

Computer-Aided Parametric Sensibility Analysis of an Amine Treatment Unit

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Amine treatment units are essential in modern refinery configurations for an efficient reutilization of amine in absorption of sulphur, which could cause acid rain and potential negative environmental impacts if released, after combustion of fuels, to the atmosphere, since on an industrial level the amine which is rich in sulphur compounds needs to be treated in order to re-use it in different processes like: oxidation of mercaptans, hydro treatment and delayed coking units. Improvement of technical performance of amine treatment units in refinery is key for obtaining clean products and efficient sulphur removal, because of this, it is necessary to determine the optimal operating conditions in order to achieve the best possible performances of the units regarding the technical aspect, by the modification of several operative variables employed in every stage.

This work had as primary goal to improve the performance of an amine regeneration of a Latin-American refinery, to accomplish this, a simulation and a parametric sensitivity analysis of the unit was made. Simulation was carried out using a robust commercial process simulation software, based on real refinery configurations, through the parametric sensitivity analysis and the implementation of sensibility curves. The behaviour of the process was studied from changes in its operating parameters, as the temperature in the absorption column, reflux ratio, mass flow of steam, Sulphur concentration in rich amine, pressure, among others, in order to upgrade its technical efficiency. Results show that changes in amine composition presents a direct effect on the amount of hydrogen sulphide absorbed, absorption process presents low sensibility to changes in pressure and concentration of hydrogen sulphide in LPG affects the heat of absorption and the temperature.

1. Introduction

In the countries of South and Central America where the gross domestic product (GDP) depends largely on the exploitation of oil, this indicator is affected due to its low price, which is why refining generates more money than oil exploitation (Malagón et al., 2016). Countries such as Colombia, Brazil, Ecuador, Mexico and Peru have opted for the modernization of their refineries to increase the production of high quality derivatives, as well as their profits (BNamericas, 2017), and moving toward unconventional crude oil sources (Almeida et al., 2017). An indicator of high quality in fuels is the minimum percentage of sulphur that must be contained. For oil refineries, this challenge is even more important, since it is also necessary to improve the quality and profitability of their products (Vilarinho et al., 2016). Mercaptans are compounds present in crude oil products and these have a high sulphur content. The sodas used in the different cracking units should be removed the impurities (mercaptans, hydrogen sulphide, gases) that have been absorbed in previous processes to be sent to the residual water treatment units and thus meet the environmental and safety standards of quality (Almeida et al., 2017). Furthermore, these sulphur compounds are removed from the crude using amines, but these must be treated to be recirculated to the mercaptans oxidation process and to the hydrotreating unit. The purpose of the amine treatment unit is the regeneration of Dietanolamine (DEA) that contains H₂S and CO₂. H₂S and CO₂ are absorbed in sweetening processes (Qeshta et al., 2015). The amine rich with these pollutants is regenerated by stripping with steam; the regenerated amine is cooled and pumped to the absorbent towers of mercaptans

oxidation process and Coker units; On the other hand, H_2S and CO_2 are sent as acid gas to a sulphur recovery unit.

2. Process description

The rich amine is sent to the flash tank (D-1), where most of the gaseous hydrocarbons are separated, this stream is put in contact in the flash contact tower with the lean amine (main unit product) and drags some components such as of the poor amine, the gaseous components are burned. The rich amine leaving the drum, passes through a series of filters to remove impurities and light hydrocarbons, then passes to the steam stripping tower to remove heavier sulphur compounds, the tower is equipped with a steam reboiler and facilities to add steam if it was necessary. The lean amine leaves at bottom tower, part of this stream is recirculated and cooled and sent to the ejector, the purpose of this is operation is reducing the temperature and prevent amine degradation. In Figure 1, a simplified process flowsheet diagram is shown. The process consists of three main stages: flash separation, filtration and stripping.

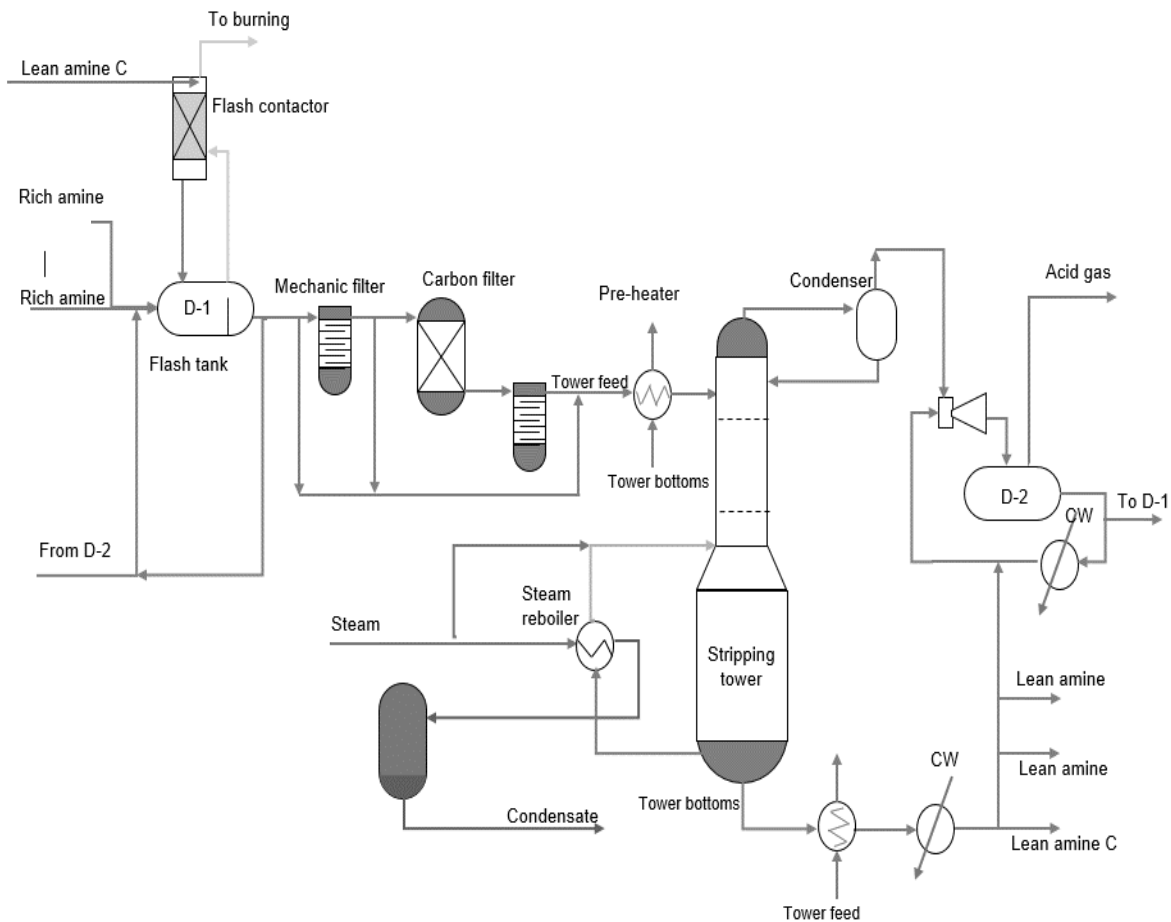


Figure 1: Simplified process flowsheet for an amine regeneration unit

2.1 Flash separation

In this stage, the rich amine coming from the oxidation units of mercaptans and Coker is fed to a flash drum where light hydrocarbon vapour is separated and sent to a flash contactor where it is placed in countercurrent contact with a poor amine (objective of the unit) with the goal of separating most of the H_2S present in the light hydrocarbons that will later be burned. The rich amine exits through the bottom of the contactor and enters the flash drum.

2.2 Filtration

The filtering is carried out by a filter system consisting of two mechanical filters and an activated carbon filter. A mechanical filter serves as a preliminary stage for the removal of impurities and other solids present in the rich

amine, the activated carbon filter removes most of the dissolved hydrocarbons that could affect later stages of the process. The last filter has the objective of removing the remnant of activated carbon present in the rich amine.

2.3 Steam stripping

The amine from the filtration stages is preheated with the bottom stream of the stripping tower, the amine vaporizes partially and enters the tower, ascends the tower plates coming into contact with the liquid stream of rich amine that comes down; this contact maintains the temperature conditions that are required to guarantee an optimum dispossession of H₂S and CO₂. The tower has facilities for the use of steam as heating source for the reboiler and to inject steam to the tower if necessary.

3. Process simulation

The process simulation was performed using a commercial simulation process. Peng-Robinson-Stryjek-Vera was used as thermodynamic model because has accuracy comparable with some dual methods using activity coefficients for the liquid-phase and equations of state for the vapour phase (Proust and Vera, 1989). The flow of steam to the reboiler controls the degree of vaporization of the amine, and directly affects the regeneration of the same, for this reason was taken as an independent variable in the sensitivity analysis, and was observed how affect operational parameters such as fraction of amine and H₂S in the bottoms and in overhead as well as reflux.

Table 1: Comparison between real and simulated data

| Component molar flow (kmol/h) | Rich amine 1 | | Rich amine 2 | | Lean amine 1 | | Lean amine 2 | | Acid gas | |
|-------------------------------|--------------|------------|--------------|------------|--------------|------------|--------------|------------|----------|------------|
| | Plant | Simulation | Plant | Simulation | Plant | Simulation | Plant | Simulation | Plant | Simulation |
| H ₂ O | 1,840 | 1,841 | 1,084 | 1,084 | 1,085 | 1,033 | 1,859 | 1,768 | 0.65 | 1.18 |
| DEA | 105.32 | 105.35 | 62.07 | 62.07 | 62.08 | 60.91 | 106.41 | 104.25 | 0.00 | 0.00 |
| H ₂ S | 5.62 | 5.62 | 12.76 | 12.76 | 1.22 | 0.00 | 2.09 | 0.00 | 16.10 | 15.98 |
| CO ₂ | 0.01 | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 | 0.00 | 0.00 | 0.02 |
| SO ₂ | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| i-butane | 0.01 | 0.01 | 0.01 | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| n-butane | 0.03 | 0.03 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 1-butene | 0.13 | 0.13 | 0.03 | 0.03 | 0.00 | 0.00 | 0.00 | 0.00 | 0.03 | 0.02 |
| i-butene | 0.00 | 0.00 | 0.04 | 0.04 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 | 0.00 |
| Cis-2-butene | 0.00 | 0.00 | 0.02 | 0.02 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Trans-2-butene | 0.00 | 0.00 | 0.03 | 0.03 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Propane | 0.30 | 0.30 | 0.04 | 0.04 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.03 |
| Propene | 0.44 | 0.44 | 0.53 | 0.53 | 0.00 | 0.00 | 0.00 | 0.00 | 0.24 | 0.14 |
| Ethane | 0.00 | 0.00 | 0.01 | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Ethylene | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 1,3-butadiene | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |

4. Results and discussion

4.1 Process simulation results

The results of the simulation show an adequate representation of the process on a real scale, the data taken as a reference correspond to real data of amine treatment unit in a Latin American refinery. The corresponding data can be visualised in Table 1.

4.2 Parametric sensitivity analysis

In Figure 2 can be seen that the tower operates in a critical area where small changes in the steam flow will produce considerable changes in the amount of H₂S that is removed and leaves the top of the tower. Figure 3 shows a decrease in the molar fraction of the DEA in the gas phase stream leaving the top of the stripping tower, a decrease in the amount of steam causes a decrease in the amount of steam of water that leaves the top of the stripping tower, consequently the proportion of DEA in the top will increase. On the other hand, it can also be observed that at values above 43,000 kg/h there would not be an appreciable change in the DEA concentration.

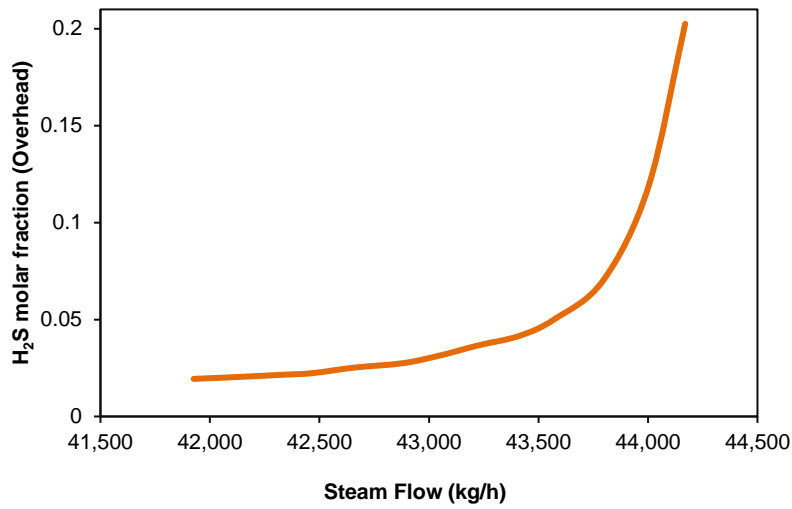


Figure 2: Steam flow H₂S molar fraction (Overhead)

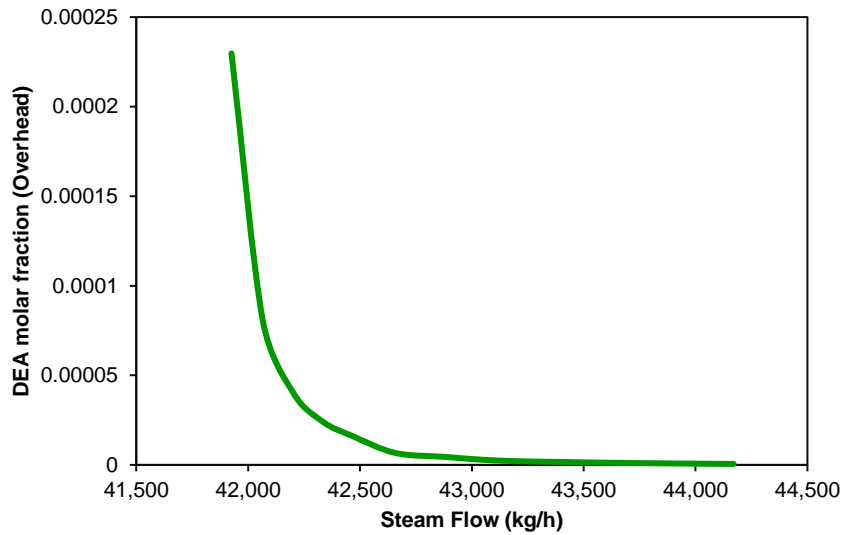


Figure 3: Steam flow vs DEA molar fraction (Overhead)

The flow of steam to which the tower regularly operates is 44170 kg/h, a linear trend of the molar fraction of DEA at the bottoms can be observed figure 4, decreasing while increasing the steam flow, increasing the amount of evaporated DEA and therefore a smaller proportion of it in the bottoms. It can also be seen that moderate changes in the steam flow (<450 kg/h) do not incur an appreciable change in the DEA molar concentration in the bottom tower stream flow, this is due to the low volatility of the tower (boiling point 535,15 K).

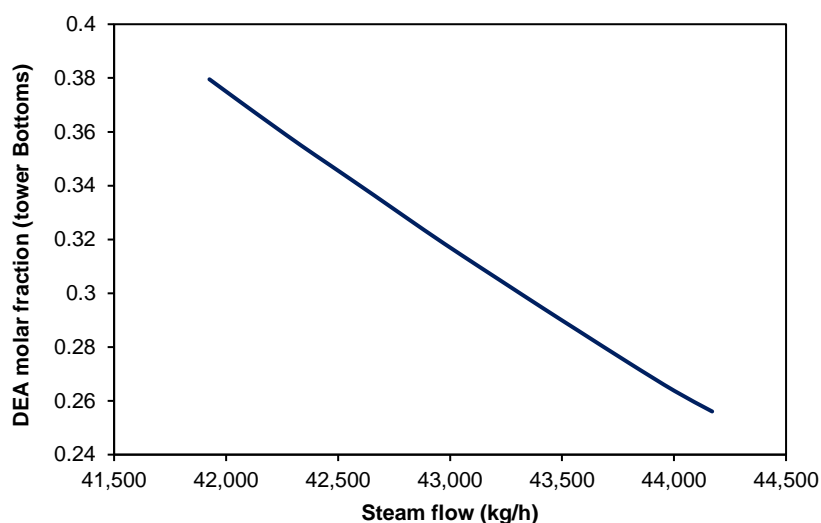


Figure 4: Steam flow vs DEA molar fraction (Tower bottoms)

Figure 5 is the last generated sensitivity curve and it shows a decrease in the reflux of the tower when the steam flow increases, the results are consistent with the actual operation of this type of towers, as the steam flow increases, it also leads to a higher vaporization of the amine on the part of the reboiler consequently a smaller flow of the same one must be lead to the same to maintain the same conditions of separation.

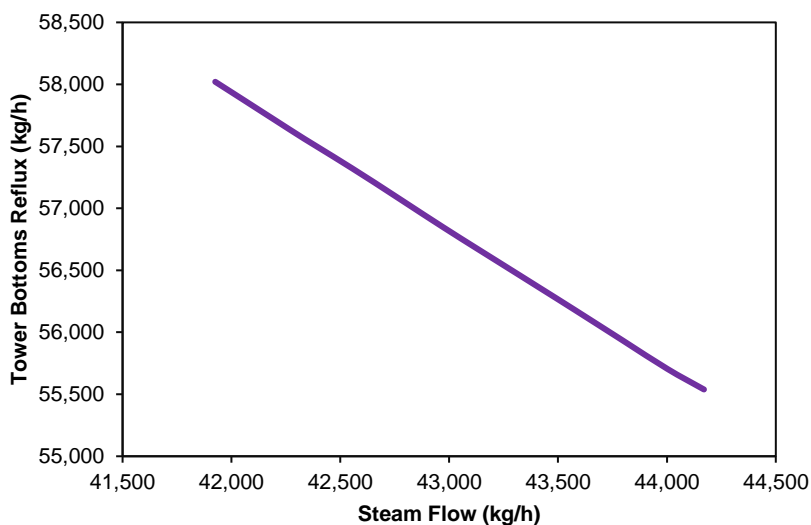


Figure 5: Steam flow vs tower bottoms reflux

5. Conclusions

The sensitivity analysis carried out previously shows that in Figure 2 the vapour flow is inversely proportional to the DEA fraction at the top of the tower, besides it was observed that small changes in the steam flow do not present appreciable changes in the concentration of DEA. On the other hand, in Figure 3 it was observed that by making small operational changes of the steam flow in a specific area it is possible to identify the amount of H₂S eliminated. Finally, in Figure 4 it was possible to determine that the decrease of the molar fraction of DEA is preceded by an increase in the steam flow in the power supply to the tower. Something to emphasize because with values above 43,000 kg/h did not generate appreciable changes in the concentration of DEA. In addition, in Figure 5 it was identified that the steam flow is inversely proportional to the reflux of the tower.

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