Evaluating the Exergetic Performance of the Amine Treatment Unit in a Latin-American Refinery

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ABSTRACT: Recently, exergy analysis has attracted great attention of the scientific community as an attractive tool for evaluating energetic efficiency of any process. In this work, the simulation of the amine treatment unit in a Latin-American refinery was performed in order to apply the exergy analysis tool to identify alternatives of improvement. The industrial amine treatment unit was simulated using Aspen plus software, which provided extended energy and mass balances. To calculate irreversibilities of the process and global exergy efficiencies per stages, the general methodological procedure of exergy analysis was used. To this end, physical and chemical exergeries were found for compounds involved within the process. The values estimated for total irreversibilities, exergy of utilities, and exergy of wastes in the treatment of the sulfur-rich amine allowed us to analyze the stages that require reductions in waste generation and utility consumption. For a processing capacity of 72.08 t/h of rich amine, results revealed that the overall exergy efficiency was 83.81% and the total irreversibility was 1.69 × 10^5 MJ/h, where 23.6% corresponds to the total exergy by residues (3.98 × 10^5 MJ/h). The novel strategy to use exergy analysis for process optimization proved to be useful to detect critical stages and prioritize actions to improve.

1. INTRODUCTION

Nowadays, it is a key challenge to preserve the environment while meeting the continuously increasing global energy demands caused by population growth.1,2 To face such challenges, it requires approaches for minimizing energy consumption or increase overall performance at the individual-process-plant level.3,4 The improvement of energetic performance of processing plants such as refineries can contribute to long-term sustainability of energy resources.5 Exergy analysis is an effective method based on the second law of thermodynamics, which is used to systematically locate and quantify inefficiency sources. Once the locations of the system’s inefficiencies are identified, improvement can be made to reduce exergy loss of the system.

Exergy accounts for the usefulness and is mathematically defined as the maximum amount of work that can be produced by a system as reaching equilibrium with the environment.6,7 Many researchers and engineers conduct exergy analysis as a method for analyzing, designing, and improving systems and processes.8,9,10 In this work, exergy analysis is implemented in the amine treatment unit of a refinery to increase the energetic efficiency of the process stages and to reduce its irreversibilities. The purpose of the amine treatment unit is the regeneration of diethanolamine (DEA) that contains H₂S and CO₂,10 which are absorbed in sweetening processes.11

2. MATERIALS AND METHODS

2.1. Methodology. The modeling of the amine treatment unit relied on the information gathered from previous studies and scientific literature, as well as on the collaboration of experienced engineers that work on this field. The simulation of the process was performed using Aspen Plus. Substances present in the real process were selected directly from the software database, so there was no need to create any hypothetical compound because they were all included in the simulator’s library. In addition, key operating parameters required to run the simulation (e.g., inlet mass flowrate) were introduced. The selected fluid package was Peng–Robinson–Stryjek–Vera used to calculate thermodynamic properties of compounds involved within the process. This thermodynamic model has been shown to give comparable results to other methods using activity coefficients for the liquid-phase and equations of state for the vapor phase.12

2.2. Process Simulation. The simulation flowsheet was built, consisting of the separation equipment, adsorption and gas stripping towers, vessels, and others, all of which were selected from the simulator model palette to represent the actual unit in an appropriate way. Then, all process data were

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entered for streams and equipment, for example, temperature, pressure, mass or molar flowrate, and processing capacity, among others. After running the simulation, the software provided the extended mass and energy balances for the entire unit including detailed process data such as mass composition of each stream and thermodynamic properties.

2.3. Process Description. The sulfur-rich amine is sent to a flash drum, where most of the light hydrocarbons dragged by the amine stream are separated. This stream is put in contact with lean amine (product of the main unit) in a flash contactor to absorb the hydrogen sulfide that could have been flashed. The rich amine leaving the drum passes through a series of filters to remove impurities and light hydrocarbon particles. The resulting stream is sent to the stripping tower to eliminate the hydrogen sulfide and carbon dioxide by vapor heating. This column is equipped with a steam boiler and with facilities to inject live steam directly to the tower if necessary. A part of the lean amine leaves the bottom of the tower, and part of the stream is recirculated to the reboiler. The rest of the stream is cooled and leaves as the main product of the unit. The hydrogen sulfide and carbon dioxide (acid gas) leave the tower from its top, followed by cooling, and then enters into a condensate drum, where the condensed liquids serve as the tower reflux. An ejector drags the acid gas, which then goes into a flash drum, where some amine in the stripping is flashed and recirculated to the initial amine flash drum. Finally, the acid gas leaves from the drum top as waste. Figure 1 depicts a simplified process flow diagram. The process consists of three main stages: flash separation, filtration, and stripping.

2.3.1. Flash Separation. In this stage, the rich amine is fed into a flash drum, where the light hydrocarbon vapors are separated and sent to a flash contactor. In such contactors, vapors flow in countercurrent with lean amine (main product) in order to absorb the largest amount of H₂S in the light hydrocarbons. The sulfurous acid leaves the system for further burning. The rich amine leaves the bottom of the contactor and enters into the flash drum.

2.3.2. Filtration. The filtering is carried out by a system consisting of two mechanical filters and an activated carbon filter. A mechanical filter is used 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 the later stages of the process. The last filter has the objective of eliminating the remnant of activated carbon present in the rich amine.

2.3.3. Stripping. The amine coming from the filtration stage is preheated with the bottom stream of the stripping tower in a heat exchanger, and then, it is sent to the tower. As a common principle of any tower, the liquid amine descends through the tower plates and makes contact with the vapors that ascend. Such a contact maintains the temperature conditions required to guarantee an optimal disposition of H₂S and CO₂. The tower has facilities for the use of steam as a heating source for the reboiler and for injecting steam to the tower if necessary.

2.4. Exergy Analysis. The exergy analysis is a thermodynamic analysis technique based on the second law of thermodynamics, which provides a computer-aided tool to evaluate, analyze, and compare systems. In addition, the exergy analysis methodology quantifies the global efficiency and per stages that allow to measure how close is any process to ideality. The main advantages of this tool are as follows:

i. Address the impact of an energy resource on the environment,
ii. Effective method for the analysis and design of energy systems
iii. Meet the principles of conservation of mass and energy along with the second law of thermodynamics
iv. Allow to find the most efficient way to use an energy resource, determine the best locations, types, and true magnitudes of the waste.

For an exergetic balance in the steady state, the destroyed exergy is related to the net irreversibility of mass flow, work, and heat transfer, given by eq 1.

\[ \text{Ex}_{\text{destroyed}} = \text{Ex}_{\text{net-mass}} + \text{Ex}_{\text{net-heat}} + \text{Ex}_{\text{net-work}} \]  

\[ \text{Ex}_{\text{work}} = W \]  

Figure 1. Simplified process flow diagram of the amine treatment unit.
According to eq 2, the exergy associated with work in a system where there is constant volume is equal to the same work of the system. Regarding exergy by heat transfer, this can be calculated based on the efficiency of Carnot using eq 3. On the other hand, the total input of exergy in a system is related to the inlet streams of the process and/or industrial services required by the system as expressed in eq 4, while the total output exergy is associated with the main product streams and/or waste streams, as shown in eq 5.

\[
E_{\text{heat}} = \sum_i \left( 1 - \frac{T_0}{T} \right) Q_i \tag{3}
\]

Irreversibilities in the process can be calculated with eq 6 by subtracting the total exergy from the products to the total input of exergy. Finally, the exergetic efficiency of a process or stage can be estimated by eq 7 based on the irreversibility and the total exergy entering into the system. The percentage of irreversibilities per each stage \((i)\) can be calculated by eq 8.

\[
E_{\text{destroyed}} = \sum \text{Ex}_{\text{total-in}} - \sum \text{Ex}_{\text{products-out}} \tag{6}
\]

\[
\eta_{\text{exergy}} = 1 - \left( \frac{\text{Ex}_{\text{destroyed}}}{\sum \text{Ex}_{\text{total-in}}} \right) \tag{7}
\]

\[
\% \text{ Ex}_{\text{destroyed},i} = \left( \frac{\text{Ex}_{\text{destroyed},i}}{\sum \text{Ex}_{\text{total-deestroyed}}} \right) \times 100% \tag{8}
\]

Table 1. Comparison between Real and Simulated Data

| component | feed-rich amine A | feed-rich amine B | product lean amine A | product lean amine B | acid gas |
|-----------|------------------|------------------|----------------------|----------------------|---------|
|           | real (kmol/h)    | simulated        | real (kmol/h)        | simulated            | real (kmol/h) |
| HDO       | 1840             | 1841             | 1084                 | 1084                 | 1085     |
| DEA       | 105.32           | 105.35           | 62.07                | 62.07                | 62.08    |
| H2S       | 5.62             | 5.62             | 12.76                | 12.76                | 1.22     |
| CO2       | 0.01             | 0.01             | 0.00                 | 0.00                 | 0.00     |
| SO2       | 0.00             | 0.00             | 0.00                 | 0.00                 | 0.00     |
| 1-butane  | 0.01             | 0.01             | 0.01                 | 0.01                 | 0.00     |
| 2-butane  | 0.03             | 0.03             | 0.03                 | 0.03                 | 0.00     |
| 3-butane  | 0.13             | 0.13             | 0.03                 | 0.03                 | 0.00     |
| 4-butane  | 0.00             | 0.00             | 0.04                 | 0.04                 | 0.00     |
| 2-butene  | 0.00             | 0.00             | 0.02                 | 0.02                 | 0.00     |
| 3-butene  | 0.00             | 0.00             | 0.03                 | 0.03                 | 0.00     |
| 4-butene  | 0.00             | 0.00             | 0.04                 | 0.04                 | 0.00     |
| 2-butene  | 0.00             | 0.00             | 0.02                 | 0.02                 | 0.00     |
| 3-butene  | 0.00             | 0.00             | 0.03                 | 0.03                 | 0.00     |
| 4-butene  | 0.00             | 0.00             | 0.04                 | 0.04                 | 0.00     |
| propane   | 0.30             | 0.30             | 0.04                 | 0.04                 | 0.00     |
| propene   | 0.44             | 0.44             | 0.53                 | 0.53                 | 0.00     |
| ethane    | 0.00             | 0.00             | 0.01                 | 0.01                 | 0.00     |
| ethylene  | 0.00             | 0.00             | 0.00                 | 0.00                 | 0.00     |
| 1,3-butadiene | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |

Figure 2. Simulation of the amine treatment plant.
3. RESULTS AND DISCUSSION

3.1. Process Simulation. The simulation of the process was carried out through the commercial simulation software Aspen Plus. For simplification purposes, the main sections of the process are flash separation, filtration, preheating, stripping, top circuit, and bottom circuit. The processing capacity was set in 72.08 t/h of rich amine, and the production rate was 67.82 t/h of the lean product (lean amine). An ideal separation vessel was used as the flash tank (D-1). A simple solid separator was used as the mechanical filter, and carbon filter simulation was performed using a component splitter fractionator in order to remove some remaining hydrocarbons. Stripping tower simulation was carried out using a refluxed absorber column equipped with a reboiler which exchanges heat with low-pressure steam as the heating source. The final flash tank (D-2) allows us to remove acid gas from the amine stream. Other equipment and operations such as recycling accessories, pumps, and utilities were used for accurate modeling of the real amine treatment unit. Figure 2 shows the simulation flowsheet provided by the software. In order to validate the results collected from the process simulation, a comparison of such values was performed with the real plant data and summarized in Table 1.

3.2. Exergy Analysis. Table 2 reports the result of the chemical, physical, and total mass exergy of the system for each current. The exergy balance shows that the total chemical and physical exergy of the process was 8.58 × 10⁶ and 7.38 × 10⁴ MJ/h, respectively. These results were used to calculate the exergetic parameters such as irreversibilities, exergy of wastes, exergy of utilities, and efficiency.

3.2.1. Exergy Analysis Per Stage. Figure 3 shows the exergy analysis from the process stages of the amine treatment unit. It was found that exergetic efficiency of the flash, filtration, preheating, stripping, and bottom circuit stages exceeds 90%, suggesting that there is no high waste of heat or work during the equipment operation in each stage. On the other hand, the section of the top circuit presents the lowest exergetic efficiency of the system with 4.1%, which affected the overall efficiency of the process. In addition, the highest percentages of irreversibilities were found at the bottom circuit, stripping, and top circuit stages with contribution to total irreversibilities of 39, 21, and 20% respectively. These results may be associated with heat or work losses and wastes. As shown in Figure 3, the exergy of wastes reached the highest values in the top circuit (1.90 × 10⁴ MJ/h), followed by the bottom circuit (1.47 × 10⁴ MJ/h) and filtration stages (4.88 × 10³ MJ/h).

3.2.2. Global Exergy Analysis. Figure 4 shows the global exergy analysis of the amine treatment unit. It was estimated that the overall process efficiency is 83.81%, a high value that suggested low process irreversibilities (1.68 × 10⁴ MJ/h). The total exergy of wastes most contributed to total irreversibilities corresponding to 23.6% (3.98 × 10⁴ MJ/h). In addition, the total exergy of utilities was calculated as 2.17 × 10⁴ MJ/h, which was lower than the exergy of wastes. These results allowed to identify process improvements in order to reduce the main sources of irreversibilities. In this sense, it is proposed

![Figure 3. Exergetic analysis per process stages in the amine treatment unit.](Image)

Table 2. Chemical, Physical, and Total Mass Exergies of Main Process Streams

| Stream                  | Chemical Exergy (MJ/h) | Physical Exergy (MJ/h) | Total Mass Exergy (MJ/h) |
|-------------------------|------------------------|------------------------|--------------------------|
| Mixed amine             | 9.51 × 10⁶             | 1.81 × 10⁵             | 9.51 × 10⁶               |
| Lean amine              | 9.55 × 10⁷             | 2.90 × 10⁷             | 9.55 × 10⁷               |
| HC                      | 1.75 × 10⁵             | 1.59 × 10⁴             | 1.77 × 10⁴               |
| Rich amine              | 9.47 × 10⁶             | 2.30 × 10⁵             | 9.48 × 10⁵               |
| Filter                  | 4.50 × 10⁴             | 0.00 × 10⁵             | 4.50 × 10⁵               |
| From F-2004             | 3.91 × 10⁵             | 1.07 × 10⁵             | 3.91 × 10⁵               |
| Rich amine to E-1       | 4.97 × 10⁵             | 2.28 × 10⁴             | 4.97 × 10⁵               |
| A intercambiador        | 9.56 × 10³             | 3.12 × 10³             | 9.59 × 10³               |
| Cold lean amine         | 9.30 × 10³             | 1.97 × 10³             | 9.32 × 10³               |
| Mixed amine to T-2      | 9.48 × 10⁵             | 6.53 × 10⁵             | 9.48 × 10⁵               |
| Refluximed amine        | 4.66 × 10⁶             | 2.37 × 10⁴             | 4.89 × 10⁶               |
| Reflux                  | 4.67 × 10⁷             | 2.58 × 10⁵             | 4.70 × 10⁵               |
| Hot lean amine          | 9.30 × 10⁶             | 3.12 × 10⁵             | 9.33 × 10⁵               |
| Sour gas                | 1.69 × 10⁵             | 1.17 × 10⁵             | 1.81 × 10⁵               |
| Steam                   | 2.29 × 10⁵             | 3.20 × 10⁴             | 5.49 × 10⁵               |
| AE                      | 8.40 × 10⁵             | 2.23 × 10⁵             | 8.42 × 10⁵               |
| Cond                    | 1.89 × 10⁵             | 3.92 × 10³             | 5.81 × 10⁵               |
| Water to TAE            | 8.40 × 10⁵             | 4.42 × 10²             | 8.84 × 10⁵               |
| Cold lean amine         | 9.30 × 10³             | 2.78 × 10²             | 9.31 × 10³               |
| Lean amine to P-2009    | 1.21 × 10⁶             | 3.61 × 10⁵             | 1.21 × 10⁶               |
| AE2                     | 5.24 × 10³             | 1.39 × 10⁴             | 5.25 × 10⁴               |
| Water to TAE2           | 5.24 × 10³             | 1.44 × 10⁴             | 5.38 × 10⁴               |
| Sour gas to U-123/4     | 1.37 × 10⁵             | 1.17 × 10⁴             | 1.37 × 10⁵               |
| To D-2007               | 1.48 × 10⁴             | 2.32 × 10³             | 1.48 × 10⁵               |
| Carbon                  | 6.98 × 10⁵             | 0.00 × 10⁵             | 6.98 × 10⁵               |

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to incorporate a new process stage or redesign the top and bottom circuit stages in order to reuse the wastes leaving the system and reduce waste generation.

4. CONCLUSIONS

In this work, an amine treatment unit of a cracking plant from a Latin-American refinery was simulated. The processing capacity was 72.08 t/h of rich amine in order to produce 67.82 t/h of lean amine. The comparison of simulated and real process data allowed us to validate the accuracy of the simulation. The exergy analysis showed a global exergetic efficiency of 83.81% that is significantly high for any energy-intensive process. Also, the exergy efficiency per stages was higher than 90% in most stages, except in the top circuit with an efficiency of 4.1%. Such a low value can be explained by the high amount of acid gas released as waste from the process. The total process irreversibilities were calculated in 1.68 × 10^5 MJ/h, while total exergy of wastes and total exergy of utilities reached 3.98 × 10^5 and 2.17 × 10^4 MJ/h, respectively.

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