

Nonequilibrium Dynamic Modeling of Hydrogen Sulfide Absorption Using Diglycolamine Solution

A. Ghaemi* , Sh. Shahhosseini

School of Chemical Engineering, Iran University of Science and Technology, Narmak, Tehran, Iran

Abstract

In this research, reactive absorption of hydrogen sulfide using diglycolamine solution in an industrial tray column was investigated. A nonequilibrium stage model has been developed based on dynamic film model for modeling of hydrogen sulfide reactive absorption into diglycolamine solution. In the model, simultaneous heat and mass transfer and reactions rate were considered. The model equations including partial and ordinary differential equations were solved numerically using the method of lines technique. The simulation results are presented in steady and unsteady state conditions. An industrial absorption column was employed to obtain the experimental data in both low and high pressure. The model results were evaluated using the steady state experimental data. A comparison of the experimental and simulation results showed that the average of correlation coefficient error for high pressure absorption process is 8.5 percent whereas the average of correlation coefficient error for low pressure absorption process is 7 percent.

Keywords: *Reactive Absorption, Nonequilibrium Modeling, Film Model, Hydrogen Sulfide (H₂S), Diglycolamine (DGA)*

1. Introduction

Hydrogen sulfide is the most common sulfur-containing compound encountered in natural gas, light and middle oil sweetening, heavy oil hydro-treating, coal gasification plants, wastewater treatment plants and in various non-petroleum applications such as non-condensable gas of the pulp and paper industry. It is a major air pollutant when it is emitted into the atmosphere because of its toxic and corrosive characters. In addition, the presence of H₂S usually prohibits direct

use of these gases due to the formation of SO₂ upon combustion and the problems it causes in downstream processing. This means that it must be removed down to very low concentration levels in the gas stream prior to use [1-3].

There are several commercial treatment techniques that can be used for H₂S removal, such as adsorption by activated carbon, condensation, chemical oxidation, incineration or catalytic combustion, wet absorption and biofiltration techniques. In

* Corresponding author: aghaemi@iust.ac.ir

recent years, several investigations have focused on the removal of H₂S from natural or synthetic fuel gases because of environmental concerns [4-8].

Absorption methods for industrial gas purification are the most wide-spread in commercial practices. H₂S removal methods are of special importance because these compounds are present as impurities in many gaseous mixtures. The cost of purifying a gaseous mixture is generally very high. Modern technological methods based on physical and chemical absorption use highly efficient organic solvents characterized by a relatively high ability to dissolve acid gases and low ability of dissolving other gaseous components [1, 9].

In the absorption method, hydrogen sulfide is removed using liquid absorbents based on chemical or physical absorption at low temperatures. Alkanolamines and their aqueous solutions absorb hydrogen sulfide at lower temperature. Diglycolamine selectively removes H₂S from natural gas streams [10].

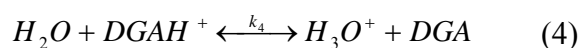
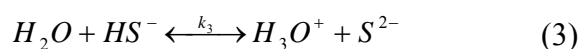
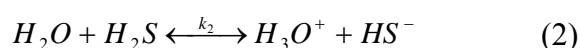
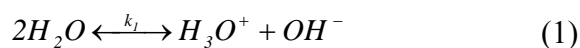
Several mathematical models with different complexity and accuracy have been proposed for absorption in the literature [11-16]. Overall, two types, of models have been reported in the literature; equilibrium and nonequilibrium stage models [12-13]. Traditional equilibrium stage models are suitable for nonreactive systems. These models assume a theoretical stage in which the liquid and gas phases attain equilibrium. Mass and heat transfer are actually rate phenomena driven by chemical potential and temperature gradients respectively. Therefore, a number of nonequilibrium models have been developed [14-16]. Nonequilibrium models are more rigorous

and complex than equilibrium models, especially rate-based models that imply actual rates of multicomponent mass and heat transfer and chemical reactions are directly taken into account [17].

In the present research, the potential of diglycolamine solution for absorption of H₂S from natural gas streams has been investigated. A rigorous nonequilibrium dynamic model has been used based on dynamic film model for reactive absorption of H₂S which can predict concentrations of the species and temperatures of the phases along the column height. The model results were evaluated using experimental data, obtained from an industrial absorption column.

2. Chemical reactions of H₂S absorption

For H₂S-DGA-H₂O system, the following equilibrium reactions occur in the bulk of the liquid phase.



Reaction (5) is instantaneous, since it involves a proton transfer. The chemical reaction rate constants are functions of temperature [18].

3. The process modeling

Mathematical models of absorption processes include some equations to compute heat and mass transfer rates between bulk and films of both phases. In these models, the absorption column is divided to several imaginary stages. These stages are linked to each other by mass and energy balances. In each nonequilibrium stage the gas and the liquid phase exchange heat and mass at the vapor-liquid interface that is normally described using a two-film model as illustrated in Fig. 1 [19-21]. In this model, it is assumed that the fluids are ideally mixed and have uniform concentrations and temperatures in the bulk areas. Since chemical reactions take place in both phases, unsteady state balance equations should include some reaction source terms as shown in equations 6 and 8.

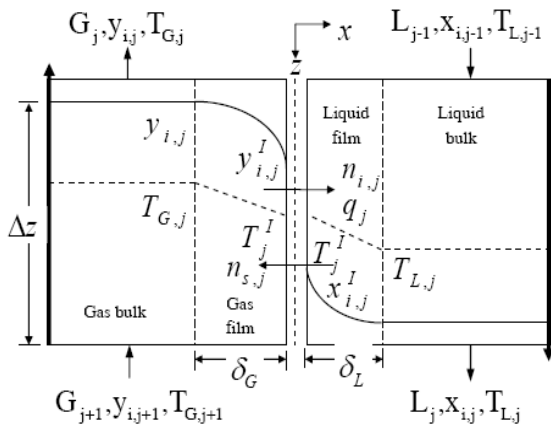


Figure 1. Schematic diagram of a two-film model as applied to a stage of an absorption tower.

$$\frac{d}{dt} u_{L,i,j} = \frac{1}{\Delta z} [L_{j-1} x_{i,j-1} - L_j x_{i,j}] + (N_{i,j}^B a + R_{L,i,j}^B \phi_L) A \quad i = 1, \dots, n \quad (6)$$

$$u_{L,i,j} = x_{i,j} U_{L,i,j} = x_{i,j} (\phi_L C_{L,i,j} A) \quad i = 1, \dots, n \quad (7)$$

Where, U is specific molar hold up, z is axial column coordinate, L is liquid molar flow rate, x is liquid molar fraction, N is molar flux, B is bulk of the phases, a is specific gas liquid interfacial area, $R_{L,i}$ is total component reaction rate, ϕ_L is specific liquid holdup, A is column cross section, $C_{L,i}$ is molar concentration, n is number of the component, j is the stage number and Δz is the segment height. Hold up of the gas phase can often be neglected due to the low gas density. Thus, the component balance for this phase is:

$$0 = \frac{1}{\Delta z} [G_{j+1} y_{i,j+1} - G_j y_{i,j}] - (N_{i,j}^B a - R_{G,i,j}^B \phi_G) A \quad i = 1, \dots, n \quad (8)$$

The energy balances written for continuous systems are as follows:

$$\frac{\partial E_L}{\partial t} = -\frac{1}{\Delta z} [L_{j-1} h_{L,j-1}^B - L_j h_{L,j}^B] + (q^I a - R_L^B \phi_L \Delta H_{RL}^0) A \quad (9)$$

$$0 = \frac{1}{\Delta z} [G_{j+1} h_{G,j+1}^B - G_j h_{G,j}^B] - (q^{gf} a - R_G^B \phi_G \Delta H_{RG}^0) A \quad (10)$$

Heat transfer rate across the vapor-liquid interface is equal to the sum of convection and conduction terms plus the product of the liquid molar held up to the specific molar enthalpy:

$$q^{gf} = -\frac{\lambda^{gf}}{\delta^{gf}} (T^i - T^{gb}) + \sum_{i=1}^m N_i^{gf} h_i^{gf} \quad (11)$$

$$q^{lf} = -\frac{\lambda^{lf}}{\delta^{lf}}(T^{lb} - T^i) + \sum_{i=1}^m N_i^{lf} h_i^{lf} \quad (12)$$

The energy fluxes across the interface are linked by the continuity equation:

$$0 = q^{gf} - q^{lf} \quad (13)$$

The liquid and gas bulk mole fractions sum to unity:

$$\sum_{i=1}^n x_i^B = \sum_{i=1}^n y_i^B = 1 \quad (14)$$

In this research, unsteady-state film model has been applied for calculation of molar fluxes. In the liquid film, diffusion and reactions were considered using the following continuity equation:

$$\frac{\partial C^f}{\partial t} = \frac{D}{\delta^2} \frac{\partial^2 C^f}{\partial \xi^2} + R^f \quad (15)$$

Where the dimensionless film coordinate ξ is defined as:

$$\xi = \frac{x}{\delta} \quad (16)$$

The partial differential equation (eq. 15) was solved for H₂S using superposition principle and the method of separation of variables [20] as follow:

$$C_{H_2S}^f(\xi, t) = \sum_{n=1}^{\infty} e^{-q_n t} \sin(\pi n \xi) a_n + \sum_{n=1}^{\infty} \left[\int_0^t e^{-q_n(t-\tau)} f_n(\tau) d\tau \right] \sin(\pi n \xi) + C_{H_2S}^l(t) + \xi [C_{H_2S}^b(t) - C_{H_2S}^l(t)] \quad (17)$$

Parameters of equation (17) have been applied by Kenig et al. [20]. Differentiating equation (17) and then multiplying by

diffusion coefficient results in an expression for molar fluxes as shown below:

$$N_{H_2S} = -\frac{D_{H_2S}}{\delta} \frac{dC_{H_2S}^f}{d\xi} \quad (18)$$

The film thickness is a parameter of the model, which must be calculated using the following equation:

$$\delta = \frac{D_{H_2S}}{k_L} \quad (19)$$

Where D_{H_2S} is diffusion coefficient of hydrogen sulfide in liquid phase, k_L is mass transfer coefficient in liquid side. In the present work, Reid et al. [24] and Onda et al. [19] correlations were applied for calculation of diffusion and mass transfer coefficient, respectively.

4. Determination of the parameters and physical properties

The accuracy of the simulation results depends on the model parameter computational methods, which are related to equilibrium thermodynamics, column hydrodynamics, chemical kinetics, and physical properties. Phase equilibrium is assumed at the interface between the phases, with interfacial compositions calculated from the following equation:

$$y_{i,j}^I = K_{i,j} x_{i,j}^I \quad i = 1, \dots, n \quad (20)$$

Where, $K_{i,j}$ is the vapor-liquid equilibrium constant, which is determined from thermodynamic models. Reactive separation processes occur mostly in aqueous systems with electrolyte species. In the present work, the model of Kent and Eisenberg [22] was

used to describe the electrolyte system.

Liquid phase diffusion coefficients are found applying Nernst-Hartley equation, which describes transfer properties in weak electrolyte systems [23]. Gas phase diffusion is estimated by Wilk-Lee equation [24]. The influence of the process hydrodynamics is taken into account by applying mass transfer, interfacial area, liquid hold up and pressure drop correlations [25-26]. In each stage physical properties such as viscosity and diffusion coefficients for mixture are calculated depending on the stage conditions. The average of correlation coefficient error was supposed to be the criterion for choosing the number of the stages, which resulted in the lowest error. The equation applied to calculate the average of correlation coefficient error is:

$$R_{ave} = \frac{100}{p} \times \sum_{i=1}^p \left| \frac{(R_{Exp.})_i - (R_{sim.})_i}{(R_{Exp.})_i} \right| \quad (21)$$

Where, p is the number of process variables and $(R_{Exp.})_i$ and $(R_{sim.})_i$ are correlation coefficients for the experimental and simulation process variables, i , respectively. R_{ave} is the average error for the process.

5. Numerical method

Nonequilibrium dynamic modeling of the process leads to a system of partial and ordinary differential equations. The equations were transformed to a set of ordinary differential equations by discretizing them in the direction of the spatial variable (column height). The resulting system of ordinary differential equations coupled with algebraic equations was solved using method of lines. It was assumed that the column was composed of 40 stages.

6. Results and discussion

The simulation results were validated against the experimental data of an industrial column. The experimental data were obtained from a tray tower in which hydrogen sulfide was absorbed in aqueous diglycolamine solution. Representative inlet and outlet data for the low pressure tower (LP) and the high pressure tower (HP) operational conditions are summarized in Table 1. The column has 40 trays, with the height of 15 meter.

Table 1. Operating data of an industrial absorber.

Parameter	Value (LP)	Value (HP)
Inlet gas flow rate, G(mol/s)	159.07	1099.70
Inlet liquid flow rate, L(m ³ /s)	0.00826	0.00826
Inlet gas temperature, TG(K)	303.5	301.22
Inlet liquid temperature, TL(K)	303.5	303.5
Inlet gas composition, y_i (mol %)	H ₂ S:17.8, CO ₂ :0.7, C1:40.35, C2 :40.35, SO ₂ :0.8	H ₂ S:4.8, CO ₂ :0.4, C1:47.15, C2 :47.15, SO ₂ :0.8
Inlet liquid loading, H ₂ S (mol/mol amine)	0.114	0.114
Outlet gas composition, H ₂ S (ppm)	20	10
Amine molarity, (mol/m ³)	2670.67	2670.67
Absorber pressure, P(bar)	3.95	21.56

Fig. 2 shows H_2S mole fraction in the gas phase along the column height. This figure implies partial pressure of H_2S at the inlet stream is higher than other parts of the column, so concentration gradient is very high there. Therefore the absorption rate is higher and most of the H_2S is absorbed at the bottom of the column.

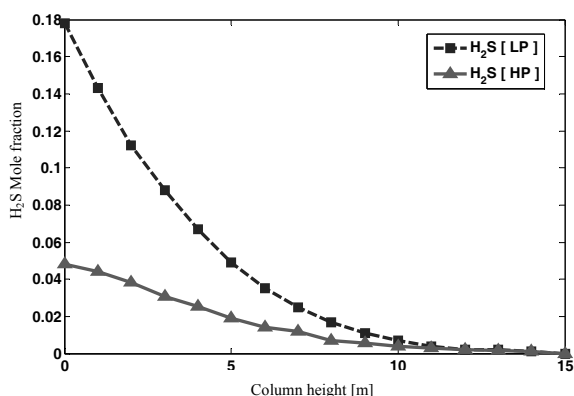


Figure 2. H_2S mole fraction in the gas phase along the column height.

Fig. 3 depicts liquid H_2S concentration along the column height. As shown in the figure, the amount of absorbed H_2S by the solution has been increased from the top to the bottom of the column. Due to the high absorption of H_2S the concentration of the solution is greater at the downside of the column.

The temperature gradient for the liquid phase is shown in Fig. 4. Absorption of H_2S is an exothermic process and this causes an increase in the temperature of both phases at the downside of the column. Most H_2S absorption occurs at the downside of the column and the absorbed heat causes the high temperature variations at the downside compared to the other parts of the column. The temperature of the gas phase is increased at the entrance of the column and then

decreased with the movement of the gas into the upside of the column. The reason is the low heat capacity of the gas phase compared to the liquid phase. First, the liquid temperature rises because it absorbs H_2S in contact with the entering gas. Then, because of temperature differences between the phases, the heat is transferred from the liquid phase into the gas phase. Due to the low heat capacity of the gas phase, the temperature of the gas increases as it enters into the column. As gas continues its upward movement, the gas phase temperature becomes higher than the liquid phase temperature and henceforth the direction of the heat transfer is changed and the heat transfers from the gas phase into the liquid phase. Consequently, the gas phase temperature is decreases from the middle of the column to the top.

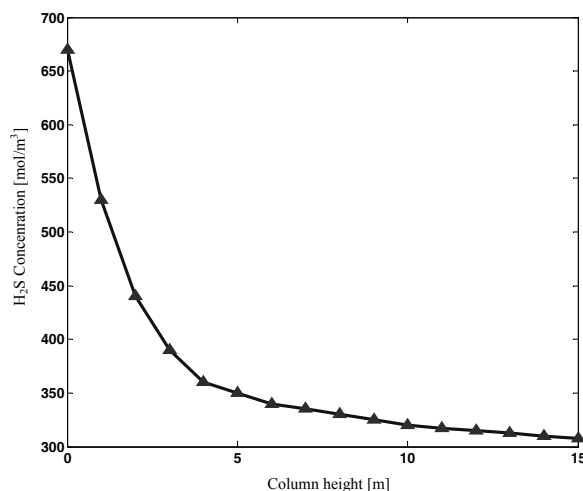


Figure 3. Concentration of H_2S in the liquid phase along the column height.

The simulation results for low and high pressure absorber are presented in Table 2. It shows that the model has good agreement with experimental results for both columns.

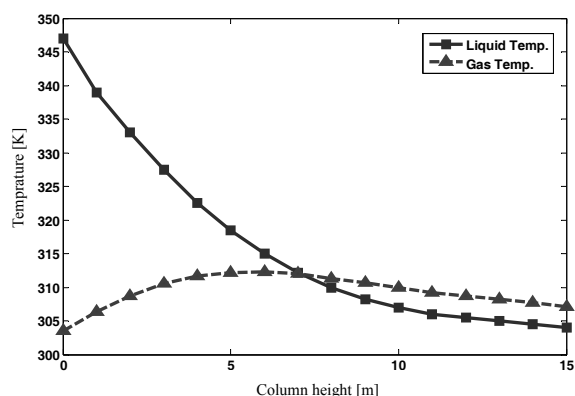


Figure 4. Temperature gradients of liquid and gas phases along the column height.

Table 2. Simulation results for low and high pressure conditions of the absorber column.

Process Data	HP	R_{ave} %	LP	R_{ave} %
T_G [K]	305.1	0.35	306.2	0.71
G [mol/s]	1042.8	6.32	135.92	2.83
L [m ³ /s]	0.0091	4.21	0.0092	3.15
T_L [K]	347.4	4.92	347.4	4.92
C_{H_2S} [mol/m ³]	702.3	15.38	675.3	15.58
y_{H_2S}	12 ppm	20	23ppm	15

Hydrogen sulfide concentration in different stages versus time is shown in Fig. 5. It indicates that the steady state condition can be met after a while in terms of concentration. The 40th element and the 1st element are considered as the bottom element and top element of the column, respectively. The results illustrate that the hydrogen sulfide in diglycolamine solution has been consumed due to the reaction between these two substances, which causes the high hydrogen sulfide absorption rate at the initial elements. It also results in the reduction of hydrogen sulfide at the top elements, which in turn, can cause the absorption rate to decline.

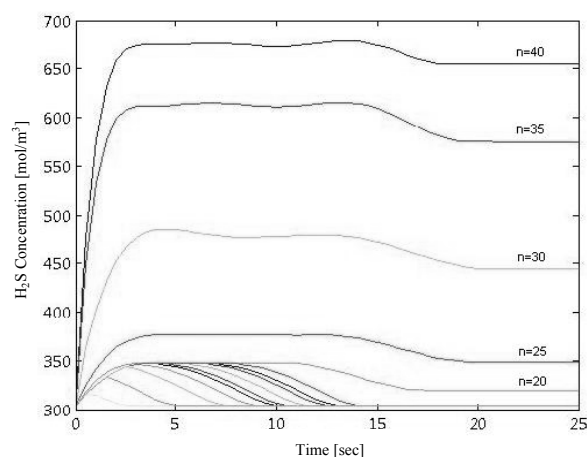


Figure 5. Variation of H_2S concentration at different stages versus time.

Fig. 6 demonstrates the variation of liquid phase temperature in comparison with time in different elements of the column. It shows solvent variation temperature at the bottom elements is quite high compared to the top ones. It might be attributed to the fact that the main part of the absorption occurs at the bottom of the column and the heat of absorption can cause this temperature gradient in this region in comparison with the other sections.

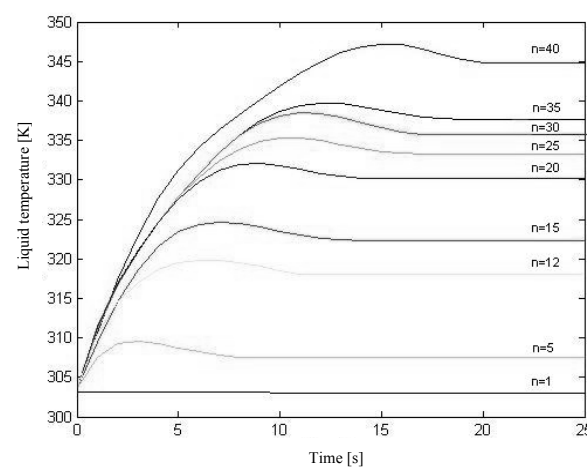


Figure 6. Variation of liquid phase temperature in different stages versus time.

In the current process, enhancement of solution temperature brings about reduction of hydrogen sulfide concentration at the outlet gas flow leading to an increase in absorption rate through the temperature promotion.

Furthermore, increasing the column pressure causes the hydrogen sulfide concentration to decrease in gas flow outlet, which results in increasing the separation performance in absorption column. Increasing the column pressure causes the hydrogen sulfide absorption rate to enhance in the liquid phase. In addition, the results demonstrate that with amine flow rate enhancement, more acidic gases transfer to the amine solvent. This is because of increasing the absorption ability of liquid phase. Transfer of acidic gas from gas to the liquid phase causes the hydrogen sulfide to decrease in the gas phase, which means that with increasing the amine flow rate, hydrogen sulfide concentration decreases in the gas phase. Additionally, variation of amine mass fraction, in constant flow rate, has a positive effect on absorption process. According to Table 3, promotion in amine mass fraction increases the absorption ability of the liquid leading to lower hydrogen sulfide partial pressure in gas outlet.

7. Conclusions

In this work, a nonequilibrium dynamic model that takes heat and mass transfer and chemical reactions in both phases into account has been introduced. The model generally describes the reactive separation processes and, especially, represents reactive absorption of H₂S into diglycolamine solution. The model can predict mole

fraction and concentration of all components that exist in liquid and gas phases and also temperature of the phases along the column in both steady-state and dynamic conditions. The simulation results showed that the method of lines technique was rigorous and suitable for numerical solution of the presented model. The model has been validated against experimental data that have been obtained employing an industrial absorption column. Comparison of simulation and experimental results showed that the model successfully predicts the process behavior. The results showed that an increase in the column pressure, liquid phase temperature and amine concentration as well as liquid flow rate can enhance the absorption ability of the process.

Nomenclature

α	[M ² /m ³]	Total area of the gas-liquid interface
A_T	[m ²]	Cross-sectional area
c	[mol/m ³]	Molar concentration
E	[J/mol]	Specific energy hold up
G	[mol/s]	Gas phase molar flow rate
h	[J/mol]	Molar enthalpy
H	[J/mol]	Specific enthalpy
k	[-]	Equilibrium relation constant
L	[mol/s]	Liquid molar flow rate
N	[mol/m ² s]	Interfacial molar flux
q	[J/m ² s]	Heat flux
R	[mol/m ³ s]	Reaction rate
T	[K]	Temperature
U	[mol/m]	Specific molar hold up
x	[mol/mol]	Liquid phase mole fraction

y	[mol/mol]	gas phase mole fraction
Δz	[m]	Segment height
δ	[m]	Film thickness

References

- [1] Chung, Y. Ch., Ho, K. L. and Ping Tseng, Ch., "Hydrogen sulfide gas treatment by a chemical-biological process: Chemical absorption and biological oxidation steps", *J. Environ. Sci. Health*, B38, 663, (2003).
- [2] Stepova, K. V., Maquarrie, D. J. and Krip, I. M., "Modified bentonites as adsorbents of hydrogen sulfide gases", *Appl. Clay Sci.*, 42, 625, (2009).
- [3] Rajagopal, K., Lacerda, R., Slobodcicov, I. and Campagnolo, E., "Modeling and simulation of hydrogen sulfide removal from petroleum production lines by chemical scavengers", *Chem. Eng. Comm.*, 196, 1237, (2009).
- [4] Chaiprapat, S., Mardthing, R., Kantachote, D. and Karnchanawong, S., "Removal of hydrogen sulfide by complete aerobic oxidation in acidic biofiltration", *Proc. Biochem.*, 46, 344, (2011).
- [5] Asaoka, S., Yamamoto, T., Kondo, S. and Hayakawa, S., "Removal of hydrogen sulfide using crushed oyster shell from pore water to remediate organically enriched coastal marine sediments", *Bioresource Technol.*, 100, 4127, (2009).
- [6] Gercel, O., Koparal, A. S., Bakır, U. and Gutveren, O., "Removal of hydrogen sulfide by electrochemical method with a batchwise operation", *Sep. Purif. Technol.*, 62, 654, (2008).
- [7] Sahu, R. C., Patel, R. and Ray, B. C., "Removal of hydrogen sulfide using red mud at ambient conditions", *Fuel Proc. Technol.*, xxx, (2011).
- [8] Maa, H., Hogendoorn, J. A. and Versteeg, G. F., "The removal of hydrogen sulfide from gas streams using an aqueous metal sulfate absorbent", *Sep. Purif. Technol.*, 43, 183, (2005).
- [9] Mandal, B. P., Guha, M., Biswas, A. K. and Bandyopadhyay, S. S., "Removal of CO₂ by absorption in aqueous MDEA/MEA and AMP/MEA solutions", *J. Chem. Eng. Sci.*, 56, 621, (2002).
- [10] Higler, A., Taylor, R., and Krishna, R., "Modeling of a reactive separation process using a nonequilibrium stage model", *J. Comput. Chem. Eng.*, 22, 111, (1998).
- [11] Brettschneider, O., Thiele, R., Faber, R., Thielert, H., and Wozny, G., "Experimental investigation and simulation of the chemical absorption in a packed column for the system NH₃-CO₂-H₂S-NaOH-H₂O", *J. Sep. Purif. Technol.*, 39, 139, (2004).
- [12] Seader, J. D., "The rate-based approach for modeling staged separations", *J. Chem. Eng. Prog.*, 85, 41, (1989).
- [13] Baghli, N. A., Pruess, S. A., Yesavage, V. F. and Selim, M. S., "A rate based model for the design of gas absorbers for the removal of CO₂ and H₂S using aqueous solutions of MEA and DEA", *J. Fluid phase Equilibria*, 185, 31, (2002).
- [14] Kenig, E. Y., Kucka, L. and Gorak, A., "Rigorous modeling of reactive absorption processes", *J. Chem. Eng. Technol.*, 26, 631, (2003).

- [15] Kucka, L., Muller, I., Kenig, E.Y. and Gorak, A., "On the modelling and simulation of sour gas absorption by aqueous amine solutions", *J. Chem. Eng. Sci.*, 58, 3571, (2004).
- [16] Kloeker, M., Kenig, E. Y., Hoffmann, A., Kreis, P., and Gorak, A., "Rate-based modeling and simulation of reactive separations in gas/vapour liquid systems", *J. Chem. Eng. Proc.*, 44, 617, (2005).
- [17] Asprion, N., "Nonequilibrium rate-based simulation of reactive systems: Simulation model, heat transfer, and influence of film discretization", *J. Ind. Eng. Chem. Res.*, 45, 2054, (2006).
- [18] Dingman, J. C., Jackson, J. L., Moore, T. F. and Branson, J. A., "Equilibrium data for H₂S-CO₂-diglycolamine agent-water system", 62th International Conference on Gas Processors, San Francisco, p. 14, (1983).
- [19] Onda, K., Takeuch, H. and Okumoto, Y., "Transfer coefficient between gas and liquid phase in packed columns", *Journal Engineering of Japan*, 1, 56, (1968).
- [20] Kenig, E.Y., Schneider, R., and Gorak, A., "Multicomponent unsteady-state film model: A general analytical solution to the linearized diffusion-reaction problem", *Int. J. Chem. Eng.*, 83, 85, (2001).
- [21] Ghaemi, A., Shahhosseini, Sh. and Ghanadi, M., "Nonequilibrium dynamic modeling of carbon dioxide absorption by partially carbonated ammonia solutions", *Chem. Eng. J.*, 149, 110, (2009).
- [22] Kent, R. L. and Eisenberg, B., "Better data for amine treating", *International Conference on Hydrocarbon process*, 55, 87, (1976).
- [23] Taylor, R. and Krishna, R., *Multi-component Mass Transfer*, John Wiley, New York, (1993).
- [24] Reid, R. C., Prausnitz, J. M. and Poling, B. E., *The properties of gases and liquids*, New York, McGraw-Hill, (1987).
- [25] Pherock, R. and Moniuk, W., "Plate efficiency in the process of absorption with chemical reaction-experiments and example calculations", *Int. J. Chem. Eng.*, 39, 37, (1988).
- [26] Kister, H. Z., *Distillation design*, 1st ed., McGraw-Hill, (1992).