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Optimization of post-combustion CO₂ process using DEA–MDEA mixtures

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ABSTRACT

This paper presents optimal operating conditions for the post-combustion CO₂ capture process utilizing aqueous amine solutions obtained using a process simulator (HYSYS). Three alkanolamine solutions (Methyldiethanolamine MDEA, Diethanolamine DEA and MDEA–DEA mixture) are considered to study the performance of the capture process.

The design problem addressed in this paper requires specifying the optimal operating conditions (inlet and outlet temperature of the lean solution stream on the absorber, CO₂ loading, amine composition and flow rates, among others) to achieve the given CO₂ emission targets at a minimum total annual cost. A detailed objective function including total operating costs and investment is considered.

The influence of the variation of CO₂ reduction targets and the mixing proportion of amines on the total annual cost is analyzed in detail. Numerical results are presented and discussed using different case studies.

The results demonstrate that process simulators can be used as a powerful tool not only to simulate but also to optimize the most important design parameters of the post-combustion CO₂ capture process.

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Keywords: Simulation and optimization; HYSYS process simulator; DEA; MDEA; Post-combustion CO₂ capture

1. Introduction

It is widely known that the main cause of global warming is greenhouse gases, mainly CO₂, emitted into the environment. The major sources of CO₂ emissions are fossil fuel power plants, automobiles and other industrial sources. Therefore, several efforts have been made recently to develop new cleaner technologies to mitigate the negative impact of CO₂ emissions on climate change.

In electrical power plants, the amine-based CO₂ capture from flue gas is especially well-suited for retrofitting existing power plants because it does not require significant changes in equipment configuration. The major challenge, however, is minimizing the operating cost and investment (Pellegrini et al., 2010; Oyenekan and Rochelle, 2007). For this reason, it is in its infancy and is several years away from commercial development.

Many articles have been published to address the modeling, parametric simulation and optimization of CO₂ capture processes (Ali et al., 2005; Oi, 2007; Suppapitnarm et al., 2000; Khakdaman et al., 2008; Abu-Zahra et al., 2007a,b; Kvamsdal et al., 2009; Aliabad and Mirzaei, 2009; Freguia, 2002; Freguia and Rochelle, 2003; Rahimpour and Kashkooli, 2004).

Detailed mathematical modeling of a post-combustion CO₂ process using amines is a complex task because it requires developing accurate and rigorous models to describe all plant equipment, including an absorber, stripper, CO₂ compression system and heat transfer equipment. Moreover, the development of a systematic algorithmic procedure to find optimal solutions using realistic cost functions with process simulators is difficult due to the recycle structures contemplated in the flow sheet (Oi, 2007; Vozniuk, 2010). In addition, non-linear and non-convex constraints in the models that correspond to all process equipment may lead to convergence problems.

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Currently, parametric analysis using process simulators is one of the most popular approaches to optimize CO₂ capture processes coupled to electrical power plants. Various approaches have been proposed to overcome convergence problems (Oi, 2007; Vozniuk, 2010).

Freguia (2002) and Freguia and Rochelle (2003) analyzed the relationships between the reboiler heat duty and the L/G parameter in the absorber and the reboiler heat duty and the stripper pressure.

Other published works analyzed the effect of flue gas flow rate, CO₂ concentration, solvent flow rate, solvent composition, absorber pressure and temperature, CO₂ recycle stream characteristics, stripper reboiler pressure, heat exchange between rich and lean solvent streams, stripper condenser temperature and other important process parameters (Aroonwilas et al., 1999; Desideri and Paolucci, 1999; Rao and Rubin, 2006; Singh et al., 2003; Fisher et al., 2005). In general, these works employed parametric optimizations instead of optimizing all process variables simultaneously. Additionally, different objective functions were considered for optimization.

Ali (2004) analyzed an existing coal-fired power plant (500-MW unit from Ontario Power Generation (OPG) in Canada) coupled with a CO₂ capture plant using monoethanolamine (MEA). ASPEN PLUS was used to model the process. It is emphasized that pressure profiles must be calculated for the absorber and stripper to assess the hydrodynamic performance of the column to achieve realistic designs. Later, Alie et al. (2005) proposed a decomposition strategy to improve the convergence of the previous model developed in ASPEN. The strategy provided good initialization points for the convergence of the entire flow sheet. The authors applied the proposed strategy to optimize the reboiler heat duty parametrically using MEA.

Khakdaman et al. (2008) applied a process simulator to study a revamping of a gas-sweetening plant performance to improve process efficiency. Given the plant operating conditions, the study was performed using a mixture of amines (DEA and MDEA) instead of using only one amine (DEA). They concluded that for a given CO₂ recovery and heat duty in the stripper, the capacity of the gas-sweetening plant improves when a blended solution with equal portions of DEA and MDEA is used. Similar conclusions regarding the performance of a CO₂ capture plant coupled to a thermo-electrical Gas Turbine Power Plant using a blended DEA–MDEA solution have been reported by Corti et al. (1998a,b, 1999) and Manfrida (1999).

Abu-Zahra et al. (2007a,b) performed parametric optimizations of a capture plant coupled to a 600-MWe bituminous coal fired power unit. The process is an absorption/desorption unit using MEA. Absorber and regenerator units were simulated with ASPEN and coupled to an ad hoc software for column design. The objective function was the thermal energy consumption and the minimum was found at a lean MEA loading of 0.3 using a 40 wt% MEA solution (0.32 for 30%) at a stripper pressure of 210 kPa with an energy consumption of 3.0 GJ/ton CO₂ (3.29 for a 30 wt% MEA solution). The following parameters were considered: CO₂ solvent loading, CO₂ removal percentage, MEA concentration, stripper operating pressure and lean solvent temperature. The optimization variables were cooling water and heat demands and solvent mass flow rate. The flue gas is assumed to have the following properties: 101.6 kPa at 48 °C with a CO₂ concentration of 13.30 vol%; and for the wet gas, it is assumed that 90% of the CO₂ has been removed.

Oi (2007) also applied parametric simulations in ASPEN to optimize a post-combustion CO₂ capture process. The flue gas inlet temperature was assumed at 40–50 °C; 82–90% CO₂ removal is fixed; captured CO₂ is compressed at 110 bar and 40 °C, while a 30 wt% MEA solution was considered. The following parameters were studied: stripper pressure, solvent circulation flow rate, height of absorber packing.

A significant amount of research has also focused on selecting the amine solvents (including mixtures) to increase CO₂ absorption. Different alkanolamine solutions have also been studied for CO₂ capture process optimization. This research line focuses on the development of sterically hindered amines to minimize the energy needed to regenerate the solution and to degrade from oxidization and to maximize capacity and CO₂ absorption rates. The amine functionalization can be obtained by adding chemical groups into the amine solution. Another ongoing research study focuses on developing new solvents using blends of simple amines to combine the advantages of each amine. For example, the use of MEA requires a significant amount of energy for solvent regeneration and severe operational problems, such as corrosion and solvent degradation. However, it is more economical and has a higher CO₂ capture efficiency and absorption rate. Other type of amines, such as DEA, DIPA and AMP, react with CO₂ at moderate rates while avoiding the significant problems of corrosion and solvent degradation. Finally, MDEA reacts with CO₂ at a slow rate but has the best operational performance. Thus, it is clear that blending different amines to achieve low energy consumption for solvent regeneration is an important when optimizing the process. Blending amines leads to significant savings in process costs by combining the desirable characteristics of different solvents and discarding unfavorable ones.

According to the aforementioned, there is a strong dependence between the type of amine, CO₂ loadings and residence time (gas flow velocity and column dimensions). Therefore, it is interesting to investigate post-combustion CO₂ capture with mixtures of amines. The key factor is to determine the operating conditions and the mixture composition that simultaneously maximize the advantages of both amines and minimize their disadvantages to improve the whole overall performance of the process. Moreover, the need to evaluate different solvent types economically and quickly leads to defining a procedure that optimizes the main operating variables and solvent characteristics using an easy, flexible and robust tool.

In this paper, a set of optimal operating conditions of the post-combustion process to satisfy different CO₂ emission targets at minimum total annual costs is obtained by using a process simulator. Specifically, in contrast to previously mentioned works, the following variables will be simultaneously optimized: inlet and outlet temperatures of the lean solution stream of the absorber, CO₂ lean loading and amine flow rates. The optimal values corresponding to the mixture compositions (DEA and MDEA) for different CO₂ recovery targets will be obtained by parametric optimization. In addition, another goal of this paper is to show the potential use of process simulators to simultaneously optimize the operating conditions of a post-combustion CO₂ process.

This paper is organized as follows: Section 2 briefly describes the CO₂ capture process. Section 3 presents the optimization problem formulation. Section 4 outlines the assumptions and mathematical model. Section 5 discusses the obtained results and shows the set of optimal solutions corresponding to different CO₂ recoveries and solvent compo-

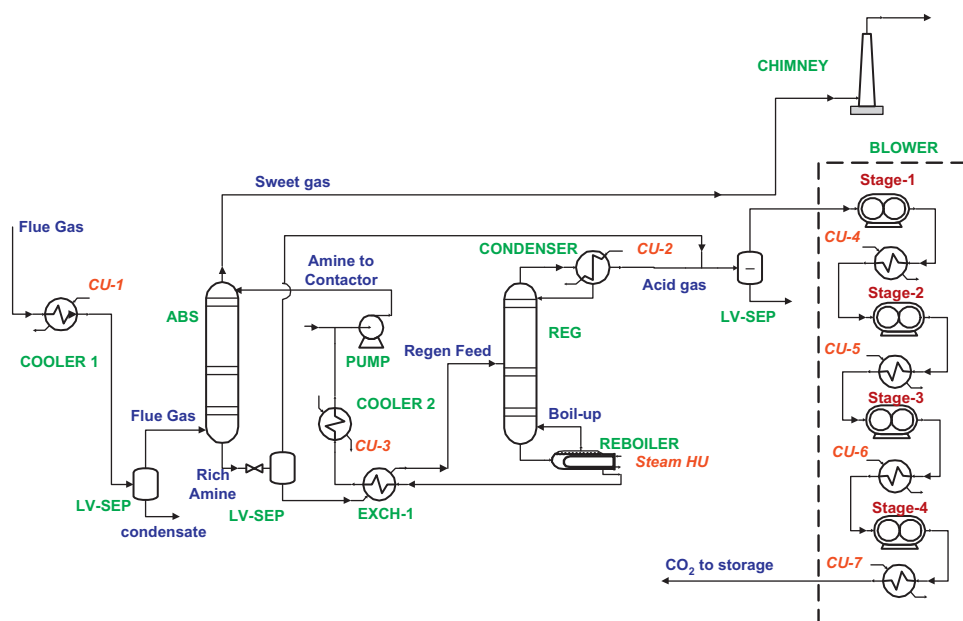


Fig. 1 – Schematic flow sheet of a conventional post-combustion CO₂ capture process.

sitions. Finally, future work and conclusions are presented in Section 6.

2. Process description

Fig. 1 shows a schematic flow sheet of the conventional post-combustion CO₂ capture process considered for the optimization.

As shown in Fig. 1, the acid gas containing CO₂ enters the absorber [ABS] at the bottom and flows upward. The sweet gas leaves the top of the absorber tower. The lean amine without acid gases (coming from the regenerator unit [REG]) enters the top of the absorber. The rich amine carrying the acid gases leaves the bottom of the absorber, passes through the lean/rich amines heat exchanger [EXCH-1] and then flows through the filter to remove solid impurities. The rich solution then flows downward through this stripper column [REG]. Acid gases are removed from the stream and condensed steam returns to the regenerator as reflux. Purified amine leaves the regenerator and goes through the amine–amine heat exchanger [EXCH-1] and solution cooler [COOLER 2] before returning to the absorber.

The volume of flue gas to be treated in common thermo-electric generation plants becomes extremely high in absorber and regenerator columns. Therefore, there are technical and economic restrictions that impose a maximum flue gas flow rate for processing (Chapel et al., 1999; Iijima, 2002; Desideri and Paolucci, 1999). For example, another processing train should be added if the volume of flue-gas is high. Therefore, it is very common to use two, three or more capture trains in real plants. Indeed, all of the trains must be equivalent for convenience in maintenance and operation. For modeling purposes, then, it is necessary to select the number of trains and the equipment capacities. The volume of recovered CO₂ strongly influences the selection of compressors (number of units and capacities).

Some mixtures of amines were investigated to optimize gas-sweetening plants (generally for plant revamping in petrochemical plants). The use of mixtures of primary (MEA) or secondary (DEA) amines with a tertiary (MDEA) amine is

very attractive because the mixtures may reduce process costs (or improve CO₂ removal efficiency). Certainly, MEA or DEA amines react rapidly with CO₂ to form carbamate ions. However, the reactions are highly exothermic (mainly MEA) and the heat required in the reboiler to regenerate both amines is greater than that required for tertiary amines (MDEA).

The CO₂ loading factor, which is defined as the ratio between total moles CO₂/total moles amine in the liquid phase, is one of the most important parameter in CO₂ capture utilizing amines. This parameter strongly depends on the type of amine. Primary and secondary amines react in a 2/1 mol amine/mol CO₂ ratio, which limits loading to 0.5 mol CO₂ to mol of amine, while 1 mol of tertiary amines reacts with 1 mol of CO₂, which considerably improves the load limit.

Finally, the reaction of tertiary amines leads to the formation of bicarbonate and protonated amine instead of carbamate. These reactions are slower than the formation of carbamates using primary or secondary amines. Therefore, higher residence times are required to achieve the same CO₂ removal if a tertiary amine is used. The reactions between tertiary amines and CO₂ do not produce carbamate ions, but indirectly contribute to bicarbonate formation and amine protonation. These reactions are relatively slower than carbamate formation from primary and secondary amines; thus, high residence times are necessary to achieve the same performance. The reboiler heat duty of the regenerator unit is strongly influenced by amine type and composition.

From the process configuration point of view, it is important to mention that heat integration between both columns (absorption and regeneration) as well as other structural changes, such as bifurcations of the lean amine stream to feed different points in both columns, are being discussed in the literature (Ali, 2004; Jassim and Rochelle, 2006), but they are still in a conceptual phase and are difficult to implement at an industrial scale.

According to the aforementioned comments, it is easy to observe the strong relationship among all process variables; and they should be considered when analyzing the entire process.

In the next section, the optimization problem proposed in this work is presented.

3. Optimization problem formulation

The optimization problem can be stated as follows. Given the composition, temperature and flow rate of the flue gases leaving a combined cycle power plant, the steam pressure and temperature to be used on the reboiler and the temperature of the cooling water, the objective is to determine the optimal design of the post-combustion process to satisfy the CO₂ absorption level to minimize the plant's total annual cost. The main optimization variables of the processes are the inlet and outlet temperature of lean solution stream on the absorber, CO₂ loading and lean and rich amine flow rates. CO₂ recovery targets and amine compositions will be considered as model parameters.

4. Hypothesis and mathematical model

The following hypotheses are assumed to develop the mathematical model.

- An Equilibrium Stage Model (ESM) is assumed. Although ESMs are known to give qualitatively different results from rate-based models (RBMs), ESMs are less complex to solve than RBMs. Thus, ESMs have been assumed as a first approximation to implement the optimization strategy. The proposed methodology will be then extended to RBM.
- CO₂ recovery is assumed as given (80, 85, 90 and 95%).
- Mixtures of DEA and MDEA amines are considered. The total amines concentration assumed is 40 wt% and blending proportions ranging between 40% MDEA (0% DEA) and 40% DEA (0% MDEA).
- Flue gas coming from a combined cycle power plant is considered. Therefore, a low CO₂ concentration in the flue gases is assumed.
- Flue gas composition does not include NO_x, SO_x, O₂, or SH₂.
- Adiabatic absorption process is considered.
- Pressure drops inside the absorber and regenerator units are not calculated throughout the optimizations. They are assumed according to values obtained from previous simulations for different flow rates and operating conditions. Hydrodynamic conditions are then checked in all solutions to detect flooding or weeping conditions.
- A CO₂ stream with 99% of purity is assumed at the top of regenerator unit.
- The specifications of the product CO₂ for storage are 303.13 K, 70.3 bar, 1649.95 kg mol/h, 0.7667 mass fraction (CO₂), 0.2332 mass fraction (H₂O), 0.001 mass fraction (N₂).
- Cooling water is available at 298 K.
- The number of equilibrium stages for both columns are assumed as model parameters.
- A modified SRK model with improved VLE calculations is used for flue gas streams at high pressure.
- The Li–Mather model is used as an Electrolyte Solution model to compute the VLE and the heat of mixing. This model shows a strong predictive capability over a wide range of temperatures, pressures, acid gas loadings and amine concentrations. The framework of the thermodynamic model is based on two types of equilibria: liquid–vapor phase equilibrium and chemical equilibrium.
- Fugacity coefficients for all molecular species are computed using the Peng–Robinson state equation.
- The costs associated for the compression stages are included.

4.1. Mathematical model

The mathematical model considers the mass and energy balances including logical constraints to ensure model convergence. For example, constraints avoiding temperature crossovers between hot and cold streams have been introduced. Among others, the model includes constraints used to compute stage efficiency, charge balance, equilibrium solubility, phase enthalpy, equilibrium reactions, phase equilibrium involving calculations of Peng–Robinson fugacity and Clegg–Pitzer equation activity coefficients as well.

The total annual cost (TAC) is the objective function to be minimized. It includes the operating costs and investment in all equipments and is defined as follows:

$$\text{TAC} = \text{TAOC} + \text{TIC} \cdot \text{CRF} \cdot \phi$$

where TAOC, TIC, ϕ and CRF refer to the total annual operating cost, the total investment cost, the maintenance factor and the capital recovery factor, respectively. The TIC is estimated using detailed cost equations for all relevant equipment. Appendix A presents many of the used cost functions, like the one used for heat exchangers, condensers, pumps, reboiler and compressors. Investments corresponding to absorber and regenerator units are also included.

4.2. Model implementation and used optimization algorithms

As mentioned earlier, HYSYS V.3.2 marketed by Hyprotech, which is now part of Aspen Technology (ASPEN HYSYS), has been used to model and optimize the process. HYSYS V.3.2 allows the user to implement models using macro languages and several HYSYS® logical operations like SET, ADJUST, RECYCLE and SPREADSHEET, which were used to model specific equipment and implement some restrictions and stream relationships for process optimization.

The mixed optimization option available in HYSYS was employed to solve the resulting mathematical model. It attempts to take advantage of the convergence characteristic of the BOX method and the efficiency of the SQP method. The BOX method is a sequential search technique that solves problems with non-linear objective functions subject to non-linear inequality constraints. No derivatives are required. This method is not efficient in terms of the required number of function evaluations. It generally requires a large number of iterations to converge on the solution. However, if applicable, this method can be very robust. The deterministic SQP method is efficient and robust, especially when reasonable initial points are provided. Thus, the mixed method starts the optimization with the BOX method using a very loose convergence tolerance (50 times the desired tolerance). After convergence, the SQP method is then used to locate the final optimal solution.

Finally, it should be mentioned that global optimal solutions cannot be guaranteed due to the non-convexities in the model. For instance, the presence of bilinear terms in energy balances may lead to local solutions instead of global solutions. A global optimization algorithm should be used to directly guarantee the solution optimality.

Table 1 – Model parameter values used for optimization.

Flue gases (fluid package and stream conditions)	
Property package	SRK
Vapor	SRK
EOS enthalpy method specification	Equation of state
Components	O ₂ , CO, CO ₂ , H ₂ , H ₂ O, CH ₄ and N ₂ .
Pressure	1.2 atm
Temperature	200 °C
Inlet flue gas flow-rate	2.8×10^4 [kg mol/h]
CO ₂ composition	4 vol%
Absorber	
Number of stages	10
Pressure	1.0 atm
Total pressure drop	0.2 atm.
Solving method	HYSIM inside-out
Maximum number of iterations	10,000
Equilibrium error tolerance	1.00×10^{-5}
Heat/spec. error tolerance	5.00×10^{-4}
Regenerator	
Condenser	(Full reflux)
Reboiler	
Number of stages	10
Feed stage	5
Pressure	2 atm
Total pressure drop	0.2 atm
Solving method	HYSIM inside-out
Maximum number of iterations	10,000
Equilibrium error tolerance	1.00×10^{-5}
Heat/spec. error tolerance	5.00×10^{-4}
Tray sizing utility	
HETP	0.971 [m]
HETP correlation	Incropera and De Witt (1990)
Section height	Number of stages \times HETP
Max flooding	70%
Packing type	Ballast rings (metal, random) 1 in.

5. Discussion

As mentioned in Section 3, the goal is to simultaneously optimize operating conditions and mixture composition (precisely DEA and MDEA) in order to satisfy different CO₂ recoveries at minimum total cost. Thus, the tradeoff between advantages and disadvantages of both amines is also included in the optimization problem.

The optimization problems were solved by assuming the model parameters listed in Table 1 and using an Intel Core 2 Quad Extreme QX9650 3 GHz 1333 MHz processor and a 4-GB RAM.

As follows, numerical results corresponding to the optimal operating conditions of the post-combustion CO₂ process are presented and discussed. It should be noted first, however, that all figures show the optimal values corresponding to the optimal set of solutions achieved by various CO₂ emission targets with different proportions of amines. For clarification, optimal values (all simultaneously obtained) of the main decision variables are presented and discussed separately (Figs. 2–13). Thus, the solution set corresponding to the optimal values of the main process variables for specific values of CO₂ recovery target and mixture proportion can be directly obtained from Figs. 2–13.

5.1. Optimal total cost values

Figs. 2 and 3 illustrate the total optimal specific costs as a function of the MDEA percentage in the aqueous blended amine solutions and CO₂ recovery targets, respectively.

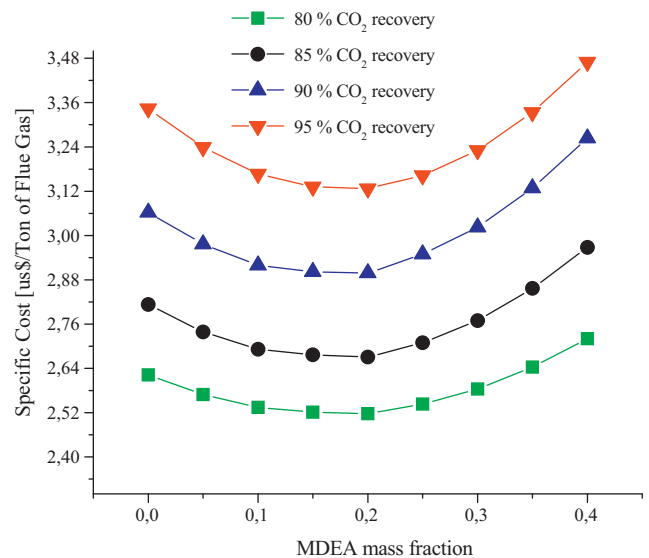


Fig. 2 – Specific total cost vs. MDEA mass fraction.

Fig. 2 shows that the minimum cost corresponds to a mixture with the same amounts of DEA and MDEA (wet weight: 20% MDEA and 20% DEA in water) while different amine proportions (compositions) involve higher specific costs. Certainly, for 80% CO₂ recovery and for single DEA amine solution, the total cost is 2.250 (US\$/ton). Lower costs are achieved by increasing the MDEA composition. The lowest specific cost (2.146 US\$/ton) is reached for a solution containing equal masses of MDEA and DEA (20% MDEA, 20% DEA and 60% water). If the amount of MDEA is then increased, the minimum costs increase. In other words, by increasing the MDEA after the point corresponding to equal masses of amines, it is not possible to achieve optimal operating conditions to decrease the total cost below 2.146 US\$/ton. The cost corresponding to a single MDEA solution (40 wt%) is 2.350 (US\$/ton).

Despite the asymmetry of the curve shown in Fig. 2, there are different operating conditions with the same total costs. In fact, there exist at least two operating points with the same total costs but with different mixture compositions and operating conditions (illustrated in the following figures). Moreover, the variation of the specific cost is not higher than

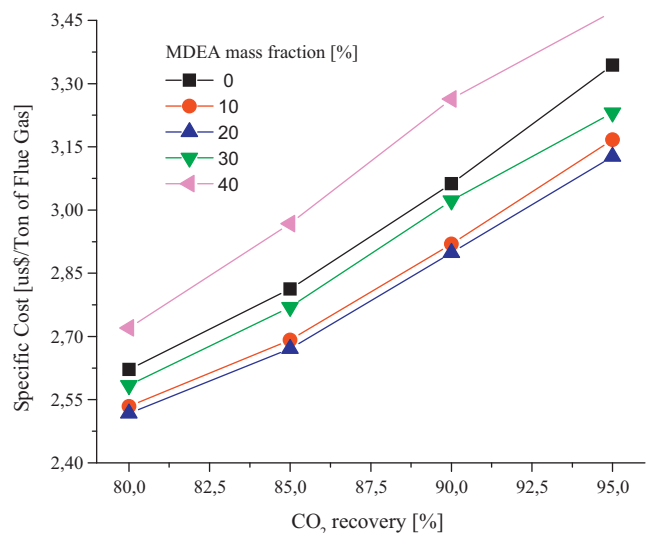


Fig. 3 – Specific total cost vs. CO₂ recovery target.

Table 2 – Optimal costs for 90 and 80% CO₂ recoveries (50 wt% MDEA and 50% DEA in solution).

	90% CO ₂ recovery 50% MDEA	80% CO ₂ recovery 50% MDEA
Investment [US\$/s]	0.15190	0.13564
Heating utility [US\$/s]	0.22654	0.20406
Cooling utility [US\$/s]	0.06202	0.06391
Electricity [US\$/s]	0.30493	0.27334
Total [US\$/s]	0.74539	0.67696

5% for a great range of operating conditions and mixtures compositions for a given CO₂ recovery.

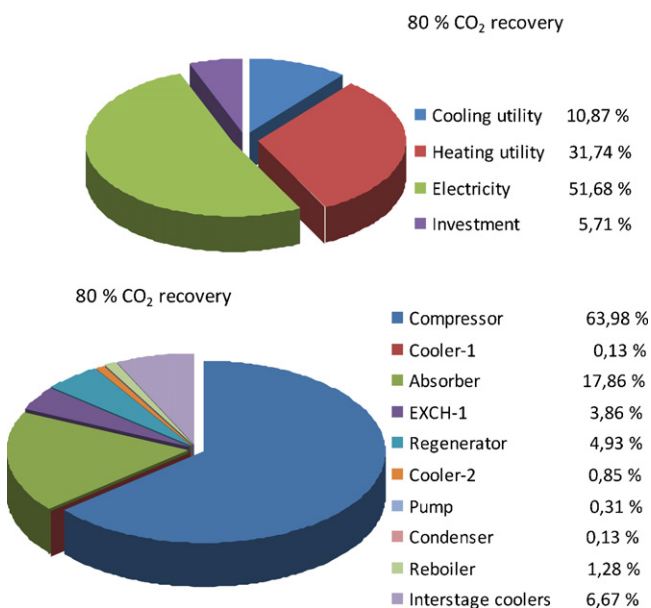
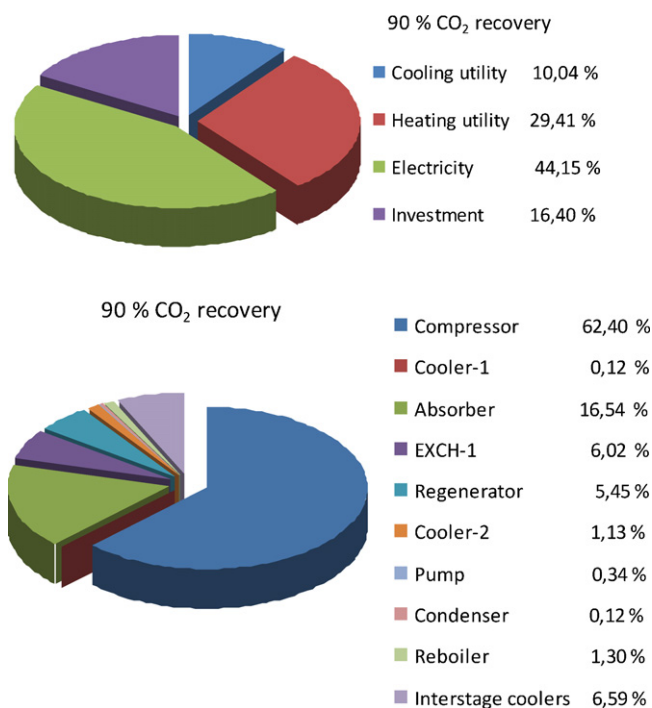
These results demonstrate that after simultaneous variation of all operating conditions (at least those manipulated here), it is possible to find an extensive operation range with optimal operating conditions. They are useful for analyzing the final selection, which takes into account other costs and technological aspects. In fact, as described later, there are other factors that influence the total cost but are difficult to introduce into the model (the cost associated with corrosion and degradation, among others). Thus, even though the results presented here do not consider such factors, they provide preliminary designs and knowledge about the process. The final design must be selected after performing a deeper analysis considering all practical aspects.

Table 2 compares the total costs involved for two CO₂ recoveries (80 and 90%).

As expected, the minimum total cost for 90% CO₂ recovery is higher than that for 80% CO₂ recovery. The increases in investment and operating costs to reach 90% CO₂ recovery compared to 80% CO₂ recovery are 10% and 20%, respectively.

Figs. 4 and 5 show how the total specific costs listed in Table 2 are distributed.

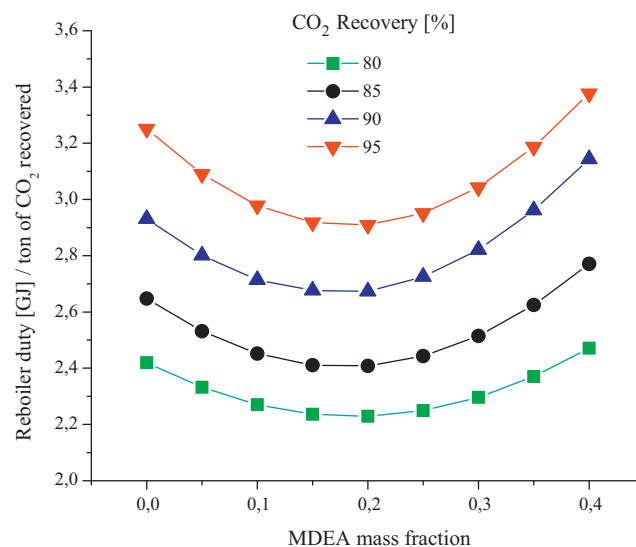
From these figures, it can be concluded that, independent of CO₂ recoveries, the specific cost is greatly influenced by electricity and heating utility costs. The contributions of the cooling utility specific cost and total investment to the total specific cost are similar (10.87 and 5.71%, respectively). Compressors and absorber units represent approximately 64 and

**Fig. 4 – Cost distribution for 80% CO₂ recovery and 40 wt% amine solution (20% MDEA/20% DEA/60% water).****Fig. 5 – Cost distribution for 90% CO₂ recovery and 40 wt% amine solution (20% MDEA/20% DEA/60% water).**

18% of the total specific investment, respectively, while regenerator units and amine heat exchangers have almost the same contributions (4–5% each).

5.2. Optimal reboiler heat duty in the regenerator unit

Figs. 6 and 7 show the reboiler heat duty as a function of mixture proportions in the solvent and CO₂ recoveries, respectively. According to Fig. 6, the minimum reboiler duty is obtained when amines are mixed in equal quantities for any CO₂ recovery target. As previously mentioned, the minimum total cost is also obtained when the solution contains the same mix proportions of amines. As it will be shown later, this proportion of amines leads to the minimum amine flow rate (Fig. 12). Moreover, as seen by comparing Figs. 2 and 3 to Figs. 6 and 7, the dependence of total cost and reboiler duty on CO₂ recoveries and mix proportion of

**Fig. 6 – Optimal reboiler heat duty vs. MDEA mass fraction.**

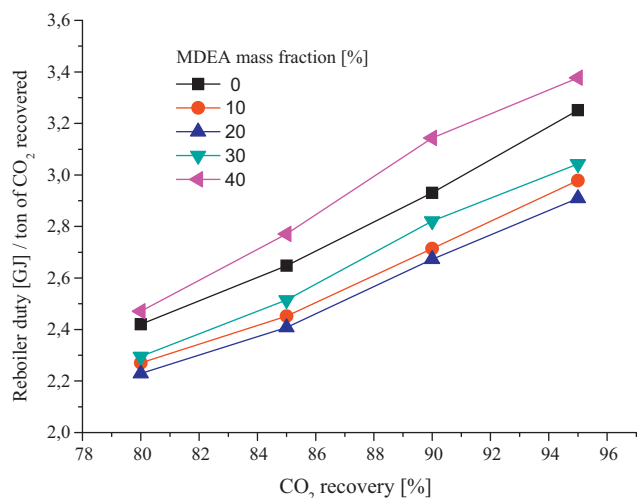


Fig. 7 – Optimal reboiler heat duty vs. CO₂ recovery target.

DEA and MDEA follows the same trend of optimal relationships.

Similar qualitative conclusions were reached by other researchers in experimental works. In fact, Sakwattanapong et al. (2005) analyzed the variation of the stripper heat duty due to the amine type used under fixed operating conditions experimentally. They also explained the observed functionalities by considering three different contributions to the total heat duty: the heat of absorption, the sensible heat for heating the amine and the latent heat to vaporize water. DEA is advantageous because it has greater reaction heat than MDEA; moreover, DEA also requires lower CO₂ partial pressure than MDEA to establish the driving force for stripping. Many authors have suggested that this implies higher vapor water production and consequently higher vaporization heat when DEA is used (Aliabad and Mirzaei, 2009; Sakwattanapong et al., 2005; Chakma, 1995).

This work also explains the combination effect on reboiler heat duty when a solution of DEA and MDEA is used; the heat of reaction is reduced according to the proportion of MDEA added to the mixture. They found that this relationship is not linear (due to the combination of the three contributions above mentioned), and the reduction rate decreases rapidly with the added MDEA. In fact, they found that beyond the equi-molar proportion, the reduction is practically negligible.

Zhang et al. (2008) reported the following ordered ranking of absorption capacities of CO₂ into different aqueous amine solutions (single solutions): DETA > AMP > MEA > DEA > MDEA. It can be concluded that DEA absorption capacity is about twice higher than that of MDEA based on their published data.

These reported properties may partially account for the reduction of the cost and the existence of an optimal mixture composition which minimizes the total cost, as occurred in our study (Fig. 2). In fact, going from 0 wt% MDEA (40% DEA) to 20 wt% MDEA in the total mixture composition (20 wt% MDEA/20 wt% DEA/60% water), the rate of the heat duty decreases progressively and the capture rate falls at a faster rate.

Idem et al. (2009) analyzed the heat duty in an experimental pilot plant using different alkanolamines (MEA and RS-1) to determine the operating conditions that minimize heat consumption. From their research results, they emphasized that the minimal steam requirements can only be obtained by optimizing process operating conditions and solvent type simultaneously.

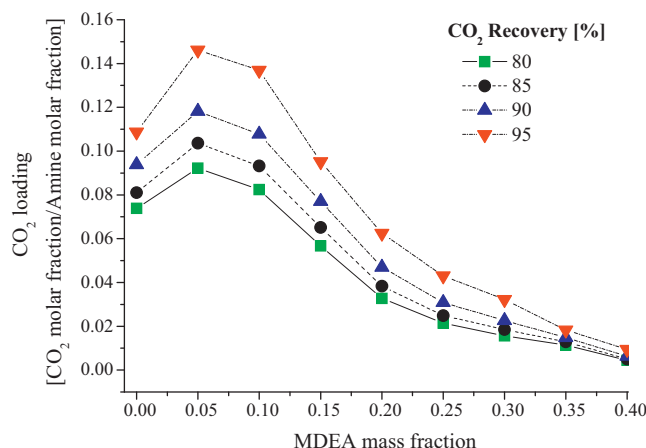


Fig. 8 – Optimal CO₂ loading vs. MDEA mass fraction.

Aroonwilas and Veawab (2007) analyzed a 500-MW coal-fired supercritical power plant integrated to a post-combustion CO₂ capture unit. They used a parametric approach and an in-house simulation model for plant optimization and concluded that a mixed alkanolamine solution is better because the heat consumption is reduced when the complex is adequately integrated. According to their result, combining the low heat requirement of MDEA with the fast absorption rate of MEA produces a potential cost reduction due to the tradeoff between the energy consumption during solvent regeneration and the lower performance of CO₂ capture (compared with MEA). Again, the authors emphasized that the optimal composition or mixing ratio must be achieved by simultaneously considering the main process variables and blending proportions.

5.3. Optimal CO₂ loading

CO₂ removal efficiency depends on CO₂ loading, among other variables. For example, removal efficiency increases as CO₂ loading decreases because less CO₂ loading leads to an increased thermodynamic driving force for the mass transfer process, which results in reaction kinetics that dominate CO₂ absorption performance. Therefore, for greater CO₂ loading, CO₂ removal efficiencies decrease. MDEA presented lower CO₂ absorption performance than DEA, using different CO₂ loading factors.

Fig. 8 shows optimal values corresponding to the CO₂ loading as a function of the proportion of amines used for each CO₂ recovery percentage. Fig. 9 illustrates the optimal CO₂ loading

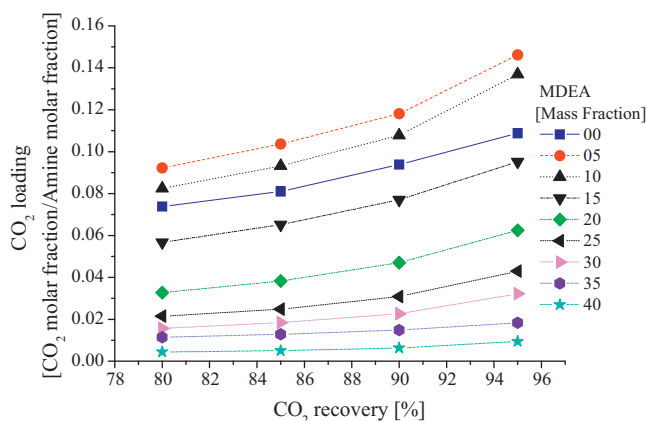


Fig. 9 – Optimal CO₂ loading vs. CO₂ recovery target.

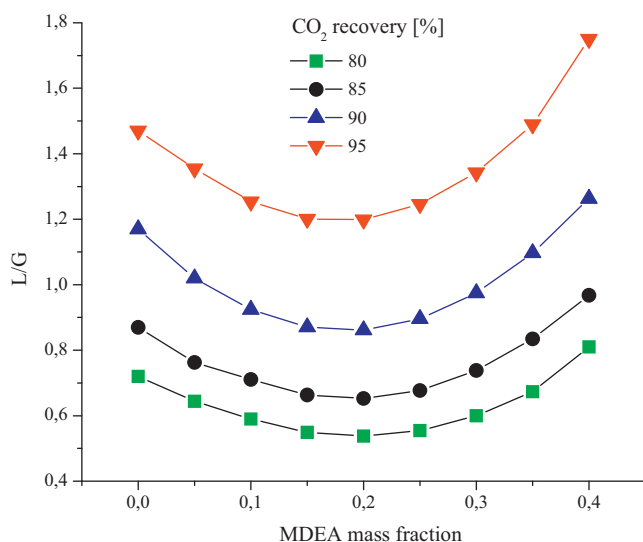


Fig. 10 – Optimal L/G ratio vs. MDEA mass fraction.

charge as a function of CO₂ recovery with the mixing proportion as parameter. It is clear that even when all process variables are simultaneously optimized, CO₂ loading for optimal performance tends to decrease when MDEA is increased.

Figs. 10 and 11 show L/G values using both CO₂ recovery and blend proportion as parameters.

In addition to CO₂ loading, the performance evaluation was extended to cover a range of liquid loads. The results show the significant impact of a liquid load on CO₂ absorption performance. CO₂ removal efficiency decreases as the liquid load decreases.

In terms of the effect of the blended amines on absorption performance, it is concluded that all process variables, including the regenerator unit, should be considered for analysis. Aroonwilas and Veawab (2007) analyzed absorption performance experimentally using different mixtures of amines. One of the studied mixtures was a MDEA/DEA amine solution. The authors examined the absorption performance for a given total concentration, different mixing proportions and CO₂ loadings of the feed solution to the absorber. They concluded that absorption performances of blended solutions ranged between the performances attained by their precursors. This result also appears to be influenced by variations in CO₂ loading in a similar way to that of single alkanolamine

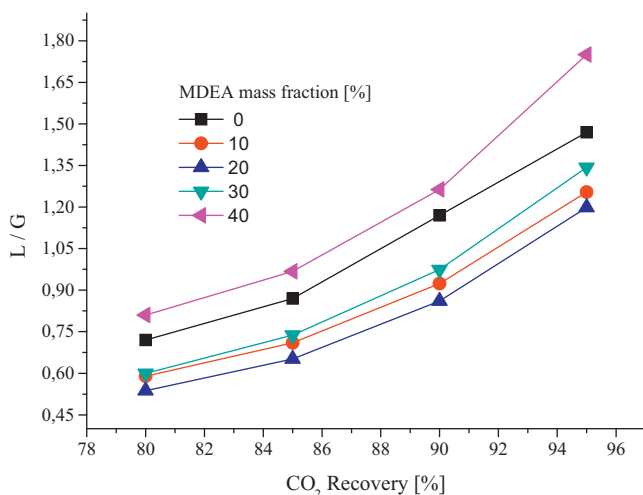


Fig. 11 – Optimal L/G ratio vs. CO₂ recovery target.

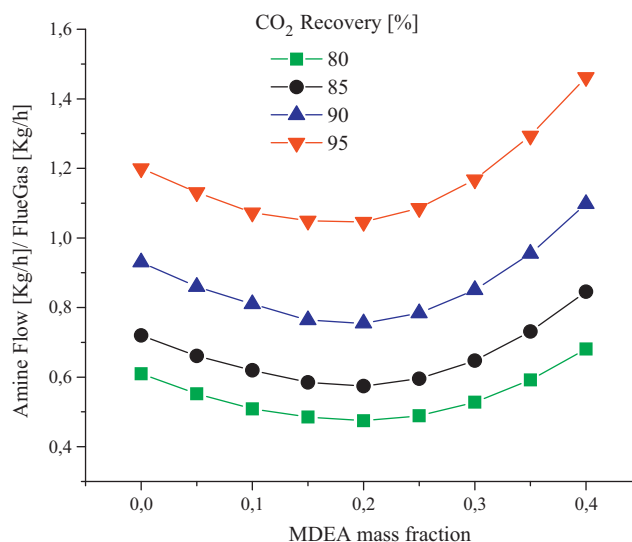


Fig. 12 – Optimal amine flow-rates vs. MDEA mass fraction.

systems. That is, as CO₂ loading increased, CO₂ absorption efficiency decreased. Indeed, it was noted that CO₂ concentration profiles of blended solutions approached the profiles of rate promoters (DEA) at low CO₂ loading. Once CO₂ loading increased, however, the profiles of blended solutions moved towards the profiles of MDEA. Finally, the authors found that the mixing ratio also played an essential role in controlling the absorption performance. CO₂ removal efficiency increased with the mixing ratio of DEA to MDEA at different CO₂ loadings. They suggested that blended alkanolamines performance can be customized to fit a specific removal target by varying the mixing ratio. It is important to highlight that these significant advances in the knowledge of such behaviors were obtained by conducting experiments in a bench-scale absorption unit without taking into account the regenerator unit. In this work, it is proved that there exists an optimal value of the mixing proportion of amines (20 wt% MDEA/20 wt% DEA/60 wt% water) to reach the desired CO₂ reduction targets when the whole process is studied, which clearly reflects the importance of optimizing the entire process simultaneously.

5.4. Optimal amine flow rates

Similarly, Figs. 12 and 13 show the optimal variation of the amine flow rate parametrically on the CO₂ recovery and

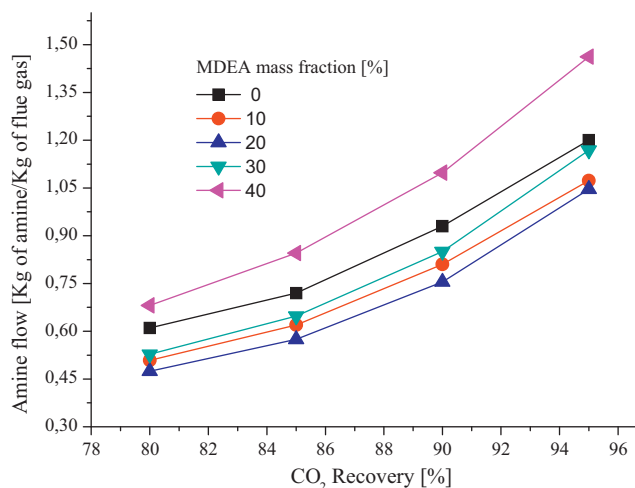


Fig. 13 – Optimal amine flow-rates vs. CO₂ recovery target.

blended amine proportion. Again, it can be seen that functionalities of the optimal amine flow rate on such parameters correspond to total cost (Figs. 2 and 3).

Finally, it is important to mention that the resulting model has also been solved using the Kent–Eisenberg and NRTL models for VLE and the Heat Mixing. Depending on the flue gas specifications, the former provided similar solutions to those obtained by Li–Mather model. However, poor solutions were obtained using the NRTL model. Certainly, many molecular parameters were not available for this system.

6. Conclusion. Future work

In this paper, a conventional post-combustion CO₂ process has been investigated. The whole process has been modeled and optimized using a process simulator (HYSYS). It has been shown that it is possible to use rigorous models and cost functions and implement an optimization procedure for simultaneous optimization of the main process variables using process simulators. It is also concluded that optimal values of such parameters follow well-defined trends as a function of CO₂ recovery targets. More specifically, given the total DEA/MDEA mixture composition (40 wt% amine) and flue gas conditions of a typical Combined Gas Cycle Power Plant, the space of optimal solutions to reach the desired CO₂ reduction targets can be described using only simple equations. Despite the accuracy of the obtained solutions, important aspects such as hydrodynamic and pressure drop computations should be considered in the optimization problems. The concentration of the mixed DEA/MDEA solution has a strong influence on the hydrodynamic behavior of the absorber column, which is intrinsically related to residence time and thus to CO₂ removal efficiency.

The dependence of effective mass-transfer area on the alkanolamine type should also be considered. Thus, equilibrium stage models assumed in this paper for absorber and regenerator units should be extended to non-equilibrium stage models.

Also, it is known that the selection of alkanolamines for a given service must take into account additional characteristics, such as solvent solubility and its relationships with corrosion properties, degradation, foaming and molecular weight. In this paper, these factors were not taken into account. Flue gas impurities, especially oxygen, sulfur oxides and nitrogen dioxide react in different ways depending on the amine being used. Annual amine degradation and oxidation rates are also important factors to be considered.

Considering all variables that affect the process performance, the strong nonlinearity of the process behavior and the number of near optimal process conditions characterized by different compositions of amines and/or different process operating conditions, it is obvious that the final and optimal design cannot be chosen easily. It may be argued that more experimental work considering all factors must be done to incorporate new process trends and decision variables. However, analytical works using optimization models are important because they can be used to guide experimental works efficiently because considering new variables (in addition to the above referenced experimental works) simultaneously is quite difficult at a pilot plant scale.

In future work, all of the above-mentioned aspects will be included into the model to obtain more realistic designs; for example, the use of parallel trains according to the gas flow rate to be processed may be considered.

Moreover, regression models based on a family of optimal solutions will also be proposed to describe the whole process with simple mathematical models. These models will then be incorporated into rigorous optimization mathematical models (MINLP and/or GDP models) to determine optimal process arrangements. Thus, simple models will be used in a pre-processing phase (solution procedure) to determine upper and lower bounds as well as initial values for robust process optimization.

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Appendix A.

The investment of equipment C_i^0 [US\$/s] is computed as:

$$C_i^0 = \frac{C_i \text{CRF } \phi}{N3600} \quad (\text{A.1})$$

where CRF is the capital recovery factor (18.2%) which is computed considering 25 years and interest tax of 5.52%. N and ϕ refer, respectively, to the total plant operating time (8000 h) and maintenance factor (1.06). The cost equations to compute C_i are presented as follows.

A.1. Heat transfer area investment

The investment corresponding to different heat transfer areas C_i (condensers, amine heat exchangers and reboiler) is computed as conventional heat exchanger equipments (tube and shell the two first and kettle the third one). Precisely, the following detailed cost equations are used:

$$C_i = C_{i,\text{basis}} \left(\frac{A_i}{A_{i,\text{basis}}} \right)^{0.6} \quad (\text{A.2})$$

$i = \text{condensers, amine heat exchangers, reboiler}$

where $C_{i,\text{basis}}$ and $A_{i,\text{basis}}$ refer to the known cost. The correlation to compute the $C_{i,\text{basis}}$ is taken from Henao (2005). Precisely, it is computed as follows:

$$C_{i,\text{basis}} = C_{\text{Eq}} \circ F_{\text{CM}} \quad (\text{A.3})$$

$$F_{\text{CM}} = B_1 + B_2 \cdot F_M \cdot F_P \quad (\text{A.4})$$

F_P is computed by the following equation:

$$\text{Log}(F_P) = C_1 + C_2 \log(P) + C_3 (\text{Log}(P))^2 \quad (\text{A.5})$$

$$\text{Log}(C_{\text{Eq}}) = K_1 + K_2 \log(A_i) + K_3 (\log(A_i))^2 \quad (\text{A.6})$$

The values corresponding to the constants K_j , C_k and B_l are: $K_1 = 3.4338$, $K_2 = 0.14450$, $K_3 = 1.0790 \times 10^{-2}$, $C_1 = -6.4990 \times 10^{-2}$, $C_2 = 5.250 \times 10^{-2}$, $C_3 = 1.4740 \times 10^{-2}$, $B_1 = 1.8$, $B_2 = 1.5$.

Table 3 – Constant values.

K1	4.391
K2	0.285
K3	0.184
1	2.500
B2	1.720

A.2. Pump investment

The cost equation used to compute pump investment is basically the same to those used for heat exchanger investment:

$$C_i = C_{i,\text{basis}} \left(\frac{W_i}{W_{i,\text{basis}}} \right)^{0.6} \quad (\text{A.7})$$

where $C_{i,\text{basis}}$ and $W_{i,\text{basis}}$ refer to the known cost. The correlation to compute the $C_{i,\text{basis}}$ is similar to Eq. (A.3) and is also taken from Henao (2005).

A.3. Absorber and regenerator investments

$$\text{CM} = \text{CE} F_{\text{CM}} \quad (\text{A.8})$$

$$\log[\text{CE}] = K_1 + K_2 \log(L) + K_3 [\log(L)]^2 \quad (\text{A.9})$$

where L refers to the column length. F_{CM} is computed as follows:

$$F_{\text{CM}} = B_1 + B_2 F_P F_M \quad (\text{A.10})$$

F_P factor depends on the pressure (P) and is calculated by Eq. (A.11):

$$\text{If } P \geq 3.7 \text{ bar, then } F_P = 0.5146 + 0.6838 \times \log(P) + 0.2970 \times (\log(P))^2 + 0.0235 \times (\log(P))^6 + 0.0020 \times (\log(P))^8$$

$$\text{If } -0.5 \leq P \leq 3.7 \text{ (bar), then } F_P = 1.00 \quad (\text{A.11})$$

$$\text{If } P \leq -0.5, \text{ then } F_P = 1.25$$

$$F_M = 1(\text{material}) \quad (\text{A.12})$$

Using as reference a column diameter of 4.00 m, the corresponding constant values are listed in Table 3.

A.4. Column spray distributor

It is computed by:

$$\text{CM} = \text{CE} F_{\text{CM}} \quad (\text{A.13})$$

where CE and F_{CM} factors are calculated by the following equations:

$$\text{CE} = (K_1 + K_2 D + K_3 D^2) N F_q \quad (\text{A.14})$$

where D , N and F_q refer to the diameter, number of trays and correction factor due to number of trays (Table 4), respectively.

$$F_{\text{CM}} = B_1 + B_2 F_P F_M \quad (\text{A.15})$$

Table 4 – F_q correction factor values.

Number of trays	F_q
1	3.00
4	2.50
7	2.00
10	1.50
>20	1.00

Table 5 – Constant values used for column spray distributor cost.

K1	235.0000
K2	19.8000
K3	75.0700
B1	0.00
B2	1.20
FP	1

The corresponding constant values by assuming a column height of 4 m are listed in Table 5 and are taken from Turton et al. (1998).

A.5. Column packing

The column packing cost is calculated as follows:

$$\text{CM} = \text{CE} F_{\text{CM}} \quad (\text{A.16})$$

$$\log(\text{CE}) = K_1 + K_2 \log(\text{PH}) + K_3 [\log(\text{PH})]^2 \quad (\text{A.17})$$

$$F_{\text{CM}} = B_1 + B_2 F_P \quad (\text{A.18})$$

where PH refers to the packing height. Constant values are listed in Table 6 and are valid for a column diameter of 4 m (Henao, 2005).

A.6. Heating and cooling energy costs

The cost equations to compute energy costs are taken from Chemical Engineering (2006):

$$C_{S,u} = a \text{CEPCI} + b C_{S,f} \quad (\text{A.19})$$

where $C_{S,u}$ is the price of the utility, a and b are utility cost coefficients, $C_{S,f}$ is the price of the fuel in \$/GJ, and CEPCI is an inflation parameter for projects in the U.S.

The constants (a) and (b) for the cooling utility cost are computed as follows:

$$a = 0.0001 + 3.0 \times 10^{-5} q^{-1} \quad (\text{A.20})$$

where q refers to the flow-rate (m^3/s)

$$b = 0.003$$

Table 6 – Constant values used for column packing cost.

K1	3.9986
K2	0.9833
K3	0.0000
FP	1.00
B1	0.00
B2	1.00

For heating utility cost:

$$a = 2.7 \times 10^{-5} m_s^{-0.9} \quad (\text{A.21})$$

where m_s is the steam flow-rate (kg/s)

$$b = 0.0034 p^{0.05} \quad (\text{A.22})$$

where p refers to the steam pressure (bar).

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