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# Post-combustion CO<sub>2</sub> capture process: Equilibrium stage mathematical model of the chemical absorption of CO<sub>2</sub> into monoethanolamine (MEA) aqueous solution

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## ABSTRACT

This paper deals with the modeling and optimization of the chemical absorption process to CO<sub>2</sub> removal using monoethanolamine (MEA) aqueous solution. Precisely, an optimization mathematical model is proposed to determine the best operating conditions of the CO<sub>2</sub> post-combustion process in order to maximize the CO<sub>2</sub> removal efficiency. Certainly, the following two objective functions are considered for maximization: (a) ratio between the total absorbed CO<sub>2</sub> and the total heating and cooling utilities and (b) ratio between total absorbed CO<sub>2</sub> and the total amine flow-rate.

Temperature, composition and flow-rate profiles of the aqueous solution and gas streams along the absorber and regenerator as well as the reboiler and condenser duties are considered as optimization variables. The number of trays or height equivalent to a theoretical plate (HETP) on the absorber and regenerator columns as well as the CO<sub>2</sub> composition in flue gas are treated as model parameters. Correlations used to compute physical-chemical properties of the aqueous amine solution are taken from different specialized literature and are valid for a wide range of operating conditions. For the modeling, both columns (absorber and regenerator) are divided into a number of segments assuming that liquid and gas phases are well mixed.

GAMS (General Algebraic Modeling System) and CONOPT are used, respectively, to implement and to solve the resulting mathematical model.

The robustness and computational performance of the proposed model and a detailed discussion of the optimization results will be presented through different case studies. Finally, the proposed model cannot only be used as optimizer but also as a simulator by fixing the degree of freedom of the equation system.

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**Keywords:** Post-combustion CO<sub>2</sub> capture process; Equilibrium stage mathematical model; Mathematical programming; Optimization and simulation

## 1. Introduction

The earth global warming, which is directly related to the worldwide demand of electricity, has been drastically increased during the last years as consequence of the growing levels of greenhouse gases emission levels. Unfortunately, this trend is expected to continue growing significantly during the next decades. Carbon dioxide (CO<sub>2</sub>) is considered to be one of

the main contributors to the greenhouse effect and it is emitted in a number of ways. Fossil fuel combustion for electricity generation, industry and transportation is the largest source of CO<sub>2</sub> emissions.

Many specialists predict for next decades that the coal and gas natural will dominate the electricity generation. Precisely, predictions indicate that coal is abundantly available to be used as a primary source of energy for next 160 years,

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approximately three times that of natural gas. Therefore, the reduction of CO<sub>2</sub> emissions is a global challenge and requires collective actions and close cooperation between industries and researchers.

The options to capture CO<sub>2</sub> from exhaust flue gas generated by the combustion of fossil fuel depend on the source of CO<sub>2</sub> emissions. Specifically, in the electricity and heat sector, there are three feasible technologies currently proposed: (1) pre-combustion capture, (2) post-combustion capture and, (3) oxi-fuel combustion capture. The conditions of the flue gas to be treated (CO<sub>2</sub> concentration and pressure) and the fuel type (solid or gas) are determinant factors in selecting the capture system. As follows, a brief description of each technology is presented.

Post-combustion process, which will be studied in this paper, includes various techniques: (a) scrubbing with aqueous amine solutions (MEA, MDEA, DEA); (b) combined amine-membrane techniques; (c) molecular sieves and (d) pressure and temperature swing adsorption (PTSA) using zeolites. These techniques separate CO<sub>2</sub> separated from a flue gas environment containing other components (NO<sub>x</sub> and SO<sub>2</sub>). Chemical composition of flue gas depends on the type of fossil fuel used. For example, coal emits more NO<sub>x</sub> and CO<sub>2</sub> per unit of useful energy produced than natural gas.

Each one of the mentioned techniques has its own advantages and disadvantages. For example, scrubbing processes are placed at the end of the pipe treatment which allow to retrofit existing fossil fuel plants easily. Another advantage of this technique is that a relatively pure CO<sub>2</sub> stream is obtained and the CO<sub>2</sub> recovered can be used for other purposes. However, the main drawbacks of this process are the high amount of energy required to regenerate the amine solvent, corrosion and excessive solvent degradation especially in gas stream containing O<sub>2</sub>.

During the last time, some of the main areas in which research efforts are being concentrated are: (a) selection and development of new type amines, (b) experimental works at pilot plant scales and (c) modeling, simulation and optimization of CO<sub>2</sub> capture processes. All these areas are strongly connected among them. Research advances in all these areas will lead to increase the CO<sub>2</sub> absorption efficiency or to minimize the total cost of the CO<sub>2</sub> capture process.

### 1.1. Selection and development of new type amines

The development of new absorbents with low environmental impact, in order to reach lower CO<sub>2</sub> capture cost and better performance is receiving considerable at the present time. Primary, secondary, tertiary, sterically hindered alkanolamines including their mixtures are widely used as reactive in chemical absorption processes.

The selection of type of solvent depends on the following factors: gas composition and condition, gas impurities specification, life cycle cost, space, salt deposition, byproduct, losses, hydrocarbon absorption, etc. In this research area, significant efforts are being made in the study of the influence of the alkanolamines properties on the CO<sub>2</sub> absorption efficiency.

Precisely, research activities on degradation, corrosion, chemical kinetics and reaction mechanisms as well are receiving special attention (Lepaumier et al., 2009a,b,c, 2010; Bello and Idem, 2006; Dubois et al., 2009; Davis and Rochelle, 2009; Sexton and Rochelle, 2009; Dawodu and Meisen, 2009; Supap et al., 2009; Edali et al., 2009; Kittel et al., 2009; Puxty et al., 2009a,b; Manjula and Amornvadee, 2009).

### 1.2. Modelling, simulation and optimization CO<sub>2</sub> capture processes

The application of the mathematical programming techniques as well as advanced process modeling tools for simulation and optimization of chemical processes have been also received much attention during recent years. They are powerful tools for gaining valuable insights on the complex processes in order to determine feasible and optimal process designs. Certainly, process alternatives and variable modifications can be easily evaluated in short times without the need for pilot-scale experimentations which are generally costly.

Specifically, in post-combustion CO<sub>2</sub> absorption process, a great number of mathematical models have been recently developed according to different purposes. A brief classification of the proposed models including some of the most recent articles is presented as follow.

#### 1.2.1. Steady and unsteady simulations

Rate-based and equilibrium mathematical models have been developed to simulate the steady and unsteady state of the post-combustion process (Edali et al., 2009; Lee et al., 1997; Lawal et al., 2009; Oyenekan, 2007; Plaza et al., 2010; Zhang et al., 2009; Huttenhuisa et al., 2009; Gabrielsen et al., 2007; Ziaii et al., 2009a,b; Ströhle et al., 2009; Greer et al., 2010; Pellegrini et al., 2010). In those articles, authors analyzed many types of amines (MEA, MDEA, DEA, MDEA-PZ), flue gas compositions and used different process simulators to implement the models (Aspen Hysys, Chemcad, Matlab). Other authors developed and implemented their own simulation algorithms. In general, authors investigated the performance of different packings and operating conditions by simulating the pilot-scale column experiments. The models included correlations for estimating liquid and vapor phase mass transfer coefficients and an effective interfacial area as well. In some cases, the absorption and regeneration processes are studied separately (stand-alone processes).

#### 1.2.2. Operating conditions optimization

In regards to this area, only few articles dealing with the simultaneous optimization of operating conditions of CO<sub>2</sub> capture processes have been recently published (Ba-Shammakh et al., 2007; Sirikitputtisak et al., 2009; Halim and Srinivasan, 2009; among others).

Ba-Shammakh et al. (2007) applied mathematical programming to develop a MINLP model for the production planning of refinery processes to achieve maximum operational profit while reducing CO<sub>2</sub> emissions to a given target through the use of different CO<sub>2</sub> mitigation options, e.g., post-combustion process using aqueous amine solutions (MEA). The proposed model includes the following options: flow-rate balancing (decreasing the inlet flow rate to a unit that emits more CO<sub>2</sub>), fuel switching (changes in a certain operation to run with a different fuel that emits less CO<sub>2</sub> emissions, such as natural gas), and installation of a CO<sub>2</sub> capture process [e.g., the monoethanolamine (MEA) process]. The objective of the MINLP model is to determine suitable CO<sub>2</sub> mitigation options for a given reduction target while meeting the demand of each final product and its quality specifications, while simultaneously maximizing profit. In this study, a global optimization algorithm is used on the different case studies considered.

Sirikitputtisak et al. (2009) developed a multi-period mathematical model to optimize the energy planning for Ontario

(Canada). The proposed model deals with discrete and continuous decisions and involves both time-dependent and time-independent constraints. The model considers fluctuation of fuel prices, CO<sub>2</sub> emission reduction target, flexibility of fuel balancing and fuel switching of the existing boilers and option purchasing of Carbon credit if the reduction target is not achievable.

The following are some conclusions obtained by the proposed model. The purchasing of new generating units consists of Coal and NGCC without CCS as well as a nuclear unit. This changes when emission reduction constraint is applied. The strategy is shifted to more NGCC units with installed CCS to reduce amount of emission. While natural gas is more expensive than coal, the less capital on operation and maintenance in addition to less emission makes it a better addition to the fleet where CO<sub>2</sub> emission is concerned. Fuel switching is also used in most of the cases where CO<sub>2</sub> emission reduction is indicated. Finally, according to the authors, the proposed model may be easily extended to other provinces and even countries.

Halim and Srinivasan (2009), proposed a simulation-optimization framework combining HYSYS process simulator and simulated annealing technique to investigate the CO<sub>2</sub> removal by using DEA aqueous solution. Authors applied the proposed methodology to generate Pareto optimal solutions reflecting the trade-off between CO<sub>2</sub> capture efficiency and operating cost.

### 1.2.3. Thermodynamic modeling (liquid-vapor equilibrium)

The vapor-liquid equilibrium (VLE) models for the reacting systems (amines/CO<sub>2</sub>/H<sub>2</sub>O) should be modeled with high accuracy. In fact, good predictions of the liquid-vapor equilibrium are crucial to develop mathematical model for simulation and optimization. Rigorous electrolyte Non-Random Two-Liquid (eNRTL) models are widely regressed to represent the thermodynamic behavior of such systems. For example, data regression system (DRS) of Aspen Plus is widely utilized to approximate model parameters to the experimental data. DRS reports not only the regressed parameters, but calculates error in the parameter values and provides a parameter correlation matrix. In most of cases, the proposed models are successfully applied to correlate simultaneously the excess enthalpy, vapor-liquid equilibria, and low temperature activity coefficients. The following articles are some of the most recently published (Tang et al., 2009; Faramarzi et al., 2009; Munkejord et al., 2009; Puxty et al., 2009a,b).

### 1.2.4. Flexibility and process control

Several dynamic models have been developed in order to study the control and behavior of the absorption process. Not only dynamic models of stand-alone CO<sub>2</sub> absorption process have been developed but also mathematical models of CO<sub>2</sub> capture processes coupled to a power plant operating at varying load (Kvamsdal et al., 2009; Chalmers et al., 2009; Ziaii et al., 2009a,b; Greer et al., 2010).

Kvamsdal et al. (2009) presented a dynamic absorber model to study operability in absorber columns during the course of dynamic operation. Two transient operational scenarios were investigated: start-up and load reduction. Also authors discussed issues regarding the operability of the absorber column in case of load-varying upstream power-plants.

**Table 1 – Process conditions for validation.**

	Flue gas	Lean amine
Temperature (K)	332.38	313.32
Total flow-rate (kg/s)	0.158	0.642
H <sub>2</sub> O % mass	1.93	63.34
CO <sub>2</sub> % mass	24.15	6.18
MEA % mass	0	30.48
N <sub>2</sub> % mass	73.92	0
O <sub>2</sub> % mass	0	0

Chalmers et al. (2009) presented a detailed review about flexible operation of coal fired power plants with post-combustion CO<sub>2</sub> capture.

### 1.3. Experimental works at pilot plant scales

This research area is closely connected with the two research lines mentioned above (1.4 and 1.5). Pilot-scale experiments are an important and necessary research activity because they are used to validate results obtained from basic investigations and to demonstrate the technical feasibility of the process under study. The technology itself and the process are validated in the pilot plants while their commercial abilities are proven in demonstration plants. Particularly in CO<sub>2</sub> capture processes, pilot plants are used to study the behavior of different solvents, the mode of start up and operating process conditions.

Recent advances of research projects involving pilot-scale experiments in testing alternative solvents for the CO<sub>2</sub> post-combustion capture can be found in (Cottrell et al., 2009; Kishimoto et al., 2009; Idem et al., 2009; Knudsen et al., 2009; Tobienssen et al., 2008; Mangalapally et al., 2009; Dugas et al., 2009; Chen et al., 2006).

The present work deals precisely with the modeling and optimization of post-combustion CO<sub>2</sub> capture. Precisely, an equilibrium stage mathematical model is developed to optimize the operating conditions to remove CO<sub>2</sub> from flue-gases in a stage column. The proposed model cannot only be used as optimizer but also as a simulator by fixing the degree of freedom of the equation system.

The mathematical model to be presented in this work is the first basic step of a more ambitious project aimed at determining the optimal synthesis and design of electricity power plant including the capture of the CO<sub>2</sub> due to the fuel combustion. The final goal is to develop a mathematical model which will be combinatorial in nature and which will be based in a superstructure where all the alternatives of interest will be embedded and optimized simultaneously.

The General Algebraic Modeling System (GAMS) which is a high-level algebraic modeling system for large scale optimization is used for implementation and solving the resulting mathematical model. In general, mathematical programming tools such as GAMS, AMPL and others have shown to be powerful and the optimality capacities of such tools are greater than simulator's capacities, specially when the optimization problem is large, combinatorial and highly non-linear.

The paper is outlined as follows. Section 2 briefly describes the post-combustion process. Section 3 introduces the problem formulation. Section 4 summarizes the assumptions, the mathematical model and the resolution procedure. Section 5 presents applications of the developed NLP model and results analysis. Finally, Section 6 presents the conclusions and future work.

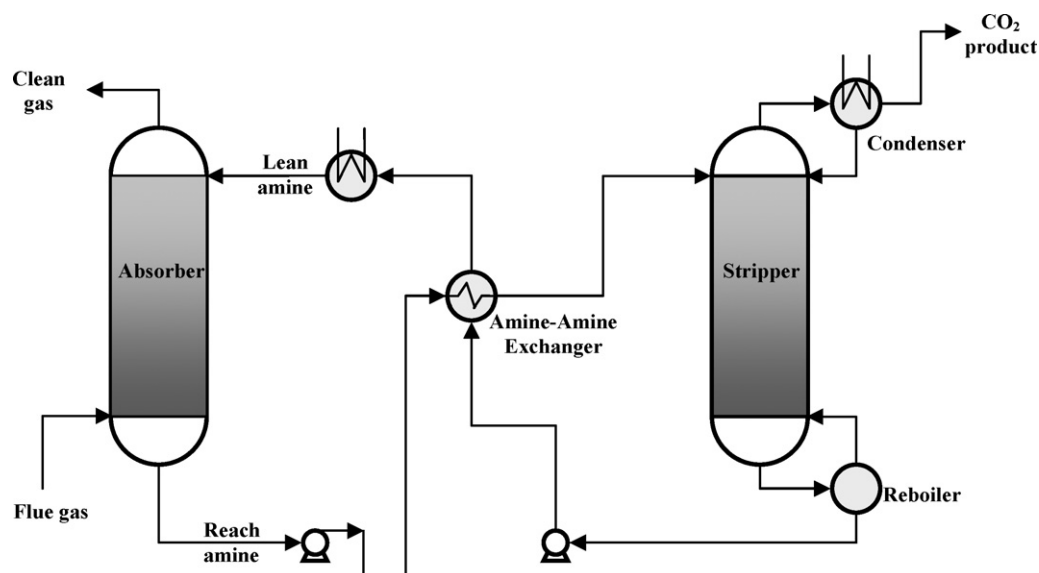


Fig. 1 – Flow diagram of the conventional CO<sub>2</sub> post-combustion process.

## 2. Process description

Fig. 1 shows a simplified flow diagram of the conventional CO<sub>2</sub> post-combustion process.

As is shown, the flue gases coming from a power plant, previously cooled and cleaned from impurities, react chemically in the Absorber (1) with the lean amine solution and then they are emitted to the atmosphere. The rich amine solution leaving the absorber is then heated with the lean amine solution coming from the regenerator unit.

The total process cost depends strongly on the type of solvent, absorber characteristics and the total heating and cooling utilities used. The solvent should be selected taken into account the chemical binding energy, the solvent load and the absorption/desorption temperatures. Corrosion and degradation of the solvent are also critical aspects which have strong influence in the operating and maintenance costs. For example, the amine concentration is limited in order to avoid corrosion problems. This limit concentration could be increased if corrosion inhibitors are used. The CO<sub>2</sub> absorption rates depend mainly on the absorber surface area. In fact, the specific surface area and the pressure drop have large effects on the CO<sub>2</sub> absorption efficiency, costs and energy use of the whole post-combustion process.

## 3. Problem formulation

The problem can be stated as follows. Given the flue gas conditions (composition, temperature and flow-rate), the goal is to determine the optimal operating conditions in order to maximize the absorption efficiency. The following two process efficiencies will be considered for optimization. The first one is defined as the ratio between the total absorbed CO<sub>2</sub> and the total heating and cooling utilities (exchanger, condenser and reboiler heat duties). The second one is defined as the ratio between total absorbed CO<sub>2</sub> and the total amine flow-rate.

Precisely, temperature, composition and flow-rates profiles of aqueous solution and flue gas streams along the column as well as the heat transferred in the reboiler, condenser and heat exchanger will be simultaneously optimized. Exploit-

ing the advantages of the proposed model, the influence of the absorber height and CO<sub>2</sub> composition in flue gas on the absorption performance is also investigated.

## 4. Hypothesis and mathematical model

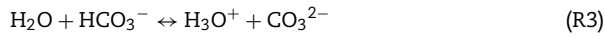
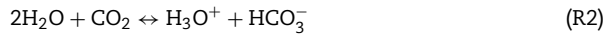
In this section, the adopted hypothesis and the mathematical model for the entire process are presented.

### 4.1. Assumptions

The mathematical model was developed on the basis of following assumptions:

1. Equilibrium Stages are assumed for absorber and regenerator. Liquid and vapor phases are well-mixed.
2. The number of theoretical stages for both columns is a model parameter.
3. The column height depends on the number of theoretical stages.
4. Dependence of stage efficiency with gas and liquid velocities and enhancement factor, among others, is considered.
5. Dependence of the reaction heat with CO<sub>2</sub> loading and temperature is considered (Oyenekan, 2007).
6. Murphree efficiencies for CO<sub>2</sub> and H<sub>2</sub>O in each stage are considered.
7. Ideal behavior in the liquid phase.
8. Real behavior in the vapor phase. Fugacity coefficients are computed by using Peng–Robinson equations of state for multi-components (Peng and Robinson, 1976).
9. CO<sub>2</sub> and water can only be transferred from liquid phase to vapor phase and vice-versa.
10. Vaporization of the amine is neglected.
11. Reactions take place in liquid phase.
12. Dependence of heat capacities with the temperature and composition for liquid and vapor streams are considered. The correlations are taken from (Greer, 2008).
13. Dependence of aqueous alkanolamine solution density with the temperature is taken into account.

14. The following reactions are considered:



$$\sum x_{iz} = 1 \quad i = \text{CO}_2, \text{H}_2\text{O}, \text{MEA}, \text{MEA}^{\text{H}^+}, \text{MEACOO}^-, \text{HCO}_3^-, \text{H}_3\text{O}^+, \text{OH}^- \quad \forall z \quad (5)$$

Energy balance in stage “z”:

$$L_{z+1}h_z - L_z h_z + V_{z-1}H_{z-1} - V_z H_z + \Delta H_R - \Delta H_{\text{H}_2\text{O}} = 0 \quad \forall z \quad (3)$$

where  $H$  and  $h$  are enthalpies of vapor and liquid respectively  $\Delta H_R$  and  $\Delta H_{\text{H}_2\text{O}}$  refer respectively to the reaction heat released and vaporization heat of water (Greer, 2008; Hilliard, 2008):

Chemical equilibrium constants:

$$K_m = \prod_i (a_{iz})^{\nu_i} = \prod_i (x_{iz} \gamma_{iz})^{\nu_i} \quad \forall m, \quad m = \text{R}_1, \text{R}_2, \text{R}_3, \text{R}_4, \text{R}_5, \text{R}_6 \quad (6)$$

$$K_m = a + \left(\frac{b}{T}\right) + c \ln(T) + dT \quad \forall m, \quad m = \text{R}_1, \text{R}_2, \text{R}_3, \text{R}_4, \text{R}_5, \text{R}_6 \quad (7)$$

#### 4.2. Mathematical model

By adopting the mentioned assumptions, the following mathematical model is derived.

#### 4.3. Absorber model

Fig. 2 shows a generic stage “z” used to model the absorber and regenerator columns. Thus, the mathematical model is developed by using an index “z” and the total number of stages is fixed by “Z” which is a model parameter. The nomenclature of some of the main optimization variables is also illustrated in Fig. 2. Due to space limitations, only the main model constraints are here presented. Readers, who are interested on the complete mathematical model, are kindly invited to contact the authors.

Overall mass balance in stage “z”:

$$L_{z+1} - L_z + V_{z-1} - V_z = 0 \quad \forall z \quad (1)$$

where  $L$  and  $V$  refer to the liquid and vapor molar flows.

Species mass balance in stage “z”:

$$L_{z+1}x_{iz} - L_z x_{iz} + V_{z-1}y_{jz-1} - V_z y_{jz} = 0 \quad \forall z \quad (2)$$

$x_i$  and  $y_j$  refer to the mole fraction of component “i” in liquid and vapor phases respectively.

$$\sum y_{jz} = 1 \quad j = \text{CO}_2, \text{H}_2\text{O}, \text{N}_2, \text{O}_2 \quad \forall z \quad (4)$$

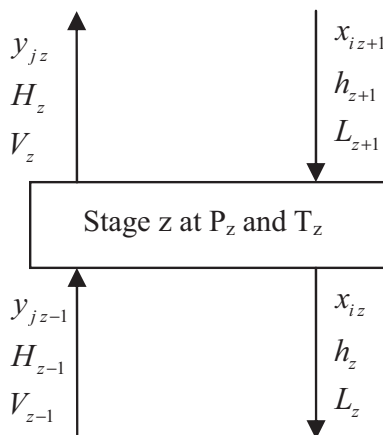


Fig. 2 – Generic stage “z”.

$K_m$  are chemical equilibrium constants from reactions (R1)–(R5).  $T$  is absolute temperature (K).  $a_{iz}$ ,  $\gamma_{iz}$ ,  $\nu_i$  are activity, coefficient activity and estequiometric coefficient to component “i” in reaction “m”, respectively. Liquid phase has ideal behavior, therefore the activity coefficients are considered equal to one (Kent–Eisenberg model). The coefficients used in Eq. (7) are taken from Aboudheir et al. (2003).

Phase equilibrium relationship:

$$y_{\text{CO}_2 z} \varphi_{\text{CO}_2 z} P_z = H_{\text{CO}_2 z} [\text{CO}_2]_z \quad \forall z \quad (8)$$

$$y_{\text{H}_2\text{O} z} \varphi_{\text{H}_2\text{O} z} P_z = p_{\text{H}_2\text{O} z} [\text{H}_2\text{O}]_z \quad \forall z \quad (9)$$

where  $[i]_z$  is the molar concentration of specie “i” in stage “z”. ( $\varphi$ ),  $P_z$  and  $p_{\text{H}_2\text{O} z}$  refer to fugacity coefficient, total pressure and partial pressure of water, respectively.

Charge balance in stage “z”:

$$[\text{MEA}^{\text{H}^+}]_z + [\text{H}_3\text{O}^+]_z = [\text{MEACOO}^-]_z + [\text{HCO}_3^-]_z + 2[\text{CO}_3^{2-}]_z + [\text{OH}^-]_z \quad \forall z \quad (10)$$

Ionic mass balance relationship in stage “z”:

$$\alpha [\text{MEA}]_z^0 = [\text{CO}_2]_z + [\text{MEACOO}^-]_z + [\text{HCO}_3^-]_z + 2[\text{CO}_3^{2-}]_z \quad \forall z \quad (11)$$

$$[\text{MEA}]_z^0 = [\text{MEA}]_z + [\text{MEA}^{\text{H}^+}]_z + [\text{MEACOO}^-]_z \quad \forall z \quad (12)$$

The superscript (0) means initial condition.  $\text{CO}_2$  loading ( $\alpha$ ) is defined as the ratio between total  $\text{CO}_2$  and total amine.

Murphree and stage efficiencies:

The non-ideal behavior of stages is considered by Eqs. (13) and (14) as follows:

$$\eta_z = \frac{V_z y_{iz} - V_{z-1} y_{iz-1}}{V_z y_{iz}^* - V_{z-1} y_{iz-1}} \quad \forall z \quad (13)$$

where  $y_{iz}^*$  is the equilibrium composition of molecular specie considered leaving the stage z.

Stage efficiency is dependent on  $\text{CO}_2$ -amine reaction rate constants, gas and liquid properties (density, viscosity, diffu-

sivity, and surface tension), packing type and size and overall bed dimensions. It is estimated as follows:

$$\eta_z = (1 - e^{[(h/a)((G'/RTk_G\rho_G) + (\lambda L'/k_L\rho_L E))])_z \quad \forall z \quad (14)$$

where,  $G'$  and  $L'$  are gas and liquid velocities ( $\text{kg/m s}^2$ ),  $\rho^G$  and  $\rho^L$  are gas and liquid densities ( $\text{kg/m}^3$ ),  $\lambda$  is the stripping factor ( $\lambda = m/(L/G)$ ),  $h$  is the height of the stage (m),  $E$  is the enhancement factor,  $k_G$  is the gas-side mass transfer coefficient ( $\text{Kmol/Pa s m}^2$ ) and  $k_L$  is the liquid-side mass transfer coefficient [ $\text{Kmol/s m}^2(\text{Kmol/m}^3)$ ].

Enhancement factor:

The Enhancement factor is given by Eq. (15). It may be considered as a correction to the liquid-side mass transfer coefficient due to pseudo-first order reaction.

$$E_z = \frac{\sqrt{D_{\text{CO}_2}(k_{r,\text{CO}_2-\text{MEA}}[\text{MEA}] + k_{r,\text{CO}_2-\text{OH}}[\text{CO}_2])}}{k_L} \quad \forall z \quad (15)$$

The forward constants ( $k_{r,\text{CO}_2-\text{MEA}}$  and  $k_{r,\text{CO}_2-\text{OH}}$ ) of the parallel and kinetically controlled reactions ((R6)–(R7)) are taken from Kucka et al. (2002) and Freguia (2002). The diffusivity of  $\text{CO}_2$  in the aqueous MEA solution ( $D_{\text{CO}_2}$ ) was calculated using the Stokes–Einstein relationship presented in Greer (2008). The mass transfer coefficients ( $k_L$  and  $k_G$ ) are determined by correlations given by Onda et al. (1968).

$\text{CO}_2$  removal efficiency:

$$ef(\%) = \left(1 - \frac{\text{CO}_2^{\text{out}}}{1 - \text{CO}_2^{\text{out}}} \times \frac{1 - \text{CO}_2^{\text{in}}}{\text{CO}_2^{\text{in}}}\right) \times 100 \quad (16)$$

Effective area ( $a$ ) for mass transfer:

Several correlations are widely used to compute the effective area in packed reactive absorption columns. The correlations consider different functionality between the effective area and process variables. In this paper, numerical results obtained by considering three correlations will be presented. Precisely, output results considering the following three correlations will be later compared (Section 5.1.2 Example 1).

$$a = \frac{a_w}{a_t} = 1 - \exp\left(-1.45\left(\frac{\sigma_c}{\sigma}\right)^{0.75}\left(\frac{L}{a_t\mu^L}\right)^{0.1}\left(\frac{L^2 a_t}{(\rho^L)^2 g}\right)^{-0.05}\left(\frac{L^2}{\rho^L \sigma a_t}\right)^{0.2}\right) \quad (17a)$$

$$a = a_w = \exp(4.73)(u^G)^{0.061}\left(\frac{L \times M^L}{1000 \times A}\right)^{0.148} \quad (17b)$$

$$a = a_t \times 0.310 \frac{\sigma^{0.5}}{H^{0.4}} \left(\left(\frac{\mu^L L}{\rho^L \sigma}\right) \times \left(\frac{6G}{a_t \mu^G}\right)\right)^{0.392} \quad (17c)$$

where  $\sigma$ ,  $\mu^L$ ,  $\mu^G$ ,  $a_t$ ,  $u^G$ ,  $A$ ,  $\sigma$  refer, respectively, to surface tension, liquid and gas viscosities, specific dry area of packing, superficial gas velocity, cross-sectional area of column. Eqs. (17a)–(17c) were developed by Onda et al. (1968), Wilson (2004) and Bravo and Fair (1982).

#### 4.4. Stripper model

Basically, the same constraints involved by the absorber model are considered. Due to space limitations they are not here included.

The mathematical model also includes mass and energy balances corresponding to the condensers, heaters and

reboiler. Finally, it considers constraints to compute the Henry's law constant ( $H$ ), enthalpies, reaction heats ( $\Delta H_R$ ), viscosity, vapor pressures, fugacity coefficients and surface tension among others.

The optimization model involves approximately 3000 variables and constraints. The model was implemented in General Algebraic Modeling System GAMS (Brooke et al., 1996). The generalized reduced gradient algorithm CONOPT 2.041 was here used as NLP solver (Drud, 1992). It should be noticed that global optimal solutions cannot be guaranteed due to some non-convex constraints involved in some of the mathematical model (bilinear terms, logarithms, etc.).

## 5. Applications of the NLP models

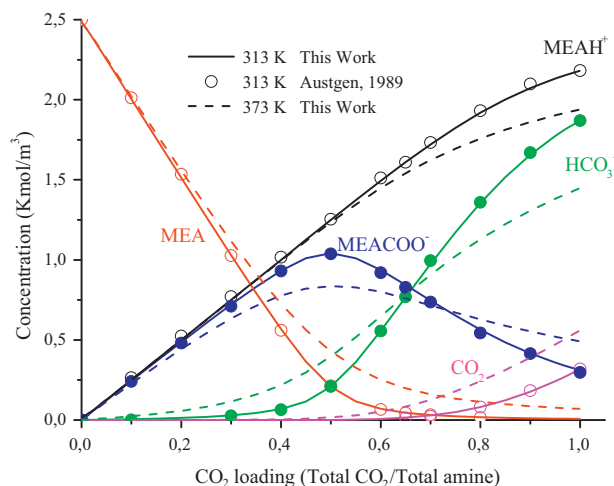
In this section, the validation of the proposed model and optimization results are discussed through two examples. Precisely, the first example deals with the model validation while in the second example the results obtained by solving an optimization problem are presented. All solutions have been obtained by using Intel Core 2 Quad Extreme QX9650 3 GHz 1333 MHz processor and 4 GB RAM.

### 5.1. Example 1. Validation model

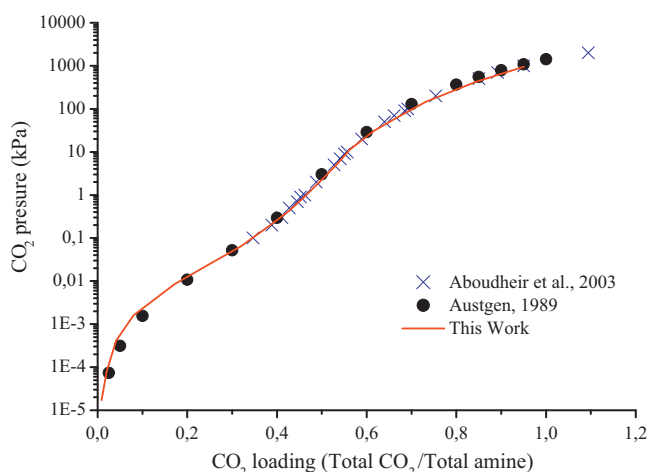
Detailed solutions of the  $\text{CO}_2$  absorption with MEA including not only variable values at the inlet/outlet of equipments but also internal profiles (temperature, compositions, flow-rates) are not available in the open literature. Therefore,  $\text{CO}_2$ -MEA vapor liquid equilibrium (VLE), absorber and regenerator units are validated separately using experimental data found in the literature. Next, each validation is presented.

#### 5.1.1. VLE model validation

The model output results of the VLE equilibrium model were compared to those reported by Austgen and Rochelle (1989) and Aboudheir et al. (2003). Fig. 3 compares the individual species concentrations corresponding to different  $\text{CO}_2$  loading, initial concentration of 2.5M MEA at 313 K. In addition, the influence of the temperature on the equilibrium concentrations is also presented (373 K). The variation of the  $\text{CO}_2$  pressure with the  $\text{CO}_2$  loading is illustrated in Fig. 4.



**Fig. 3 – Model validation of the liquid-phase concentration in 2.5M MEA with  $\text{CO}_2$  loading from 0 to 1 at 313 K and 373 K.**



**Fig. 4 – Model validation of CO<sub>2</sub> equilibrium partial pressure over 2.5 M MEA solutions to 313 K.**

**Table 2 – Absorber specifications for validation.**

Column type	Packed
Diameter (m)	0.427
Total packing height (m)	6.1
Stages number	10
Packing specifications	
Type of packed	IMTP#40
Specific area (m <sup>2</sup> /m <sup>3</sup> )	145
Nominal packing size (m)	0.04
Void fraction	0.97

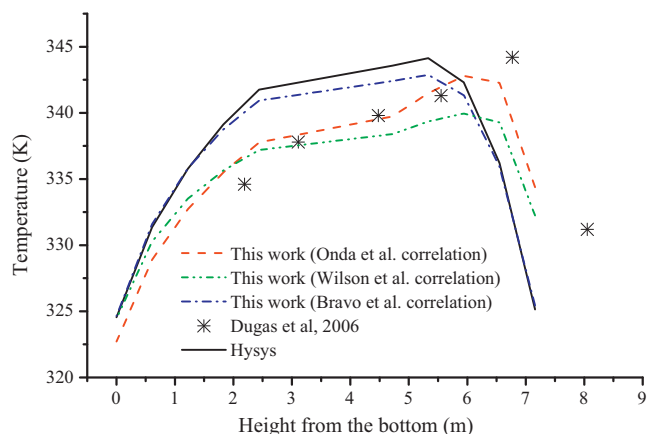
As it can be seen, the comparison show a good agreement between the values predicted by the model and those reported in the literature.

5.1.2. Validation of absorber column

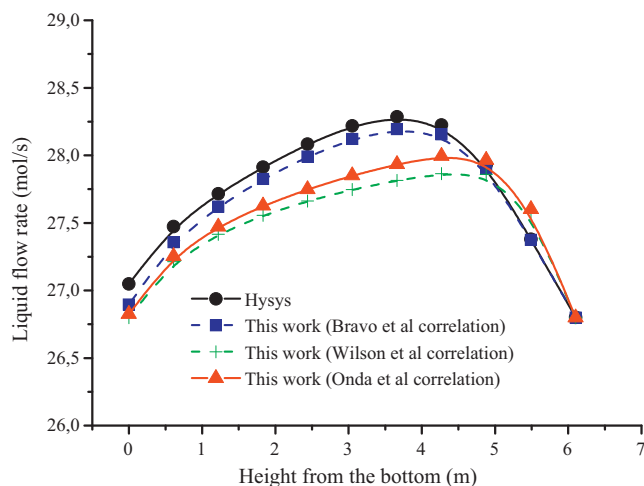
The validation of the absorption column was performed by using experimental data (pilot plant) reported by Dugas (2006) and simulation results obtained by using a process simulator (HYSYS).

Tables 1 and 2 show the specifications of the flue gas and model parameters corresponding to the absorber column and packing specifications used for validation.

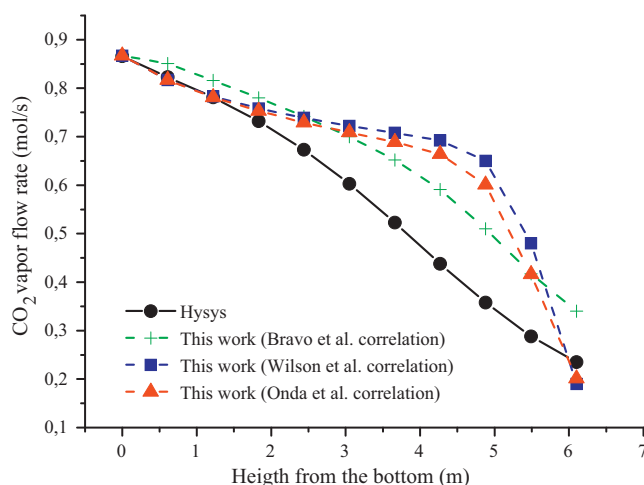
Figs. 5–8 show the comparison of the temperature and flow-rate profiles. Precisely, only experimental temperature profile is illustrated because it was only available in the open literature (Fig. 5). The flow-rate profiles (liquid, gas and CO<sub>2</sub>



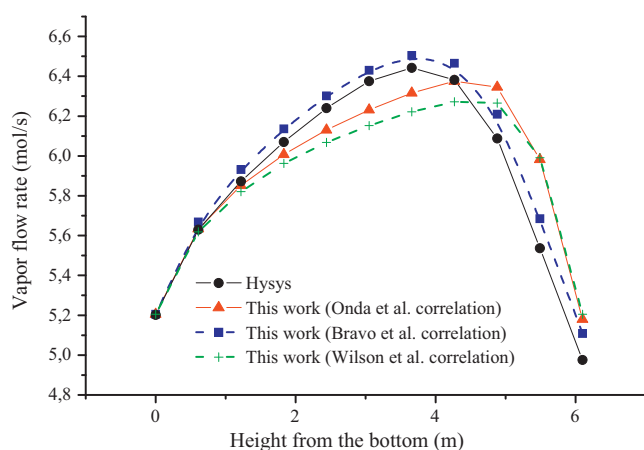
**Fig. 5 – Temperature distribution along the absorber (model validation).**



**Fig. 6 – Liquid flow rate distribution along the absorber (model validation).**



**Fig. 7 – Vapor flow rate distribution along the absorber (model validation).**



**Fig. 8 – CO<sub>2</sub> flow rate distribution along the absorber (model validation).**

vapor flow-rates) obtained from the proposed model are also compared to those obtained by HYSYS for a more “complete validation” (Figs. 6–8). On the other hand, solutions obtained by the developed model considering different published correlations to compute the effective area for mass transfer are also illustrated.

**Table 3 – Comparison between model output results with experimental data and HYSYS simulations.**

Variable	Hysys	This work (Bravo and Fair, 1982)	This work (Wilson, 2004)	This work (Onda et al., 1968)	Dugas (2006)
Solvent loading in the middle	0.3966	0.3952	0.4498	0.4417	0.392
Rich solvent loading (mol/mol)	0.4815	0.4480	0.4958	0.4919	0.5390
Gas outlet temperature (K)	325.1	325.4	332.2	331.4	331.2
Average temperature (K)	336.4	336.0	335.0	335.9	335.2
Maximum temperature (K)	344.1	342.9	339.3	341.0	344.2
CO <sub>2</sub> removal efficiency (%)	95.3	86.6	89.1	96.2	–

**Table 4 – Model parameter for validation (regenerator unit).**

Rich amine	
Temperature (K)	342
Total flow-rate (Kg/s)	0.700
H <sub>2</sub> O % mass	59.00
CO <sub>2</sub> % mass	11.00
MEA % mass	30.00
Column type	Packed
Diameter (m)	0.427
Total packing height (m)	6.1
Stages number	10
Packing specifications	
Type of packed	IMTP#40
Specific area (m <sup>2</sup> /m <sup>3</sup> )	145
Nominal packing size (m)	0.04
Void fraction	0.97

Fig. 5 shows the temperature distribution in the liquid phase through the absorber. From this figure, it can be clearly observed that the solutions obtained by the model considering the empirical correlation developed by Bravo and Fair (1982) are very close to those obtained by the HYSYS simulator. Same qualitative conclusions are obtained for liquid and vapor flow-rate distributions through the absorber and also for CO<sub>2</sub> flow rates (Figs. 6–8).

Finally, Table 3 compares the output values of the main model parameters obtained from: (a) proposed model (considering the three mentioned empirical correlations), (b) HYSYS simulator and (c) pilot-scale plant (Dugas, 2006).

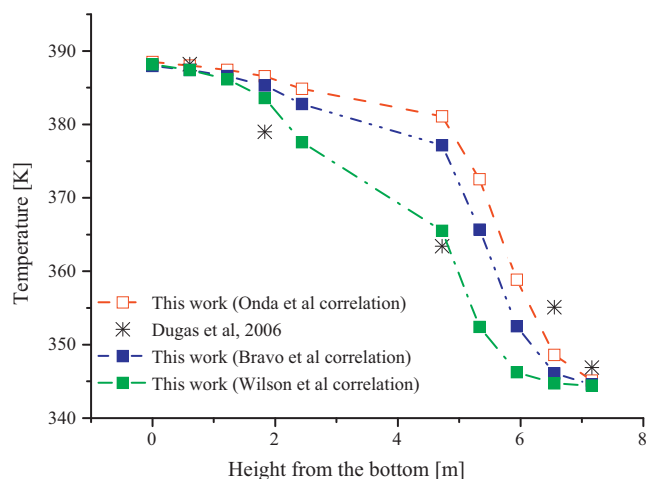
According to the results, it is possible to conclude that experimental data obtained in pilot-scale plant as well as solutions obtained by HYSYS simulator can be accurately predicted by the developed model. For example, according to Figs. 5–8 the temperature and liquid/vapor flow-rate profiles in the absorber are very close to those obtained by HYSYS when the mathematical model is solved by considering the correlation developed by Bravo and Fair (1982). It should be mentioned that the other correlations also predict good output results. On the other hand, according to Table 3, it is possible to conclude that the experimental data reported by Dugas (2006) are well predicted when the correlation developed by Onda et al. (1968) is taken into account.

### 5.1.3. Regenerator unit validation

Table 4 shows the model parameters used for the validation.

**Table 5 – Validation results (regenerator unit).**

	Hysys	This work	Experimental data [Tobienssen et al., 2008; Freguia and Rochelle 2003; Dugas et al., 2006]
Reboiler temp. [K]	387.13	390.61	391.11
Reboiler heat duty [MJ/h]	649.21	790.04	749.07
Inlet temp. at condenser [K]	342.12	345.05	336.14

**Fig. 9 – Model validation of regenerator unit.**

In Table 5 numerical values of some process variables obtained by the proposed model are compared with experimental data [Tobienssen et al., 2008; Freguia and Rochelle, 2003; Dugas, 2006]. Fig. 9 compares experimental and simulated temperature profiles along the regenerator. Then, it is possible to conclude that simulated values are in good agreement with the experimental data.

### 5.2. Example 2. Optimal operating conditions in absorber to maximize the CO<sub>2</sub> recovery

As mentioned in Section 3, the proposed mathematical model is used to solve two optimization problems for the flue gas conditions listed in Table 1. To do this, it was necessary to “relax” the variable values which were fixed to perform the model validation. Precisely, the optimal operating conditions are determined for the following two objective functions:

- (1) OF1: Total Heat Duty/CO<sub>2</sub> recovery [kJ/mol]. The optimization direction is the minimization. So, the optimization criterion is to recover the maximum CO<sub>2</sub> contained in flue gases by using the minimum total heating and cooling utilities.
- (2) OF2: CO<sub>2</sub> Recovery/amine solution flow-rate [%/(mol/s)]. The optimization direction is the maximization. So, the optimization criterion is to recover the maximum CO<sub>2</sub> contained in flue gases by using the minimum amine solution flow-rate.



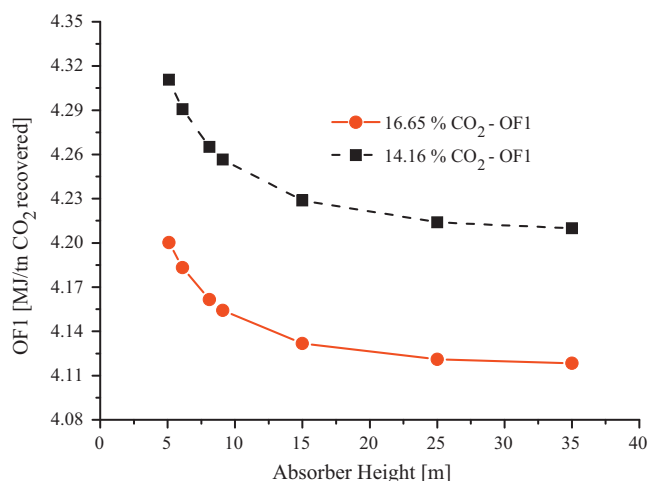


Fig. 10 – Optimal objective function OF1 values vs. absorber height.

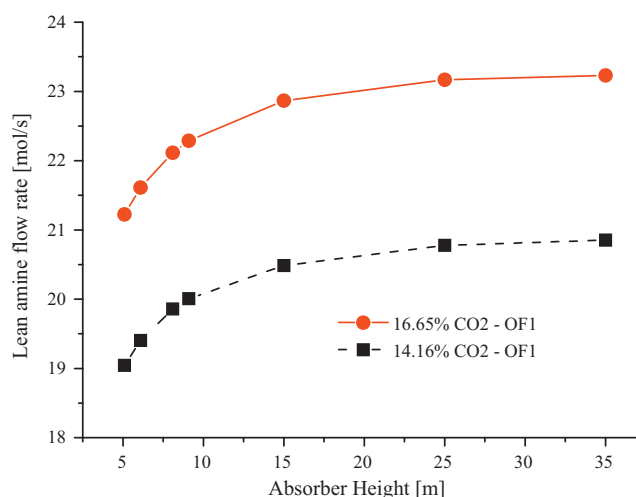


Fig. 13 – Optimal values of lean amine flow rate vs. absorber height.

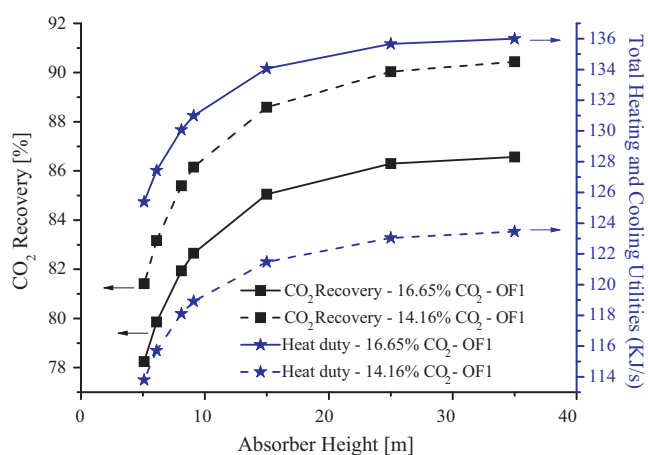


Fig. 11 – Optimal values of CO<sub>2</sub> recovery and total heating and cooling utilities vs. absorber height.

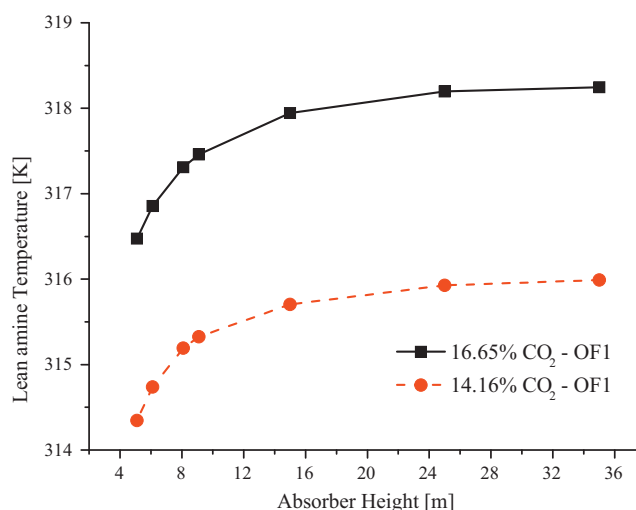


Fig. 14 – Optimal values of lean amine temperature vs. absorber height.

As follows, solutions obtained for both optimization problems are presented.

5.2.1. Optimal operating conditions by considering OF1

Figs. 10-14 show the optimal values corresponding to FO1, heating and cooling total utilities, amount of CO<sub>2</sub> recovered, CO<sub>2</sub> lean loading and amine solution flow-rates for different

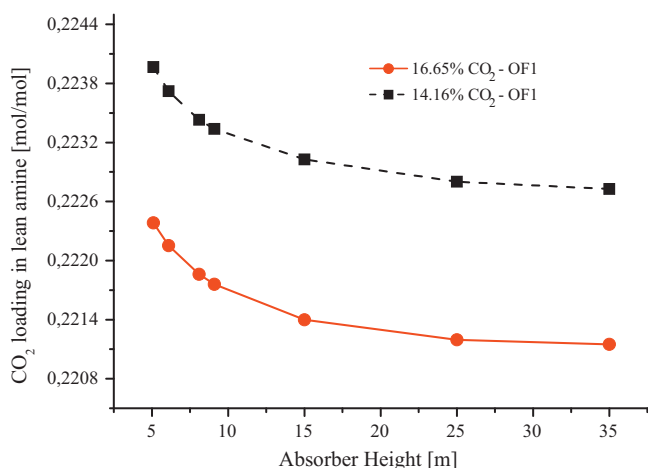


Fig. 12 – Optimal values of CO<sub>2</sub> lean loading vs. absorber height.

absorber heights and the flue gas composition (mainly CO<sub>2</sub> concentration).

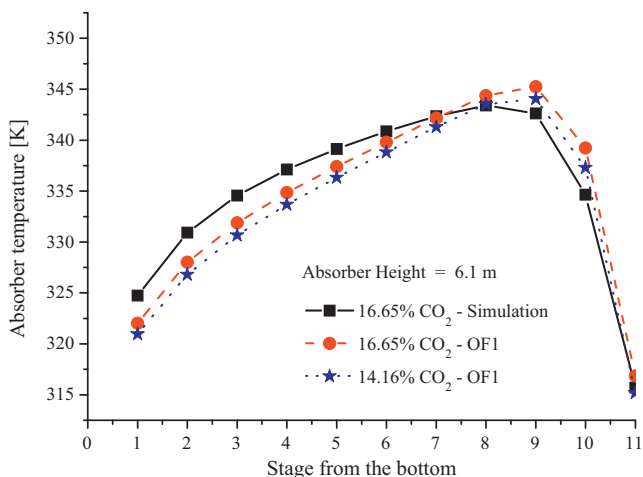
From these figures it can be seen that the optimal OF1 value decreases as the absorber height increases (Fig. 10). Despite that both total utilities and amount of CO<sub>2</sub> recovered increase with the increasing of the absorber height, the amount of CO<sub>2</sub> recovered increases faster than the total utilities (Fig. 11).

On the other hand, the CO<sub>2</sub> lean loading decreases as the absorber height increases (Fig. 12) as consequence of the increasing of the amine solution flow-rate (Fig. 12) which improves the CO<sub>2</sub> removal from the gas phase.

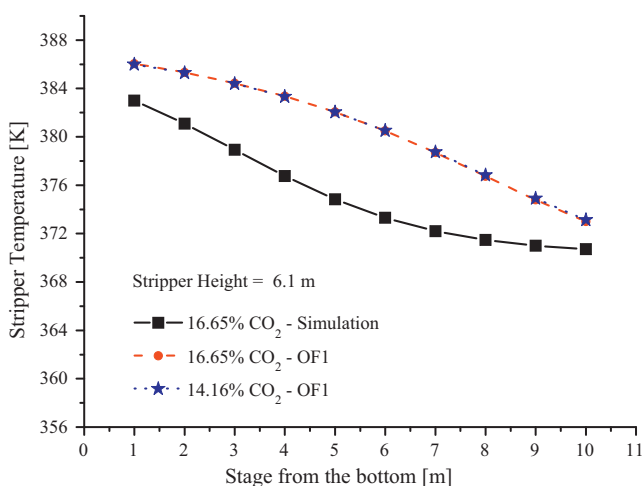
According to Fig. 14 the absorber height has a slight influence on the inlet temperature of the rich amine solution at the absorber.

The optimal CO<sub>2</sub> loading and temperature profiles along the absorber and regenerator obtained by considering an absorber height of 6.1 m are illustrated from Figs. 15-18. That is, these profiles correspond to only one point illustrated previously in Figs. 10-14.

By comparing the results obtained for both assumed CO<sub>2</sub> compositions, it can be concluded that CO<sub>2</sub> composition has slight influence on the temperature behaviors at the absorber and stripper. In fact, the CO<sub>2</sub> loading and temperature profiles in the stripper are not influenced by varying the CO<sub>2</sub> composi-



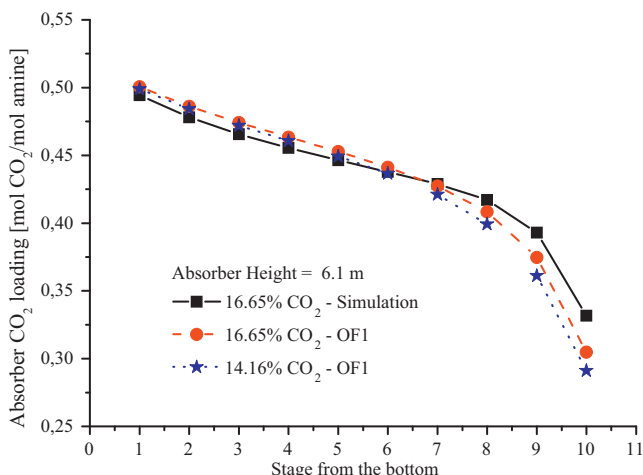
**Fig. 15 – Optimal values of temperature profile along the absorber (6.1 m).**



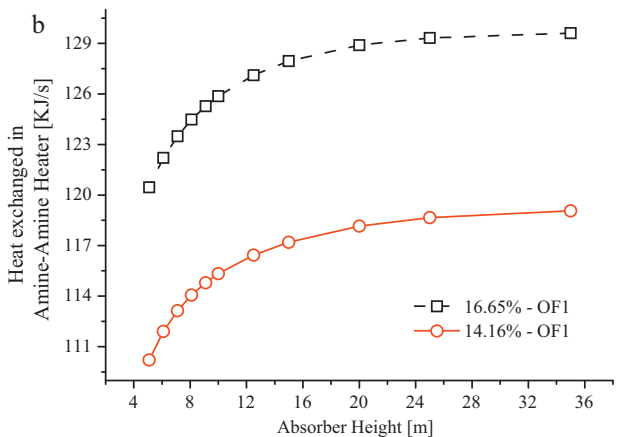
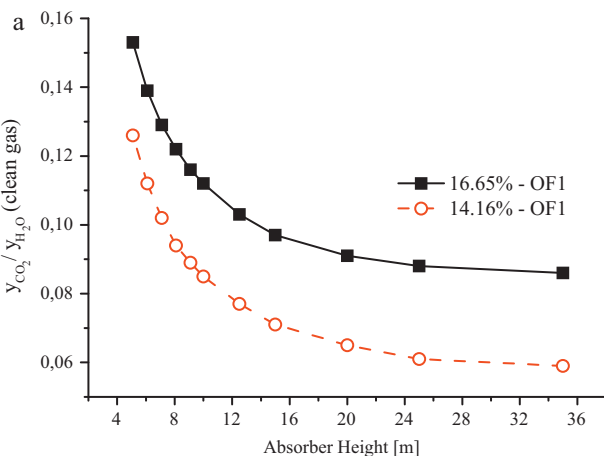
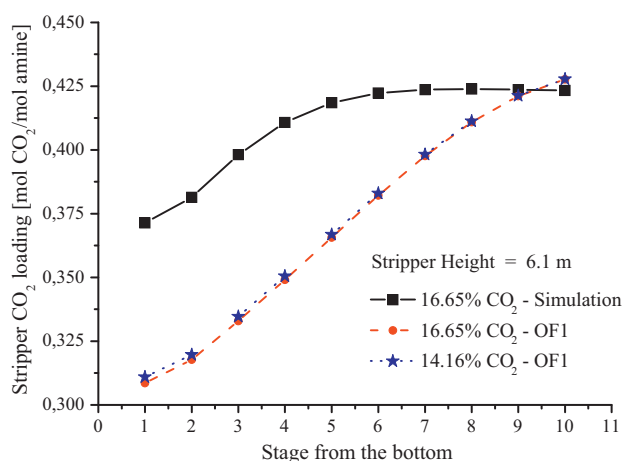
**Fig. 16 – Optimal temperature distribution along the stripper (6.1 m).**

tion from 16.65% mass fraction to 14.16% mass fraction. On the other hand, slight differences of these profiles can be observed in the absorber.

Fig. 18a illustrates the optimal ratios in clean gas between  $y_{CO_2}$  and  $y_{H_2O}$  corresponding to OF1.



**Fig. 17 – Optimal CO<sub>2</sub> loading distribution along the absorber (6.1 m)**



**Fig. 18 – Optimal CO<sub>2</sub> loading distribution along the stripper (6.1 m). (a) Optimal ratio of  $y_{CO_2}/y_{H_2O}$  vs. absorber height (OF1). (b) Optimal heat transferred in amine-amine heat exchanger vs. absorber height (OF1).**

Finally, heats transferred in amine-amine heaters for different flue-gas CO<sub>2</sub> compositions (14.16 and 16.65% mass fraction) are shown in Fig. 18b. As can be seen, the heat transfer increases with the increasing of the absorber height which leads to minimize the ratio between the total heat duty (heating and cooling utilities) and CO<sub>2</sub> recovery.

5.2.2. Optimal operating conditions by considering OF2

The optimal solutions obtained by solving the proposed model using the objective function OF2 are presented.

According to Figs. 19–23, the obtained results show the same profile behaviors to those obtained by using OF1 but of course with different numerical values. As is expected, the

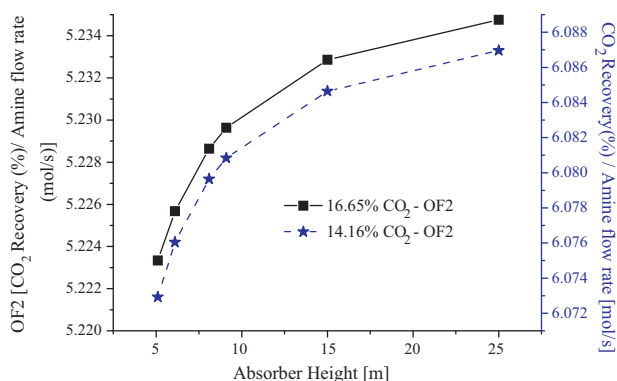


Fig. 19 – Optimal values of objective function OF2 vs. absorber height.

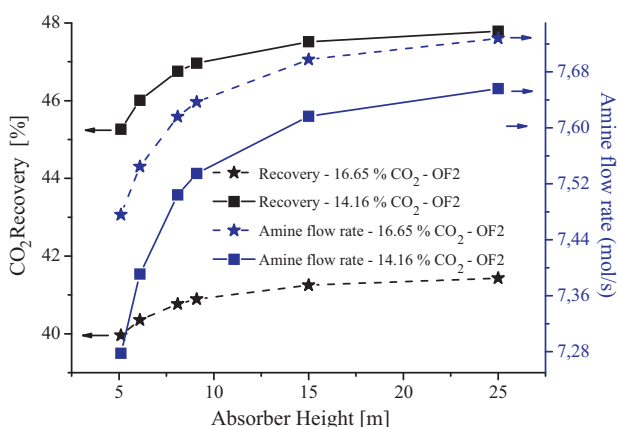


Fig. 20 – Optimal values of CO<sub>2</sub> recovery and amine flow rate vs. absorber height.

OF2 and amine flow-rate increase with the increasing of the absorber height. On the other hand, the CO<sub>2</sub> lean loading decreases as the absorber height increases improving the CO<sub>2</sub> recovery (Figs. 20 and 21). Finally, higher total heating and cooling utilities are needed to reach the maximum CO<sub>2</sub> recovery when the absorber height is increased (Fig. 22).

5.2.3. Optimal heat transfer areas involved by OF1 and OF2

Figs. 22 and 23 illustrate the heating and cooling utilities vs. absorber height corresponding to both OFs (OF1 and OF2). The corresponding ratios between the heat transfer area of heating

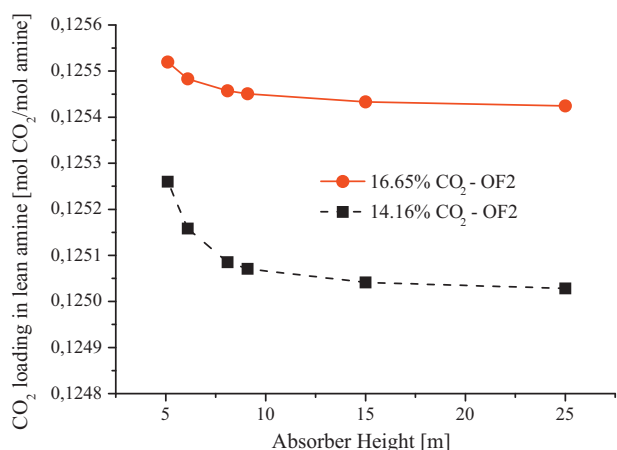


Fig. 21 – Optimal CO<sub>2</sub> loading distribution vs. absorber height.

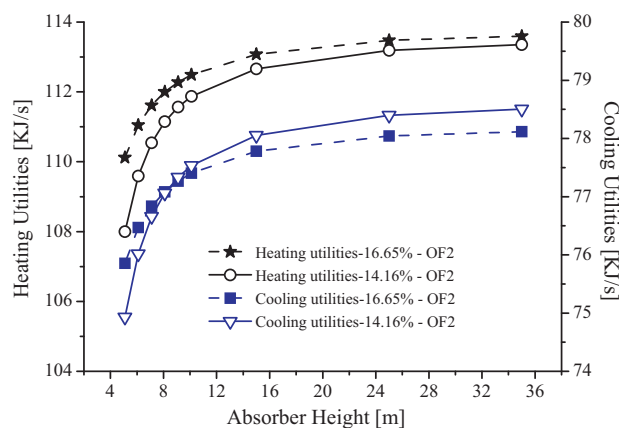


Fig. 22 – Total heating and cooling utilities vs. absorber height (OF1 and OF2).

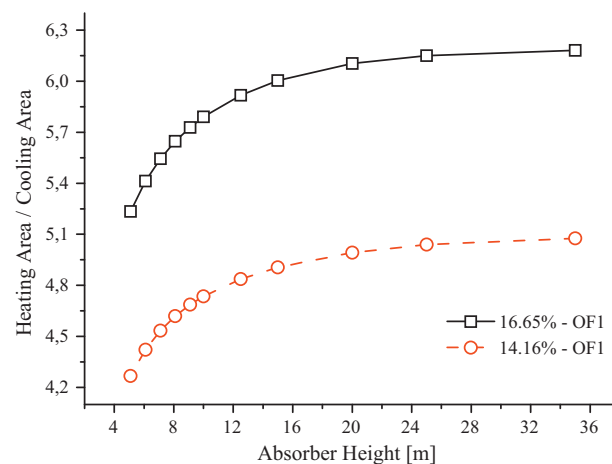


Fig. 23 – Optimal ratio between heating and cooling areas vs. absorber height (OF1).

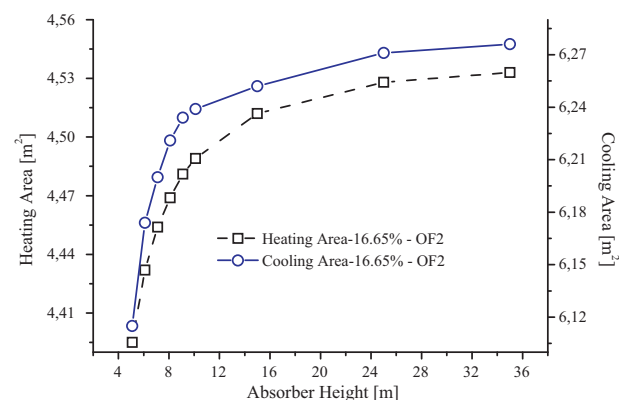


Fig. 24 – Optimal heating area vs. absorber height and optimal cooling area vs. absorber height (OF2).

and cooling process are shown in Figs. 23 and 24. As expected, higher CO<sub>2</sub> recoveries require higher total heat transfer areas at the reboiler and heat exchangers.

Finally, from computational performance point of view, it can be mentioned that global optimal solutions cannot be guaranteed due to the non-convex constraints involved in the mathematical model. Large nonlinear optimization problems are characterized by convergence problems (infeasible solutions) and local optimal solutions. Scaling on variables and equations as well as a systematic initialization procedure have been implemented in order to guarantee the model conver-

gence. In fact, initial values and bounds are provided by a simplified mathematical model where the number of stages is considered as continuous variable which reduces drastically the model size (number of equations and variables).

## 6. Conclusions: future works

This paper presented a deterministic NLP mathematical model. The process has been modelled by considering detailed energy and mass balances. Also, detailed correlations taken from specific literature were considered to model the L-V equilibrium, equilibrium reaction constants, among others.

The proposed mathematical model is a useful tool to be used to study the conventional CO<sub>2</sub> post-combustion process. The model cannot only be used to optimize but also to simulate the entire process when the degree of freedom of the equation system is fixed. The robustness and flexibility of the model as well as the used NLP solver (CONOPT) have been examined by solving many examples which were conducted by varying the parameters values.

Despite the good agreement between the model output results to those obtained by experimental works, it is interesting to extend the proposed model (equilibrium model) into a more rigorous one (non-equilibrium model or "Rate" based model) in order to generate more realistic results. For this purpose, the penetration and film theories as well as an economic objective function will be considered. Also, the coupling of the post-combustion process into power plants will be particularly studied. In fact, the future model will allow not only to optimize the operating conditions of the integrated process will be studied but also the configuration plant. These aspects will be focused in future works.

## Acknowledgements

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