

Experimental validation of a rigorous model for CO₂ post-combustion capture system using monoethanolamine (MEA)

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1 Introduction

Given the advantages inherent in fossil fuels, such as their availability, relatively low cost, and the existing infrastructure for delivery and distribution, they are likely to play a major role in energy production in the near- to medium-term future. On the other hand, combustion of fossil fuels such as coal and natural gas are major sources of CO₂ pollution, which cause considerable damage to the environment of our planet. Increased concerns about the impact of CO₂ emissions have led to a number of measures around the globe to address this problem. The countries that have ratified the Kyoto protocol are obliged to meet specified emissions-reduction targets, though at this point in time without the participation of the United States, who are responsible for a large portion of the world CO₂ emissions. The Bush administration, has, however, independently proposed a number of initiatives that address this problem. The most viable and commercially available CO₂ capture technology for power conversion is in general the post-combustion technology. In this process the CO₂ is captured from the flue gases after the conversion of fuel into power. Typically, the CO₂ concentrations are 3–5% in gas-fired power plants and 13–15% in coal plants. In order to properly understand the mechanisms associated with this removal technology, for accurate plant design, and for process improvement, precise modeling of this entire process is of utmost importance.

1.1 Specific system description

In a post combustion CO₂ absorption plant, the exhaust gas enters the bottom of a reaction column, the absorber, where it is met by a liquid trickling downwards in the opposite direction (see Figure 1). The liquid contains the amino-compound that is able to absorb the CO₂ to form a new compound by a chemical reaction in the liquid phase. As the liquid reaches the bottom of the absorber it is loaded with CO₂ and is subsequently transferred to the top of a new tower, called the regenerator column or desorber, where it flows down to meet upcoming vapor. This vapor contains the energy required to regenerate the gas by the reverse chemical reaction to form the pure CO₂ gas. The amine solution at the bottom of the regeneration column is then brought back to the absorption tower to complete the cycle.

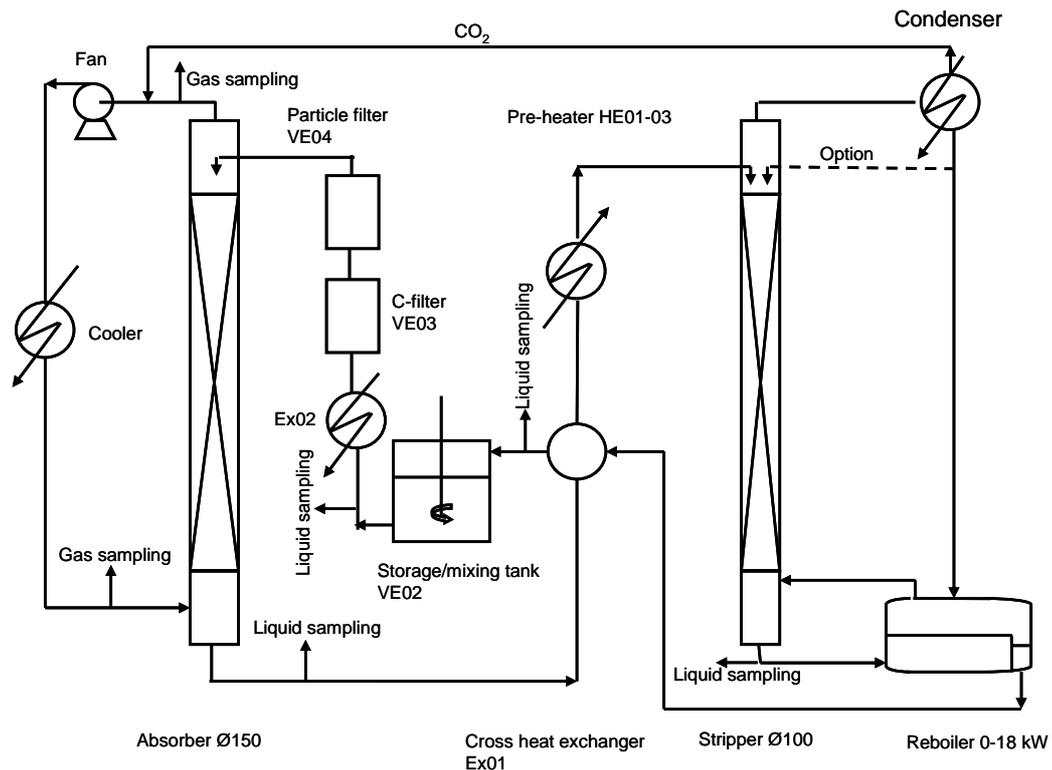


Figure 1: Simplified process flow sheet

The objective of this work is to validate a rigorous simulation program with data from a pilot plant available in our labs. The developed model yields a predictive tool for CO₂ absorption of flue gases with the use of monoethanolamine (MEA). The model is written entirely in FORTRAN 90. A rigorous gas/liquid interface model is developed based on the penetration theory using advanced numerical techniques. Simpler and faster interfacial models can also be used in the present simulator. Emphasis has been put on the adaptability of the code for different systems. All subprograms within the main module are developed using standardized syntax and unit operations are modularized to ease changing spread sheet configuration if that is required.

The simulation results are tested against measurements performed in our in house pilot plant facility. This is a system that has been operated continuously and includes an absorber and a desorber. A future paper will include the validation of the model against data from the desorber section of the pilot rig. The developed model is written primarily for modeling flue gas systems from post combustion CO₂ removal units at ambient pressure.

2 Model theory

2.1 Description of flow model for packing:

In order to obtain a mathematical model describing the mass transfer with simultaneous chemical reaction in a differential absorber, the following assumptions were made regarding the flow model:

The flow field for both liquid and vapor phases are considered as of that for plug flow. For industrial packed bed reactors, the flow fields are highly turbulent in both phases. It is therefore reasonable to assume that there are negligible radial gradients in temperature and concentration along the tower.

Axial diffusion is negligibly small in comparison with the effect of convective flux. In this work, backmixing is assumed to be negligible.

Vapor in the gas phase condenses at the walls and at the gas-liquid interface releasing heat of condensation instantaneous to the liquid phase.

All reactions are restricted to the liquid phase.

The gas film is in steady for all interfacial mass transfer models.

The packing has one liquid and one gas feed stream.

The packing has one liquid and one gas exit stream.

All other units can be two phase. If a stream is two phase prior to the packing, a flash will be calculated, vapors will be bypassed to the overhead vapor stream.

No radial effects are present in the column.

For a steady state 1-D model disregarding effects of axial and radial diffusion in both phases, the general continuity equation reduces to the following where positive is defined as along the direction of flow for both phases.

3 Experimental section

3.1 Description of the laboratory pilot plant.

In our laboratory scale CO₂ pilot plant, the exhaust gas enters the bottom of the absorption column, where it is met by a liquid trickling downwards in the opposite direction. The liquid contained during this test program 30 wt% MEA. As the liquid reaches the bottom of the absorber it is loaded with CO₂ and is subsequently transferred to the top the regenerator column, where it flows down to meet upcoming vapor from an electric heated reboiler. This vapor contains the energy required to regenerate the liquid to form almost pure CO₂ gas. The regenerated amine solution from the reboiler outlet is then brought back to the absorption tower to complete the cycle.

Again, the simplified flow sheet for the pilot rig is illustrated in Figure 1. A detailed flow chart of the pilot plant can be found upon request from the authors.

3.2 Data analysis and assumptions for the pilot rig absorber.

Figure 1 shows the absorber column. Density and component concentrations as well as pressure and temperature were measured for the liquid inlet. Except for the amine concentration, same properties were measured for the absorber outlet. It was assumed that the amount of amine condensed or evaporated in the tower was too small for accurate measurements. Therefore the MEA concentration at the outlet of the absorber was given the same value as for the measured liquid inlet concentration. Within the absorber, 5 temperature measurements were taken for each run, calibrated to within an accuracy of about 0.1°C. Inlet and outlet liquid and gas temperatures were measured, yielding a total of 7 temperatures for the column profiles. It was, however, impossible to determine if the temperature probes within the

column measured the liquid or gas phase. The temperature plots for the two phases used therefore the same internal temperatures, while the gas or liquid temperatures at the inlets were added to the set.

The recycled carrier gas for CO₂ consists mainly of nitrogen and water vapor. A flow meter prior to the absorber measured the calibrated CO₂ content on a dry basis. It was assumed that the gas feed line was saturated with water at the given inlet temperature and the amount obtained by using steam table data (Irvine and Liley, 1984). The inlet gas wet basis partial pressures were then obtained using the assumption of the following relationship:

$$y_{CO_2,in} = y_{CO_2,in,dry} (1 - y_{H_2O,in}^{Sat.}) \quad (1.1)$$

$$y_{H_2O,in}^{Sat.} = \frac{p(T_{l,in})_{H_2O}^{Sat.}}{P_{tot,in}} \quad (1.2)$$

$$y_{N_2,in} = 1 - (y_{H_2O,in}^{Sat.} + y_{CO_2,in}) \quad (1.3)$$

Where $y_{CO_2,dry}$ is the calibrated value measured by the CO₂ flow meter. The dry temperature for the measurement is assumed the given value at saturation at 10°C. The amount of MEA obtained in the gas feed line is the saturation pressure at the inlet temperature, this was thought as a negligible amount.

4 Results and discussion

Due to the nature of the rate based framework, the scale-up of the model from lab scale systems to industrial scale units will not require any additional parameter fittings. The hydraulic parameters will be recalculated for the new and larger systems and adjusted accordingly. In the case for an equilibrium stage model, new residence time profiles need to be assumed, which requires significant user experience [ref. rate based literature?]. Another feature with the rate based two phase model is that one will obtain temperature profiles throughout the packing, for both liquid and gas phases. For the equilibrium model this difference is neglected and calculations are carried out with average stage temperatures for each stage.

4.1 Model Verification: Absorber

The obtained experimental data from the pilot plant was used in conjunction with simulation results as basis for the model verification. The model was tested against all the obtained experimental data, which included 15 data acquisition periods, during the continuous pilot rig operation. The following data were used as basis for the model verification for the absorber:

- The fully described incoming liquid stream and incoming gas stream to the absorber: *molar flow rate, F; component molar composition, xi and yi, temperature and pressure; T, p.*

- The fully described outlet liquid stream and outlet gas stream of the absorber: *molar flow rate, F ; component molar composition, x_i and y_i , temperature and pressure; T, p .*
- 5 temperature-meters through the absorber packing to yield a temperature profile.

The identical fully defined inlet liquid and gas streams were inserted to the simulator. Comparisons were made with the simulation results. This included the calculated outlet streams from the absorber, component concentrations as well as temperature profiles.

The basis for data comparisons has been set using a specified simulator setup. The base case interfacial mass transfer model is the complete numerical solution of the penetration model, with 11 interfacial adaptive gridpoints. The equilibrium model is tuned to fit data obtained from SINTEF/NTNU data [Ma'mun et al., 2005; Castor report, B.]. The total absolute standard deviation of the fit obtained for the model compared to the experimental data is 20.58 %, and with a relative absolute deviation of 22.6 %. The model fitting was performed using Levenberg-Marquardt's method with an in-house software package, Modfit [Hertzberg, Mejdell].

4.2 Temperature profiles (loading ranges 1, 2, and 3) and CO₂ absorption rates.

The temperature profiles for 4 experimental datasets vs. the model predictions are shown in figures 5.1-5.4. These datasets were picked because they cover almost the whole experimentally obtained loading range for MEA, 0.18-0.47. The temperature profiles for the remaining datasets show similar profiles. Complete datasets and evaluations can be obtained from the authors upon request.

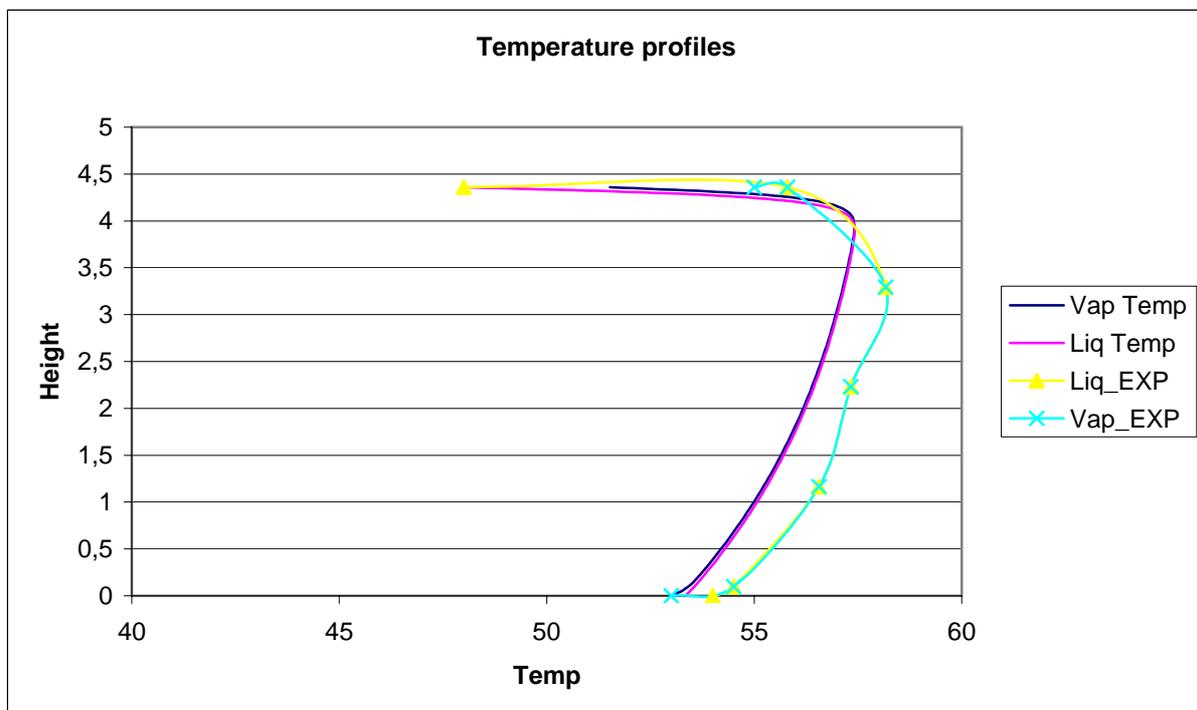


Figure 5.1 Loading range 1 (14.03.2005 par 1): experiment: 0.217-0.333, simulated: 0.217-0.334

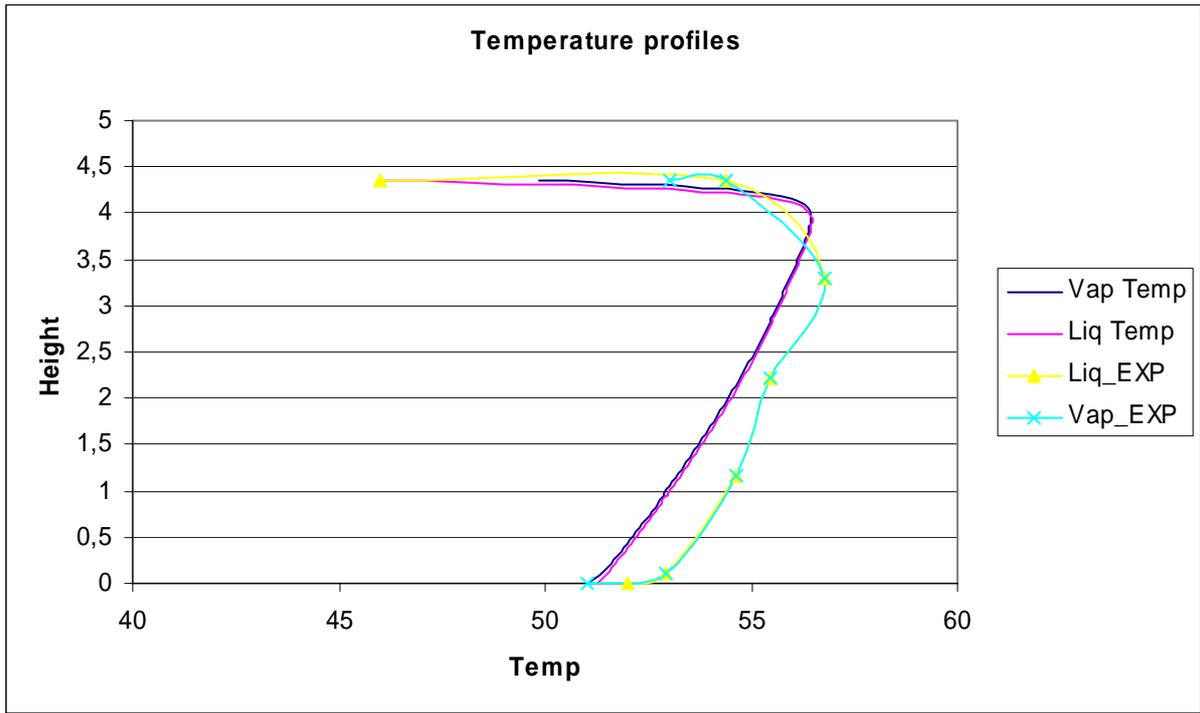


Figure 5.2 Loading range 2 (16.03.2005 par 1): experiment: 0.307-0.400, simulated: 0.307-0.409

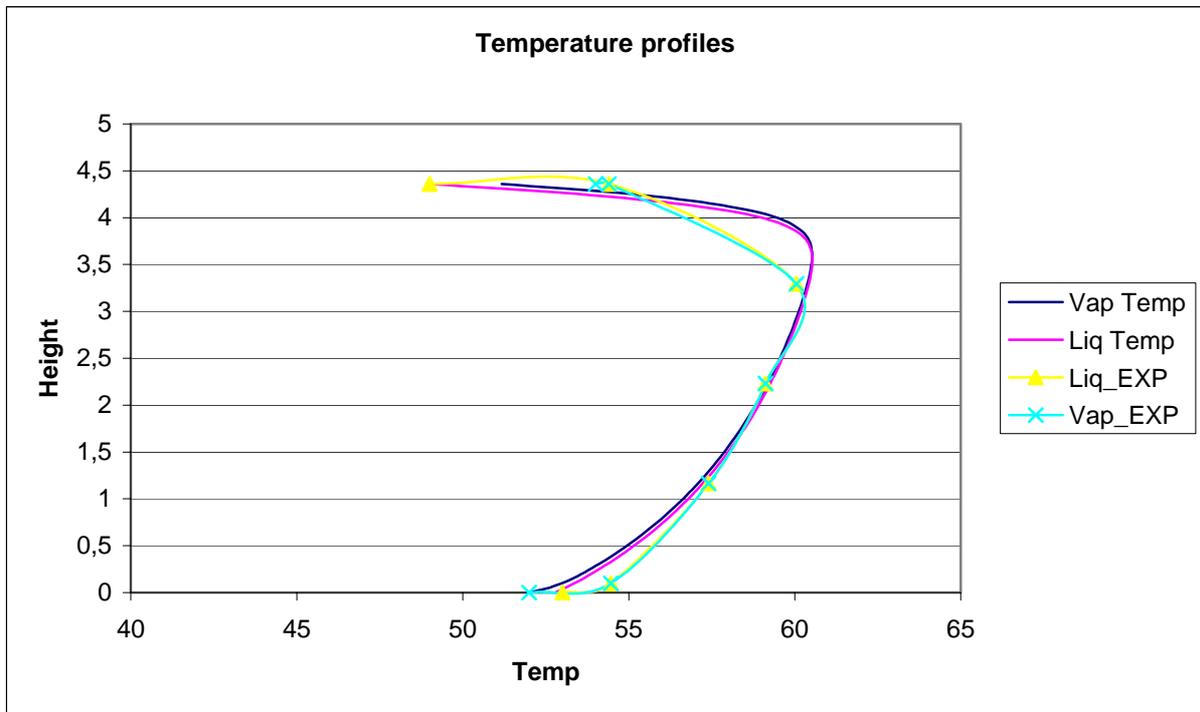


Figure 5.3 Loading range between 1 and 2 (11.03.2005 par 1): experiment: 0.284-0.345, simulated: 0.284-0.347

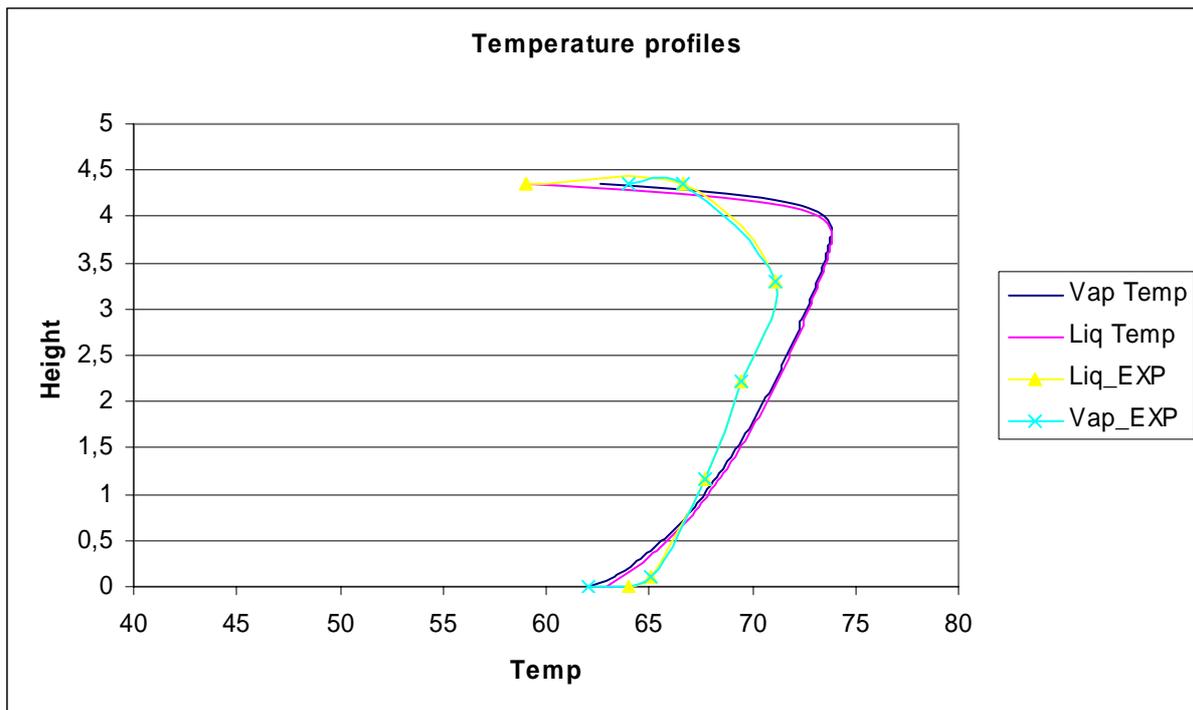


Figure 5.4 Loading range 3 (17.03.2005 par 2): experiment: 0.357-0.434, simulated: 0.357-0.441

The temperature profiles from simulations and experimental data, which give important information as to how the absorption takes place throughout the column, show that the curves are very similar at the lower loading ranges. At the higher loading ranges, range 3 (rich loading above 0.40), the temperature comparisons with the experimental data show larger deviations. Figure 5.5 shows a quantitative comparison of the CO₂ loading of the liquid leaving the column with the corresponding values predicted by the model. The inlet loadings are the same. 15 runs are included. Figure 5.6 and 5.7 show the calculated mass transfer rates for the 3 loading ranges, compared to the experimental liquid side mass transfer, and both liquid phase and gas phase transfer, respectively. It is clear that the deviations start becoming larger as the loading range increases. The 3rd loading range indicated by the red crosses and black crosses in figures 5.6 and 5.7 show the largest deviations. At the lower loading ranges (up to 0.40 indicated by the blue triangles and diamonds) the simulated data show very good agreement with the experimental data.

The trends shown in these simulations are very reasonable. There are several possible sources of errors at the larger loading regime. The use of the complete numerical solution of the penetration model should account for the different reaction regimes that can appear throughout the packing. At the higher loading the enhancement due to reaction cannot be assumed being the same as the Hatta number, which is usually assumed for a reaction in the pseudo 1st order regime. The reaction rate become less accurate at increased temperatures, and an Arrhenius extrapolation might not be valid, as shown by Aboudheir et al. [Aboudheir et al. 2003]. An even more important effect is the uncertainties associated with the equilibrium data.

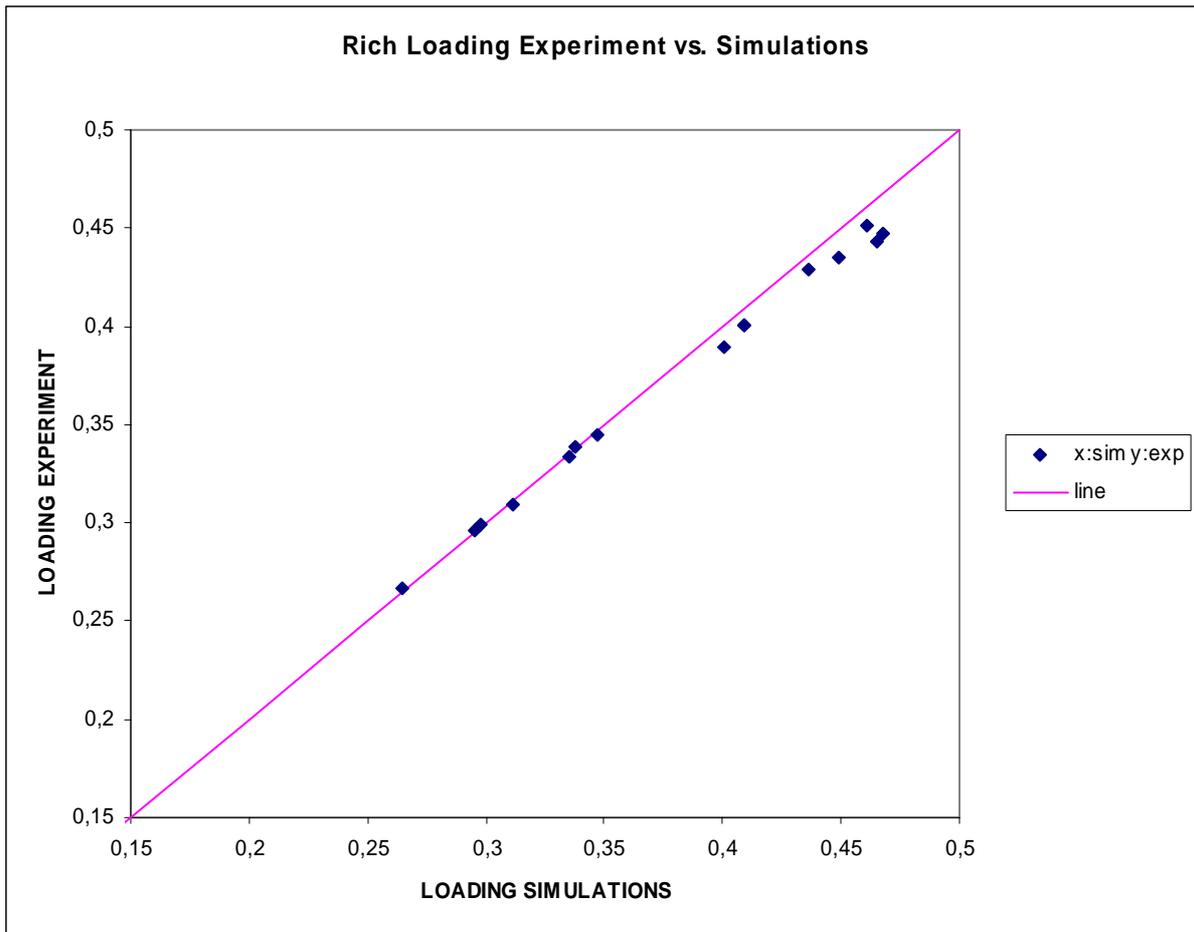


Figure 5.5 Rich loading values for the set of runs throughout loading ranges 1 to 3.

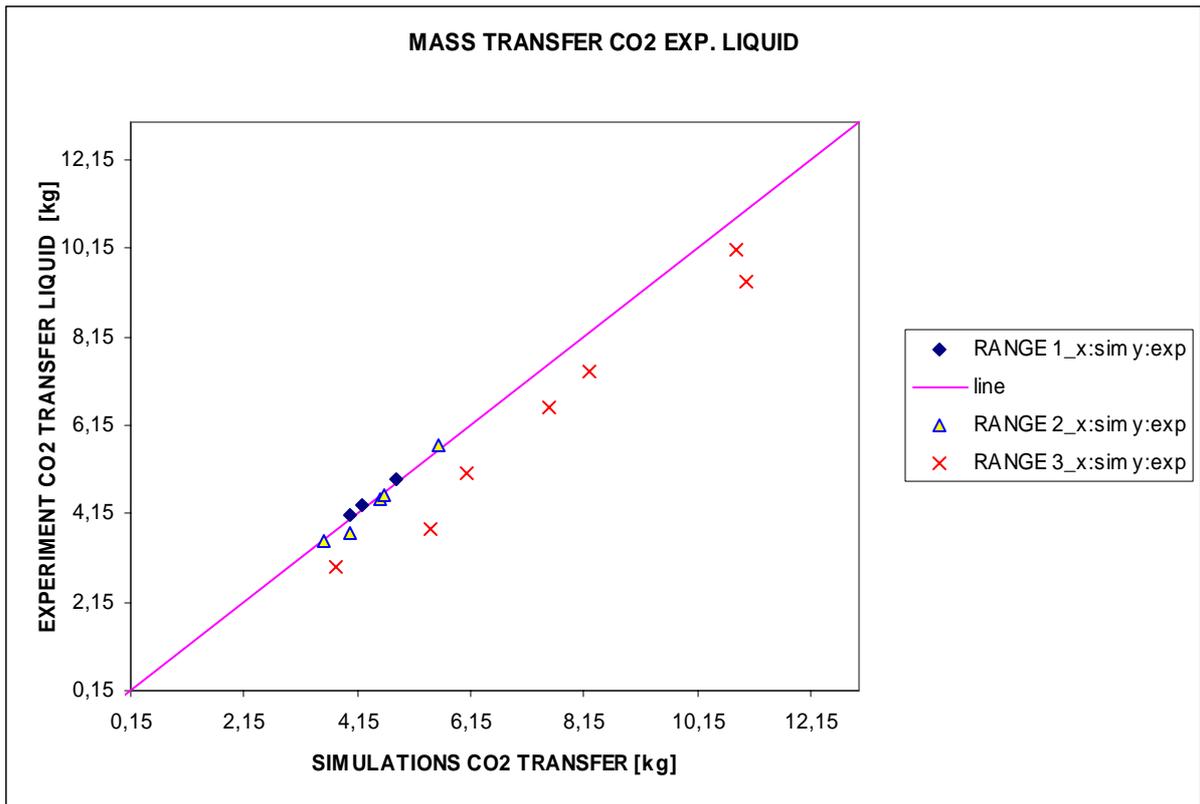


Figure 5.6 Simulation results compared to experimentally calculated mass transfer rates [kg/h] based on the liquid side.

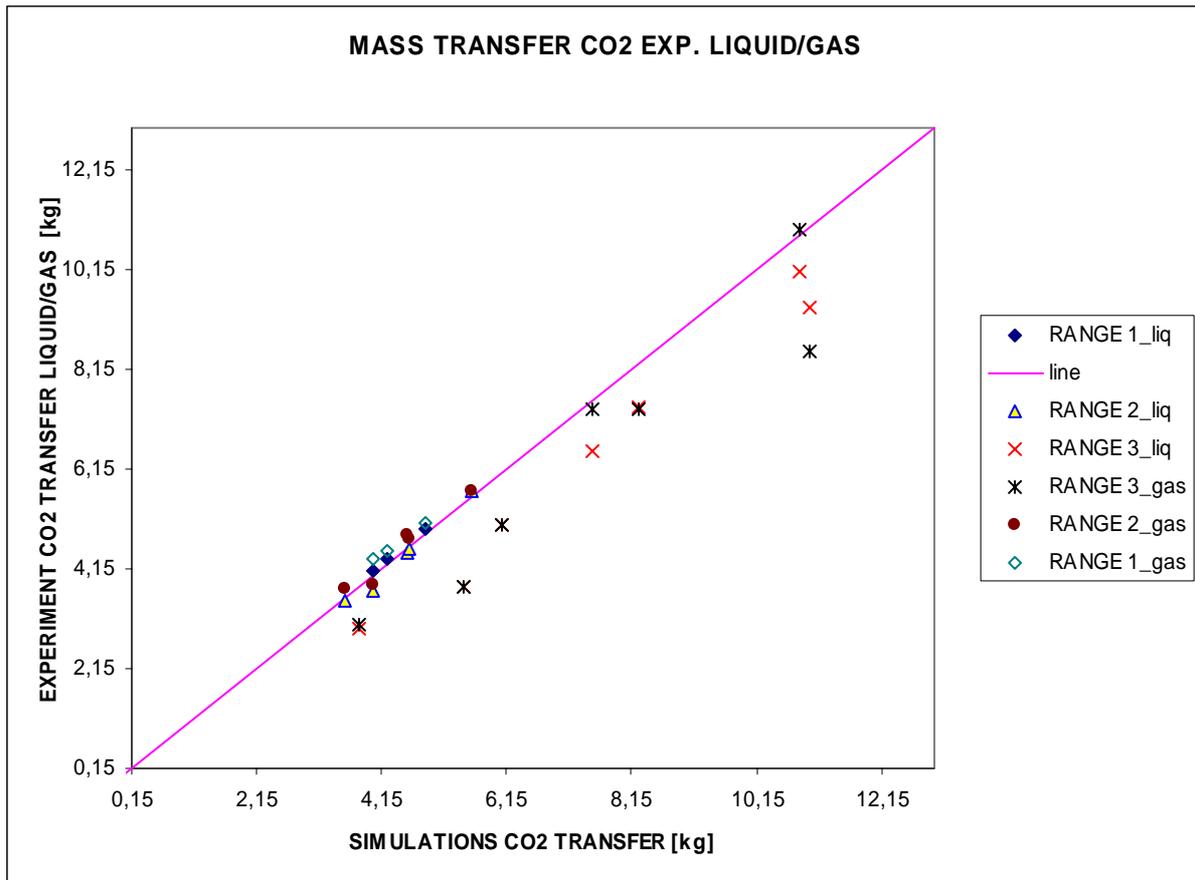


Figure 5.7 Simulation results compared to experimentally calculated mass transfer rates [kg/h] based on the liquid side and the gas side.

5 Conclusion

The objective of this work has been two fold:

1. To obtain high quality data from our post-combustion pilot rig located in our labs, both for the absorber and the stripper, as well as the complete process during continuous operation over a large time period.
2. To validate a rigorous simulation program with the obtained experimental data from the pilot rig.

The obtained experimental data from the pilot plant was used in conjunction with simulation results as basis for model verification. The model was tested against all the obtained experimental data during the continuous pilot rig operation.

The developed model yields a predictive tool for CO₂ absorption of flue gases with the use of monoethanolamine (MEA). The model is written entirely in FORTRAN 90. A gas/liquid interface model is developed based on the penetration theory using advanced numerical techniques. Simpler and faster interfacial models can also be used in the present simulator, however care should be taken when a priori assuming interface reaction regimes. Emphasis has been put on the adaptability of the code for different systems.

The temperature profiles from simulations and experimental data show that the curves obtained are very similar at the lower loading ranges. At the higher loading ranges, range 3 (rich loading above 0.40), the temperature comparisons with the experimental data show larger deviations. At the lower loading ranges up to 0.40 mole CO₂/mole MEA the simulated mass transfer data show very good agreement with the experimental data. The highest loading range, from 0.40 up to 0.45 mole CO₂/mole MEA show the largest deviations.

6 References

Aboudheir , A; Tontiwachwuthikul, P.; Chackma, A.; Idem, R.; Chem. Engng. Sci. 2003, 58, 5195-5210.

Castor report, A: Modeling tools for the simulation of CO₂ absorption/desorption process.

CASTOR Deliverable from SINTEF and NTNU, 2005

Castor report, B: Characterisation and selection of solvents

CASTOR Deliverable D2.2.3 from SINTEF and NTNU, 2005

Jou, F.-Y.; Mather, A. E.; Otto, F. D. The Solubility of CO₂ in a 30 Mass Percent Monoethanolamine Solution. *Can. J. Chem. Eng.* **1995**, 73, 140-147.

Modfit, A general multi-response non-linear model fitting program, Hertzberg, T., Mejdell, T.

Ma'mun, S.; Nilsen, R.; Juliussen, O.; Svendsen, H. F. Solubility of Carbon Dioxide in 30 mass % Monoethanolamine and 50 mass % Methyldiethanolamine Solutions, *J. Chem. Eng. Data* **2005**, 50 (2), 630 -634.

"Steam and Gas tables", Irvine, T. F. Jr.; Liley, P. E.; 1984 Academic Press Inc.