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CHALLENGES AND SOLUTIONS OF GAS SWEETENING UNIT IN POLYPROPYLENE PLANT USING PROCESS SIMULATION: A CASE STUDY

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Abstract

Gas sweetening units using amines are an important part of lots of industries. They provide clean burning fuels and valuable chemical feedstock. The integration of these units with petrochemical plants has increased their importance and complexity over the years. The advantages of computer simulation models as tools for designing and troubleshooting gas treating plants is increasingly obviously. This paper discusses the major problems faced in operation of the amine gas sweetening unit in polypropylene plant using a process simulation tool, HYSYS version 10. Several highlighted problems in such a plant have been investigated and discussed; then a number of proposed modifications have been suggested to overcome these problems and increase the productivity of the plant as designed. The results showed that the proposed modifications have a high impact on the amine sweetening unit efficiency. The modified procedures were applied, and the lab analysis showed good agreement with the simulation results.

Keywords: *Simulation; MDEA; Gas sweetening; Amine system; Troubleshooting.*

1. Introduction

Gas sweetening using amines is a key operation in gas processing facilities, refinery operations, petrochemical plants, and other industries; aiming to maintain efficient operation and meet sales specifications [1]. The amine system is designed as a closed-circuit system and directed primarily to remove hydrogen sulfide, carbon dioxide and other acidic components from gaseous hydrocarbon streams. It takes great attention due to high pressure for environmental compliance and high quality of acid gas removal [2]. However, many operational problems face the amine-based gas sweetening process; such as intense corrosion, capacity reduction, instability of operation, amine degradation, carryover and excessive foaming [3-4]. The occurrence of such problems in gas sweetening units will consequently result in a reduction in treating efficiency and hence, higher amounts of acid gases in the resulted gas stream. Some of these problems have taken great attention from the researchers over the years; for example, corrosion problems have been addressed by Mogul [5] who introduced thermoplastic coating to insulate process equipment from corrosion-inducing conditions. Further corrosion control methods have been introduced and discussed by other researchers [6-9]. On the other hand, the foaming problem has been discussed in details by Gondule *et al.* [10]; from the view point of causes, disadvantages and how to control it. They reported that foaming could be a result of contamination in the absorbing solvent or feed gas. Possible contaminants may be corrosion products, corrosion inhibitors, well treating fluids, liquid hydrocarbons, amine degradation products, organic acids, foam reducing agents or other finely divided solids. Foaming results in many negative effects such as reduction in mass transfer area, efficiency and absorption capacity. Even more, carryover of amine solution to the downstream plant could be a result of foaming [11-13]. Sarker [14] has discussed the theoretical effect of various process variables on the performance of the gas sweetening process. The studied variables were amine circulation rate and concentration; temperature and pressure of single and mixed amine solvents; and sweetening stages. Over the years, some other research work has addressed the probable problems in amine based sweetening units and introduced the suggested solutions [2, 15-17]. However, most of the previous works were focused on the natural gas sweetening units. In this work, the research was focused on the challenges facing the gas sweetening unit in an existing petrochemical plant.

Process streams and feedstocks for polymerization units are needed to be of high purity, to avoid negative effects on catalyst activity and functionality. Furthermore, polymer quality and yield could also be affected negatively by improper treatment or sweetening of the monomer feedstock stream [18]. Therefore, the sweetening unit is an important purification unit for removing carbon dioxide and other acid gases.

In this work, the troubleshooting in the amine based sweetening unit, specially using methyl diethanolamine (MDEA) as a solvent, in a petrochemical plant was studied. Many solutions were suggested in order to overcome operational problems and increase the productivity of the plant to reach its designed value. HYSYS software version 10 was used in this work as the simulation tool. It is expected that the introduced solutions and modifications can handle huge amounts of CO_2 out of the feed gas stream.

2. Case study and process description

The case study taken in this research work is for the MDEA sweetening unit in polypropylene production plant located in Egypt. Propane is fed to the dehydrogenation unit for the production of propylene, which is the feedstock for the polypropylene production plant.

During propane dehydrogenation reaction, CO_2 is formed due to the hydrolysis reaction, and reconversion of coke lay down on the catalyst (caused by thermal cracking) with steam during the operation cycle. Propylene stream containing CO_2 should be purified to overcome the acid gas negative effects on catalyst activity and functionality as well as polymer quality and yield. Moreover, this gas stream will undergo liquefaction process that requires operation under a very low temperature (-90°C) and a low pressure reaching 3 bar. At these conditions, CO_2 can freeze on the exchanger surface (cold box), and cause plugging of the pipes and reduction in plant efficiency. So, the amine sweetening process is constructed prior to the liquefaction process. Figure1 shows a block diagram for the propane dehydrogenation plant (PDH).

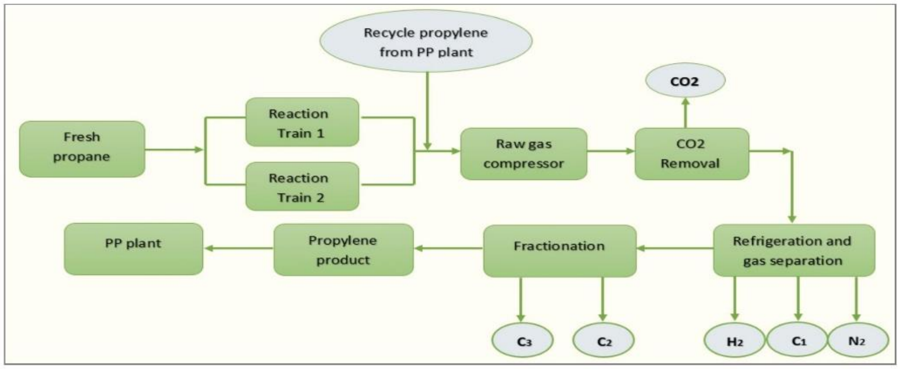

Figure 1. Block diagram of the main processes of PDH plant

As shown in Figure 1, PDH plant consists of reaction section and heat recovery, natural gas compression, a CO_2 removal unit, refrigeration and gas separation, and fractionation processes, in addition to polypropylene (PP) production plant.

2.1. Processes chemistry

The processes chemistry of this case study includes two parts. The first part describes how the CO_2 gas is produced from the propane dehydrogenation reaction section, while the second part describes how methyl diethanol amine solvent absorbs the CO_2 in the presence of piperazine as an activator in the CO_2 removal unit. The dehydrogenation of propane to propylene takes place in two series reactors; super heating reactor; called steam reformer, and an oxy-reactor. This is performed in two identical, parallel reaction trains, (train I and train II). Dehydrogenation is a strongly endothermic reaction, in which propane is converted to propylene and hydrogen according to the reaction described in Equation 1 [19-21].

$$C_3H_8 \rightleftharpoons C_3H_6 + H_2 \tag{1}$$

Within the reformer reactor, the heat required for the reaction is provided by super heating steam. Approximately 75% of overall propylene production is accomplished in this reactor. Side reactions like cracking and hydrolysis can lead to the formation of lower hydrocarbons like methane, ethane, and ethylene as addressed in Equations 2- 4 [19, 21].

$$C_3H_8 \rightarrow C_2H_4 + CH_4 \tag{2}$$

$$C_3H_8 + H_2 \rightarrow C_2H_6 + CH_4 \tag{3}$$

$$C_2H_4 + H_2 \rightarrow C_2H_6 \tag{4}$$

These cracking reactions are primary of thermal cracking type, which can result in the formation of small amounts of coke (Equation 5). Therefore, the platinum oxide catalyst used (PtO_2) should be regenerated regularly to burn off the coke. However, the presence of steam during reaction lowers coke lay down on the catalyst; allowing longer operation cycles as well as quick and simple regeneration.

$$CH_4 \rightarrow C + 2H_2 \tag{5}$$

The product gas emerged from the reformer reactor is admitted to the oxy-reactor for more conversion of propane to propylene by oxidative dehydrogenation. Within the oxy-reactor, selective conversion of hydrogen, as well as further conversion of propane, takes place. The oxygen is admitted to the oxy-reactor to provide the endothermic heat requirement for dehydrogenation of propane. However, the equilibrium can be shifted in forwarding direction by removal/conversion of hydrogen for the formation of H_2O as presented in Equation 6. The formation of H_2O is an exothermic reaction, which provides the heat of reaction for further endothermic conversion of paraffins to olefins; this consequently leads to an increase in propane conversion as presented in Equation 1.

$$H_2 + {}^1/_2 O_2 \rightarrow H_2O \tag{6}$$

Combustion of propane and propylene may exist according to Equations 7, and 8.

$$C_3H_8 + 5\,O_2 \rightarrow 3\,CO_2 + 4\,H_2O \tag{7}$$

$$C_3H_6 + {}^9/_2\,O_2 \rightarrow 3\,CO_2 + 3\,H_2O \tag{8}$$

Besides the above reactions, carbon monoxide (CO) and carbon dioxide can be formed as described in Equations 9-12.

$$C + {}^1/_2\,O_2 \rightarrow CO \tag{9}$$

$$C + H_2O \rightarrow CO + H_2 \tag{10}$$

$$2CO \rightarrow C + CO_2 \tag{12}$$

The CO_2 produced with the propylene product (Equations 7,8, and 12) from the reaction section is removed in the CO_2 removal unit while the other side product gases are removed in the refrigeration and the fractionation units as shown in Figure 1.

In the CO_2 removal unit, CO_2 is absorbed in an absorption tower using piperazine-activated MDEA as a solvent. This solvent selectively absorbs CO_2 contained in the gas produced from the oxy-reactor. The main problem associated with MDEA usage without activator is the lower rate of the absorption process. Therefore, the activator is required to increase the absorption rate. Although MDEA can be activated through many ways like Mono-ethanol amine, but activating MDEA with piperazine (PZ) will increase the absorption process rate to be many times faster, compared to Mono-ethanol amine. The needed dose of piperazine to achieve the required purity of the process gas is small [9, 22].

Many reactions can take place during the CO₂ absorption process using activated MDEA solution in the sweetening unit. These reactions are presented by the following equations [4, 23-27].

$$CO_2 + \mathrm{MDEA} + H_2O \leftrightharpoons \mathrm{MDEA}H^+ + HCO_3{}^- \tag{13}$$

$$CO_2 + OH^- \leftrightharpoons HCO_3{}^- \tag{14}$$

$$CO_2 + \mathrm{PZ} + H_2O \leftrightharpoons PZCOO^- + H_3O^+ \tag{15}$$

$$CO_2 + \mathrm{MDEA} + PZ \leftrightharpoons \mathrm{MDEA}H^+ + PZCOO^- \tag{16}$$

$$CO_2 + PZCOO^- + H_2O \leftrightharpoons PZ(COO^-)_2 + H_3O^+ \tag{17}$$

$$CO_2 + \mathrm{MDEA} + PZCOO^- \leftrightharpoons \mathrm{MDEA}H^+ + PZ(COO^-)_2 \tag{18}$$

$$HCO_3{}^- + H_2O \longrightarrow CO_3^{2-} + H_3O^+ \tag{19}$$

$$\mathrm{MDEA} + H_3O^+ \longrightarrow \mathrm{MDEA}H^+ + H_2O \tag{20}$$

$$2H_2O \longrightarrow H_3O^+ + OH^- \tag{21}$$

$$PZ + H_3O^+ \longrightarrow PZH^+ + H_2O \tag{22}$$

$$PZCOO^- + H_3O^+ \longrightarrow PZH^+COO^- + H_2O \tag{23}$$

where:

- Equation (13) is the basic catalyzed hydration reaction of MDEA solution
- Equation (14) is the formation reaction of bicarbonate
- Equation (15) represents the formation of mono-carbamate reaction by PZ
- Equation (16) is the reaction of formation of mono-carbamate by PZ/MDEA
- Equation (17) is the formation of di-carbamate reaction
- Equation (18) represents the formation reaction of di-carbamate by $PZCOO^-/MDEA$
- Equation (19) is the formation reaction of carbonate reaction
- Equation (20) represents the protonation reaction of MDEA
- Equation (21) is the dissociation of water reaction
- Equation (22) is the protonation reaction of piperazine
- Equation (23) represents the protonation reaction of mono-carbamate.

In the regeneration tower in the sweetening unit, the mono and di-carbamate are transformed into free piperazine and CO₂. In the presence of piperazine, the heat required to separate CO₂ from the carbamate (Equations 15-18) increases in the regeneration process according to carbamate stability (Equation 24). In case of absence of the piperazine, bicarbonate ($\mathrm{HCO_3}^-$) and carbonate ($\mathrm{CO_3^{2-}}$) are only formed with CO₂ in the absorber (Equations 13, 14, and 19) and are easily separated in the regenerator using a lower amount of heat according to Equations 25 and 26 [2, 28].

$$PZCOO^- + H_2O \rightleftharpoons CO_2 + PZ + OH^- \tag{24}$$

$$HCO_3{}^- \leftrightharpoons CO_2 + OH^- \tag{25}$$

$$CO_3^{2-} + H_2O \rightleftharpoons CO_2 + 2OH^- \tag{26}$$

2.2. CO₂ removal unit

As discussed previously, CO₂ gas must be removed to achieve the purity specification of the propylene product. For this purpose, the CO₂ removal unit is constructed. Traces of H₂S, which may present due to sulphur contained in the propane feed, could also be removed during the sweetening process. The flow diagram of this unit, which is the focus of the present work is illustrated in Figure 2.

The used MDEA solvent contains 20 to 40 mole percent of MDEA and 5 to 6 mole percent piperazine, while balance constitutes of water. The rich solvent is regenerated and then, stripped from CO₂/H₂S traces. However, it is noted that lean solvent is not fully free of CO₂/H₂S and contains some observable residual amount of them.

As shown in Figure 2, the sour compressed gas from the process gas compressor is admitted to the bottom of the absorber column and contacted counter currently with the lean MDEA solution which is admitted to the top of the absorber column, at a pressure of 3106 kPa and a temperature of 65°C. The treated gas from absorber top is routed to the fractionation unit after knocking out of potential liquid carry over in treated gas knock out the drum. In the absorber, a small quantity of water is added to the absorber to balance the loss of vapor leaving the system with the gas streams. The regeneration of the MDEA solution is carried out at a low pressure of 348.1 kPa and an elevated temperature of 95°C in the stripper. The CO_2 content in the treated gas outlet from the absorber top is reduced to 1300 ppm. The rich solution is let down to a lower pressure across control valve rich MDEA (Rich aMDEA LV) and routed to the high-pressure flash drum (HP Flash Drum). This flash drum operates at a pressure in between the absorber and stripper operating pressures and normally higher than the partial pressure of CO_2 in the feed gas to the absorber. This ensures that CO_2 is not lost through the flash gas containing absorbed hydrocarbons which are routed back to the raw gas compressor unit for recompression. The bottom product of the high-pressure flash drum is heated in the solvent heat exchanger with the lean solution from the stripper bottom to a temperature of 95°C and fed to the stripper.

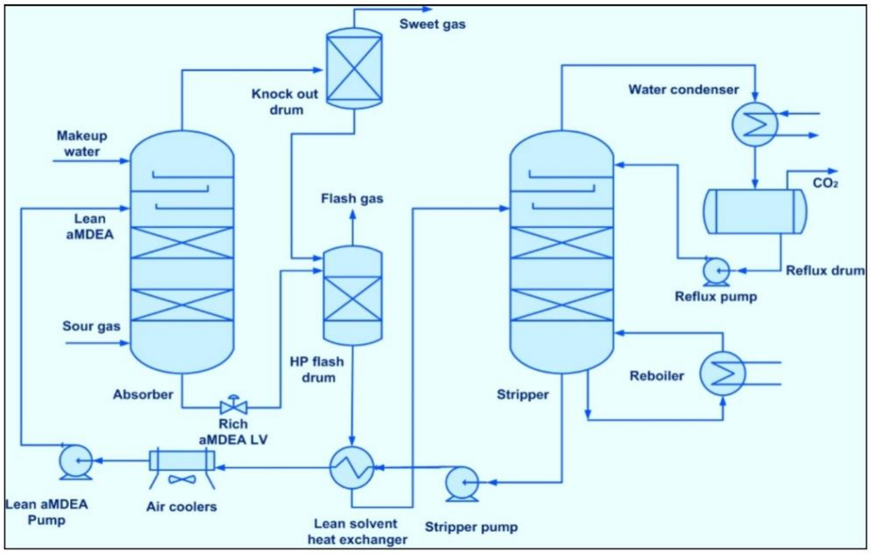

Figure 2. Process flow diagram of CO_2 removal unit

The stripper reboiler supplies the necessary heat required to strip off the CO_2 from the stripper top. The reboiler is heated with a stream of process gas at a temperature of 137°C. Overhead vapors from stripper are partially condensed, then received in a reflux drum. The condensed liquid is returned as reflux to the stripper while the vapor phase containing CO_2 is routed to the auxiliary boiler, where it is incinerated in the burners. Inflammable components in the vapors and C_3H_8 are to be burned in the boiler furnace. The regenerated solution from the stripper bottom shows a very low residual loading of CO_2. The heat from this hot stream is recovered in the solvent heat exchanger. The bottom product out from the stripper should be cooled to absorber operating temperature using air cooler. Anti-Foam agent is added as required to the absorber column and to the stripper column.

2.3. Refrigeration and gas separation unit

The refrigeration and gas separation unit include gas dryers and gas chilling processes. In the gas drying process, water is removed by molecular sieves and emerged from the CO_2 removal unit to prevent the hydrate formation in the process gas before cooling it in the cold box of the chilling process. Purpose of the cold box is to separate un-condensable process gas components like hydrogen, nitrogen, and methane from propane and propylene containing hydrocarbon phase by partial condensation. The hydrocarbon phase will be condensed while hydrogen, nitrogen, and methane remain in the gas phase. The temperature of the process gas is reduced to approximately -85°C. Due to refrigeration, more hydrocarbons will condense out of the process gas.

The CO_2 removal unit has some troubles that affect the sweetening and subsequent units. These troubles can lead to the isolation of the cold box in the refrigeration and gas separation units. This means much propane and propylene losses directed to the fuel gas network via cold box bypass. Additionally, the side products emerged from the reaction section can cause many problems. The main problems that affect the CO_2 removal process are the foaming and the solid compounds formation.

2.4. Amine sweetening unit operational issues

The different highlighted operational issues in the studied existing sweetening unit and in the subsequent units (Refrigeration and gas separation) are summarized as follows:

1. The fast rise of the level in the coolers of treated natural gas.
2. High amine losses and amine carryover into equipment downstream of the absorber in the forward refrigeration and gas separation unit.
3. Decrease of acid gas removal system efficiency and an increase of the CO_2 content in treated natural gas.
4. High differential pressure across the absorber.
5. Increase in the pressure drop across the drier in service.
6. Freezing out (hydrate formation) in the cold box.

Most of these problems (2, 3, and 6) are an indication of the inefficient removal of acid gases in the MDEA sweetening unit. This will lead also consequently to increase propane and propylene losses in the fuel gas network via cold box bypass in the refrigeration and gas separation unit. The remaining problems may happen due to the passage of liquid droplets (amine and water) at high gas velocities with the vapor from a packing section to the packing above (carryover), then, towards the equipment located downstream of the acid gas removal column. By this effect, lower volatile liquid is withdrawn to the packing above where liquid with higher volatility is present. It is detrimental that packing efficiency will be reduced. Carryover is also detrimental when nonvolatile impurities are carried upward to contaminate the overhead product from the column. There are many probable causes for inefficient acid gas removal as reported in the literature. Foaming, carryover, and amine degradation may lead to such problems [2, 5, 9].

The present study has discussed the problem of foam and amine carryover at the head of the acid gas absorber and showed that its origin comes from the stable foam in the columns. This phenomenon is primarily due to contaminants, under-sizing of the acid gas absorber, and the reaction of an amine with the side products of the oxy-reactor. Contaminants can be obtained from two sources. One of these sources is degradation products of the MDEA resulting from thermal decomposition, while the other source is degradation products of the MDEA by the formation of the non-regenerable products. The degradation of the MDEA by thermal decomposition is a problem when the MDEA is subjected to high temperatures. This problem occurs in the reboiler, where the high temperatures can cause localized overheating. Under the action of heat, the MDEA decomposes and gives in particular ethylene oxide which is extremely reactive. The ethylene oxide can be polymerized and react with the MDEA, and the anti-foam used. The products of these reactions, which are found in a solid or liquid form, deactivate the solution of MDEA and favor the effect of corrosion and foaming of the amine solution. In addition to the reaction of the MDEA with CO_2 where it forms regenerable products, the MDEA also reacts irreversibly with CO_2. The reactions are very slow and complex. Corrosion products settle on the column packing and cause an inflexibility of the valves which are constrained in their movement by a fibrous texture, that, limit the flow of the liquid and increase the speed of the gas, generating possible aerosols thus favoring the formation of stable foam. A bad filtration may cause activated carbon filter particles to deeply circulate with the system leading to a foaming problem. Any contaminants which may cause the surface tension of the solution to decrease will increase foaming possibility in the solution. Also, any contaminants which may cause the solution viscosity to increase will help in foam formation. Contaminants in addition to all of the above reasons can be formed from the reaction between the activated

MDEA solution specially piperazine and side reactions out from oxy-reactor plus free oxygen according to lab results.

Under-sizing of the acid gas absorber is achieved as the gas velocity starts to increase. That will carry more liquid droplets with the outlet vapor causing the carry-over problem. Many experimental studies of carry-over were conducted and showed that the dominant variable affecting carry-over is gas velocity through the two-phase zone on the packing. The carryover is a significant factor in determining the limits of flooding of a column. Therefore, to size a column and avoid its flooding, it is necessary to know the maximum flows of gas and liquid, which can be introduced into the column. The maximum gas flow rate and consequently the maximum gas speed correspond to the flooding of the column should be determined. For optimal value, the speed of gas must be below the value for which the flooding occurs. In general, it is recommended to operate at 80% of the conditions of the flooding. The column diameter is obtained then, by knowing the gas flow rate, the selected speed (at 0.80 the speed of vapor at flooding) and to the packing active section.

The reaction of an amine with the side products of the oxy-reactor (amine degradation) may exist directly or alternatively if H_2S is present in the feed. Oxygen can react with a sulfur species first, followed by a subsequent reaction with the amine. The product distribution of the various carboxylic acids depends on the oxygen concentration, the operating temperature and the amine used.

The temperature of the absorber may be an important indirect parameter causing foaming; if the absorber temperature is reduced to reach the dew point of heavy hydrocarbons in the feed gas, then condensable hydrocarbons may exist in the gas stream. These condensates result in foaming, which is responsible for the sweetening reduced efficiency.

The increased foaming tendency requires a lower circulation rate of the MDEA solvent and more antifoam doses. Normally the circulation rate of the solvent is 180 m^3/h, but when the foaming increases a decision of decreasing the circulation rate to around 100 m^3/h may be taken to control foaming problems. The lower circulation rate minimizes the MDEA carryover from sweet gas knockout drum to the downstream refrigeration and gas separation unit.

Foaming also makes liquid levels of columns and vessels unstable. When liquid levels become unstable, the reduction of the circulation rates saves the running pumps from being stopped. So, the reduction of the solvent circulation rate is better than having carryover or complete stop of the solvent circulation rate.

The presented troubleshooting results accordingly in some consequences in CO_2 removal unit and in the subsequent refrigeration and gas separation unit due to MDEA decreased concentration. These consequences on CO_2 removal unit are summarized in the following points:

- Reduction in the CO_2 removal unit capacity until 80% of the design capacity.
- Excess of MDEA consumption.
- Corrosion of the equipment included in the CO_2 removal unit

However, the problems consequences in the subsequent refrigeration and gas separation unit can be summarized in the following:

- Contamination of the molecular sieves contained in the drier's unit shutdown for the defrosting and the drying of cryogenic exchangers.
- Replacement and repairs of several cold box cores.
- Several interventions of maintenance.

Addition of more antifoam does not prevent the foam; it only stops the generation of the foam, while the cause of foam formation still exists. Many problems may be resulted by using antifoams with unlimited use; corrosion and pollution of the mechanical equipment are the main problems [13,29,30]. If corrosion inhibitors are added to the amine system, these inhibitors do not cause foaming, but stabilize the foam; these consequently increase the foaming tendency [13,31,32].

In this work, some modifications were proposed and studied to the sweetening unit to overcome the operational problems mentioned above.

2.5. Economic study formulations

HYSYS version 10, with Acid gas – chemical solvents as a fluid package was used as the simulation software in the present research work. It was applied to build the original and the modified sweetening unit. It is also used to consider the economic calculations needed to evaluate the introduced modifications. The effectiveness of the suggested modifications to the sweetening unit should be confirmed through an economic study. Thus, it is needed to evaluate the modifications via estimating of return on investment (ROI) and consequently the payback period. ROI is related directly to the total annual cost (TAC) which can be calculated according to the following Equation:

$$\text{Total costs} = \mathrm{C_{cap}} . Af + \mathrm{C_{op}} \tag{27}$$

where $\mathrm{C_{cap}}$ and $\mathrm{C_{op}}$ are the capital equipment and the operating costs of the process, respectively.

Af is an annualization factor used to annualize the capital equipment cost and calculated as presented in Equation 28:

$$Af = \frac{\mathrm{m}\,(1+\mathrm{m})^{\mathrm{n}}}{(1+\mathrm{m})^{\mathrm{n}}-1} \tag{28}$$

where m is fractional interest rate; n is a number of years.

The capital equipment cost includes columns, air coolers, pumps, heat exchangers and separators costs. Where the operational cost includes steam, power and cooling water costs [33]. The cost of power, cooling water, high pressure steam, and low-pressure steam are assumed by Hysis program to be \$0.078 per kWh, \$120 per million gallons, \$3.16 per million BTU and \$2.11 per million BTU, respectively.

Profitability that can be acquired from a company at a specified status is an important denominator for all business activities [34]. Return on investment (ROI) indicated in Equation 29 consists of two main terms; the first is the saving in the operating cost, which acquired in case of the modified plan. On the other hand, the second term is the increase in the total capital cost ($\mathrm{C_{Cap}}$) which includes purchased equipment, installation and foundation costs.

$$\mathrm{ROI} = \frac{\text{saving in operating cost}}{\text{increasing in } \mathrm{C_{Cap}}} \tag{29}$$

Payback period is the period required to recover the sum of the paid investment; Payback period can be calculated by applying Equation 30.

$$\text{Payback period} = {}^{1}\!/_{\mathrm{ROI}} \tag{30}$$

In this work, the capital cost is annualized in one year (n) with 5% fractional interest rate (m).

3. Results and discussion

The purpose of this study is to modify the investigated sweetening unit for overcoming its operational problems as well as to raise the plant throughput to be near the designed value. The following sections discuss the proposed modifications and their effectiveness and effects on the original plant.

3.1. Original plant simulation

To show the benefits of the proposed modifications, it is needed firstly to simulate the investigated original sweetening unit before modifications. This simulation is based on the design basis of the plant with taking into account the feed gas composition of the CO_2 removal unit and the real operational conditions of the current plant, which differs from the design basis data. The real composition of the plant feed gas was identified via lab analysis. Table 1 addresses the sour feed gas composition of the current CO_2 removal unit. The flowrate of this gas feed is 4356 kgmole/hr. The lean solvent solution which consists of 23.59 mole% methyl di-ethanol amine (MDEA), 5.42 mole% piperazine and 70.99 mole % water are applied with a flow rate of 180 m^3/hr. Aspen HYSYS version 10 was used as the simulation software, and the chosen fluid package for simulation is acid gas – chemical solvents package. The simulated plant under consideration is presented in Figure 3.

Table 1. CO_2 removal plant sour gas feed composition

Components	Mole fraction	Components	Mole fraction
Methane	0.028700	1-Butene	0.000099
Ethane	0.015000	1,3-Butadiene	0.000000
Ethylene	0.000999	M-Acetylene	0.000999
Propene	0.197422	Nitrogen	0.000699
Propane	0.476371	Oxygen	0.0000999
n-Butane	0.000300	CO_2	0.0359000
i-Butane	0.003300	CO	0.0006990
Propadiene	0.000000	Hydrogen	0.235188
i-Butene	0.004300	Total	1.0

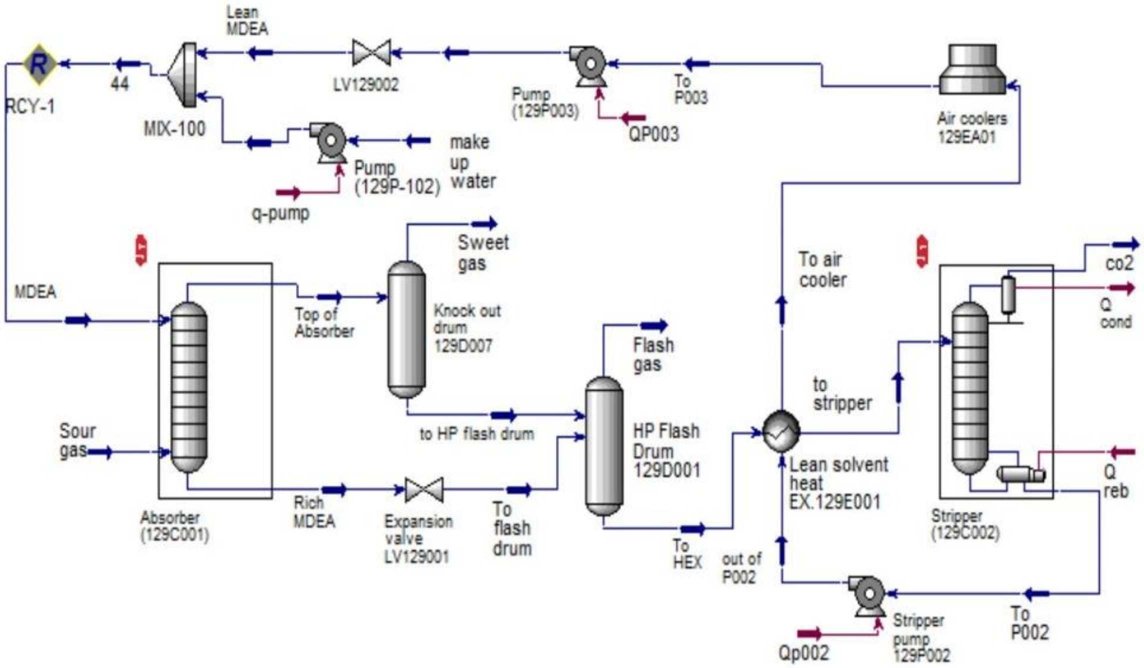

Figure 3. Simulation of original CO_2 removal unit

3.2. Proposed modifications

A modification for the sweetening unit was proposed in order to overcome operating problems and increase the productivity of the plant to reach its designed value. It was found that the CO_2 concentration out from the reaction section unit increased more than expected which lead to series problems in sweetening unit (carryover, foaming, and MDEA degradation). Therefore, modification included changes in process configuration and some operating conditions, was proposed, in order to achieve purity specification of the propylene product.

A comparative process simulation by HYSYS was done for the modified cases; design basis process and the modified process. The suggested modifications are as follows:

1) Using MDEA without an activator
2) Replacement of the old absorber with a larger one which contains three beds of structured packing
3) Increasing of MDEA circulation rate.
4) Addition of two pumps around equipped with two stages of side air coolers
5) Addition of a reclamation unit.

For improving the sweetening process, the operating parameters should be investigated, and the optimum condition should be identified. Depending on the feed gas composition, temperature and pressure along with the sweet gas requirements. The most sensitive operating parameters taken into consideration include rich amine temperature, amine circulation rate, gas/liquid contact time, and influence of MDEA activator.

3.2.1. Using MDEA without an activator

For alleviating the foaming problems or reducing their bad impacts, some operational practices were carried out in this study to investigate the causes of this problem. One of these trials was to cut oxygen feed to the reaction section of the PDH plant. The results showed that there is no foaming formed by avoiding oxygen to reach the reaction section. Therefore, it is confirmed that the main source of the foaming problem was the side products of MDEA reaction in the presence of oxygen outside the oxy-reactor. Accordingly, the action should be taken is using MDEA without piperazine activator. Since as declared in the reaction mechanism, piperazine activates MDEA and gives more amounts of activated MDEA ($MDEA^+$) as illustrated in Equations 16, 18, and 20. These activated amounts can react with the side products and produce solid compounds that can contribute to foaming formation. The MDEA is used in the modified suggested sweetening process model without activator using the Hysis program and the results showed that the foaming height is decreased from 680 mm to 180 mm as illustrated in Table 2. Also, the field results illustrated that using of MDEA without activator is a good idea to decrease the foaming. Thus, for the newly modified plant, MDEA should be used without activator with taking into account the possibility of increasing solvent circulation rate and volume of the absorber itself, which can be taken as alternatives for eliminating the foaming issues.

Table 2. Comparison between original and modified sweeting processes regarding sweet gas compositions, MDEA strength and foaming properties

Components	Simulation results of sweet gas composition, mole fraction	
	Original plant	Modified plant
Methane	0.02980	0.030342
Ethane	0.01560	0.015801
Ethylene	0.00100	0.000968
Propene	0.18880	0.183448
Propane	0.49380	0.503309
n-Butane	0.00030	0.000317
i-Butane	0.00340	0.003487
Propadiene	0.00001	0.000000
i-Butene	0.00380	0.003652
1 Butene	0.00009	0.000085
1,3 Butadiene	0.00010	0.000000
M-Acetylene	0.00000	0.000855
Nitrogen	0.00080	0.000742
Oxygen	0.00010	0.000083
CO2	0.00130	0.000106
CO	0.00070	0.000742
Hydrogen	0.24430	0.249196
MDEAmine	0.00000	0.000045
H2O	0.01610	0.006822
Lab MDEA strength, foaming		
MDEA strength (mole %)	23.59	24.1
Lab foam test height (millimeter)	680	180
Lab test breakdown (sec)	40	<30

3.2.2. Replacement of the current absorber with a larger one

Since the reaction of CO_2 with MDEA is slow in the absence of activator, the column diameter, and packing height must be adjusted to give sufficient time for the reaction to take place. By consulting certain experts in the gas industry field, it was confirmed that the replacement of the existing absorber by another large one more effective might bring a solution to the foaming problem and consequently, as well as the problem of amine carryover. For this study, the old absorber tower with two packing beds is replaced by a larger one with three structured packing beds in the modified sweetening process. The results of the simulation gave decreasing in the CO_2 concentration in the outlet sweet gas as described in Table 2

3.2.3. Increasing of MDEA circulation rate

Increasing the MDEA solvent circulation rate for a given absorber column will lead to an increase of the CO_2 pickup [14]. This usually holds true for MDEA in an absorber column of a fixed diameter, even though, the liquid residence time will decrease with increasing solvent circulation rate. In this research work, a new modification was proposed to increase the circulation rate from 180 to 220 m^3/h. This suggested modification cannot be achieved without increasing the length of the tower itself by adding a new packing in order to improve effectively the absorption process. The simulated results of the modified plant presented in Figure 4 display that CO_2 concentration in the treated gas decreases from 1200 ppm to 106 ppm by increasing the solvent circulation rate from 140 m^3/h to 220 m^3/h respectively. It is also noticed that increasing of MDEA rate above 220 m^3/h has no effect on the CO_2 concentration in the treated gas.

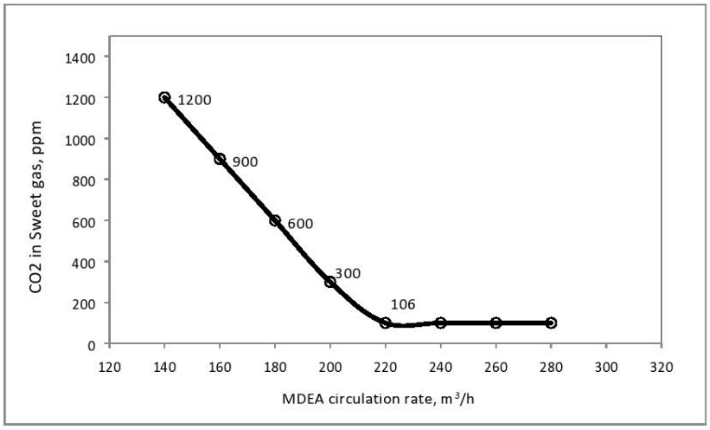

Figure 4. Relationship between MDEA circulation rate and CO2 concentration in sweet gas

3.2.4. Addition of two pumps around equipped with two stages of side air coolers

Usually, the only parameter available for controlling the absorber temperature is the lean amine temperature. Since the CO_2 reaction with MDEA is kinetically controlled; a hotter column increases the reaction rate. However, once the lean amine temperature reaches about 90°C at the operating pressure, the decrease in solubility of the CO_2 in the amine solution will usually become the overriding factor, and the net CO_2 pickup will begin to decrease.

To overcome the degradation problem of the solvent, it is required to control the temperature profile of the absorber.

In this work, it is suggested to add air cooler after each packing. This will help in controlling the temperature increase of the MDEA ascribed to the exothermic reaction between CO_2 and the amine. Therefore, the outlet MDEA temperature of the first packing section can return back to the desired operating feed condition. Then, the MDEA will be pumped again back to the second packing of the absorber as shown in the modified sweetening process shown in Figure 5. This procedure will be repeated with the same sequence for the three packing sections of the absorber. For raising the absorption capacity of the MDEA solvent solution, the down flowing liquid is drawn off from absorber column below the 1st and 2rd absorber packing sections and cooled down in external air coolers. According to Figure 5, below the 2nd packing, the MDEA solution is drawn off and circulated by rich MDEA circulation pump (Pump 129P002) via rich MDEA air cooler (129EA02) back to the absorber column (MDEA recycle 1 in Figure 5). Below the 1st packing, the MDEA solution is drawn off and circulated by rich MDEA circulation pump (pump 129P003) via rich MDEA air cooler (129EA03) back to the absorber column (MDEA recycle 2 in Figure 5). Applying this suggested solution for controlling the temperature of the absorber increased the net CO_2 pickup as illustrated in Table 2.

3.2.5. Addition of a reclamation unit

As proposed before, the modified sweetening plant should include a Reclaimer vacuum distillation separation unit (Reclaimer 129D008). The function of this Reclaimer is to permit cleaning up of amine, which is contaminated with heat stable salts. This can be realized by converting the amine salts to sodium salts and boiling the amine away from the resulting salt solution. Figure 5 presents the simulated modified plant, which includes the new reclamation system. The simulated Reclaimer feed rate (stream 55 in figure 5) is taken as 25% of the out stream of the stripper pump 129P002. According to Figure 5, a slip amine stream from booster pump (129P002) is routed to the Reclaimer to fill it with the amine. The medium pressure (MP) steam is used for heating the contents to nearly 98°C. The Reclaimer is operating at a vacuum pressure -0.2 bar. This will help in evaporating the water and volatile MDEA while making up with lean MDEA to hold levels. The overhead vapor is cooled and partially condensed in condenser 129E004. The condensed liquid is separated in separator 129D009. The condensed liquid is pumped back to the stripper by condensate pump 129P017. When enough heavier components have accumulated in the Reclaimer, the inlet liquid feed of the Reclaimer is stopped, then, the sludge in the Reclaimer is dumped, and the cycle can be repeated. Figure 5 shows the simulation of the CO_2 removal unit after including all the proposed modifications for improving the sweetening process as well as solving some of the operational issues.

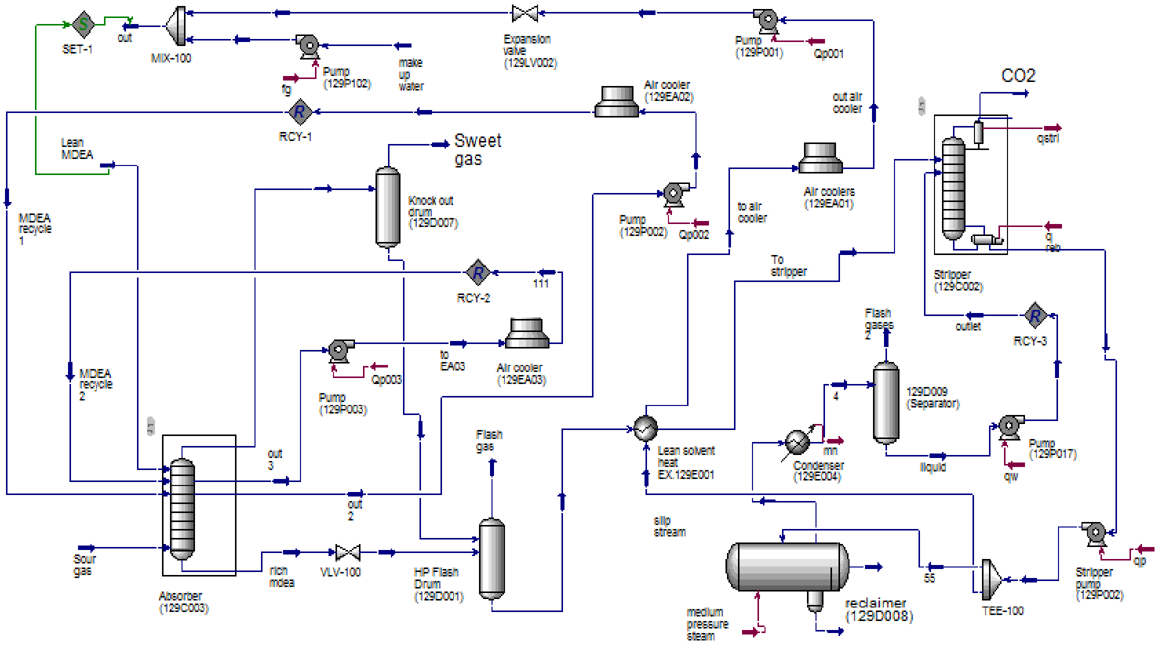

Figure 5. Simulated suggested modified CO_2 removal unit

In this work, by using the HYSYS program, it is found that the amount of sludge formed corresponds to the loss in the amount of MDEA. The actual concentration of MDEA used by

HYSYS is 23.59 mole% in the existing sweetening unit and 24.1 mol% in the modified unit. In the existing and the modified sweetening unit, the MDEA concentration is increased by an amount compensated by the sludge. This amount equals 14 mole% of the amine (loss in the amine).

3.3. Economic evaluation of the original and the modified sweetening unit

HYSYS program was used to calculate the total capital and operating costs of the original and the modified plants. The results showed that there is saving in operating costs in case of the modified plant. As shown in Table 3, according to the proposed modifications of using MDEA solution without activator, saving in operating cost is $ 2 919 802.23 per year.

Table 3. Capital and operating costs of the original and modified plats

Items	Operating cost	
	Original case	Modified case
Electricity (US$/year)	597 460.41	495 209.39
Cooling water (US$/year)	317 180.8	105 099.98
High pressure steam (US$/year)	5 456 825.57	
Medium pressure steam (US$/year)		2 851 355.18
Total operating cost (US$/year)	6371466.78	3 451 664.55
Saving in operating cost (US$/year)	2919802.23	
	Capital cost (US$)	
	Original case	Modified case
Knock out drum 129D007	188 700	188,700
Stripper pump 129P002	124 300	124,300
Lean solvent heat EX.129E001	531 800	531,800
Pump(129P003)	520 200	520,200
Pump (129P102)	165 800	165,800
Air coolers129EA01	585 700	585,700
HP Flash Drum 129D001	401 000	401,000
Stripper (129C002)	19 419 600	19 419 600
Main Tower_@Absorber (129C001)	194 600	
New Main Tower_@Absorber (129C003)		430 900
Reclaimer (129D008)		242 500
Separator (129D009)		161 000
Air cooler (129EA02)		159 000
Condenser (129E004)		118 200
Pump (129P002)		105 200
Pump (129P001)		427 300
Air cooler (129EA03)		163 600
Pump (129P017)		51 700
Total capital cost (US$)	22 131 700	23 796 500
Total capital cost (US$/year)	23 238 285	24 986 325
Total annual cost (US$/year)	29 609 751.78	28 437 989.55
Increasing in capital cost (US$)	1 664 800	
Return on Investment (ROI) (year^{-1})	(2 919 802.23/1 664 800) =1.75	
Payback period (year)	(1/1.75) = 0.571	

This is because the heat required for the regeneration of MDEA in the case of amine-free activator is small compared with that required if amine is used with the activator [22]. Another example of a variation of operating cost is the steam type used in the reboiler of the stripper (Reboiler @ Stripper (129C002)). In the modified plant, the applied steam is of intermediate pressure type, which costs approximately the half value of the high-pressure steam used in the current plant as described in Table 3. This steam used to separate CO_2 from the rich solvent stream (MDEA+CO_2). Besides the reduction of operational costs, more benefits can be ascribed to the modified plants such as higher absorptive power of solvent that leads to removal of a high amount of CO_2 with lower energy consumption and higher stability [13]. Nevertheless, the lower reaction time in the absence of the MDEA activator is the greatest disadvantage of the proposed modification. This drawback can be solved by increasing the absorber volume as well as the amine circulation rate.

As illustrated in Table 3, the capital cost of the modified plant is increased by 1 664 800 US$. This increment is attributed to the addition of new equipment such as an additional absorber, a separator, condenser, two air coolers, three pumps, and a Reclaimer vacuum unit. However, the calculated return on investment (ROI) and the payback period are 1.75 year^{-1} and 0.571 years respectively (see the last two rows of Table 3). This very low value of payback period indicates that the modified plant with applying the amine solvent without activator is more profitable than the original plant.

3.4 Validation of the proposed modified sweetening unit

All the previous suggested modifications in the existing gas sweetening unit in this work are implemented in the plant. The results of the operation agree with the simulation results obtained in this work. A comparison is made between the results of the original and modified CO_2 removal unit from the viewpoint of the sweet gas composition, the strength of MDEA and foaming properties. The results illustrate that CO_2 concentration in the outlet sweet gas for the modified plant decreases from 1300 ppm to 106 ppm compared to the old plant. This consequently diminishes the potential formation of hydrate in cold box refrigeration system. Consequently, this leads to reducing the tendency towards foaming formation inside the absorber. These results are confirmed by lab tests which indicated the reduction of foam height from 680 millimeters at 40 sec in case of original unit to 180 millimeter at <30 sec for the absorber tower as illustrated in Table 2. Therefore, it is strongly recommended to apply the introduced modification of the investigated and similar plants to increase the plant profitability as well as to improve the plant performance.

4. Conclusion

The main objective of the present study is to enhance the sweetening unit owned to one of the biggest companies in the Middle East, particularly in the gas treatment sections. Additionally, this work investigates how to solve some encountered operational problems of this sweetening plant. Some experimental practices and analysis were undertaken to explore the sources of the solvent carry over the problem, and the obtained results showed that this problem is related primarily to the characteristics of MDEA solvent used for acid gas removal via absorption. Such characteristics are a tendency to foam, the presence of hydrocarbons and solid particles, in addition to the under-sizing of the acid gas removal columns.

The present study introduces some modifications in order to alleviate or eliminate effectively the problems in the acid gas removal section. These modifications include the following: Using MDEA without activator, replacing the current absorber with a larger one includes three structured packing instead of two packing bed, adding two pumps around with two stages of side air coolers, adding a reclamation unit, and increasing amine solvent circulation rate. The original and modified plants were simulated by using HYSYS software version 10. Compared to the original plant, results showed that the modified plant has a higher strength of lean MDEA and lower CO_2 concentration in the outlet sweet gas. This, in turn, increases the absorption capacity for CO_2, reduces the tendency towards foaming formation inside the absorber, and diminishes the potential formation of hydrate in the cold box. However, the proposed modification for the sweetening unit under consideration can solve effectively the encountered operational problems. The economic studies of the modified and original plants show that the modified plant is more profitable. Therefore, it is strongly recommended to apply the proposed modifications to the plant under investigation or similar plants in order to raise their economics and performances as well as to solve their operational problems.

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