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Comparison of Aspen HYSYS and Aspen Plus simulation of CO₂ absorption into MEA from atmospheric gas

Lars Erik Øi*

Telemark University College, N-3901 Porsgrunn, Norway, lars.oi@hit.no

Abstract

A CO₂ capture process based on MEA absorption has been simulated with Aspen HYSYS and Aspen Plus. Both rate-based simulations and simulations with specified Murphree efficiencies have been performed. The differences between the equilibrium models and between Aspen HYSYS and Aspen Plus were small. The removal efficiency was calculated to be lower and the temperature profiles were slightly different in the rate-based calculations. The simulations were close to equivalent if the aim is to calculate CO₂ removal efficiency as a function of circulation rate, number of column stages and inlet temperature.

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Keywords: absorption; CO₂; simulation; amine; efficiency

1. Introduction

The most mentioned method for CO₂ capture from exhaust gas is by absorption in an amine based solvent like MEA (monoethanolamine) followed by desorption. The principle for a CO₂ removal process based on absorption in MEA followed by desorption is shown in Fig. 1. The basis is a process for removing 85 % CO₂ from the exhaust from a 400 MW natural gas fired combined cycle power plant.

There have been published very few studies comparing different simulation tools for CO₂ absorption at atmospheric conditions. One of the few references comparing different simulation programs for CO₂ removal from atmospheric gas is Luo et al. [1]. They tested Aspen RadFrac, ProTreat, ProMax, Aspen RateSep, CHEMASIM from BASF and CO₂SIM from SINTEF/NTNU and compared with pilot plant data. Madsen [2] and Hansen [3] have performed comparisons between the programs Aspen HYSYS, Aspen Plus and Promax at Telemark University College, and this is developed further in this work.

* Corresponding author. Tel.: +47-3557-5141; fax: +47-3557-5001.
E-mail address: lars.oi@hit.no.

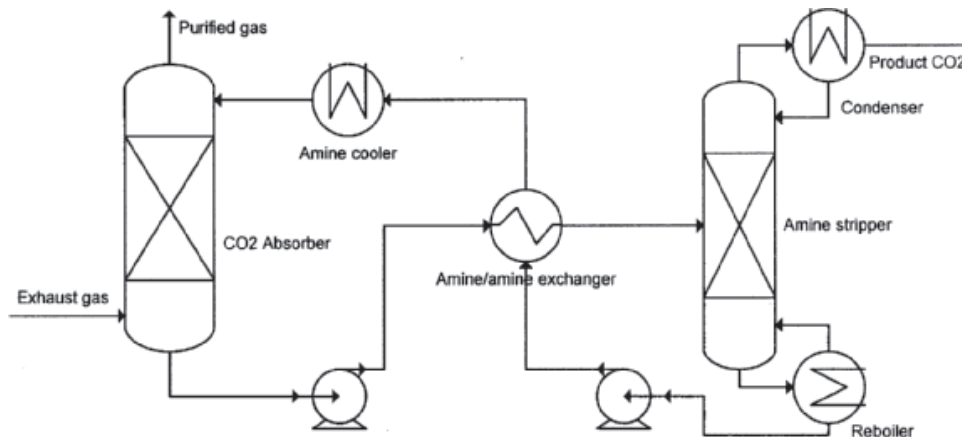


Fig. 1. Principle for CO₂ removal process based on absorption followed by desorption in amine solution

Aspen HYSYS has an amine package with Kent-Eisenberg [4] and Li-Mather [5] equilibrium models. The column models are equilibrium based and can be specified with Murphree efficiencies on each stage. Aspen Plus has an Electrolyte-NRTL equilibrium model which is based on Austgen et al. [6]. The column models can be specified with Murphree efficiencies and there is a rate-based column model available in Aspen Plus. The purpose of this paper is to compare the different programs, equilibrium models and column calculation tools for CO₂ absorption at atmospheric conditions.

2. Murphree efficiency based and rate-based simulation

2.1. Murphree efficiency

The principle of the definition of Murphree efficiency based on gas phase mole fractions for a trayed column is shown in Fig. 2. For a packed column, a tray in Fig. 2 can represent a packing height section.

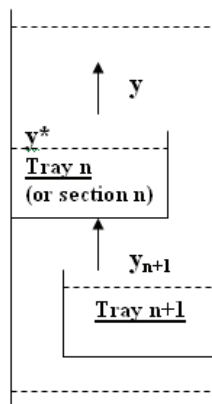


Fig. 2. Illustration of mole fractions necessary for the definition of Murphree efficiency, $E_M = (y - y_{n+1}) / (y^* - y_{n+1})$, where y^* is in equilibrium with the liquid on stage n .

The definition of Murphree efficiency is slightly different from the definition in Fig. 2 in the program Aspen HYSYS. In a column without side-draws and with the assumption of constant vapour flow through the column, the definitions are equivalent. Using Murphree efficiencies gives a more realistic description of the concentration and temperature profiles as a function of column height than using ideal equilibrium stages. When specifying Murphree efficiencies in process simulation programs, it is assumed that the gas and liquid temperatures are equal at each stage. A Murphree efficiency can be specified to e.g. 0.25 which is equivalent to order of magnitude 1 to 2 meter of packing height. Murphree efficiencies can also be estimated automatically for trays in Aspen HYSYS or from e.g. Fig. 3 as described in Øi [7].

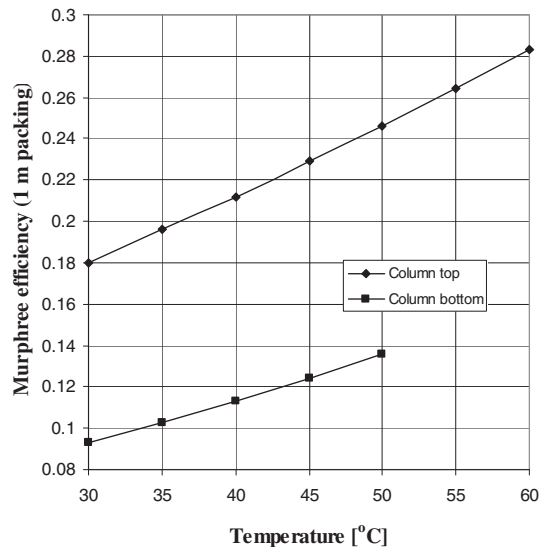


Fig. 3. Murphree efficiency per meter structured packing with specific area $250 \text{ m}^2/\text{m}^3$ from a pseudo first order expression as a function of temperature for typical column top and column bottom conditions

In Øi [7], Murphree efficiencies in structured packing with specific surface area $250 \text{ m}^2/\text{m}^3$ were estimated based on a pseudo first order expression for 1 meter of packing as a function of temperature at top and bottom conditions. At temperatures above $50 \text{ }^\circ\text{C}$, the equilibrium partial pressure of CO_2 of the liquid in the bottom exceeds the partial pressure of the incoming gas. The numbers in Fig. 3 are slightly different from the numbers in Øi [7] because the estimated influence of viscosity on the liquid diffusivity is slightly changed.

2.2. Rate-based simulation

A rate-based model separates the liquid and vapour flow in the column and is based on the calculation of heat transfer, mass transfer between the phases and chemical kinetics. Fig. 4 shows typical partial pressure and concentration profiles at a given column height (or column stage) which can be calculated by a rate-based calculation. Due to a small gas film resistance, the partial pressure decreases slightly through the gas film. At the interface it is assumed to be equilibrium. CO_2 diffuses into the liquid, and the concentration of CO_2 in the liquid decreases rapidly near the surface due to a fast reaction with the amine, and approaches the equilibrium concentration in the liquid bulk. The amine concentration decreases in the liquid film due to the same reaction.

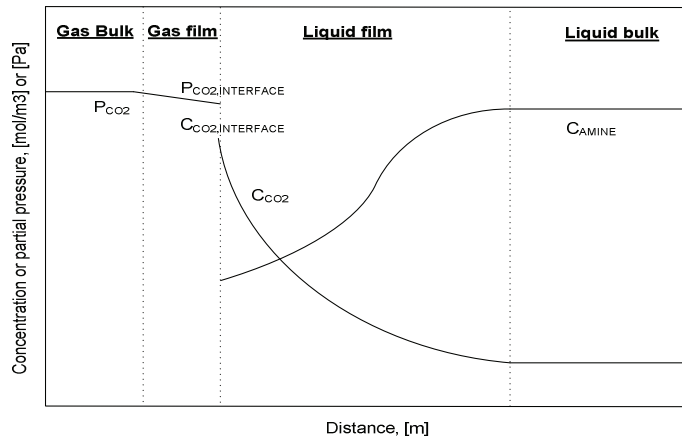


Fig. 4. Typical concentration profiles in liquid film with absorption and chemical reaction, assuming equilibrium between partial pressure and concentration of CO₂ at the interface

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 CO₂ removal using MEA is available with the Aspen Plus program.

3. Calculations and results

3.1. Specifications for base-case calculation

In the case of a model based on Murphree efficiency, the only needed specifications for an absorption column calculation are the number of stages, the Murphree efficiencies on each stage in addition to the inlet streams and a pressure profile. The Murphree efficiencies for the components except from CO₂ were set to unity. The specifications for a base-case calculation are given in Table 1. The specifications are mainly from an earlier Aspen HYSYS simulation from Øi [8].

In the Aspen HYSYS calculations, the vapour/liquid equilibrium models Kent-Eisenberg and Li-Mather were used with non-ideal gas. The equilibrium model used in Aspen Plus was Electrolyte-NRTL (Non-Random-Two-Liquid) for both types of calculations. Version 7.0 and 7.2 of the programs were used.

The Aspen Plus simulations were based on an example file from the Aspen Plus program documentation (Rate_Based_MEA_Model in Version 7.0). Most of these specifications were also used by Zhang et al. [9] in their Aspen Plus rate-based simulation of CO₂ absorption. For the rate-based calculation, some parameters were changed from the example file. The selected packing was standard metal Mellapak 250Y. The reaction condition factor was changed from 0.9 in the example file to 0.5. The interfacial area factor was kept at 1.0 and the height of one stage was 2.0 m. The stage flow option was changed from countercurrent to V-plug, which simulates the vapour in plug flow and the liquid as ideally mixed at each stage. Using the countercurrent flow option was tried, but it led to difficulties with convergence, and in some cases unrealistic temperatures appeared in top of the column.

Table 1. Specifications for base case CO₂ removal

| Specified parameter [dimension] | Value |
|--|---------------|
| Inlet gas temperature [°C] | 40 |
| Inlet gas pressure [bar (a)] | 1.1 |
| Inlet gas flow [kmol/h] | 85000 |
| CO ₂ in inlet gas [mol-%] | 3.73 |
| Water in inlet gas [mol-%] | 6.71 |
| Lean amine temperature [°C] | 40 |
| Lean amine pressure [bar (a)] | 1.0 |
| Lean amine rate [kmole/h] / [kton/h] | 120000 / 2.75 |
| MEA in lean amine [mass-%] | 29 |
| CO ₂ in lean amine [mass-%] (Loading) | 5.5 (0.263) |
| Number of stages in absorber | 10 |
| Murphree efficiency in absorber | 0.25 |
| Height of stage in rate-based calculation [m] | 2 |

Using Aspen HYSYS, 85.0 % removal grade was achieved for the base-case with the Kent-Eisenberg and 83.4 % with the Li-Mather model. Using Aspen Plus, 85.0 % was achieved for the base-case conditions with Murphree efficiency. Aspen Plus with rate-based simulation achieved 81.7 % removal, which was lower than for the calculation using Murphree efficiencies. If results with the countercurrent stage flow model had been achieved, this had probably resulted in a slightly higher removal efficiency.

3.2. Calculations of CO₂ removal grade as a function of circulation rate, number of stages and temperature

CO₂ removal grade was calculated as a function of solvent circulation rate, number of column stages and inlet gas and liquid temperature. All other parameters were kept constant. The results are shown in Figs. 5 to 7.

Fig. 5 shows that the removal grade increases slightly when the circulation rate increases. This is due to better driving force especially in the bottom part of the absorption column. The rate-based calculations show a lower removal grade at low circulation rates and a higher at high circulation rates compared to the Murphree efficiency based calculations. In Fig. 6 the removal grade increases as expected when the number of stages increases. The increase is smaller at higher number of stages because the CO₂ removal grade approaches the maximum according to equilibrium. The rate-based calculations give lower removal grade, and the dependency on the number of stages is smaller than for the Murphree efficiency based calculations. In Fig. 7 the removal grade is decreasing when the temperature increases because the solubility of CO₂ decreases with increasing temperature. Fig. 7 is based on the assumption of constant Murphree efficiencies independent on temperature. Actually, the Murphree efficiencies increase with increasing temperature as shown in Fig. 3, so that under some circumstances, the removal grade may increase with increased temperature.

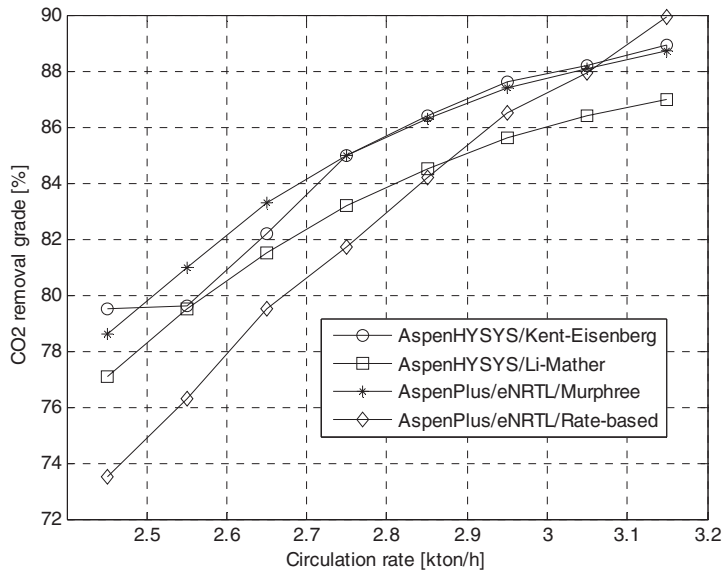


Fig. 5. Calculated absorber CO₂ removal grade as a function of amine circulation rate for different programs and equilibrium models, Murphree efficiency is 0.25 in all the calculations except for the Aspen Plus rate-based calculation

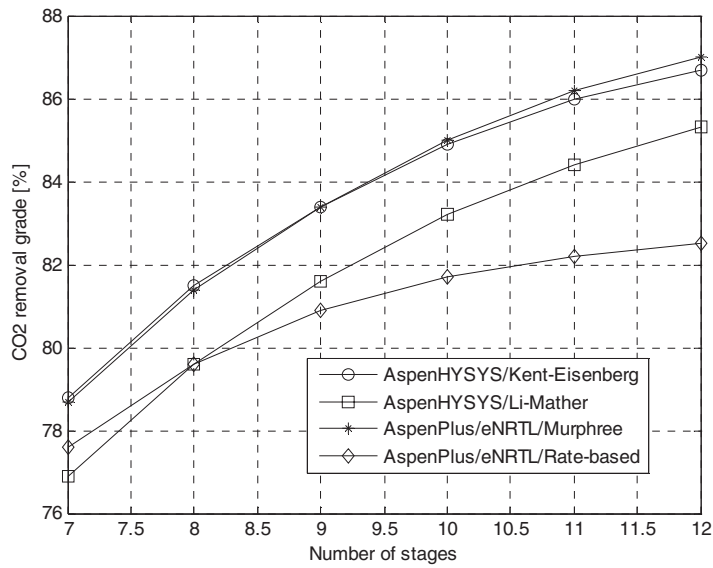


Fig. 6. Calculated absorber CO₂ removal grade as a function of number of stages for different programs and equilibrium models, Murphree efficiency is 0.25 in all the calculations except for the Aspen Plus rate-based calculation

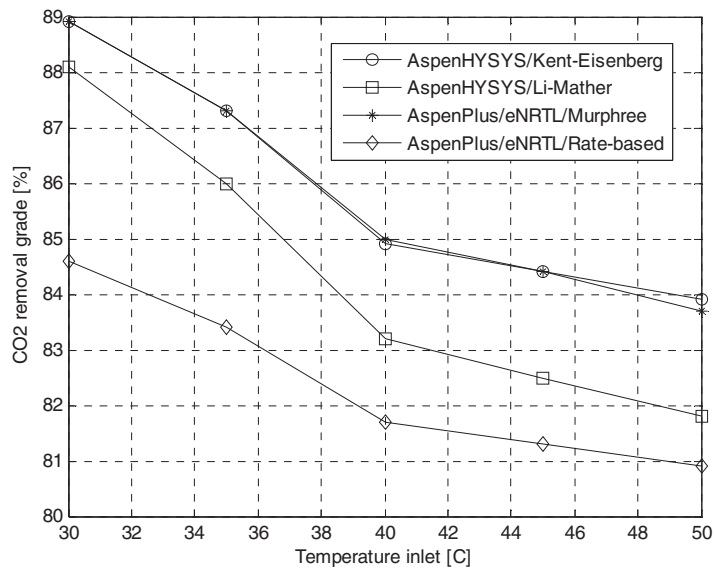


Fig. 7. Calculated absorber CO₂ removal grade as a function of inlet gas and liquid temperature for different programs and equilibrium models, Murphree efficiency is 0.25 in all the calculations except for the Aspen Plus rate-based calculation.

All the calculations using a constant Murphree efficiency of 0.25 for each stage showed similar results. The deviation in removal grade was within about 2 %-points. The differences between the equilibrium models and between Aspen HYSYS and Aspen Plus were small. This indicates that there are not important differences in the equilibrium models.

The largest deviation when using different equilibrium models was that Aspen Plus with the Electrolyte-NRTL model calculated higher temperatures in the middle of the column as shown in Fig. 8. This is probably due to higher calculated heat of absorption in the Electrolyte-NRTL model than the other equilibrium models. However, this difference did not result in large differences in CO₂ removal efficiencies.

The results from the rate-based calculations in Aspen Plus were in the same order of magnitude compared to the calculations using Murphree efficiencies. The removal grade was calculated up to 5 %-points lower in the rate-based calculations. The temperature profiles as a function of column height were slightly different as shown in Fig. 8. All the calculations showed increasing CO₂ removal grade with increasing circulating rate and number of stages, and decreasing removal grade with increasing temperature. The magnitudes of the dependencies were slightly different in the calculations using Murphree efficiencies compared to rate-based simulation. The liquid and gas temperatures are very close in the rate-based calculation (less than 1 °C difference). From this it follows that an assumption of thermal equilibrium between the gas and liquid phases is probably justified.

The rate-based calculation was less dependent on inlet temperature than the other calculations, and this is probably more reasonable. This is expected because the other models have been calculated with a constant Murphree efficiency, and the Murphree efficiency is expected to increase with increasing temperature as shown in Fig. 3.

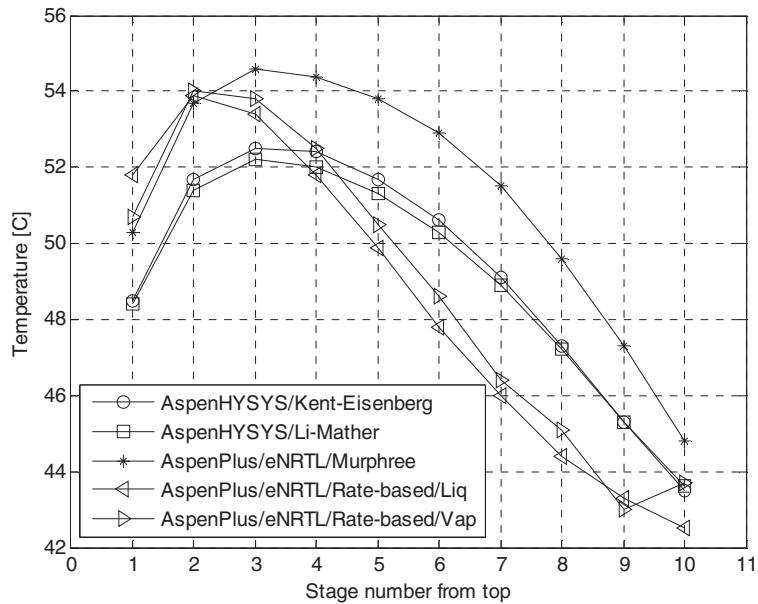


Fig. 8. Calculated absorber temperature profiles for different programs and equilibrium models, Murphree efficiency is 0.25 in all the calculations except for the Aspen Plus rate-based calculation with 2 meter /stage

3.3. Calculations of temperature profiles using varying Murphree efficiencies

In Fig. 8, the rate-based temperature profile is decreasing steeper than the temperature profiles based on Murphree efficiencies. One explanation for this is that the Murphree efficiencies are specified to be constant, while the efficiency is actually larger in the top of the column than in the bottom.

In Fig. 9, the temperature profiles are calculated in Aspen HYSYS with the Kent-Eisenberg equilibrium model and Murphree efficiencies estimated from Fig. 3. When the inlet temperatures were 40 °C, the top stage temperature was 49 °C and the bottom stage temperature was 43 °C for 10 stages. Murphree efficiencies for 49 °C at top conditions and for 43 °C at bottom conditions were specified first according to Fig. 3. The efficiencies were kept constant down to the stage with maximum temperature (stage 4). Between the maximum temperature stage and the bottom stage, the efficiency was specified to vary linearly. In the Aspen HYSYS calculation, this resulted in a slightly changed temperature profile, and the specified efficiencies were adjusted to be consistent with the new temperatures. 12 stages were selected to achieve 83.5 % removal grade in the Aspen HYSYS calculation with varying Murphree efficiency and 81.7 % in the Aspen Plus rate-based calculation at 40 °C.

In Fig. 9, the temperature profiles for inlet temperature 33 °C are also shown. 33 °C was selected because this was earlier found to give the optimum absorption efficiency [7]. This resulted in 85.5 % removal grade in the Aspen HYSYS calculation with varying Murphree efficiency and 84.0 % in the Aspen Plus rate-based calculation.

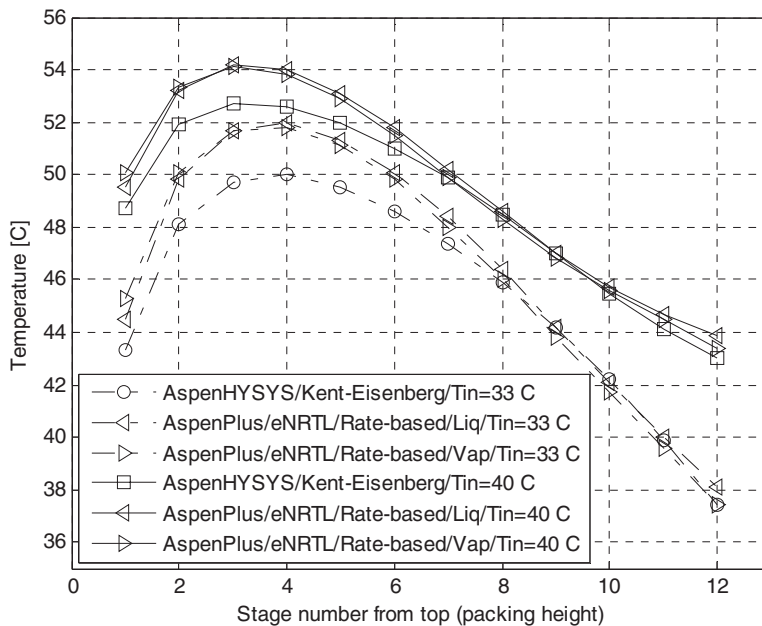


Fig. 9. Calculated absorber temperature profiles for varying Murphree efficiency using Kent-Eisenberg compared to rate-based simulation using electrolyte-NRTL

The rate-based calculations were performed with 12 stages similar to the Aspen Plus calculations with 10 stages in Fig. 8. The parameters used were similar, except that the mixed flow stage model was used in the simulations with 12 stages due to easier convergence. At the specified amine circulation rate, the Aspen Plus rate-based simulation had difficulties in achieving 85 % removal grade, even with 12 stages each with 2 meter height. The absorber height in the rate-based calculations was considerably higher (24 meter) than in the calculations based on Murphree efficiencies (12 meter with efficiencies for 1 meter packing height).

All the models showed the same temperature profile pattern with a maximum close to the top (at stage 3 or 4 from top). The difference in maximum temperature (about 2 °C) was the same as in Fig. 8 and can also here be explained with a higher heat of absorption calculated using the Electrolyte-NRTL model.

The temperature profiles using varying Murphree efficiency and rate-based simulation are very close. It is interesting to compare Fig. 9 with Fig. 8 where the Murphree efficiencies are constant (0.25) at all (10) stages. The temperature profiles are much closer especially in the lower part of the column when using varying Murphree efficiencies.

4. Discussion

Luo et al. [1] have tested Aspen RadFrac, ProTreat, ProMax, Aspen RateSep, CHEMASIM and CO2SIM. They concluded that basically all the codes were capable of giving reasonable predictions on overall CO₂ absorption rate. Also in this work, all the calculations have resulted in similar results for CO₂ absorption rate (or CO₂ removal grade) using Aspen HYSYS and Aspen Plus.

The reboiler duties, the temperature profiles and concentration profiles were less well predicted according to Luo et al. In this work, it has been shown that when using varying Murphree efficiencies and rate-based simulation, the temperature profiles in Aspen HYSYS and Aspen Plus become very similar. The desorption part including the reboiler duty has not been considered in this work.

It is not obvious whether a simulation with Murphree efficiencies or a rate-based simulation of CO₂ removal is most accurate. The advantages using Murphree efficiencies in CO₂ absorption simulations are that it is simple, and that it can utilize the equilibrium models and robust stage by stage column models already available in commercial process simulation programs. The advantages using rate-based simulations are that it can take into consideration more detailed effects of kinetics and complex heat and mass transfer in combination with equilibrium.

It is doubtful whether any of the available tools are really predictive for CO₂ absorption in structured packing without any adjustable parameters. Careful comparisons and fitting of different tools to large scale experimental data are necessary to conclude about which tools are most accurate.

5. Conclusions

A CO₂ capture process based on MEA absorption has been simulated with Aspen HYSYS and Aspen Plus with rate-based simulations and simulations with specified Murphree efficiencies. The differences between the programs Aspen HYSYS and Aspen PLUS using the equilibrium models Kent-Eisenberg, Li-Mather and Electrolyte-NRTL were small. There were some differences in removal efficiency and temperature profiles between the results based on Murphree efficiencies and rate-based simulations. A general result of the calculations performed in this work, is that all the simulations are close to equivalent if the aim is to calculate CO₂ removal efficiency as a function of e.g. circulation rate, number of column stages and temperature.

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