

Experimental verification of Equilibrium-Stage and Rate-Based Simulations

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Abstract—In this article, pilot plant data for CO₂ post-combustion capture are discussed and compared with modelling results. The objectives of this paper are to evaluate the overall performance of the CO₂ capture pilot plant using both experimental and simulation results. In addition, this work is aiming to assess the performance of two different modelling approaches (equilibrium-stage and rate-based) in representing the CO₂ capture process performance and requirement. Furthermore, an extended parametric study was carried out to evaluate both experiments and simulation tools. This work indicated that there are no major differences between the two modelling approaches in predicting the overall capture process behaviour (macro scale) for this pilot plant case. However, the simulation of the absorber and stripper columns demonstrated that the rate-based model gives a better prediction of the columns temperature profiles and mass transfer inside the columns compared to the equilibrium-stage approach (micro scale). As a result, for a detailed process design or understanding of the mass and energy profiles in the absorber and stripper columns, the rate-based approach should be applied. It was concluded that both modelling approaches can be used for predicting the capture process overall behaviour and requirement for pilot plant scale as well as for industrial scale application.

Keywords- CO₂ capture, absorption, pilot plant, MEA, equilibrium-stage, rate-based

I. INTRODUCTION

Chemical absorption is considered the best suited technological option for post-combustion capture of CO₂ in the near term [1, 2]. Chemical absorption processes for CO₂ capture are widely used in industrial applications, although not on the scale required for power stations [3]. In addition to these industrial applications, there are number of smaller lab-scale and pilot plants facilities aiming to develop and evaluate the different CO₂ capture processes [4-10].

Beside the experimental work, different modelling and simulation activities have been carried out to evaluate and understand the chemical absorption capture process [11-19]. The objectives of these modelling activities are varied from one research group to another. Carey et al 1991 [11] and Al-Baghli et al. 2001 [14] have developed rate-based models to study the behaviour of the absorption/stripping system with different solvents. Escobillana et al. 1991 [12] have validated their in-house developed model with experimental results. On the other hand, Chang et al. 2005 [19] have used a commercial simulation tool (Aspen plus) to study and optimize the performance of the CO₂ capture unit for industrial scale coal power plant. Another conventional tool (gPROMS) has been used by Lawal et al. 2008 [16] to compare the equilibrium-based approach versus the rate-based approach. In their work, they have found that the rate-based approach gives better predictions of the temperature profiles comparing to the equilibrium-based approach. However, none of these activities have included experimental results of large-scale capture process. In addition, the focus of these activities has been divided either on the columns behaviour or on the process overall behaviour.

As a part of the European project on the CO₂ capture and geological storage (CASTOR), a 1 tonne CO₂/hour CO₂ post-combustion capture pilot plant has been realised at Dong power plant in Denmark [20]. This pilot plant runs on a split stream of real flue gas from coal power plant. The general target of the pilot plant is to demonstrate long-term steady operation of CO₂ capture processes based on real flue gas conditions. In addition, it can be considered as a test facility for standard and novel solvents. The collected data and experimental results from this facility will be used for process benchmarking and models validating [21]. In this pilot plant, different tests have been done, which will enable a better understanding of the steady state operation of the chemical absorption capture process. In this work two relevant test series based on the use of monoethanolamine (MEA) as an absorbent are presented. In these tests the solvent flow rate and the stripper pressure have been varied to optimize the capture process.

In this work the focus is on the evaluation of the conventional Aspen plus modelling tools using CASTOR pilot plant data. In addition, the overall capture process (macro scale) and the absorber/stripper columns profiles are analysed and evaluated (micro scale). The goals of this work are:

1. Large-scale pilot plant experimental data analysis and evaluation,
2. The comparison of two different modelling approaches (equilibrium-stage and rate-based models) to assess their performance in presentation the CO₂ capture process, and
3. The capture process overall evaluation on macro and micro scale.

II. SIMULATION APPROACHES BACKGROUND

In this section the basis of the models, which are used in describing the absorption process is discussed. For the absorption process, two approaches are used in modelling vapour-liquid mass-transfer in a section of packing: the equilibrium-stage approach and the non-equilibrium stage (rate-based) approach (see Figure 1).

In the equilibrium-stage approach, the vapour-liquid mass transfer is modelled by creating section where it is assumed that the vapour and liquid phases are perfectly mixed and in equilibrium. This means that the liquid phase and the vapour phase leave this packing section at the same



temperature. This model is based on the theory of theoretical number stages combined with the concept of efficiency to determine the actual number of stages. These actual number of stages together with the right mass and heat transfer rate can be used for the separation column design [24, 25]. However, in the rate-based approach, the actual mass and heat transfer rates are described in a direct way using mass and heat transfer rates [24].

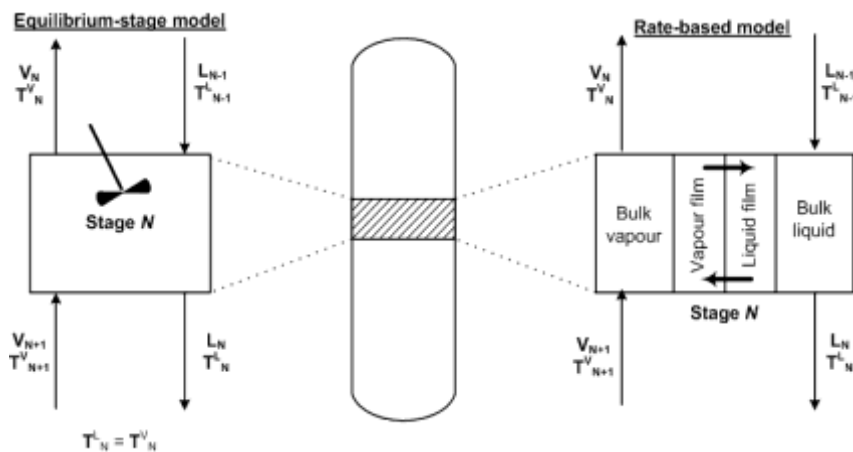
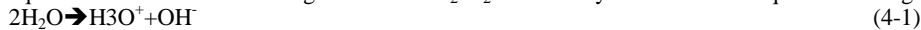


Figure 1. Equilibrium-stage and rate-based models

A. Equilibrium-Stage Simulation Approach

The equilibrium-stage approach, which is used in this article, is built in the Radfrac column model in Aspen Plus. To describe the absorber column, three equilibrium stages with no condenser or reboiler have been used. The number of equilibrium stages is based on the operating line in connection with the equilibrium line. For the absorption section three equilibrium stages are sufficient to describe the CO₂ separation process using MEA. However, for the regeneration column six equilibrium stages including the reboiler are needed. The specifications of the equilibrium-stage model for the absorber, the washing column (section) and the stripper are shown in Table I. The solvent which is used for this discussion is monoethanolamine (MEA). MEA is a primary ethanolamine, which can associate with H₃O⁺ to form an ion MEAH⁺, and can also react with CO₂ to form a carbamate ion MEACOO⁻. Chemical equilibrium is assumed with all the ionic reaction in the MEA chemistry. The following set of equilibrium reactions describing the MEA-CO₂-H₂O chemistry are used in the equilibrium-stage approach [29]:



Description	Absorber	Absorber washing section	Stripper
Calculation type	Equilibrium	Equilibrium	Equilibrium
Number of theoretical stages	3	2	6
Condenser	None	None	None ¹
Reboiler	None	None	Kettle
Pressure	~ 100 kPa	~ 100 kPa	~ 180 kPa ²
Pressure drop ³	3-8 kPa	Negligible	~ 10 kPa
Column's design specification	None	Solvent losses is fixed by varying the washing water feed flow rate	Reboiler (stage 6) temperature is fixed by varying the boil up ratio

TABLE I. SPECIFICATIONS FOR THE EQUILIBRIUM-STAGE APPROACH

The equilibrium constants for these different equilibrium reactions are built in the Aspen properties set of CO₂-MEA-H₂O system, which is originally provided from the work of Austgen et al. [28]. The CO₂ capture process using the MEA-H₂O-CO₂ system is thermodynamically described using the Electrolyte-NRTL model [28].

¹ The condenser is modeled as a separate unit

² The stripper pressure has been included in the process parametric study. This value is used for the base case.

³ The columns pressure drop has been provided based on the experimental results, so it has been changed from one simulation to another.



B. Rate-Based Simulation Approach

In the rate-based model, actual rates of mass and heat transfer as well as chemical reactions are considered. The mass transfer is described using the two-film theory using the rigorous Maxwell-Stefan theory [30]. This model has been implemented in the Aspen plus Radfrac column model using the rate-based calculation method. This model approach is based on the same properties data set (CO₂-MEA-H₂O) which is provided within Aspen plus. However, some properties modifications have been made based on the Aspen tech work [29] to make it fit with the rate-based calculations. In addition to the previously mentioned equilibrium reactions, the following four kinetic reactions have been implemented in the rate based calculation method:



Power law expressions are used in calculating the rate of the above mentioned reactions (reactions 6-9):

$$r = AT^n \exp\left(-\frac{E}{RT}\right) \prod_{i=1}^N C_i^{a_i} \quad (4-10)$$

Where:

r = rate of reaction;

A = Pre-exponential factor [unit depends on the order of the reaction];

T = Absolute temperature [K];

n = Temperature exponent [=0];

E = Activation energy [cal/mol];

R = Gas law constant [cal/mol.K];

N = Number of component in the reaction;

C_i = Concentration of component i [mol/l];

a_i = The stoichiometric number of the component i in the reaction equation.

The kinetic parameters (A and E) for the reactions (6-9) are given in Table II [29]:

Reaction number	k	E, cal/mol
6	4.32e+13	13249
7	2.38e+17	29451
8	9.77e+10	9855.8
9	2.18e+18	14138.4

TABLE II. PARAMETERS K AND E IN EQUATION (4-10) [29]

The mathematical model behind the rate-based calculations in Aspen rate-based model consists of material balances, energy balances, mass transfer, energy transfer, phase equilibrium, and summation equations [26]. To achieve these complicated calculations a large number of input parameters and specifications need to be provided for the different unit operation blocks. These input and specifications that have been used for the absorber, the stripper and the absorber washing columns are shown in Table III, Table IV and Table V, respectively. Most of these specifications are recommended to be used for the rate-based model of the CO₂ capture process by Aspen Tech [29] with some modifications to fit the model with the pilot plant specifications and results [22].

Number of stage: 17

Pressure: ~ 100 kPa

Pressure drop: Experimental value used as input

Reboiler: None

Condenser: None

Packing type: IMTP, NORTON, Metal, 50 mm

Packing height: 17 m and section diameter: 1.1 m

Mass transfer coefficient method: Onda et al 1968

Interfacial area method: Onda et al 1968

Interfacial area factor: 1.5

Heat transfer coefficient method: Chilton and Colburn

Holdup correlation: Stichlmair et al 1989

Film resistance : Discrxn for liquid film and Film for vapour film

Flow model: mixed

Design specifications: None

TABLE III. ABSORBER COLUMN SPECIFICATIONS USED IN THE RATE-BASED MEA MODEL



Number of stage: 13 includes reboiler
 Pressure: ~ 180 kPa bar
 Pressure drop: Experimental value used as input
 Reboiler: Kettle
 Condenser: None
 Packing type: IMTP, NORTON, Metal, 50 mm
 Packing height: 13 m and section diameter: 1.1 m
 Mass transfer coefficient method: Bravo et al 1992
 Interfacial area method: Bravo et al 1992
 Interfacial area factor: 2
 Heat transfer coefficient method: Chilton and Colburn
 Holdup correlation: Stichlmair et al 1989
 Film resistance : Discrxn for liquid film and Film for vapour film
 Flow model: mixed
 Design specification: Stage 13 (reboiler) temperature is fixed by varying boil up ratio

TABLE IV. STRIPPER COLUMN SPECIFICATIONS USED IN THE RATE-BASED MEA MODEL

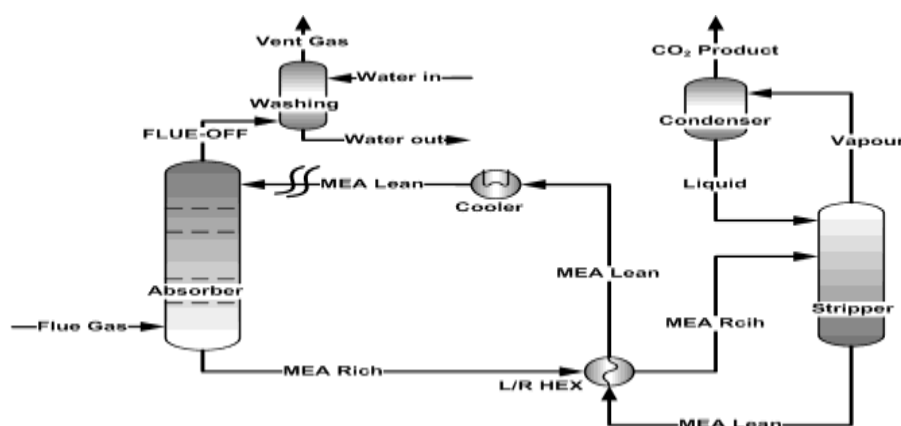
Number of stage: 3
 Pressure: ~ 100 kPa
 Pressure drop: Zero
 Reboiler: None
 Condenser: None
 Packing type: MellapakPL, Sulzer, Standard, 252Y
 Packing height: 3 m and section diameter: 1.1 m
 Mass transfer coefficient method: Bravo et al 1985
 Interfacial area method: Bravo et al 1985
 Interfacial area factor: 1.5
 Heat transfer coefficient method: Chilton and Colburn
 Film resistance : Film for both liquid film and vapour film
 Flow model: mixed
 Design specification: None

TABLE V. ABSORBER WASHING SECTION SPECIFICATIONS USED IN THE RATE-BASED MEA MODEL

The rate-based modelling approach is expected to have many advantages over the equilibrium-stage approach. It is expected to provide more realistic results [30]. The rate-based model explicitly accounts for the actual column configuration, which affects the column performance. As a result, it is expected to predict the experimental results more accurate.

C. Simulation Criteria and Limitations

The pilot plant results from the MEA test campaign within the European CO₂ capture and storage (CASTOR) project have been analysed and used in validating both the equilibrium-stage approach and the rate-based approach [20]. Dong Energy provided the measured parameters from the experiments in the pilot plant at steady state [32]. The simulations were performed using Aspen Plus, version 7 [26] with the process flow sheet shown in Figure 2.


 Figure 2. CO₂ capture with MEA absorption process: Aspen Plus simulation flow sheet


The main simulation operating specifications are provided from the experimental results. The input variables are shown in Table VI. After running the process simulation using the different models and experimental data sets, the simulation results are compared with the experimental results.

Parameter	Specifications
Flue gas	Total flow rate, composition, temperature, pressure
Lean solvent	Flow rate, composition, temperature, pressure
Lean solvent cooler	Pressure, outlet temperature
Lean/rich solution heat exchanger	Pressure drop, temperature difference approach
Absorption column	Operating pressure and pressure drop
Stripper column	Reboiler temperature, operating pressure and pressure drop

TABLE VI. PROCESS SIMULATION INPUT USING THE EXPERIMENTAL DATA

The two modelling approaches have been validated in two different levels: the macro analysis and the micro analysis. In the process macro analysis, different process output parameters have been used to evaluate the experimental results and to validate the different models. These parameters have been chosen depending on its importance for the overall process behaviour; like the regeneration energy requirement, the CO₂ removal percentage (process efficiency), the solvent rich loading. In the micro analysis, the experimental results inside the columns are evaluated. The temperature profiles in the absorber/desorber give a good indication on the effectiveness of the CO₂ absorption and desorption in the different sections of the columns. Table VII provides the output parameters from the process simulations, which has been used in the process evaluation and models validation.

Parameter	Unit
CO ₂ recovery	[%]
Rich CO ₂ loading	[mol CO ₂ /mol MEA]
Regeneration energy requirement	[kWth]
CO ₂ captured flow rate	[kg/hr]
Flue gas outlet temperature	[°C]
Absorber temperature profile	[°C]
Rich solvent temperature	[°C]
Stripper temperature profile	[°C]

TABLE VII. SIMULATIONS OUTPUT PARAMETERS

However, a general limitation has been found within ASPEN Plus tool. The vapour liquid equilibrium (VLE) data provided in the data sets does not describe the experimental results in great accuracy. Comparing the VLE data for the MEA-H₂O-CO₂ system, which has been calculated using the ASPEN model, with experimental data from Lee et al 1976 [31], has shown that the calculated loading at a given partial pressure at the stripper condition is in general higher than the experimental data (see Figure 3). However, the calculated loading at a given partial pressure at the absorber condition is in good agreement with the experimental data.

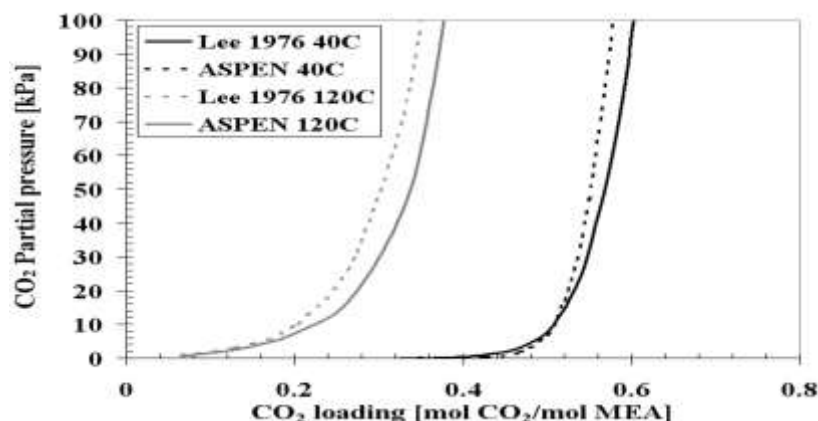


Figure 3. Experimental and calculated VLE data at 40 and 120 °C [26,31]

The disagreement between the simulation and the experimental loading has been found mainly in the high temperature conditions (stripper conditions), which will result in higher values of the lean loading comparing to the values that have been measured in the experiment. These higher values of lean loading are expected to influence the overall CO₂ recovery in the absorber. To avoid a major effect of the VLE data on the overall process behaviour and validation of the models, the process is simulated with an open tear stream (MEA-Lean). This allows the use of the experimental lean loading values as input to the absorber and on the same time operating the solvent reboiler at the temperatures based on the experimental results.



III. REFERENCE CASE DEFINITIONS

A. Pilot Plant Description

The CO₂ absorption pilot plant is located at the Esbjerg power plant, Esbjergværket (ESV). ESV is owned and operated by Dong Energy. ESV is a 400 MW pulverised coal-fired power plant equipped with deNO_x and FGD units. In 2005, the CO₂ absorption pilot plant was erected and commissioned. This plant operates on a slipstream of the flue gas, taken after the deNO_x and FGD units. The design of the pilot plant is based on the standard CO₂ production plant with minor modifications (as in Figure 2). The pilot plant key design figures are shown in Table VIII.

Parameter	Design value
Flue gas capacity	5000 Nm ³ /hr
CO ₂ captured (at 12 vol. % CO ₂)	1000 kg/hr
CO ₂ removal percentage	90 %
Maximum solvent flow rate	40 m ³ /hr
Maximum reboiler steam flow	2500 kg/hr (350 kPa)
Maximum stripper pressure	300 kPa

TABLE VIII. PILOT PLANT DESIGN FIGURES [22]

The flue gas enters the absorber tower at the bottom in a counter-current flow with the solvent. The flue gas does not require cooling due to the relatively low inlet temperature (~46 °C). The gas fan is placed downstream the absorber, which implies that the absorber is operated at a pressure slightly below atmospheric pressure. CO₂ analysers continuously monitor the CO₂ content of the absorber inlet and outlet.

The pilot plant is equipped with full height absorber and stripper columns to achieve 90% CO₂ removal and deep rich solvent regeneration. This full height makes it a real demonstration of the large scale capture process with the need only to scale up the diameter to cope with the larger gas/liquid flow rates. The absorber tower consists of four consecutive packed-beds for CO₂ absorption and an additional bed for water wash at the top. The absorber has an internal diameter of 1.1 meter. Each bed for CO₂ absorption is 4.25 meters in height and filled with IMTP 50 random packing. The water wash bed is 3.0 meters in height and filled with Mellapak 252Y structured packing.

The rich solvent from the absorber is pumped through two mechanical filters in series (25 and 350 μm) and a plate heat exchanger (heat exchanged with lean solvent from the stripper) before being fed to the stripper. The stripper has an internal diameter of 1.1 meter and consists of two 5.0 meter beds filled with random packing IMTP 50 and an additional bed for water wash at the top (3.0 meters of IMTP 50). A steam driven reboiler supplies the heat input to the stripper. The steam (350 kPa saturated) is supplied by ESV and the reboiler temperature controls the steam flow. The CO₂ gas and vapours from the stripper pass through a water-cooled condenser and a gas/liquid separator. The condensate from the separator is returned to the stripper wash section and the resultant gas, which is essentially pure CO₂ saturated with water, is returned to the ESV flue gas duct. The CO₂ product quality is monitored online by an analyser. The regenerated solvent from the stripper is cooled to its final set point temperature by a water-cooler after it has been heat exchanged with the rich solvent. A slipstream of approximately 10% of the solvent flow is passed through a carbon filter.

In order to monitor energy and cooling water consumptions as well as the general plant performance, the pilot plant is fitted with temperature sensors, pressure gauges and flow meters throughout. All of the measurements are continuously logged on a PC. Among others, the logged data includes: gas and liquid flow rates, CO₂ inlet and outlet concentrations and flow rates, pressures and temperatures both in the gas and the liquid phase of the main unit components (absorber, stripper, reboiler, lean cooler, lean/rich heat exchanger, and CO₂/water condenser), and temperature profiles in the packed columns.

B. Experimental Procedure and Results

The purposes of the experimental campaign are to study the effect of real flue gas conditions on the operation of the CO₂ capture process and to collect data on the different operating conditions of the process. The obtained data is used for the validation of the different models. To achieve these targets a parametric study has been done using the previous modelling activities as a guide line [27]. Depending on the previous modelling results; the variable parameters for the model validation were chosen. It is important to note that some of the variables, which have been investigated before, were not included in this work. These variables are considered as design specifications for the pilot plant, for example the MEA solvent concentration and lean solvent temperature. In this paper, the parametric study will be evaluated on two different levels: the macro analysis and the micro analysis. For this evaluation, two experimental tests have been carried out by changing two input variables:

- Test 1: The lean solvent flow rate (13-23 m³/h).
- Test 2: The stripper pressure (110-200 kPa).

To validate the different process models the following overall results are examined:

- Process regeneration energy requirement;
- CO₂ removal efficiency;
- Solvent rich loading; and
- Packed columns temperature profiles (the temperature measurement points for both the absorber and the stripper are shown in Figure 4).



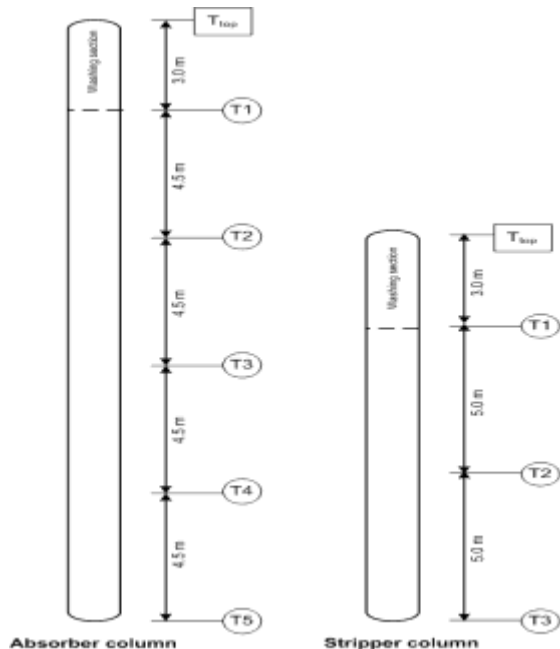


Figure 4. Temperature measurement position in the absorber and the stripper

Moreover, in addition to the temperature measurement points within the columns, the columns outlet temperatures and the solvent reboiler temperature have been registered and used for the evaluation of the calculated column temperature profile. This will be discussed in the micro-analysis section.

i. Test 1 results: varying the lean solvent flow rate

Table IX summarizes the experimental main input parameters and results of the capture process. The first tests have been done by changing the lean solvent flow rate, while keeping the carbon dioxide removal percentage constant (90 %). This has been achieved by decreasing the solvent lean loading at lower solvent flow rate. The values of the solvent lean and rich loading have been measured by analysing the liquid samples at the inlet and outlet of the absorber. The loading of the lean solvent is controlled by changing reboiler temperature.

Parameter						
Input	Solvent flow rate (m ³ /h)	23.00	19.00	16.70	14.80	12.50
	Flue gas (Nm ³ /h)	4915	5011	4939	4926	4990
	CO ₂ at inlet (mol % wet)	11.86	11.94	11.76	12.12	11.77
	Flue gas inlet temp (°C)	47.3	48.0	46.8	46.9	47.2
	Stripper pressure (kPa)	181	181	181	181	181
Results	CO ₂ at outlet (mol % wet)	1.54	1.53	1.53	1.39	1.56
	CO ₂ captured (kg/hr)	1040	1075	1070	1090	1060
	CO ₂ recovery (%)	90	90	90	91	90
	MEA Concentration (% w/w)	30.4	31.2	30.8	31.4	31.1
	Lean CO ₂ loading (mol CO ₂ /mol MEA)	0.28	0.25	0.22	0.19	0.17
	Rich CO ₂ loading (mol CO ₂ /mol MEA)	0.46	0.48	0.48	0.48	0.48
	Regeneration energy (MJ/tonne CO ₂)	3897	3722	3725	3626	3745
	Cooling water (MJ/tonne CO ₂)	3434	3204	3059	2907	1963
	Flue gas outlet temp (°C)	47.8	49.1	48.6	48.8	49.2
	Absorber temperature 1 (top) (°C)	58.8	61.2	62.1	62.9	63.2
	Absorber temperature 2 (°C)	75.0	73.7	72.9	72.3	69.8
	Absorber temperature 3 (°C)	73.0	69.6	66.9	65.3	61.3
	Absorber temperature 4 (°C)	67.5	62.6	59.3	57.4	54.3
	Absorber temperature 5 (bottom) (°C)	54.0	52.9	51.1	50.7	50.4
Stripper temperature 1 (top) (°C)	100.0	99.6	99.6	99.9	101.2	
Stripper temperature 2 (°C)	104.0	103.5	104.2	108.3	115.2	
Stripper temperature 3 (bottom) (°C)	116.0	117.6	119.1	120.1	120.8	
Reboiler temperature (°C)	118.5	119.5	120.6	121.4	122.0	

TABLE IX. SUMMARY OF PILOT PLANT TEST 1 MAIN INPUT AND RESULTS [32]



Increasing the solvent flow rates at constant flue gas flow rate leads to increasing liquid-to-gas ratios (L/G) in the absorber. The lowest regeneration energy demand (3.6 GJ/tonne CO₂) can be obtained at a solvent flow rate of 14.8 m³/h. However, it should be noted that considering the experimental uncertainty of 5%, the regeneration energy demand is nearly constant in the flow range of 12.5 to 19.0 m³/h. At the higher flow rate (23 m³/h), the specific steam demand is clearly higher. Out of the experiments, it can be concluded that the solvent rich loading is nearly constant and close to the expected equilibrium value (0.5 mol CO₂/mol MEA). This could be expected based on the height of the absorption column.

ii. Test 2 results: varying the stripper pressure (temperature)

In the second test, the stripper pressure has been varied. It can be seen from Table X that the CO₂ capture percentage varies between 88 and 93% among the different operating points. This is due to the fluctuations in the CO₂ concentration in the flue gas originating from changing boiler loads. Therefore, it was difficult to achieve a constant 90% removal in all tests.

It can be clearly seen that the regeneration energy increases as the stripper pressure is reduced from 181 kPa to 112-143 kPa. However, increasing the stripper pressure from 181 to 216 kPa does not lead to regeneration energy decrease. The higher regeneration energy at lower stripper pressures may to some extent is over exaggerated, due to not optimised solvent flow rates.

	Parameter				
Input	Stripper pressure (kPa)	216	181	143	112
	Solvent flow rate (m ³ /h)	15.00	15.50	17.00	19.00
	Flue gas (Nm ³ /h)	4917	4971	4935	4874
	CO ₂ at inlet (mol % wet)	10.98	11.29	10.22	10.32
	Flue gas inlet temp (°C)	48.2	46.3	46.4	45.0
Results	CO ₂ at outlet (mol % wet)	1.62	1.38	0.86	1.03
	CO ₂ captured (kg/hr)	995	1037	968	957
	CO ₂ recovery (%)	88	90	93	92
	MEA Concentration (% w/w)	29.7	30.3	29.5	28.7
	Lean CO ₂ loading (mol CO ₂ /mol MEA)	0.21	0.21	0.23	0.24
	Rich CO ₂ loading (mol CO ₂ /mol MEA)	0.48	0.46	0.46	0.46
	Regeneration energy (MJ/tonne CO ₂)	3738	3692	4006	4185
	Cooling water (MJ/tonne CO ₂)	3025	3323	3197	3195
	Flue gas outlet temp (°C)	49.2	48.0	47.8	47.0
	Absorber temperature 1 (top) (°C)	61.6	61.8	59.6	58.6
	Absorber temperature 2 (°C)	70.6	71.6	72.5	72.4
	Absorber temperature 3 (°C)	63.8	65.4	69.1	69.7
	Absorber temperature 4 (°C)	56.9	57.7	62.3	63.6
	Absorber temperature 5 (bottom) (°C)	51.7	50.4	51.3	51.0
	Stripper temperature 1 (top) (°C)	103.3	99.6	95.6	91.3
	Stripper temperature 2 (°C)	107.7	105.1	103.0	99.7
Stripper temperature 3 (bottom) (°C)	123.2	119.0	112.7	106.5	
Reboiler temperature (°C)	124.9	120.4	113.8	107.6	

TABLE X. SUMMARY OF PILOT PLANT TEST 2 MAIN INPUT AND RESULTS [32]

IV. PROCESS SIMULATION RESULTS VALIDATION AND DISCUSSION

The validation of the equilibrium-stage model and rate-based model for the CO₂ capture process is done by comparing the simulation results with the presented experimental data. This validation will be done on two different levels. The macro analysis is used for validating the overall capture process behaviour and requirements. The micro level is used for validating and evaluating the columns behaviour by studying the temperature profiles within the absorber and the stripper.

A. Macro Analysis

The two input parameters (the solvent flow rate and the stripper pressure) have been varied in the process simulation to evaluate the overall process behaviour. The equilibrium-stage model and the rate-based model have been used for this simulation. The overall process evaluation is done by evaluating the three following output parameters:

1. The regeneration energy;
2. The CO₂ removal efficiency; and
3. The solvent capacity (rich loading).



iii. The regeneration energy requirement

The regeneration energy requirements from the modelling prediction have been compared with the data from the pilot plant under steady-state operating conditions. Figure 5 and Figure 6 show the regeneration energy requirement as function of solvent flow rate and stripper pressure, respectively.

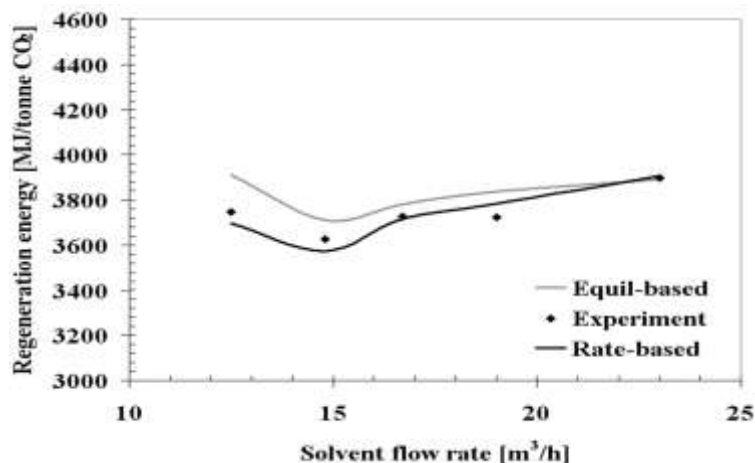


Figure 5. Regeneration energy requirement as a function of solvent flow rate for experimental and simulated results

Figure 5 shows that the regeneration energy requirement has a minimum value of 3.7 GJ/tonne CO₂ at a solvent flow rate around 15 m³/hr. This value is somehow lower than the published energy requirement for the conventional MEA process (3.8-4.0 GJ/tonne CO₂) [3, 27]. This small difference can be related to the different gas liquid ratio, operating conditions and measurement inaccuracy. The theoretical regeneration energy requirement can be divided into three parts: energy required to reverse the chemical reaction and release CO₂, energy for water evaporation and the energy required to heat up the solvent from the inlet temperature (around 105 °C) to the operating stripper temperature (around 120 °C). It is important to note that the first part, the amount of energy required to release the CO₂, is almost constant in the experiments due to the constant CO₂ removal efficiency of 90 %. This means that at lower solvent flow rate, a lower lean loading is required, which results in a higher energy requirement. However, higher solvent flow rate leads to an increase of the energy needed to heat up the solvent to the desired reboiler temperature. These two effects will increase the regeneration energy at high and low solvent flow rate, resulting in a minimum regeneration energy leading to an optimum solvent flow rate.

It can be seen from Figure 5 that the predictions of the model are in good agreement with the experimental data and closely follow the pilot plant trends. A difference of less than 5 % between the model's prediction and the pilot plant experimental data has been obtained. Comparing the equilibrium-stage approach and the rate-based approach, it can be seen that at high solvent flow rates the results of both models are almost identical. However, at lower solvent flow rate the rate-based model gives a better fit with the experimental data. This better agreement is expected due to the fact that the rate-based model includes the effect of reaction kinetics and mass transfer.

Next to the investigation of the effect of solvent flow rate, also the effect of the stripper pressure on the regeneration energy has been investigated. The increase in the stripper pressure, which is connected to the stripper temperature, results in a reduction of the regeneration energy requirement at an optimum pressure around 180 kPa (120.4 °C). This can be observed in **Error! Reference source not found.**, where the simulated and experimental data are depicted (the solvent reboiler temperature is shown between parentheses). Two effects can be noted. The first one is that a higher stripper temperature leads to an improvement in stripper efficiency. However, the second effect is that a higher pressure leads to a lower amount of CO₂ released. These two effects lead to the optimum which can be seen in Figure 6.

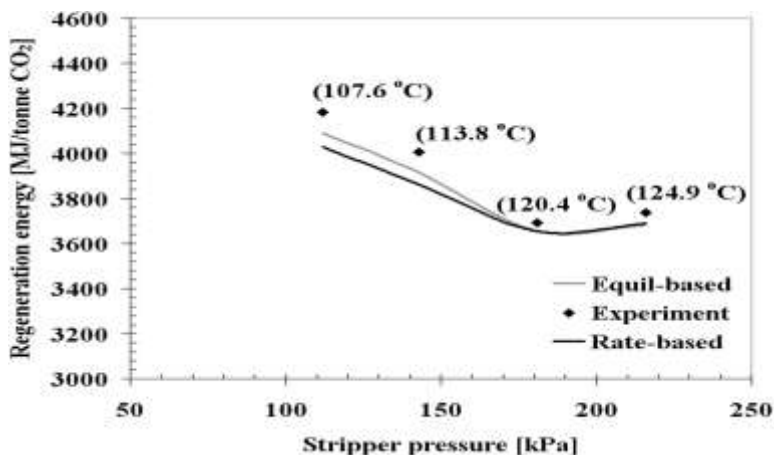


Figure 6. Reboiler duty as function of the stripper pressure and temperature for experimental and simulated results



Both modelling approaches have shown a slightly lower regeneration energy requirement comparing to the experimental results with an average difference of less than 5 %. Differences can be due to the experimental accuracy, heat losses and modelling accuracy. In general, it can be seen that the rate-based model results in lower regeneration energy comparing to the equilibrium-stage model. It is of importance to note that the regeneration energy is a function of the amount of CO₂ removed and the energy needed for heating up the solvent, the amount of steam leaving the stripper and reaction enthalpy. The reason for the difference between rate and equilibrium model can be due to the deviations in the values of the specific heat and heat of formation, which have been used in the rate-based model and the equilibrium-based model. These deviations are expected to influence the overall enthalpy in both of the absorber and the stripper.

iv. The carbon dioxide removal efficiency

In the first experimental test, the CO₂-removal percentage has been kept constant while changing the solvent flow rate (see Figure 7). The target of 90% removal (gas phase as a reference) has been achieved in the experiments by a slight increase in the reboiler temperature at lower solvent flow rate. In the experimental results, it can be seen that the CO₂ mass balances in the gas phase do not match with the CO₂ balances calculated from the liquid phase. These differences are related to measurement inaccuracy, especially in the solvent loading analysis. The simulation results of the removal efficiency are lower than the measured removal efficiencies calculated from the gas phase. The lower simulation results are connected to the fact that the simulation has been done using the measured solvent flow rate and lean solvent loading values as input. The modelled results are based on an open tear stream simulation where the lean loading is based on the experimental results. Therefore, it is logical that the simulation results are in good agreement with the CO₂ removal from the liquid phase analysis. It is tempting to conclude that the above mentioned deviation is coming from the experimental error of the measured loading and solvent flow rate. However, the measurement of the gas phase is considered more accurate that is why it is used for the evaluation of model results versus experimental CO₂ removal values.

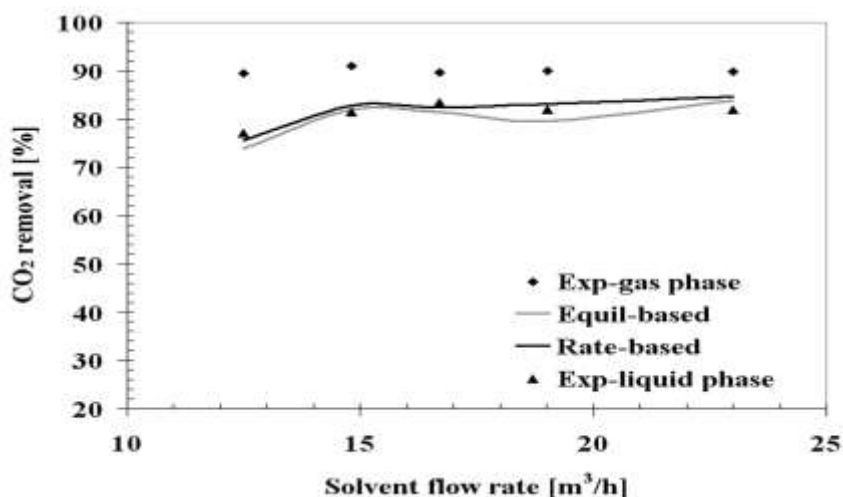


Figure 7. CO₂ removal % as function of solvent flow rate for experimental and simulated results

Regarding the stripper pressure, it can be expected that at constant temperature an increase in stripper pressure should lead to a decrease in removal efficiency. However, the experimental practice is to change both parameters trying to achieve 90% removal. However, in these experiments it was difficult to keep the CO₂ removal constant due to the fluctuations in the CO₂ concentration in the flue gas originating from changing boiler loads. In addition, at lower stripper pressure, the solvent flow rate has increased with increasing the lean loading. This has an effect on the removal efficiency. At the operating conditions, the modelling results show an agreement with the experimental data trends (see Figure 8). As stated before, the estimated removal ratios in the simulations results are lower than the measured data by almost 5 to 8 %. The rate-based approach presents a better agreement with the experimental data comparing to the equilibrium-stage model.

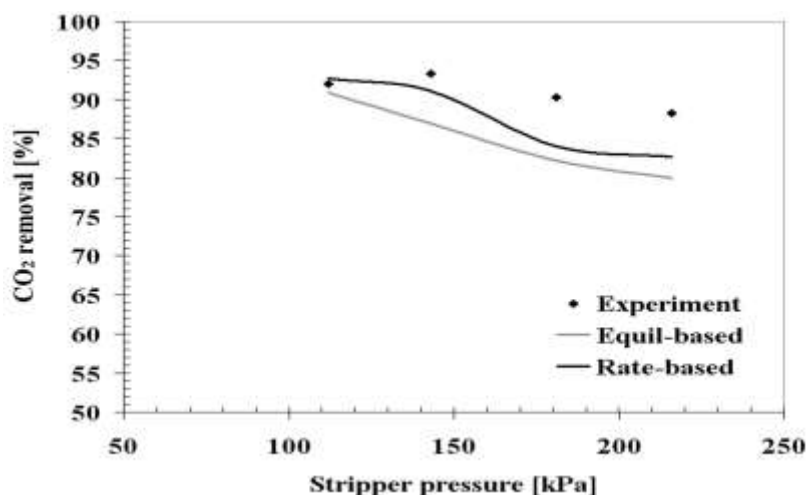


Figure 8. CO₂ removal % as function of stripper pressure for experimental and simulated results



v. The solvent capacity (rich loading)

The rich loading is the solvent loading with CO_2 at the absorber outlet. This loading is a good indication to the level of solvent saturation and gives an indication on how efficient the absorption process is. Out of the published and measured loading values [33], it is clear that the rich loading values from the experiments are very close to the maximum rich loading ($0.5 \text{ mol CO}_2/\text{mol MEA}$) that could be achieved at the specified operating absorber temperature ($40\text{-}55 \text{ }^\circ\text{C}$) and CO_2 partial pressure. This implies that the experimental process was running very close to equilibrium.

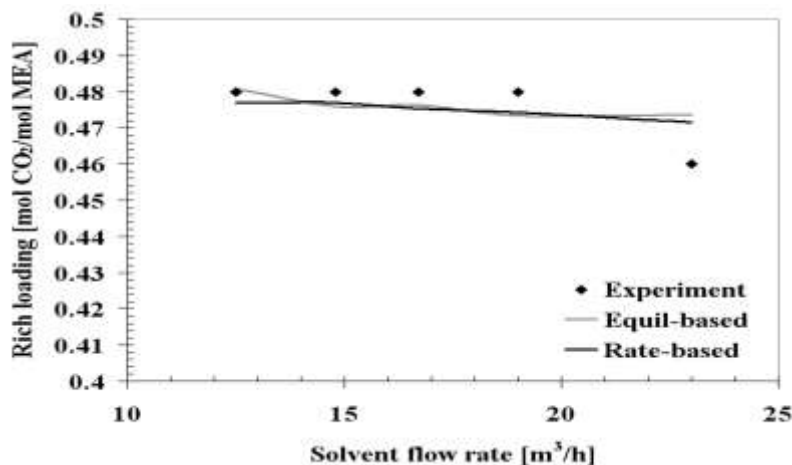


Figure 9. Solvent rich loading as function of solvent flow rate for experimental and simulated results

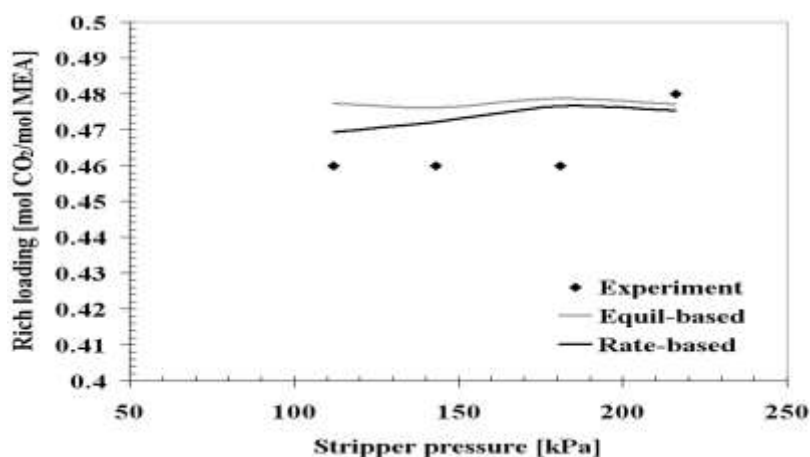


Figure 10. Solvent rich loading as function of stripper pressure for experimental and simulated results

In Figure 9 and Figure 10, it can be seen that there is a good agreement between the experimental results and the simulation values, for both modelling approaches. Comparing the two modelling approaches, it can be concluded that there is hardly any difference in the estimated rich loading between the equilibrium-stage and rate-based model. This conclusion is valid for the current situation where the absorber column is designed with a full height packing material. This indicates that for a full height system both approaches can be used for analysing and predicting the capture process requirement on macro scale.

B. Micro Analysis

The temperature profile in the absorber shows clearly the effect of the exothermal reaction between CO_2 and MEA (see Figure 11 and Figure 12). The temperature has a maximum ($70\text{-}75^\circ\text{C}$) above the 3rd bed (12.8 m of packing) after which it decreases to $58\text{-}63^\circ\text{C}$ at the absorber outlet and below 50°C after the washing section.

In Figure 11, the results show that at higher solvent flow rate the absorber outlet (top) temperature decreases. This can be due to the greater cooling capacity of the lean solvent feed at higher flow rates. It can be seen from Figure 12 that there is no major influence of stripper pressure on the absorber temperature profile. The slight differences are related to other parameters that have been changed during the experiment (the fluctuation of the CO_2 inlet concentration, the lean loading and the solvent flow rate).



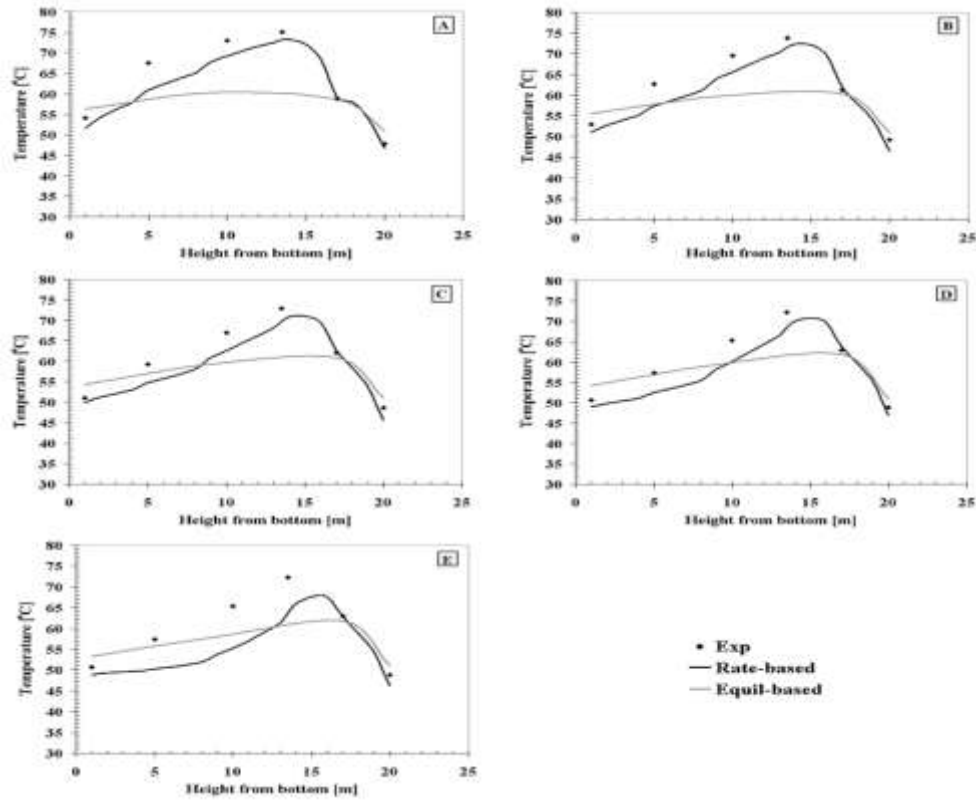


Figure 11. The absorber temperature profile at different solvent flow rates (A at 23 m³/hr, B at 19 m³/hr, C at 16.5 m³/hr, D at 14.8 m³/hr, E at 12.5 m³/hr)

The rate-based simulation results of the temperature profiles in the absorber have shown a good agreement with the experimental data. It can be observed that the predicted temperature profiles are lower than the measured values. This is related to the predicted lower CO₂ removal percentage, which leads to a lower overall heat of reaction. However, in the case of the equilibrium-stage approach, the predicted temperature profiles do not fit with the experimental data. The only points where the equilibrium-stage model shows agreement with the experimental data are at the absorber top and the bottom. This could be explained by the fact that the same gas and liquid inlet temperatures from the experimental data have been used in the simulation, also the absorber is running a near equilibrium conditions.

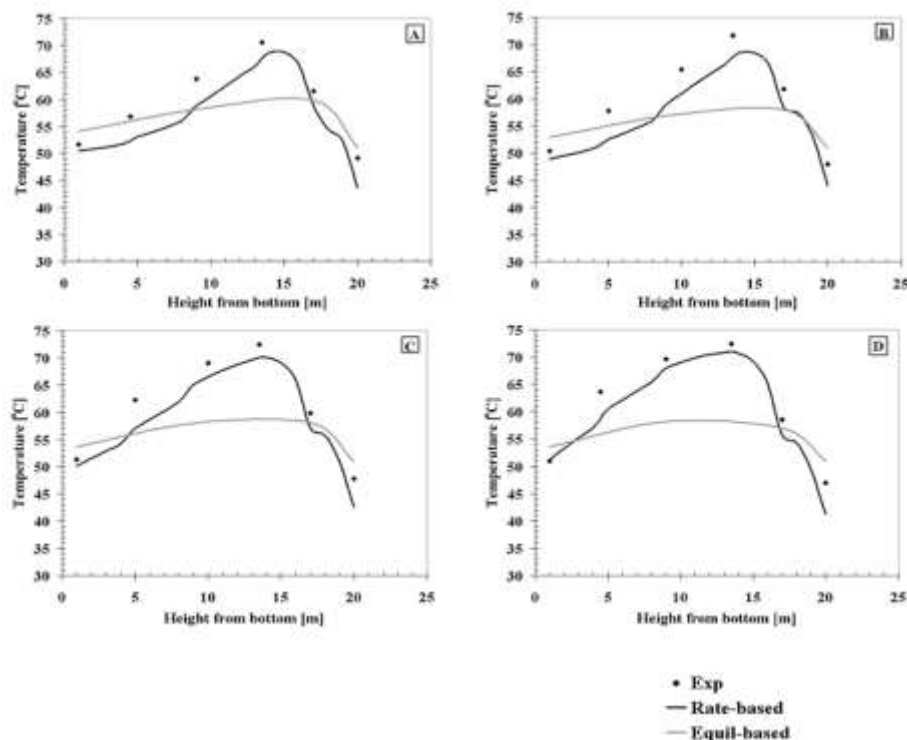


Figure 12. The absorber temperature profile at different stripper pressure (A at 220 kPa, B at 180 kPa, C at 140 kPa, D at 110 kPa)



In the stripper, the temperature decreases significantly between the bottom and the middle section of the stripper for the tests with high flow rates (16.7 to 23.0 m³/h); whereas only a minor temperature decrease is seen between the middle and top section (see Figure 13). This could indicate that most of the CO₂ is released in the bottom section. For the other two tests with low solvent flow rates (14.8 and 12.5 m³/h) the temperature decrease in the top section is more significant indicating that CO₂ also is released in the top section. Moreover, also more energy per amount of solvent is brought into the system at lower solvent flow rates to obtain a lower lean loading. In Figure 13 and Figure 14, it can be observed that the temperature profile of the equilibrium based model is less steeper compared to the rate based model. This is due to the more evenly spread of the CO₂ release over the column. Nevertheless, the internal temperature is better predicted with a rate based model than for an equilibrium based model.

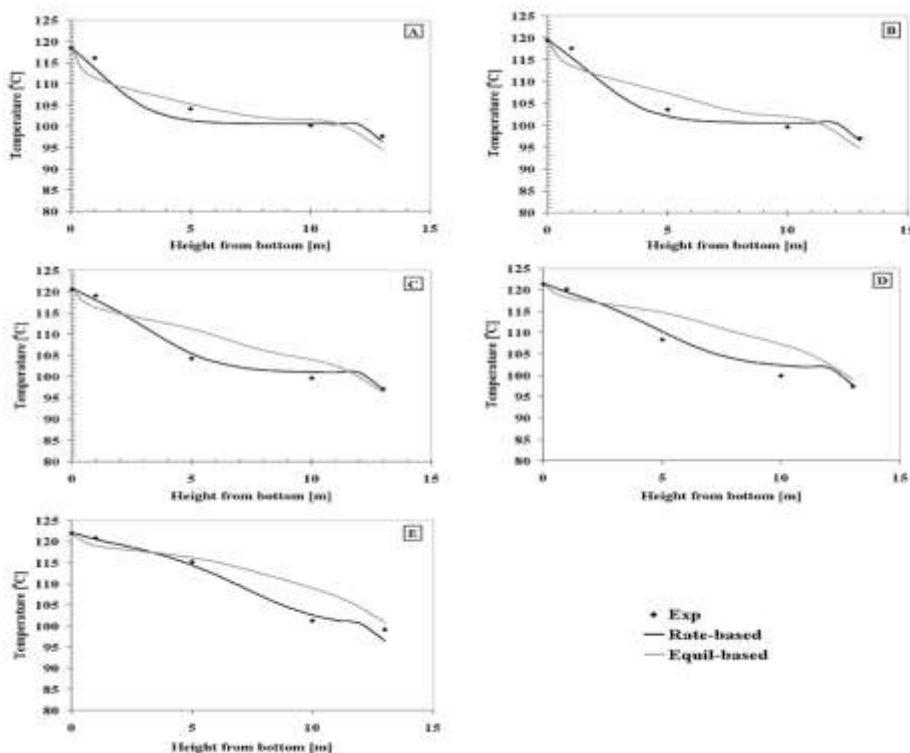


Figure 13. The stripper temperature profile at different solvent flow rates (A at 23 m³/hr, B at 19 m³/hr, C at 16.5 m³/hr, D at 14.8 m³/hr, E at 12.5 m³/hr)

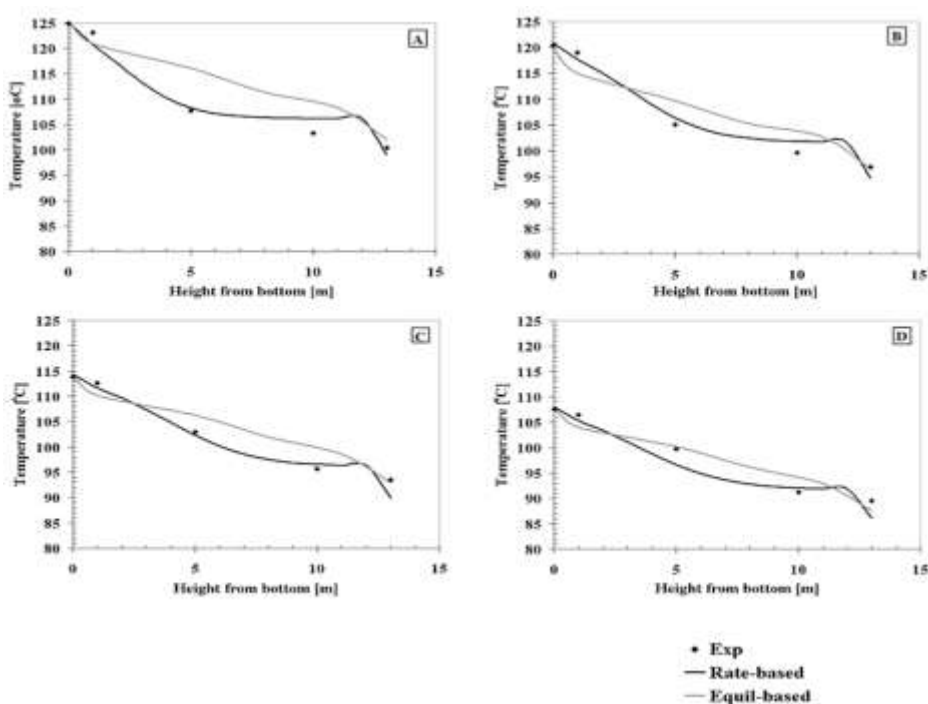


Figure 14. The stripper temperature profile at different stripper pressure (A at 220 kPa, B at 180 kPa, C at 140 kPa, D at 110 kPa)



Comparing the prediction of the temperature profile of the equilibrium based model for the absorber and the stripper, it can be stated that the equilibrium based model predicts the temperature profile of the stripper more accurate than for the absorber. This can be related to the fact that kinetic resistance is less dominant. Mass transfer rate and reaction kinetics are improved with the increase of temperature. Moreover, in the absorber the mass transfer of CO₂ is completely controlled in the liquid film. This is in contrast with the stripper, where in the lower section of the column, the mass transfer is controlled by 50 % in the gas phase and by 50 % in the liquid phase.

ACKNOWLEDGMENT

The authors would like to thank the European Project on the 'Capture and Geological Storage of CO₂ (CASTOR)' for their financial and technical support.

CONCLUSION

In this work, the pilot plant experimental results were evaluated and compared to the simulation results. Equilibrium-based and rate-based models are used for describing the reactive absorption process of carbon dioxide based on MEA. These models are implemented within the Aspen plus flow sheet simulation tool.

The process parameter variation tests indicate that the lowest regeneration energy requirement of 3.7 GJ/ton CO₂ is obtained at solvent flow rates of 12.5 to 19 m³/h. The tests also show that the specific regeneration energy requirement increases as the stripper pressure is reduced from 185 to 123-150 kPa. On the contrary, increasing the pressure from 185 to 220 kPa has no effect on the regeneration energy requirement. The results of the minimum regeneration energy requirement are in good agreement between the experimental and the simulation results.

The process validation on macro scale shows a good agreement between the experiment and simulation results from both modelling approaches. These results indicate that both the equilibrium-stage and rate-based models can predict the overall capture process in an appropriate way for a full height system. However, the equilibrium approach is advantageous due to the simple calculation approach and the simulation time saving.

The micro analysis shows that the rate-based model gives a better prediction of the columns temperature profiles and internal behaviour comparing to the equilibrium-stage approach. Out of this work, it can be concluded that for a detailed process design the rate-based approach should be applied.

In addition, the presented results support the idea of extending the use of these two models for benchmarking different CO₂ capture solvents and process conditions.

REFERENCES

- [1] H. Audus, *Leading Options for the Capture of CO₂ at Power Stations*, Greenhouse Gas Control Technologies, P. Riemer, B. Eliasson, A. Wokaun (eds.), Elsevier Science, Ltd., Kidlington, United Kingdom. 1998, pp. 91-96.
- [2] M. Simmonds, P. Hurst, *Post combustion technologies for CO₂ capture: a techno-economic overview of selected options*, Paper presented at GHGT-7. 2004; Vancouver, Canada.
- [3] C. Mariz, *Carbon dioxide recovery: large-scale design trends*. J. Can. Pet. Technol. 37 (1998) 42-47.
- [4] A. Tobiesen, O. Juliussen, H. Svendsen, *Experimental validation of a model for simulating the desorber and connected unit operations for a CO₂ post-combustion capture pilot plant using monoethanolamine (MEA)*. 8th International conference on greenhouse gas control technology. 2006, Trondheim, Norway.
- [5] J. Li, X. Liang, *CO₂ capture modelling for pulverised coal-fired power plants: A case study of an existing 1 GW ultra-supercritical power plant in Shandong, China*. Sep and Pur Tech. 94 (2012), 138-145
- [6] S. Lee, S. Maken, J. Park, H. Song, J. Park, J. Shim, J. Kim, H. Eum, *A study on the carbon dioxide recovery from 2 ton-CO₂/day pilot plant at LNG based power plant*. Fuel. 87 (8-9) (2008) 1734-1739.
- [7] A. Tobiesen, T. Mejdell, H. Svendsen, *A comparative study of experimental and modeling performance results from the CASTOR Esbjerg pilot plant*. 8th International conference on greenhouse gas control technology. 2006, Trondheim, Norway.
- [8] R. Idem, M. Wilson, P. Tontiwachwuthikul, A. Chakma, A. Veawab, A. Aroonwilas, D. Gelowitz, *Pilot Plant Studies of the CO₂ capture performance of aqueous MEA and mixed MEA/MDEA solvents at the university of Regina CO₂ capture technology development plant and the boundary dam CO₂ capture demonstration plant*. Ind. Eng. Chem. Res. 45 (8) (2005) 2414 -2420.
- [9] J. Gabrielsena, H. Svendsen, M. Michelsena, E. Stenbya, G. Kontogeorgis, *Experimental validation of a rate-based model for CO₂ capture using an AMP solution*. Chem. Eng. Sci. 62 (2007) 2397-2413.
- [10] R. Notz1, H. Mangalapally, H. Hasse, *Post combustion CO₂ capture by reactive absorption: Pilot plant description and results of systematic studies with MEA*. Int J of Greenhouse Gas Control. 6 (2012) 84-112.
- [11] T. Carey, J. Hermes, G. Rochelle, *A model of acid gas absorption/stripping using methyldiethanolamine with added acid*. Gas separation and purification. 5 (1991) 95-109.
- [12] G. Escobillana, J. Saez, J. Pérez-Correa, H. Neuburg, *Behaviour of absorption/stripping columns for CO₂-MEA system: Modelling and experiments*. Can J Chem Eng. 69 (1991) 969-977.
- [13] M. Pacheco, G. Rochelle, *Rate-based modelling of reactive absorption of CO₂ and H₂S into aqueous methyldiethanolamine*. Ind Eng Chem Res 37 (1998) 4107-4117.
- [14] N. Al-Baghli, S. Pruss, V. Yesavage, M. Selim, *A rate-based model for the design of gas absorbers for the removal of CO₂ and H₂S using aqueous solutions of MEA and DEA*. Fluid Phase Equilibria. 185 (2001) 31-43.
- [15] L. Kucka, I. Müller, E. Kenig, A. Górak, *On the modelling and simulation of sour gas absorption by aqueous amine solutions*. Chem Eng Sci. 58 (2003) 3571-3578.
- [16] C. Biliyok, A. Lawal, M. Wang, F. Seibert, *Dynamic modelling, validation and analysis of post-combustion chemical absorption CO₂ capture*. Int J of Greenhouse Gas Control, 9 (2012) 428-445.
- [17] M. Aroua, M. Haji-Sulaiman, K. Ramasamy, *Modelling of carbon dioxide absorption in aqueous solutions of AMO and MDEA and their blends using Aspenplus*. Sep Pur Tech. 29 (2002) 153-162.



- [18] S. Freguia, G. Rochelle, Modelling of CO₂ capture by aqueous Monoethanolamine. *AIChE J.* 49 (7) (2003) 1676-1686.
- [19] H. Chang, C. Shih, Simulation and optimization for power plant flue gas CO₂ absorption-stripping systems. *Sep Sci Tech.* 40 (2005) 877-909.
- [20] CASTOR project. CO₂ from capture to storage. An Integrated Project partially funded by the European Commission under the 6th Framework Programme (Contract n8 SES6-CT-2004-502586). www.co2-castor.com.
- [21] P. Feron, M. Abu-Zahra, P. Alix, O. Biede, P. Broutin, H. de Jong, J. Kittel, J. Knudsen, P. Vilhelmsen, Development of post-combustion capture of CO₂ within the CASTOR Integrated Project: Results from the pilot plant operation using MEA. 3th international conference on Clean Coal Technology for our future. 2007, Sardinia, Italy.
- [22] P. Feron, J. Knudsen, J. Kittel, H. de Jong, P. Vilhelmsen, O. Biede, J. Jensen, K. Hansen, K. Lauritsen, P. Alix, P. Report on first testing campaign with CASTOR pilot plant at Esbjerg power plant. CASTOR project deliverable D2.5.3, 2006.
- [23] M. Klöker, E. Kenig, A. Hoffmann, P. Kries, A. Górak, A. Rate-based modelling and simulation of reactive separations in gas/vapour-liquid systems. *Chem Eng Process.* 44 (2005) 617-629.
- [24] R. Taylor, R. Krishna, Review: Modelling reactive distillation. *Chem Eng Sci.* 55 (2000) 5183-5229.
- [25] B. D. Smith, Design of equilibrium stage processes (chemical engineering series). McGraw-Hill Inc. NY, USA, 1963.
- [26] Aspen Plus. Aspen Plus one version V7, Cambridge, MA, USA: Aspen technology Inc. 2008.
- [27] M. Abu-Zahra, L. Schneiders, J. Niederer, P. Feron, G. Versteeg, CO₂ capture from power plants: Part I. A parametric study of the technical performance based on mono-ethanolamine. *Int. J. Greenhouse Gas Con.* 1 (2006) 37-46.
- [28] D. Austgen, G. Rochelle, X. Peng, C. Chen, Model of vapour-liquid equilibria for aqueous acid gas-alkanolamine systems using the Electrolyte-NRTL equation. *Ind. Eng. Chem. Res.* 28 (1989) 1060-1073.
- [29] AspenTech, <support.aspentech.com>. Rate-based model of the CO₂ capture process by MEA using Aspen Plus.
- [30] R. Baur, A. Higler, R. Taylor, R. Krishna, Comparison of equilibrium stage and nonequilibrium stage models for reactive separation. *Chem Eng J.* 76 (2000) 33-47.
- [31] J. Lee, F. Otto, A. Mather, Equilibrium between carbon dioxide and aqueous Monoethanolamine solutions. *J. appl. Chem. Biotechnol.* 26 (1976) 541-549.
- [32] M. Abu-Zahra, J. Knudsen, P. Vilhelmsen, O. Biede, J. Jensen, K. Hansen, Report on second testing campaign with CASTOR pilot at Esbjerg power plant. 2007; CASTOR project deliverable D 2.5.4.
- [33] A. Kohl, R. Nielsen, Gas Purification (5th edition). Gulf publishing company, Texas, 1997.

