GHGT-10

Sensitivity study for the rate-based simulation of the reactive absorption of CO_2

Inga Tönnies, Hari Prasad Mangalapally, Hans Hasse*

Laboratory of Engineering Thermodynamics, University of Kaiserslautern, 67663 Kaiserslautern, Germany

Abstract

The most promising process for Post Combustion Carbon Capture (PCC) is reactive absorption. For the design and scale-up of this process, reliable process models are needed. To achieve this, the models need to not only reliably describe the physical and chemical equilibria in the reacting systems but also to account for both mass transfer and reaction kinetics. Consequently, the models are complex and contain a large number of input parameters for describing fluid dynamics and physico-chemical properties. In order to assess the required quality of the input, the sensitivity of the simulation results to the parameters has to be known. This paper presents results from such a sensitivity study for a typical operating point of a PCC pilot plant with 0.3 g/g monoethanolamine (MEA) in water as the solvent. A rate-based model and its input parameters are introduced and describe the pilot plant results well. The most relevant input parameters of the model are systematically varied and the influence of that variation on the simulation results is monitored. Absorber and desorber are considered separately. The results are sensitive to most of the studied parameters. High sensitivities are found for the interfacial area, the Henry's law constant and the enthalpy of absorption as well as for the parameters describing the equilibrium and kinetics of the carbamate formation and the amine protonation equilibrium.

1. Introduction

Reactive absorption is the most promising process for Post Combustion Carbon Capture (PCC) from power plant flue gases. The design, optimization and scale-up of PCC plants has to be based on modeling and simulation. Such models are developed based on information on the physico-chemical properties of the chosen reactive systems and validated using pilot plant data. Only rate-based models are suited for predictive simulations of reactive absorption. In equilibrium stage models, the stage efficiency has to be fitted in order to match pilot plant data [1]. Rate-based models, however, require a large amount of input for describing fluid dynamics and physico-chemical properties. Besides equilibrium properties like gas solubility and absorption enthalpy, transport properties and mass transfer correlations are needed, as well as information on the chemical reactions. The quality of the simulation result is determined by the quality of that input data, which is often not available or, when available, is of dubious quality. In order to assess the required quality of the input, the sensitivity of the results of the process simulation to the

parameters has to be known. That information is also needed to decide whether estimation methods can be applied to circumvent the need for experiments. This paper presents results from such a sensitivity study for a typical operating point of a PCC pilot plant with 0.3 g/g monoethanolamine (MEA) in water as the solvent.

2. Simulations

The base case used for the present study is the simulation of a run in our own pilot plant which is described in detail by Mangalapally et al. [2]. Care was taken to select the base case so that it is close to realistic operating conditions of a large scale plant (i.e. the removal rate is 0.9). At the same time, an operating point was chosen for which the plant is not oversized as this would lead to unrealistic results for sensitivities. More information on the base case experiment is given in Table 1.

For the simulations, a rate-based model from the Aspen Plus example library [3] is used. The non-idealities in the liquid phase are described by the Electrolyte-NRTL with parameters from Austgen et al. [4]. To describe the kinetic reactions, concentration based kinetics for the forward and backward reaction are used. The forward reaction kinetic constants are taken from Pinsent et al. [5] for the hydrogen carbonate reaction and from Freguia et al. [6] for the carbamate reaction and the backward reaction kinetic constants were calculated from the equilibrium constants [6, 7]. Chemical kinetics are taken into account only in the absorber. Due to the higher temperatures, it is sufficient to model the desorber assuming chemical equilibrium is reached in each segment. The reboiler at the desorber bottom is considered as an equilibrium stage. The binary mass transfer coefficients are calculated from the correlation of Bravo et al. [8] and the hold-up is calculated from the correlation of Bravo et al. [9]. The interfacial area is fixed to 320 m^2/m^3 based on measurements with an aqueous KOH-solution in our pilot plant. The absorber and desorber are simulated separately in order to study the influence of the parameter changes on both apparatuses. In the simulations, the feed stream specifications are taken from experimental data and kept constant while the parameter of interest is varied. The influence of the parameter variation on the mass flow of captured/released CO_2 is monitored. Some additional information on the simulation, including results from a study on the influence of the numerical discretization is given in the Appendix.

Table 1: Base case of the sensitivity study (operating point from LTD pilot plant)

Parameter	Value
Flue gas flow rate / kg/h	79.3
Flue gas temperature / °C	46.2
Flue gas CO_2 partial pressure / mbar	101
Solvent flow rate / kg/h	200.2
Removal rate	0.906
Absorbed/desorbed CO_2 flow/ kg/h	10.60
Reboiler duty /kW[*]	12.62
Specific reboiler duty /GJ/t_{CO2}[*]	4.29

[*]Corrected for heat losses, see [10] for details.

In Table 2, the absorbed and desorbed CO_2 mass flow and the lean and rich loadings are shown for the base case simulation and the corresponding experiment. As the absorber and desorber are simulated separately, based on experimental input data, there are slight differences in the absorbed and desorbed CO_2 mass flow from the simulation. In Figure 1, the temperature and concentration profiles of the absorber are plotted. It can be seen that the absorbed and desorbed mass flow, the loadings and the profiles are well represented by the model.

Table 2: Comparison of base case simulation with experimental values

	Experiment	Simulation
Absorbed / desorbed CO_2 mass flow / kg/h	10.60	10.82/10.36
Rich loading / mol CO_2/mol MEA	0.437	0.447
Lean loading / mol CO_2/mol MEA	0.186	0.190

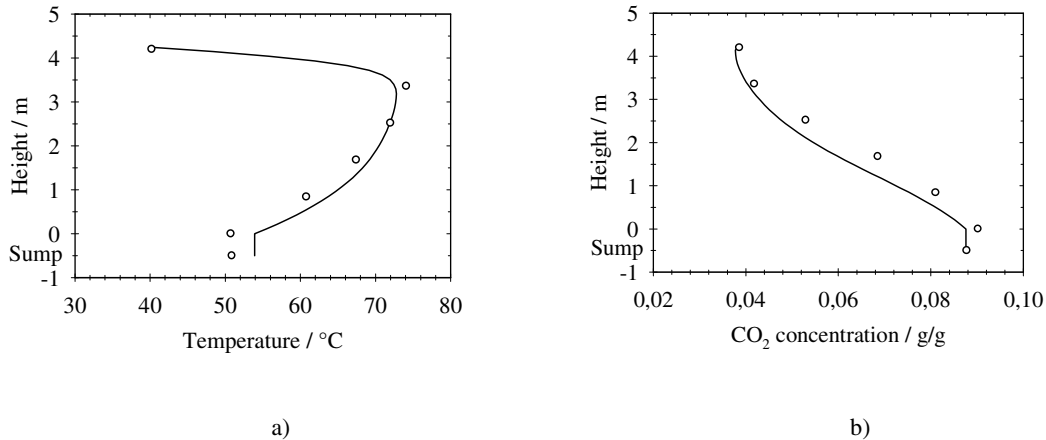a)   b)

Figure 1: Absorber a) temperature and b) CO_2 concentration profile for the base case; simulation results (lines) and experimental data (points).

For the sensitivity analysis, simulations are carried out, keeping all parameters constant except for the studied parameter, which is increased or decreased by 10% or 50%. It should be noted that the varied properties are generally not constant in the columns as they are functions of other variables like temperature and composition. The strategy to handle this problem is different for different properties. The goal was always to come close to a similar increase or decrease of the property over the entire temperature and concentration range of interest.

The studied parameters include fluid dynamic parameters, physical property parameters and reaction parameters. The fluid dynamic parameters include the interfacial area, the liquid and gas side binary mass transfer coefficients and the liquid phase hold-up. The physical property parameters include Henry's law constant, the heat of absorption, the amine ion diffusivities and the viscosity and liquid density of the solvent.

The Henry's law constant represents, here, the uncertainty of the phase equilibrium data. For simplicity, the Henry's law constant of CO_2 in the solvent is changed by changing the Henry's law constant of CO_2 in water and the viscosity of the solvent is changed by changing the pure liquid viscosity of water. The effect of a changed enthalpy of absorption is studied by varying the enthalpy of formation of CO_2. It should be noted here that contrarily to the other properties, studying the influence of this property on the transferred mass flow of CO_2 alone may not give a good indication of its importance for the process simulation, which stems also from its direct and strong influence on the enthalpy balance.

The ion diffusivities are calculated according to Nernst-Hartley [11] and are varied by changing the ion mobility for all amine species. The reaction parameters include the kinetic constants of the carbamate and bicarbonate formation and the equilibrium constants of those reactions as well as that of the amine deprotonation (acid dissociation constant of the protonated amine). When varying the kinetic constants of the forward reaction, the kinetic constants of the backwards reaction are changed simultaneously in order to obtain the same equilibrium concentrations. The

equilibrium constants are changed by adjusting the activity based equilibrium constant and the kinetic constant of the backward kinetic reaction.

In addition to the parameter variation, a short study on the influence of different mass transfer correlations from the literature was carried out.

3. Results and Discussion

Variation of mass transfer correlations

Table 3 shows the results from the study on the influence of different mass transfer correlations. Note that these correlations include both information on the mass transfer coefficients as well as on the interfacial area. The change in the mass flow of the absorbed/desorbed CO_2 compared to the base case simulation is reported. For the base case simulation a constant interfacial area of 320 m^2/m^3, as measured in our pilot plant, is used together with the mass transfer coefficients from the correlation of Bravo et al. [8]. As mentioned above, the base case simulation describes the experimental results well. The influence of the mass transfer correlations is much more important for the absorber than for the desorber. Using the correlation of Bravo et al. [8] for both mass transfer coefficients and the interfacial area leads to only slight changes of the absorbed/desorbed CO_2 mass flow compared to the base case simulation. However, drastic differences are observed for the absorber upon switching to the correlations of Bravo et al. [9]. The interfacial area in the base case simulation (which agrees with the experimental number) is 320 m^2/m^3, whereas the average value for the interfacial area in the absorber is 471 m^2/m^3 for Bravo et al. [8] and 106 m^2/m^3 for Bravo et al. [9]. This indicates that the differences between the different mass transfer correlations from the literature rather result from the differences in the correlations of the interfacial area rather than from those of the mass transfer coefficients.

Table 3: Influence of different mass transfer correlations on the mass flow of the absorbed/desorbed CO_2. Changes compared to base case simulation.

	Absorber	Desorber
Bravo et al. [8]	4.3%	2.0%
Bravo et al. [9]	-26.4%	-3.6%

Parametric Study

The results of the parametric study are summarized in Table 4 for the absorber and in Table 5 for the desorber. The change in the mass flow of the absorbed/desorbed CO_2 compared to the base case simulation is reported for the ± 10% and the ± 50% variation of the different parameters. For most properties, the change of the mass flow as a function of the change of the corresponding parameter is neither linear nor point symmetric to the origin. The signs are as expected in most cases, e.g. increasing the interfacial area is positive both for the absorber and desorber while increasing the equilibrium constant of the carbamate formation has a positive effect in the absorber but a negative effect in the desorber. For some properties which influence multiple processes in the columns, the observations are less readily explained and a more detailed discussion is given below.

For an easier comparison of the sensitivity of simulation results to the variations of the different properties, the largest absolute value observed in the ± 50% variation of the parameter is highlighted in bold in Tables 4 and 5. The exception is the liquid density which can be estimated with much better accuracy than the other parameters. For this property, the value from the ± 10% variation is used. For a more sophisticated approach, values for the accuracies with which the different parameters can be determined with the "same" effort would be needed to which the parameter variations could be related. Due to the difficulty of determining those values such an attempt was not undertaken.

Table 4: Results from the sensitivity study for the absorber: Percent change of absorbed CO_2 mass flow compared to the base case simulation for a variation of the different parameters by ± 10% and ± 50%. The bold number indicates the value which is used for the comparison. The absorber was modeled taking reaction kinetics into account.

Absorber	-50%	-10%	10%	50%
Fluid dynamics				
Interfacial area	**-15.9%**	-1.7%	1.4%	4.5%
Mass transfer coefficient, gas side	**-3.1%**	-0.3%	0.3%	1.0%
Mass transfer coefficient, liquid side	**-0.9%**	-0.1%	0.1%	0.3%
Hold-up	**-0.0%**	-0.0%	0.0%	0.0%
Physical properties				
Henry's law constant	5.2%	1.5%	-1.5%	**-7.7%**
Viscosity of solvent	**2.4%**	0.4%	-0.4%	-1.7%
Liquid density of solvent	-20.3%	**-1.9%**	1.4%	4.3%
Enthalpy of absorption	**1.2%**	0.2%	-0.3%	-1.2%
Ion diffusivities of amine species	**-1.1%**	-0.2%	0.2%	0.7%
Chemical properties				
Kinetic constant (carbamate)	**-5.0%**	-0.7%	0.5%	2.0%
Equilibrium constant (carbamate)	**-3.0%**	-0.4%	0.3%	1.2%
Equilibrium constant (amine deprotonation)	**2.0%**	0.4%	-0.4%	-2.0%
Equilibrium constant (hydrogen carbonate)	**-0.3%**	-0.1%	0.1%	0.3%
Kinetic constant (hydrogen carbonate)	0.0%	0.0%	0.0%	0.0%

Table 5: Results from the sensitivity study for the desorber: Percent change of absorbed CO_2 mass flow compared to the base case simulation for a variation of the different parameters by ± 10% and ± 50%. The bold number indicates the value which is used for the comparison. The desorber was modeled assuming that chemical equilibrium is reached in all segments.

Desorber	-50%	-10%	10%	50%
Fluid dynamics				
Interfacial area	**-5.3%**	-0.7%	0.5%	2.1%
Mass transfer coefficient, gas side	**-3.6%**	-0.4%	0.4%	1.4%
Mass transfer coefficient, liquid side	**-2.0%**	-0.2%	0.2%	0.7%
Physical properties				
Henry's law constant	**-17.8%**	-2.7%	2.4%	9.9%
Enthalpy of absorption	5.6%	1.4%	-1.8%	**-14.1%**
Liquid density of solvent	-1.3%	**-0.2%**	0.1%	0.5%
Ion diffusivities of amine species	**-0.5%**	-0.1%	0.1%	0.2%
Viscosity of solvent	**0.4%**	0.1%	-0.1%	-0.3%
Chemical properties				
Equilibrium constant (amine deprotonation)	-16.9%	-2.6%	2.4%	9.9%
Equilibrium constant (carbamate)	**13.9%**	2.3%	-2.1%	-9.2%
Equilibrium constant (hydrogen carbonate)	**1.4%**	0.3%	-0.3%	-1.3%

As discussed above, the influence of the fluid dynamic parameters is more pronounced for the absorber than for the desorber. For the absorber, the influence of the interfacial area is distinctly more important than that of the mass transfer coefficients. The mass transfer on both the liquid and the gas side play a role but the gas side resistance is more important. The results show that for reliable rate-based simulations, an improvement of the correlations for the effective interfacial area is particularly essential. In the development of such correlations, often only the product of

the mass transfer coefficient and the interfacial area is measured. In the complex rate-based simulations with kinetic reactions in the liquid film, however, it is not simply the product of the two which is important. Note that for the desorber which was modeled assuming chemical equilibrium, the situation is different. If both mass transfer coefficients are increased/decreased simultaneously by a constant factor, the resulting change in the mass flow is the same as that observed upon varying the interfacial area by that factor. For the desorber, only the product $k \cdot A$ is important. The effect of the hold-up in the absorber is negligible.

Of the studied physical property parameters, the Henry's law constant, which represents the influence of the gas solubility data, has the largest influence. The change of the equilibrium curve upon changing the Henry's law constant is shown in Figure 2. Note that changing the Henry's law constant changes the concentration of molecular CO_2 in the solvent and, hence, also affects the concentrations of all species in the reaction network.

The enthalpy of absorption shows a larger effect in the desorber compared to the absorber. In the absorber, it has an effect on the temperature profiles (not shown), but the effect on the absorbed CO_2 mass flow is rather small. For the desorber, however, the enthalpy of absorption has a large effect on the water vapor flow in the desorber at a fixed reboiler energy and therefore on the separation efficiency of the desorber. Therefore, when developing models for new solvents care has to be taken that the enthalpy of absorption is correctly represented especially at high temperatures.

The liquid density of the solvent changes the mass transfer coefficients, but more importantly the molarities of the species which are used in the concentration based kinetics. Therefore, liquid density shows a large sensitivity in the absorber while in the desorber the influence is almost negligible. The expected uncertainty of the solvent density however is low. The solvent liquid viscosity mainly affects the diffusivity of the molecular components which are calculated according to the Wilke-Chang model, but it also has a slight effect on the liquid side mass transfer coefficients. Lowering the solvent viscosity increases the diffusivities of the molecular components as they are inversely proportional. In the desorber, the effect of the diffusivities (viscosity) is almost negligible whereas in the absorber the effect is more pronounced. The effect of the ion diffusivities of the amine species is small and again larger in the absorber than in the desorber.
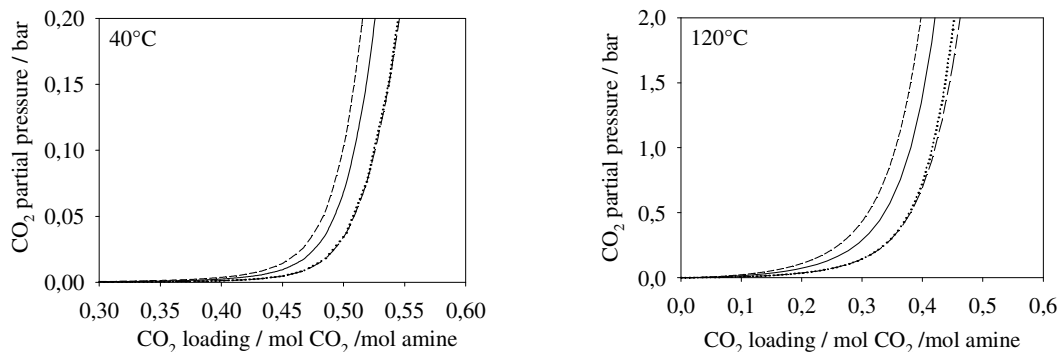

Figure 2: Solubility of CO_2 in an aqueous solution with 0.3 g/g MEA for 40°C and 120°C as calculated with different models: base case (solid line); Henry's constant decreased (long dashes) and increased (short dashes) by 50%; equilibrium constant of amine deprotonation decreased by 50% (dotted).

Of the reaction parameters, those describing the carbamate formation and the amine deprotonation have the largest effect. The hydrogen carbonate formation does not affect the results significantly because only a very small amount of hydrogen carbonate is present. The influence of the equilibrium constant of the hydrogen carbonate formation on the results is therefore low; the influence of its rate constant is negligible. Note that the values for the equilibrium constants of the carbamate formation and the amine deprotonation also have a significant effect on the gas solubility as calculated with the physico-chemical equilibrium model. This is shown in Figure 2 for the amine deprotonation.

Coincidently, a decrease of the equilibrium constant by 50% has almost the same effect as decreasing the Henry's law constant by 50%. The very strong influence of the carbamate formation and amine deprotonation equilibrium constants is a consequence of the shift of the equilibrium lines. The differences between the sensitivities in the absorber and desorber regarding these chemical equilibrium constants can be attributed to the fact that only the desorber was calculated using the assumption of chemical equilibrium.

4. Conclusions

This study gives insight into the sensitivity of the results from rate-based modelling of PCC with MEA solutions to the input parameters which are used for describing the fluid dynamics and the physico-chemical properties. The results should, at least as a point of orientation, be helpful in developing sound models for new solvents for which much of the required information is lacking. They are particularly useful for deciding which information should be measured and which can be estimated. High sensitivities are found for the interfacial area, the Henry's law constant and the enthalpy of absorption as well as for the parameters describing the equilibrium and kinetics of the carbamate formation and the amine protonation equilibrium. The accuracy of other parameters such as viscosity, diffusivity and density is less critical. The present results show the need for more reliable correlations for the interfacial area in order to improve rate-based absorption models.

Appendix: Supplementary information on the model

Reaction kinetics

The kinetic parameters of Freguia et al. [6]. are used in a previous version of the Aspen Plus example file [7] and in this work as they describe the results of our pilot plant more accurately than those of Hikita et al. [1] which are approximately 50% lower in the relevant temperature range. With Hikita's kinetic constants, the absorbed CO_2 mass flow for the base case is 5% lower than that calculated with Freguia's kinetic constants. Using concentration based kinetics in the absorber for both the forward and backward reaction is thermodynamically inconsistent because the equilibrium model uses activity based equilibrium constants. A Fortran subroutine that uses the forward concentration based kinetic constant and calculates the backward concentration based kinetic constant from the activity based equilibrium constant showed a change in the absorbed CO_2 mass flow of only 1.5%, but convergence was poor.

Discretization

The numerical discretization of the column over its height and in the liquid film is of great importance for the simulation. A systematic variation of the number of segments used for the vertical discretization of both the absorber and desorber showed that above 40 segments the absorbed and desorbed CO_2 mass flow do not change significantly. For the liquid film discretization, an unsymmetrical grid distribution as suggested by Asprion [13] is used.

$$x_i = \left(\frac{i}{n}\right)^{1/m} \tag{1}$$

x_i is the normalized film position, n is the number of film segments and m is a grid distribution factor. If m equals one, the distribution is equidistant whereas for high numbers of m, the grid distribution shifts towards the interface. The influence of the number and location of the discretization elements in the film on the removal rate is presented in Figure 3. The removal rate is strongly overestimated for low values of m and n. If m is too high, all points lie at the interface and the removal rate is overestimated as well. For the current study, a discretization of $n = 7$ and $m = 20$ was chosen in order to find a compromise between computational efficiency and accuracy.

In Aspen Plus, several options are available for defining how the bulk properties in each segment are calculated from the properties of the inlet and outlet streams. Different choices result in variations of the absorbed/desorbed CO_2 mass flow of about 1%. For the present study, the standard setting was used in which it is assumed that the bulk properties in a section are the same as those of the stream leaving the stage.

Aspen Plus also allows inclusion of a liquid film non-ideality correction, i.e. the thermodynamic factor, in the calculation of the driving force in the Stefan-Maxwell equation. As simulations carried out with and without that correction yielded practically the same results, the liquid film non-ideality was not considered in this study.
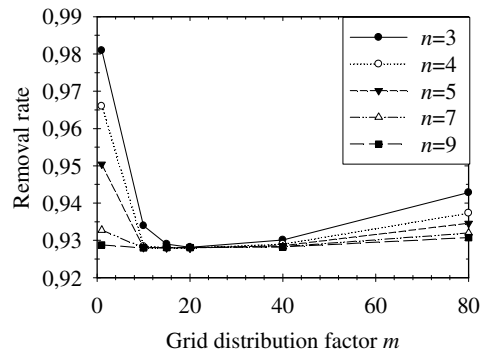

Figure 3: Removal rate in the absorber as a function of the grid distribution factor *m* and the number of film segments *n* for the base case. The experimental result for the removal rate is 0.906.

5. References

[1]   Luo X., Knudsen J.N., de Montigny D., Sanpasertparnich T., Idem R., Gelowitz D. et al. Comparison and validation of simulation codes against sixteen sets of data from four different pilot plants. Energy Procedia 2009;1:1249 – 56.

[2]   Mangalapally H.P., Notz R., Hoch S., Asprion N., Sieder G., Garcia H. et al.. Pilot plant experimental studies of post combustion CO_2 capture by reactive absorption with MEA and new solvents. Energy Procedia 2009;1:963 – 70.

[3]   Aspen Technology Inc.. Rate-based model of the CO_2 capture process by MEA using Aspen Plus. Aspen Plus Example Library 2008.

[4]   Austgen D.M., Rochelle G.T., Peng X., Chen C.C.. Model of vapor liquid equilibria for aqueous acid gas alkanolamine systems using the electrolyte NRTL equation. Ind. Eng. Chem. Res. 1989; 28(7):1060–73.

[5]   Pinsent B.R., Pearson L., Roughton F.J.W.. The kinetics of combination of carbon dioxide with hydroxide ions. Trans. Faraday Soc. 1956; 52:1512-20.

[6]   Freguia S., Rochelle G. T.. Modeling of CO_2 capture by aqueous monoethanolamine. AIChE J. 2003; 49(7):1676–86.

[7]   Aspen Technology Inc.. Rate-based model of the CO_2 capture process by MEA using Aspen Plus. Aspen Plus Example Library 2007.

[8]   Bravo J.L., Rocha J.A., Fair J.R.. Mass-transfer in gauze packings. Hydrocarbon Process. 1985; 64(1):91–5.

[9]   Bravo J.L., Rocha J.A., Fair J.R.. A comprehensive model for the performance of columns containing structured packings. I. ChemE. Symp. Ser. 1992;128: A439-57.

[10]   Notz R.. CO_2-Abtrennung aus Kraftwerksabgasen mittels Reaktivabsorption, PhD thesis, Berlin: Logos Verlag; 2009.

[11]   Horvath A. L.. Handbook of Aqueous Electrolyte Solutions. Chichester: Ellis Horwood; 1985.

[12]   Hikita H., Asai S., Ishikawa H., Honda M.. The kinetics of reactions of carbon dioxide with monoethanolamine, diethanolamine and triethanolamine by a rapid mixing method. Chem. Eng. J. 1977; 13:7-12.

[13]   Asprion N.. Simulation of mass transfer in reactive absorption. In 16th European Symposium on Computer Aided Process Engineering and 9th International Symposium on Process Systems Engineering 2006.