Comparison of Simulation Tools to Fit and Predict Performance Data of CO_2 Absorption into Monoethanol Amine at CO_2 Technology Centre Mongstad (TCM)

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Abstract

In this work, several sets of experimental data from the amine based CO_2 capture process at CO_2 Technology Centre Mongstad (TCM) have been compared with simulations of different equilibrium based models and a rate-based model. The equilibrium models (in Aspen Plus and Aspen HYSYS) were fitted by adjusting the Murphree efficiency for each stage and the rate-based model (in Aspen Plus) was fitted by adjusting the interfacial area factor. Aspen Plus (using the Electrolyte-NRTL model) and Aspen HYSYS (using Kent-Eisenberg and Li-Mather models) gave almost identical results for the capture rate and small deviations for the temperature profiles. There are however deviations both between the measured temperatures at a specified column height and between measured temperatures and the simulated temperatures. Equilibrium based models are less fundamental than rate-based models, but for the conditions in this study, the rate-based models still lack accurate input parameters like the interfacial area. The results from this study show that equilibrium and rate-based models perform equally well in both fitting performance data and in predicting performance at changed conditions.

Keywords: CO_2, amine, absorption, simulation

1 Introduction

Developing robust and predictable process simulation tools for CO_2 capture is an important step in improving carbon capture technology to reduce man-made carbon emissions. Examples of available process simulation tools for CO_2 absorption into amine solutions are the equilibrium based models in Aspen Plus and Aspen HYSYS and the rate-based model in Aspen Plus. Equilibrium based absorption models are based on the assumption of equilibrium at each stage. The model can be extended by introducing a Murphree efficiency (the ratio of the change in mole fraction from a stage to the next divided by the change assuming equilibrium). Rate-based models are based on rate expressions for chemical reactions, mass transfer and heat transfer.

At CO_2 Technology Centre Mongstad (TCM) there is an absorption column with a rectangular cross section of 3.55 times 2 meter which is equivalent to a packing diameter of 3 meter, and a packing height up to 24 meter. At TCM, performance tests of CO_2 absorption from flue gas into 30 wt-% monoethanol amine (MEA) have been run in 2013 (Thimsen et al., 2014; Hamborg et al., 2014) and in 2015 (Gjernes et al., 2017). Figure 1 shows a simplified process diagram of the amine based CO_2 absorption and desorption facility at TCM.

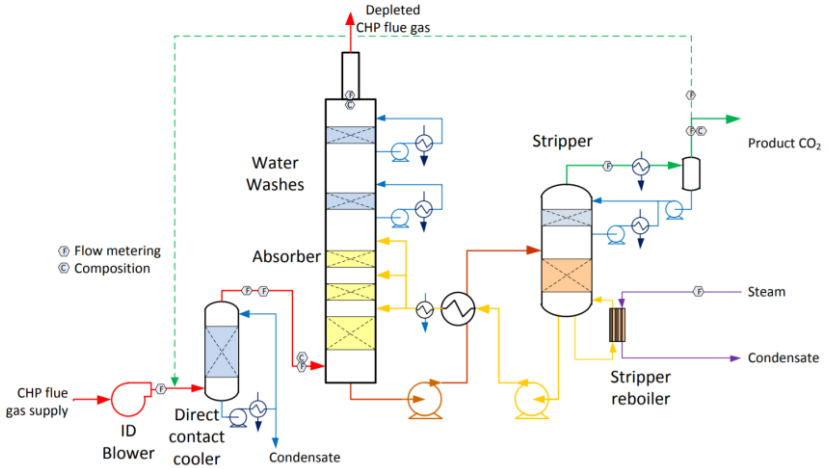

Figure 1. Simplified process diagram of the amine based CO_2 capture plant at TCM (Thimsen et al., 2014)

A performance test at TCM is normally run at constant conditions for a long period of time to obtain steady state conditions. In this work, the emphasis is on the absorber part of the process. Especially the total CO_2 capture rate (in % of incoming CO_2) in the absorption section and the temperature profile from top to bottom of the absorption section are the evaluated parameters.

The aim of this work is to compare results from simulations with performance data for CO_2 absorption into 30 wt-% MEA at TCM using different simulation tools. In this work, 4 sets of experimental data (scenarios) from the amine based CO_2 capture process at TCM have been compared with simulations of different equilibrium based models and a rate-based model. The work is based on the Master Thesis of Kai Arne Sætre (2016). Some of the results from the Master Thesis were presented as a non-published Poster at the TCCS-9 conference in Trondheim in June 2017. In the original work (Sætre, 2016) the equilibrium models (in Aspen Plus and Aspen HYSYS) were fitted to one specific scenario by adjusting the Murphree efficiency for each stage, and the rate-based model (in Aspen Plus) was fitted to another scenario by adjusting the interfacial area factor. In this work, the Murphree efficiency for each stage was adjusted in the other scenarios to achieve a good fit to the temperature profile. The interfacial area was constant in all the calculations for the rate-based model, and this gave a good fit to the CO_2 capture rate and reasonably good fit to the temperature profile.

2 Available Equilibrium and Kinetic Models

There are several equilibrium models available for the MEA/water/CO_2 system describing the relations between the vapour and liquid phase at equilibrium. Aspen HYSYS has an amine package with the Kent-Eisenberg (1976) and the Li-Mather (1994) equilibrium models. Aspen Plus has an Electrolyte-NRTL equilibrium model which is based on Austgen et al. (1989). The column models in both Aspen HYSYS and Aspen Plus can be specified with Murphree efficiencies.

In the Master Thesis work of Zhu (2015) and Sætre (2016), a Murphree efficiency for each stage (meter of packing) was estimated for a set of TCM data (Hamborg et al., 2014). Zhu (2015) found that a Murphree efficiency fitted to 0.09 for all stages obtained good agreement between measured and simulated CO_2 capture rate. Using different Murphree efficiencies for each stage, it was possible to achieve also good agreement between the measured and simulated temperature profile.

In Aspen Plus, there are several models for heat transfer, mass transfer and kinetics which can be included in a rate-based calculation. A rate-based example file for CO_2 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_2 absorption pilot plant at the University of Texas. The rate-based models used at TCM have been developed during several years, and different models have been used in the Master Thesis works of Larsen (2014), Desvignes (2015) and Sætre (2016).

There have been published very few comparisons between different simulation tools for CO_2 absorption. One reference comparing different simulation programs for CO_2 removal from atmospheric gas is Luo et al. (2009). They tested Aspen RadFrac, ProTreat, ProMax, Aspen RateSep, CHEMASIM from BASF and CO2SIM from SINTEF/NTNU and compared with pilot plant data. They claimed that all models were capable of fitting the capture rate, but the temperature and concentration profiles were less well predicted. Øi (2012) has performed comparisons between the programs Aspen HYSYS and Aspen Plus. He 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 literature, different models and tools are mentioned. In this work a simulation tool is meant as a complete collection of models for equilibrium, rate expressions and efficiencies including defined parameter values for all the models. It should be noted that most of the models used are very dependent on the parameter values.

3 Material, Methods and Specifications

3.1 Performance Data from TCM

Performance data for this work have been taken from 4 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. These scenarios were all run with anti-foam to avoid operating problems due to foaming. Only the performance of the absorber part of the process was evaluated in this work. The conditions in each scenario are mainly defined by the conditions of the inlet gas stream and the inlet amine stream to the absorption section of the absorption column. The performance test data cover measurements from all the process units in Figure 1. Each of the scenarios were run for several days to obtain measurements for steady state conditions.

The data for the 4 scenarios are listed in Table 1, Table 2, Table 3 and Table 4 (from Sætre, 2016). The data are from scenarios documented in Hamborg (2014) and Gjernes (2017), but some of the data are converted to different units to make them suitable for input to simulation programs.

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The 4 scenarios which have been selected in this work are named H14 and 6w from 2013 (Hamborg, 2014) and 2B5 and Goal1 from 2015 (Gjernes, 2017). The names have been used internally at TCM, except the H14 scenario which is based on a temperature profile with mean values from the 4 locations for each packing height of one meter. The 4 scenarios were run with amine concentrations close to 30 wt-% MEA in water. The measured MEA concentrations were 30.0 (H14), 30.4 (6w), 31.6 (2B5) and 32.4 wt-% (Goal1).

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 [ºC]	36.5	Temperature [ºC]	25.0
MEA [mol%]	10.94	CO_2 [mol%]	3.7
H_2O [mol%]	86.54	H_2O [mol%]	2.95
CO_2 [mol%]	2.52	O_2 [mol%]	13.6
Pressure [bara]	1.0313	N_2 [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 [ºC]	36.9	Temperature [ºC]	25
MEA [mol%]	11.13	CO_2 [vol%]	3.57
H_2O [mol%]	86.37	H_2O [vol%]	3.0
CO_2 [mol%]	2.5	O_2 [vol%]	13.6
Pressure [bara]	1.0313	N_2 [vol%]	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 [ºC]	36.8	Temperature [ºC]	28.2
MEA [mol%]	11.67	CO_2 [mol%]	3.57
H_2O [mol%]	85.65	H_2O [mol%]	3.7
CO_2 [mol%]	2.68	O_2 [mol%]	14.6
Pressure [bara]	1.0313	N_2 [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 [ºC]	28.6	Temperature [ºC]	25
MEA [mol%]	12.04	CO_2 [mol%]	3.62
H_2O [mol%]	85.19	H_2O [mol%]	3.1
CO_2 [mol%]	2.77	O_2 [mol%]	14.3
Pressure [bara]	1.0313	N_2 [mol%]	79
		Pressure [bara]	1.063

The results from the performance data scenarios to be compared with simulations, are the total CO_2 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 scenario, a mean value for each meter of packing was specified in the temperature profile (Hamborg, 2014).

3.2 Specifications for the Equilibrium Based Simulation Tools

When using Aspen HYSYS version 8.0, the Amine package with the Kent-Eisenberg model was used with non-ideal vapor phase. In the work of Sætre (2016) also the Li-Mather model was used, but the results with the Li-Mather model are not included in this work.

When using Aspen Plus version 8.0, the Electrolyte-NRTL (Non-Random-Two-Liquid) was used. The sample file available from Aspen Plus, was used as the basis for the Aspen Plus simulations.

In the Master Thesis work of Zhu (2015) and in Sætre (2016), a Murphree efficiency for each of the 24 stages (meter of packing) was estimated for the TCM data set (Hamborg 2014). Zhu (2015) found that a Murphree efficiency of 0.09 for all stages gave a good fit to the capture rate. This approach was used by Sætre (2016) in his work, but these results are not presented in this work. Zhu (2015) also found that a linear Murphree efficiency profile gave a better fit to the temperature profile. A Murphree efficiency of 0.23 at the top stage and then reduced linearly to 0.09 for stage 14 and constant equal to 0.01 (close to 0) for the bottom stages fitted the temperature profile very well for the H14 scenario (Zhu, 2015). This Murphree efficiency was used in all the scenarios in the work of Sætre (2016). In this work, this was found to be satisfactory only for the scenarios H14 and Goal1. The capture rate and temperature profile in the scenarios 6w and 2B5 scenarios were found to be well predicted by a linear efficiency profile with $E_M = 0.192$ at the top stage and 0.008 at the bottom. This was specified in this work for 6w and 2B5 in both the Aspen HYSYS and Aspen Plus simulation tool.

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). Especially the parameters in the Electrolyte-NRTL model are not the same in all versions. In this work, the parameters in the sample file from Aspen Plus version

8.0 (Rate_Based_MEA_Model) 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_2 absorption at the University of Texas. The specifications for the rate-based model (in the APRB_TCM2016 file) is shown in Table 5.

Table 5. Specifications for the rate-based model in the APRB_TCM2016 file

SPECIFICATION	
Calculation type	Rate-based
Number of stages	50
Efficiency type	Vaporization efficiencies
Reaction ID	MEA-NEW
Holdup	0.0001 stage 1 to 50
Reaction condition factor	0.9
Packing type	Koch metal 2x
Section diameter [m]	3
Section packed height [m]	24
Flow model	Countercurrent
Interfacial area factor	0.55 (0.5 to 1)
Film Liquid phase	Discrxn
Film Vapor phase	Film
Mass transf coeff method	Bravo et al. 1985
Heat transf coeff method	Chilton and Colburn
Interfacial area method	Bravo et al. 1985
Holdup method	Bravo et al. 1992
Add. Discretize points liquid	5

Detailed documentation of the rate-based model can be found in the Aspen Plus program documentation. References to the mass transfer, interfacial area and hold-up models are Rocha et al. (1985) and Rocha et al. (1993), and for the heat transfer coefficient method Chilton and Colburn (1935).

4 Results

4.1 General Results

The results from the simulations are mainly the capture rate and the temperature profile. There are 3 simulation tools used, and no parameters are changed in the simulation tools from scenario to scenario except for the Murphree efficiencies. Simulation results and performance data are compared for each scenario. In general, the simulated capture rate was reasonably close to the measured capture rate for all scenarios except for the Goal1 scenario. Because of that, emphasis is in this work on comparison of temperature profiles.

4.2 Scenario H14

Measured capture rate was 88.5 %. Aspen HYSYS achieved 86.9 %, Aspen Plus equilibrium based 86.9 and Aspen Plus rate-based 88.5 %. Comparison between measured and simulated temperature profile is shown in Figure 2.

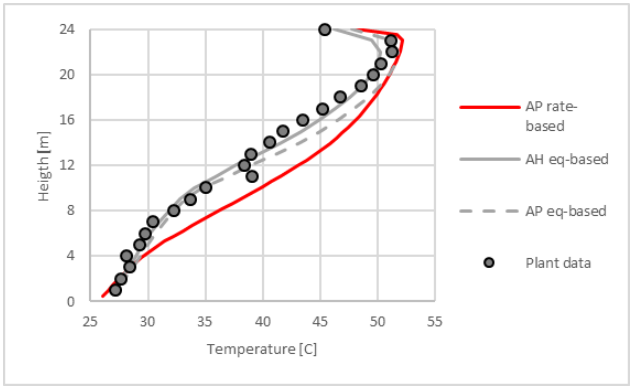

Figure 2. Comparison of plant data scenario H14 and simulated temperature profiles.

The deviation is less than 2 °C for the equilibrium models and less than 6 °C for the rate-based model. It must be noted that the Murphree efficiencies in the equilibrium based models were actually fitted to the plant data.

4.3 Scenario 6w

Measured capture rate was 88.5 %. Aspen HYSYS achieved 87.2 %, Aspen Plus equilibrium based 87.5 and Aspen Plus rate-based 86.1 %. Comparison between measured and simulated temperature profile is shown in Figure 3.

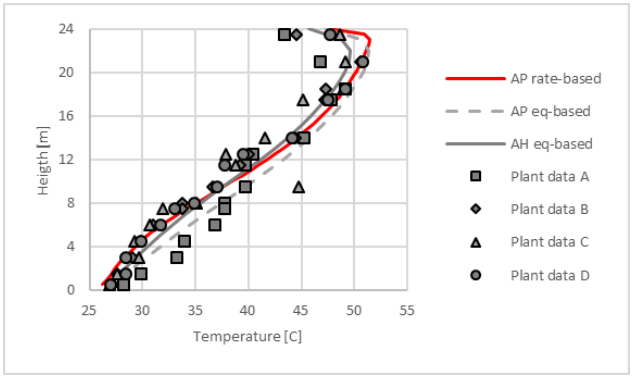

Figure 3. Comparison of plant data scenario 6w and simulated temperature profiles.

With the exception of the plant data A and one outlier temperature from plant data C, the deviations between measured and simulated temperatures were less than 3 °C. In this case the Murphree efficiencies were fitted as a linear profile from top to bottom. It must be noted that the interfacial area factor was fitted (to 0.55) for the Aspen Plus rate-based model to fit the capture rate and the temperature profile for this scenario.

4.4 Scenario 2B5

Measured capture rate was 87.2 %. Aspen HYSYS achieved 87.3 %, Aspen Plus equilibrium based 87.5 and Aspen Plus rate-based 86.0 %. Comparison between measured and simulated temperature profile is shown in Figure 4.

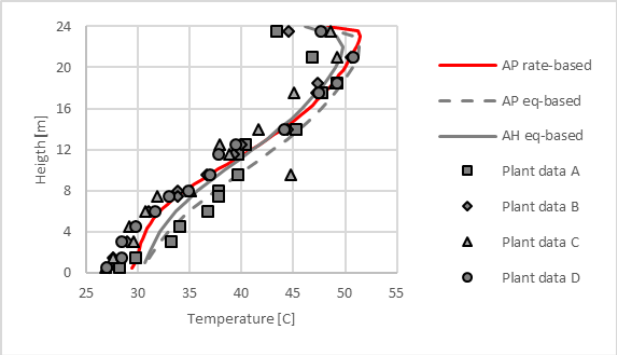

Figure 4. Comparison of plant data scenario 2B5 and simulated temperature profiles.

With the same exception of the plant data A and one temperature from plant data C, the deviations between measured and simulated temperatures were less than 2 °C. Also in this case the linear Murphree efficiency profile gave a good fit to the temperature profile. The equilibrium based temperatures were slightly less than the measured temperatures, while the rate-based temperatures were close to the measured.

4.5 Scenario Goal1

Measured capture rate was 90.1 %. Aspen HYSYS achieved 86.2 %, Aspen Plus equilibrium based 82.7 and Aspen Plus rate-based 78.9 %. This is the only case where there is a significant deviation between performance data and capture rate. The deviation is 4 %-points for the Aspen HYSYS equilibrium based model, 7 %-points for Aspen Plus equilibrium based and 11 %-points for the Aspen Plus rate-based model. Comparison between measured and simulated temperature profile is shown in Figure 5.

The deviations between measured and simulated temperatures were less than 3 °C. The Murphree efficiency profile from Zhu (2015) gave a reasonably good fit for the equilibrium based models with less than 2 °C difference between the models.

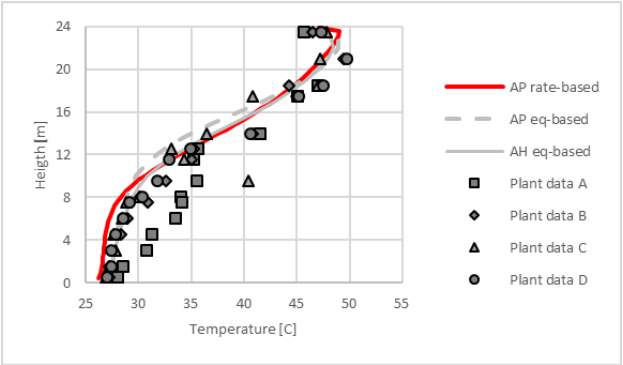

Figure 5. Comparison of plant data scenario Goal1 and simulated temperature profiles.

5 Discussion

There is very little difference in the results from different equilibrium models like Kent-Eisenberg and Electrolyte-NRTL. Sætre (2016) also simulated the 4 scenarios in this work with the Li-Mather model. The Li-Mather and Kent-Eisenberg models gave very similar results, and this has also been experienced earlier (Øi, 2012). There is a difference of approximately 2 °C in the maximum temperature in the upper part of the column between Kent-Eisenberg and Electrolyte-NRTL, but this does not seem to give differences in the removal rate. When simulating the Goal1 scenario, the maximum temperature in the simulation tools were very close to each other.

All the tools are close to similar when it comes to prediction of the total absorption rate. Fitting the models to achieve the measured absorption rate can be performed for one scenario by adjusting the Murphree efficiency for the equilibrium based models or the interfacial area factor for the rate based models. For the equilibrium based models, two sets of Murphree efficiencies were used to achieve reasonable results for all 4 scenarios. The ability to predict performance at other conditions was about the same for the different simulation tools. Luo et al. (2009) have tested Aspen RadFrac, ProTreat, ProMax, Aspen RateSep, CHEMASIM and CO2SIM. As in this work, they concluded that basically all the codes were capable of giving reasonable predictions on overall CO_2 absorption rate.

The figures show that measured temperature profiles and simulated temperature profiles are reasonably close. There are however deviations both between the measured temperatures at different locations at a specified column height and between measured temperatures and the simulated temperatures. It is not obvious that any of the simulation tools predicts the measured temperatures better than the other models.

Some references (Zhang et al., 2009; Larsen, 2014; Desvignes, 2015) have compared also the concentration profiles when comparing performance data and simulation tools. This is not done in this work. In the work of Larsen (2014) the concentration data values were too uncertain to make the comparisons significant because the uncertainty in the measured liquid concentrations were higher than the simulation uncertainties.

It has been claimed (Zhang et al., 2009) that rate-based models are superior to equilibrium based models because the rate-based models are capable of describing more detailed mechanisms. It is however factors and parameters in the rate-based models which are not known, especially specifications for fluid flow, heat transfer and mass transfer conditions in structured packings. A rate-based model has several parameters which can be used to fit the model to performance data. The most reasonable parameter to vary to fit capture efficiency is the interfacial area factor. It could also be possible to divide the column in sections with different interfacial area factors. The ability to predict performance at other conditions is however a difficult challenge. One assumption for the rate-based model is that there is ideal flow in axial direction and perfect mixing in radial direction. The large deviations in temperature measurements at different locations for each meter of packing (location A, B, C and D) indicate that this assumption is optimistic.

It is an important question whether the simulation tools with fitted parameters are able to give a predictable simulation at different conditions. Sætre (2016) tried to predict the capture rate and the temperature profiles for scenarios with 40 wt-% MEA (Desvignes, 2015) with the 3 simulation tools used in this work (which is fitted for 30 wt-% scenarios). The predictions were rather poor.

In this work, only performance data with 24 meter of packing was used. With such a high packing height, the capture rate becomes very high, and will approach equilibrium. This is indicated by the Murphree efficiencies which give the best temperature fit for scenario H14 and Goal1 were almost zero for the lowest stages. There are also available performance data for lower packing heights, e.g. 18 meter (Hamborg, 2014; Gjernes, 2017). When comparing performance data with simulation tools, comparisons using lower packing height would probably give interesting results.

6 Conclusions

It is possible to fit a rate-based model by adjusting the interfacial area factor, and to fit an equilibrium model by adjusting the Murphree efficiency for each stage. Equilibrium based models are less fundamental than rate-based models, but for the conditions in this study, the rate-based models still lack accurate input parameters like the interfacial area. The results from this study show that equilibrium and rate-based models perform equally well in both fitting performance data and in predicting performance at changed conditions. The models with fitted parameters will give a predictable simulation only when there are small changes in the process parameters.

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