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Regeneration Section of a CO_2 Capture Plant by MEA Scrubbing 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.
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 by means of MEA washing.

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.
Once emitted, CO_2 added to the atmosphere and oceans remains for thousands of years. Thus, climate changes forced by CO_2 depend primarily on cumulative emissions, making it progressively more and more difficult to avoid further substantial climate change.

"*Its concentration has increased every year since scientists started making measurements on the slopes of the Mauna Loa volcano more than five decades ago. The rate of increase has accelerated since the measurements started, from about 0.7 ppm per year in the late 1950s to 2.1 ppm per year during the last 10 years.*"

as stated by National Oceanic and Atmospheric Administration – NOAA (NOAA, 2013).
Before the Industrial Revolution in the 19th century, global average CO_2 was about 280 ppm. During the last 800'000 years, CO_2 fluctuated between about 180 ppm during ice ages and 280 ppm during interglacial warm periods. Today's rate of increase is more than 100 times faster than the increase that occurred when the last ice age ended. On May 9th, 2013, the daily mean concentration of carbon dioxide in the atmosphere of Mauna Loa, Hawaii, surpassed 400 parts per million (ppm) for the first time since measurements began in 1958.

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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 into 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.
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.
In order to obtain the best process solution, the type of amine and the amine concentration should be carefully chosen. Generally, they are mainly determined by (Kohl and Nielsen, 1997):

- pressure and temperature conditions of the gas;
- composition of the gas with respect to major and minor constituents;
- purity requirements of the treated gas;
- simultaneous or selective H_2S and CO_2 removal.

In many cases process requirements can be met by different amines: the choice is made basing on an economic analysis. It should also be considered that increasing the amine concentration will generally reduce the required solution circulation rate and therefore the plant cost, but that the acid gas vapor pressure is higher over more concentrated solutions at given acid-gas/amine mole ratios. Moreover, when the same quantity of acid gas is absorbed in a smaller volume of solution, the heat of reaction results in a greater increase in temperature and a consequently increased acid-gas vapor pressure over the solution.
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.
The correct description of the considered scrubbing system is fundamental:

- for the absorption section:
  - to choose the specific amine to be used in the chemical solution;
  - to choose the right amount of solvent to be fed;
  - to determine the height of the column;
- for the regeneration section:
  - to determine which type of regeneration (stripping or distillation) should be used;
  - to determine the height of the column;
  - to determine the energy requirement at the reboiler;
  - to study minimum energy configurations.

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) using MEA washing.

2. Modeling

2.1 Thermodynamic and chemical equilibria

A good description of vapor-liquid equilibrium (VLE) 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 (Langé et al., 2013; Moioli et al., 2013; Pellegrini et al., 2013).
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:

1) dissociation of water:

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

2) solubilization of carbon dioxide:

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

3) dissociation of the bicarbonate ion:

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

4) dissociation of the protonated monoethanolamine ion:

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

4) dissociation of the carbammate ion:

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

Table 1. Values of parameters of Eq. (6) for all the chemical equilibrium reactions considered in this work.

Reaction	A	B	C	D	Source
Eq. (1)	132.89	-13446	-22.47	0	Edwards et al., 1978
Eq. (2)	231.46	-12092	-36.78	0	Edwards et al., 1978
Eq. (3)	216.05	-12432	-35.48	0	Edwards et al., 1978
Eq. (4)	-3.038	-7008.3	0	-0.0031	AspenTech, 2010
Eq. (5)	-0.52	-2545.5	0	0	AspenTech, 2010

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) and are reported in Table 1.

To describe such vapor-liquid equilibrium 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 two assumptions:

1) 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.
2) local electroneutrality assumption: the distribution of anions and cations around a central molecule makes the net local charge null.

The local distribution of anions, cations and molecules, then, is considered as shown in Figure 1. 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 (Langé et al., 2013; Moioli et al., 2013; Pellegrini et al., 2013; Pellegrini et al., 2011a; Pellegrini et al., 2011b) of parameters allow a very good representation of the vapor-liquid equilibrium.

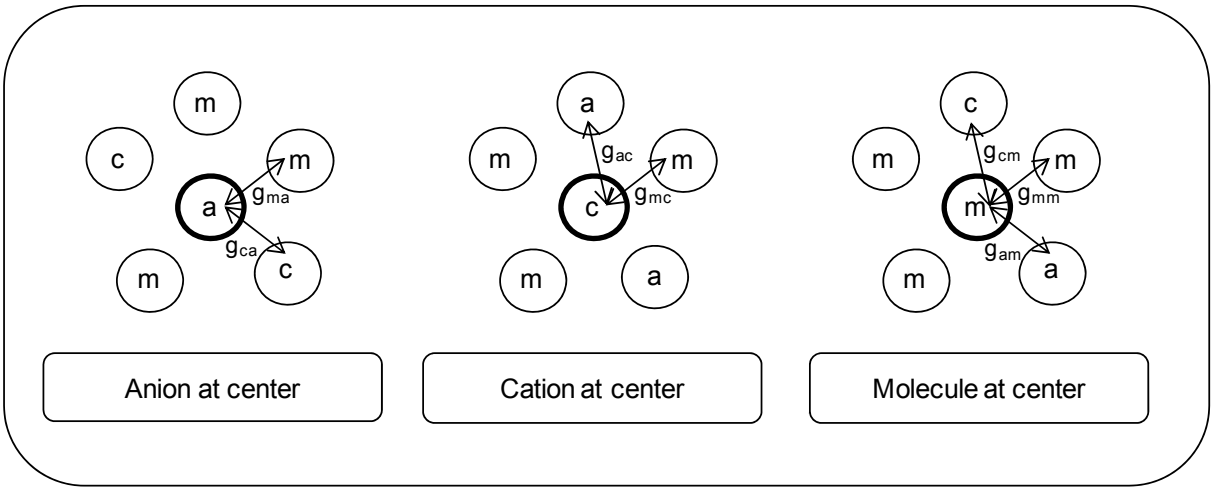

Figure 1: Different types of cell according to the Electrolyte-NRTL model.

2.2 Kinetics and mass transfer

If chemical reactions take place, a further contribution to mass transfer must be considered. 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 are then:

1) reaction between carbon dioxide and monoethanolamine in water:

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

2) reaction between carbon dioxide and the hydroxyl ion:

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

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

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

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

Table 2. Values of parameters of Eq. (1) for all the kinetic-controlled reactions considered in this work.

Reaction	A [m^3/(kmol s)]	E_{att} [kJ/mol]	Source
Eq. (9)	4.32×10^{13}	55.4603	Hikita et al., 1977
Eq. (10)	9.77×10^{10}	41.2564	Pinsent et al., 1956

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) and are reported in Table 2.
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 into 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).
The theory by Lewis and Whitman (1924) is the first approach to mass transfer analysis at vapor-liquid interface. It assumes that all the mass transfer resistances are located in two films of a finite thickness near the interface on the gas side and on the liquid side, that films are free from convection currents, so any transfer of solute through these films is affected by the process of diffusion and that in the bulk of the liquid or of the gas phase mixing by convection is so rapid that the concentration of solute in the phase can be considered uniform everywhere. According to this theory, then, a mass transfer coefficient proportional to the diffusivity of CO_2 in the aqueous phase can be derived.
The Eddy Diffusivity theory, proposed by King in 1966, is a steady state theory taking into account both molecular diffusion and turbulent transport. It assumes that there exists a primary mass transfer resistance zone where all

the species change their concentration from the value at the interface to the value in the liquid bulk and that the presence of little eddies influences the mass transfer rate. A mass transfer coefficient with a square root dependence on diffusivity is obtained, more in accordance with field data about the amine scrubbing process.

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 2.
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 Table 3. 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 4). 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).
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 3 and Figure 4), as already shown in previous works (Moioli et al., 2012).

Table 3. 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 4. 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

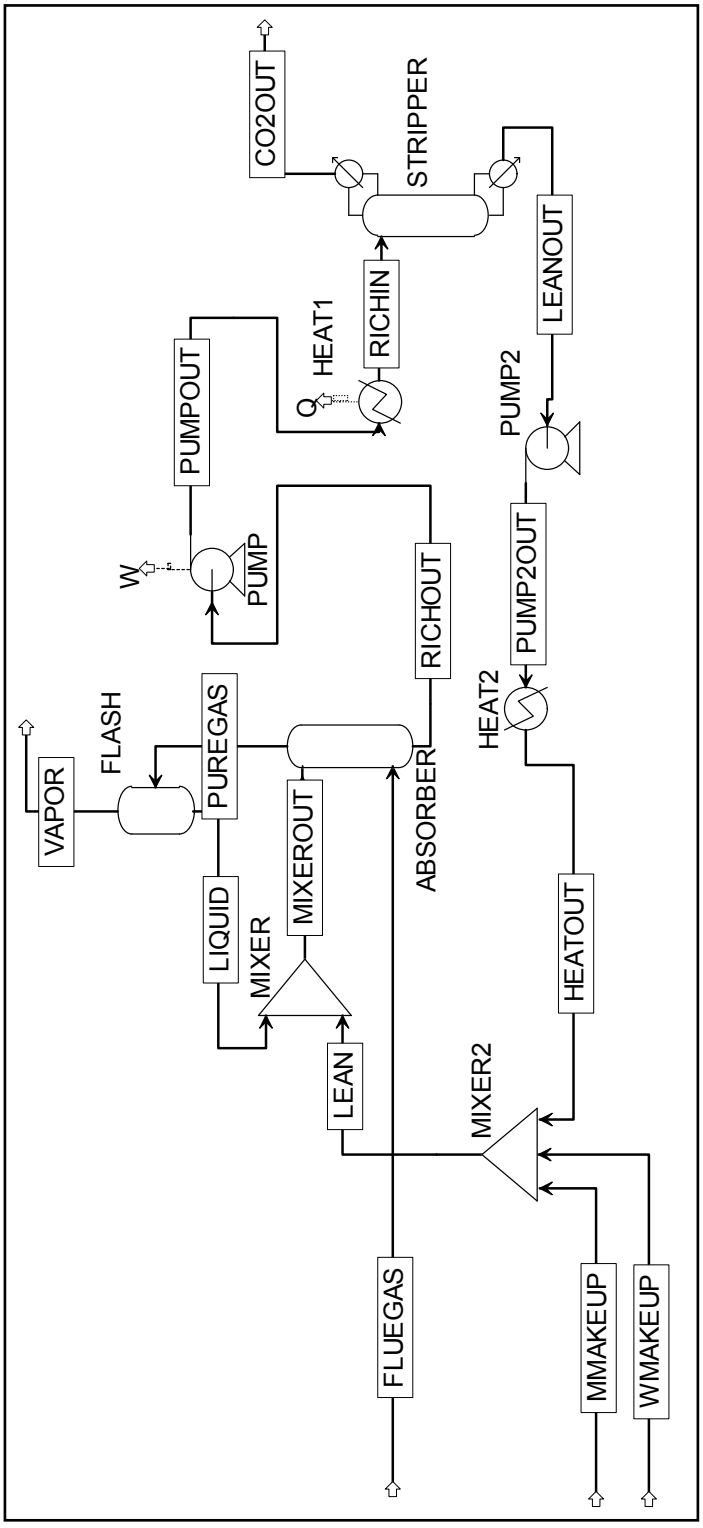

Figure 2: Scheme of the simulated process (ASPEN Plus®)

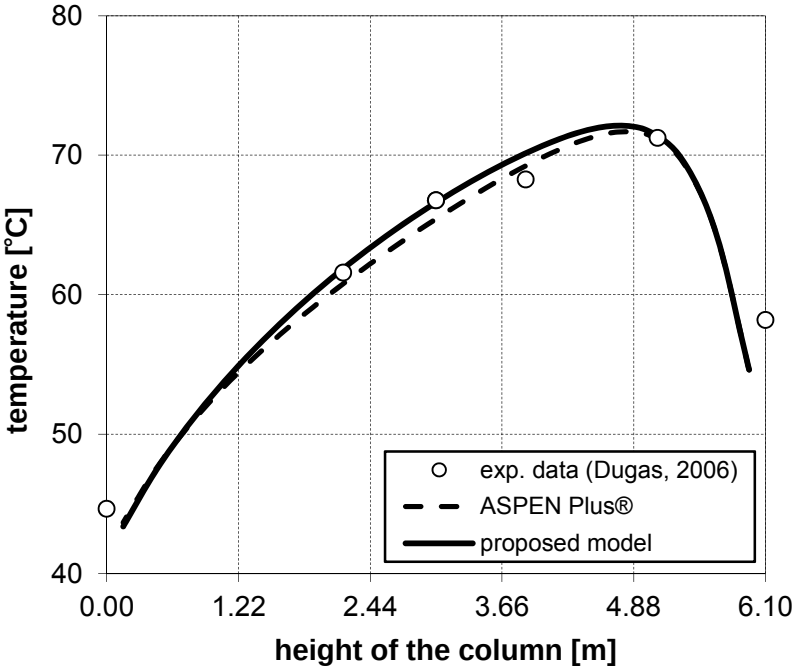

Figure 3: Temperature profile of the absorption section according to the proposed model

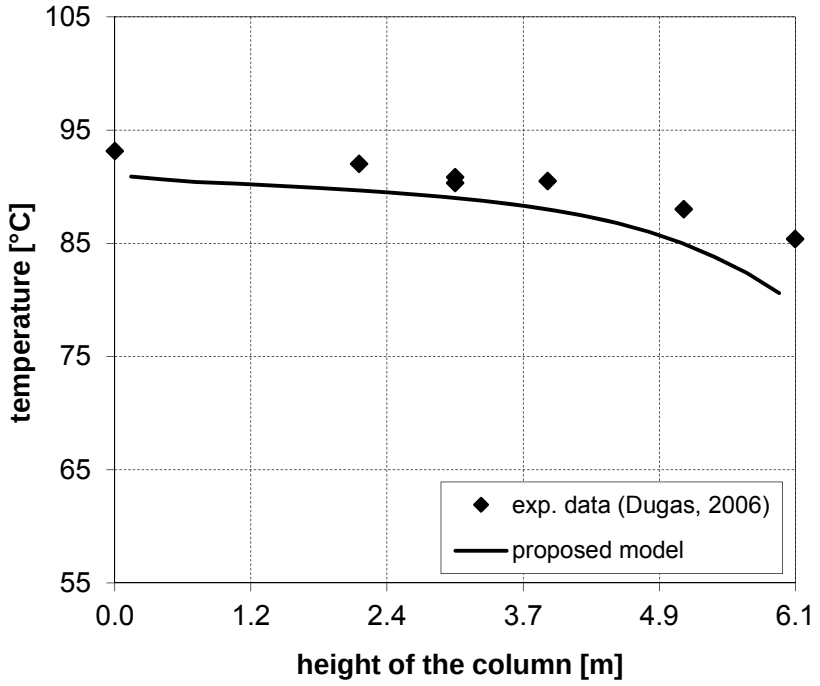

Figure 4: Temperature profile of the regeneration section according to the proposed model

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 at 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 4 shows a good reproduction of the temperature profile in the distillation column, confirming the reliability of the Eddy Diffusivity theory (King, 1966) for amine scrubbing modeling (Moioli and Pellegrini, 2013).

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.

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