

# Simulation of CO<sub>2</sub> Absorption at TCM Mongstad for Performance Data Fitting and Prediction

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## Abstract

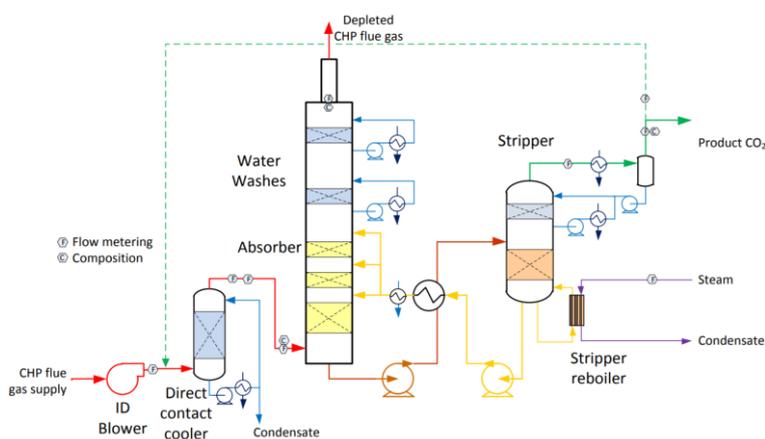
The main purpose of this work has been to fit simulated models to performance data from Test Centre Mongstad (TCM), and evaluate whether fitted parameters for one scenario (a set of experimental data at specified conditions) give reasonable predictions at other conditions. Five scenarios from the amine based CO<sub>2</sub> absorption process at TCM have been simulated in a rate-based model in Aspen Plus and an equilibrium based model in Aspen HYSYS and Aspen Plus. It was evaluated whether a fitted interfacial area (for the rate-based model) or an E<sub>M</sub>-profile (Murphree efficiency on each of 24 stages for the equilibrium based model) gave a good prediction of CO<sub>2</sub> removal rate and temperature profile for other conditions. An indication of the predictive performance of the rate-based model is that the interfacial area fitted to the different scenarios had to be varied between 0.29 and 1.0 to obtain the experimental CO<sub>2</sub> removal efficiency. Using a specific E<sub>M</sub>-profile was able to predict both the CO<sub>2</sub> removal and the temperature profile for all the scenarios reasonably well. An E<sub>M</sub>-factor multiplying all the E<sub>M</sub> values in an E<sub>M</sub>-profile from another scenario was fitted to values between 0.60 and 1.02 for all the scenarios.

*Keywords: CO<sub>2</sub>, amine, absorption, simulation*

## 1 Introduction

The CO<sub>2</sub> Technology Centre Mongstad (TCM) close to Bergen is the world's largest test facility for CO<sub>2</sub> capture technology. For testing of CO<sub>2</sub> absorption into amine based solvents, there is an absorption column with a rectangular cross section equivalent to a packing diameter of 3 meter, and a packing height up to 24 meter. There have been performed performance tests of CO<sub>2</sub> absorption from flue gas into 30 wt-% monoethanol amine (MEA) in 2013 (Thimsen et al., 2014; Hamborg et al., 2014) and in 2015 (Gjernes et al., 2017; Faramarzi et al., 2017). Figure 1 shows the principle of the amine based CO<sub>2</sub> absorption and also the desorption facility at TCM. In this work, especially the total CO<sub>2</sub> capture rate (in % of incoming CO<sub>2</sub>) in the absorption section and the temperature profile from top to bottom of the absorption section are the evaluated parameters.

The first aim of this work is to compare results from simulations with performance data for CO<sub>2</sub> absorption into 30 wt-% MEA at TCM using different simulation tools. The second aim, which is specific for this work, is to test whether fitted parameters for one scenario (a set of experimental data at specified conditions) give reasonable predictions at other conditions. The work is based on the Master Thesis of Sofie Fagerheim (2019) and on earlier work at the University of South-Eastern Norway.



**Figure 1.** Simplified process diagram of the amine based CO<sub>2</sub> capture plant at TCM (Thimsen et al., 2014)

In earlier work (Sætre, 2016; Røsvik, 2018; Øi et al., 2018) the equilibrium models (in Aspen Plus and Aspen HYSYS) were fitted to one specific scenario by adjusting the Murphree efficiency ( $E_M$ ) for each stage, and the rate-based model (in Aspen Plus) was fitted to another scenario by adjusting the interfacial area factor. In literature there is very little research on predicting CO<sub>2</sub> absorption with models fitted for other conditions.

In this work, 5 sets of experimental data (scenarios) from the amine based CO<sub>2</sub> capture process at TCM have been compared with simulations of different equilibrium based models and a rate-based model. The  $E_M$ -profile was then adjusted with an  $E_M$ -factor in the other scenarios to achieve a good fit to the temperature profile.

## 2 Process simulation tools and CO<sub>2</sub> absorption models

There are several process simulation tools available for CO<sub>2</sub> absorption processes. The key content in these programs are models for vapour/liquid equilibrium calculations and efficient flow-sheet solvers. Some of the programs (especially the programs with rate-based tools) also include models for chemical, heat transfer and mass transfer kinetics. Commercially available programs are Aspen Plus, Aspen HYSYS, ProTreat, ProMax and ChemCad. Some companies have internal programs, SINTEF use the program CO2SIM.

There are different equilibrium models used for the MEA/water/CO<sub>2</sub> system describing the relations between the vapour and liquid phase at equilibrium. Aspen Plus has an Electrolyte-NRTL equilibrium model which is based on Austgen et al. (1989). The new version of Aspen HYSYS has a new acid gas model. This work is mainly based on the earlier models in Aspen HYSYS which is based on the amine package with the Kent-Eisenberg (1976) and the Li-Mather (1994) equilibrium models.

Aspen Plus has included rate-based models. For CO<sub>2</sub> absorption, there are several models available for heat transfer, mass transfer and kinetics which can be included in a rate-based simulation. A specific rate-based example file for CO<sub>2</sub> removal using MEA is available with the Aspen Plus program. The parameters in this file are mostly based on the work of Zhang et al. (2009) who fitted Aspen Plus simulations to experimental runs at a CO<sub>2</sub> absorption pilot plant. Different rate-based models have been developed for TCM in the Master Thesis works of Larsen (2014), Desvignes (2015) and Sætre (2016). The gCCS program has been used for dynamic simulations at TCM (Bui et al., 2020).

Equilibrium based absorption models are based on the assumption of equilibrium at each stage. The model can be extended by using a Murphree efficiency (the ratio of the change in mole fraction from a stage to the

next divided by the change assuming equilibrium). An advantage using Murphree efficiencies compared to rate-based simulations is that it is simpler and fewer parameters have to be specified. In the Master Thesis work of Zhu (2015), Sætre (2016) and Røsvik (2018), a Murphree efficiency for each stage (meter of packing) was estimated for one set (scenario) of TCM data (Hamborg et al., 2014). Zhu (2015) fitted a constant Murphree efficiency to 0.09 in Aspen HYSYS for all stages to obtain the experimental CO<sub>2</sub> capture rate. Using different fitted Murphree efficiencies for each stage, good agreement between the measured and simulated temperature profile was also obtained.

There are a few comparisons between different simulation tools for CO<sub>2</sub> absorption in literature. Luo et al. (2009) tested Aspen RadFrac, ProTreat, ProMax, Aspen RateSep, CHEMASIM from BASF and CO2SIM from SINTEF/NTNU by comparing with pilot plant data. The result was that all models were capable of fitting the CO<sub>2</sub> capture rate, but the temperature and concentration profiles were not well predicted. When comparing Aspen HYSYS and Aspen Plus, Øi (2012) claimed that there were small differences between the tested equilibrium models, and that a rate-based and equilibrium based model with estimated Murphree efficiencies gave similar results. In the work by Øi et al. (2018), different models were compared for 4 scenarios from TCM. The results showed that equilibrium and rate-based models perform equally well in both fitting performance data and in predicting performance at changed conditions.

## 3 Data, Methods and Specifications

### 3.1 Performance Data from TCM

Performance data for this work have been taken from 5 sets of conditions (scenarios) at TCM. They are from campaigns in 2013 and 2015 for approximately 30 wt-% MEA in water. 24 meter of packing height (the maximum available) was used in these scenarios.

The data (mainly conditions of the inlet gas stream and the inlet amine stream to the absorption section) for the 5 scenarios are listed in Table 1 to Table 5. Table 1 to 4 are for the same conditions as in Øi et al. (2018). The data are from scenarios documented in Hamborg et al. (2014), Gjernes et al. (2017) and Faramarzi et al. (2017), but some of the data are converted to make them suitable for input to simulation programs.

The 5 scenarios which have been selected in this work are named H14 and 6w from 2013 (Hamborg et al., 2014), 2B5 and Goal1 from 2015 (Gjernes et al., 2017) and F17 from 2015 (Faramarzi et al., 2017). The names have been used internally at TCM, except the H14 and F17 scenarios. The 5 scenarios were run with amine concentrations close to 30 wt-% MEA in water.

**Table 1** Scenario H14 experimental input data for process simulations.

Input data to the simulations			
Amine inlet		Flue gas inlet	
Flow rate [kg/h]	54900	Flow [kmol/h]	2022
Temperature [°C]	36.5	Temperature [°C]	25.0
MEA [mol%]	10.94	CO <sub>2</sub> [mol%]	3.7
H <sub>2</sub> O [mol%]	86.54	H <sub>2</sub> O [mol%]	2.95
CO <sub>2</sub> [mol%]	2.52	O <sub>2</sub> [mol%]	13.6
Pressure [bara]	1.0313	N <sub>2</sub> [mol%]	79.75
		Pressure [bara]	1.063

**Table 2** Scenario 6w experimental input data for process simulations.

Input data to the simulations			
Amine inlet		Flue gas inlet	
Flow rate [kg/h]	54915	Flow [kmol/h]	2005
Temperature [°C]	36.9	Temperature [°C]	25
MEA [mol%]	11.13	CO <sub>2</sub> [mol%]	3.57
H <sub>2</sub> O [mol%]	86.37	H <sub>2</sub> O [mol%]	3.0
CO <sub>2</sub> [mol%]	2.5	O <sub>2</sub> [mol%]	13.6
Pressure [bara]	1.0313	N <sub>2</sub> [mol%]	79.83
		Pressure [bara]	1.063

**Table 3** Scenario 2B5 experimental input data for process simulations.

Input data to the simulations			
Amine inlet		Flue gas inlet	
Flow rate [kg/h]	49485	Flow [kmol/h]	2022
Temperature [°C]	36.8	Temperature [°C]	28.2
MEA [mol%]	11.67	CO <sub>2</sub> [mol%]	3.57
H <sub>2</sub> O [mol%]	85.65	H <sub>2</sub> O [mol%]	3.7
CO <sub>2</sub> [mol%]	2.68	O <sub>2</sub> [mol%]	14.6
Pressure [bara]	1.0313	N <sub>2</sub> [mol%]	78.08
		Pressure [bara]	1.063

**Table 4** Scenario Goal1 experimental input data for process simulations.

Input data to the simulations			
Amine inlet		Flue gas inlet	
Flow rate [kg/h]	44391	Flow [kmol/h]	2017
Temperature [°C]	28.6	Temperature [°C]	25
MEA [mol%]	12.04	CO <sub>2</sub> [mol%]	3.62
H <sub>2</sub> O [mol%]	85.19	H <sub>2</sub> O [mol%]	3.1
CO <sub>2</sub> [mol%]	2.77	O <sub>2</sub> [mol%]	14.3
Pressure [bara]	1.0313	N <sub>2</sub> [mol%]	79
		Pressure [bara]	1.063

**Table 5** Scenario F17 experimental input data for process simulations.

Input data to the simulations			
Amine inlet		Flue gas inlet	
Flow rate [kg/h]	57434	Flow [kmol/h]	2558
Temperature [°C]	37.0	Temperature [°C]	29.8
MEA [mol%]	11.44	CO <sub>2</sub> [mol%]	3.70
H <sub>2</sub> O [mol%]	86.27	H <sub>2</sub> O [mol%]	3.70
CO <sub>2</sub> [mol%]	2.29	O <sub>2</sub> [mol%]	14.60
Pressure [bara]	1.0313	N <sub>2</sub> [mol%]	78.00
		Pressure [bara]	1.0100

The results from the performance data scenarios to be compared with simulations, are the total CO<sub>2</sub> capture rate and the temperature profile measured for every meter of the packing. The temperature was measured at different locations for each meter of packing, and the different locations were named A, B, C and D.

For the H14 and F17 scenario, a mean value for each meter of packing was specified in the temperature profile (Hamborg, 2014; Faramarzi 2017).

### 3.2 Specifications for the Equilibrium Based Simulation Tools

When using Aspen HYSYS, the Amine Package with the Kent-Eisenberg model was used with non-ideal vapor phase. The Acid Gas model, which is the recommended equilibrium model in the last Aspen HYSYS version was used as a check. When using Aspen Plus, the Electrolyte-NRTL (Non-Random-Two-Liquid) model was used. The figures in this work show only results from Aspen Plus.

In the Master Thesis work of Zhu (2015), Sætre (2016) and Røsvik (2018) a Murphree efficiency for each of the 24 stages (meter of packing) was estimated for the TCM data set (Hamborg et al., 2014). Different approaches for fitting the E<sub>M</sub> profile to the temperature profile was a constant E<sub>M</sub> for every stage (Zhu, 2015) and a linear Murphree efficiency profile (Øi, 2012). A high Murphree efficiency at the top stages and then gradually reduced to a constant equal to 0.01 (close to 0) for the bottom stages fitted the temperature profile very well for the H14 scenario (Zhu, 2015; Sætre, 2017; Røsvik, 2018). Fagerheim (2019) fitted two other E<sub>M</sub> profiles, SF1 and SF2 to the performance data. The SF1 and SF2 profiles has E<sub>M</sub> = 0.01 on the 5 lowest stages compared to the Zhu profile which has E<sub>M</sub> = 0.01 on the 10 lowest stages. These profiles were specified in both the Aspen HYSYS and Aspen Plus simulation tool. The different E<sub>M</sub> profiles used in this work are presented in Table 6.

**Table 6** Murphree efficiency profiles used in this work

Murphree efficiency profiles in the packed column from top to bottom					
EM	0,1	Zhu	Lin	SF1	SF2
1	0.1	0.2300	0.17	0,2450	0,2400
2	0.1	0.2192	0.17	0,2425	0,2350
3	0.1	0.2085	0.17	0,2400	0,2300
4	0.1	0.1977	0.17	0,2375	0,2250
5	0.1	0.1869	0.17	0,2350	0,2200
6	0.1	0.1800	0.16	0,2325	0,2150
7	0.1	0.1762	0.15	0,2300	0,2300
8	0.1	0.1546	0.14	0,2000	0,2000
9	0.1	0.1438	0.13	0,1700	0,1700
10	0.1	0.1331	0.12	0,1400	0,1400
11	0.1	0.1223	0.11	0,1100	0,1100
12	0.1	0.1115	0.10	0,0800	0,0800
13	0.1	0.1007	0.09	0,0500	0,0550
14	0.1	0.0900	0.08	0,0475	0,0525
15	0.1	0.0100	0.07	0,0450	0,0500
16	0.1	0.0100	0.06	0,0425	0,0475
17	0.1	0.0100	0.05	0,0400	0,0450
18	0.1	0.0100	0.04	0,0375	0,0425
19	0.1	0.0100	0.03	0,0350	0,0400
20	0.1	0.0100	0.02	0,0001	0,0001
21	0.1	0.0100	0.01	0,0001	0,0001
22	0.1	0.0100	0.01	0,0001	0,0001
23	0.1	0.0100	0.01	0,0001	0,0001
24	0.1	0.0100	0.01	0,0001	0,0001

### 3.3 Specifications for the Rate-Based Tool

The specifications in the rate-based Aspen Plus simulation tool at TCM have been developed during several years and different versions have been used (Larsen, 2014; Desvignes, 2015; Sætre 2016). In this work, the same parameters as in Øi et al. (2018) were used. Most of these specifications are based on the work by Zhang et al. (2009) where Aspen Plus rate-based simulations were fitted to pilot scale experiments of CO<sub>2</sub> absorption at the University of Texas. Detailed documentation of the rate-based model can be found in the Aspen Plus program documentation.

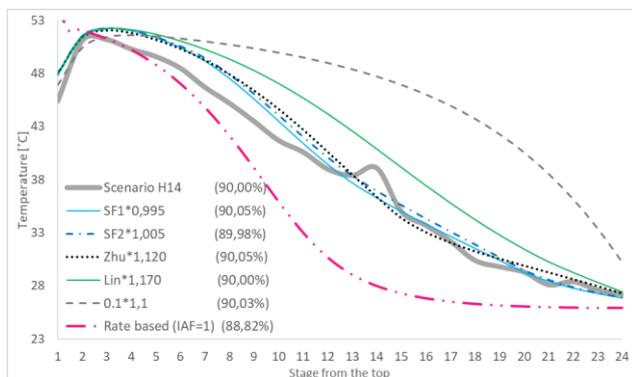
## 4 Results and discussion

### 4.1 General Results

The results shown for each model in the scenario figures are the capture rate and the temperature profile. The model parameters (in the case of the rate-based model the interfacial area factor) are adjusted to achieve the specified capture rate. In the case of using an E<sub>M</sub> profile, all the E<sub>M</sub> values were multiplied with an E<sub>M</sub>-factor which is the only parameter. In some cases it was not possible to obtain the specified capture rate. In that case the parameter was adjusted to come as close as possible to the specified capture rate. The emphasis in this work is on comparison of the temperature profiles.

### 4.2 Scenario H14

Comparisons between measured and simulated temperature profiles are shown in Figure 2. In the figure, the number after each model is the E<sub>M</sub>-factor (adjusted to achieve the capture rate given in the parenthesis). The broad solid line is representing the experimental data as an average of 4 measured temperatures at each stage. The non-smooth form of the experimental line indicates that there is some uncertainty in the measurements.

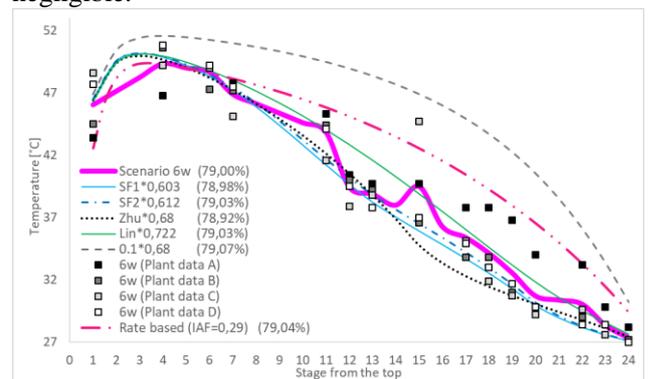


**Figure 2.** Comparison of plant data scenario H14 and simulated temperature profiles (Fagerheim, 2019).

The model with constant E<sub>M</sub> overpredicts the temperature to a large degree in the lower part of the column. The rate-based model (with interfacial area 1.0) underpredicts the temperature. The model with a linear E<sub>M</sub> profile gives a reasonable temperature profile. The adjusted E<sub>M</sub> profiles give the best fit. This is as expected because all the E<sub>M</sub> values (24 parameters) are actually fitted to this scenario. In the work of Øi et al. (2018), the rate-based model gave a temperature profile closer to the experimental line for the H14 scenario using Aspen HYSYS. In that case, an interfacial area of 0.55 was used, but this does not achieve the capture rate in the Aspen Plus simulations. Even with an interfacial area factor of 1.0, the Aspen Plus simulations only achieved a capture rate slightly below the experimental value of 90 %. The slight difference between the results using Aspen HYSYS and Aspen Plus, is probably due to different vapour/liquid equilibrium models.

### 4.3 Scenario 6w

Comparisons between measured and simulated temperature profiles are shown in Figure 3. The experimental temperatures are shown in the figure, and the broad solid line shows the average. It is clear that the uncertainty in the experimental temperatures are not negligible.

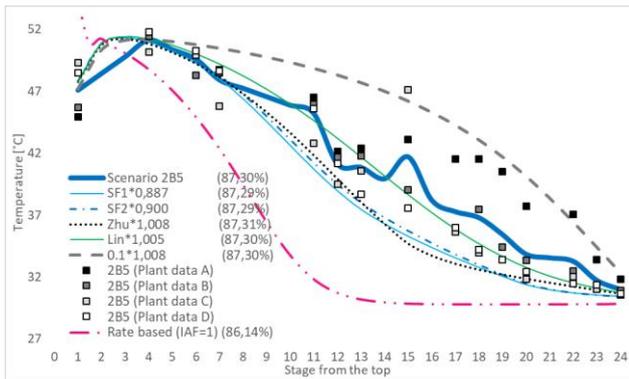


**Figure 3.** Comparison of plant data scenario 6w and simulated temperature profiles (Fagerheim, 2019).

In this scenario all the models except the constant E<sub>M</sub> model give reasonable temperature profiles. In this case, the rate-based model overpredicts the temperature in the lower part of the column. The interfacial area had to be adjusted to 0.29 to achieve the experimental capture rate. The models with E<sub>M</sub> profiles fitted to the H14 scenario, had to be adjusted with factors from 0.60 to 0.72 to obtain the experimental capture rate.

### 4.4 Scenario 2B5

Comparisons between measured and simulated temperature profiles are shown in Figure 4. The figure shows a higher uncertainty in the experimental temperatures than the other scenarios.



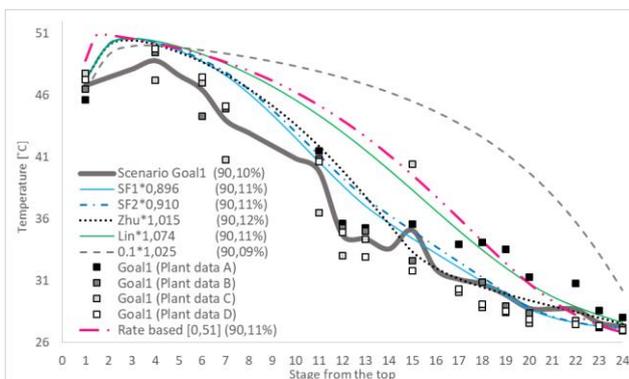
**Figure 4.** Comparison of plant data scenario 2B5 and simulated temperature profiles (Fagerheim, 2019).

As in the H14 scenario, the model with constant  $E_M$  overpredicts the temperature in the lower part of the column and the rate-based model underpredicts the temperature. The interfacial area in the rate-based model had to be adjusted to 1.0 to (almost) achieve the experimental capture rate.

The  $E_M$  profile models give a good fit with an adjustment factor between 0.89 and 1.01. The uncertainty in the data is too large to conclude which model is closest to the experimental data.

#### 4.5 Scenario Goal1

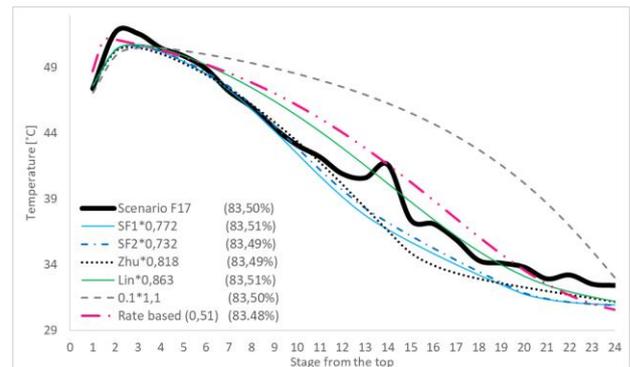
Comparisons between measured and simulated temperature profiles are shown in Figure 5. In this scenario all the models overpredicts the temperature in the middle of the column. The rate-based model and the linear model overpredicts the temperature with about 10 K. The  $E_M$  profile models overpredicts the temperature with less than about 3 K. The interfacial area was adjusted to 0.51, while the other models were adjusted with factors between 0.90 and 1.02.



**Figure 5.** Comparison of plant data scenario Goal1 and simulated temperature profiles (Fagerheim, 2019).

#### 4.6 Scenario F17

Comparisons between measured and simulated temperature profiles are shown in Figure 6. The broad solid line is representing the experimental data. The experimental line which is smoother than in the earlier scenarios indicates that the experimental uncertainty is lower in the F17 scenario. There is however an outlier in the experimental temperature on stage 14 in all the scenarios. The linear model is closest to the experimental data for this scenario. The rate-based model overpredicts the temperature slightly in the middle part of the column.



**Figure 6.** Comparison of plant data scenario F17 and simulated temperature profiles (Fagerheim, 2019).

The  $E_M$  models underpredicts the temperature with up to 3 K in the lower part of the column. The interfacial area was adjusted to 0.51, while the other models were adjusted with factors between 0.72 and 0.86.

#### 4.7 General discussion

Only the results using the Electrolyte-NRTL model in Aspen Plus were shown in the figures in this work. Earlier work has shown that different equilibrium models give similar results (Sætre, 2016; Øi et al., 2018), and this has also been confirmed in simulations in Fagerheim (2019).

Some references (Zhang et al., 2009; Larsen, 2014; Desvignes, 2015) have compared also the concentration profiles when comparing performance data and simulation tools. This may give additional information for analysis.

Only performance data with 24 meter of packing was used in this and earlier work. The low Murphree efficiency on the lowest stages indicate that the number of stages in the column is too high. Equilibrium based and rate-based models could also be fitted to performance data for lower packing heights which are available for e.g. 18 meter packing height (Gjernes, 2017).

This work indicates that equilibrium based models give better predictions at other conditions. This is probably not a general conclusion. Equilibrium based models are very empirical and are probably only useful when the conditions do not change much. Some have claimed (Zhang et al., 2009) that rate-based models are superior to equilibrium based models. There are several factors and parameters in the rate-based models which are not well known, typically specifications for fluid flow, heat transfer and mass transfer mechanisms in structured packings. When the knowledge of these factors becomes better known, the rate-based models can probably be made more predictive.

## 5 Conclusions

Five different scenarios from the CO<sub>2</sub> capture process at TCM have been simulated in a rate-based model in Aspen Plus and in an equilibrium-based model in Aspen HYSYS and Aspen Plus. In the rate-based model, the performance data was fitted by changing only the interfacial area factor to obtain the experimental CO<sub>2</sub> removal efficiency. The simulated temperature profile from top to bottom of the absorption column was then only qualitatively correct compared to the measured temperature profile. In the equilibrium based model, a Murphree efficiency ( $E_M$ ) was specified for each of 24 stages (meter of packing) to fit both the CO<sub>2</sub> removal efficiency and the temperature profile for one scenario. In this work different  $E_M$ -profiles (different  $E_M$  values on each stage) were examined to fit the temperature profile for a given scenario. The  $E_M$ -profiles were then used to fit performance data for other scenarios by adjusting only an  $E_M$ -factor which multiplies all the  $E_M$  values in an  $E_M$ -profile.

It was evaluated whether a fitted interfacial area (for the rate-based model) or a fitted  $E_M$ -profile (for the equilibrium based model) for one scenario gave a good prediction for other scenarios. The rate-based model fitted for a certain scenario was not able to predict performance well for all other scenarios. An indication of this was that the interfacial area in the different scenarios had to be varied between 0.29 and 1.0 to obtain the measured CO<sub>2</sub> removal efficiency. Using a  $E_M$ -profile fitted for a specific scenario was able to predict performance better for all the scenarios. By multiplying the specified  $E_M$ -profile with an  $E_M$ -factor (only one parameter), the fit at a new scenario was reasonably accurate. The fitted  $E_M$ -factor for each scenario had to be varied between 0.60 and 1.02 to obtain the measured CO<sub>2</sub> removal for all the scenarios.

The performance (CO<sub>2</sub> removal efficiency and temperature profile) was reasonably fitted and simulated for each scenario by all the models. None of the models are however expected to predict accurate performance for conditions far from the fitted scenario without any additional adjustment.

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