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Regeneration Section of CO_2 Capture Plant by MEA Scrubbing with a Rate-Based Model

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CO_2 capture from exhaust gas of power plants, natural gas and refinery gas can be successfully achieved by chemical absorption with alkanolamines. CO_2 capture from exhaust gas is often obtained by absorption with monoethanolamine (MEA) which is the most frequently used solvent for this purpose.

Our paper focuses on the regeneration section, where the amine solution is separated from the absorbed CO_2 and recirculated to the absorber. Since regeneration is obtained in a stripper or a distillation column, it is the most energy demanding unit of the plant, so a careful modeling is required.

Thermodynamics, kinetics and mass transfer influence the chemical absorption process. Acidic gases and amines are weak electrolytes, which partially dissociate in the aqueous phase: the high non-ideality of the liquid phase must be properly taken into account, by employing a γ/ϕ method.

Kinetics and mass transfer can be described using two different approaches: the “equilibrium-based stage efficiency” model or the “rate-based” one. ASPEN Plus® uses the rate-based model, but the prediction of mass transfer coefficients is based on the film theory by Lewis and Whitman, while other theories can more conveniently be used, i.e. the Eddy Diffusivity theory.

Since ASPEN Plus® simulator is suitable to be user customized, it has been chosen as framework for the model proposed in this work, that was validated by comparing simulation results with experimental data of a pilot plant for the purification of exhaust gas from power plant.

1. Introduction

Many gas streams commonly present in industrial plants - natural gas, syngas, exhaust gases and refinery gases - contain significant quantities of acid gases, mainly CO_2 and H_2S. Their presence is very undesirable due to corrosion, operational, economical and/or environmental reasons. As a matter of fact, carbon dioxide should be removed for different productions (ammonia, hydrogen, etc.) to avoid poisoning of the catalyst. Moreover, CO_2 is a powerful greenhouse gas, whose massive presence in the atmosphere is the cause of gradual global warming. In order to limit this problem and to accomplish the requirements of the Kyoto protocol, an important CO_2 removal is then realized in the treatment of combustion gases at power plants.

Industrially, absorption is probably the most used gas purification technique, involving the transfer of a substance from the gaseous phase to the liquid one through the phase boundary. The absorbed material may dissolve physically in the liquid or react chemically with it. Using aqueous amine solvents, the mass transfer is promoted by chemical reactions: acid gases can react directly or through a mechanism due to acid-base ionic species in solution.

The mass transfer from the bulk of the gas phase to the bulk of the liquid phase is mainly influenced by:

1) Diffusion of the reactant from the bulk of the gas phase to the gas-liquid interface;
2) Diffusion of the reactant from the gas-liquid interface to the bulk of the liquid phase;
3) Simultaneous reaction between dissolved gas and liquid reactant;
4) Diffusion of reaction products in the bulk of the liquid phase promoted by the concentration gradient due to chemical reactions.

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Molecules of alkanolamines are characterized by one hydroxyl group and one amino group. The former helps in reducing the vapor pressure and increasing the water solubility, while the latter provides the necessary alkalinity in water solutions to make the acid gas absorption occur (Kohl and Nielsen, 1997). Indeed, the solubility of acid gas in water is highly influenced by the presence of the amine.

The equilibrium solubility of an acid gas that does not react in the liquid phase is governed by the partial pressure of this gas over the liquid. In a reactive solvent, on the contrary, when an acid gas is absorbed, it is partially consumed by chemical reactions. As a consequence, the CO_2 bulk concentration in the liquid phase is low and the rate of absorption of the acid gas is significantly affected by the amine. Chemical reactions enhance the mass transfer driving force, i.e. the difference between the gas concentration in the liquid at the gas-liquid interface and the unreacted gas concentration in the bulk of the liquid phase.

This work focuses on CO_2 capture from exhaust gases of power plants by absorption with monoethanolamine (MEA). This amine is the most frequently used solvent for this process, due to its relatively high loading, i.e. the ratio of moles of absorbed acid gas per mole of amine.

Experimental data for the system CO_2-H_2O-MEA have been collected over the past two decades. In order to reproduce these data, many thermodynamic models were developed, in particular the one proposed by Kent and Eisenberg (Kent and Eisenberg, 1976) and the Electrolyte-NRTL model (Chen et al., 1979; Chen et al., 1982; Chen and Evans, 1986; Mock et al., 1986).The latter can be used to reproduce experimental data for a wider range of temperatures and loadings.

Kinetics and mass transfer can be described using two different approaches: the “equilibrium-based stage efficiency” model or the “rate-based” one (Pellegrini et al., 2011c). The “equilibrium-based stage efficiency” approach corrects the performance of a theoretical stage by a factor called “stage efficiency”. The “rate-based” model avoids the approximation of efficiency, by analysing the mass and heat transfer phenomena that occur on a real tray or actual packing height. ASPEN Plus® (AspenTech, 2010) uses the rate-based model, but the prediction of mass transfer coefficients is based on the film theory (Lewis and Whitman, 1924), while other theories can more conveniently be used, i.e. the Eddy Diffusivity theory (King, 1966).

A proper design of the absorption and the regeneration units is then needed. Since ASPEN Plus® simulator is suitable to be user customized, it has been chosen as framework for the model proposed in this work, that was validated by comparing simulation results with experimental data of a pilot plant for the purification of exhaust gas from power plants (Dugas, 2006).

2. Modeling

2.1 Thermodynamic and chemical equilibria

A good description of vapor-liquid equilibrium is crucial for a correct design of unit operations involving mass transfer from one phase to the other (Pellegrini et al., 2010).

Chemical reactions in the liquid phase should be taken into account when describing the VLE. The generation of ionic species, moreover, makes the system highly non ideal.

As a matter of fact, acid gases and amines partially dissociate in the aqueous phase because they are weak electrolytes. The liquid phase is then composed of a moderately volatile solvent (water), a non volatile solvent (MEA), very volatile molecular species (acid gas) and non volatile ionic species (Moioli et al., 2013; Pellegrini et al., 2013a, 2013b).

Physical VLE involves only molecular species, i.e., CO_2, H_2O and MEA. Chemical reactions occurring in the liquid phase involve both molecular and ionic species and can be described according to the following equilibrium relations:

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

$$2H_2O + CO_2 \xrightleftharpoons{K_{a,CO_2}} HCO_3^- + H_3O^+ \tag{2}$$

$$H_2O + HCO_3^- \xrightleftharpoons{K_{a,HCO_3^-}} CO_3^{2-} + H_3O^+ \tag{3}$$

$$MEAH^+ + H_2O \xrightleftharpoons{K_{a,MEAH^+}} MEA + H_3O^+ \tag{4}$$

$$MEACOO^- + H_2O \xrightleftharpoons{K_{carb}} MEA + HCO_3^- \tag{5}$$

The equilibrium constants K_j are strongly dependent on temperature T:

$$\ln K_j = A_j + \frac{B_j}{T} + C_j \ln T + D_j T \tag{6}$$

where A_j, B_j, C_j, D_j are parameters whose values can be found in literature (Edwards et al., 1978; Moioli et al., 2012; Pellegrini et al., 2011a; Pellegrini et al., 2011b).

To describe such Vapor-Liquid Equilibrium (VLE) systems, a γ/ϕ approach is used. The vapor phase is represented by means of an Equation of State (EoS), in particular the SRK EoS (Soave, 1972). The liquid phase, on the other hand, is described by means of an activity coefficient model. For the considered system, the Electrolyte-NRTL model (Chen et al., 1979; Chen et al., 1982; Chen and Evans, 1986; Mock et al., 1986) has been used.

The model is based on the assumptions of like-ion repulsion assumption, i.e.: the local composition of cations around other cations is zero and, similarly, the local composition of anions around other anions is zero. This idea is based on the assumption that repulsive forces between ions of the same charge are strong, therefore they are extremely relevant for near species. The other assumption is based on local electroneutrality: the distribution of anions and cations around a central molecule makes the net local charge null.

The considered model provides an expression for the excess Gibbs free energy, taking into account molecular and ionic interactions among all species in liquid phase.

The model is characterized by a large number of parameters, that take into account interactions between molecule and molecule, molecule and ion pair, ion pair and ion pair. Proper values (Moioli et al., 2013; Pellegrini et al., 2013a, 2013b; Pellegrini et al., 2011a; Pellegrini et al., 2011b) of parameters can allow a very good representation of the vapor-liquid equilibrium.

2.2 Kinetics and mass transfer

If chemical reactions take place, a further contribution to mass transfer should be taken into account. Besides diffusion limitations also kinetics of reactions between CO_2 and MEA (Eq. (7)) and between CO_2 and OH^- (Eq. (8)) should be taken into account, since chemical equilibrium conditions are not attained.

The reactions that are considered are then:

$$CO_2 + MEA + H_2O \xrightarrow{k_{c,MEA}} MEACOO^- + H_3O^+ \tag{7}$$

$$CO_2 + OH^- \xrightarrow{k_{c,OH^-}} HCO_3^- \tag{8}$$

For these two reactions, the rate equations can be written as follows:

$$R_{CO_2+MEA} = k_{c,MEA}[CO_2][MEA] \tag{9}$$

$$R_{CO_2+OH^-} = k_{c,OH^-}[CO_2][OH^-] \tag{10}$$

The rate constants are expressed according to the Arrhenius relationship:

$$k_c = A\exp\left(-\frac{E_{att}}{RT}\right) \tag{11}$$

The values of the pre-exponential factor and of the activation energy are taken from literature (Hikita et al., 1977; Pinsent et al., 1956).

When dealing with the absorption + regeneration system involving CO_2 and amines, mass and heat transfer limitations should be taken into account.

There are two main approaches to modeling: the “Equilibrium” and the “Rate-based” models.

The Equilibrium model divides the column in different segments, each considered well mixed in the liquid and vapor phases. The departure from equilibrium is taken into account by introducing efficiency.

The Rate-based model is a non-equilibrium model, where the rate of absorption or desorption is finite, as in a real process. This model is already implemented in ASPEN Plus® process simulator and is used in this work.

Several theories were developed to describe transfer limitations (King, 1966; Lewis and Whitman, 1924). Among these, film theory is used by default by ASPEN Plus®, while the Eddy Diffusivity allows to obtain the correct dependence of mass transfer coefficient on diffusivity of carbon dioxide in the liquid phase (Moioli et al., 2013).

3. Validation of simulation results with experimental data from a pilot plant

The model has been tested by simulating an experimental pilot plant (Dugas, 2006), consisting of an absorber and a regenerator. The scheme is shown in Figure 1.

The pilot plant has two columns of the same dimensions. Each column has an inside diameter of 42.7 cm and two 3.05 m beds of packing with a collector plate and a distributor between the beds. The main characteristics of the absorber and of the regenerator are reported in Table1. The absorber removes CO_2 from the flue gas by means of a solution of monoethanolamine 30% w/w (2.141E-2 kmol/s) at the operating conditions of 313.15 K and 1.70 bar. The feed (5.128E-3 kmol/s), entering the absorption column at 332.18K and 1.03 bar, is composed of carbon dioxide, nitrogen, water and oxygen, in order to reproduce the composition of a typical exhaust gas coming out of a coal fired power plant (Table 2). The lean solvent is fed to the absorption column with a loading equal to 0.286. After CO_2 removal from the flue gas, the loading becomes 0.539. Then the rich solvent enters the top of the distillation column for regeneration.

For a detailed description of the plant please refer to test # 47 of literature (Dugas, 2006).

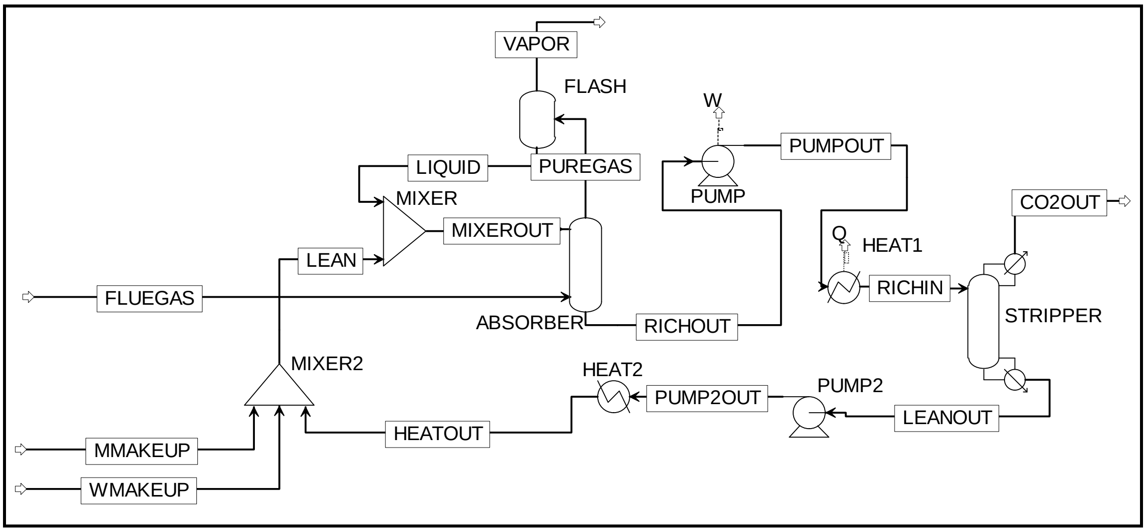


Figure 1: Scheme of the simulated process

Table 1. Characteristics of the absorption and regeneration sections of the experimental pilot plant (Dugas, 2006).

Parameter	Absorption column	Regeneration column
diameter [m]	0.427	0.427
packing height [m]	6.10	6.10
packing type	IMTP #40	Flexipac 1Y
pressure [bar]	1.01	0.69

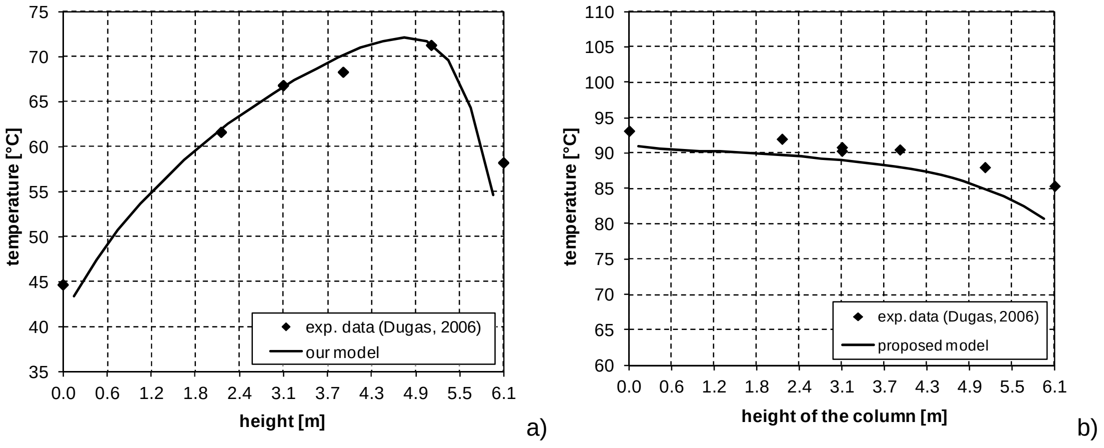
Table 2. Composition (mole fraction) of the flue gas entering the purification plant.

Component	FLUE GAS
water	0.016
carbon dioxide	0.1841
nitrogen	0.7528
oxygen	0.0471

The proposed model has been validated by comparing the obtained results with the experimental data from the pilot plant. The first and most important check has been performed on the absorption column (Moioli et al., 2012b). This unit, indeed, is not influenced by specifications that should be given in order to fulfill the remaining degrees of freedom (as in a distillation column), because only the characteristics of the column and the streams fed to it should be given as an input. As a consequence, the data can be more easily compared.

In the absorption process considerable heat is released, because of exothermic reactions of the acid gas in the amine solution. The temperature profile along the column presents a bulge due to the cold inlet gas absorbing heat from the rich solution (Kohl and Nielsen, 1997). The position of the bulge depends on the value of the liquid to gas ratio and is well predicted. A very good agreement between the proposed model and the experimental temperature profile has been obtained (see Figure 2), as already shown in previous works (Moioli et al., 2012).

The proposed model, then, has been applied to the regeneration section, in order to prove its reliability also for simulating the complete purification plant. The rich solvent is fed to the regeneration column, that is generally a distillation column or a stripping one. In the simulated case, a distillation column characterized by a partial reboiler and a partial condenser has been simulated. The solvent to be purified is fed to the top of the unit, with the liquid reflux coming from the partial condenser. It is a full reflux unit, since the only product obtained from the top of the regeneration section is a gaseous stream with a very high concentration of carbon dioxide, while all the liquid, practically water, is recycled to the column. The lean amine solution exits from the bottom of the unit. Few losses of amine occur, since MEA is characterized by low volatility, though the heat of reaction with CO_2 is important, the desorption representing the main expense of the process. A proper description of this unit is fundamental to study minimum energy configurations and has been achieved: Figure 2b shows a good reproduction of the temperature profile in the distillation column, confirming the reliability of the Eddy Diffusivity (King, 1966) theory for amine scrubbing modeling.



a) b)

Figure 2: Temperature profile of a) the absorption section and b) the regeneration section according to the proposed model

4. Conclusions

Mass transfer significantly influences the process of absorption of acid gases in amine aqueous solutions. In this work the Eddy diffusivity theory is taken into account, in order to perform simulations of both the absorption and the regeneration units with the correct dependence of the mass transfer coefficient on CO_2 diffusivity.

The model has been verified by comparing simulation results with experimental data of a pilot plant (Dugas, 2006), showing a good prediction of experimental data also for the regeneration unit.

The possibility of using a reliable model, tested on experimental data, allows engineering companies to design more accurate plants and to choose the right amount of amine solvent to be used. For this reason, this work can result very helpful if applied to design acid gas purification plants with amines.

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