

# Optimal design and sensitivity analysis of post-combustion CO<sub>2</sub> capture process by chemical absorption with amines



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## ABSTRACT

This paper focuses on the optimization of the specific total annual cost (operating costs and investments) of a post-combustion CO<sub>2</sub> capture plant with chemical absorption and on the sensitivity analyses of all of the model parameters. Using a mathematical programming approach and a detailed model the optimal design of the entire process (absorption, amine regeneration, compression stage, and energy recovery system) is investigated. For a more general discussion, two optimal designs that differ on how the total operating cost is computed are discussed. In the former case, the operating cost includes the MEA and H<sub>2</sub>O make-ups and cooling water costs. In the second case the cost of the steam required in the reboiler and the total electricity cost are also included. In both cases, the entire process is simultaneously optimized in order to determine the optimal sizes of each process unit and the operating conditions that minimize the specific total cost. The solutions obtained for both objective functions are compared in detail. Then, sensitivity analyses are performed in order to identify and to investigate how the two optimal designs are modified with the variations of the model parameters. Among others, the results revealed that the specific total cost varies from –0.10 to 7.7% when the parameters are  $\pm 2.5\%$  of their nominal values. However, significant differences are observed in the optimal sizes in several process units (variations up to 118.30% depending on the case) and also in the requirements of steam, electricity and cooling water (variations up to 27.60% depending on the case). The numerical results that support the conclusions are presented and discussed through several optimization solutions.

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## 1. Introduction

CO<sub>2</sub> emissions from fossil fuel based power plants are considered to be one of the most significant contributors to the greenhouse gases emission to the atmosphere. It is widely accepted that the CO<sub>2</sub> emission rate must be significantly reduced in order to mitigate the greenhouse gases effect. For this, more research effort is needed to improve and develop CO<sub>2</sub> capture and storage processes.

Pre-combustion, post-combustion and oxi-fuel technologies are the main and feasible CO<sub>2</sub> capture options. In particular, the chemical absorption with MEA is considered to be as the most

mature technology to be implemented in the short-term not only for already existing power plants but also for new ones. However, it is an intensive energy process because of the large amount of steam required for the amine regeneration which is the major drawback of this alternative. In this process, there are several trade-offs that must not be ignored (investments and operating costs, desired CO<sub>2</sub> capture levels and energy penalties). The current research efforts are to contribute towards achieving significant savings of the CO<sub>2</sub> avoiding costs. In this sense, a sensitivity analysis is essential to identify the model parameters and variables that considerably affect the overall process efficiency, total energy consumption or process total cost.

Several articles have been published addressing the study of CO<sub>2</sub> capture processes taking into account different assumptions and/or scenarios and methodologies (Abu-Zahra et al., 2007a; Eslick and Miller, 2011; García-Gusano et al., 2015; Harkin et al., 2010; Karimi et al., 2011; Lee et al., 2013; Liu et al., 2016; Mores et al., 2012a, 2014; Nuchitprasittichai and Cremaschi, 2013; Rao and Rubin, 2002; Razi et al., 2013; Sipöcz and Tobiesen, 2012). In

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addition, some authors studied the whole CO<sub>2</sub> capture process including the absorption, desorption and compression stages (Abu-Zahra et al., 2007a; Damartzis et al. 2016; Dinca, 2016; Lee et al., 2013; Molina and Bouallou, 2015; Mores et al., 2012a; Nuchitprasittichai and Cremaschi, 2013; Rao and Rubin, 2002; Rivera-Tinoco and Bouallou, 2010; Rodriguez et al., 2011; Sipöcz et al., 2011; Ystad et al., 2012) and other authors focused on the absorption or regeneration units considering stand-alone process (Karimi et al., 2011; Mores et al., 2011; Razi et al., 2013; Greer et al., 2010). In addition, there are articles dealing with the study of the power plants coupled to CO<sub>2</sub> capture processes (Eslick and Miller, 2011; Sipöcz and Tobiesen, 2012; Harkin et al., 2012; Manassaldi et al., 2014; Mores et al., 2014; Cormos et al., 2015).

Sipöcz and Tobiesen (2012) presented thermodynamic and economic analyses of a 440 MWe NGCC plant with an integrated CO<sub>2</sub> removal plant, using an aqueous solution of monoethanolamine (MEA). The authors included absorber intercooling and lean vapor recompression in the flow sheet of the CO<sub>2</sub> capture plant and considered the recirculation of the exhaust gas recirculation (EGR) in the gas turbine which leads to increase the CO<sub>2</sub> content in the exhaust gases compared to conventional operating gas turbines. The results showed that EGR in combination with a reduced specific reboiler duty adds significant benefits in term of operating and investment costs.

Liang et al. (2015) presented comparative studies of stripper overhead vapor integration-based configurations for post-combustion CO<sub>2</sub> capture. Precisely, they compared the total equivalent work of five process configurations (conventional process, split flow with overhead exchanger, simple vapor recompression, split flow with vapor recompression and improved split flow with vapor recompression) via simulation runs using ProMax3.2 software. The simulation results for all processes show that the simple vapor recompression configuration seems to be the worst one because the total equivalent work is higher than the baseline process. The split flow with vapor recompression and the improved split flow with vapor recompression were both the best configurations, with a minimum total equivalent work of 0.808 GJ/t CO<sub>2</sub> and 0.805 GJ/t CO<sub>2</sub>. The total equivalent work was significantly reduced by 17.21 and 17.52%, respectively, compared to the baseline configuration.

Greer et al. (2010) developed an in-house dynamic model for simulation of the de-absorption process using Matlab software. The model included the mass and energy balances, Henry's law, Peng–Robinson equation of state, enhancement factor and correlations of physico-chemical properties as a function of temperature. A typical 400 MW natural gas power station producing one million tonnes of CO<sub>2</sub> per year was used. The main model parameters were the column size and pressure, temperature, flow-rate and composition of entering streams. For the simulation, an inlet loading of 0.46 was used where the majority of the MEA was in the form of MEAH<sup>+</sup> and MEACOO<sup>-</sup>. An outlet loading of 0.27 was achieved with a reboiler reflux of 30.00% and a reboiler temperature of 400 K. This required an energy consumption of 4.25 MJ per kg of CO<sub>2</sub> removed, which was in line with other literature sources. Also, the authors observed that the process performance was not significantly influenced by the increasing of the height of the stripper because it reaches the equilibrium quickly. It was also observed that the slower spatial movement of the fluids within the tower results in a fluid retention time of some hours. Furthermore, the reaction rates, diffusion and fluid properties are all strong function of the temperature. Finally, the authors highlighted the necessity to optimize the entire process from the total cost point of view.

Nuchitprasittichai and Cremaschi (2013) proposed a simulation-optimization framework combining a process simulator with a surface response methodology and they studied how the total cost

of the post-combustion capture process using amines is affected by the CO<sub>2</sub> concentration in the flue gas stream and by the utility costs. For the assumed model parameters, the simulation results obtained revealed that the specific total cost (expressed in terms of US\$/tn CO<sub>2</sub> recovered) depended more on the CO<sub>2</sub> concentration in flue gas than on the utility costs. The higher CO<sub>2</sub> concentrations the lower specific total costs. The fluctuations in the utility costs do not exhibit a significant impact on the minimum CO<sub>2</sub> capture cost.

Razi et al. (2013) applied multi-scale simulations to study alternative absorber designs in an MEA based CO<sub>2</sub> capture plant for the following two cases: a) for CO<sub>2</sub> capture from a gas-fired power plant and b) for CO<sub>2</sub> capture from a coal-fired power plant. In both cases, a power output of 400 MWe and a 90.0% of CO<sub>2</sub> recovery target were assumed. Also, the authors considered the absorber as the major contributor to CAPEX (CAPital EXPenditures) and they investigated the implications of the absorber's design on the cost of the exhaust gas blower and on the cost related to the pumping of the solvent. For this, simulation runs in Aspen RateSep were carried out. Obtained results revealed that large electrical energy savings in the feed gas blower can be obtained if the absorber pressure drop is reduced. This reduction can be obtained by reducing the velocity and therefore by increasing the column cross sectional area requiring a little bit volume of packing which results in a slight increase of the investment. In addition, for the two case studies a) and b) the optimal values of the flooding velocities for which the total costs reached minimum values were 71.0 and 74.0%, respectively.

Rao and Rubin (2002) and Lee et al. (2013) proposed the use of multi-objective optimization techniques. Rao and Rubin (2002) studied the total cost involved by a typical MEA-based absorption system taken into account the pipeline transport of liquefied CO<sub>2</sub> to geological storage sites. In contrast to the previous authors, Rao and Rubin considered probability distributions of the model inputs instead of single deterministic values. They have shown that the CO<sub>2</sub> avoidance cost strongly depends on the assumptions considered for the designs of the power and capture plants, on the interactions with other systems of control of other pollutants and on the methods used for the CO<sub>2</sub> storage. Lee et al. (2013) evaluated and compared the entire CO<sub>2</sub> capture process performances for different solvents (MEA and DEA). By comparing the Pareto fronts of each amine, they concluded that the use of DEA is preferred since both the thermal energy penalty (reboiler heat duty) and the total investment cost related to DEA (diethanolamine), are lower than that related to MEA (monoethanolamine) for CO<sub>2</sub> capture. They concluded that the quantitative results are highly dependent on the robustness of the thermodynamic models for the amine-CO<sub>2</sub> systems available in the process simulator. Therefore, more efforts should be done in order to develop new solvents and to refine thermodynamic models of the existing solvents and perform the corresponding sensitivity analyses.

Recently, Dinca (2016) analyzed solvents based on MEA, DEA and MEA–DEA blended, with a view to reducing the CO<sub>2</sub> generated by burning coal in the pilot installation CFBC (circulating fluidized bed combustion). The experimental results were successfully compared with the ones obtained when the program Aspen Plus-Hysys 3.2 was used. Using the same process simulator (Aspen Plus software), Molina and Bouallou (2015) simulated the CO<sub>2</sub> absorption by aqueous ammonia through a membrane contactor and comparing the different process that used ammonia solution as solvent. Results revealed that membrane contactor can achieve promising performance for CO<sub>2</sub> post-combustion capture by ammonia.

Sipöcz et al. (2011) successfully applied Artificial Neural Networks (ANN) to generate a simple model to predict the optimum operating conditions of CO<sub>2</sub> capture plant using MEA process. The

authors used data obtained from CO2SIM simulator to train the ANN model. A back propagation learning algorithm based on a trial-and-error method. The trained model was then used for finding the optimum operation for the reference plant with respect to the lowest possible specific steam duty and the maximum CO<sub>2</sub> capture rate. Two different algorithms have been used and compared for the training of the ANN and, a sensitivity analysis was carried out to find the minimum number of input parameters needed while maintaining sufficient accuracy of the model.

Harkin et al. (2010) proposed a combined pinch analysis and linear programming optimization to determine targets for the energy penalty of existing power plants. The authors determined the amount of electricity which may be exported from a power station, when a portion of the steam and electricity is used to run an amine-based solvent carbon capture plant. Several retrofit cases, with increasing levels of integration have been investigated.

Recent results presented in Mores et al. (2014) allowed to conclude that local and global sensitivity analyses should be performed in order to evaluate the relative importance of each one of the model parameters. This qualitative conclusion is also in full agreement to that concluded in the detailed review study conducted recently by Koronaki et al. (2015) who highlighted the need to perform sensitivity analysis on the operational windows defined by the bounds taken from literature.

In this context, this paper presents a detailed discussion on how each one of the model parameters affects the optimal solution sets. This paper is a natural continuation of the author's earlier work in this subject (Mores et al., 2014, 2012a, 2012b, 2012c). The main contribution of this paper is the fact that, using a detailed mathematical model and a simultaneous optimization algorithm, all the parameters of the model related to the calculations of the costs, physicochemical properties, sizes of the process-units and operating conditions will be considered for the sensitivity analyses. In contrast to the majority of the published papers, the sensitivity analysis is performed considering that the sizes of the process units (heat transfer areas, packing volumes and power capacities) and utility requirements (steam, cooling water, electricity and MEA/water make up streams) are considered as optimization variables. In addition, the study is performed taken into account all the process units of the entire CO<sub>2</sub> process (absorption, amine regeneration and CO<sub>2</sub> compression) instead of standalone processes. Thus, the use of detailed models for sensitivity analysis is valuable because the interactions of all parameters are considered simultaneously and therefore more precise guidelines and better understanding of the process behavior can be obtained. Qualitative and quantitative results presented in this paper will provide valuable insights for the design of new CO<sub>2</sub> capture plants. This study must be interpreted as a sensitivity analysis of the model parameters on the optimal designs. As one of a model result, a rank list of all the model parameters ordered according to their influence level on the proposed objective functions is obtained.

For a much better presentation and discussion of the results, the parameters will be grouped in three sets, depending on their characteristics. The first ones are related to the design and operating conditions (e.g. composition, temperature, pressure and flow-rate of flue gas and solvent streams, heat transfer coefficients, final pressure, among others). The second set corresponds to the physicochemical parameters which may also affect the results. For instance, a sensitivity analysis on these values is useful in order to conclude about the convenience of use fixed values or if these parameters must be replaced by correlations. Finally, the third set is related to the purchased equipment cost as well as the specific cost of the different utility requirements (steam, cooling water and electricity).

The paper is outlined as follows. Section 2 briefly describes the capture process and defines the problem statement. Section 3 introduces the mathematical model and the main assumptions. Section 4 and 5 present and discuss the results of different study cases. Finally, Section 6 presents the conclusions and future works.

## 2. Process description and problem statement

Fig. 1 illustrates a typical flow-sheet of the CO<sub>2</sub> capture process by chemical absorption. As shown, in the first section (I) the flue gas stream, which is previously cooled at absorption conditions, is delivered into the bottom of the absorption column by the blower [BLO]. A clean gas stream and a rich solvent stream are the result of the gas–liquid contact in the absorption section (II), where mass transfer with chemical reaction is developed. In Section 3 the rich solvent is heated while the lean solvent is cooled. The last fed the top of the absorber [ABS] while the hot rich solution is regenerated into the stripping section (IV), which is constituted by a regeneration column [STP], a condenser [CND] and a reboiler [REB]. The last process section includes compressor [COMP], coolers [IC] and CO<sub>2</sub> pumps [CO2P] in order to compress the concentrated CO<sub>2</sub> stream and deliver it for transport and storage.

There exist several trade-offs among the dimensions of columns [ABS] and [STP], the total heat transfer area involved by [AC], [ECO], [REB], [CND] and [IC], heating utility required (steam) by [REB], CO<sub>2</sub> emission level and electric power consumption by [COMP], [BLO], [AP] and [CO2P].

In this paper, the proposed optimization problem (OP) consists on the minimization of the specific total annual cost (sTAC) and can be formally stated as follows.

$$\text{To minimize : } \text{sTAC} = \frac{\text{TAC}}{G^{\text{out}} y_{\text{CO}_2}^{\text{out}}} \quad (\text{OF})$$

$$\text{Subject to : } \begin{aligned} h_j(\underline{x}) &= 0, & j &= 1, \dots, J \\ g_k(\underline{x}) &\leq 0, & k &= 1, \dots, K \end{aligned}$$

where  $\underline{x}$  denotes the vector of continuous variables such as heat duties, electricity consumption, dimensions of equipment, flow-rates, temperatures, compositions and pressures, which are simultaneously optimized.  $h_j(\underline{x})$  refers to equality constraints (mass, momentum and energy balances, investment and operating costs and correlations to compute physicochemical properties (see Table 1) and  $g_k(\underline{x})$  is a set of inequality constraints defined in order to circumscribe a feasible operating region. TAC refers to the total annual cost,  $G^{\text{out}}$  and  $y_{\text{CO}_2}^{\text{out}}$  are, respectively, the flow-rate and CO<sub>2</sub> molar fraction of the product stream (CO<sub>2</sub> concentrated stream). A detailed description of the mathematical model can be found in Mores et al. (2012a, 2012b, 2012c). Finally, the model parameters (known and fixed values) are listed from Table 2–4. Given the flue gas specification to be treated (flow-rate, temperature and composition), the goal in problem OP is to determine the optimal operating conditions (flow-rate, temperature and composition of each stream including cooling and heating utilities) and the size of each piece of equipment (heat transfer area required by economizers, coolers, condenser and reboiler, diameter and height of absorber and stripper, power of pumps, blowers and compressors and volume of MEA and H<sub>2</sub>O make-up tanks) in order to minimize the specific total cost (sTAC). At this point, it is necessary to introduce the following comments in regards to the cost-items considered to compute the TAC and to the CO<sub>2</sub> capture level (CL) involved in the objective function (OF).

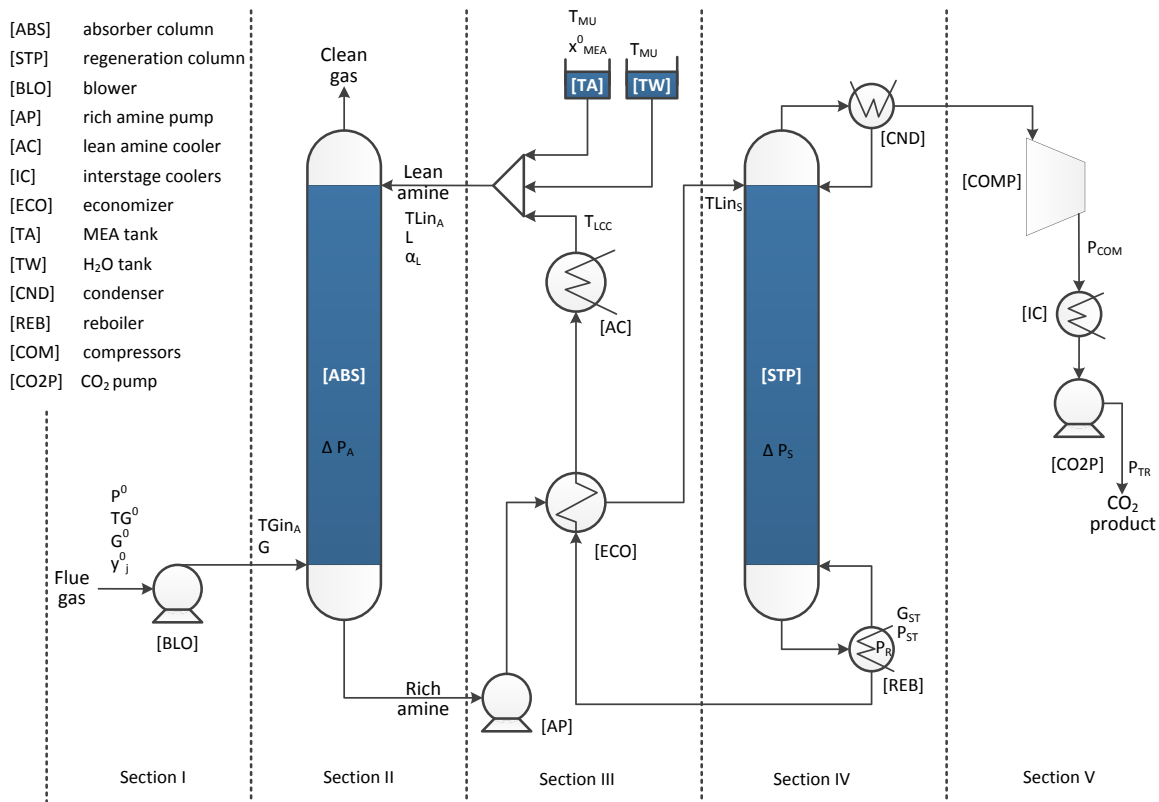


Fig. 1. Schematic diagram of the CO<sub>2</sub> capture process to be studied.

- The total annual cost (TAC) in OF is computed considering investment and operating costs (CAPEX and OPEX). It should be mentioned that, in several articles, OPEX does not include the cost related to the electricity supplied in mechanical devices (compressors, pumps and blowers) and the cost of the steam required to regenerate the solvent because they consider that electricity and steam are supplied by the power plant for which the CO<sub>2</sub> capture plant is coupled (Abu-Zahra et al., 2007a; Fisher et al., 2005; Rao and Rubin, 2006, 2002; Romeo et al., 2008). Nevertheless, in other articles both costs are included in the calculation of the OPEX (Karimi et al., 2011; Mores et al., 2012a; Nuchitprasittichai and Cremaschi, 2013). Thus, the optimal solutions will be different in both scenarios. Because of the fact that the CO<sub>2</sub> capture plant is always coupled to power plants, then the first proposal to compute the total cost seems to be more realistic than the second one. However, for the sake of generality and a more complete discussion of results both options are analyzed and discussed in two case studies.
- A target of 90% of CO<sub>2</sub> capture level (CL) is commonly assumed to produce an almost pure CO<sub>2</sub> stream. However, this CO<sub>2</sub> capture level is rarely justified (Mac Dowell and Shah, 2013; Rao and

Rubin, 2006). In this work, the CL is considered as an optimization variable and it is directly involved in the OF with the aim to obtain their optimum values. However, a minimum value of 80.0% was imposed. As will be presented later, in all of the optimization results considering ranges in typical operating conditions, the CL was higher than the lower bound. Certainly, the optimal CO<sub>2</sub> capture levels obtained varied from of 82.2 to 94.6%.

### 3. Mathematical model and assumptions

A previous mathematical model presented recently in Mores et al. (2012a, 2012b, 2012c) is used to solve the OP. The mentioned model was already verified with experimental data reported by other authors. Briefly, the model involves mass, momentum and energy balances. In addition, several correlations are used to represent the mass transfer phenomena. Table 1 lists all of the sources from where the correlations used in this paper have been taken. Section 3.1 and Section 3.2 summarize the model assumptions and the numerical values assumed for all of the parameters including also their justifications.

#### 3.1. Assumptions

The following modeling aspects are taken into account:

- The system frontiers are clearly defined in Fig. 1. As shown, the CO<sub>2</sub> transport and storage are not considered in the model. Similarly, the pretreatment of the flue gas which mainly consist in SO<sub>x</sub>, NO<sub>x</sub> and particulate matter removal and flue gas cooling, is also not included.

Table 1  
Sources used for correlations.

Item	Source
Column pressure drops	(Robbins, 1991)
Kinetic and equilibrium constants	(Aboudheir et al., 2003; Kucka et al., 2002; Liu et al., 1999)
Flooding gas velocity	(Leva, 1992)
Effective surface area, and mass transfer coefficients	(Onda et al., 1968)
CO <sub>2</sub> solubility in amine solution	(Greer, 2008; Liu et al., 1999)

**Table 2**  
Numerical values of the input data for design and operating conditions.

Parameter		Unit	Value
<i>Exhaust flue gas stream</i>			
Flow rate	$C^0$	[kmol/s]	8.0
Pressure	$p^0$	[kPa]	101.3
Inlet temperature (absorber bottom)	$T_{GinA}$	[K]	318.15
<i>Composition</i>			
CO <sub>2</sub>	$y^0_{CO_2}$	[molar fraction]	0.0422
H <sub>2</sub> O	$y^0_{H_2O}$	[molar fraction]	0.0845
O <sub>2</sub>	$y^0_{O_2}$	[molar fraction]	0.1166
N <sub>2</sub>	$y^0_{N_2}$	[molar fraction]	0.7567
<i>Absorption solvent</i>			
Temperature (absorber top)	$T_{LinA}$	[K]	313.15
Temperature (stripper top)	$T_{LinS}$	[K]	368.15
MEA concentration	$x^0_{MEA}$	[molar fraction]	0.115
Make-up temperature	$T_{MU}$	[K]	298.15
Available steam pressure	$P_{ST}$	[kPa]	375.00
Available cooling water temperature	$T_{CW}$	[K]	298.15
Reboiler pressure	$P_R$	[kPa]	165.0
CO <sub>2</sub> compression pressure	$P_{COM}$	[MPa]	7.3
Transport pressure	$P_{TR}$	[MPa]	15.5
<i>Heat transfer coefficients</i>			
Reboiler	$U_R$	[kW/m <sup>2</sup> K]	1.0813
Economizer	$U_{ECO}$	[kW/m <sup>2</sup> K]	0.7632
MEA cooler	$U_{AC}$	[kW/m <sup>2</sup> K]	0.7155
Condenser/intercoolers	$U_{CND}, U_{IC}$	[kW/m <sup>2</sup> K]	0.3871
Work equivalence factor	$f_{ext}$	–	0.25

- Physicochemical properties (densities, heat capacities, diffusivities, viscosities, reaction heats, surface tensions and latent heats) are assumed as constant values. In particular, solvent density is assumed to be equal to the water density at 298.15K while the rest is computed as an average of those results obtained by using correlations employed in previous works (Mores et al., 2012b, 2012c).
- The absorption and regeneration columns are randomly packed with ceramic Intalox saddles which have the following characteristics: 1) nominal diameter: 50 mm; 2) void fraction: 79%; 3) specific area: 118 m<sup>2</sup>/m<sup>3</sup> and, 4) dry packing factor: 121.4 m<sup>2</sup>/m<sup>3</sup>.
- The heights of both columns are computed using HTU–NTU concept and the diameters are determined by considering restrictions on the gas velocity. Precisely, the gas velocity can range between 60.0 and 85.0% of gas flooding velocity.
- The calculation of the heat transfer areas is based on the following hypothesis: 1) the overall heat transfer coefficients and heat capacities are constant throughout the exchanger. 2) Heat losses and pressure drops are negligible. 3) Geometry and fouling of the heat exchanger are not taken into account.

**Table 3**  
Model parameters assumed for the stream properties.

Physicochemical properties			
<i>Liquid streams</i>			
Molar density	$\rho^L$	[kmol/m <sup>3</sup> ]	55.56
Surface tension	$\sigma$	[N/m]	6.0E-02
Heat capacity	$C_p^L$	[kJ/mol]	8.0E-02
Diffusivity	$D^L$	[m <sup>2</sup> /s]	3.5E-09
Viscosity	$\mu^L$	[kg/m s]	1.0E-03
Reaction heat	$\Delta H_{RX}$	[kJ/mol]	80.00
Latent heat of water	$\lambda_{H_2O}$	[kJ/mol]	44.00
Latent heat of MEA	$\lambda_{MEA}$	[kJ/mol]	60.00
<i>Gas stream</i>			
H <sub>2</sub> O diffusivity	$D^G_{H_2O}$	[m <sup>2</sup> /s]	3.0E-05
CO <sub>2</sub> diffusivity	$D^G_{CO_2}$	[m <sup>2</sup> /s]	2.0E-05
Heat capacity	$C_p^G$	[kJ/mol]	3.0E-02
Viscosity	$\mu^G$	[kg/m s]	1.6E-05
Compressibility factor	$z$	–	1.00
Fugacity coefficient	$\phi$	–	1.00

- The compression train configuration comprises four compression stages with intercooling to 318.15 K. The design is based on a 450 K maximum temperature limit and a maximum compression ratio of 3. It is assumed that the stages have equal compression ratios, which are considered as optimization variables.
- The total annual cost used includes capital and operating costs.
- Six-tenth rule is used to compute the cost of each individual piece of equipment (absorber and stripper columns, heaters, coolers, blowers, compressors and pumps).
- MEA make-up, H<sub>2</sub>O make-up, cooling water, electricity and steam costs are considered to compute variable operating costs.
- Electricity and steam costs, which depend on the fuel price, are computed by means of correlations suggested by Ulrich and Vasudevan (2006).
- The total energy penalties include the equivalent electric requirement and the electric power required by blowers, compressors, amine pumps and CO<sub>2</sub> pumps. The power losses due to steam extraction depend on the steam and returning condensate conditions as well as the turbine efficiency. In this work, the thermal energy penalties expressed as equivalent electric requirement ( $W_{ext}$ ) is defined as 25.0% of the regeneration heat ( $Q_R$ ) as is suggested in Rao and Rubin (2006, 2002).

### 3.2. Numerical values of the used input parameters

#### 3.2.1. Design and operating parameters

Numerical values taken from the specific literature were assumed for the design and operating parameters. Exhaust flue gas composition arises from considering ideal combustion of natural gas while the flue gas flow-rate is lower than a maximum permissible value given by a maximum absorber diameter which is defined as 12.8 m by Chapel et al. (1999). On the other hand, in order to consider a feasible operating region, the values assumed for solvent (concentration and temperature) and working pressures at different points of the process (reboiler, compressor) have been taken from the literature (Abu-Zahra et al., 2007b; Chapel et al., 1999; Fisher et al., 2005; Mac Dowell and Shah, 2013; Oyekan and Rochelle, 2009, 2007; Rao and Rubin, 2002; among others). The most common value for the solvent concentration and the inlet solvent temperature at the absorber were considered which are 30% w/w of MEA and 313.15 K, respectively.

The exhaust flue gas exits the HRSG (Heat Recovery Steam Generator) at high temperature and is usually cooled between 313.15 and 323.15 K (Fisher et al., 2005; Karimi et al., 2011; Rao and Rubin, 2006, 2002). In this case, this temperature is fixed at 318.15 K.

Typical values suggested in the literature for the reboiler pressure range from 130 to 200 kPa (Abu-Zahra et al., 2007b; Oyekan and Rochelle, 2009, 2007; Rao and Rubin, 2002). In this work, the value of pressure is fixed at 165 kPa.

In regard to the compression pressure, several authors suggest that the CO<sub>2</sub> concentrated stream should be compressed up to 8.6 MPa and then pumped to 14.0 MPa (Fisher et al., 2005; Rao and Rubin, 2006, 2002). Other authors have reported compression pressures between 6 and 8.6 MPa while the CO<sub>2</sub> final pressures required for transport vary from 11 to 20 MPa (Amrollahi et al., 2011; Bernier et al., 2010; Eslick and Miller, 2011; Lee et al., 2013; Sipöcz and Tobiesen, 2012; Ystad et al., 2012). The mentioned parameters may have a significant influence not only on the specific cost but also on the overall process efficiency. For instance, they are strongly related to the acquisition cost of compressors/CO<sub>2</sub> pumps and electric energy supply for these mechanical devices. In particular, the product pressure strictly

**Table 4**  
Model parameters used to compute the cost-items (specific costs).

Equipment	Unit		Cost	Characteristics
CO <sub>2</sub> pump	[MUSS/kW]	C <sub>CO2P</sub>	0.9801	Centrifugal, CS
Vessel of absorber/stripper	[MUSS/m <sup>2</sup> ]	C <sub>VA</sub> , C <sub>VS</sub>	0.0640	Vertical vessel, SS
Compressor	[MUSS/kW]	C <sub>COM</sub>	0.0424	Centrifugal, SS
Reboiler	[MUSS/m <sup>2</sup> ]	C <sub>R</sub>	0.0149	Kettle, SS-SS
Blower	[MUSS/kW]	C <sub>BLO</sub>	0.0135	Centrifugal (turbo), CS
Economizer	[MUSS/m <sup>2</sup> ]	C <sub>ECO</sub>	0.0104	Floating head, SS-SS
Packing column	[MUSS/m <sup>3</sup> ]	C <sub>PA</sub> , C <sub>PS</sub>	0.0095	Intalox Saddles, ceramic
Condenser, MEA cooler, intercoolers	[MUSS/m <sup>2</sup> ]	C <sub>CND</sub> , C <sub>AC</sub> , C <sub>IC</sub>	0.0072	Floating head, CS-SS
MEA pump	[MUSS/kW]	C <sub>AP</sub>	0.0058	Centrifugal, SS
Tank	[MUSS/m <sup>3</sup> ]	C <sub>TA</sub> , C <sub>TW</sub>	0.0045	Floating roof, CS
<b>Raw materials and utilities</b>				
Cooling water	[US\$/tn]	C <sub>W</sub>	0.0703	
MEA make-up	[US\$/tn]	C <sub>MEA</sub>	1858.4	
Fuel	[US\$/GW]	C <sub>FUEL</sub>	3.3175	
Man power cost	[MUSS/y]	C <sub>MP</sub>	0.6633	
<i>Other cost parameters (Abu-Zahra et al., 2007a)</i>				
Lang factor			5	
Interest rate	[%]		8	
Lifetime	[y]		25	
Operating hours	[h/y]		8000	
Operators	[op/shift]		3	
Operator salary	[US\$/op. y]		30,000	

depends on the final disposal requirements (pipelines transport and storage). For the local sensitivity analyses, 7.3 and 15.5 MPa are selected as fixed values for the compression and transport pressures, respectively.

Low pressure steam is required by the reboiler of the amine regeneration section. If the steam is supplied by a power generation plant (steam turbine cycle), its quality will depend on the extraction points (HRSG, Intermediate Pressure/Low Pressure –IP/LP– crossover pipe). There are several trade-offs between amount and quality of steam, heat transfer area required in the reboiler and power plant efficiency. For instance, the amount of steam required to regenerate the amine decreases as the steam quality increases, but the power plant efficiency decreases. Additionally, in order to avoid solvent degradation as well as corrosion problems, an upper bound for the saturation steam pressure should be considered and suggested values ranged from 300.0 to 450.0 kPa (Amrollahi et al., 2011; Bernier et al., 2010; Lee et al., 2013; Rao and Rubin, 2002; Ystad et al., 2012). In this work, steam extraction pressure is set to 375.0 kPa at saturated steam conditions.

On the other hand, for a given level of amine regeneration on the stripper unit, higher solvent temperatures could lead to reduce the energy required in the reboiler, which implies lower efficiency penalties on the power plant. Typical values reported by several authors range from 363.15 to 373.15 K (Bernier et al., 2010; Lee et al., 2013; Mac Dowell and Shah, 2013). 368.15 K is the selected value to do the proposed local sensitivity analysis.

Table 2 summarizes the numerical values assumed for each one of the design and operating parameters.

### 3.2.2. Physicochemical parameters

The physicochemical properties of each process stream (densities, diffusivities, viscosities, heat capacities, reaction heats, latent heats, surface tensions) are required to describe the mass transfer phenomena. As was mentioned earlier, there are a number of uncertainties in the correlations used and limitations in the range for which they are valid. In this work, for each one of the properties listed in Table 3, is assumed an average value of those computed by using different correlations reported in the literature at various operating conditions.

### 3.2.3. Numerical values for the parameters related to the investment and operating costs

Finally, the cost model used to compute the investment and operating costs also plays an important role to perform a cost-effectiveness analysis of any chemical or industrial process. In this regards, it should be mentioned that more than one correlation can be found in the open literature to compute the capital cost of a same process unit. All of the correlations depend on several characteristics such as the type of equipment and construction material as well as the associated uncertainties. In this paper, correlations taken from Henao (2010); Matche (2007); McCollum and Ogden (2006) and Seider (2009), are used for the calculation of investment. Data assumed to compute raw material and utility costs are taken from Rao and Rubin (2006, 2002) and Ulrich and Vasudevan (2006). Details of the characteristics assumed for each process-unit, parameters and their corresponding numerical values are summarized in Table 4.

## 4. Results

As mentioned earlier, the proposed optimization problem consists of determining the optimal operating conditions and size of each process-unit that minimize the specific total annual cost sTAC (US\$/tn of CO<sub>2</sub> captured). For a more general discussion, two different optimization problems, which only differ in the cost-items considered to compute the total annual cost TAC are investigated. In the first optimal design the calculation of the sTAC, objective function hereafter named as OF1, includes the costs related to the water and amine make-ups, cooling water and the investments of the process units. In the second optimal design the calculation of the sTAC, objective function hereafter named as OF2, includes the costs involved in the OF1 plus the cost of the steam supplied in the reboiler and the cost of the total electricity required by the pumps, blowers and compressors.

Once the optimal solutions were obtained, local and global sensitivity analyses are then performed to identify which are the model parameters that significantly affect the total specific cost and the optimal design (sizes and operating conditions) when the OF1 and OF2 are investigated.

#### 4.1. Optimal designs obtained by minimizing the sTAC for Case Study 1 and 2

The total investment (CAPEX) and total operating cost (OPEX) including the optimal distribution of the cost-items obtained for OF1 and OF2 are summarized in Table 5. Additionally, the corresponding optimal operating conditions and process unit sizes are listed in Table 6.

#### 4.2. Local sensitivity analyses

The local sensitivity analysis is based on the relative marginal values (RMV<sub>j</sub>) defined by Eq. (1):

$$RMV_j = \frac{\partial OF / OF}{\partial P_j / P_j} = M \left( \frac{P_j}{OF} \right) \quad (1)$$

where M refers to the marginal parameter. As indicated in Eq. (1), RMV computes the local gradients of the objective function, in regard to infinitesimal parameter variation ( $P_j$ ) and its sign indicates the direction of the change of the objective function. The RMV of each parameter is additionally provided by GAMS as a result and can be successfully applied for sensitivity analysis in several processes (Mussati et al., 2006; Druetta et al., 2013, 2014).

Tables 7 and 8 list the relative marginal values of each one of the parameters used as input data (Tables 2–4) obtained for the Case Study 1 and Case Study 2, respectively. The RMV are arranged according to their influences on the objective function, beginning with the highest value. The parameters with RMVs lower than 0.01 are not included. For a more complete discussion, the RMV listed in Tables 7 and 8 are then compared by categories from Fig. 2–4. Precisely, Fig. 2 includes the RMVs of the unit costs and Figs. 3 and 4 include the RMVs of the design/operating conditions and physicochemical properties, respectively.

#### 4.3. Global sensitivity analysis

For nonlinear models, the values of the KKT multipliers reported by GAMS are based on a linearization around the optimal solution

and therefore they are only valid for local sensitivity analyses. Thus, the rank lists presented in Tables 7 and 8 are only useful to identify the most sensitive parameters in the “neighborhood” of the current optimal solutions, but they do not are valid for a wider range of variation. In order to get a more accurate and complete picture, a global sensitivity analysis is then required. In order to perform this, the operating parameters  $P_j$  with higher RMV values are varied from  $-2.5$  to  $+2.5\%$  of the nominal value while the remaining parameters are kept constant. Precisely, Table 9 presents the results of the percentage changes on the sTAC, CAPEX, OPEX and CL, Tables 10 and 11 report the corresponding changes on the design variables and utility requirements, respectively. The results included in these tables correspond for  $-2.5$  and  $+2.5\%$  of variations from the nominal values. Hereafter, “nominal value” will be referred as NV. In addition, the analysis is also extended for values of parameters that are widely used by other authors and reported in the literature, described in Section 3.2.1 and summarized in Table 12. The results are plotted in Fig. 5 for OF1 and in Fig. 6 for OF2 and they will be discussed in detail in the Section 5.3.

## 5. Discussion of results

### 5.1. Optimal results obtained by minimizing the sTAC for Case Study 1 and Case Study 2

Table 5 illustrates how the total annual cost is distributed in operating costs (OPEX) and investments (CAPEX) for the Case Study 1 (OF1) and Case Study 2 (OF2). As expected, the results reveal that the specific total annual cost sTAC obtained by OF2 is much higher than that obtained by OF1 as consequence of the high increase of the operating cost because of the inclusion of the steam and electricity costs in computing TAC. The trade-offs existing between the TAC and the amount of the captured CO<sub>2</sub> in the Case Study 2 lead to a CO<sub>2</sub> capture level (CL) of 89.1% (Table 6) involving a TAC of 44.9 MUS\$/y while in Case Study 1 the CL increases up to 93.7% involving a TAC of 24.6 MUS\$/y. Thus, the CL in OF1 increases in about 4.6% and the TAC decreases in about 45.2% when compared with OF2. As listed in Table 5, the contribution of the CAPEX in the TAC computed by the two OFs is practically similar: 120.2 MUS\$ in OF1 and 116.5

**Table 5**  
Optimal cost distribution obtained for OF1 and OF2.

			OF1	OF2
Specific total annual cost (sTAC)		[US\$/ton CO <sub>2</sub> ]	61.2	117.8
Total annual cost (TAC)		[MUS\$/y]	24.6	44.9
Total investment (CAPEX)	1.35 IFC	[MUS\$]	120.2	116.5
Equipment acquisition cost (C <sub>inv</sub> )		[MUS\$]	24.1	23.3
Total direct manufacturing cost (DMC)	2.688 C <sub>inv</sub>	[MUS\$]	64.8	62.8
Total indirect manufacturing cost (IMC)	0.375 DMC	[MUS\$]	24.3	23.5
Investment on fix capital (IFC)	DMC + IMC	[MUS\$]	89.1	86.3
Working investment	0.25 IFC	[MUS\$]	22.3	21.6
Start-up cost + initial MEA cost	0.10 IFC	[MUS\$]	8.9	8.6
Total operating cost (OPEX)	0.104 IFC + 2.445 C <sub>MP</sub> + 1.050C <sub>RM</sub>	[MUS\$/y]	13.3	34.0
Raw material and utility cost (C <sub>RM</sub> )		[MUS\$/y]	2.3	22.3
Cooling water		[MUS\$/y]	0.9	0.9
MEA make up		[MUS\$/y]	1.3	1.3
Electricity		[MUS\$/y]	–	9.4
Low pressure steam		[MUS\$/y]	–	10.7
Man power cost (C <sub>MP</sub> )		[MUS\$/y]	0.7	0.7
Total production cost		[MUS\$/y]	9.9	29.7
Fixed charge	0.030 IFC	[MUS\$/y]	2.7	2.6
Direct production cost	0.045 IFC + 1.400 C <sub>MP</sub> + 1.000 C <sub>RM</sub>	[MUS\$/y]	7.2	27.1
Plant overead cost	0.024 IFC + 0.780 C <sub>MP</sub>	[MUS\$/y]	2.7	2.6
General expenses	0.005 IFC + 0.265 C <sub>MP</sub> + 0.050 C <sub>RM</sub>	[MUS\$/y]	0.7	1.7

**Table 6**  
Main optimal design and operating variables obtained for OF1 and OF2.

Optimal design and operating variables			OF1	OF2
CO <sub>2</sub> captured		[tn/y]	400,892	381,322
Overall CO <sub>2</sub> recovery	CL	[%]	93.7	89.1
Absorber CO <sub>2</sub> recovery	$\eta_A$	[%]	96.4	93.5
Regeneration stage CO <sub>2</sub> recovery	$\eta_R$	[%]	56.0	56.6
Flue gas temperature	TG <sup>0</sup>	[K]	303.15 <sup>a</sup>	304.51
Lean amine CO <sub>2</sub> loading	$\alpha_L$	[mol CO <sub>2</sub> /mol MEA]	0.1911	0.1931
Lean amine temperature	T <sub>LCC</sub>	[K]	313.61	313.64
Liquid gas flow rate ratio, mass base	L/G	[-]	1.2	1.1
Absorber pressure drop	$\Delta P_A$	[kPa]	15.3	13.8
Stripper pressure drop	$\Delta P_S$	[kPa]	2.2	3.6
Packing volume of absorber	V <sub>A</sub>	[m <sup>3</sup> ]	1686	1456
Packing volume of stripper	V <sub>S</sub>	[m <sup>3</sup> ]	69	113
Surface area of absorber	AS <sub>A</sub>	[m <sup>2</sup> ]	2306	2184
Surface area of stripper	AS <sub>S</sub>	[m <sup>2</sup> ]	324	355
Reboiler heat transfer area	A <sub>R</sub>	[m <sup>2</sup> ]	2566	2211
Condenser heat transfer area	A <sub>CND</sub>	[m <sup>2</sup> ]	4065	4176
Economizer heat transfer area	A <sub>ECO</sub>	[m <sup>2</sup> ]	2664	2508
MEA cooler heat transfer area	A <sub>AC</sub>	[m <sup>2</sup> ]	2395	2115
Intercoolers heat transfer area	A <sub>IC</sub>	[m <sup>2</sup> ]	70	45
Volume of water tank	V <sub>TW</sub>	[m <sup>3</sup> ]	962	915
Volume of MEA tank	V <sub>TA</sub>	[m <sup>3</sup> ]	16	15
Amine pump work	W <sub>AP</sub>	[kW]	14.5	14.0
Blower work	W <sub>BLO</sub>	[kW]	3848.2	3499.9
CO <sub>2</sub> pump work	W <sub>CO2P</sub>	[kW]	241.1	229.3
Compression work	W <sub>COM</sub>	[kW]	5004.7	4704.3
Compression ratio	cr	–	2.6	2.6
Specific reboiler duty	$\dot{Q}_R$	[GJ/tn CO <sub>2</sub> ]	5.2	4.8
Total equivalent work	W <sub>e</sub>	[kWh/kg CO <sub>2</sub> ]	0.5425	0.5089
Steam extraction (equivalent work)	W <sub>ext</sub>	[kW]	18075.0	15808.5
Total mechanical work	W	[kW]	9108.4	8447.5
Cooling water consumption	L <sub>CW</sub>	[kg/s]	453.1	415.0
Steam flow-rate	G <sub>ST</sub>	[kg/s]	33.8	29.5
MEA make-up flow rate	L <sub>A</sub>	[kg/s]	0.025	0.037
Water make-up flow rate	L <sub>W</sub>	[kg/s]	11.136	10.592

<sup>a</sup> Lower bound.

MUS\$ in OF2. By comparing the results listed in Table 6, they reveal that in order to minimize the sTAC computed by OF2, the model tends to decrease the sizes of all pieces of equipment (absorber, reboiler, economizer, tanks and coolers) except the size of the stripper (surface area and packing volume) and condenser. However, despite of this, the CAPEX only decreases about 3.1% in comparison to the OF1. On the other hand, the contribution of the total operating cost (OPEX) in OF2 and OF1 are, respectively, 34.0 and 13.3 MUS\$/y representing about 54.1 and 75.7% of the TAC. The reason of this can be seen by comparing the results presented in Table 6, which lists the corresponding optimal operating conditions and sizes of each process unit. As shown, despite the fact that the OPEX computed in OF2 is much more higher than in OF1, the requirements of the electricity, steam and water requirements (W, G<sub>ST</sub> and L<sub>CW</sub>) in OF2 are lower compared to OF1 (7.3, 12.7 and 8.4%, respectively), which clearly confirm that the inclusion of these costs is the main reason of the OPEX increase.

An interesting observation to highlight from the obtained optimization results reveal is that even when a great number of input parameters have been assumed in the developed model, the optimal operating variables (rich and lean CO<sub>2</sub> loadings, ratio between the solvent and flue gas flow-rate, specific reboiler duty, cooling water consumption, electric and thermal penalties, etc.) obtained for both OFs are in accordance with those obtained by other authors. In fact, the obtained values are in the ranges of those reported by Abu-Zahra et al. (2007b), Alie et al. (2005), Amrollahi et al. (2012), Esmaili and Roozbehani (2014), Fisher et al. (2005), Mangalapally and Hasse (2011), Ystad et al. (2012), in spite of the differences on process configurations and operating conditions like

CO<sub>2</sub> recovery, final disposal pressure, compression pressure, amine flow-rate, inlet gas temperature, among others.

## 5.2. Local sensitivity analyses

The relative marginal values of each one of the parameters used as input data (Tables 2–4) are listed in Tables 7 and 8. They are arranged according on how they affect the objective function, beginning from the parameter that has the largest effect. For a more clear discussion of results, the RMV are then classified and compared by categories from Fig. 2–4. Precisely, Fig. 2 refers to the unit costs, Fig. 3 presents the design and operating conditions and finally, Fig. 4 compares the physicochemical properties. The parameters with RMVs lower than 0.01 are not included.

### 5.2.1. Influence of the unit costs on the sTAC

In this study, it is assumed that due to the fact that a stand-alone CO<sub>2</sub> capture is here addressed, the electricity and steam required are provided by the power plant to which the CO<sub>2</sub> capture plant is coupled. Taking into account this, the electricity and steam costs are computed in OF2 in terms of the fuel price using the correlation proposed by Ulrich and Vasudevan (2006) as already described earlier in the Section 3.1. The fuel price volatility is an important aspect that may have a strong influence on the optimal design and its inclusion in the sensitivity analysis is needed. Here, for simplicity, the fuel price is analyzed in a deterministic manner.

As expected, Fig. 2 clearly shows that the fuel cost exhibits the highest RMV indicating that it has the most significant influence on the OF2 in comparison with the rest of unit costs. It can be also



**Table 7**  
Local sensitivity analysis for OF1.

Parameter		RMV
CO <sub>2</sub> molar fraction (flue gas stream)	$y_{CO_2}^0$	-0.6490
Cooling water temperature	$T_{CW}$	0.5526
Solvent temperature (top of stripper)	$T_{Lin_S}$	0.5438
Solvent temperature (top of absorber)	$T_{Lin_A}$	-0.4787
Flue gas flow rate	$G^0$	-0.4296
Flue gas pressure	$p^0$	-0.4120
Gas temperature (absorber bottom)	$T_{Gin_A}$	-0.3005
Compressor cost	$C_{COM}$	0.2439
Absorber vessel cost	$C_{VA}$	0.2313
Fugacity coefficient	$\varphi$	-0.1475
Reboiler pressure	$P_R$	-0.1369
MEA concentration	$x_{MEA}^0$	-0.0983
Density (liquid stream)	$\rho^L$	-0.0946
Stripper vessel cost	$C_{VS}$	0.0712
Surface tension	$\sigma$	0.0701
Blower cost	$C_{BLO}$	0.0663
Man power cost	$C_{MP}$	0.0661
Compressibility factor	$z$	0.0649
Heat capacity (liquid stream)	$Cp^L$	0.0608
MEA make-up cost	$C_{MEA}$	0.0576
Reboiler cost	$C_R$	0.0574
Reaction heat	$\Delta H_{RX}$	0.0517
Steam pressure	$P_{ST}$	-0.0471
Diffusivity (liquid stream)	$D^L$	-0.0443
Economizer cost	$C_{ECO}$	0.0410
Cooling water cost	$C_W$	0.0402
Condenser cost	$C_{CND}$	0.0366
CO <sub>2</sub> compression pressure	$P_{COM}$	0.0348
Heat transfer coefficient of reboiler	$U_R$	-0.0345
Cost of packing material (absorber)	$C_{PA}$	0.0285
MEA cooler cost	$C_{AC}$	0.0266
Heat transfer coefficient of economizer	$U_{ECO}$	-0.0246
Diffusivity of water (gas stream)	$D_{H_2O}^G$	-0.0231
Heat transfer coefficient of condenser	$U_{CND}$	-0.0219
H <sub>2</sub> O latent heat	$\lambda_{H_2O}$	0.0191
Transport pressure	$P_{TR}$	0.0164
Heat transfer coefficient of MEA cooler	$U_{AC}$	-0.0160
CO <sub>2</sub> pump cost	$C_{CO_2P}$	0.0145
Viscosity (gas stream)	$\mu^G$	0.0137
Tank cost	$C_{TW}, C_{TA}$	0.0104

noted that the cost of MEA make-up is more influential than the cost of the cooling water. In addition, the two objective functions (OF1 and OF2) are also significantly influenced by the unit costs related to the investments of the compressors and absorber vessel (high RMV values). Also, for both OFs it is observed that the influence of the column vessel cost (absorber and stripper) is higher than the packing cost. This result is in accordance with those reported by Abu-Zahra et al. (2007a), Karimi et al. (2011), Romeo et al. (2008), among others. On the other hand, the influence of the investment cost parameters in OF2 is lower than in OF1. Indeed, each marginal value is approximately 50% of the obtained value when OF1 is minimized. Moreover, the equipment acquisition cost reduction is reached by the decrease of the majority of the process-unit sizes (absorber column volume, exchange areas of coolers and heaters, tank volumes and power of mechanical devices).

### 5.2.2. Influence of design and operating parameters on the sTAC

This section shows how the OF1 and OF2 are influenced by the design and operating process parameters. From Fig. 3 it is observed that temperatures of the process streams have greater RMV than the operating pressures. In fact, OF1 and OF2 are significantly affected by the cooling water temperature and the solvent temperatures in both columns (absorber and regenerator), followed by the flue gas temperature, reboiler pressure and MEA concentration. Finally, the two OFs are much less affected by the steam pressure,

**Table 8**  
Local sensitivity analysis for OF2.

Parameter		RMV
Flue gas pressure	$p^0$	-0.7998
CO <sub>2</sub> molar fraction (flue gas stream)	$y_{CO_2}^0$	-0.4887
Cooling water temperature	$T_{CW}$	0.3159
Fuel cost	$C_{FUEL}$	0.3064
Flue gas flow rate	$G^0$	-0.2297
Solvent temperature (top of absorber)	$T_{Lin_A}$	-0.2195
Solvent temperature (top of stripper)	$T_{Lin_S}$	-0.1919
Gas temperature (absorber bottom)	$T_{Gin_A}$	0.1826
Reaction heat	$\Delta H_{RX}$	0.1481
Fugacity coefficient	$\varphi$	-0.1362
Compressor cost	$C_{COM}$	0.1285
Reboiler pressure	$P_R$	-0.1268
Absorber vessel cost	$C_{VA}$	0.1224
Density (liquid stream)	$\rho^L$	0.1014
Heat capacity (liquid stream)	$Cp^L$	0.0788
Surface tension	$\sigma$	0.0801
H <sub>2</sub> O latent heat	$\lambda_{H_2O}$	0.0650
MEA concentration	$x_{MEA}^0$	-0.0621
Diffusivity (liquid stream)	$D^L$	-0.0505
Transport pressure	$P_{TR}$	0.0504
Compressibility factor	$z$	0.0470
Stripper vessel cost	$C_{VS}$	0.0411
Man power cost	$C_{MP}$	0.0361
Blower cost	$C_{BLO}$	0.0343
CO <sub>2</sub> compression pressure	$P_{COM}$	0.0319
Heat capacity (gas stream)	$Cp^G$	0.0300
MEA make-up cost	$C_{MU}$	0.0299
Reboiler cost	$C_R$	0.0287
Diffusivity of water (gas stream)	$D_{H_2O}^G$	-0.0245
Economizer cost	$C_{ECO}$	0.0216
Condenser cost	$C_{CND}$	0.0203
Cooling water cost	$C_W$	0.0201
H <sub>2</sub> O molar fraction (flue gas stream)	$y_{H_2O}^0$	0.0182
Heat transfer coefficient of reboiler	$U_R$	-0.0172
Viscosity (liquid stream)	$\mu^L$	-0.0152
Viscosity (gas stream)	$\mu^G$	0.0148
Cost of packing material (absorber)	$C_{PA}$	0.0142
MEA cooler cost	$C_{AC}$	0.0135
Heat transfer coefficient of economizer	$U_{ECO}$	-0.0130
Heat transfer coefficient of condenser	$U_{CND}$	-0.0122

CO<sub>2</sub> compression and CO<sub>2</sub> final pressures as well as the values of heat transfer coefficients.

From the results illustrated in Fig. 3 and the RMV listed in Tables 7 and 8, the following trends have been observed:

- If the cooling water temperature (RMV > 0) increases the driving force for heat transfer decreases resulting in higher heat transfer area and water demand and therefore higher investment and operating costs.
- It is widely accepted and the specific literature suggests that the solvent temperature ( $T_{Lin_A}$ ) should be as low as possible to increase the absorption rate (which means improve the absorption efficiency). However, when the entire process is optimized considering the total investment (CAPEX) and total operating cost (OPEX) in the two objective functions, the obtained negative relative marginal values reveal that the increase of the  $T_{Lin_A}$  leads to reduce the sTAC at expense of decreasing the CL as well as CAPEX and OPEX.
- The influence of the rich solvent temperature ( $T_{Lin_S}$ ) is different for OF1 and OF2. As will be clearly discussed in the Section 5.3.3, the increase of  $T_{Lin_S}$  leads to the following effects: 1) TAC increases faster than the decrease of CL, and consequently the sTAC increases when OF1 is minimized; 2) both, TAC and CL diminishes in order to reduce sTAC when the OF2 is minimized. Similar qualitative conclusions are also obtained for the flue gas temperature ( $T_{Gin_A}$ ).

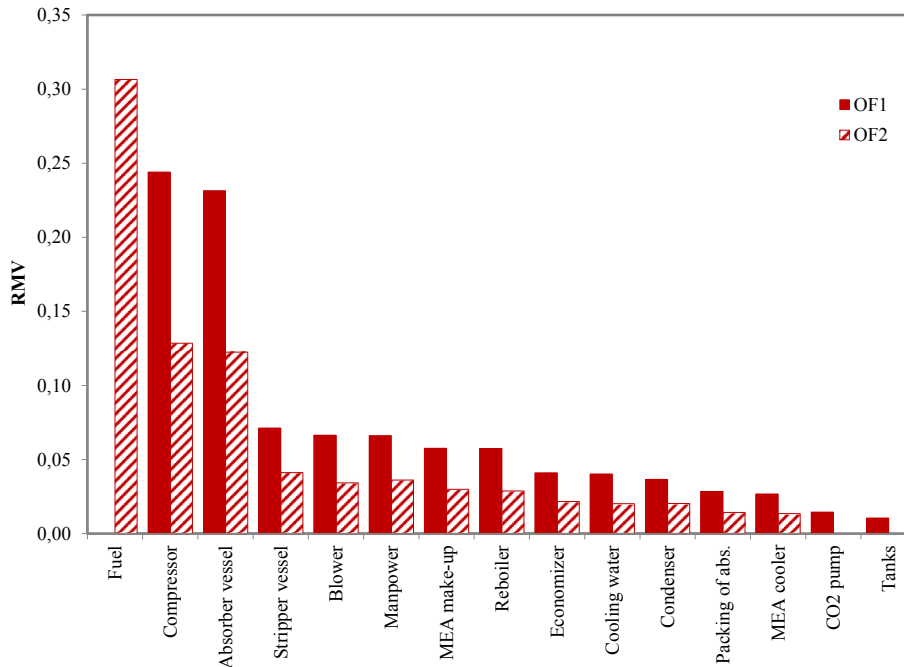


Fig. 2. Relative marginal values obtained for the specific costs.

- As expected, as the reboiler pressure increases ( $RMV < 0$ ) and the compression and final pressures decrease ( $RMV > 0$ ), the STAC decreases because of the reduction of both the electricity required by compressors and the external heating utility required in the reboiler. However, serious degradation rates and corrosion problems can appear if the reboiler operates at high pressure, aspects that were not included in the mathematical model.
- For OF1, the steam pressure  $P_{ST}$  has a negative RMV indicating that the total annual cost per unit of  $CO_2$  captured decreases with the increase of this parameter. This is caused by the

reduction of the sizes of the most of the process units (e.g. volume of columns and reboiler, economizer and MEA cooler areas, among others). However, as it was mentioned earlier, there are technological constraints like maximum temperatures and pressures to reduce amine degradation and corrosion problems, which limit the value of the steam pressure (temperature). However, for OF2, this parameter has a positive sign. It can be explained by the fact that the steam price is computed in terms of the steam pressure and the fuel cost, resulting in a cost rise with the increase of the fuel price or the steam pressure. Then, for the cost set adopted in this work and considering

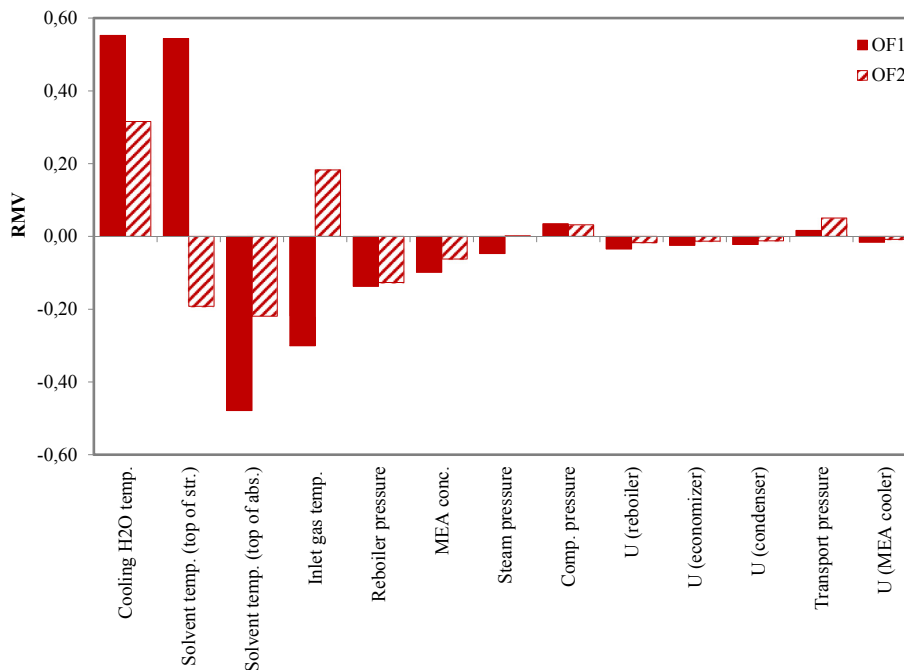


Fig. 3. Relative marginal values obtained for the design and operating variables.

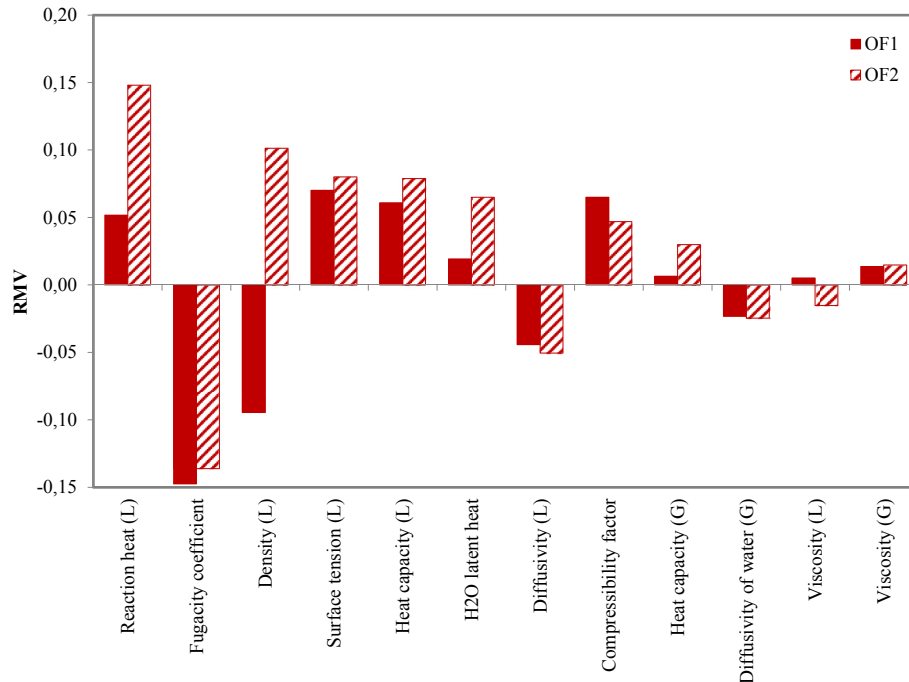


Fig. 4. Relative marginal values obtained for the stream properties.

that the fuel price has the greatest RMV, the influence of the steam pressure on the OF2 is practically negligible ( $RMV < 0.01$ ) in the “neighborhood” of the NV. However, as will be discussed later in the global sensitivity, its effect is much more significant for a wide range of values that includes values suggested by other authors.

- The solvent concentration ( $x_{MEA}^0$ ) has a negative relative marginal value. Therefore, its increase improves the absorption rate and decreases the amine solvent flow-rates resulting in a lower sTAC. However, higher concentrations may cause serious corrosive problems and MEA degradation, similarly to that described above for the reboiler pressure.
- As the pressure of flue gas stream coming from the power plant ( $P^0$ ) increases, the absorber pressure drop decreases resulting in lower blower cost. Also, the increase of the  $CO_2$  concentration ( $y_{CO_2}^0$ ) and/or the flue gas flow-rate ( $G^0$ ), which implies a greater quantity of  $CO_2$  available to be captured, positively impacts on the minimization of the sTAC since the increase of CL is faster than the increase of TAC. However, it should be mentioned

that the flue gas specification (pressure, flow-rate and composition) cannot be easily changed because they are defined by the power generation section, except if the process configuration is modified, e.g. if exhaust gas recirculation to the gas turbine is considered. Such analysis is out of the scope of this paper.

- As it is also expected, the results show that the increase of the heat transfer coefficients (U) has a positive effect on the reduction of sTAC as a consequence of the lower heat transfer area requirements. The relative marginal values decrease in the following order: reboiler, economizer, condenser and MEA cooler. Similar qualitative conclusions are obtained for each heat exchanger cost.

### 5.2.3. Influence of fixed values of physicochemical properties on the sTAC

Fig. 4 shows that the reaction heat  $\Delta H_{RX}$  and the fugacity coefficients are the most important parameters related to the liquid and gas phases and they affect the OF2 in an opposite direction but

Table 9

Global sensitivity analysis. Percentage change of the cost components when operating conditions are  $\pm 2.5\%$  of their nominal values.

	sTAC		CAPEX		OPEX		TAC		CL		
	OF1	OF2	OF1	OF2	OF1	OF2	OF1	OF2	OF1	OF2	
TGin <sub>A</sub> [K]	-2.5	7.503	6.842	-3.408	-4.651	-1.724	-3.932	-2.497	-4.106	-9.301	-10.248
	+2.5	0.185	0.458	1.235	0.234	0.932	0.410	1.071	0.367	0.885	-0.090
TLin <sub>A</sub> [K]	-2.5	1.560	0.747	1.298	1.423	1.841	0.749	1.592	0.913	0.031	0.165
	+2.5	-0.874	-0.381	-1.163	-1.167	-0.800	-0.308	-0.967	-0.517	-0.094	-0.136
TLin <sub>S</sub> [K]	-2.5	-0.977	1.000	-0.956	-0.759	-0.685	2.131	-0.809	1.429	0.169	0.425
	+2.5	2.233	0.071	2.316	2.410	1.881	-0.734	2.081	0.030	-0.149	-0.041
P <sub>R</sub> [kPa]	-2.5	0.356	0.327	0.306	0.327	0.307	0.231	0.306	0.255	-0.049	-0.072
	+2.5	-0.330	-0.306	-0.282	-0.269	-0.285	-0.197	-0.284	-0.214	0.046	0.092
P <sub>ST</sub> [MPa]	-2.5	0.122	-0.002	0.139	0.141	0.094	-0.037	0.115	0.006	-0.007	0.008
	+2.5	-0.113	0.005	-0.129	-0.131	-0.087	0.039	-0.107	-0.002	0.007	-0.007
P <sub>COM</sub> [MPa]	-2.5	-0.089	-0.081	-0.109	-0.111	-0.075	-0.080	-0.091	-0.087	-0.002	-0.006
	+2.5	0.086	0.078	0.106	0.108	0.073	0.076	0.088	0.084	0.002	0.006
P <sub>TR</sub> [MPa]	-2.5	-0.041	-0.126	-0.051	-0.052	-0.036	-0.154	-0.043	-0.129	-0.001	-0.003
	+2.5	0.041	0.126	0.050	0.051	0.035	0.154	0.042	0.129	0.001	0.003

**Table 10** Global sensitivity analysis. Percentage change of design variables when operating conditions are  $\pm 2.5\%$  of their nominal values.

	Section 1		Section 2		Section 3		Section 4		Section 5																
	[BLO]/Power		[ABS]/Volume		[AC]/Area		[ECO]/Area		[AP]/Power		[TA], [TW]/Volume		[STP]/Volume		[REB]/Area		[CND]/Area		[COMP]/Power		[IC]/Area		[CO2P]/Power		
	OF1	OF2	OF1	OF2	OF1	OF2	OF1	OF2	OF1	OF2	OF1	OF2	OF1	OF2	OF1	OF2	OF1	OF2	OF1	OF2	OF1	OF2	OF1	OF2	
TG <sub>inA</sub> [K]	-2.5	-53.03	-48.35	-41.56	-39.18	42.25	28.00	50.70	34.10	63.10	41.69	-9.30	-10.25	2.76	-1.92	17.08	10.83	2.21	-4.05	-9.15	-10.06	-3.29	-9.30	-10.25	
	+2.5	10.99	1.30	7.96	-0.02	0.97	3.32	-3.31	-0.82	-3.65	1.16	0.89	-0.09	1.86	1.58	0.09	0.63	0.90	0.31	0.89	-0.08	0.60	0.89	-0.09	
TL <sub>inA</sub> [K]	-2.5			0.39	77.81	83.11	-1.31			-1.09				2.26	1.08			0.55							
	+2.5			-0.15	-52.97	-54.08	0.57			0.55				-0.43	-0.12			-0.02							
TL <sub>inS</sub> [K]	-2.5			-0.14	-1.96	23.94	19.87	-45.82	-48.22	-0.68	-3.32			1.00	9.13	5.44	9.11	-7.91	-4.46			0.69	-3.94	4.66	
	+2.5			-0.60	1.00	-33.25	-31.62	118.35	130.59	-0.71	2.58			2.42	-7.46	-3.26	-5.35	12.10	8.26			-0.01	2.86	2.24	
P <sub>R</sub> [kPa]	-2.5			0.33	0.39	-1.76	-1.53	4.79	5.24	-7.07	-6.52			3.00	2.68	-2.60	-2.91	2.22	1.73	0.77	0.72	1.65	1.54		
	+2.5			-0.32	-0.47	1.69	1.38	-4.35	-4.90	6.97	6.21			-2.84	-1.68	2.73	3.18	-2.08	-1.64	-0.75	-0.67	-1.59	-1.06		
P <sub>ST</sub> [kPa]	-2.5														3.46	3.53									
	+2.5														-3.17	-3.23									
P <sub>COM</sub> [MPa]	-2.5																			-0.74	-0.73	0.47	0.79	2.22	
	+2.5																			0.72	0.72	-0.46	-0.76	-2.22	
P <sub>TR</sub> [MPa]	-2.5																							-4.73	
	+2.5																							4.73	

with a similar magnitude of influence. Certainly, the increase of  $\Delta H_{RX}$  leads to increase OF2 but the increase of the fugacity coefficients leads to decrease OF2. As a first conclusion, it is possible to suppose that the assumptions considered for  $\Delta H_{RX}$  and for the ideal gas behavior expressed in terms of compressibility and fugacity coefficients should be carefully analyzed.

Another conclusion that can be drawn from Fig. 4 is that the obtained RMV values of the parameters associated with the calculation of the physicochemical properties in the liquid phase are higher than in the gas phase for both OF1 and OF2 (except fugacity coefficients). In addition, a comparison of the RMVs obtained for OF1 and OF2 indicates that the effect of the majority of properties (density, surface tension, heat capacity, water latent heat, diffusivity and viscosity) on the sTAC is more pronounced in OF2 than in OF1. Despite the fact that the RMVs are low, they indicate that the results are dependent on the accuracy of the fixed values. Therefore, the optimal solutions may change if correlations instead of fixed values are used. In other words, the considerations of the dependences of such parameters with the temperature and concentration ( $CO_2$  loading) may lead to more precise results, especially if these parameters are then treated as optimization variables.

The reaction heat ( $\Delta H_{RX}$ ) deserves a special analysis. It is known that the higher the  $\Delta H_{RX}$ , the higher reboiler duty and, as consequence, the higher steam requirements to regenerate the solvent. Thus, in the RMV rank list sorted according to decreasing order of importance, the RMV of  $\Delta H_{RX}$  changes from the 22nd in OF1 (Table 7) to the 9th order in OF2 (Table 8). This clearly shows that the use of a correlation to compute the  $\Delta H_{RX}$  considering the  $CO_2$  loading and temperature may be more preferred than the use of a fixed value especially if the optimal design of new  $CO_2$  capture plants is addressed.

Once the most influential parameters have been identified via local sensitivity analysis, it is then important to perform a global sensitivity analysis to conclude about the importance of such parameters, (especially, the assumed operating parameters) in a wider range of values, as presented below.

### 5.3. Global sensitivity analysis

In this section, the percentage changes of the objective functions when a parameter varies  $-2.5$  and  $+2.5\%$  from the NVs (listed in Tables 2–4) are shown in Tables 9–11. The empty cells represents numerical values lower than 0.5%. As mentioned earlier, there are a wide variety of numerical values that several authors assumed for several parameters. Because of this, and for the sake of generality and a more complete discussion, Figs. 5 and 6 plot the variation of the sTAC for OF1 and OF2 for a more full range of values of the parameters which are listed in Table 12.

For a more general way to present the results, the actual value of each parameter ( $P_j$ ) which is plotted in the x-axis and is computed by the Eq. (2), is expressed in terms of the run number "a". The minimal value ( $P_j^b$ ) and the uniform increments ( $\Delta P_j$ ) are indicated in Table 12. Thus, for instance, the reboiler pressure at the NV (165.00 kPa) is computed by Eq. (2) considering  $a = 5.00$ ,  $\Delta P = 7.00$  kPa and  $P_j^b = 130.00$  kPa.

$$P_j = P_j^b + a\Delta P_j \quad a = 0, 1, 2, \dots, 10 \quad (2)$$

#### 5.3.1. Effect of the flue gas temperature at the bottom of absorber (TG<sub>inA</sub>)

Before beginning to analyze the obtained results, it is first important to briefly explain how some of the temperatures are related between them and which are parameters and variables. The chemical reaction between MEA and  $CO_2$  is exothermic. Then, the absorption capacity increases as the temperature of the gas at the

**Table 11**Global sensitivity analysis. Percentage change of the utility and material demand when operating conditions are  $\pm 2.5$  of their nominal values.

	Cooling water		Process water		MEA make-up		Electricity		Steam		
	OF1	OF2	OF1	OF2	OF1	OF2	OF1	OF2	OF1	OF2	
TG <sub>inA</sub> [K]	-2.5	22.59	13.27	-9.30	-10.25	-9.10	-6.64	-27.58	-25.85	20.25	13.63
	+2.5	-0.33	0.53	0.89	-0.09	0.88	-0.06	5.15	0.49	-0.12	0.63
TLin <sub>A</sub> [K]	-2.5	12.86	13.49				-0.82				
	+2.5	0.29	0.00				0.86				
TLin <sub>S</sub> [K]	-2.5	-0.35	-1.01							5.10	6.79
	+2.5	3.73	4.68							-3.48	-4.41
P <sub>R</sub> [kPa]	-2.5	1.34	1.27					0.41	0.36	0.31	
	+2.5	-1.27	-1.24					-0.40	-0.36	-0.28	
P <sub>ST</sub> [kPa]	-2.5										
	+2.5										
P <sub>COM</sub> [kPa]	-2.5							-0.35	-0.36		
	+2.5							0.34	0.35		
P <sub>TR</sub> [kPa]	-2.5										
	+2.5										

absorber inlet (TG<sub>inA</sub>) decreases. The decrease of TG<sub>inA</sub> is limited by the cooling water T<sub>CW</sub>. Then, it was assumed that the temperature of the flue gas stream entering to the blower (TG<sup>0</sup>) which is a model variable should be at least 5.0 K higher than the available cooling water temperature which is a model parameter (T<sub>CW</sub> = 298.15 K). This relationship is imposed by the following inequality constraint: TG<sup>0</sup> ≥ T<sub>CW</sub> + 5.0 K.

As shown in Table 9, independently of the two objective functions, the decrease of the NV of TG<sub>inA</sub> in about -2.5% has much more effect than the increase of the NV of TG<sub>inA</sub> in about +2.5%. In fact, the differences in the percentage variations of sTAC are: 7.503 vs. 0.185% for OF1 and 6.842 vs. 0.458% for OF2.

Fig. 5 shows the presence of a minimum value of sTAC computed by OF1 (61.218 MUS\$/tn of CO<sub>2</sub> captured) which is obtained at TG<sub>inA</sub> = 319.74 K, near of the NV (318.15 K). Here, it is interesting to mention that for range of value of TG<sub>inA</sub> from 310.20 (-2.5% of the NV) to 318.15 K, the inequality constraint imposed between TG<sup>0</sup> and T<sub>CW</sub> is turned into an equality constraint indicating that the minimum temperature difference of 5.0 K was achieved, and therefore TG<sup>0</sup> = 303.15 K. By increasing the TG<sub>inA</sub> from 310.20 to 318.15 K, both the total annual cost (TAC) and CO<sub>2</sub> recovery (CL) increase in about 2.5% and 9.3%, respectively (Table 9). These increase are more pronounced than that observed from 318.15 (NV) to 326.10 K (+2.5% of the NV) where the TAC and the CL increase less than 1.1% (Table 9). However, it should be highly emphasized that in the former temperature range (310.20–318.15 K), all of the design and operating variables in all process sections (I to V) showed considerably changes independently of the objective function considered, as clearly shown in Tables 10 and 11. In fact, for OF1 and for 310.2 K (-2.5% of the NV) greater values are found for the heat transfer area of amine cooler [AC], economizer [ECO], reboiler [REB] and condenser [CND] compared to that obtained for 318.15 K (NV). The increases are 42.25, 50.70; 17.08 and

2.21%, respectively. In contrast, decreases of about 9.3% are observed for the volumes of amine and water tanks [TA and TW] and 3.29% in the heat transfer area involved in the coolers [IC] in the compression stage (Section 5). Also, the sizes of the blower [BLO], compressor [COMP], amine pump [AP] and CO<sub>2</sub> pump [CO2P] expressed in terms of power capacities are also significantly modified, according to the following detail: the power of [BLO], [COMP] and [CO2P] are 53.03; 9.15 and 9.30% lower than the power in the reference case (i.e. at the NV) while the power of the [AP] is 63.10% greater. Regarding to the separation columns, the volume of absorber [ABS] is 41.56% lower than the size at the NV while the stripper [STP] volume is only 2.76% higher. Also, it is interesting to comment that the packing volume of the [STP], the power of [AP] and the transfer areas of [REB] and [AC] reached minimum values at TG<sub>inA</sub> = 319.74 K (results not shown). Regarding to the utility requirements, it is concluded that both the cooling water and steam demands increase in about 22.59 and 20.25%, from 453.10 to 555.46 kg/s and from 33.78 to 40.62 kg/s, respectively. On the contrary, the total electricity requirement decreases in about 27.58% (from 9108.44 to 6596.65 kW), the MEA and water make-ups both decrease from 0.025 to 0.023 kg/s in MEA and from 11.136 to 10.100 kg/s in water.

As mentioned earlier, variations on the optimal design and utility requirements are also modified when TG<sub>inA</sub> increases 2.5% of the NV but with a lower level of influence compared to -2.5% of NV.

Similar qualitative conclusions can be derived from Table 9, 10 and 11 for OF2 when TG<sub>inA</sub> varies from 310.20 (-2.5% of the NV) to 318.15 K with the main difference that the sTAC reached its minimum value of 117.655 US\$/tn at TG<sub>inA</sub> = 316.56 K (Fig. 6).

From these results, it is clear that the cold gas temperature (TG<sub>inA</sub>) has a great influence in the minimization of costs and strongly depends on the available cooling water temperature.

**Table 12**

Selected ranges used for global sensitivity analyses for OF1 and OF2.

Parameter (P <sub>j</sub> )	Unit	Minimum (P <sub>j</sub> <sup>l</sup> )	Nominal value (taken from Table 12)	Maximum	Parameter variation (ΔP <sub>j</sub> )
Solvent temperature (top of stripper)	TLin <sub>S</sub> [K]	363.15	368.15	373.15	1.00
Solvent temperature (top of absorber)	TLin <sub>A</sub> [K]	303.15	313.15	323.15	2.00
Gas temperature	TG <sub>inA</sub> [K]	310.20	318.15	326.10	1.60
Reboiler pressure	P <sub>R</sub> [kPa]	130.00	165.00	200.00	7.00
Compression pressure	P <sub>COM</sub> [MPa]	6.00	7.30	8.60	0.26
Steam pressure	P <sub>ST</sub> [MPa]	300.00	375.00	450.00	15.00
Transport pressure	P <sub>TR</sub> [MPa]	11.00	15.50	20.00	0.90

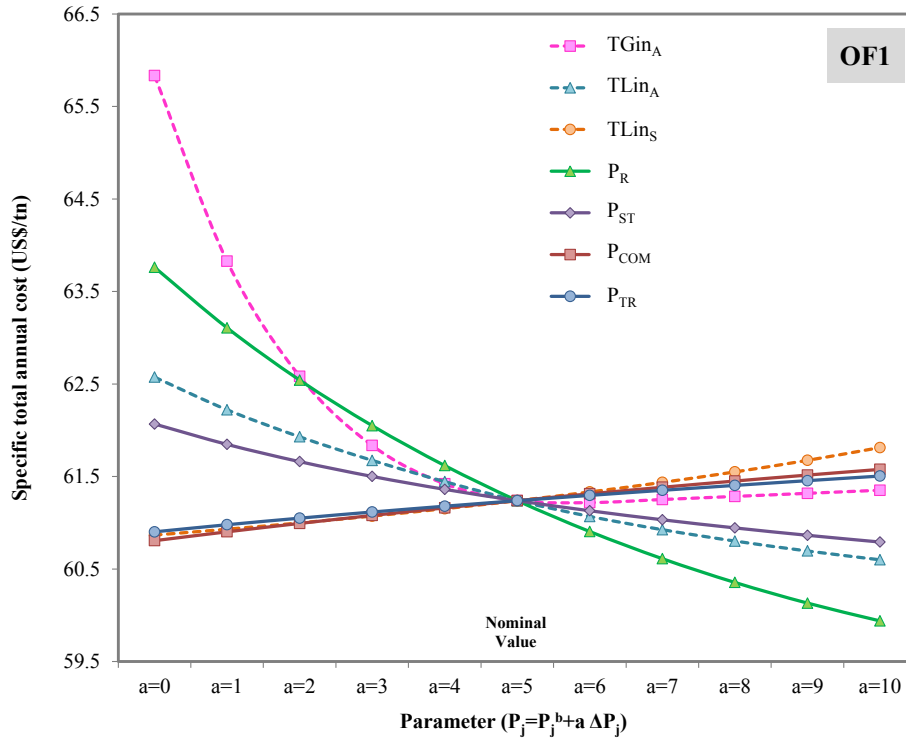


Fig. 5. Global sensitivity analysis corresponding for OF1.

5.3.2. Effect of the solvent temperature at the top of absorber ( $TLin_A$ )

In a similar manner to that observed for the  $TGin_A$ , independently of the objective functions, the decrease  $TLin_A$  in about 2.5% of the NV has also more effect than the increase in about +2.5% of

the NV but with a small difference in the percentage variations in the sTAC as well as in the sizes of process units and utility requirements.

As shown in Table 9, the percentage variations of sTAC computed by OF1 for  $TLin_A = -2.5\%$  of the NV (305.32 K) is 1.56% which is also

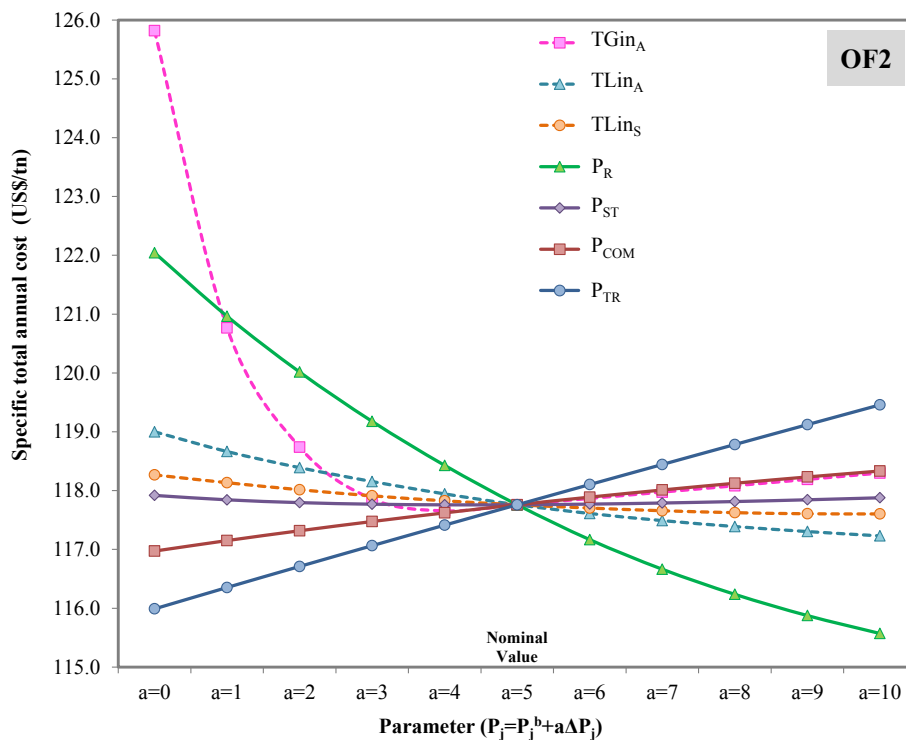


Fig. 6. Global sensitivity analysis corresponding for OF2.

about twice as high as for that obtained (0.87%) for  $T_{LinA} = +2.5\%$  of the NV (320.97 K), affecting the  $sTAC$  in opposite direction, the lower values of  $T_{LinA}$  the higher values of  $sTAC$ . A similar conclusion is also obtained for OF2. In addition, the results listed in Table 9 indicate that if  $T_{LinA}$  increases  $+2.5\%$  of the NV both the TAC and the CL slightly decrease and these trends are similar for both OFs.

For OF1, the increase of  $sTAC$  in about 1.56% for  $T_{LinA} = -2.5\%$  of the NV is because of the slight increase of both the TAC in about 1.59% (from 24.6 to 24.9 MUS\$/y) and the  $CO_2$  captured in about 0.03% (from 93.709 to 93.738%). In addition, according to Table 9, the CAPEX and OPEX increase, respectively, in about 1.3% (120.2–121.8 MUS\$) and 1.8% (from 13.3 to 13.5 MUS\$/y). The main reason of the CAPEX's increase is the increase of the [AC] in more than 77% (Table 10). In fact, slight reductions of about approx. 1.15% of the heat transfer area of the [ECO] and power capacity of [AP] are obtained. Also, slight increase in about 2.26 and 0.55% in the packing volume in the stripper and the heat transfer area in the condenser [CND] are obtained.

Regarding to the increase of the OPEX, it is concluded from Table 11 that the cooling water requirement is the utility that considerably increases. In fact, it decreases 12.86% with respect to the NV. No influence of  $T_{LinA}$  in the cost related to the MEA and water make-ups is observed.

For OF2, the  $sTAC$  increases 0.75% (from 117.8 to 118.7 US\$/tn of  $CO_2$  captured) when  $T_{LinA}$  is 2.5% lower than the NV (305.32 K) (Table 9). The increase of the TAC is about 0.91% (from 44.9 to 45.3 MUS\$/y) as consequence of the increase of CAPEX in about 1.42% (from 116.5 to 118.2 MUS\$) and OPEX in about 0.79% (from 34.0 to 34.3 MUS\$/y), as shown in Table 10. In a similar manner to that observed for OF1, the CAPEX is also only strongly affected by the increase of the heat transfer area of the [AC] in about 83.11% (from 2115.00 to 3872.86  $m^2$ ). The sizes of the remaining process units practically do not vary. On the other hand, the cooling water required by the cooler is the major contributor to the OPEX. In fact, for  $T_{LinA} = 305.32$  K it increases in about 13.49% (from 414.98 to 470.96 kg/s), not affecting the remaining utility requirements compared to that obtained at the nominal value (Table 11).

### 5.3.3. Effect of the solvent temperature at the top of stripper ( $T_{LinS}$ )

This is another parameter that leads to significant changes in the design variables in the Section 3 of the process ([AC] and [ECO]) when it is decreased or increased with respect to its nominal value independently of the objective function. As shown in Table 9, the influence of an increase of  $T_{LinS}$  in  $+2.5\%$  of its NV on the OF1 is more pronounced than in OF2 (2.23 vs. 0.07%) in contrast to that happens for  $-2.5\%$  where the magnitudes are similar but opposite in trends ( $-0.98$  for OF1 vs. 1.00 for OF2).

More precisely, for  $+2.5\%$  of the NV, the CAPEX in OF1 increases in about 2.32% (from 120.2 to 123.0 MUS\$). This increase is because of the variations of the heat transfer areas of the [AC] and [ECO] which are effected in opposite manner (Table 10). While the percentage change of the heat transfer area in the [ECO] considerably increases (118.35%, from 2663.73 to 5816.18  $m^2$ ), the percentage change of the heat transfer area in the [AC] has the potential to decrease ( $-33.35\%$ , from 2395.39 to 1598.89  $m^2$ ) resulting in a net increase in the CAPEX. On the other hand, a net increase of the OPEX in approx. 1.88% (from 13.3 to 13.5 MUS\$/y) can be also observed as a result of the increase in the cooling water requirement ( $+3.73\%$ , from 453.10 to 470.00 kg/s), and decrease of the steam used in the reboiler ( $-3.48\%$ , from 33.78 to 32.61 kg/s), as indicated in Table 11.

Similar qualitative conclusions can be also derived for  $-2.5\%$  for OF1 and for  $\pm 2.5\%$  for OF2.

### 5.3.4. Effect of the operating pressure in the reboiler ( $P_R$ )

In Table 9 it can be seen that, for OF1 and OF2, the decrease of the TAC is about 0.52% while the increase of the CL is approx. 0.13%

as the reboiler pressure ( $P_R$ ) increases from  $-2.5\%$  of NV (160.9 kPa) to  $+2.5\%$  of NV (169.1 kPa) which lead to a small decreases in the OFs: 0.69% for OF1 and 0.63% for OF2. However, these reductions necessarily also imply several changes in the optimal sizes of the majority of the process units and utility consumptions (Tables 10 and 11) and consequently in their corresponding costs (Table 9). The magnitudes of the variations in the heat transfer areas, power capacities and operating conditions in the majority of the process units for both OF1 and OF2 are similar. For instance, while the heat transfer area of the [AC], [REB] and power capacity of the [AP] decrease for  $-2.5\%$  of NV and they increase for  $+2.5\%$  of NV. The remaining process unit sizes at 160.9 kPa are smaller than the sizes at 165.0 kPa while their capacities at 169.1 kPa are higher than it at 165.0 kPa (Table 10).

These qualitative behaviors can also be observed for the utility requirements in Table 11. In fact, the cooling water and electricity required in OF1 and OF2 increase for  $P_R = -2.5\%$  of NV and they decrease for  $P_R = +2.5\%$  of NV. The steam is only influenced in OF1 while the MEA and water make-ups are not influenced by  $P_R$  for OF1 and OF2.

### 5.3.5. Effect of the steam pressure ( $P_{ST}$ ), compression and transport pressures ( $P_{COM}$ and $P_{TR}$ )

In contrast to the previous case, the percentage changes observed in Table 9, 10 and 11 clearly reveal that the influence of  $P_{ST}$  in OF1 and OF2 is practically negligible. In fact, for both OFs, the percentage variations of the OPEX, CAPEX, TAC, CL and  $sTAC$  are lower than 0.5%. Similar conclusion can be also derived for the effect of compression and transport pressures ( $P_{COM}$  and  $P_{TR}$ ).

Finally, from the obtained results listed from Tables 5–11 and plotted in Figs. 5 and 6, it is possible to conclude that, the reboiler pressure ( $P_R$ ) and the stream temperatures ( $T_{GinA}$ ,  $T_{LinA}$  and  $T_{LinS}$ ) are the most important operating parameters that affect OF1 and OF2 and, depending of the case, with different magnitudes and trends. Precisely, they can be arranged in decreasing order of importance (absolute values) as follows: a) for OF1:  $T_{GinA} > T_{LinS} > T_{LinA} > P_R > P_{ST} > P_{COM} > P_{TR}$  and b) for OF2:  $T_{GinA} > T_{LinA} > T_{LinS} > P_R > P_{ST} > P_{COM} > P_{TR}$ . Thus, the only difference in both order lists is the position of  $T_{LinA}$  and  $T_{LinS}$ . From stream temperatures, the mentioned orders are different to those reported in the Local Sensitivity Analyses through the RMV (Tables 7 and 8), and this may be because when the range is extended some inequality constraints, included in order to define a space of feasible solutions, become in equality constraints and vice-versa equality constraints become in inequality constraints, depending on the case. In the majority of the optimization results, the variations of the TAC were higher than the small changes of the  $CO_2$  capture levels. Finally, it should also be noted that slight variations of the model parameters imply considerable of optimal values of the sizes, operating conditions and utility requirements.

The obtained results clearly showed the benefits of performing a global sensitivity analysis not only considering parameters related to the operating conditions but also parameters related with the physicochemical properties and design as well.

## 6. Conclusions

This paper presented optimization results obtained for an amine-based  $CO_2$  post-combustion capture process. Using a NLP detailed mathematical model, the entire process (absorption, desorption and compression stages) was optimized in order to determine the optimal design that leads to the minimum specific total annual cost. For the sake of generality and a more complete discussion of results, two different ways to compute the total annual cost were considered. In one of the objective functions (OF1)

the costs related to the water and amine make-ups, cooling water and the investments of the process units were considered to compute the TAC and in the other objective function (OF2) the cost of the steam supplied in the reboiler and the cost of the total electricity required by pumps, blowers and compressors were also included. For each objective function, the optimal sizes of process units and operating conditions were simultaneously optimized and a comparison of the obtained results was presented. Then, based on the relative marginal values (RMV) reported by GAMS which are valid in the “neighborhood” of the current values, the influence of each model parameter on the specific total annual cost and the optimal design was investigated in detail. Finally, a global sensitivity analysis was also performed, by varying each parameter within the range between  $-2.5$  and  $+2.5\%$  of each nominal value.

From a qualitative point of view and for the model cost considered in this paper which is complete and detailed enough, the results revealed that the specific total annual cost varied from 0.01 to 7.70% when the majority of the operating parameters varied  $\pm 2.5\%$  around of each nominal value. Certainly, the TAC and the CO<sub>2</sub> removal levels did not changed significantly. However, despite of this, the sizes of the several process units, heating and cooling utilities and electricity requirements are significantly influenced when the model parameters are varied around the nominal values used in this paper, which have been assumed from a wide variety of numerical values used by other authors.

For instance, when the TLIn<sub>5</sub> was increased in about 2.5% of the nominal value (from 368.15 to 377.35 K) the specific total cost slight increases in approx. 2.23% as consequence of an increase of the CAPEX in about 2.32% and OPEX in 1.88% while the CO<sub>2</sub> recovery remains almost constant (approx. 93.6%). Nevertheless, the percentage change of the heat transfer area in the economizer considerably increased in about 118.35% while the percentage change of the heat transfer area in the amine cooler has the potential to decrease in approx.  $-33.25\%$ . In addition, the cooling and heating utilities, that is cooling water and steam, increased in about  $+3.73\%$  (from 453.10 to 447.34 kg/s) and decreased 3.48% (from 33.78 to 32.61 kg/s), respectively.

The results presented in this paper provide useful guidelines to help the reader to identify and to determine how influential the model parameters are on the sizes of the process units and on the utility requirements when the entire post-combustion CO<sub>2</sub> capture process by chemical absorption with amines is simultaneously optimized.

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