Design and Optimization of a Process Based on Extractive Distillation for the Sweetening Natural Gas

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For the sweetening natural gas process, the most used scheme at industrial field is the chemical absorption by alcohol amines. Recently, Lastari et al., (2010) proposed a design using the cryogenic extractive distillation by employing like entrainer the same hydrocarbon liquefied fractions of the process. In this work, it was used the Aspen Plus One 7.0 ® simulator, considering non-equilibrium trays to model these schemes, coupled to a multi-objective stochastic optimization procedure, using Differential Evolution (DE) as main algorithm. The optimization is focused on minimizing the Total Annual Costs (TAC) and maximizing the acid gas removal interpreting the information with Pareto fronts. Finally a post-optimization analysis was performed considering a dynamic study by singular value decomposition (SVD) technique, thermodynamic efficiency and greenhouse gases generation studies for several representative spots for each Pareto. The process performance was focused on breaking the CO_2- ethane azeotrope, following the next procedure: assessment of pure different entrainers (propane, n-butane, n-pentane and n-hexane) on three arrangements with and without thermally coupled. We compare the performance of these sequences with the conventional system using chemical absorption by mono-ethanol amine (MEA) like benchmark problem. A comparison between Pareto fronts analysis showed that cryogenic extractive distillations reached out bigger CO_2 removals with lower TACs than chemical absorption.

1. Introduction

The removal of acid gases from natural gas is called sweetening process. This action is used when the sour source has mainly CO_2, hydrogen sulfide or both. The aim to remove these gases is to avoid some operational and safety drawbacks for the next steps related with the natural gas treatment; for instance decreasing the heating value of the liquefied natural gas, preventing the solidification during the cryogenic processing, and others. Moreover, the usage of schemes for CO_2 separation also has had fairly interest in different fields, such as on removal systems by coupling with power generation plants that use natural gas,(Øi 2007). In addition to this example, another relevant scheme for CO_2 separation is used for EOR (Enhanced Oil Recovery), where the CO_2 is utilized to extract the oil under the underground. Finally, the abatement of CO_2 can be performed by producing other products like biodiesel (Iancu et al. 2012), turning the process sustainable.

To figure out the problem of sweetening the natural gas, currently there are a big amount of processes proposed; such as the chemical absorption with amines, direct conversion, physical absorption, membrane permeation process, and low temperature distillation processes. Of these alternatives, absorption using amines is the most widely used process. However, for high CO_2 feedstock, this process requires a significant amount of solvent.

The low temperature distillation that separates CO_2 from hydrocarbons in a series of distillation columns has the potential to overcome some of the above drawbacks. There are two significant technical challenges in applying this process: (i) the formation of solid CO_2 during the separation of methane in the demethanizer column; and (ii) the existence of an azeotrope in the CO_2 recovery column. However, these challenges can be gotten over by recycling some of the natural gas liquid (NGL) product, which is produced in the solvent recovery column, as a entrainer, *Figure 1.*
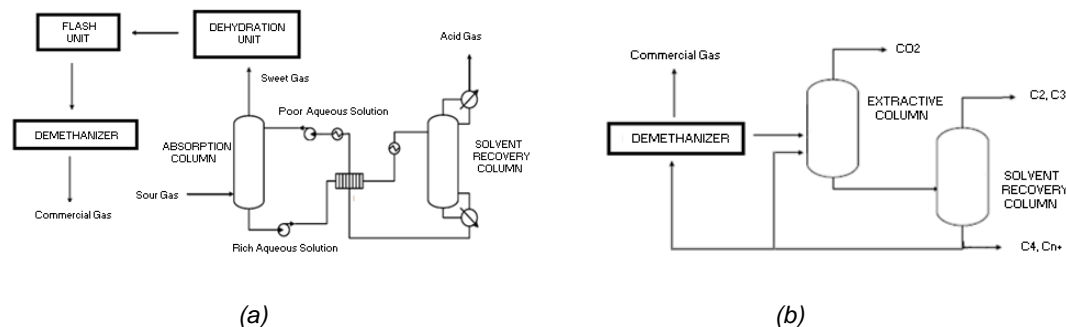

(a)   *(b)*

Figure 1: (a). General scheme of the traditional chemical absorption method; (b). General principle of the cryogenic extractive distillation by recycling some NGL.

In the alternative and traditional configurations, distillation columns are required; this unit operation is characterized for its huge energy consumption and low thermodynamic efficiency. Thus, inside the process design area the thermally coupling concept seems as a good proposal for making up alternative schemes with important energy savings, and even more in those cases where process integration is not possible. In this study we proposed the usage of thermally coupled distillation sequences in the alternative configurations. We compare the performance of these sequences with the conventional system using chemical absorption by mono-ethanol amine (MEA)) like benchmark problem.

2. Methods

The methodology followed during this work can be described in the next consecutive sections. The Aspen Plus 7.0 simulator, Excel 2007and Visual Basic 6.3 were utilized for optimization procedure.

2.1 Design of the schemes

For the prediction of the thermodynamic properties, we selected two properties methods: (i) Peng Robinson for the cryogenic extractive distillation sequences (ii) AMINES package for the traditional chemical absorption.

These thermodynamic models were chosen after an extensive and testable literature review. We decided to use the non- equilibrium model for the trays separation included in Aspen Plus [R] (Rate-Based) because on this way we can consider finite heat and mass transfer; therefore the efficiencies of the trays vary along the columns; as consequence the energy requirements predicted are more realistic than using an ideal model. Several studies using the non-equilibrium model show that these simulations match with the experimental information (He et al., 2010), and etc. We fixed the sour natural gas feed (high CO_2 concentration), and we considered the ethane the only relevant hydrocarbon in the natural gas because we focused on breaking the CO_2 - ethane azeotrope (considering that the methane has already removed in another unit operation). In general terms, the demethanizer column has too thermodynamic constraints for optimization purposes (Lastari et al., 2010). Moreover after the methane, the ethane is the second major component
We can see the feed composition in the Table 1 (Morales et al., 2005).

Table 1: Feed Composition (% Mole Base)

CO_2	Ethane
32.22	67.78

In order to select the best entrainer for each type of sequence, a sensitivity analysis was carried out fixing two aspects: the purity of the product streams and the percentage of the CO_2 removal. While doing the comparison, we detected the suitable ranges in the decision variables for the optimization step.
The criteria in this step to be satisfied are shown in the Table 2.

Table 2: Criteria to be satisfied in the configurations.

Purity CO_2 Stream	Sweet Gas Stream	Solvent Stream	% CO_2 Removal (Alternative Sequences)
0.9	0.9	0.93	96, 97,98, 98.5, 99, 99.5 and 99.9

In the case of the thermally coupled distillation sequences, we used the methodology proposed by Hernández and Jiménez (1996) for starting configurations.

2.2 Optimization Procedure

For each sequence, four solvents were considered in the step below; then, the best two sequences per case were selected for the optimization and due to the complex nature of the models of this type of systems a metaheuristic algorithm called Differential Evolution (DE) has been applied. We selected DE by means of the Hybrid Multi-Objective algorithm made by Srinivas and Rangaiah (2007). DE requires the next parameters: Population Size (Np), Crossover factor (Cr) and Mutation or Differentiation Factor (F). We used the starting values proposed by Rangaiah (2010); then Np = 10 Decision Variables, F = 0.8 and Cr = 0.9. The stopping criterion (number of generations equal to 160) was fixed for all the optimizations. The Objective Functions were minimizing the Total Annual Cost (TAC) and maximizing the removal of CO2. The TAC function is represented for the Equation 1. Simulations with lower purities than those established in the criteria set in step one were penalized.

The correlations and data for TAC were taken from Turton et al.,(2009).

$$TAC = \sum \left[\left(\frac{Capital\ Cost}{Time\ of\ Investment} \right)_i + (Cost\ of\ Utilities)_i \right]$$

(1)

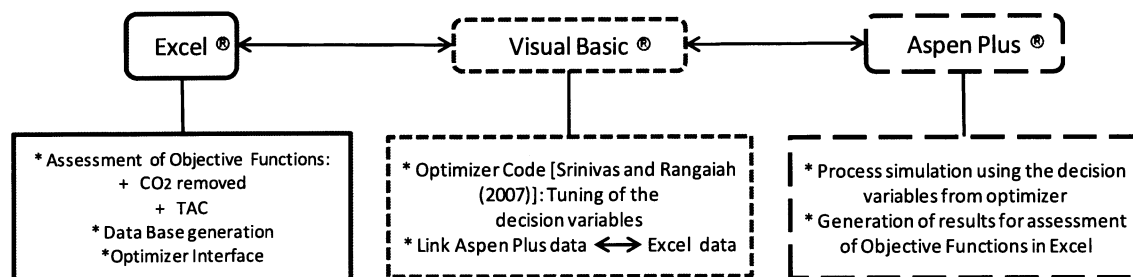The optimization was made under the next interface

Figure 2: Flowchart of the general interface procedure for the optimization.

2.3 Step 3: Post-Optimization Analysis

After the formal optimization, we obtained Pareto fronts (% CO_2 Removed versus TAC) and we chose ten representative spots for each Pareto front (optimal sequences for different % CO_2 removed) and carried out three different studies: (i) **Dynamic Analysis by Singular Value Decomposition (SVD):** under this study, we used the concept of Dominant Time Constant defined by Skogestad and Morari (1987) to generate the gain matrix of the process; next by means of a frequency response, we accomplished the SVD, (Klema and Laub, 1980), with a constant disturbance on the control variable directly related with the product streams; (ii) **Thermodynamic Efficiency:** this study was based on the methodology described by Seader and Henley (2006); (iii) **CO2 Emissions:** this analysis was performed based on the work of Gadalla et al. (2005), focused on the CO2 emissions generating by the steam used on the reboiler of the columns.

3. Case studies

Three different schemes using cryogenic extractive distillation were simulated, each of them with four pure solvents: propane, n-butane, n-pentane and n-hexane.

The pressure and temperature of operation were taken from the Lastari et al. (2010) paper.

For the chemical absorption process, an amine aqueous solution was used as entrainer. This amine aqueous solution has only water and methanol-amine (MEA). All the conditions for this process were taken from POGC (2002). The sequences studied are depicted in the *Figure 3.*

(a) 12 Decision Variables

(b) 12 Decision Variables

(c) 14 Decision Variables
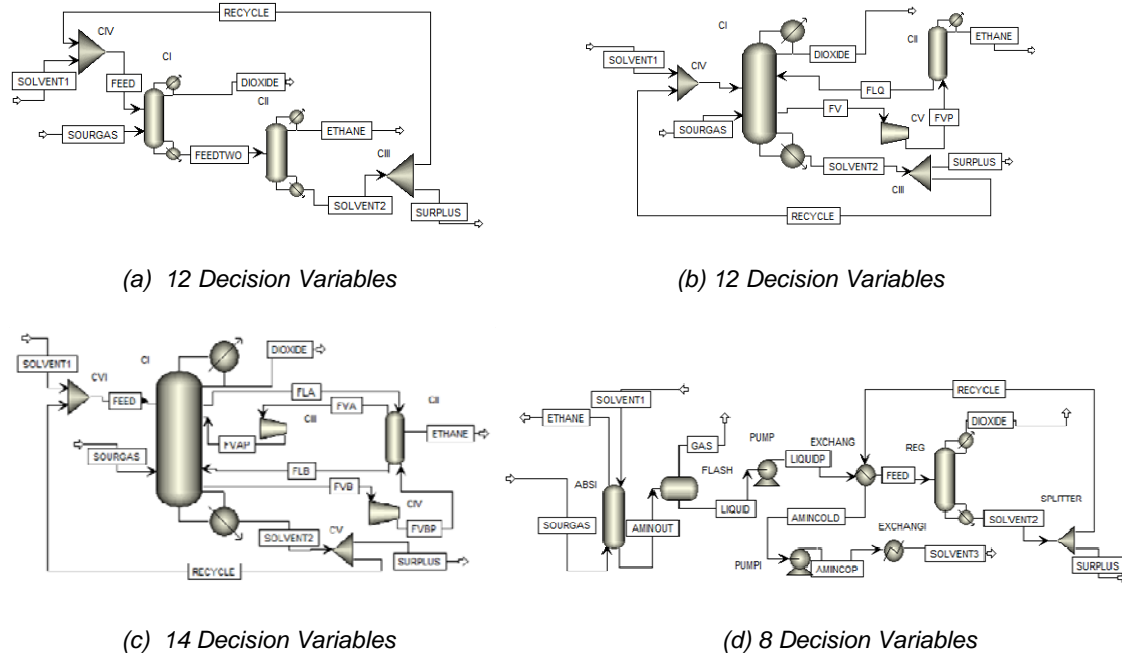

(d) 8 Decision Variables

Figure 3: (a) Conventional Cryogenic Extractive Sequence (Alt_1); (b) Thermally Coupled Extractive Sequence with Side Rectifier (Alt_2); (c) Petlyuk Extractive Sequence (Alt_3), (d) Chemical Absorption (Conv.)

4. Results and Discussions

The results can be analysed in a better way if we divide them in three major categories based on the methodology below.

4.1 Step 1: Design of the Schemes by Sensitivity Analysis
The methodology is illustrated by considering a single case just focused on the best option obtained and reporting the general and more relevant results for each stage of each section.
The sensitivity analysis, showing the behaviour of the four solvents for the sequence Alt_2, is depicted in *Figure 4*. We can observe that n-butane and n-pentane are the most promising sequences, and then they are chosen for the next study.
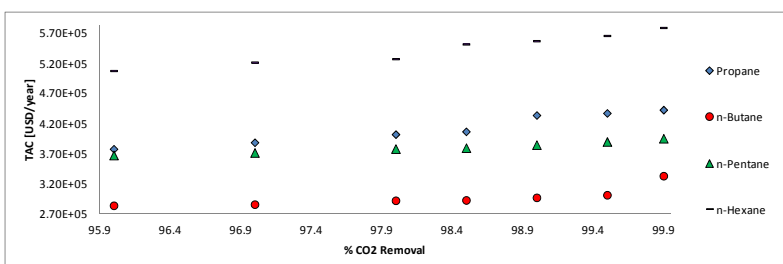

Figure 4: Sensitivity Analysis for the sequence Alt_2.

In general terms, we found that for all the sequences, Alt_1, Alt_2 and Alt_3, the best entrainers were the n-butane and n-pentane; moreover, the n-hexane had the worst performance.
A possible reason for which n-hexane did not work is because of the high boiling point of this heavy solvent; according to the vapour composition profiles in Alt_2 using n-hexane, the behaviour of this system was more similar to absorption than distillation.
For the case of propane, it had a better performance than n-hexane because of a greater transition from the liquid solvent to the vapour phase. However it was not better than n-butane or n-pentane, probably

because the low boiling point closer to the ethane. Finally n-butane had better responses in most of the cases.

4.2 Step 2: Optimization Procedure

The optimization for the two solvents on sequence Alt_2 is shown in *Figure 6.a.*The trend in this section is according to the last one. We can note there is a zone of operation just before the inflexion point where the percentage of recovery is too high and the TAC is still reasonable.
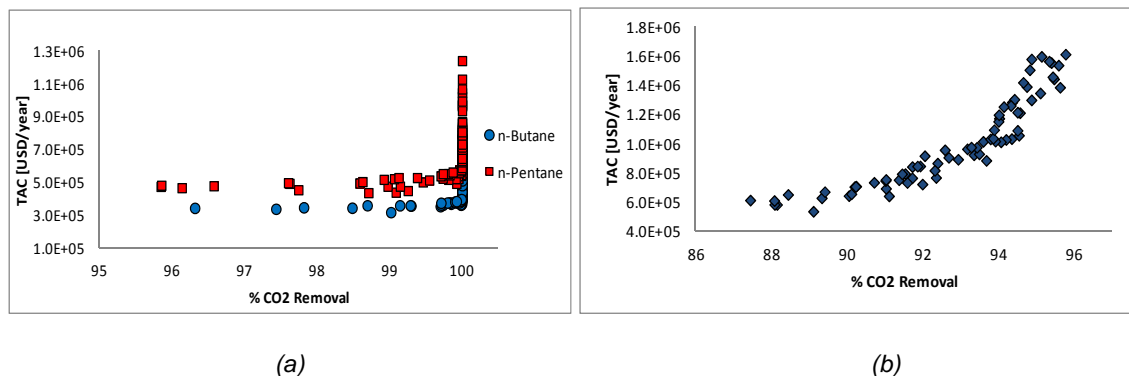

(a)   (b)

Figure 6: (a) Final Pareto Front for Alt_2; (b) Final Pareto Front for the Chemical Absorption

In all the Pareto fronts obtained, they followed the same tendency than step 1. Also we can describe that Alt_1 and Alt_2 reached out the highest percentage of CO_2 removals meeting the purities criteria, and slightly lower TACs for Alt_2. The worst in this issue was the Conv., with the highest TAC and poor CO_2 removals, *Figure 6.b*. The Pareto fronts for Alt_3 were not clear, and most of their optimal points did not meet the purity criteria. All this could reflect the need of a major quantity of generations.

4.3 Step 3: Post-Optimization Analysis

As an example, we show some post-optimization results for the Alt_2 using n-butane (the best sequence found). We can see that the points with less percentage of removal have better dynamic behaviour for this scheme (lower Condition Number and higher Minimum Singular Value); meanwhile the spots in the middle (just before inflexion point) have intermediate behaviour, *Figure 7*. In addition to this, the thermodynamic efficiency and CO_2 emissions for these intermediate points are quite good, *Figure 8*.
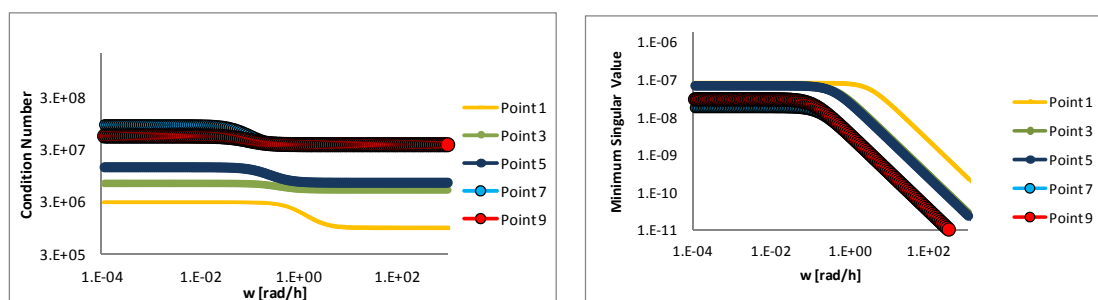

Figure 7: Some points representing the dynamic behaviour of the sequence Alt_2 using n-butane.
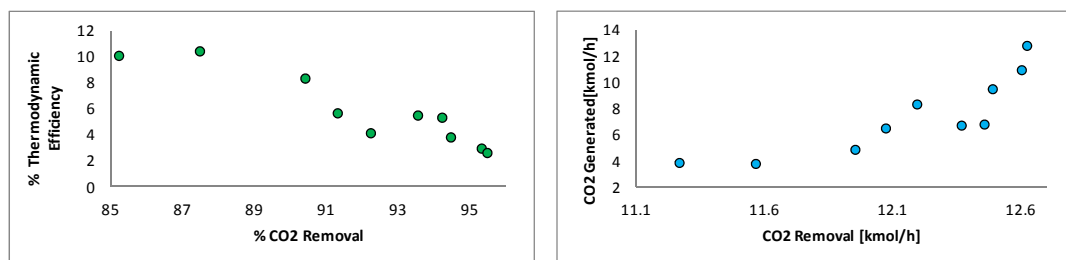

Figure 8: Points representing the static behaviour of the sequence Alt_2 using n-butane.

In general, comparing the dynamic behaviour, we noted that each sequence has a particular trend, but it can be seen that with the solvent n-butane, the points with lower removal (from 95 % to 99 %) have better dynamic features, and with solvent n-pentane occurs with higher removal (from 99 % to 100 %). Also the extreme spots have worse dynamic parameters and lower efficiency (mainly for high removals). The emissions tendency was similar to the TAC profile, and just the alternatives seem to be sustainable (lower CO_2 generation than CO_2 removal). The alternatives' thermodynamic efficiencies were lower than chemical absorption ones because of the use of cryogenic units in alternative arrangements.

5. Conclusions

According to the analyzed data, we can conclude that the alternative sequences had a better generalized performance than the conventional chemical absorption scheme. The Alt_2 arrangement turned out the best option for sweetening the natural gas with high CO_2 concentration. Using sensitivity analysis followed by a formal optimization resulted in a robust but efficient tool for finding the feasible and suitable range of operation for each sequence since different points of view like costs, control, and more.

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