Exergy study of amine regeneration unit using diethanolamine in a refinery plant: A real start-up plant

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ABSTRACT

Refinery plants use diethanolamine (DEA) solutions for gas sweetening. The role of DEA is to absorb H2S from sour gas. Amine Regeneration Units (ARU) are used to regenerate the rich Amine with H2S from refinery units to Lean Amine. An ARU unit of a Middle Eastern refinery that began official production in 2020 was simulated using Aspen HYSYS V.11, and an exergy study was conducted on different equipment. Whereas energy is transformed from one form to another, the exergy is destroyed in an irreversible process. The total exergy was equal to the physical and chemical exergy. The physical exergy was calculated using HYSYS, and the chemical exergy was calculated using a series of equations embedded in Excel. The DEA concentration used was 25 wt%. The exergy destruction rates, destruction efficiency, and percentage share of destruction of each piece of equipment were calculated. The regenerator exhibited the highest destruction rate of 13459.73 kW, and a percentage share of 79.61% of the total destruction. The overall exergy efficiency was 99.7%. The DEA concentration decreased from 25% to 20% as a result of system losses during start-up. Therefore, a case study was conducted to test the effect of this decrease in the H2S concentration in the sweet gas, and no effect was observed. An exergy study was conducted using an DEA of 20%. The distribution of the equipment destruction did not change. The total destruction loss increased by 2057.08 kW. From the exergy and operation point of view, the best scenario was to use a 25% concentration, to prevent destruction losses and operation problems.

1. Introduction

The hydrogen sulfide produced in the refinery industry is considered a hazardous pollutant and is toxic, corrosive, and acidic in nature. It causes severe damage to equipment as a result of its corrosiveness and may cause human death [1, 2]. Sulfur recovery unit (SRU) plants recover elemental sulfur from harmful H2S [3, 4] to prevent any acidic gas emissions from violating environmental regulations [5, 6, 7]. Recently, most plants have used the modified Claus process for sulfur recovery [8]. H2S is usually removed by an amine scrubber unit that follows the modified Claus process [6]. The CO2/H2S removal amine unit normally consists of equipment such as exchangers, coolers, a lean amine (LA)/rich amine (RA) heat exchanger, an absorber, a stripper, and pumps. The acidic gases come into contact with the amine solution in the absorber, where H2S is absorbed in the amine solution. Sweet gases are present at the top of the absorber. Then, the RA that exits the bottom is regenerated in the stripper and recycled again within the process [9]. A simple schematic of the amine scrubbing process is depicted in Figure 1.

The selection of an extremely effective chemical solvent that can meet beneficial requirements such as a high absorption capacity, high chemical and thermal stability, rapid reaction kinetics, and large regeneration energy savings is one of the most pivotal factors in chemical absorption [6]. Aqueous solvents of alkanolamine such as diethanolamine (DEA) and methyl DEA (MDEA) have been used as industrial chemical absorbents in scrubber units [10], but these amine solvents require large amounts of energy for their regeneration [11]. Aqueous solutions of MDEA and DEA are widely used in industrial treatment, especially for acid gas streams containing H2S and CO2. MDEA has high selectivity for H2S rather than CO2; therefore, in the presence of both acid gases, MDEA is used to absorb H2S and desorb CO2, while DEA is usually used if H2S is by itself [12, 13, 14, 15].

The world’s rapidly expanding population and mounting industrialization have led to a dramatic increase in energy consumption [16].
MDEA is widely used as a chemical absorbent because of its lower energy requirements [17, 18]. Optimum energy consumption is a key factor in community development. From an energy point of view, the optimization of energy consumption is currently deemed a significant indicator for the evaluation of a community's development level. Hence, energy optimization and loss prevention become crucial in various industries. Chemical processes with high energy consumption may cause an increment in both production and operation costs, and thereby decreasing system efficiency [19].

Exergy is a new concept for energy that implies the energy destruction by irreversible processes. This concept is not consistent with the common energy conservation concept in any process. Exergy is the work or power produced by the energy usage with respect to the natural environment. Some exergy components such as kinetic and potential components are similar to those for energy. The exergy can also be divided into chemical and physical exergy components. In comparison with the chemical and physical exergies, the lowest values for the kinetic and potential energies can be ignored. In most cases, the chemical exergy is always higher than the physical exergy [20]. Chemical and physical exergies are considered to be the maximum amounts of work that can be obtained from a substance. The difference between them is that for chemical exergy, the substance is changed from the environment state to the dead state only by an exchange and heat transfer with the environment. For physical exergy,
the substance is changed from its initial state to the environment state only by thermal interaction with the environment [21].

Rostami and Tavan, Hashemi et al., and Zarei performed exergy studies on SRU plants considering the overall exergy of the SRU, difference between individual sections, and individual pieces of equipment [19, 20, 22]. The literature survey revealed that there is no remarkable study involving energy and exergy analyses of amine scrubber units and ARU units. Mohamadi-Baghmolaie et al. conducted an exergy study on different compositions of a mixture of DEA and MDEA and examined a blended mixture of CO₂ emissions from the exit sweet gas [9].

The exergy studies of Amine units using special packages in HYSYS is not accurate. For example: The authors conducted a complete exergy study on the SRU plant using a special package for sulfur in HYSYS V.11 called SULSIM. They computed the exergy of all the equipment, including the reactors, exchangers, and condensers. They found a problem concerning the amine scrubber unit. The SRU package considered the unit as a block without considering the different pieces of equipment. Figure 2 shows the output from the SRU simulation and shows that the sour gas from the SRU unit was directed to the “Amine Absorber & Regenerator” block, while the sweet gas was directed to the incinerator for the final oxidation of any gas containing H₂S to SO₂. Stream 1 B was recycled again and mixed with the feed to the SRU. It is clear from Figure 2 that the amine absorber and regenerator block are not present in the detailed equipment of the amine scrubber unit. No studies were found related to the individual DEA solution and the effect of a decrease in the original concentration due to operational problems. Therefore, an industrial ARU unit was simulated with Aspen HYSYS V.11, and the results of the simulation were compared to industry data. The ARU is designed to regenerate the Rich Amine (RA) from all the refinery units to Lean Amine (LA). The LA is then recycled for gas sweetening in all the refinery units. The ARU of the SRU plant is a special unit in the Sulfur unit itself and is not a part of the common ARU unit for the refinery. The tail gas in the SRU Amine unit contains H₂S and CO₂. Therefore, the Amine scrubber unit employs the selective H₂S solvent MDEA to maximize hydrogen sulfide absorption rather than CO₂. DEA was not used in this case, although it has higher selectivity because it absorbs both H₂S and CO₂. Carbon dioxide must be left with the exit sweet gas and not with the RA. The gas sweetening in all other refinery units uses DEA solvent. The DEA concentration in the solvent solution was 25% by weight. After model validation, exergy analyses (chemical and physical) were conducted. The local irreversibility values for the equipment and distributions of destroyed exergy between devices were compared, and the exergy efficiencies of the different pieces of equipment were calculated. The concentration of DEA decreased to approximately 20% as a result of system losses. The same exergy study was also conducted on an DEA solution with a concentration of 20% to determine the changes that occurred in the different exergy calculations. The authors studied for the first time the ability to work with an DEA solution at a very low concentration (20%) without increasing the H₂S composition in the tail sweet gas outlet from the absorber. Researchers have recently focused on exergy studies to determine the destroyed energy from different process fields and to try to find the best solutions to prevent this destruction in irreversible processes.

2. Materials and methods

2.1. Simulation step

Amine regeneration unit is simulated using Aspen HYSYS software V.11 and simulation output that describes the plant is shown in Figure 3 with the feed characteristics tabulated in Table 1. Figure 3 shows the output from the simulation and can be considered to be a process flow diagram for the plant.

2.2. Simulation sections

The Rich amine received from other refinery process units and absorbers is regenerated to lean amine in regenerator column, where acid gas from overhead is sent to Sulphur recovery unit (SRU) to be processed further. The rich amine solution is pumped by the Rich Amine Pump (P1) to the tube side of the (lean/rich Amine heat exchanger E1) and fed to the Amine regenerator. Regenerator reboiler supplies the heat to the regenerator to strip H₂S off from the rich amine solution. The overhead vapor from the regenerator is cooled down to 55 °C. In the regenerator overhead condenser. The acid gas from Regenerator Re reflux Drum is then routed to SRU. Lean amine solution leaving the Amine regenerator is transferred to the shell side of E1 and cooled down to about 88.2 °C. After cooled down at E1, lean amine is pumped by (Amine charge pump P2) flowing to lean Amine Air Cooler.

2.3. Simulation criteria

The fluid package used in the simulation was “Chemical Solvent.” This package was suitable for the component feed. An inappropriate selection for the fluid package would cause a deviation in the results. The regenerator was simulated as a distillation tower, which also required some information (the number of trays, connections for the inlet and outlet streams, bottom pressure, top pressure, bottom temperature, and top temperature), and the column was based on specifications such as the flow rates or top and bottom component fractions. E1 is simulated as a normal heat exchanger. This required some values for the cold and hot side streams such as the flow rates of the streams, temperatures, and pressure drops. P1 and P2 were selected as the pumps.

Figure 3. Amine regeneration unit.
Table 1. Feed characteristics.

| Stream description | Rich Amine |
|--------------------|-------------|
| Temperature        | 103         |
| Pressure           | 5.3         |
| Mass flow          | 496025.8    |

| Total Weight Comp. Fraction |
|-----------------------------|
| DEA                         | 0.245       |
| Water                       | 0.734       |
| H2                          | 0.000       |
| NH3                         | 0.000       |
| H2S                         | 0.020       |
| CO2                         | 0.000       |

2.6. Exergy destruction calculation equations for equipment

The exergy in, exergy out, and exergy destruction equations based on the equipment types in the studied unit are presented in Table 2.

2.7. Material and energy balance concepts

The ARU unit had a large amount of equipment, including a distillation column with a condenser and reboiler (the regenerator), one heat exchanger, two pumps, and an air cooler. This paper attempts to use an approach for the material and energy balance in the plant that will be useful for readers.

2.7.1. Material balance equations

The general material balance equation is as follows:

\[ \text{Input} - \text{output} + \text{generation} - \text{consumption} = \text{accumulation}. \quad (7) \]

In the case of steady-state conditions, no accumulation exists, and the equation can be written as follows:

\[ \text{Input} + \text{generation} = \text{output} + \text{consumption}. \quad (8) \]

2.7.2. Material balance assumptions

The plant runs under steady-state conditions in the case of a non-reactive system with no generation or consumption in the system.

2.7.3. Material balance equations used in plant

The reactive systems follow Eq. (2). The continuous nonreactive system follows the following equation:

\[ \sum_{\text{input}} m_i = \sum_{\text{output}} m_i. \quad (9) \]

Otherwise, the equation is written as follows:

\[ \sum_{\text{input}} m_i = \sum_{\text{output}} m_i. \quad (10) \]

2.7.4. Energy balance equations

The overall energy balance equation is as follows:

\[ \Delta H + \Delta E_k + \Delta E_p = Q - W. \quad (11) \]

The enthalpy difference is calculated based on the following equation:

\[ \Delta H = \sum_{\text{output}} m_i H_i - \sum_{\text{input}} m_i H_i. \quad (12) \]

The kinetic energy is calculated based on the following equation:

\[ \Delta E_k = \sum_{\text{output}} m_i \gamma_i - \sum_{\text{input}} m_i \gamma_i. \quad (13) \]

The potential energy is calculated based on the following equation:

\[ \Delta E_p = \sum_{\text{output}} m_i g \gamma_i - \sum_{\text{input}} m_i g \gamma_i. \quad (14) \]

Table 2. Exergy calculations.

| Equipment   | Exergy in         | Exergy out        | Exergy destruction |
|-------------|-------------------|-------------------|--------------------|
| P1          | \( E_{138} + Q \times \text{P1} \) | \( E_{139} \) | \( E_{138} + Q \times \text{P1} - E_{139} \) |
| E1          | \( E_{139} + E_{41} \) | \( E_{41} \) | \( E_{139} + E_{41} - E_{41} \) |
| Regenerator | \( E_{40} + Q \times \text{Reboiler} \) | \( E_{41} + E_{153} + Q \times \text{Condenser} \) | \( E_{40} + Q \times \text{Reboiler} - E_{41} - E_{153} - Q \times \text{Condenser} \) |
| P2          | \( E_{42} + Q \times \text{P2} \) | \( E_{42, \text{out}} \) | \( E_{42} + Q \times \text{P2} - E_{42, \text{out}} \) |
| Air Cooler  | \( E_{42, \text{out}} \) | \( E_{43} \) | \( E_{42, \text{out}} - E_{43} \) |
2.7.5. Energy balance assumptions

- Because the plant contained a large amount of equipment, it was necessary to use assumptions for each piece of equipment.
- If there was no temperature change, phase change, or chemical reaction, there was no significant change in pressure from the inlet to the outlet, and $\Delta H = 0$ (the mechanical energy balance was more useful in this case).
- If a temperature change, phase change, or chemical reaction occurred, $\Delta H \neq 0$, $(\Delta E_k, \Delta E_p)$ could be neglected.
- If there were no great vertical distances between the inlets and the outlets, $\Delta E_p = 0$.
- If the system and its surroundings were at the same temperature or the system was perfectly insulated, then $Q = 0$ and the process was adiabatic.
- If the energy was not transmitted across the system boundary by a moving part, an electric current, or radiation, $W_s = 0$.

2.7.6. Plant equipment energy balance equations

The following equation was used for the pumps:

$$\Delta H = W_s.$$  \hspace{1cm} (15)

The following equation was used for the condenser and reboiler:

$$\Delta H = Q'.$$  \hspace{1cm} (16)

The following equation was used for the mixers, waste heat boilers, and adiabatic reactors:

$$\Delta H = 0.$$  \hspace{1cm} (17)

Felder et al. reported the material and energy balance equations for different processes and equipment, as well as the assumptions for each case [23, 25].

2.8. Detailed equipment equations

2.8.1. Distillation (regenerator)

A distillation column can be described using several material and energy balance equations. Figure 4 shows a typical distillation column.

The overall material balance can be found as follows:

$$F = D + W,$$  \hspace{1cm} (18)

where $F$, $D$, and $W$ are the feed, distillate, and residue rates, respectively (kg/h).

The component material balance can be found as follows:

$$F x_f = D x_d + W x_w,$$  \hspace{1cm} (19)

where $x_f$, $x_d$, and $x_w$ are the distillate compositions in the feed, distillate, and residue, respectively.

The overall heat balance can be found as follows:

$$F h_f + Q_r = D h_d + W h_w + Q_c,$$  \hspace{1cm} (20)

where $Q_r$ and $Q_c$ are the reboiler duty and condenser duty, respectively, and $h_f$, $h_d$, and $h_w$ are the specific enthalpies (J/kg) for the feed, distillate, and residue, respectively.

$$Q_c = V \frac{\lambda_{\text{mix}}}{\mu} = \left( m \ cp \Delta T \right)_{\text{water}}$$  \hspace{1cm} (21)

Here, $c_p$ is the sensible heat (J/kg °C).

$$V = L + D$$  \hspace{1cm} (22)

Here, $V$ and $L$ are the rates of the vapor at the top plate and liquid flow returning to the top plate (kg/h), respectively.

$$Q_r = m_{\text{steam}} \lambda_{\text{steam}}$$  \hspace{1cm} (23)

Here, $\lambda_{\text{mix}}$ and $\lambda_{\text{steam}}$ are the latent heat of vaporization (J/kg) values for the overhead mixture and reboiler steam, respectively.

2.8.2. Heat exchanger equations

The material balance equations were presented in Eq. (10). The general equation for the heat transfer across a surface is as follows:

$$Q = U A \Delta T_{\text{lm}}$$  \hspace{1cm} (24)

where $Q$, $U$, $A$, and $\Delta T_{\text{lm}}$ are the heat transfer per unit time (W), overall heat transfer coefficient (W/m² °C), area of heat transfer (m²), and log mean temperature difference (°C), respectively. The log mean temperature difference was calculated using the following equation:

![Figure 4. Tray distillation column.](image-url)
\[ \Delta T_{\text{m}} = \frac{(T_1 - t_2) - (T_2 - t_1)}{\ln \left( \frac{T_1 - t_2}{T_2 - t_1} \right)} \]  

(25)

where \( T_1 \) is the hot-fluid inlet temperature, \( T_2 \) is the hot-fluid outlet temperature, \( t_1 \) is the cold fluid inlet temperature, and \( t_2 \) is the cold fluid outlet temperature.

### 2.8.3. Pump equation

The total energy required can be calculated from the following equation:

\[ gz + \frac{\Delta P}{\rho} - \frac{\Delta P_f}{\rho} - W = 0, \]

(26)

where \( W \) is the work done (J/kg), \( \Delta z \) is the elevation difference between \( z_1 \) and \( z_2 \) (m); \( \Delta P \) is the system pressure difference between \( P_1 \) and \( P_2 \) (N/m²); \( \Delta P_f \) is the pressure drop due to friction, including miscellaneous losses and equipment losses (N/m²); \( \rho \) is the liquid density (kg/m³); and \( g \) is the acceleration due to gravity (m/s²) [24]. Figure 5 shows the piping system.

### 3. Results and discussion

#### 3.1. Validation results

The validation results are listed in Table 3, which clearly shows that the industrial and simulation results were very close. Different simulations showed that the key factor in the simulations was the suitable selection of the package, which provided high accuracy. In this simulation, the highest deviation existed in temperature of stream 153, with a deviation of 8.93%. Approximately no deviation existed in the composition of the components. The chemical solvent package was selected for this case.

#### 3.2. Calculations for DEA concentration of 25%

##### 3.2.1. Physical and chemical exergy calculations for streams

The physical and chemical exergy calculations for the streams were based on the equations of section (2.5 Exergy Calculations). HYSYS calculated the molar flow rates, mass flow rates, and mass exergy for the streams, which are presented in Table 4.

The physical exergy, chemical exergy, and total exergy for the streams were calculated using the equations in section 2.5 (Exergy Calculations) and listed in Table 5.

The values for \( Q_{\text{P}1}, Q_{\text{P}2}, Q_{\text{Reboiler}}, \) and \( Q_{\text{Condenser}} \) were 89.52, 173.11, 40238.92, and 19910.56 kW, respectively. The physical exergy, chemical exergy, and total exergy calculations for the streams were based on the equations in section 2.5 (Exergy Calculations) and listed in Table 6.

The values for \( Q_{\text{P}1}, Q_{\text{P}2}, Q_{\text{Reboiler}}, \) and \( Q_{\text{Condenser}} \) used for the exergy calculations were 89.52, 173.11, 40238.92, and 19910.56 kW, respectively. The physical exergy, chemical exergy, and total exergy calculations for the streams were based on the equations in section 2.5 (Exergy Calculations) and listed in Table 7.

The exergy calculations for the streams with an DEA concentration of 20% were similar to those for the DEA concentration of 25%. The chemical exergy values were higher than the physical exergy values. The percentage share of the destruction for the chemical exergy exceeded 99% in all the streams.

##### 3.2.2. Exergy destruction and exergy efficiency of equipment

The exergy destruction calculations for the equipment were based on the equations in Table 2. The exergy efficiencies for the equipment and percentage shares of destruction were calculated based on section 2.5 (Exergy Calculations) and are presented in Table 6.

The highest destruction rate was observed in the Regenerator, with a value of 13459.73 kW and a percentage share of 79.61% of the total destruction, followed by Air Cooler with a value of 2096.65 kW and percentage share of 12.40% of the total destruction. The percentage of destruction is shown in Figure 6. The overall exergy efficiency was 99.70%.

#### 3.3. Calculations for DEA concentration of 20%

##### 3.3.1. Physical and chemical exergy calculations for streams

The physical and chemical exergy calculations for the streams were based on the equations in section 2.5 (Exergy Calculations). HYSYS calculated the molar flow rates, mass flow rates, and mass exergy for the streams, which are presented in Table 7.

The values for \( Q_{\text{P}1}, Q_{\text{P}2}, Q_{\text{Reboiler}}, \) and \( Q_{\text{Condenser}} \) used for the exergy calculations were 89.52, 173.11, 40238.92, and 19910.56 kW, respectively. The physical exergy, chemical exergy, and total exergy calculations for the streams were based on the equations in section 2.5 (Exergy Calculations) and listed in Table 8.

The exergy calculations for the streams with an DEA concentration of 20% were similar to those for the DEA concentration of 25%. The chemical exergy values were higher than the physical exergy values. The percentage share of the destruction for the chemical exergy exceeded 99% in all the streams.

##### 3.3.2. Exergy destruction and exergy efficiency of equipment

The exergy destruction calculations for the equipment were based on the equations in Table 2. The exergy efficiencies for the equipment and percentage shares of destruction were calculated based on section 2.5 (Exergy Calculations) and are presented in Table 9.

The highest destruction rate was observed in the Regenerator, with a value of 15571.65 kW and a percentage share of 82.11% of the total destruction, followed by Air Cooler with a value of 2034.29 kW and percentage share of 10.73% of the total destruction. The percentage of destruction is shown in Figure 7. The overall exergy efficiency was 99.98%. The destruction efficacy was compared with the destruction rate. Although the Air Cooler had a destruction energy higher than that of E1, its efficacy was lower than that of E1.

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Table 2. Usually, the chemical exergy magnitude is higher than that for the physical exergy. The percentage share of the destruction of chemical exergy exceeded 99% in all the streams.

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Figure 5. Piping system.
The refinery and SRU plant started its official operation in 2020 and faced problems. The actual operational DEA concentration of the plant decreased from the original design of 25% by weight to 20% due to system losses. The amine concentration may have decreased during the start-up, especially for three possible reasons: amine degradation, foaming, and flooding. In the degradation phenomenon, amines are transformed into undesirable products that cannot be recovered with normal regeneration. Amines can be degraded for many reasons. One of these is the make-up water used to prepare the amine solution. Others include suspended solids, non-volatile contaminants, lower and higher molecular weight hydrocarbons, additives and antifoaming agents, corrosion inhibitors, make-up water and water impurities, and inorganic and organic acids. Before the start-up of any plant, flushing and cleaning procedures, and degreasing are performed. In many cases, this is not done properly. Undesirable compounds are present, especially in the start-up, when defects occur during the cleaning of the unit. Consequently, many of these contaminants exist in the system, causing amine degradation. Foaming is one of several amine degradation problems. Foaming causes a portion of the amine to exit from the top of the tower instead of following its normal path from the bottom, causing DEA loss and decreasing the concentration. Other degradation problems include a

### Table 3. Simulation validation.

| Stream | Property | Design | Simulation | Dev | Design | Simulation | Dev |
|--------|----------|--------|------------|-----|--------|------------|-----|
|        | Temperature (°C) | 65.00  | 65.00    | 0.00 | 54.90  | 50.00    | 8.93 |
|        | Pressure (kg/cm²g) | 10.50  | 10.50  | 0.00 | 0.80  | 0.80  | 0.00 |
|        | Mass flow (kg/h) | 487058.6 | 485811 | 0.26 | 9801.8 | 10214.8 | -4.21 |

### Table 4. HYSYS calculations for streams.

| Stream number | Molar flow (Kmol/h) | Mass flow (kg/h) | Mass exergy (KJ/kg) |
|----------------|---------------------|-----------------|-------------------|
| 138 (RA)       | 21670.31            | 496026          | 10.81             |
| 139            | 21670.31            | 496026          | 11.27             |
| 140            | 21670.31            | 496026          | 36.36             |
| 153 (AG)       | 304.57              | 10214.8         | 42.28             |
| 141            | 21365.74            | 485811          | 63                |
| 142            | 21365.74            | 485811          | 28.84             |
| 142-Out        | 21365.74            | 485811          | 29.86             |
| 143            | 21365.74            | 485811          | 13.3              |

### Table 5. Stream exergies.

| Stream number | Eph (kW) | Ech (kW) | Etot (kW) | Percentage share of Ech in Etot |
|----------------|----------|----------|-----------|--------------------------------|
| 138 (RA)       | 1489.19  | 941842.64| 943331.83 | 99.84                          |
| 139            | 1552.67  | 941842.64| 943395.31 | 99.84                          |
| 140            | 5009.74  | 941842.64| 946852.38 | 99.47                          |
| 153 (AG)       | 119.97   | 65480.33 | 65600.30  | 99.82                          |
| 141            | 8501.25  | 877388.64| 885889.89 | 99.04                          |
| 142            | 3891.50  | 877388.64| 881280.15 | 99.56                          |
| 142-Out        | 3891.50  | 877388.64| 881280.15 | 99.56                          |
| 143            | 1794.85  | 877388.64| 879183.49 | 99.80                          |

### 3.3.3. Case study for actual DEA concentration

The refinery and SRU plant started its official operation in 2020 and faced problems. The actual operational DEA concentration of the plant decreased from the original design of 25% by weight to 20% due to system losses. The amine concentration may have decreased during the start-up, especially for three possible reasons: amine degradation, foaming, and flooding. In the degradation phenomenon, amines are transformed into undesirable products that cannot be recovered with normal regeneration. Amines can be degraded for many reasons. One of these is the make-up water used to prepare the amine solution. Others include suspended solids, non-volatile contaminants, lower and higher molecular weight hydrocarbons, additives and antifoaming agents, corrosion inhibitors, make-up water and water impurities, and inorganic and organic acids. Before the start-up of any plant, flushing and cleaning procedures, and degreasing are performed. In many cases, this is not done properly. Undesirable compounds are present, especially in the start-up, when defects occur during the cleaning of the unit. Consequently, many of these contaminants exist in the system, causing amine degradation. Foaming is one of several amine degradation problems. Foaming causes a portion of the amine to exit from the top of the tower instead of following its normal path from the bottom, causing DEA loss and decreasing the concentration. Other degradation problems include a

### Table 6. Exergy destruction and exergy efficiency results.

| Equipment | Destructed exergy (kW) | Percentage share | Exergy Efficiency (%) |
|-----------|------------------------|------------------|-----------------------|
| Regenerator | 13459.73   | 79.61            | 98.64                 |
| Air Cooler  | 2096.65    | 12.40            | 99.76                 |
| E1          | 1152.67    | 6.82             | 99.94                 |
| F2          | 172.79     | 1.02             | 99.98                 |
| P1          | 25.62      | 0.15             | 100.00                |
| Sum         | 16907.45   | 100.00           | 99.70                 |
reduced solution capacity and plant performance, the corrosion effect of degradation products, construction capital/material issues, the environmental effects of degradation products, and the fouling effect of degradation products. The third reason for the decrease in concentration is the flooding phenomenon that occurs with high sour gas feed flow rates, which also causes a portion of the DEA to exit with the sweet gas from the top. During the start-up period, foaming and flooding phenomena were observed several times in the plant absorbers [25]. A study was conducted on the simulation absorber to check the H$_2$S concentration in sweet gas; the H$_2$S concentration was not affected.

### 3.4. Comparison of DEA concentrations of 25% and 20%

A comparison between the DEA concentrations of 25% and 20% is shown in Table 10. The total destroyed exergy with 25% DEA was less than that with 20% by 2057.08 kW. This was an indication that it would be better to work with a higher concentration from an exergy point of view. The main contributor to this decrease was the regenerator. The destruction value for the DEA concentration of 20% was higher than that for the 25% concentration by 2057.08 kW, which was approximately the same overall difference between concentrations.

### Table 7. HYSYS calculations for streams.

| Stream number | Molar flow (kmol/h) | Mass flow (kg/h) | Mass exergy (kJ/kg) |
|---------------|---------------------|------------------|---------------------|
| 138 (RA)      | 22697.00            | 496025.80        | 10.51               |
| 139           | 22697.00            | 496025.80        | 10.97               |
| 140           | 22697.00            | 496025.80        | 36.16               |
| 153 (AG)      | 374.18              | 11474.62         | 70.31               |
| 141           | 22322.82            | 484551.18        | 62.48               |
| 142           | 22322.82            | 484551.18        | 28.08               |
| 142-Out       | 22322.82            | 484551.18        | 29.11               |
| 143           | 22322.82            | 484551.18        | 12.97               |

### Table 8. Stream exergies.

| Stream number | $E_{in}$ (kW) | $E_{ch}$ (kW) | $E_{tot}$ (kW) | Percentage share of $E_{ch}$ in $E_{tot}$ |
|---------------|---------------|---------------|----------------|-----------------------------------------|
| 138 (RA)      | 1448.14       | 782250.45     | 783698.59      | 99.82                                   |
| 139           | 1511.82       | 782250.45     | 783762.26      | 99.81                                   |
| 140           | 4981.70       | 782250.45     | 787232.15      | 99.37                                   |
| 153 (AG)      | 224.10        | 65632.52      | 65856.62       | 99.66                                   |
| 141           | 8499.58       | 717722.64     | 726132.22      | 98.84                                   |
| 142           | 3780.06       | 717722.64     | 721502.71      | 99.48                                   |
| 142-Out       | 3780.06       | 717722.64     | 721502.71      | 99.48                                   |
| 143           | 1745.77       | 717722.64     | 719468.41      | 99.76                                   |
It was necessary to identify the main reason for the difference in the destruction values in the regenerator. The destruction exergy in the regenerator was calculated from the equation $(E_{140} + Q_{Reboiler} - E_{141} - E_{153} - Q_{Condenser})$, as listed in Table 2. The condenser duty with 25% exceeded that with 20% by 2149.01 kW, which was approximately the total destruction difference between the cases (2057.08 kW). This refers to the main contributor, because some other small values may increase or decrease. Table 11 lists the streams related to the regenerator destruction calculations.

It can be observed from Table 11 that some exergies calculated for streams with the 25% concentration exceeded those with the 20% concentration by significant values. The $E_{140}$ stream can be considered as an example. The $E_{140}$ value of the stream at 25% was higher than that at 22% by 159,620.24 kW. The total exergy was the summation of the physical and chemical exergy values. The $E_{ch}$ value with 25% was higher than that with 20% by only 28.04 kW. Therefore, it was not the main contributor. The $E_{ch}$ value at the 25% concentration was higher than that with the 20% concentration by 159,592.19 kW. $E_{ch}$ was the cause of this difference. The composition of the components had the main effect on the $E_{ch}$ value calculated using the equation $\sum x_i e^{0}_{che} + RT_0 \sum x_i \ln x_i$. The DEA standard chemical exergy was much higher than that of water.

The $e^{0}_{che}$ values for DEA and $H_2O$ are 2718.1 kJ/mol and 0.90 KJ/kmol, respectively. Consequently, the chemical exergy at the 25% concentration was much higher than that with the 20% concentration. The difference between the mole fractions of these compositions with $e^{0}_{che}$ is listed in Table 12.

### 4. Summary and conclusions

Amine Regeneration Units (ARU) are used to regenerate the rich Amine with $H_2S$ from refinery units to Lean Amine. The LA is used for gas sweetening in refinery units. The ARU unit that is part of a refining plant in the Middle East that started its official production in 2020 was simulated with HYSYS V.11 to conduct an exergy study on the original DEA concentration of 25 wt%. The main calculations concerned the exergy destruction, exergy efficiency, and percentage share of the destruction of each piece of equipment. The total exergy destruction was 16907.45 kW. The highest destruction rate was observed in the Regenerator, with a value of 13459.73 kW and percentage share of 79.61% of the total destruction, followed by Air Cooler, with a value of 2096.65 kW and percentage share of 12.40% of the total destruction. The overall exergy efficiency was 99.70%. The DEA concentration decreased to 20 wt% due to start-up problems (amine degradation, foaming, and flooding). A case study was conducted on the actual situation to determine whether the sweet gas at the outlet of the absorber was affected by high $H_2S$ concentrations. No effect was observed from the $H_2S$ concentration point of view. An exergy study was conducted using the DEA concentration of 20 wt%. The total exergy destruction was 18964.53 kW. The same percentage of the destruction distribution was found for the equipment. It was found that the highest destruction rate was in the regenerator, with a value of 15571.65 kW and percentage share of 82.11% of the total destruction. The second highest was Air Cooler, with a value of 2034.29 kW and percentage share of 10.73% of the total destruction. The overall exergy efficiency was 99.30%. The comparison between the cases showed an increase in the total destruction by 12.17% at the 20% concentration (2057.08 kW).

### Table 9. Exergy destruction and exergy efficiency results.

| Equipment  | Destructed energy (KW) | Percentage share | Exergy Efficiency (%) |
|------------|-------------------------|------------------|-----------------------|
| Regenerator| 15571.65                | 82.11            | 98.12                 |
| Air Cooler | 2034.29                 | 10.73            | 99.72                 |
| E1         | 1159.63                 | 6.11             | 99.92                 |
| P2         | 173.11                  | 0.91             | 99.98                 |
| P1         | 25.84                   | 0.14             | 100.00                |
| Sum        | 18964.53                |                  | 99.30                 |

### Table 10. Comparison between destruction values for DEA concentrations of 25% and 20%.

| Concentration | Equipment  | 25  | 20  | Difference |
|---------------|------------|-----|-----|------------|
|               | Destructed energy (KW) | Destructed energy (KW) |               |
| P1            | 25.62      | 25.84 | -0.23 |
| E1            | 1152.67    | 1159.63 | -6.96 |
| Regenerator   | 13459.73   | 15571.65 | -2111.93 |
| P2            | 172.79     | 173.11 | -0.32 |
| Air Cooler    | 2996.65    | 2034.29 | 62.36 |
| Sum           | 16907.45   | 18964.53 | -2057.08 |
should be considered based on their destruction values. The regenerator had the highest destruction value by 13459.73 kW with an DEA concentration of 25%, and the lower exergy efficiency by 98.64%. From an exergy point of view, the best scenario was to use a 25% concentration because it saved 2057.08 kW.

Declarations

Author contribution statement

Ahmed Y. Ibrahim: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Fatma H. Ashour: Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data.

Mamdouh A. Gadalla: Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data.

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Data availability statement

Data included in article/supplementary material/referenced in article.

Declaration of interests statement

The authors declare no conflict of interest.

### Table 11. Regenerator streams.

| Stream     | Conc | E_{in} | E_{out} | E_{net} |
|------------|------|--------|---------|---------|
| Inlet      | 140  | 25     | 5009.74 | 94184.64 | 946852.38 |
|            |      | 20     | 4981.70 | 782250.45 | 787323.15 |
| Difference |      |        | 28.04   | 159592.19 | 159620.24 |
| Q_Reboiler | 25   | 40157.11 |        |         |
|            | 20   | 40238.92 |        |         |
| Diff       |      |        | -81.80  |         |         |
| Outlet     | 141  | 25     | 8501.25 | 877388.64 | 885889.89 |
|            |      | 20     | 3780.06 | 717722.64 | 721502.71 |
| Difference |      |        | 4721.18 | 159666.00 | 164387.18 |
| 153        | 25   | 119.97 | 65480.33 | 65500.30 |
|            | 20   | 224.10 | 65632.52 | 65856.62 |
| Difference |      |        | -104.13 | -152.20  | -256.32 |
| Q_Condenser| 25   | 22059.58 |        |         |
|            | 20   | 19910.56 |        |         |
| Diff       |      |        | 2149.01 |         |         |

### Table 12. Standard chemical exergy values and mole fraction of DEA [9, 26].

| DEA Concentration | ex^0_{chem} (KJ/kmol) | 25 wt% | 20 wt% |
|-------------------|-----------------------|--------|--------|
| Components        |                       | Mole Fr. |        |
| DEA               | 2718.10               | 0.05    | 0.04   |
| H2O               | 0.90                  | 0.93    | 0.94   |
| H2                | 236.09                | 0.00    | 0.00   |
| NH3               | 337.90                | 0.00    | 0.00   |
| H2S               | 812.00                | 0.11    | 0.01   |
| CO2               | 19.48                 | 0.00    | 0.00   |

### Additional information

No additional information is available for this paper.

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