

# Improved rate-based modeling of the process of CO<sub>2</sub> capture with PZ solution

*Stefania Moioli\*, Laura A. Pellegrini*

*Dipartimento di Chimica, Materiali e Ingegneria Chimica “G. Natta”, Politecnico di Milano, Piazza Leonardo  
da Vinci 32, I-20133 Milano, Italy*

\*Corresponding author. Tel.: +39 02 2399 3237; fax: +39 02 7063 8173.

E-mail addresses: [stefania.moioli@polimi.it](mailto:stefania.moioli@polimi.it) (S. Moioli), [laura.pellegrini@polimi.it](mailto:laura.pellegrini@polimi.it) (L.A. Pellegrini)

## **Abstract**

In recent years the interest in the development of CO<sub>2</sub> capture technology has increased due to global warming, which is mainly due to emissions of carbon dioxide and which causes climate changes to the atmosphere and the Earth.

Commercial software packages are based on different methods for the column calculations, such as equilibrium or rate-based approaches. The commercial simulation software ASPEN Plus<sup>®</sup> has been used as a framework for the modeling, based on the rate-based approach with the Eddy diffusivity theory. The proposed model has been validated by comparison with experimental data.

An improvement in the prediction of mass transfer coefficients has been obtained by linking an external Fortran user subroutine to the software.

*Keywords:* CO<sub>2</sub> capture, PZ kinetics, rate-based model, PZ scrubbing, Eddy diffusivity theory.

## 1. Introduction

In recent years the interest in the development of CO<sub>2</sub> capture technology has increased due to global warming, which is mainly due to emissions of carbon dioxide and which causes climate changes to the atmosphere and the Earth.

One of the most used techniques to achieve CO<sub>2</sub> removal is absorption by chemical solvents, as amines. In the last years traditional amine solutions have been used in mixture with specific activators (as piperazine (PZ)) in order to enhance the absorption process. In particular, the use of PZ-blended solutions, as PZ-activated MDEA solvent, has been considered to be a possible way to improve the absorption characteristics of traditional amine solutions. Recently, also the use of a solvent composed of water and only PZ has become to be considered advantageous because of the improved capacity and rate of reactions, characteristics of piperazine. The concentration of PZ is limited by its solubility (Freeman et al., 2009), at the operating temperatures, since its melting point is very high (106°C). However, the use of this species as pure compound in water has not been widely analyzed in literature yet. For this reason, a reliable model able to well represent the absorption of CO<sub>2</sub> is needed and has been studied in this work.

Commercial software packages (AspenTech, 2010a, 2010b) are based on different methods for the column calculations, such as equilibrium or rate-based approaches. It is commonly accepted that a rate-based approach has a potential for the most accurate description of the phenomenon (Kohl and Nielsen, 1997), but thermodynamics and mass transfer with kinetics should be properly taken into account. In this paper the rate-based approach has been considered, with a theory for mass transfer different from the traditionally used film theory (Lewis and Whitman, 1924; Moioli and Pellegrini, 2013).

Simulations of the proposed model, based on the Eddy Diffusivity theory (King, 1966), have been performed with the commercial simulation software ASPEN Plus<sup>®</sup>, properly modified and used as a framework for modeling.

The obtained tool has been used for validation by comparison with experimental data (Plaza, 2012), showing an improvement in the prediction of mass transfer.

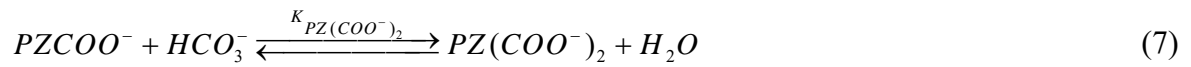
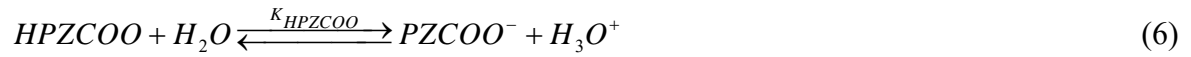
## **2. Modeling of PZ scrubbing systems**

The mass transfer phenomenon of the PZ scrubbing process is promoted by chemical reactions in the liquid phase. From the bulk of the gas phase to the bulk of the liquid phase different steps occur, involving the diffusion of the component from the bulk of the gas phase to the gas-liquid interface, the diffusion of reagents from the gas-liquid interface to the bulk of the liquid phase, the simultaneous reaction between the dissolved gas and the liquid reactant and the diffusion of reaction products in the bulk of the liquid phase promoted by the concentration gradient due to chemical reactions (Bergman and Yarborough, 1978). Indeed, the presence of the amine dramatically influences the solubility of the acid gas in water (Kohl and Nielsen, 1997), making the amine scrubbing process advantageous.

As a consequence, an accurate description of the phenomenon, in terms of thermodynamics, kinetics and mass transfer, is fundamental for a reliable representation of the absorption process.

## 2.1 Thermodynamic modeling

Piperazine reacts twice with the absorbed carbon dioxide, producing cations and anions in the liquid phase other than those generated by water dissociation. When dealing with amine scrubbing systems, chemical equilibrium reactions should be considered for the thermodynamic description of the process. The set of reactions is then composed of Eqs. (1)-(7):



The system is composed of solvent species (i.e.: H<sub>2</sub>O and PZ, respectively), acid gas molecular species (CO<sub>2</sub>) and ions, which are not interested by vapor-liquid equilibrium, as shown in Figure 1.

The system is highly non-ideal due to the presence of ions in the liquid phase, which do not undergo to vaporization, and can be accurately described by means of a  $\gamma/\phi$  approach (Khoo

and Tan, 2006; Langé et al., 2013; Pellegrini et al., 2013). In this work the Electrolyte-NRTL model developed by Chen et al. (Chen et al., 1979; Chen et al., 1982), Chen and Evans (Chen and Evans, 1986) and Mock et al. (Mock et al., 1986) for the liquid phase and the SRK (Soave, 1972) (Equation of State) EoS for the vapor phase have been used. Unlike the liquid phase, the vapor phase shows a negligible deviation from ideality, so an EoS can be used. In particular, the Soave-Redlich-Kwong, which can also be successfully employed to describe the behavior of carbon dioxide in mixture with n-alkanes (De Guido et al., 2014; Pellegrini et al., 2012b), has been chosen. The used thermodynamic model is based on parameters both for the vapor phase (Pellegrini et al., 2012a) and for the liquid phase. For this latter, in particular, it requires a large number of parameters, since it takes into account interactions between molecule and molecule, molecule and ion pair, ion pair and ion pair. Moreover, the values of parameters related to species with a high concentration should be carefully chosen. A test on values implemented in an ASPEN Plus® (AspenTech, 2010b) template file has shown a good agreement with experimental data (Dash et al., 2011b), so default parameters have been maintained. Figure 2 reports some of the experimental points and the obtained trends used for comparison. In this work all the values published by Dash et al. (2011b) have been considered, though not all of them have been shown in this paper for the sake of conciseness.

In order to model the system, which takes into account the presence of reactions, the chemical equilibrium constants have been obtained by considering the following expression (with  $T$  in [K]):

$$\ln K_j = A_j + \frac{B_j}{T} + C_j \ln T + D_j T \quad (8)$$

The values of parameters have been taken from literature (Edwards et al., 1978) for reactions of dissociation of water, of dissociation of carbon dioxide and of dissociation of the

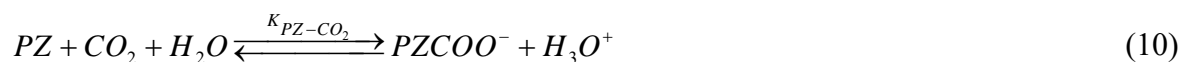
bicarbonate ion. For the reaction of protonated PZ (Eq.(4)), experimental data can be found in literature (Hetzer et al., 1968; Lide, 1996, 2008; Pagano et al., 1961; Paoletti et al., 1963; Pickett et al., 1953; Schwarzenback et al., 1952) and have been considered for comparison with all the available correlations (AspenTech, 2010b; Bishnoi and Rochelle, 2000b, 2002a; Cullinane and Rochelle, 2005a; Dash et al., 2011a; Derks et al., 2005a; Derks et al., 2005b; Hetzer et al., 1968; Hillard, 2004, 2008; Liu et al., 1999), reported in Table 1.

As shown in Figure 3, the different correlations give values of the chemical equilibrium constant for the reaction involving piperazine very different one from the others in the range of temperatures between 320 K to 350 K and none of them can be considered reliable. Data (Hetzer et al., 1968; Lide, 1996, 2008; Pagano et al., 1961; Paoletti et al., 1963; Pickett et al., 1953; Schwarzenback et al., 1952) have then been used to regress new parameters (Figure 4), in order to obtain an expression for the equilibrium constant whose results are closer to experimental data.

The following regressed correlation has been used for modeling:

$$\ln K_{PZH^+} = -9.6416 - \frac{5008.4}{T[K]} \quad (9)$$

For the reaction (Eq. (5)) involving the formation of the piperazine carbamate from piperazine and bicarbonate, no experimental data are available. Values of parameters found in literature (Bishnoi and Rochelle, 2000b, 2002b; Cullinane and Rochelle, 2005b; Dash et al., 2011c; Derks et al., 2005b; Hillard, 2004, 2008) and the ones reported in the example by ASPEN Plus<sup>®</sup> have been considered. However, many authors do not consider reaction Eq. (5), but prefer to consider the reaction:



which becomes Eq. (5) if summed to Eq. (2). The resulting equilibrium constant, that is the product of the equilibrium constant of these two reactions, can be compared to equilibrium constants directly calculated from Eq. (5).

Values of parameters are reported in Table 2 (for each source, if two lines are present, the first line refers to Eq. (2), the second one to Eq. (10); otherwise Eq. (5) is considered).

A comparison among all the analyzed correlations has shown differences, but a new correlation cannot be obtained because experimental data are not available. The expression by Bishnoi and Rochelle (Bishnoi and Rochelle, 2000b) has been considered for simulation.

As for the reaction of dissociation of HPZCOO, values of the equilibrium constant expression by ASPEN Plus<sup>®</sup> have been maintained, since no experimental data are available and found correlations (Bishnoi and Rochelle, 2000b, 2002b; Cullinane and Rochelle, 2005b; Dash et al., 2012; Derks et al., 2005b; Hillard, 2008), reported in Table 3, are quite different one from the others in the range of operating temperature of absorption columns.

Each PZ can be bonded to two molecules of CO<sub>2</sub>, involving the formation of the piperazine dicarbamate, according to Eq. (7). As for Eq. (6), the correlation by ASPEN Plus<sup>®</sup> has been maintained. No experimental data are available and literature correlations (Bishnoi and Rochelle, 2000b, 2002b; Cullinane and Rochelle, 2005b; Dash et al., 2011b; Derks et al., 2005b; Hillard, 2004), reported in Table 4, do not show a unique trend. Some researchers have considered Eq. (11) instead of Eq. (7): however the equilibrium constant can be obtained by summing the inverse of Eq. (2) to Eq. (11).





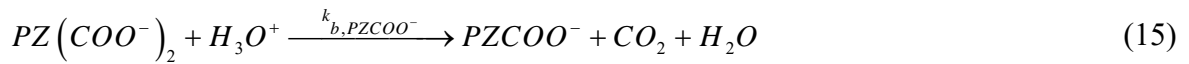
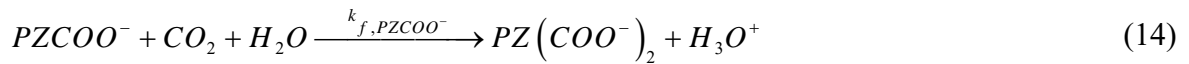
As for Henry's constants, an expression analogous to Eq. (9) with parameters from ASPEN Plus® (AspenTech, 2010b) has been considered.

## 2.2 Mass transfer with kinetics modeling

### 2.2.1 Kinetic-controlled reactions

Absorption of carbon dioxide in PZ solution involves finite rate reactions. These reactions are quite fast, but chemical equilibrium is not attained, so a proper kinetic characterization is important for a reliable description of the phenomenon (Moioli et al., 2012; Pellegrini et al., 2011a).

Piperazine reacts twice with carbon dioxide, producing a carbamate ion and a dicarbamate one, according to the following kinetic-controlled mechanism:



Moreover, carbon dioxide reacts also with the hydroxyl ion following a mechanism already known in literature (Eqs. (16)-(17)) with kinetic constants calculated according to the Arrhenius form (Eq. (18)) with parameters taken from Pinsent et al. (Pinsent et al., 1956).



$$k_j = A_j \exp\left(-\frac{E_{att,j}}{RT}\right) \quad (18)$$

It should be pointed out that all reactions involving carbon dioxide are kinetic-controlled reactions, though characterized by different rates, according to literature.

The kinetic constant for the reaction of carbon dioxide and piperazine in water is used in some works (Bishnoi and Rochelle, 2000a; Samanta and Bandyopadhyay, 2007; ZareNezhad and Eggeman, 2006; Zhang et al., 2001). However, as shown in Figure 5, at elevated temperatures results of the compared correlations are quite different, so the expression by ASPEN Plus<sup>®</sup> has been maintained for modeling. The kinetic constant of the backward reaction has been obtained by considering the one of the forward reaction and the equilibrium constants of reactions Eq. (2) and Eq. (5).

Also for the kinetic constant of carbon dioxide and PZCOO<sup>-</sup> no experimental data are available in literature and only a comparison among different models (Bishnoi and Rochelle, 2000b; Samanta and Bandyopadhyay, 2007; ZareNezhad and Eggeman, 2006) can be done: curves obtained according to Dang and Rochelle, Bishnoi and Rochelle and ASPEN Plus<sup>®</sup> overlap. According to Dang and Rochelle the kinetic constant of this reaction can be considered equal to ¼ of the kinetic constant of the reaction involving PZ and CO<sub>2</sub>. In this work  $k_{f,PZ}$  by ASPEN Plus<sup>®</sup> has been used, so  $k_{f,PZCOO^-} = 0.25 \cdot k_{f,PZ}$  has been considered. It should be pointed out that simulations performed also with  $k_{f,PZCOO^-}$  by ASPEN Plus<sup>®</sup> have shown that this reaction does not exert a strong influence on the behavior of the absorption column (the profiles of temperature and composition with the two  $k_{f,PZCOO^-}$  result almost the

same). However, for a complete description of the process, this reaction has been taken into account.

The kinetic constant of the backward reaction has been computed by considering the one of the forward reaction and the equilibrium constants of Eq. (2) and Eq. (7).

### **2.2.2 Diffusion with reaction**

As mentioned in Section 1, different approaches can be used to represent the absorption column, depending on the desired accuracy. Apart from “rule of thumb” designs, used only for quick hand calculation estimates (Kohl and Nielsen, 1997), methods based on “equilibrium-based stage” approach or “rate-based stage” approach are commonly considered for modeling (Pellegrini et al., 2011b).

According to the “equilibrium-based stage” approach a theoretical stage is considered, in which the liquid and the gas attain equilibrium, and the performance of this stage is adjusted to represent a real tray by the use of a correction factor, the “tray efficiency”. With nonreactive systems, the tray efficiency can be determined by considering gas and liquid properties, tray design and fluid dynamics; with reactive systems the correlation for tray efficiency is more complex because the reactions affect both the vapor-liquid equilibrium relationship and the rate of absorption. However, the “equilibrium-based stage” approach is widely used also in amine scrubbing modeling, because it is not demanding in terms of computational time.

The “rate-based stage” approach analyses the mass and heat transfer phenomena that occur in a real tray or section of packing (Krishnamurthy and Taylor, 1985a, 1985b, 1985c, 1985d). The method considers each real tray individually, and is based on separate mass and heat balances for each phase, which are solved simultaneously with mass and energy balances on

the tray. The deep insight into the mass transfer phenomenon requires to consider mass transfer theories. Film theory (Lewis and Whitman, 1924) is widely used, but other theories, such as the Eddy Diffusivity theory (King, 1966), have been developed and can be successfully employed for the description of the phenomenon of diffusion with reaction in case of amine scrubbing. Because of the large number of simultaneous equations to be solved, the “rate-based stage” approach is more demanding in terms of computational time and convergence is not always easily achievable. However, it is considered the most reliable method for amine scrubbing modeling, because developed on theoretical basis.

As for mass transfer modeling, ASPEN Plus® performs calculations with the “rate-based stage” approach, with kinetic controlled reactions and basing the prediction of mass transfer coefficients on a mass-transfer theory, without need of the stage efficiency concept. By default, film theory (Lewis and Whitman, 1924) is used and, for the mass transfer coefficient, a linear dependence on diffusivity of carbon dioxide is obtained:

$$k^{\circ}_l = \frac{D_{CO_2}}{\delta} \quad (19)$$

whereas for amine scrubbing systems a square root dependence on  $D_{CO_2}$  is observed.

So the Eddy Diffusivity theory (King, 1966) has been introduced to obtain a correct prediction. It takes into account a parallel turbulent transport, through an Eddy Diffusivity, which is added to the molecular diffusivity and which is:

$$E = \varepsilon x^2 + b \quad (20)$$

where  $x$  is the distance normal to the interface.

Considering the contribute of Eddy diffusivity to mass transfer and the presence of chemical reactions, the mass balance equation for carbon dioxide can be expressed as (Moioli et al., 2014; Moioli et al., 2013):

$$\frac{\partial}{\partial x} \left[ (D_{CO_2} + \varepsilon x^2) \frac{\partial [CO_2]}{\partial x} \right] - R_{CO_2} = 0 \quad (21)$$

where  $R_{CO_2}$  is the rate of consumption of carbon dioxide due to chemical reactions occurring in the liquid phase.

The mass transfer coefficient, obtained by analytically solving Eq. (21), shows a square root dependence on diffusivity of carbon dioxide in the amine solution, in better agreement with data on amine scrubbing systems (Austgen, 1989). The derived expression for the mass transfer coefficient is:

$$k_l = \frac{\pi}{2} \sqrt{\frac{1}{2} \left( k_{f,OH^-} [OH^-]_i + k_{f,PZ} [PZ]_i + k_{f,PZCOO^-} [PZCOO^-]_i \right) D_{CO_2}}$$

For a detailed description of the mathematical passages to obtain this expression, please see the Appendix Section.

The developed model has been implemented by means of an external Fortran subroutine in the process simulator ASPEN Plus<sup>®</sup>, that, among the commercial process simulators, is the only one that can be easily user customized.

The mass transfer area, fundamental for calculation, has been estimated by using the default correlation already implemented in ASPEN Plus<sup>®</sup>. It should be underlined that the adaptive Interfacial Area Factor provided in ASPEN Plus<sup>®</sup> has been set equal to 1, in order to avoid any influence of adjustment parameters.

### 3. Results

Experimental data from different test runs of a pilot plant (Plaza, 2012) have been used for comparison with simulation results of the proposed model.

The plant is characterized by an absorption column, operating at atmospheric pressure. It presents two sections of structured packing, each one of 3.05 m and the diameter is 0.427 m. A gaseous stream containing CO<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub> and H<sub>2</sub>O is fed to the absorber with the aim of removing CO<sub>2</sub> by means of a PZ aqueous solution with a composition of PZ in the solvent varying for each case. Table 5 reports the detailed conditions and concentrations of the gaseous stream obtained by Plaza (2012). Characteristics of the amine solution fed to the absorption column (Plaza, 2012) are reported in Table 6.

Simulation results of some test runs, along with experimental data, are shown in Figure 6 and in Figure 7. The latter reports only the comparison between ASPEN Plus<sup>®</sup> default and the proposed model results, since no experimental values of CO<sub>2</sub> vapor molar fraction are available.

### 4. Discussion

All the tests of the “Nov. ‘08” campaign reported by Plaza (Plaza, 2012) have been taken into account. According to the source (Plaza, 2012), other tests have been performed but not published.

The temperature profile of all the considered cases is in good agreement with experimental data. As shown in Figure 6, experimental values do not show a unique temperature profile: sometimes two points are present at the same height of the column. This feature is due to the

fact that experimentally both the temperature of the vapor phase and the temperature of the liquid phase had been measured, as reported in the considered source (Plaza, 2012). Since the source does not differentiate experimental data of the two phases, all of them have been considered.

Figure 7 shows the vapor molar fraction profiles obtained with ASPEN Plus<sup>®</sup> default and with the modified method. The use of the Eddy Diffusivity theory, with a square root dependence on the CO<sub>2</sub> diffusivity in the solvent, makes the simulator estimate a lower absorption of carbon dioxide along the column. This is in agreement with simulations of other amine systems (Moioli et al., 2014; Moioli et al., 2013), for which experimental values of composition along the column can be found in literature (Naami et al., 2012).

Though no experimental data of removal of carbon dioxide are available (Plaza, 2012), the particular temperature profile characteristic of the absorption column can be used as an index of the model reliability. The increase in temperature is due to the heat released because of the exothermic reactions that occur in the liquid phase, while the position of the bulge depends on the ratio between the liquid and the vapor flows in the column (Kohl and Nielsen, 1997). A proper description of the temperature profile can be useful to determine the accuracy of the model. This peculiarity is confirmed also when dealing with other amine scrubbing systems (Moioli et al., 2014; Moioli et al., 2013): a model able to well represent the temperature profile can well reproduce the amount of absorbed acid gas and consequently the molar fraction of the purified gaseous stream.

The calculated temperature profile presents a trend more in accordance with experimental data than ASPEN Plus<sup>®</sup>. Results of simulation of different runs show that the proposed model is able to reproduce the trend of temperature along the column, with a good representation of the position and of the extension of the bulge, which are different for the cases reported in Figure 6.

## 5. Conclusions

Mass transfer significantly influences the absorption process of acid gases in aqueous amine solutions, in particular when removal of carbon dioxide is performed.

In this paper ASPEN Plus<sup>®</sup>, a commercial simulation software, has been used as a framework for simulation, by integrating the proposed model with an external subroutine where the Eddy diffusivity theory (King, 1966) instead of film theory (Lewis and Whitman, 1924) has been taken into account to model the amine scrubbing system. Being the absorption process involving CO<sub>2</sub> characterized by kinetic-controlled reactions, proper kinetic expressions have been considered.

The use of this tool on different case studies taken from a pilot plant (Plaza, 2012) shows an improvement in the representation of the absorption phenomenon.

## Appendix

In the following the mathematical passages to obtain the expression for flux of carbon dioxide starting from Eq. (21) are reported.

A new kinetic constant ( $k_{f,PZcst}$ ,  $k_{f,PZCOO^-cst}$  and  $k_{f,OH^-cst}$ ), composed of the kinetic constant and the concentration of the other reactants assumed constant, can then be defined. Since, according to IPFO theory, the amine concentration is constant in the reaction sub-layer, also the concentration of products of amine is constant. Being the kinetic constant of the forward and the backward reactions related to the chemical equilibrium constant of the considered reaction, the rate of consumption of carbon dioxide can be written as follows:



$$R_{CO_2} = k_{f,PZcst} \left( [CO_2] - [CO_{2,eq}]_i \right)$$

where  $[CO_{2,eq}]_i$  is the carbon dioxide concentration at equilibrium. Considering all the kinetically controlled reactions of the system the total rate of consumption of carbon dioxide is:

$$R_{CO_2} = k_{f,CO_2} \left( [CO_2] - [CO_{2,eq}]_i \right)$$

$$\text{with } k_{f,CO_2} = \left( k_{f,OH^-cst} + k_{f,PZcst} + k_{f,PZCOO^-cst} \right).$$

Then:

$$\frac{\partial^2 [CO_2]}{\partial r^2} - \frac{\pi^2}{4\mathcal{E}} \left( 1 + tg^2 \left( r \frac{\pi}{2} \right) \right) k_{f,CO_2} \left( [CO_2] - [CO_{2,eq}]_i \right) = 0$$

$\left( [CO_2] - [CO_{2,eq}]_i \right)$  and  $-\frac{\pi^2}{4\mathcal{E}} k_{f,CO_2}$  can be substituted, by obtaining:

$$\frac{\partial^2 y}{\partial r^2} + a \left( 1 + tg^2 \left( \frac{\pi}{2} r \right) \right) y = 0$$

This is a homogeneous linear differential equation with variable coefficients:

$$a_0(r) y'' + a_1(r) y' + a_2(r) y = 0$$

$$y = C_1 z(r) \int \frac{\exp\left(-\int \frac{a_1(r)}{a_0(r)} dr\right)}{z^2(r)} dr + C_2 z(r)$$

Since in this case  $a_1(r) = 0$  :

$$y = C_1 z(r) \int \frac{1}{z^2(r)} dr + C_2 z(r)$$

The following expression can be assumed for  $z(r) \neq 0$ :

$$z(r) = \alpha \left( \operatorname{tg} \left( \frac{\pi}{2} r \right) \right)$$

Then:

$$\alpha \frac{\pi^2}{2} \operatorname{tg} \left( \frac{\pi}{2} r \right) \left( 1 + \operatorname{tg}^2 \left( \frac{\pi}{2} r \right) \right) + a \left( 1 + \operatorname{tg}^2 \left( \frac{\pi}{2} r \right) \right) \alpha \left( \operatorname{tg} \left( \frac{\pi}{2} r \right) \right) = 0$$

$$\operatorname{tg} \left( \frac{\pi}{2} r \right) \left( 1 + \operatorname{tg}^2 \left( \frac{\pi}{2} r \right) \right) \left( \alpha \frac{\pi^2}{2} + a \cdot \alpha \right) = 0$$

In order to satisfy the condition, it must be:

$$\left( \alpha \frac{\pi^2}{2} + a \cdot \alpha \right) = 0$$

This equation is satisfied for any value of  $\alpha$  and when  $a = -\frac{\pi^2}{2}$ . A particular solution is

identified, with  $\alpha$  equal to 1:

$$z(r) = \operatorname{tg} \left( \frac{\pi}{2} r \right)$$

Then:

$$y = C_1 \operatorname{tg} \left( \frac{\pi}{2} r \right) \int \frac{1}{\operatorname{tg}^2 \left( \frac{\pi}{2} r \right)} dr + C_2 \operatorname{tg} \left( \frac{\pi}{2} r \right)$$

$$y = -\frac{2}{\pi} C_1 \left( 1 + \frac{\pi}{2} r \left( \operatorname{tg} \left( \frac{\pi}{2} r \right) \right) \right) + C_2 \operatorname{tg} \left( \frac{\pi}{2} r \right)$$

$$[CO_2] - [CO_{2,eq}]_i = -\frac{2}{\pi} C_1 \left( 1 + \frac{\pi}{2} r \left( \operatorname{tg} \left( \frac{\pi}{2} r \right) \right) \right) + C_2 \operatorname{tg} \left( \frac{\pi}{2} r \right)$$

$C_1$  and  $C_2$  can be evaluated considering the boundary conditions:

$$[CO_2] = [CO_2]_i \quad \text{when} \quad x = 0$$

and:

$$[CO_2] = [CO_2]_i^* \quad \text{when} \quad x \rightarrow \infty$$

Then the flux of carbon dioxide becomes:

$$N_{CO_2} = \frac{\pi}{2} \sqrt{\varepsilon D_{CO_2}} \left( [CO_2]_i - [CO_{2,eq}]_i \right)$$

under condition that:

$$a = -\frac{\pi^2}{2}$$

$$-\frac{k_{f,CO_2} \pi^2}{4\varepsilon} = -\frac{\pi^2}{2} \quad \Rightarrow \quad \varepsilon = \frac{k_{f,CO_2}}{2}$$

The expression for the flux of carbon dioxide is:

$$N_{CO_2} = \frac{\pi}{2} \sqrt{\frac{1}{2} \left( k_{f,OH^-} [OH^-]_i + k_{f,PZ} [PZ]_i + k_{f,PZCOO^-} [PZCOO^-]_i \right) D_{CO_2}} \left( [CO_2]_i - [CO_2]_{i,eq} \right)$$

with the correct dependence on diffusivity of carbon dioxide.

## References

AspenTech, 2010a. ASPEN HYSYS®. AspenTech, Burlington, MA.

AspenTech, 2010b. ASPEN Plus®. AspenTech, Burlington, MA.

Austgen, D.M.A., 1989. Model of Vapor-Liquid Equilibria for Acid Gas-Alkanolamine-H<sub>2</sub>O Systems. PhD Thesis, University of Texas, Austin, Texas.

Bergman, D.F., Yarborough, L., 1978. 71st Annual Meeting of AIChE, Miami Beach, Florida.

Bishnoi, S., Rochelle, G., 2000a. Carbon dioxide absorption promoted by piperazine. Abstracts of Papers of the American Chemical Society 219, U751-U751.

Bishnoi, S., Rochelle, G.T., 2000b. Absorption of carbon dioxide into aqueous piperazine: reaction kinetics, mass transfer and solubility. Chem. Eng. Sci. 55, 5531-5543.

Bishnoi, S., Rochelle, G.T., 2002a. Absorption of carbon dioxide in aqueous piperazine/methyldiethanolamine. AIChE J. 48, 2788-2799.

Bishnoi, S., Rochelle, G.T., 2002b. Thermodynamics of piperazine/methyldiethanolamine/water/carbon dioxide. Ind. Eng. Chem. Res. 41, 604-612.

Chen, C.C., Britt, H.I., Boston, J.F., Evans, L.B., 1979. Extension and application of the Pitzer equation for vapor-liquid equilibrium of aqueous electrolyte systems with molecular solutes. AIChE J. 25, 820-831.

Chen, C.C., Britt, H.I., Boston, J.F., Evans, L.B., 1982. Local composition model for excess Gibbs energy of electrolyte systems. Part I: single solvent, single completely dissociated electrolyte systems. AIChE J. 28, 588-596.

Chen, C.C., Evans, L.B., 1986. A local composition model for the excess Gibbs energy of aqueous electrolyte systems. AIChE J. 32, 444-454.

Cullinane, J.T., Rochelle, G.T., 2005a. Kinetics of Carbon Dioxide Absorption into Aqueous Potassium Carbonate and Piperazine. Ind. Eng. Chem. Res. 45, 2531-2545.

Cullinane, J.T., Rochelle, G.T., 2005b. Thermodynamics of aqueous potassium carbonate, piperazine, and carbon dioxide. Fluid Phase Equilib. 227, 197-213.

Dash, S.K., Samanta, A., Samanta, A.N., Bandyopadhyay, S.S., 2011a. Absorption of carbon dioxide in piperazine activated concentrated aqueous 2-amino-2-methyl-1-propanol solvent. *Chem. Eng. Sci.* 66, 3223-3233.

Dash, S.K., Samanta, A., Samanta, A.N., Bandyopadhyay, S.S., 2011b. Vapour liquid equilibria of carbon dioxide in dilute and concentrated aqueous solutions of piperazine at low to high pressure. *Fluid Phase Equilib.* 300, 145-154.

Dash, S.K., Samanta, A.N., Bandyopadhyay, S.S., 2011c. Solubility of carbon dioxide in aqueous solution of 2-amino-2-methyl-1-propanol and piperazine. *Fluid Phase Equilib.* 307, 166-174.

Dash, S.K., Samanta, A.N., Bandyopadhyay, S.S., 2012. Experimental and theoretical investigation of solubility of carbon dioxide in concentrated aqueous solution of 2-amino-2-methyl-1-propanol and piperazine. *Journal of Chemical Thermodynamics* 51, 120-125.

De Guido, G., Langè, S., Moioli, S., Pellegrini, L.A., 2014. Thermodynamic method for the prediction of solid CO<sub>2</sub> formation from multicomponent mixtures. *Process Saf. Environ.* 92, 70-79.

Derks, P.W., Hogendoorn, K.J., Versteeg, G.F., 2005a. Solubility of N<sub>2</sub>O in and density, viscosity, and surface tension of aqueous piperazine solutions. *J. Chem. Eng. Data* 50, 1947-1950.

Derks, P.W.J., Dijkstra, H.B.S., Hogendoorn, J.A., Versteeg, G.F., 2005b. Solubility of carbon dioxide in aqueous piperazine solutions. *AIChE J.* 51, 2311-2327.

Edwards, T.J., Maurer, G., Newman, J., Prausnitz, J.M., 1978. Vapor-Liquid Equilibria in Multicomponent Aqueous Solutions of Volatile Weak Electrolytes. *AIChE J.* 24, 966-976.

Freeman, S.A., Dugas, R., Van Wagener, D., Nguyen, T., Rochelle, G.T., 2009. Carbon dioxide capture with concentrated, aqueous piperazine. *Energy Proc.* 1, 1489-1496.

Hetzer, H.B., Robinson, R.A., Bates, R.G., 1968. Dissociation constants of piperazinium ion and related thermodynamic quantities from 0 to 50°. *Journal of Physical Chemistry* 72, 2081-2086.

Hillard, M.G., 2004. Thermodynamics for aqueous piperazine/potassium carbonate/carbon dioxide characterized by the Electrolyte NRTL Model within ASPEN Plus®. M.S.E. Thesis, The University of Texas, Austin, Texas.

Hillard, M.G., 2008. A predictive thermodynamic model for an aqueous blend of potassium carbonate, piperazine and monoethanolamine for carbon dioxide capture from flue gas. PhD Thesis, The University of Texas, Austin, Texas.

Khoo, H.H., Tan, R.B.H., 2006. Life Cycle Investigation of CO<sub>2</sub> Recovery and Sequestration. *Environmental Science & Technology* 40, 4016-4024.

King, C.J., 1966. Turbulent Liquid Phase Mass Transfer at a Free Gas-Liquid Interface. *Ind. Eng. Chem. Fundam.* 5, 1-8.

Kohl, A.L., Nielsen, R., 1997. *Gas Purification*, 5th ed. Gulf Publishing Company, Book Division, Houston, Texas, USA.

Krishnamurthy, R., Taylor, R., 1985a. A Nonequilibrium Stage Model of Multicomponent Separation Processes .1. Model Description and Method of Solution. *AIChE J.* 31, 449-456.

Krishnamurthy, R., Taylor, R., 1985b. A Nonequilibrium Stage Model of Multicomponent Separation Processes .2. Comparison with Experiment. *AIChE J.* 31, 456-465.

Krishnamurthy, R., Taylor, R., 1985c. A Nonequilibrium Stage Model of Multicomponent Separation Processes .3. The Influence of Unequal Component-Efficiencies in Process Design-Problems. *AIChE J.* 31, 1973-1985.

Krishnamurthy, R., Taylor, R., 1985d. Simulation of Packed Distillation and Absorption Columns. *Ind. Eng. Chem. Proc. Des. Dev.* 24, 513-524.

Langé, S., Pellegrini, L.A., Moioli, S., Picutti, B., Vergani, P., 2013. Influence of Gas Impurities on Thermodynamics of Amine Solutions. 2. Mercaptans. *Ind. Eng. Chem. Res.* 52, 2025-2031.

Lewis, W.K., Whitman, W.G., 1924. Principles of Gas Absorption. *Ind. Eng. Chem.* 16, 1215-1220.

Lide, D.R., 1996. *Handbook of Chemistry and Physics*, 77th ed. CRC Press, Boca Raton.

Lide, D.R., 2008. *Handbook of Chemistry and Physics*, 88th ed. CRC Press, Boca Raton.

Liu, Y.D., Zhang, L.Z., Watanasiri, S., 1999. Representing vapor-liquid equilibrium for an aqueous MEA-CO<sub>2</sub> system using the electrolyte nonrandom-two-liquid model. *Ind. Eng. Chem. Res.* 38, 2080-2090.

Mock, B., Evans, L.B., Chen, C.C., 1986. Thermodynamic Representation of Phase Equilibria of Mixed-Solvent Electrolyte Systems. *AIChE J.* 32, 1655-1664.

Moioli, S., Pellegrini, L.A., 2013. Regeneration Section of CO<sub>2</sub> Capture Plant by MEA Scrubbing with a Rate-Based Model. *Chem. Eng. Trans.* 32, 1849-1854.

Moioli, S., Pellegrini, L.A., Gamba, S., 2012. Simulation of CO<sub>2</sub> Capture by MEA Scrubbing with a Rate-Based Model, 20<sup>th</sup> International Congress of Chemical and Process Engineering CHISA 2012, Prague, Czech Republic.

Moioli, S., Pellegrini, L.A., Gamba, S., Li, B., 2014. Improved rate-based modeling of carbon dioxide absorption with aqueous monoethanolamine solution. *Front. Chem. Sci. Eng.*, doi:10.1007/s11705-11014-11415-11700.

Moioli, S., Pellegrini, L.A., Picutti, B., Vergani, P., 2013. Improved rate-based modeling of H<sub>2</sub>S and CO<sub>2</sub> removal by MDEA scrubbing. *Ind. Eng. Chem. Res.* 52, 2056-2065.

Naami, A., Edali, M., Sema, T., Idem, R., Tontiwachwuthikul, P., 2012. Mass Transfer Performance of CO<sub>2</sub> Absorption into Aqueous Solutions of 4-Diethylamino-2-butanol, Monoethanolamine, and N-Methyldiethanolamine. *Ind. Eng. Chem. Res.* 51, 6470-6479.

Pagano, J.M., Goldberg, D.E., Fernelius, W.C., 1961. A thermodynamic study of homopiperazine, piperazine and N-(2-Aminoethyl)-Piperazine and their complexes with copper (II) ion. *Journal of Physical Chemistry* 65, 1062-1064.

Paoletti, P., Ciampolini, M., Vacca, A., 1963. Thermochemical studies. VII. Heats and entropies of stepwise neutralization of piperazine and triethylenetetramine. *Journal of Physical Chemistry* 67, 1065-1067.

Pellegrini, L.A., Langé, S., Moioli, S., Vergani, P., 2013. Impurities on Thermodynamics of Amine Solutions: Part 1. Aromatics. *Ind. Eng. Chem. Res.* 52, 2018-2024.

Pellegrini, L.A., Moioli, S., Gamba, S., 2011a. Energy saving in a CO<sub>2</sub> capture plant by MEA scrubbing. *Chem. Eng. Res. Des.* 89, 1676-1683.

Pellegrini, L.A., Moioli, S., Gamba, S., Ceragioli, P., 2012a. Prediction of vapor-liquid equilibrium for reservoir mixtures with cubic equations of state: binary interaction parameters for acidic gases. *Fluid Phase Equilib.* 326, 45-49.

Pellegrini, L.A., Moioli, S., Gamba, S., Ceragioli, P., 2012b. Prediction of volumetric properties of fluids for oil and gas applications. *Fluid Phase Equilib.* 317, 52-58.

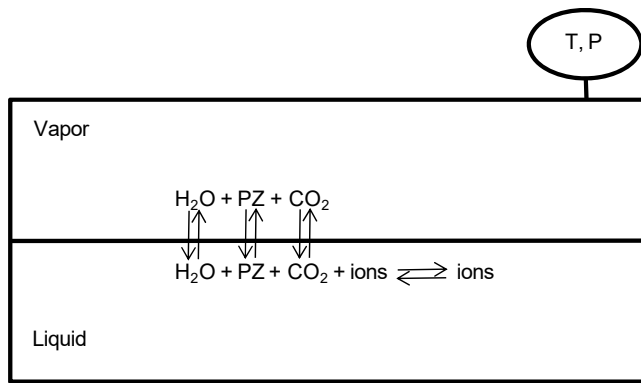
Pellegrini, L.A., Moioli, S., Picutti, B., Vergani, P., Gamba, S., 2011b. Design of an Acidic Natural Gas Purification Plant by means of a Process Simulator. *Chem. Eng. Trans.* 24, 271-276.

Pickett, L.W., Corning, M.E., Wieder, G.M., Semenov, D.A., Buckley, J.M., 1953. The vacuum ultraviolet spectra of cyclic compounds. III. Amines. *Journal of American Chemical Society* 75, 1618-1622.

Pinsent, B.R.W., Pearson, L., Roughton, F.W.J., 1956. The kinetics of combination of carbon dioxide with hydroxide ions. *Trans. Faraday Soc.* 52, 1512-1518.

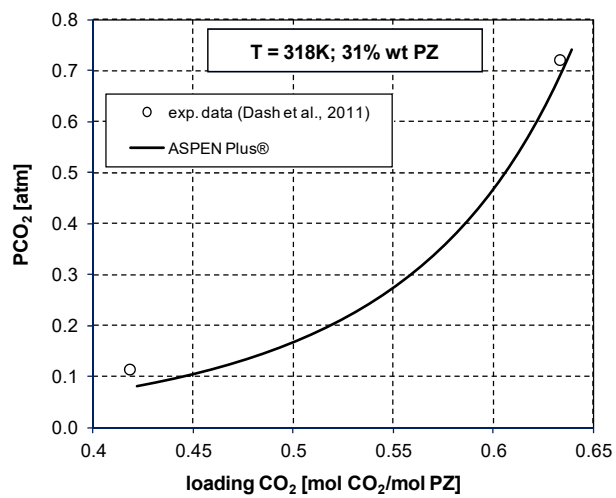


- Plaza, J.M., 2012. Modeling of Carbon Dioxide Absorption Using Aqueous Monoethanolamine, Piperazine and Promoted Potassium Carbonate. PhD Thesis, The University of Texas, Austin, Texas.
- Samanta, A., Bandyopadhyay, S.S., 2007. Kinetics and modeling of carbon dioxide absorption into aqueous solutions of piperazine. *Chem. Eng. Sci.* 62, 7312-7319.
- Schwarzenback, G., Maissen, B., Ackerman, H., 1952. Metallkomplexe mit Polyaminen VII: Diamine und Silber(I). *Helvetica Chimica Acta* 23, 2333-2336.
- Soave, G., 1972. Equilibrium constants from a modified Redlich-Kwong equation of state. *Chem. Eng. Sci.* 27, 1197-1203.
- ZareNezhad, B., Eggeman, T., 2006. Application of Peng–Rabinson equation of state for CO<sub>2</sub> freezing prediction of hydrocarbon mixtures at cryogenic conditions of gas plants. *Cryogenics* 46, 840-845.
- Zhang, X., Zhang, C.F., Qin, S.J., Zheng, Z.S., 2001. A kinetics study on the absorption of carbon dioxide into a mixed aqueous solution of methyldiethanolamine and piperazine. *Ind. Eng. Chem. Res.* 40, 3785-3791.

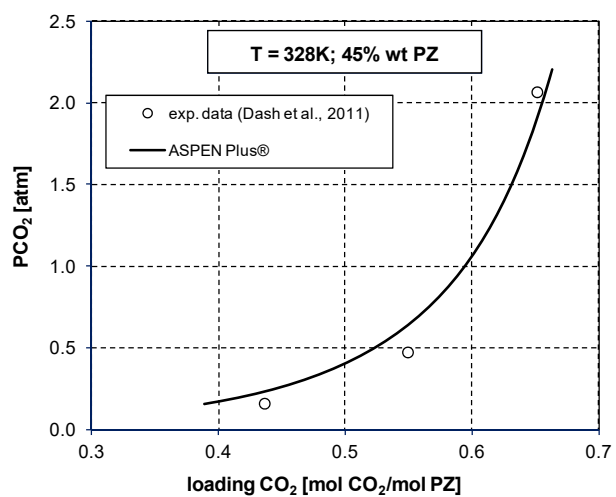


**Figure 1.** Vapor-liquid equilibrium in a closed system involving the presence of acid gases and amine solutions.

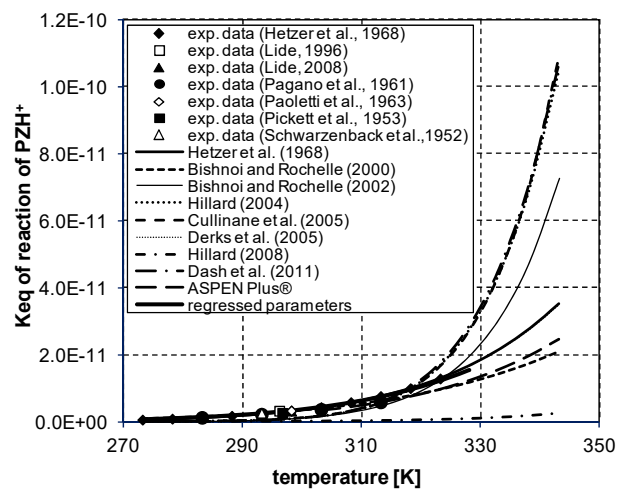
a)



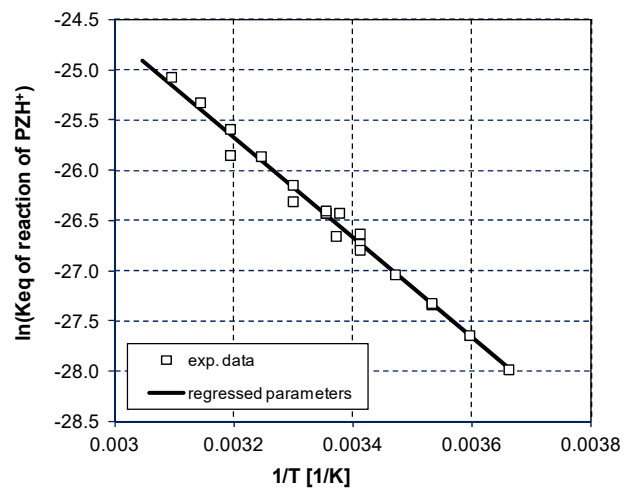
b)



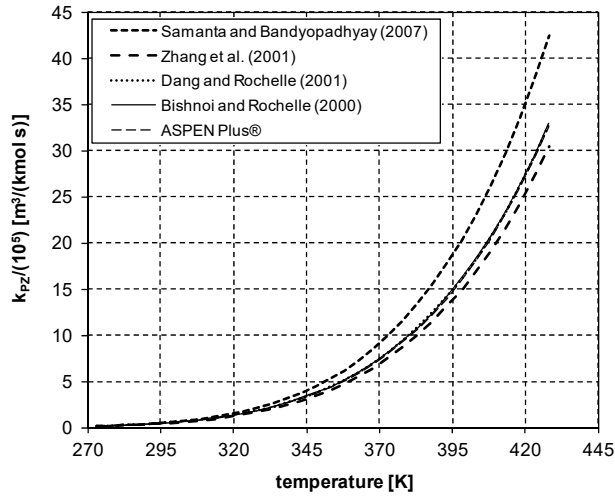
**Figure 2.** CO<sub>2</sub> partial pressure vs. loading in a) 31% wt PZ solution at 308K and in a b) 45% wt PZ solution at 328K.



**Figure 3.** Equilibrium constant for the reaction of protonated piperazine.

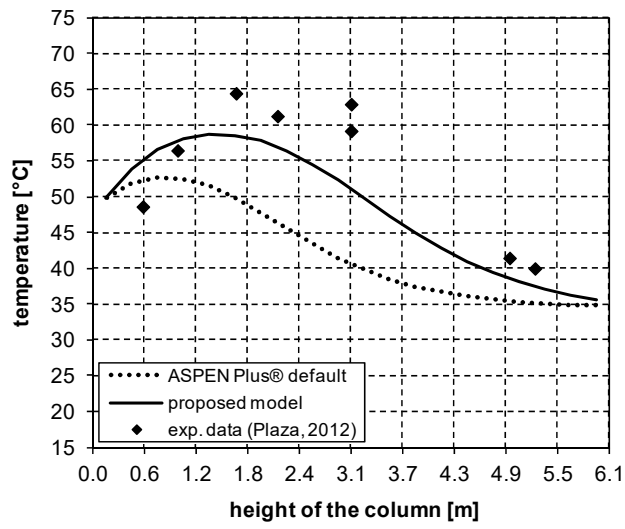


**Figure 4.** Comparison of regressed correlation with experimental data.

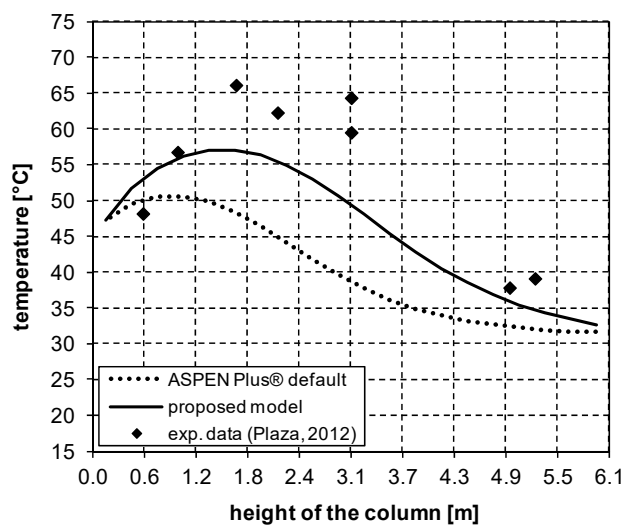


**Figure 5.** Kinetic constant of the reaction of CO<sub>2</sub> and PZ in water according to different sources in literature.

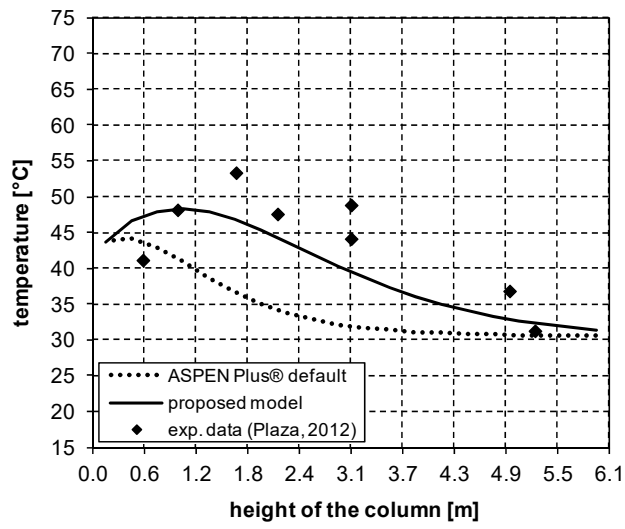
a)



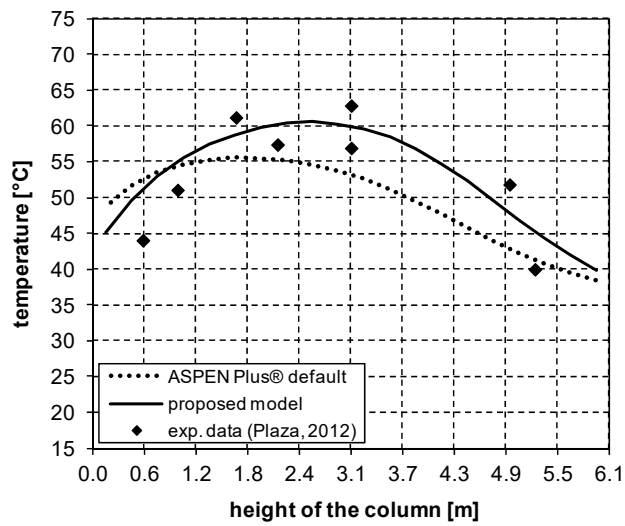
b)



c)

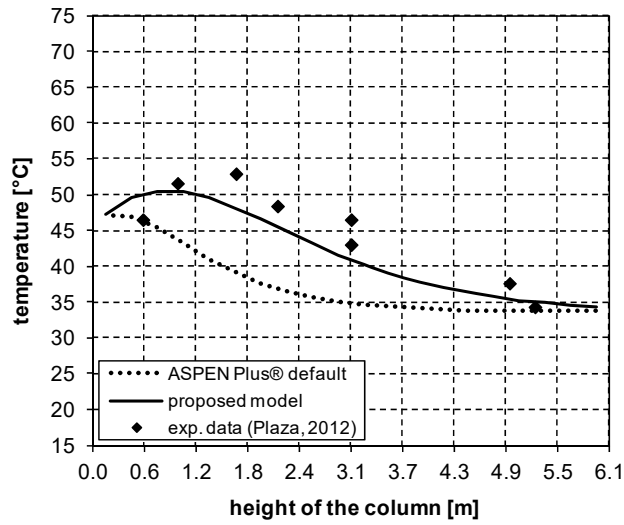


d)

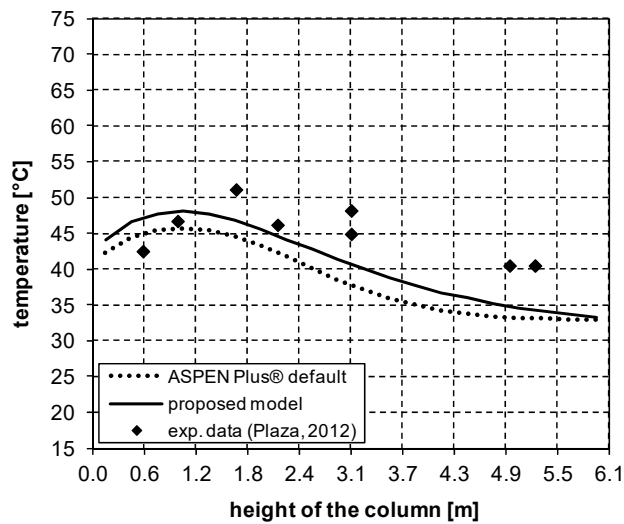




e)

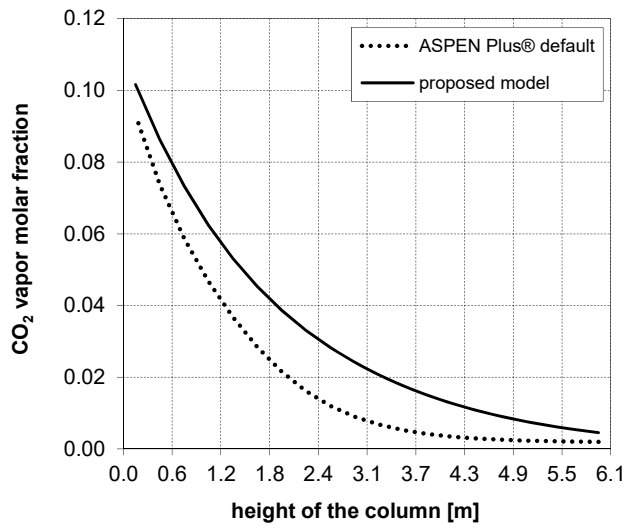


f)

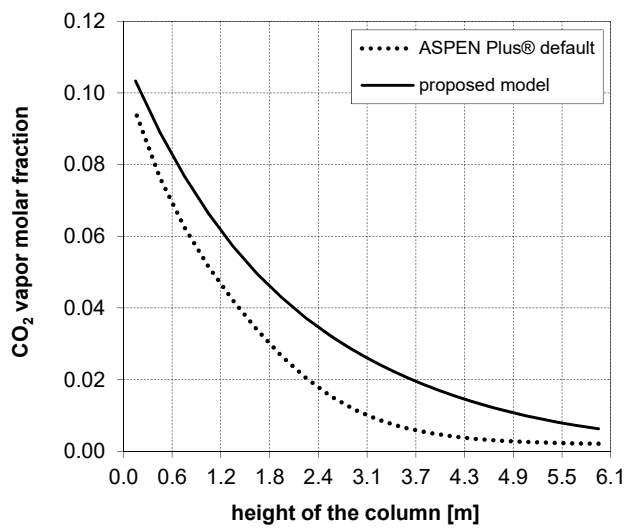


**Figure 6.** Results of simulations and experimental data (Plaza, 2012) of temperature profiles along the absorption column of the simulated pilot plant for a) test 1, b) test 2, c) test 6, d) test 8, e) test 9 and f) test 11 of “Nov. ‘08” campaign.

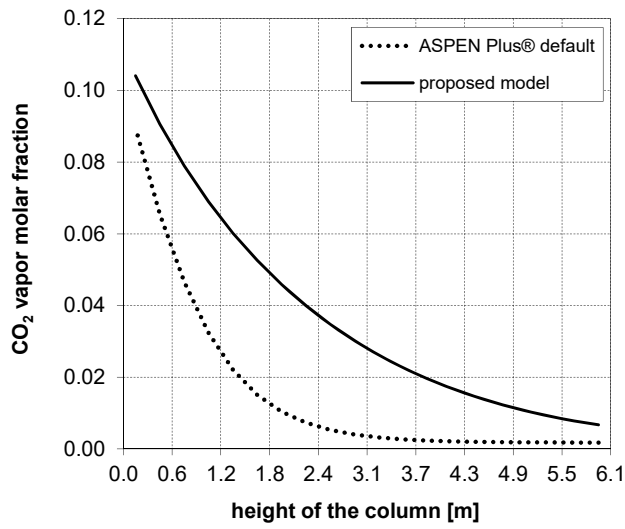
a)



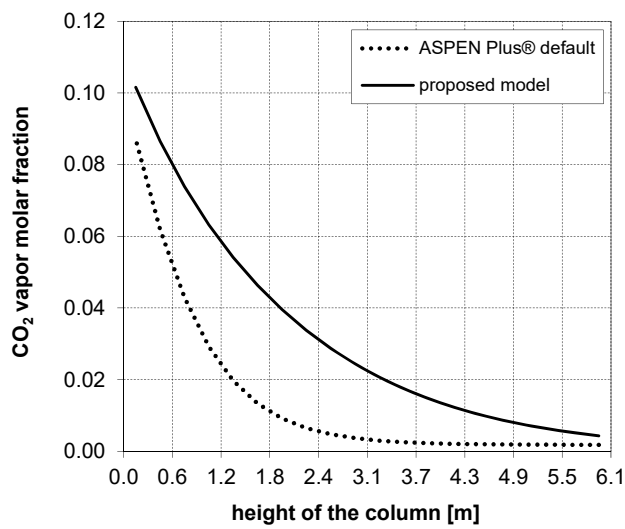
b)



c)



d)



**Figure 7.** Results of simulations of CO<sub>2</sub> vapor molar fraction profiles along the absorption column of the simulated pilot plant for a) test 1, b) test 2, c) test 6 and d) test 9 of “Nov. ‘08” campaign.

**Table 1.** Values of parameters A, B, C and D for the equilibrium constant of the reaction of protonated piperazine.

source	A	B	C	D
Bishnoi and Rochelle (2000)	-11.91	-4351	0	0
Bishnoi and Rochelle (2002)	4.964	-9714.2	0	0
Derks et al. (2005)	18.135	3814.4	0	-0.0151
Cullinane et al. (2005)	241.5	-21928	-34.35	0
Hillard (2004)	482	-33449	-69.8	0
Hillard (2008)	-64.4	-4899	8.9	0
Hetzer et al. (1968)	6.1316	1656.59	0	- 0.00656
Liu et al. (1999)	-22.086	459.37	0	0
Dash et al. (2011)	514.314	-34910.9	-74.602	0
ASPEN Plus®	-4.08	-7773.20	0.00	0.00

**Table 2.** Values of parameters A, B, C and D for the equilibrium constant of the reaction of piperazine carbamate ion.

source	A	B	C	D
Derks et al. (2005)	-4.6185	3616.1	0	0
Hillard (2004)	-610	36512	87.08	0
Hillard (2008)	1025	1606	-214	0.657
ASPEN Plus <sup>®</sup>	-4.62	3616.10	0.00	0.00
Bishnoi and Rochelle (2000)	-29.31	5615	0	0
	231.4	-12092	-36.78	0
Bishnoi and Rochelle (2002)	-41.583	9288.2	0	0
	231.4	-12092	-36.78	0
Cullinane et al. (2005)	-10.15	21980	44.42	0
	231.4	-12092	-36.78	0
Dash et al. (2011)	466.497	1614.5	-97.54	0.2471
	231.465	-12092.1	-36.782	0

**Table 3.** Values of parameters A, B, C and D for the equilibrium constant of the reaction of dissociation of HPZCOO.

source	A	B	C	D
Bishnoi and Rochelle (2000)	-8.21	-5286	0	0
Bishnoi and Rochelle (2002)	-13.041	-3961.6	0	
Cullinane et al. (2005)	-25.91	-5700	0	
Derks et al. (2005)	14.042	3443.1	0	0
Hillard (2008)	668	3465	-156	0.594
Dash et al. (2012)	6.822	-6066.9	-2.29	0.0036
ASPEN Plus <sup>®</sup>	-14.042	-3443.1	0	0

**Table 4.** Values of parameters A, B, C and D for the equilibrium constant of the reaction of piperazine dicarbamate.

source	A	B	C	D
Derks et al. (2005)	0.3615	1322.3	0	0
Hillard (2004)	-251	14080	36.78	0
ASPEN Plus <sup>®</sup>	0.3615	1322.3	0	0
Bishnoi and Rochelle (2000)	-30.78	5615	0	0
	231.4	-12092	-36.78	0
Bishnoi and Rochelle (2002)	-44.7	9288.2	0	0
	231.4	-12092	-36.78	0
Cullinane et al. (2005)	-13.26	1990	0	0
	231.4	-12092	-36.78	0
Dash et al. (2011)	-11.563	1769.4	-1.467	0.0024
	231.465	-12092.1	-36.782	0

**Table 5.** Characteristic of the gaseous stream (Plaza, 2012) entering the absorption column for all the analyzed cases.

run	T [°C]	P [atm]	flow [ACFM]	yH <sub>2</sub> O	yCO <sub>2</sub>	yN <sub>2</sub>	yO <sub>2</sub>
1	15	1	350	0.005261	0.120000	0.691098	0.183710
2	0	1	350	0.001873	0.120000	0.693740	0.184412
3	0	1	350	0.001873	0.120000	0.693740	0.184412
4	21	1	350	0.007682	0.120000	0.689210	0.183208
5	7	1	350	0.003082	0.120000	0.692797	0.184161
6	-5	1	350	0.001287	0.120000	0.694196	0.184533
7	22	1	350	0.008168	0.120000	0.688831	0.183107
8	7	1	350	0.003082	0.120000	0.692797	0.184161
9	21	1	350	0.007682	0.120000	0.689210	0.183208
10	22	1	350	0.008168	0.120000	0.688831	0.183107
11	14	1	350	0.004930	0.120000	0.691356	0.183778
12	7	1	350	0.003082	0.120000	0.692797	0.184161
13	-9	1	350	0.000942	0.120000	0.694465	0.184605
14	8	1	350	0.003302	0.120000	0.692626	0.184116



**Table 6.** Characteristic of the amine solution (Plaza, 2012) entering the absorption column for all the analyzed cases.

<b>run</b>	<b>T [°C]</b>	<b>P [atm]</b>	<b>PZ molal concentration</b>	<b>lean loading [mol CO<sub>2</sub>/mol PZ]</b>	<b>L/G</b>
1	35	1	7	0.26	5.50
2	32	1	8	0.31	5.50
3	28	1	9	0.25	5.00
4	34	1	8	0.39	5.60
5	38	1	7	0.28	4.40
6	31	1	7	0.30	6.20
7	34	1	7	0.31	5.80
8	38	1	7	0.30	4.60
9	34	1	7	0.27	7.00
10	36	1	7	0.33	6.00
11	33	1	4	0.32	7.40
12	33	1	4	0.27	7.20
13	42	1	4	0.26	5.80
14	39	1	4	0.26	4.90