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A sensitivity analysis and a comparison of two simulators performance for the process of natural gas sweetening

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ABSTRACT

Chemical processes simulation is an important instrument for the design, optimization and control of industrial plants. Simulation cases can be accomplished with relatively low costs and the absence of risks for the operators. However, the precision of the results depends on the similarity between the simulation performed and the process considered. In this article, two simulators, Aspen Hysys V8.6 and Aspen Plus V8.6, are employed to simulate the process of natural gas sweetening using diethanolamine (DEA). Additionally, a parametric sensitivity analysis is performed to define the optimal operative range for the process. The required data and the conditions of the operating units are taken from a gas conditioning plant in northern Argentina. Finally, a comparison between the block of obtained results from both simulations is also detailed.

1. Introduction

The natural gas is a non-renewable source used in a wide range of applications due to its combustible characteristics. These range for domestic purposes to industrial issues for example the generation of electricity or as raw material for the petrochemical products obtainment. The natural gas is composed for a mix of hydrocarbons, mainly methane, but also ethane, propane, butane and superiors. Also, it includes impurities such as water vapor, sulphurated components, carbon dioxide, nitrogen or heavier hydrocarbons. Its specific composition varies according to the site where it has been obtained (Martínez, 2000).

The composition of a natural gas stream is restricted in order to accomplish the adequate conditions to be transported and used. These restrictions are ruled by local entities in each country or according to the costume preferences. With the aim of satisfying these bound values, the natural gas streams are treated in different process sectors. One of the sectors is the sweetening stage, where the acid gases of the sour natural gas are removed using different technologies.

As mentioned before, the sweetening process is made to remove the acid gases: H_2S and CO_2. Under proper conditions, these gases cause the corrosion of natural gas pipelines. Additionally, the presence of acid gases reduces the calorific power of the gas which implies economic losses and the decrease of the global energy efficiency. In Argentina, the specification values are ruled by the government through the ENARGAS (*Ente Nacional Regulador del Gas*).

Many works have been published following the aim of studying the sweetening process. In their work, Polasek and Bullin (1990) studied a natural gas sweetening unit with the simulator Tsweet. The sensibility of the system respect to the operating conditions and the parameters of the process are studied. In their analysis, one of the parameters considered was the H_2S/CO_2 relation in the gas to treat. De la Cruz-Guerra et al. (1996) show a thermodynamic kinetic model for the optimization of a sweetening sector. The optimal acid gas composition in order to reduce the global energy consume, detect energy saving opportunities and minimize the operating costs are considered in their work. Panahi et al. (2010) analyzed the design, simulation and optimization of a CO_2 capture unit using amines. The operation and the optimal control of the process in order to reach the proximity to the optimal operating conditions

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are established in the study. In their research, UniSim simulator is used and the mathematical function minimized is the global energy consume.

Various processes for the natural gas sweetening have been developed. They are characterized mainly for the type of absorbent used. In the case of chemical absorbents, the gas to be treated is put in countercurrent contact with an active component. The main disadvantages related to the use of chemical solvents are the high demand of energy, the corrosive nature of the solutions and the limit for the acid gases absorption, due to the stoichiometry of the reactions. In the treatment of natural gas, aqueous alkanolamines solutions are used to remove H_2S and CO_2.

Alkanolamines are components derived from ammonia (NH_3), organic bases where one, two or three alkyl groups may replace the hydrogens of ammonia to give primary, secondary and tertiary amine molecules, respectively. Initially, the monoethanolamine (MEA) was a very popular solvent for the sweetening process. This last was substituted for the diethanolamine (DEA) due to the best in-practice obtained results. However, in the last times the methyldiethanolamine (MDEA) has gained more popularity. Mixtures of amines are also used in the industry (Al-Lagtah et al., 2015).

Abbas et al. (2011) consider that the most common absorbent, between primary and secondary amines, is DEA. According to them, DEA is less expensive, easy to install and operate than MEA and become a solvent widely used for sweetening. It is a secondary amine with lower reactivity, less corrosive and has a low heat of reaction than MEA. It means that DEA is easier in processing and easier to regenerate than MEA is. Pino Morales (2004) states that DEA is used when the acid gas mole concentration in the sour gas is less than 10% and operating pressure greater than 3500 kPa.

If the costs of regeneration are taken into account, tertiary amines (i.e. MDEA) are much more attractive (Van Loo et al., 2007). However, MDEA is a tertiary amine that reacts slowly with the CO_2, then more absorption equilibrium stages, respect to primary and secondary amines, are required. Consequently, MDEA is preferred for those cases where CO_2 and H_2S are presented simultaneously, due to its high selectivity for the H_2S (Erdmann et al., 2012).

This article describes the development of the steady simulation for a natural gas sweetening process using DEA as solvent. In particular, the article focuses in the CO_2 removal from a sour natural gas stream. Once the simulation case is performed in Aspen Hysys v8.6, a parametric sensitive analysis of the main operative variables is run. For the purpose, the Acid Gas thermodynamic package is used. The analysis allows to determine the incidence of the reboiler pressure in the regeneration of the solvent. As mentioned, other decisive variables are also evaluated.

Firstly, the simulation is performed using Aspen Hysys V8.6 simulator, then Aspen Plus V8.6 simulator is also employed. Both are commercial products of AspenTech Inc. In the Aspen Plus simulator, the knowledge of chemical reactions is required in order to execute the simulation. The study allows to establish a comparison of the results with the aim of determining the differences and a conclusion respect to the feasibility or simplicity in the use of each process simulator.

2. Process description

Fig. 1 represents a simple amine treating facility (Lunsford and Bullin, 1996). The acid gas (SOUR GAS) is introduced for the bottom of the contactor tower (ABSORBER). There, it is put in contact with a descendent flux of an aqueous amine solution (LEAN AMINE). The contact occurs in counter-current. The acid components are absorbed by the amine solution, so the sweet gas leaves the absorber through the top of the tower (SWEET GAS). The liquid stream conformed for the amine solution and the absorbed complex component leaves the tower through the bottom. This last stream (RICH AMINE) is sent to a flash tank where the hydrocarbons that could contain are separated as vapor (FLASH).

Once the absorption has occurred, the rich amine solution fluxes through a heat exchanger with the aim of increasing its temperature up to 90–100 °C (LEAN/RICH EXCHANGER). The heated rich amine solution is introduced to a regenerator tower (STRIPPER), where the acid gases are removed. In this stage, dissolved acid gases and water that the rich amine could contain are also removed. The internal pressure value of the contactor tower must be kept as high as possible in order to increase the reboiler temperature. The maximum value of temperature is given for the degradation temperature range of the amine solvent employed. A pump is included in the flowsheet for keeping the value of pressure over the absorber pressure (CIRCULATION PUMP). Finally, an air cooler (TRIM COOLER) reduces the lean amine temperature before being sent back to the contactor tower (Behroozsarand, 2011).

2.1. Process conditions

The steady state simulation for the sweetening process is performed using the two cited simulators. The specifications of the gas to be treated are shown in Table 1 and its composition in Table 2. For the study, a typical sour gas of the northern region of Argentina is used. The main characteristic of the gas is the absence of H_2S, then the process focuses is the absorption of CO_2. For the reasons exposed, DEA is the amine selected for this process; its conditions are given in Table 3.

3. Steady simulation in Aspen Hysys

Once the components involved in the process and the fluid thermodynamic package are charged in the simulator the next step is to add the operating units. The logical operator ‘recycle’ is introduced in order to properly run the simulation, see Fig. 2. The absorber tower includes 20 internal trays; tray 1 is at the top of the tower and tray 20 at the bottom. The sour gas is fed in the tray 20 while the amine aqueous in tray 1. The stripper tower has 20 trays, a condenser and a reboiler. The amine solution to regenerate is fed in tray number 3.

In the case of Aspen Hysys, the fluid package selected is the Acid Gas. Specifically, the Acid Gas property package was developed with the Peng-Robinson equation-of-state for vapor phase and the electrolyte non-random two-liquid (eNRTL) activity coefficient model for electrolyte thermodynamics (Song and Chen, 2009). The property package contains the eNRTL model parameters and other transport property model parameters identified from regression of extensive thermodynamic and physical property data for aqueous amine solutions (Zhang and Chen, 2011; Zhang et al., 2011). The thermodynamic fluid package includes the chemical reactions system without the necessity of specifying them into the simulation software.

After performing the simulation, different variables profiles have been obtained for both absorber and stripper towers. The flowsheet diagram for the sweetening process simulation is shown in Fig. 3. Basically, it is conformed for an absorber and a regenerator tower (Erdmann et al., 2012).

Fig. 4 shows the CO_2 mole fraction and temperature profiles through the absorber tower trays. The CO_2 concentration profile shows that its elimination is progressively performed up to the complete removal. The temperature profile shows an increase of the values towards the bottom of the tower, where the highest quantity of CO_2 is removed.

Fig. 5 shows the mole fraction and temperature profiles in the stripper tower. From the temperature profile, the highest value of

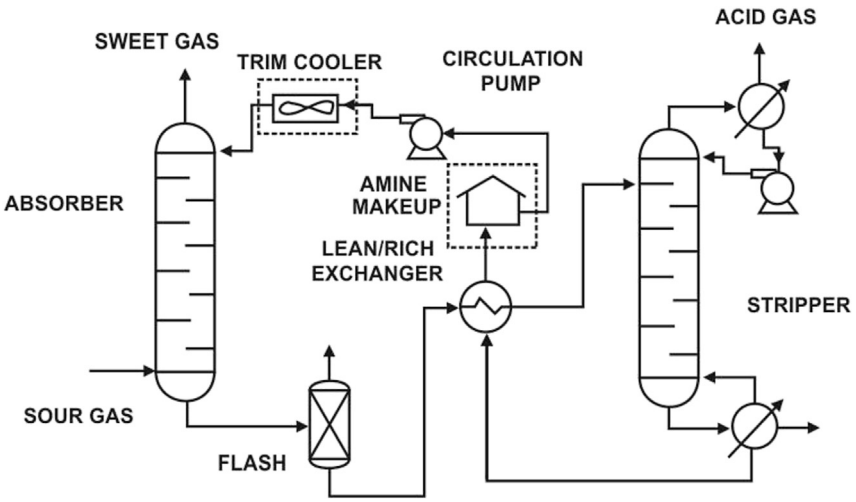

Fig. 1. Schematic of a simple amine sweetening plant (Lunsford and Bullin, 1996).

Table 1
Conditions of the Sour Gas stream.

Sour Gas	
Temperature	30 °C
Pressure	6895 kPa
Molar Flow	1627 kmol h^{-1}

Table 2
Composition of the Sour Gas stream.

Component Mole fraction	
C1	0.8618
C2	0.0621
C3	0.0203
iC4	0.0039
nC4	0.0052
iC5	0.0022
nC5	0.0013
C6	0.0004
C7	0.0007
C8	0.0001
C9	0.0001
CO_2	0.0346
H_2O	0.0020
N_2	0.0052

Table 3
Conditions and compositions of the DEA stream pumped to the ABSORBER.

DEA TO ABS	
Temperature	35 °C
Pressure	6860 kPa
Std Ideal Liq Vol Flow	53.9 m^3 h^{-1}
CO_2 Mass Frac.	0.0018
Water Mass Frac.	0.7187
DEA Mass Frac.	0.2795

125 °C is observed in the reboiler. From the concentration CO_2 profile, the highest values of concentration are observed in the last 3 trays. A special behavior is observed in tray 3, where the rich amine is fed.

3.1. Sensitivity analysis

Case 1: In the regenerator tower, the reboiler pressure is modified and the effects of this action are perceived in the following variables:

- Temperature of the regenerated amine stream
- CO_2 and H_2O mole fractions in the regenerated amine stream

For the first modification, the analysis allows to determine the limit value for the operating pressure before the degradation of the amine. The results are shown in Fig. 6. The best performances of the stripper tower are obtained by high values of pressure because they favor the removal of the acid gas. However, the increase of the pressure increases the values of temperature that may produce corrosion and the chemical degradation of the amine. For the majority of the alkanolamines units, a temperature between 115 and 126 °C is enough to separate the acid gases for the solution (Maddox, 1982), so then the pressure value should not overcome the limit of 226 kPa. For lower values than 226 kPa, a temperature cross is observed in the heat exchanger which makes the process unrealistic.

From the composition profile, see Fig. 7, a particular behavior of the CO_2 and H_2O is observed. For increasing values of pressure a decrease of the CO_2 mole fraction in the regenerated amine is observed. However, from higher values than 373 kPa, the concentration increases quickly. Since low concentration values are needed, a pressure between 196 and 390 kPa are equitable for the case. The amine load remains constant in the range studied.

Case 2: In the absorber tower, the amine concentration in the lean amine stream is modified in order to evaluate the impact in the CO_2 percentage in the sweet gas stream. This analysis has been performed for different values of standard ideal liquid volume flows. Fig. 8 illustrates the effect of the lean amine composition on the sweet gas composition for different values of lean amine liquid flows.

For the operating conditions in the absorber tower, if the mass fraction is increased then it is possible to reduce the lean amine flow to a 10 m^3 h^{-1}. In the other curves, a particular behavior is observed, as the mass fraction is increased in the lean amine solution, the removed CO_2 tends to be same. So the graphic represents a decision graph when selecting the appropriate flow and lean amine composition.

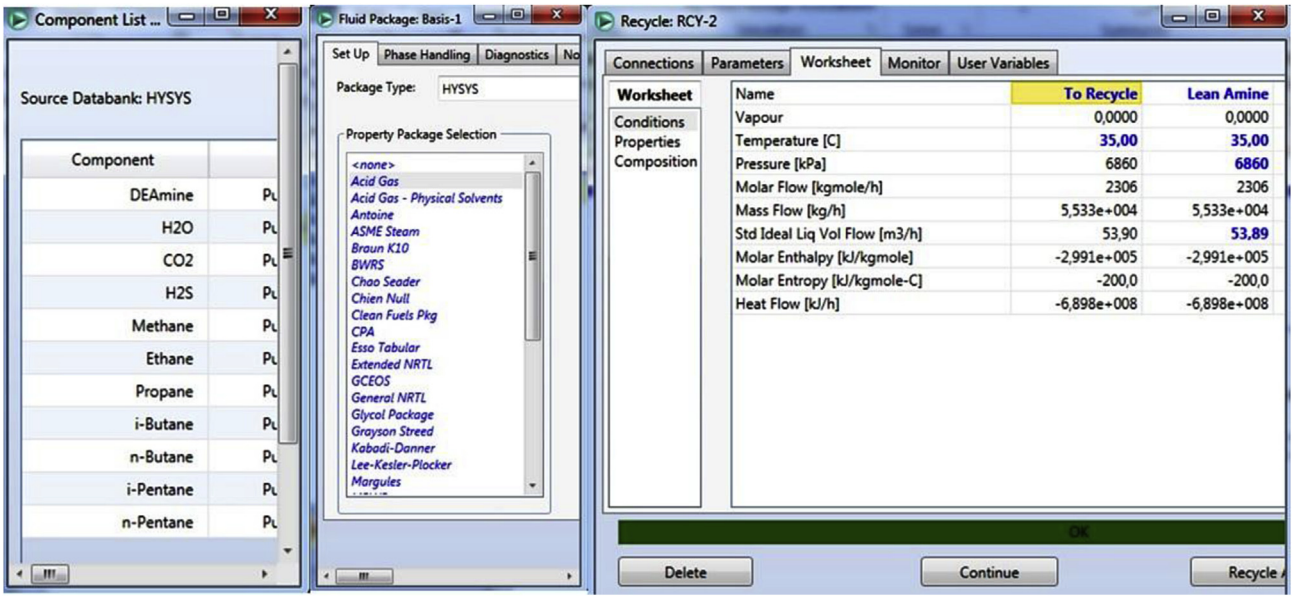

Fig. 2. Selection of components, fluid package and Recycle operator in Aspen Hysys 8.6.

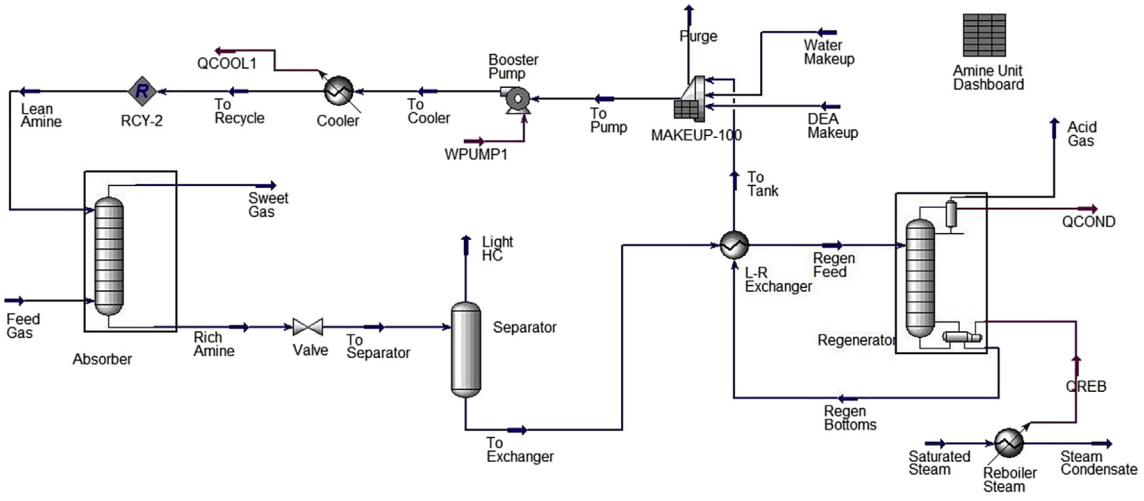

Fig. 3. Sweetening process in Aspen Hysys v8.6.

Case 3: The sour gas mole flow is modified to evaluate the impact on the CO_2 percentage in the sweet gas stream. This analysis has been performed for different lean amine (DEA + water) compositions. Fig. 9 illustrates the effect of the sour gas mole flow in the sweet gas composition for different values of DEA mass fractions.

With a DEA mass fraction of 0.3, the mole flow can be increased up to 7200 kmol h^{-1} obtaining a gas under specification. 2500 kmol h^{-1} of gas with 0.1 of DEA mass fraction and 11000 kmol h^{-1} of 0.6 DEA are necessary for obtaining a gas with 2% of CO_2. Lunsford and Bullin (1996) state that mass fractions higher than 0.4 tend to pick up a large amount of acid gases and may cause extreme corrosive conditions. For these reasons, increasing the amine concentration is not a viable option. In contrast, mass fractions of 0.1 and 0.2 reduce to 2800 and 5000 kmol h^{-1}, respectively, the capacity of the plant.

From the analysis of the cases exposed, an optimum range for the proper treatment of the gas can be established. The reboiler pressure must be set between 196 and 226 kPa. The 0.3 DEA lean amine stream can be reduced up to 12 m^3 h^{-1} with a capacity for the gas of 7200 kmol h^{-1}.

3.2. Steady simulation in Aspen Plus

Contrarily to Aspen Hysys V8.6 simulator, Aspen Plus V8.6 does not include a specific package with all of the chemical reactions between the acid gases and the alkanolamines. However, chemical reactions involving electrolytes can be defined in order to accomplish the simulation.

The sort of reactions that occurs in an absorber tower is electrolytic. In that sense, Aspen Plus has an Electrolyte-NRTL equilibrium model which is based on Austgen et al., 1989 equation (Øi, 2012). Therefore, with Aspen Plus is possible to simulate any type of electrolytic system.

The process to remove the acid gases is modeled with the RedFrac option. As mentioned before, the tower operates to high values of pressure and low values of temperatures in order to favor

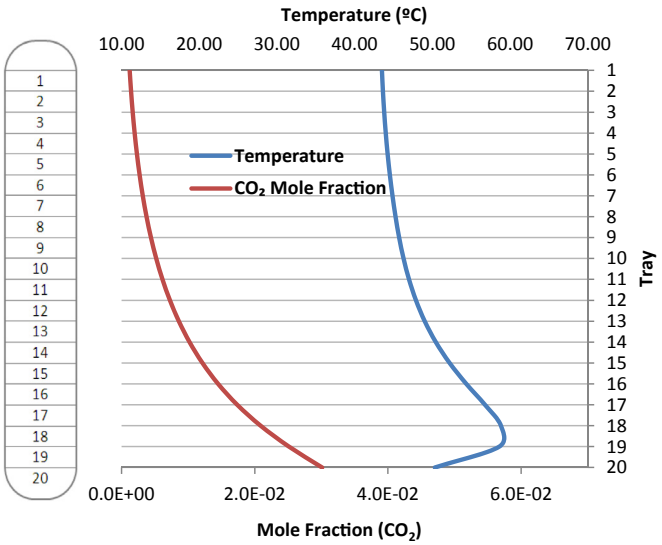

Fig. 4. CO_2 concentration and temperature profiles in the absorber tower.

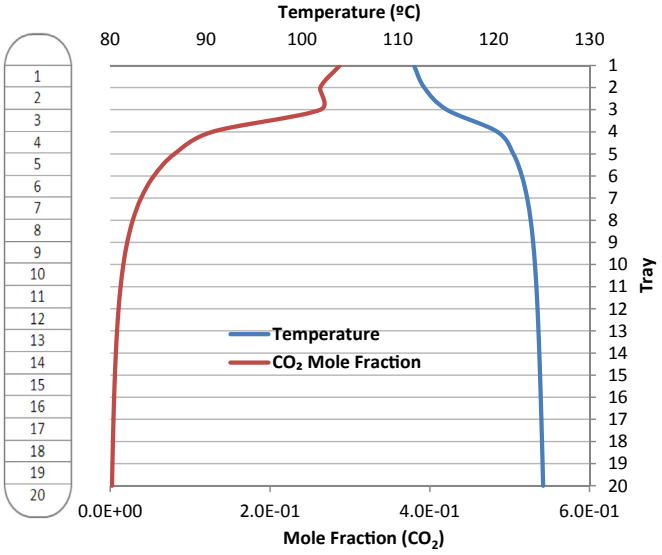

Fig. 5. CO_2 concentration and temperature profile in the stripper tower.

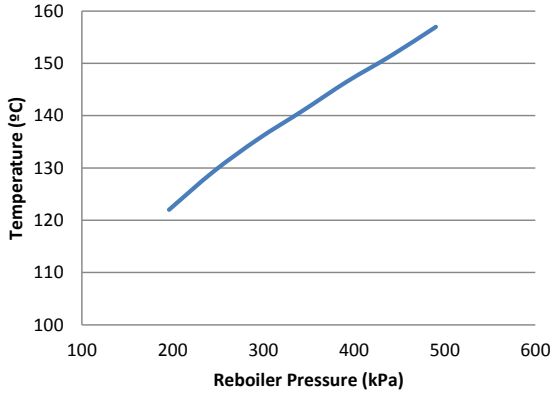

Fig. 6. Temperature of the regenerated amine versus reboiler pressure.

the chemical reactions.

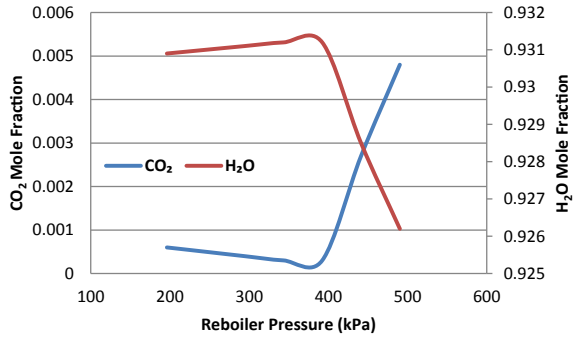

Fig. 7. CO_2 and H_2O concentration in the regenerated amine versus reboiler pressure.

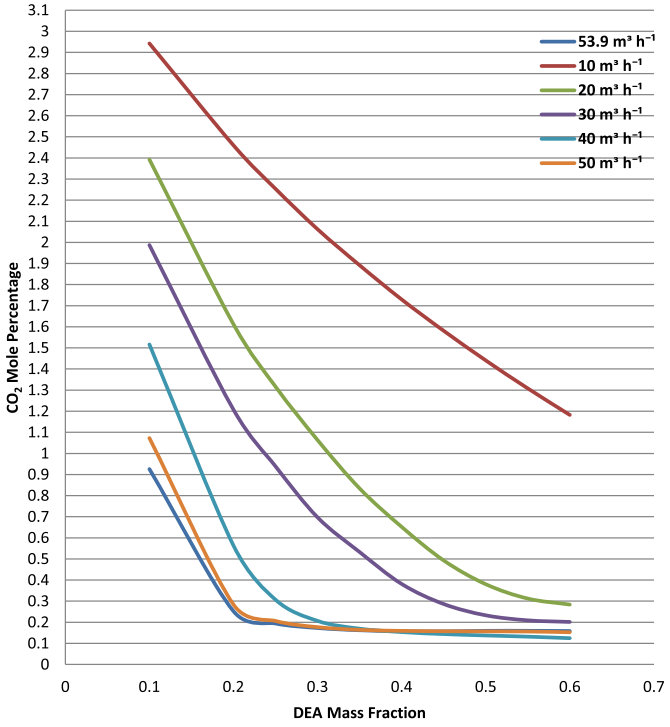

Fig. 8. CO_2 concentration in the sweet gas versus lean amine concentration, for different lean amine liquid flows.

With the aim of simulating the gas sweetening process in Aspen Plus, the definition of a global reactions system is required. The reaction system includes all of the electrolyte reactions that occur in the process.

In this case, the reactions are of equilibrium nature, and they allow to explain the mechanism of the electrolyte formation. In their work, Xu Zhang et al. (2002) define the group of those reactions as follows:

$$DEACOO^- + H_2O \leftrightarrow DEA + HCO_3^-$$

$$CO_2 + 2H_2O \leftrightarrow HCO_3^- + H_3O^+$$

$$HCO_3^- + H_2O \leftrightarrow CO_3^{2-} + H_3O$$

$$DEAH^+ + H_2O \leftrightarrow DEA + H_3O^+$$

$$2H_2O \leftrightarrow OH^- + H_3O^+$$

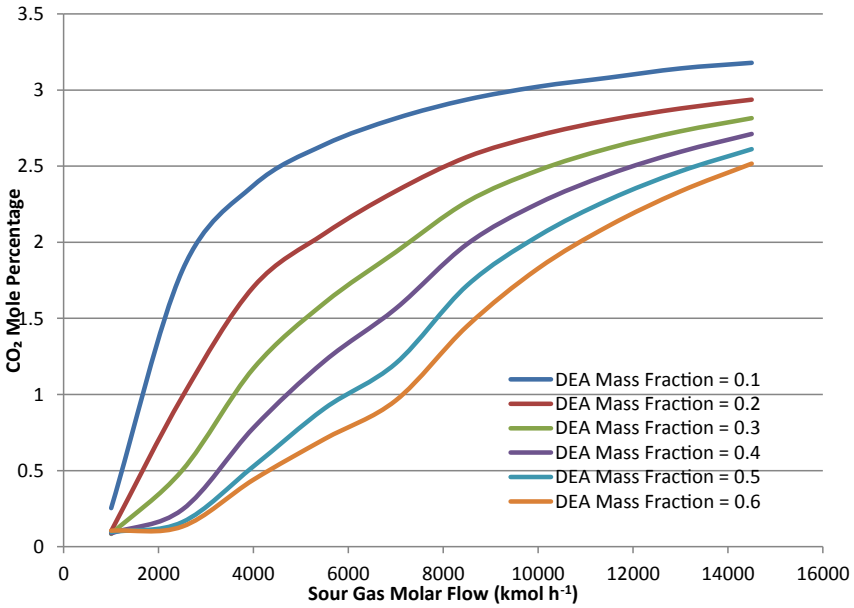

Fig. 9. CO_2 concentration in the sweet gas versus sour gas mole flow, for different lean amine mass fractions.

To define the reactions system in the absorber tower, the two first reaction of the global system are replaced by the next irreversible kinetic reactions:

$$CO_2 + DEA + H_2O \rightarrow DEACOO^- + H_3O^+$$

$$CO_2 + OH^- \rightarrow HCO_3^-$$

On the other side, to define the reactions of the regenerator tower, the two first reactions of the global system are replaced for the next irreversible kinetic reactions:

$$DEACOO^- + H_3O^+ \rightarrow CO_2 + DEA + H_2O$$

$$HCO_3^- \rightarrow CO_2 + OH^-$$

The values of the constraints and the kinetic parameters needed are obtained from the Aspen Plus database. The conditions employed for the gas to sweet and for the amine solvent are those used in the previous simulation case so then is possible to establish a comparison between the results. The developed flowsheet for the sweetening process simulation is shown in Fig. 10.

3.3. Aspen Plus vs. Aspen HYSYS

In this section, the obtained results with Aspen Plus are compared with those obtained using Aspen HYSYS. The comparison is generalized as follows:

- Concentration of CO_2 in the sweet gas stream
- Temperature profile in the absorber tower
- CO_2 profile in the absorber column
- Temperature profile in the stripper tower
- CO_2 profile in the stripper tower

In both simulations, the sweet gas is under specification. That means that for both cases the CO_2 mole percentage in the sweet gas is lower than 2%. Moreover, the concentration of CO_2 was technically equal to zero for the sweetened gas.

For the case of the temperature profile, the obtained results are shown below. Fig. 11 shows the temperature profile while Fig. 12 shows the CO_2 concentration profile for the absorber column.

For the first case, the relative error of Aspen Plus results respect to Aspen Hysys results was calculated. The highest relative error, of about 15%, is found in the middle trays. In the CO_2 profile, it is observed that the same point was found with both simulations, in tray 13.

The stripper tower temperature profile is shown in Fig. 13 while the stripper CO_2 concentration profile is shown in Fig. 14. For the first case, the highest relative error is approximately 8%, in tray number 4. However, almost the same behavior of the curves can be seen. On the other hand, the same behavior in the composition

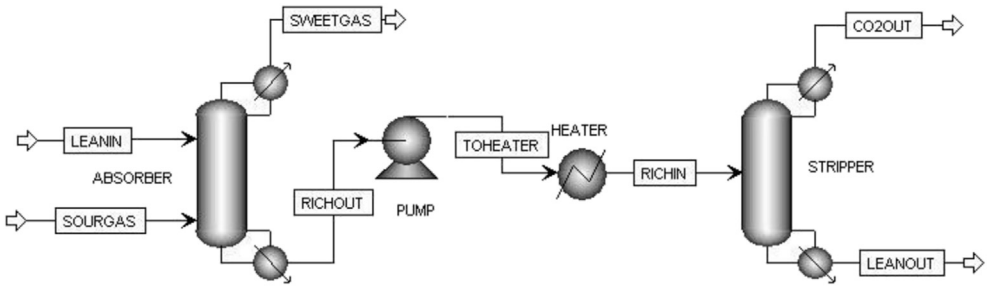

Fig. 10. Sweetening process in Aspen Plus v8.6.

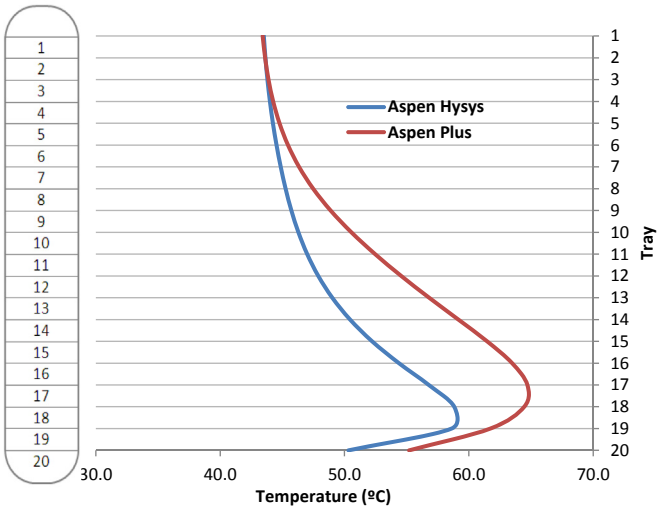

Fig. 11. Temperature profile in the absorber tower.

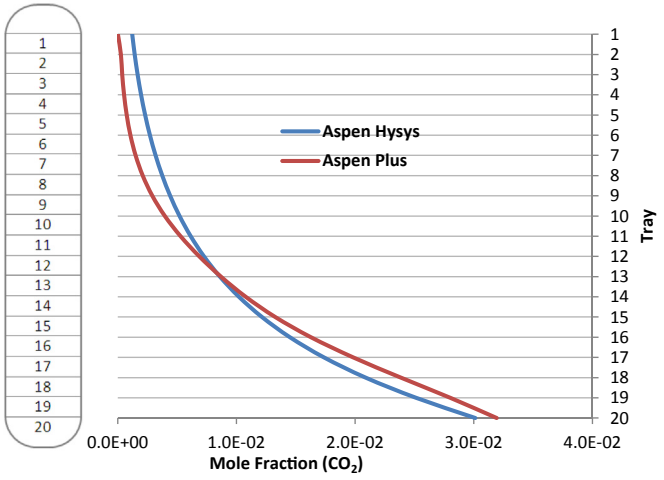

Fig. 12. CO_2 profile in the absorber tower.

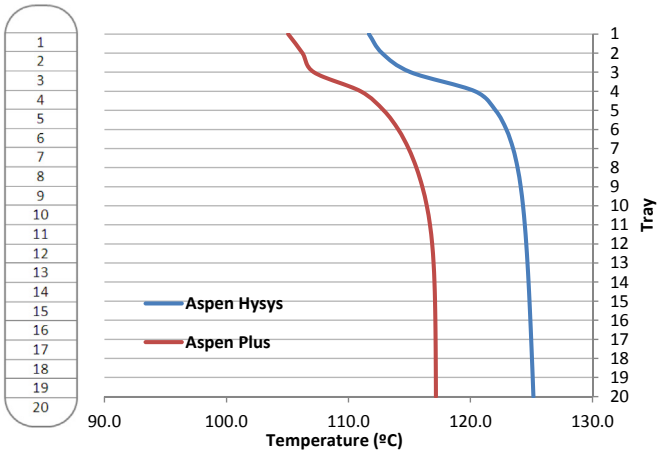

Fig. 13. Temperature profile in the stripper tower.

curves and low percent errors were obtained in the simulations performed separately.

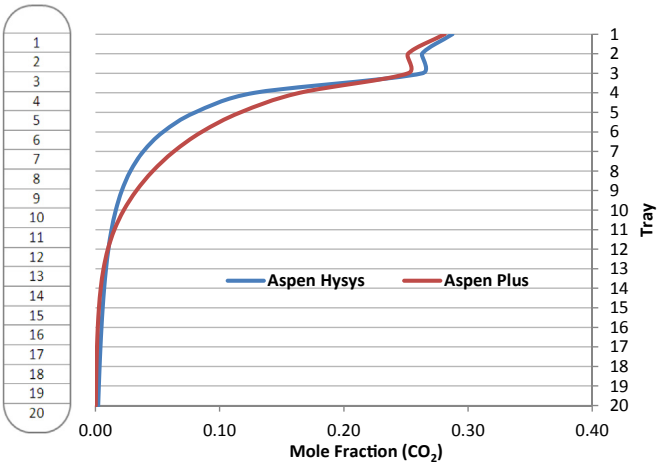

Fig. 14. CO_2 profile in the stripper tower.

The main differences between the obtained profiles are due to the property package used. Aspen Hysys V8.6 employs a specific fluid package improved for the process under study: the Acid Gas thermodynamic package. On the other side, Aspen Plus employs the Electrolyte NRTL block. In this simulator, the operator must introduce manually the block of chemical reactions that take place depending on the alkanolamine used. The difference in the procedure may origin dissimilarities in the obtained results.

The main drawback using Aspen Plus is that the operator must change the set of chemical reactions that can drive to discrepancies. Particularly, if the block of chemical reaction does not describe the exact behavior of the reactants involved, especially with mixtures of alkanolamines. Apart from these discordances, in both simulations the concentration of CO_2 in the sweet gas is reduced up to zero.

In the absorber, the temperature profile shows good approximation between the simulators. According to real data, the results are quite closed to those observed in practice. The higher values of temperatures are observed at the bottom trays, where the highest quantity of CO_2 is removed.

In the stripper tower, the profile temperature of the liquid stream has almost the same behavior in both cases. For the Aspen Hysys simulation case, higher temperatures are observed and a decrease of the temperature in tray 3 where the inlet stream is fed. The highest values of temperature are reached in the reboiler.

4. Conclusions

The steady state of the sweetening process has been simulated using two different simulators, Aspen Hysys v 8.6 y Aspen Plus v 8.6. A parametric sensitivity analysis has been performed and a proper optimal operative range for the process was studied.

The temperature of the regenerated amine and its composition are highly sensible to the reboiler pressure variation. If the flow of the lean amine increases, the CO_2 in the gas decreases substantially until a certain value where the decrease is not significant. The molar flow of the sour gas can be increased up to a 400% with the lean amine stream considered. From this study, further analyses can be done considering new decision variables.

The main difference between the simulators lies on the use of the fluid package. It is observed that the obtained profiles in both cases are quite similar and the relative error between the simulators does not exceed a 15%.

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