Rigorous Modeling of a CO_2-MEA Stripping System

Claudio Madeddu*[a], Massimiliano Errico[b], Roberto Baratti[a]

[a]Università degli Studi di Cagliari, Dipartimento di ingegneria Meccanica, Chimica e dei Materiali, Via Marengo 2, 09123, Cagliari, Italy
[b]University of Southern Denmark, Department of Chemical Engineering, Biotechnology and Environmental Technology, Campusvej 55, DK-5230 Odense M, Denmark
c.madeddu@dimcm.unica.it

The complexity of the phenomena involved in CO_2 chemical absorption and solvent regeneration systems results in the necessity to develop reliable models to describe the steady state and the dynamic behavior of the process. In the present work, the modeling of the regeneration section of a post-combustion CO_2-MEA system have been examined. A rigorous rate-based approach, considered as mandatory for a reliable description of this type of process, was applied, where the two-film theory with chemical reaction was used to describe the gas/liquid interfacial material and energy transfer occurring in the packed column. The column was modeled as a convective-reactive system, with appropriate energy and material balances for each component. Particular emphasis was given to the definition of the correct number of segments for the discretization of the packing height. The effect of the axial diffusion/dispersion was analysed by means of the evaluation of the material and thermal Peclet number, and the results showed a plug-flow like behavior. The influence of the backmixing due to the countercurrent was also taken into account by varying the number of segments up to the achievement of an asymptotic behavior, confirming the correctness of the results obtained by the evaluation of the Peclet numbers. The model was validated with experimental data from a pilot-plant facility and the reproduction of the experimental values was deemed acceptable. The more detailed discretization allows to better describe the internal fluxes of the stripper column and has important implications in the design and in the extension to transient systems.

1. Introduction

The post-combustion CO_2 capture by means of absorption with amines is currently considered the most mature technology for the reduction of the carbon dioxide emissions produced by combustion processes.
The complexity of the process, involving both transport phenomena and chemical reactions, the strong interconnection between absorber and stripper, the potential of reducing the energy consumptions and the environmental sustainability of the process are still issues of great interest in the research community.
In the modeling of a carbon capture and storage post-combustion system, up to now, more attention has been given to the absorption process compared to the stripping one. As stated by Zhang et al. (2009), "the performance of the absorber is much more dependent on accurate modeling of the transfer phenomena and rates", compared to the stripper.
On the other hand, the stripper is now recognized as the most crucial point in the system from an economical point of view and its optimization is one of the keys for minimizing the energy consumption. As the reboiler duty represents by far the highest operating cost of the plant, as it drives the entire thermal swing, it is also the value that has the largest potential for improvement. Different works on the stripper are focused mainly on the search for the operative conditions that minimize the reboiler duty or in the search for new plant schemes to improve the energy utilisation through Process Integration (Neveaux et al., 2013).
The development of a model able to correctly describe its behavior is an essential step to successively identify new possible ways to minimize the energy consumption. As highlighted by Tobiesen et al. (2008), the higher complexity of the solvent regeneration section of the plant, compared to the absorption one, due to the addition of the condenser and the reboiler, leads to the necessity of a detailed model of the entire process, in order to have a better understanding of the phenomena that happens inside the equipment and to improve the

interpretation of the obtained results. At the same time, only few experimental data sets for the stripper are available in the open literature. This makes model validation and verification more difficult.

Different stripper models have been proposed in the literature, spacing from the simple equilibrium stage model (Mores et al., 2011) to the rigorous rate-based model, based either on the two-film theory (Tobiesen et al., 2008) or on the eddy diffusion (Moioli and Pellegrini, 2013).

This work had the aim to analyse the solvent regeneration part of a CO_2-MEA system with a rigorous rate-based model, paying attention to some key-parameters that influenced both the profiles along the column and the outputs. In particular, the effect of the number of segments for the discretization of the axial domain, whose importance was evidenced by Errico et al. (2016) for the chemical absorption, was taken into account. This parameter was correctly defined evaluating the material and thermal Peclet numbers, whose values indicated the absence of axial diffusion/dispersion, so a plug-flow like behavior. Moreover, the eventual effect of the backmixing due to the countercurrent was considered through the simulations at different numbers of discretization points. The results highlighted how the evaluation of the reaction rates and the internal fluxes was modified and how this was reflected on the column behavior. The model was validated using experimental values from a pilot-plant facility.

2. Process description

In the case of a CO_2 post-combustion capture with MEA system, the absorption process is followed by the solvent regeneration one. The CO_2-rich solvent from the absorber is firstly heated and then sent to the top of the stripper, that can be either a packed or a plate column, where it meets a vapor, generated by a reboiler, flowing countercurrent from the bottom. From the stripper bottom, the lean solvent is sent to the reboiler and then recirculated to the absorption section; from the top of the column, the CO_2-rich vapor flow is sent to a condenser where water is recovered as reflux. After the condenser, the gas is sent to compression and subsequent storage.

The complex nature of the system is characterised by mass transfer with chemical reactions. As it is the opposite of the absorption process, in which the kinetic reactions are exothermic, the stripping reactions are endothermic. So, in this case, heat is provided by the vapor flow. Consequently, the vapor condensates, reducing the temperature of the system from the bottom to the top. From another perspective, an interphase flow of water from the vapor to the liquid phase is expected throughout the column, as a consequence of the condensation process.

In this work, the plant considered was the CO_2 capture facility described in the work of Tobiesen et al. (2008). The column (diameter=0.1 m) is packed with 3.89 m of Mellapak 250Y (void fraction=0.987, dry specific area=256 m^2/m^3) and equipped with both condenser and reboiler. The reflux from the condenser is entirely mixed with the liquid from the stripper bottom and then sent to the reboiler. Different runs with different rich solvent loadings and operative conditions have been tested and analysed from the experimental campaign. Due to space limitations, the feed data and the operative conditions for the simulation correspond to Run 1 of the experimental campaign and are reported in Table 1.

2.1 Thermodynamics and chemical reactions

The strong non-ideal behavior of the liquid phase was taken into account by means of the Electrolyte-NRTL model, while the Henry's law and the Redlich-Kwong EoS were employed to describe CO_2 solubility and vapor properties, respectively.

For what concerns the chemical reactions, a set of three equilibrium reactions, Eq(1-3), and two reversible reactions involving CO_2, Eq(4-5), were selected:

Table 1: Input data for the simulations – Run 1 from (Tobiesen et al., 2008)

Feed data	Value	Operative conditions	Value
Molar flow [kmol/h]	10.7121	Condenser/Top pressure [kPa]	196.96
Pressure [kPa]	196.96	Pressure drop [kPa]	1
Temperature [K]	389.81	Condenser temperature [K]	288.15
CO_2 [mole fraction]	0.03484	Reboiler duty [kW]	11.6
H_2O [mole fraction]	0.85493		
MEA [mole fraction]	0.11023		
Loading [mol CO_2/mol MEA]	0.31607		

$$2H_2O \leftrightarrow H_3O^+ + OH^- \tag{1}$$

$$H_2O + HCO_3^- \leftrightarrow H_3O^+ + CO_3^{2-} \tag{2}$$

$$H_2O + C_2H_8NO^+ \leftrightarrow H_3O^+ + C_2H_7NO \tag{3}$$

$$C_3H_6NO_3^- + H_3O^+ \leftrightarrow C_2H_7NO + CO_2 + H_2O \tag{4}$$

$$HCO_3^- \leftrightarrow CO_2 + OH^- \tag{5}$$

The equilibrium constants for reactions Eq(1-3) were evaluated using the standard Gibbs free-energy change, while the kinetic constants for reactions Eq(4-5), described by means of a second-order law expression, were taken from Errico et al. (2016), in which the authors made a calibration of the original kinetics parameters from the work of Hikita et al. (1977), and Pinsent et al. (1956), respectively.

2.2 Rate-based model

For a rigorous description of the different phenomena involved in the process, including contemporarily phase equilibrium at the vapor-liquid interface, material transfer by diffusion, chemical reactions and energy transfer, the rate-based approach is recognized as the most correct for the CO_2-MEA system description (Neveaux et al., 2013).

In this work, the Aspen Plus RADFRAC Model - Rate-Based Mode was used for all the simulations. The model was based on the two-film theory and implied the evaluation of the wet surface area, the material and heat transfer coefficients and the liquid and vapor hold-up. Furthermore, the model allowed to rigorously describe the liquid film, where all the reactions are concentrated, using the Nernst-Planck equation. Finally, both liquid and vapor bulk were modeled as perfectly mixed using the so-called "Mixed Flow" model.

The correlations used for the evaluation of the transport properties in structured packing, together with the setup parameters for the rate-based model, were described in detail in a previous work (Errico et al., 2016) and not reported here.

3. Model validation

The model represented a plug-flow reactor approximated as a series of n-CSTRs. Mathematically speaking a DAEs (Differential Algebraic Equation) system was obtained.

Therefore, for the solution of this system it was necessary to define a correct number of CSTRs, i.e., number of segments for the discretization of the axial domain. This important parameter was mainly influenced by two phenomena: the axial diffusion/dispersion and the backmixing due to countercurrent. If just one of this factor had an important effect on the system, there would have been no need to use a high number of segments; on the other hand, if both factors were negligible, the column behavior would have resembled a pure plug-flow reactor and then the necessity of a high number of segments for the correct description of the process.

It should be noted that the two degrees of freedom of the system were saturated by the condenser temperature and the reboiler duty.

3.1 Effect of the axial diffusion/dispersion – Peclet number analysis

In order to investigate if the axial diffusion/dispersion had an effect on the system, the Peclet number was evaluated. This nondimensional group is defined as the ratio between the material (energy) transport by convection and the material (energy) transport by diffusion. High values of the Peclet number correspond to a pure plug-flow like behavior, then the necessity of a high number of segments to discretize of the axial domain rises. On the other hand, low values of the Peclet number imply that the axial diffusion/dispersion has an important effect on the process and so the number of segments has no influence on the system solution.

The Peclet number, defined in Eq(6), was evaluated for both the phases and for both the material and the energy transport. In particular, for what concerns the material transport, the single components and the whole mixture were considered. In all the cases, the nondimensional group was computed with respect to the equivalent diameter of the packing, that for Mellapak 250Y is 0.01277 m. The equivalent diameter was chosen as characteristic length instead of the column height because it gives information on what happens at a microscopic level, being the axial diffusion/dispersion a microscale phenomenon.

$$Pe_{d_{p,eq}} = \frac{N\, d_{p,eq}}{\epsilon\, h\, S\, C\, \mathcal{D}}$$
(6)

where   N: molar flow [kmol/h],

        $d_{p,eq}$: packing equivalent diameter [m],

        ϵ: void fraction [m^3/m^3],

        h: fractional hold-up [m^3/m^3],

        S: cross-sectional area [m^2],

        C: molar density [kmol/ m^3],

        $\mathcal{D}$: diffusivity [m^2/h].

The lowest value of the Peclet number obtained was 431 for the CO_2 in the vapour phase. This result indicated a stripper fluid dynamic behavior close to that of a plug-flow reactor. This meant that, for a correct description of the system, a high number of segments was needed for the solution of the DAEs system.

3.2 Effect of the backmixing due to countercurrent – Variation of the number of segments

The Peclet number does not take into account the effect of the backmixing due to the countercurrent, which is included in the material and energy balances of the system. Then, to see if the backmixing had an effect on the process, the plant had to be simulated varying the number of segments until an asymptotic behavior was reached. If the backmixing had an important influence on the system, the pure plug-flow assumption would have not been valid anymore, even with high Peclet number values. On the other hand, if the backmixing effect was negligible, a high number of segments would have been needed for a correct description of the process.

Figure 1 a) reports the comparison between the liquid temperature experimental data and profiles obtained from the model varying the number of segments. The number of segments was varied until two consecutive profiles were overlapped. As it is possible to notice, the profiles obtained with 10 segments and 70 segments are evidently different, meaning that the backmixing does not have effect on the process. The agreement between the experimental data and the model is good, as it is demonstrated by the evaluation of the standard error, defined as the square root of the mean squared error, which in the case of 70 segments is 0.23 K. The output results, reported in Table 2, corroborate the good quality of the model.
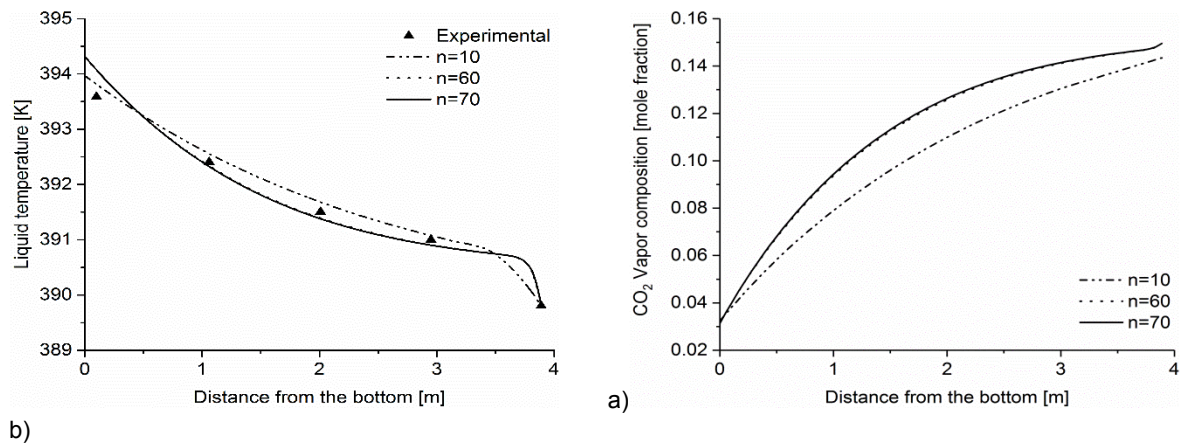

Figure 1: Variation of the a) liquid temperature and b) CO_2 vapor composition profile with the number of segments

Table 2: Comparison between the experimental output and the model results

Data	Experimental	Model (n=70)
Lean solvent		
Temperature [K]	394.15	395.24
CO_2 [mole fraction]	0.02372	0.02601
H_2O [mole fraction]	0.86773	0.86274
MEA [mole fraction]	0.10855	0.11125
Loading [mol CO_2/mol MEA]	0.21852	0.2338
Gas from condenser		
Molar flow [kmol/h]	0.11588	0.09809

The effect of a higher number of segments in the simulations is even more evident for what concerns the CO_2 vapor composition, reported in Figure 1 b), where a higher extent of the stripping reaction is highlighted. This is because the more detailed discretization permits a better evaluation of the reaction rates, generating more accurate results. Furthermore, along the column, there can be several transitions between the desorption and the absorption processes and using a low number of segments can lead to an under/over-estimation of the net fluxes (Kenig et al., 1999), as can be seen in Figure 2 a) and 2 b), where the CO_2 reaction flow rate and the H_2O interphase transfer flow rate are shown.
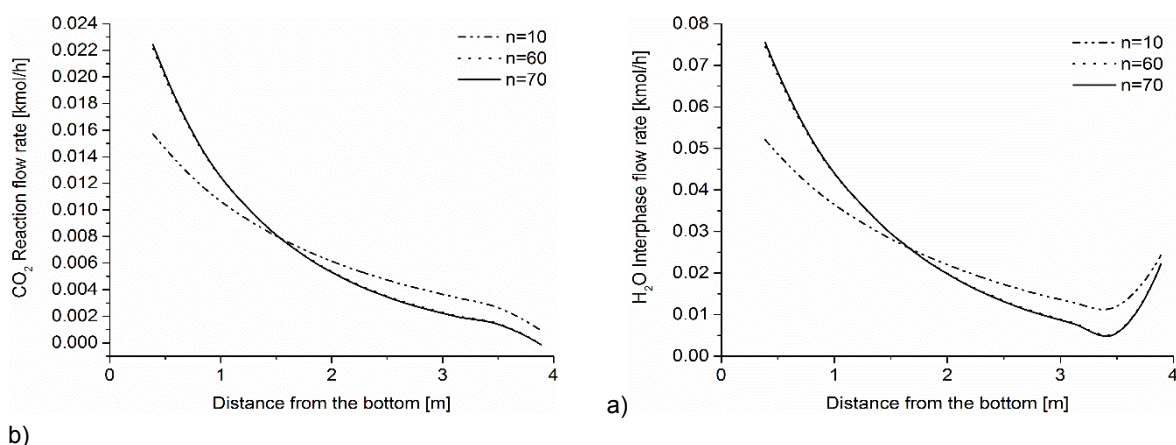

b)   a)

Figure 2: Variation of the a) CO_2 reaction flow rate and b) H_2O interphase flow rate profile with the number of segments

It can clearly be seen that the profiles obtained with 10 segments are significantly different from those at 70 segments, justifying again this analysis. As already mentioned, the process is characterized by an interphase transfer of water from the vapor to the liquid phase throughout the column, as a consequence of the condensation.

This result has evident implications in design, because it can lead to an under/over-estimation of the column dimensions and required duty, and in the assessment of control system structures, because the profiles would be different from the real ones.

The investigation of the correct number of segments to be used in the simulations is a key part in the modeling of this process, as it leads to obtain a more robust and more correct model from a numerical point of view.

4. Conclusions

The modeling of the post-combustion carbon capture CO_2 by means of liquid amine solutions process represents a challenging topic in the literature.

The integration of the technology at an industrial scale is mainly limited by the high energy consumption in the regeneration section that reduces the overall efficiency of the plant. In particular, the reboiler duty used in the solvent regeneration section represents the major operative cost in the entire process.

Prior to the search for solutions that optimize the system, a rigorous and reliable model of the stripper is needed. This is because a deep understanding of the process, characterized by simultaneous material and

energy transport and chemical reactions, is fundamental in order to propose new plant schemes or to find the best operative conditions.

In this work, the regeneration section was modeled using a rate-based approach. When this kind of model is employed, the definition of an appropriate number of segments for the discretization of the axial domain is an important step for the correctness of the model itself. Following a similar procedure presented in a previous work (Errico et al., 2016), the Peclet numbers for both the material and the energy transport were evaluated to study the eventual effect of the axial diffusion/dispersion. The high values of the nondimensional group suggested a plug-flow like behavior of the column, and then a high number of discretization segments was necessary for the solution of the resulting DAEs system.

Moreover, the possible presence of the backmixing due to the countercurrent was investigated simulating the plant with different number of segments. The asymptotic behavior for the profiles of the considered plant was reached with 70 segments, confirming the correctness of the plug-flow behavior assumption. A good agreement between the experimental values and the model results was found for what concerns both the liquid temperature profiles and the output lean solvent and top gas product. Furthermore, through the analysis of the CO_2 vapor composition profiles, an important result was found: the model with a higher number of segments allows to highlight a higher extent of the stripping reaction for the same fixed duty. This result has important implications for the eventual design of new plants and was found thanks to the more detailed discretization of the column height, that leads to a better description of the internal fluxes in the column. The proposed model is suitable for the extension to study the stripper from a dynamic point of view.

Acknowledgments

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