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Simulation Model Evaluation of CO₂ Capture by Aqueous MEA Scrubbing for Heat Requirement Analyses

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Abstract

Carbon dioxide is a powerful greenhouse gas, whose massive presence in the atmosphere causes gradual global warming. Absorption by means of chemical solvents is the most commonly used process for CO₂ removal. It can be applied to gaseous streams in power plants, natural gas, and refinery gas. Amine scrubbing is widely considered the most mature technology for PCC (post-combustion CO₂ capture), and 30% wt. MEA aqueous solution can be taken as the baseline solvent to be used as reference for studies focused on modelling and simulation. Thermodynamics, kinetics and mass transfer influence the chemical absorption process. The thermodynamic model exerts an influence also on the determination of the overall heat of absorption of the acid gas in the solvent, being the heat released at chemical equilibrium related to the extent of reactions. Its estimation is of paramount importance, since it is directly related to the energy requirement at the reboiler of the solvent regeneration column and determines the temperature profile along the absorber. The model used in this work has been previously validated by comparison with data of absorption performances with regard to mass transfer phenomenon. In this work, results obtained from simulations have been checked against experimental data, by focusing on the thermodynamic framework and its influence on the evaluation of the reboiler duty, for possible energy saving solutions in scale-up design.

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1. Introduction

According to the United Nations climate panel, the temperature on Earth will increase between 1.8°C and 4°C by the year 2100 due to global emissions of greenhouse gases. Carbon dioxide is thought to be one of the most important of these gases, with the main contribution to global CO₂ emission being combustion of fossil fuels for power production. Fossil fuels currently supply more than 85% of world's energy [1,2], 40% of which is produced in power plants [1], and it has been estimated that the supply of primary energy will continue to be dominated by fossil fuels for several decades. Therefore, the energy industry is facing the challenge of how reducing greenhouse gas emissions while ensuring the power supply.

Post-combustion CO₂ capture (PCC) is well recognized as an effective way of absorbing more than 80% of carbon dioxide emissions from fossil fuel-fired power plants [3], by means of chemical absorption processes. CO₂ removed from the flue gas can be stored in depleted oil fields or saline aquifers, instead of being sent to the atmosphere [4].

Amine scrubbing is widely considered the most mature technology for PCC: 30% wt. MEA aqueous solution can be taken as the baseline solvent and used as reference for studies focused on modelling and simulation. The greatest advantage of MEA is its relatively high loading, while its main drawbacks are chemical instability, high volatility and corrosivity. Moreover, being the enthalpy of reaction high, a high energy requirement at the reboiler of the solvent regeneration column is needed. The heat duty at the reboiler includes also the sensible heat required to raise the temperature of the solvent to that of the regenerated solution leaving the reboiler and the condenser duty, which is mainly the heat of vaporization of the water leaving the stripping section of the column, condensed and returned to the stripper as reflux.

This paper focuses on CO₂ capture from flue gas by absorption with monoethanolamine (MEA) which is industrially the most used solvent for post-combustion CO₂ removal and one of the preferred solvents for CO₂ removal from gas streams at low pressures.

In this work, results obtained from simulations have been checked against data from experimental campaigns of a pilot plant, paying particular attention to the thermodynamic model and its influence on the evaluation of the reboiler duty. The correct estimation of the reboiler duty can allow an engineering company to properly design and optimize carbon capture plants for energy saving and design.

Nomenclature

A	binary interaction parameter
B	binary interaction parameter
MEA	MonoEthanolAmine
P	pressure
P _{CO₂}	partial pressure of carbon dioxide
PCC	post-combustion capture
T	temperature
X	concentration in the liquid phase

Greek Symbols

ϕ	fugacity coefficient
γ	activity coefficient

Subscripts

<i>j</i>	molecular, electrolyte, cation or anion species
<i>k</i>	molecular, electrolyte, cation or anion species

2. Simulation Tool

Thermodynamics, kinetics and mass transfer influence the chemical absorption process. CO₂ and MEA are weak electrolytes, which partially dissociate in the aqueous phase: the high non-ideality of the liquid phase must be properly taken into account when dealing with vapor-liquid equilibrium (VLE) and a γ/ϕ approach is often used also by commercial process simulators. The software ASPEN Plus[®], provided with the Electrolyte-NRTL model [5-8] and the possibility of introducing user subroutines, has been chosen for simulation.

The thermodynamic model exerts an influence also on the determination of the overall heat of absorption of the acid gas in the solvent, being the heat released at chemical equilibrium related to the extent of reactions. Its estimation is of paramount importance, since it is directly related to the energy requirement at the reboiler and it determines the temperature increase along the absorber.

In ASPEN Plus[®] the “rate-based” model can be used to avoid the approximation of stage efficiency, by analyzing the mass and heat transfer phenomena that occur. In this simulation software, the prediction of mass transfer coefficients is based on the film theory by Lewis and Whitman, while other theories can more conveniently be used, *i.e.* the Eddy Diffusivity theory. Due to the suitability of ASPEN Plus[®] to be user customized, the simulator has been chosen as framework and has been integrated with an in-house kinetic/mass transfer Fortran subroutine and with fine-tuned binary interaction parameters for the Electrolyte-NRTL thermodynamic model.

3. Process Modeling

For process modeling, by coupling thermodynamics and mass transfer, three different simulation approaches (a, b, c) may be considered:

- “ASPEN Plus[®] default”: ASPEN Plus[®] default model, taken from the example “Rate-Based Model of the CO₂ Capture Process by MEA using Aspen Plus” [9];
- “proposed model (VLE default)”: ASPEN Plus[®] default Electrolyte-NRTL model, taken from the example “Rate-Based Model of the CO₂ Capture Process by MEA using Aspen Plus” for chemical and vapor-liquid equilibrium calculations, coupled with a mass transfer model implemented in an external subroutine linked to the simulator;
- “proposed model”: the Electrolyte-NRTL model, with fine-tuned binary interaction parameters that allow for a good description of both VLE and heat of absorption, coupled with a mass transfer model implemented in an external subroutine linked to the simulator.

A detailed description of the theoretical basis of the mass transfer concept and of the routine used for simulation can be found in previous papers [10-13].

For Vapor-Liquid-Equilibrium calculations, values of adaptive parameter $A_{j,k}$ and $B_{j,k}$ [14-16] for binary interaction parameters in the NRTL contribution to the liquid phase activity coefficient have been previously regressed against vapor-liquid equilibrium experimental data [17-24], considering chemical reactions as reported in [25]. The regression had been performed for parameters related to pairs H₂O-(MEA⁺-MEACOO⁻), (MEA⁺-MEACOO⁻)-H₂O, H₂O-(MEA⁺-HCO₃⁻), (MEA⁺-HCO₃⁻)-H₂O, being the ones that most affect this system.

Considering all the experimental data, the resulting AAD% in the estimation of CO₂ loading is equal to 7.6334 % for ASPEN Plus[®] default parameters and is equal to 5.3056 % for the proposed parameters.

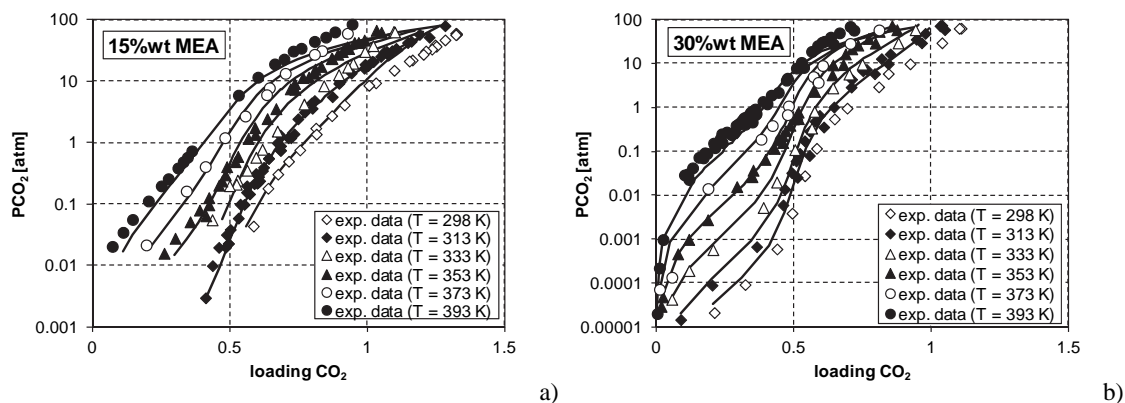


Fig. 1. Vapor-Liquid Equilibrium for the CO₂-MEA-H₂O system estimated by ASPEN Plus[®] parameters and experimental data for a) 15% wt. MEA aqueous solution and b) 30% wt. MEA aqueous solution.

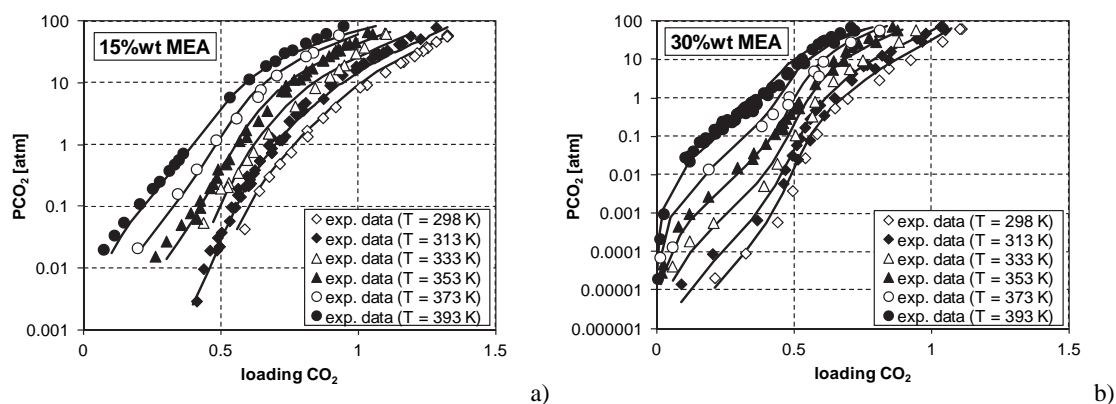


Fig. 2. Vapor-Liquid Equilibrium for the CO₂-MEA-H₂O system estimated by proposed parameters and experimental data for a) 15% wt. MEA aqueous solution and b) 30% wt. MEA aqueous solution.

Fig. 1 and Fig. 2 (P_{CO_2} is expressed in logarithmic scale in order to cover the overall range of partial pressures of CO₂ analyzed, since many data on gas solubility are available for wide ranges of temperature, pressure and amine concentration) report results of VLE calculations for 15% wt. and for 30% wt. MEA solution. The obtained parameters exert an influence not only on the VLE representation of the process, but also on the heat of absorption, which is strongly related to the energy requirement of the CCS plant. Therefore, those parameters have been validated by checking results also against literature-available experimental data of the heat of absorption [26-28].

Heat of absorption has been calculated by simulating an isothermal and isobaric simple flash, considering a vapor-liquid separation unit composed of two streams entering the unit (CO₂ and solvent) and two streams exiting the same unit (one stream for the vapor phase and one stream for the liquid phase). Input variables are temperature and pressure of the two fed streams and of the separation unit, the molar flow rate and the composition of the CO₂ and of the solvent streams.

The amount of heat released during the operation, which consists in the heat of absorption of carbon dioxide in the solvent, and the characteristics of the streams coming out of the separation unit, are the output of the simulation. The amount of carbon dioxide absorbed in the solvent and the heat of absorption per mole of CO₂ can be obtained as results of the analysis.

Results of heat of absorption obtained from calculations are shown in Fig. 3 for pressures up to about 5 bar, covering the pressure range of interest for the capture plant treating flue gas streams from power plants, since usually both the absorption and the desorption sections operate at pressures lower than 5 bar.

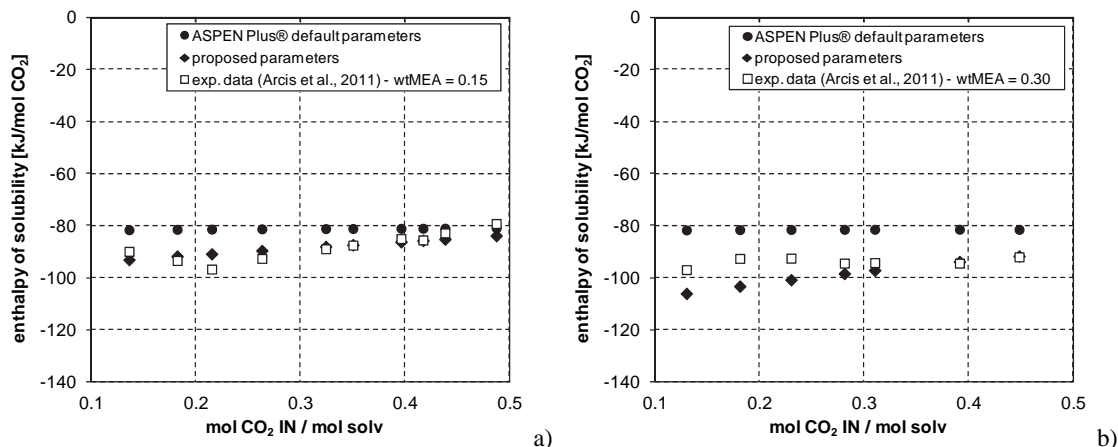


Fig. 3. Comparison between results of calculations using ASPEN Plus® default and the proposed parameters and experimental data by Arcis et al. [27] for mol CO₂ IN / mol solv up to 0.5, pressure up to 5 bar and T = 322.5 K for a) 15% wt. MEA aqueous solution and b) 30% wt. MEA aqueous solution.

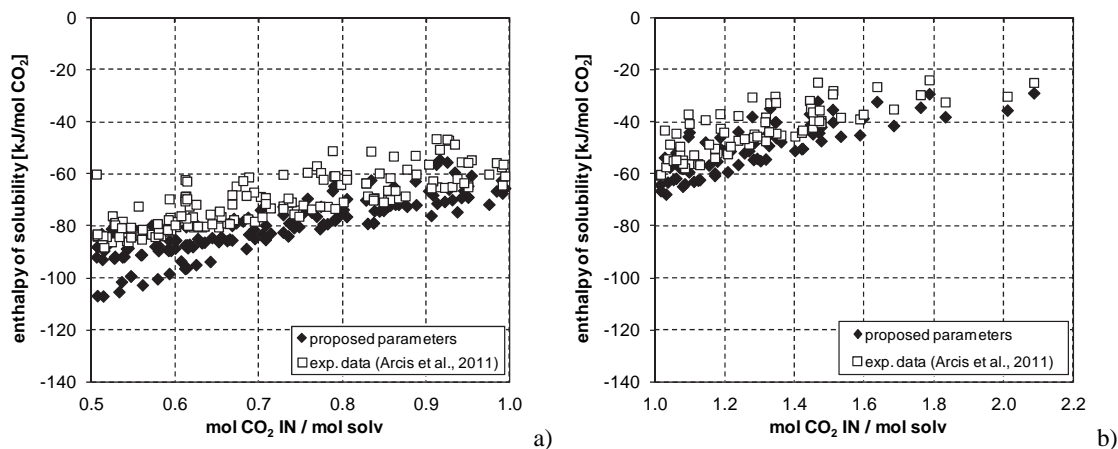


Fig. 4. Results of calculations and experimental data by Arcis et al. [27] for a) mol CO₂ IN / mol solv between 0.5 and 1 and b) mol CO₂ IN / mol solv higher than 1.

Fig. 4 shows both the results of heat of absorption calculations and the comparison with experimental data [27] for higher loadings. Generically, the absorption of CO₂ is a combination of chemical reactions and physical dissolution. Two characteristic domains exist: one corresponding to an unsaturated solution, where all the injected carbon dioxide is dissolved into the liquid, and one corresponding to a saturated solution, so that only part of the injected CO₂ is dissolved in the liquid phase. The solubility of the gas into the solution is limited by the reactions stoichiometry to a maximum loading of 0.5. For low CO₂ loadings, the enthalpy values can be considered almost constant [29], as in Fig. 3, while for higher values a change of the enthalpy behavior occurs. Due to possible

carbamate hydrolysis, the loading may exceed 0.5 for increasing partial pressures of carbon dioxide, so that the dissolution process becomes controlled by the reaction of carbon dioxide with the amine to form a carbonate, and not by the formation of the carbamate. The solubility can be extended to loadings higher than 0.5, though the change in the governance of the reaction causes a change in the energetic behavior [27], with a different trend (Fig. 4).

4. The Influence of Thermodynamic Parameters on the Prediction of Process Performances

An analysis of the results from the estimation of the performances of the absorption column of a CO₂ capture plant obtained with different thermodynamic parameters has been carried out in order to check the main differences with the experimental data.

Data of a pilot plant by Notz et al. [30] have been taken into account. Models “*proposed model (VLE default)*” and “*proposed model*” had not been validated yet on the basis of these data. The absorber has five packing sections, each one equipped with four elements of the structured packing Sulzer Mellapak 250Y and comprising a liquid redistributor at the top and a collector at the bottom. The overall height of the packed sections is 4.2 m. A washing section is installed at the top of the absorber above the lean solvent feed in order to reduce amine losses, in an additional packed section. The diameter of the column is 0.125 m.

The characteristics of the streams entering the column are reported in Table 1.

Table 1. Characteristics of the streams fed to the absorption column.

	<u>FLUEGAS</u>		<u>LEANIN</u>	
	mole fraction	mass fraction	mole fraction	mass fraction
molar flow rate [kmol/s]	72		200.1	
T [°C]	48.01		40.03	
P [mbar]	1004.49			
composition	mole fraction	mass fraction	mole fraction	mass fraction
Nitrogen	0.7460366	0.743	0	0
Oxygen	0.0887822	0.101	0	0
Water	1.11E-01	0.071	0.86949	0.673
Carbon dioxide	0.054326	0.085	0.027452	0.052
MEA	0	0	0.104599	0.275

According to Notz et al. [30], the accuracy of the temperature measurement is 0.1 K, the one of the pressure measurement is about 1-2 mbar and the one of the main flow measurement devices is 0.2-1% of the measured value. Though being this plant is of high interest for research purposes, the CO₂ removal rate is equal to 75.9%, below the 85-90% value usually considered as reference value. This is due to the characteristics of the experimental column, whose height does not correspond to the one of an industrial-scale plant [30].

Both thermodynamics and mass transfer play a fundamental role in the rigorous description of the chemical absorption process, as shown by results reported in Fig. 5 and in Fig. 6. Considering the two methods which use the same mass transfer model (“*proposed model*” and “*proposed model (VLE default)*”), the profile of carbon dioxide along the column both for the vapor phase and for the liquid phase shows a similar trend: the two curves slightly decrease as the gaseous stream flows inside the column (Fig. 5). Because of the adjusted values of thermodynamic parameters, results obtained with method c) are closer to data published by Notz et al. [30] than results obtained with method b).

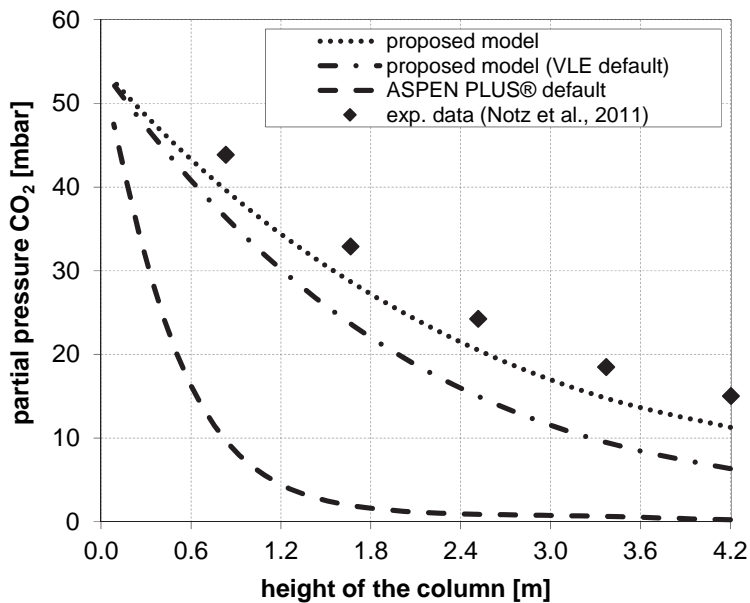


Fig. 5. Results of calculations and comparison with experimental data from Notz et al. [30] for CO₂ partial pressure profile along the column.

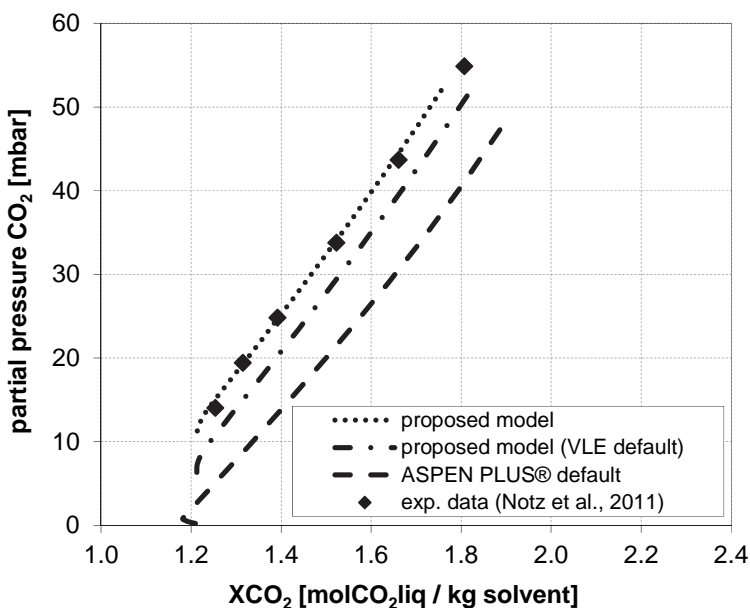


Fig. 6. Results of calculations and comparison with experimental data from Notz et al. [30] for CO₂ partial pressure profile and CO₂ liquid concentration (apparent composition) profile in the absorber column.

The values of thermodynamic parameters, therefore, play a fundamental role in determining the amount of carbon dioxide which is transferred from one phase to the other. In designing industrial columns, the difference between the

experimental datum and the value resulting from calculations can be significant and can lead to overestimate or underestimate the height of absorption columns, with consequent higher costs. This issue can become important also when dealing with the optimization of the energy requirement for carbon capture from different flue gases resulting from different energy sources [31]. Therefore, the influence of these thermodynamic parameters should be taken into account.

5. Conclusions

A detailed study is fundamental to properly assess the simulation framework of a chemical absorption system. Particular attention to the influence that the value of thermodynamic parameters of the chosen method (Electrolyte-NRTL) can exert on the estimation of equipment performances has been paid.

The study has been carried out by considering both the vapor and liquid composition occurring at vapor-liquid equilibrium at different temperatures and the heat required for absorption or desorption in the system. To this aim, a simulation with a flash vessel has been set up, and different operating conditions have been considered, with both the “*proposed model (VLE default)*” and the “*proposed model*”.

Simulations of the absorption column of a pilot plant have been then performed in order to check the representation of the absorption phenomenon by testing the model with experimental data of a CO₂ capture unit. Determining whether calculation results agree with experimental data is very important, since simulation software is used for process design of industrial plants.

The model can be further used to focus the research on the environmental impact of carbon dioxide capture, which is often related to the primary source used for energy generation.

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