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Revamping of An Acid Gas Absorption Unit: An Industrial Case Study

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Abstract

This work evaluates the efficiency of the aqueous mixture of Methyl Diethanolamine (MDEA) and Diethanolamine (DEA) at various mass concentrations to remove CO_2 and H_2S from natural gas in an industrial sweetening unit in Fajr Jam Gas Refining Company located in the south of Iran and gives recommendations for modifying the process. The sweetening unit includes absorber and desorption towers, flash drum, lean and rich amine exchanger, kettle type reboiler and a reflux drum. The considered process is simulated by Promax simulator (version 3.2) taking into account operational constraints and sustainability of the environment. The validity of simulation has been evaluated by comparison between simulation results and the plant data. The main objective of this work is the modification of natural gas sweetening unit to achieve lower energy consumption. Thus, the effect of amine circulating rate and MDEA to DEA ratio on steam consumption in the regeneration tower, CO_2 and H_2S concentration in the treated gas, and the acid gas loadings have been investigated. Therefore, substitution of DEA solvent in the unit with the aqueous mixture of DEA and MDEA is proposed. In the examined cases, the mass concentration of MDEA and DEA lies between 15-45 wt % and 0-30 wt%, respectively, with the reference cases having MDEA 0 wt.% and DEA 31.6 wt.%. The results show that in the proposed cases of alternative mixtures including cases 1 (MDEA15 wt% and DEA 30 wt%), 2 (MDEA 20 wt% and DEA 25 wt%), and 3 (MDEA 25 wt% and DEA 20 wt%) the amount of reduction in amine circulation rate are between 11.1%v/v and 19.4%v/v compared to the original amine circulation rate. Likewise, steam consumption decreases between 24.4 %wt/wt and 27 %wt/wt. Influence of anti-foam injection for the different cases were also studied and it was found that anti-foam with the concentration of 5000 ppmv is more suitable for the optimum operation and is a more cost effective.

Keywords: Sweetening unit, Process simulation, Promax, Amine circulating, Foaming

1. Introduction

Removing impurities such as H_2S, CO_2 and other sulfuric components like the RSH (mercaptans) from natural gas is necessary from environmental and safety viewpoints[1]. CO_2 decreases heating value of gas and consequently its price. To avoid human health threatening and corrosion issues in transport pipelines and refining facilities, many restrictions have been imposed in which, the largest allowable molar concentration of CO_2, and H_2S in the gas stream should not be exceeded than 2 vol.% and 4 ppmv, respectively[1].

Despite the progressive improvement in technologies related to the separation of impurities in gaseous stream, the absorption by Alkanoamine solvents is the most widely commercialized processes in many industries [2]. These chemicals provide necessary water solubility and alkalinity for absorbing acid gases impurities by their Hydroxyl and Amino groups, respectively [1]. Although primary and secondary amines have more alkalinity and reactivity compared to tertiary amines [3], in terms of energy saving, stability and solvent losses, tertiary amines are more desirable [4]. Tertiary amines like MDEA are able to selectively absorb H_2S and do not directly react with CO2 [1]. There are many limiting factors such as the specification of sweet gas, required energy for reclaiming the solvent, circulation rate and concentration of the solvent along with its ability to absorb the acid gases which should be taken into account for selecting optimum operating conditions in which the process works qualitatively [2, 5, 6]. Many approaches introduced to modify the amine-based absorption-desorption process and decrease the operational cost of that process. Galindo et al. (2012) investigated the performance of the aqueous mixture of DEA and MEA to absorb CO_2 in an amine-based post-combustion process[7]. The results showed that DEA offers the possibility to operate the stripping column at a lower temperature level, hence the more energy saving. Qiu et al (2014) investigated effects of the number of trays and operating pressure of the absorber in a natural gas sweetening process. They used a modified based MDEA absorbent and their results showed that improving absorption pressure and tray number would reduce the circulation rate, energy and operational cost [8]. Sohbi et al (2007) focused on the change in the amine concentration and the circulation rate in a natural gas sweetening plant by using a mixture of amines (DEA and MDEA). Their results revealed that 40 wt% MDEA with 10 wt% DEA is the best option in terms of water losses [9]. Younas et al (2014) investigated the change in amine concentration and circulating flow rate in a natural gas sweetening process by Promax software. They determined that MDEA 45 wt% with the flow of 360 (m^3/h) is the optimum conditions for their processes [10].

Røkke et al. (2014) proposed different CO_2 absorption unit [11]. The Aspen-Hysys simulator was used to design the proposed processes as well as cost estimation and optimization. The results showed that the vapours recompression configuration gives both the lowest energy consumption and the best net present value. Al-lagtah et al. (2015) analyzed Lekhwair gas sweetening process by Aspen-Hysys simulator to increase profitability and sustainability [12]. The results showed that conventional split-loop by carrying out side draw from stripper to the absorber and optimizing the flow rate of this side draw, the intermediate side draw in the stripper, and the feed stage in the absorber could decrease operating cost up to 50% compared to the conventional process. Fouad and Berrouk (2013) investigated the use of amine solvents that consist of two tertiary amines namely MDEA and TEA [13]. Their results showed that the mixture containing 40 wt% MDEA and 5 wt% TEA reduces operating cost up to 3% considering the sweet gas specifications in terms of H_2S and CO_2 concentrations.

Since the required energy to regenerate rich amine is directly related to the type and rate of circulation solvent, applying the optimal rate and solvent composition are two critical factors to reduce operational cost and increase product quality. Thus, the objective of this work is the modification of natural gas sweetening unit in Jam Gas Refining Company to achieve lower energy consumption. The main idea is the substitution of DEA solvent in the unit with an aqueous mixture of DEA and MDEA. To compare the efficiency of the aqueous solution of DEA and mixture of MDEA and DEA to capture CO_2 and H_2S, the process is simulated by Promax simulator (version 3.2) developed by Bryan Research & Engineering considering operational constraints including product specification, corrosion prevention resulted from increasing acid gases loading, degradation of solvent by increasing regeneration tower temperature and energy saving. The validity of simulation is evaluated by comparison between simulation results and plant data. Then, the effects of amine circulating rate and MDEA to DEA ratio on the performance of sweetening process are determined. Besides, due to unexpected foaming and excess consumption of anti-foam to prevent foaming which is currently a critical problem in the refinery, a foaming test has been done to evaluate proposed mixture in terms of their tendency for formation of the foam.

2. Process Description

The plant includes eight parallel sweetening trains that is worked separately, albeit they are similar except for their amine solvents. Table 1 shows the feed composition which supplies from three sources i.e. South Pars, Nar and Kangan gas reservoirs. Fig. 1 shows the schematic flow diagram of the process. These sweetening units include absorber (T-4101) and desorption towers (T4102), flash drum(S-4102), lean and rich amine exchanger (E-4101), kettle type reboiler (E-4102) and a reflux drum(S-4103). In the conventional sweetening process, sour gas is fed to a drum to separate water and heavy hydrocarbon liquid from the natural gas stream (S-4105). The stabilized sour gas is fed to the bottom of the absorber and in counter-current contact with the solvent; CO_2 and H_2S are removed from the gas stream. The rich amine solution leaves the absorber at the bottom and feeds to a flash drum equipped with a throttling valve that expands the high-pressure absorber rich amine by decreasing the pressure of the gas before entering the flash drum. The purpose of the drum is to remove the most dissolved hydrocarbon gas and some acid gases. This horizontal flash drum is worked as a hydrocarbon recovery unit and could prevent foaming. A lean/rich heat exchanger serves as a preheater to heat the cold rich amine stream from the flash drum by the exchange of heat from the hot lean amine stream which exits from the regenerator. After that, the preheated rich solution flows into the regenerator column where rich solution is stripped at low pressure and high temperature. The regenerated lean amine stream is pumped via P-4101 back into the top of the absorption column after passing through the air cooler (E-4104). The air cooler is used to ensure that the lean stream is sufficiently cooled before recirculate to the amine cycle. The regenerator tower is equipped with the kettle type reboiler, a number of stainless steel condenser tubes that utilize to cool down the acid gas stream before entering to the reflux drum. At the bottom of the tower, the reboiler supplies the necessary heat to heat up the semi-rich amine to its boiling point and at the top of the tower, the reflux stream provides the condensing condition so that acid gas stripping is done and the solvent is regenerated. A pump (P-4103) is used to recycled back the condensed mixture of amine and water collected in the reflux drum to the regenerator tower. The outlet gas stream from the top of reflux drum that mainly consists of H_2S and CO_2 is fed to an incinerator and the exhausted steam that used to boiling the solution accumulated in a drum, sending to the utility unit to reproduce steam. However, there is a plan to install Sulfur Recovery Unit in near future to abide with the environmental regulations.

Fig. 1- Schematic flow diagram of the gas sweetening plant.

Table 1- Feed gas flow rate, composition and condition of the considered plant

3. Process simulator

Process simulation is a model-based representation of chemical processes and unit operations. Simulation software describes a process in flow diagrams where unit operations are connected together with the mass and energy streams. Based on the simulated process and inputs, the software solves the mass and energy balance equations to find the operating point. The main goal of a process simulation is to find the optimal condition of the simulated process. Promax which has been developed by Bryan Research and Engineering Company (TX, USA), introduced as a popular process simulator software for designing, troubleshooting, analyzing and optimizing the chemical processes. In this research, the sour gas-sweetening unit is simulated by Promax software. Figure 2 shows the flow diagram of simulated sweetening process in Promax.

Fig. 2- Simulated process flow diagram.

3.1. Simulation Constraints

In the present work, amine circulation rate, and MDEA to DEA ratio at constant total concentration have been used as manipulated variables to investigate the performance of sweetening process. Generally, the mass concentration of MDEA and DEA lays between 45 wt % to 15wt % and 0 wt % to 30 wt% in the considered cases, respectively. Many restrictions and constraints should be accounted to select the optimal case. Based on the refinery management policies, operational limitations and safety issues are considered as a constraint. The total amount of H_2S in outlet stream from refinery must be lower than 4ppmv. In addition, the total molar concentration of CO_2 in refinery outlet must be lower than 2% molar. Since some of the trains have been equipped with Merox unit, the amount of CO_2 must be lower than 30 ppmv in those trains to prevent caustic loss in Merox tower. In addition, to meet pipeline specification, the concentration of amine mixture recommended being lower than 45 wt% and the amount of DEA in amine blend must not be greater than 30 wt% due to preventing corrosion in instruments. Moreover, rich and lean loading that are respectively define, as the total mole of acid gases divided to the total mole of solvents in rich and lean amine must be respectively lower than 0.04 (acid gas mole/amine mole) and 0.5 to prevent corrosion. In addition, the maximum amine circulation rate for this process in the high-pressure amine pump could not be exceeded than 360 m^3/hr and the minimum rate must be more than 160 m^3/hr. According to the mechanical design constraints to prevent amine degradation, the bottom and top temperature of regenerator should not be upper than 126 and 112°C, respectively.

4. Results and discussion

4.1. Field test data and simulation validity

In this section, the simulation results of the considered sweetening unit and the plant data are compared to evaluate the reliability and accuracy of the software. In the first step, the feed stream is defined as presented in Table 1. In this unit, the absorber is a valve tray tower with 32 trays in which amine stream enters from the top of the tower on tray number 1 and gas stream enters from the bottom. A throttling valve is used before entering the exhausted rich amine from the absorber to the flash drum to supply more than 7700 kPa (g) pressure drop for better flashing and releasing acid gases and dissolved hydrocarbons in the amine. To reach the high energy recovery, a lean rich exchanger provides the counter current flow of lean regenerated amine from the acid gas stripper tower and the rich flash drum outflow stream. Generally, to run the kettle type reboiler and total condenser amine in the regenerator either reboiler steam or a tower specification should be determined. Since the aim of this work was reducing energy consumption, setting lean loading or amount of reboiler's steam could not be helpful; thus setting the temperature in the top of the regenerator tower used to consider the effects of substitution of the new solvents in different circulation rates.

Presence of high amount of CO_2 in the absorber outlet stream causes the caustic loss in the Merox tower. In this plant for preventing this undesirable effect, the DEA solvent has been used as a sweetening agent to reduce the amount of CO_2 less than the 30 ppm. Consequently, the high amounts of amine circulation rate and regeneration steam were always two inevitable side effects for years. Consequently, the idea of substituting the mixture of MDEA and DEA for DEA solution has been proposed to simultaneously benefit from the advantages of MDEA such as lower required energy for regeneration and DEA ability in absorbing CO_2. Utilizing lower energy for solvent regeneration could prevent the formation of amine degradation products and heat stable salts[14]. According to the field test data collected from four of eight trains in the refinery's laboratory and daily log sheet from the control room while each of these trains had the maximum feed, the average amount of the steam consumption and amine circulation rate were 57 ton/hr and 359 m^3/hr , respectively. Table 2 reported the conditions of aforementioned trains in which different concentrations of the DEA solvent have been used in almost the same operating conditions. Moreover, as impurities level would affect solvent performance and the simulation prediction, the plant data are based on the results that have been obtained after overhaul when the solvent was fresh (without effective amount of by-products).

Table 2. Operational condition of DEA trains

Since the scale-up is a challenge in chemical engineering, many cases in different conditions have been used to determine whether the simulation is validated. It is observed that in all cases, the results of the simulations have a great agreement with the plant data. This confirms how the simulations were successful in anticipating the process behavior while utilizing the alternative solvent.

Table 3. The comparison between simulation results and plant data.

Table 3 reveals the data related to one of the mentioned trains to prove the validity of the simulation. Finally, by implementing the simulation results on the real plant data with 10.5 Millions standard cubic meter per day ($MMSCMD$) of the feed gas, it has observed that the alternative mixtures of 25 wt% MDEA and 20 wt% DEA decrease CO_2 and H_2S concentration in the treated gas considerably without violating the constraints. The specifications of outlet gas from the absorption tower and simulation results are compared in Table 4.

Table 4 shows the comparison between simulation results and DEA plant data from Fajr Jam Gas Refining Company.

Table 4. Result of testing the 20 wt% MDEA 25 wt% DEA in on of the rifinery's train

4.2. Simulation results

Since the regenerating energy requirement is directly associated with the type and the rate of circulation absorbent, applying the optimized rate and composition of this solvent, are the two critical factors in reducing operational cost and enhancement quality of process product. Blending diverse typical amines such as MDEA and DEA leads to make an absorbent mixture with characteristics of both secondary and tertiary amines simultaneously, e.g. achieves lower regeneration energy consumption, lower corrosion rate, higher reactivity toward CO_2 and COS[1]. Furthermore, DEA is more corrosive as compared to MDEA solution since forming the heat stable salt and amine degradation products strengthen the corrosion nature of the DEA more than MDEA solvent [15]. Therefore, mixing ratio plays an important parameter in the design and operation of amine gas treating processes. In this section, the effect of amine ratio and amine circulating rate on the performance of conventional sweetening units are investigated under steady-state conditions. Table 5 presents the considered solvents.

Table 5. Considered solvents.

In the sweetening process, amine circulation rate has a main effect on the acid gas loading. Increasing amine circulation rate decreases the number of equilibrium stages in the absorption tower. On the other hand, it increases the cost of pumping of the solution, regeneration, heating and cooling. Figures 3 and 4 show the effect of amine circulating rate on the H_2S and CO_2 concentration in the outlet gas stream from absorption tower. It is obvious that increasing amine circulation rate decreases H_2S concentration in the outlet gas stream. Due to the low solubility of CO_2 in MDEA, decreasing DEA concentration in the solution decreases amine's CO_2 loading, so the aqueous solution of MDEA presents minimum CO_2 absorption. Considering MDEA as a base solution, increasing the amine circulation rate from 230 to 320 m3/hr reduces the CO_2 concentration from 6949.5 to 6466.4 ppmv in the treated gas. Higher CO_2 absorption, due to increased circulating rate of MDEA solution, increases H_2S concentration in the treated gas about 9%. The results show that aqueous solution of MDEA is more effective to absorb H_2S compared to the aqueous mixture containing 40 wt% MDEA and 5 wt% DEA. Because of higher acidity of CO_2 compared to H_2S and higher selectivity of MDEA toward H_2S compared to DEA[1], the aqueous mixture containing 40 wt% MDEA and 5 wt% DEA could absorb higher CO_2 compared to MDEA solution, so applying 230 m^3/hr solutions in the system decreases CO_2 concentration to 3452.1 ppmv in the treated gas. With respect to the presented results, it is observed that increasing DEA concentration decreases CO_2 concentration in the treated gas, albeit increasing DEA concentration increases H_2S concentration in the absorber outlet gas stream and after reaching a maximum point H_2S concentration decreases gradually. The results show that minimum H_2S concentration in the treated gas is achieved by using the solution containing 15 wt% MDEA and 30 wt% DEA. However, as regards to the Sale Gas Pipeline Specifications for CO_2 and H_2S, other cases in some and the cases 2 and 3 in all rates from 230 to 320 m^3/hr are appropriate. Additionally, the more concentration of the DEA solvent would be associated with intensifying the possibility of corrosion in facilities.

Fig. 3- Effect of amine circulating rate on the H_2S concentration

Fig. 4-Effect of amine circulating rate on the CO_2 concentration

The rich amine is usually regenerated at high temperature and low-pressure conditions. Since carbon dioxide and hydrogen sulphide reactions are reversible and exothermic, increasing temperature shifts the absorption reactions toward the left side[1]. In the regeneration tower, carbon dioxide and hydrogen sulphide are released, and the regenerated solution is recycled to the absorption tower. In the industrial unit with utility facilities, the heat of regeneration is supplied by steam, so steam consumption is one of the main parameters that have a significant effect on the operational cost. Figure 5 shows steam consumption in ton/hr in the regeneration step versus amine circulation rate for all the cases which are described in Table 5. Generally, increasing amine circulation rate increases rate of required steam in the regeneration tower. In addition, since the DEA solvent requires higher energy to strip acid gases during regeneration, increasing DEA concentration in the aqueous solution of DEA and MDEA would lead to enhance the amount of required steam in the tower's reboiler in order to reach expected lean loading. Table 6 reveals the information about the amount of differences in required steam consumption and also the percentage reduction in solvent circulation rate that properly shows how the mixing MDEA with DEA can reduce the energy saving.

Fig. 5- Amount of used steam in the regeneration step.

Table 6. Amount of reduction in solvent circulation rate and steam consumption for different cases.

Figures 6 and 7 respectively show rich and lean loading of the aqueous mixture of DEA and MDEA at the different mass ratios. Loading is defined as the moles of absorbed acid gases to the moles of applied solvent [16]. Figure 6 reveals that there is a considerable difference between rich loading of solutions at the same amine circulating rate. Having the lower MDEA reactivity toward CO_2, the lower rich loading appears in samples containing higher MDEA. Figure 7 shows the lean loading of the cases. Lean loading has the significant effect on the purity of treated gas in the absorption tower. As can be seen from the figure, in the same amine circulation rate, the stripping of the cases contains more MDEA is easier.

Fig. 6- Rich loading of aqueous mixtures of DEA and MDEA

Fig. 7 Lean loading of aqueous mixtures of DEA and MDEA

5. Foaming Tendency

Foaming in the absorber column has been reported as a common and severe problem in sweetening plants as it imposes extra maintenance and operational costs in terms of installing reclaimer and amine clean up setting to prevent excessive loss of solvent, column pluggage, premature flooding, and process instability. Moreover, foaming can cause reducing the product quality and separation efficiency since it decreases concentration difference between trays, and results in off-specification of products and high pressure drop [17, 18]. Many problems including mal-operation, heat stable salts, amine degradation products, and entering oil cuts and other contaminates from feed or water make-up have been reported as the main factors in foam formation [18-20]. Figure 8 shows the foaming height as a criterion for foaming tendency of the cases and the cases foam subsidence time after 5 minutes with applying 10000 ppm PN-30 antifoam based on ASTM D892-Standard Test Method for Foaming Characteristics of

Lubricating Oil [21]. The data in Figure 8 illustrate that cases 2 and 5 and 7 without utilizing the antifoam have the more foaming height. There is an almost similar result in case of using 5,000 and 10,000 ppm antifoam as a foam breaker. It appears that in all cases increasing antifoam concentration from 5000 to 10,000 ppm slightly decreases foam height or foam tendency. In conclusion, since in almost all cases utilizing much more antifoam would not certainly lead to big differences in foaming height, being the process more cost effective could be achievable in lower concentration.

Fig. 8- The foaming height of aqueous mixtures of DEA and MDEA.

6. Conclusion

In this work, the aqueous mixture of MDEA and DEA was evaluated to replace the DEA solution for removal of CO_2 and H_2S from natural gas in an industrial case. The gas sweetening process was simulated by Promax simulator based on the equipment design and the field data. The results show that although increases DEA concentration decreases acid gas concentration in the treated natural gas, it raises required energy for regeneration. Consequently, a higher amount of steam is used in the regeneration tower's reboiler. Hence, in order to select proper mixture a number of factors have been considered. H_2S content is the first and of the most important parameter that cases 6 and 7 are not acceptable in all rates similar to case 5 below the 290 (m3/hr). The second factor is CO_2 content in product as the lower CO_2 content, is more desirable. It is obvious that cases 1, 2, 3 are more acceptable based on a lower CO_2 content excellence. The third factor that has been affected on picking the appropriate solvent is rich and lean loading that should be lower than the standard values. As can be seen from the Figure 6 for the majority of rates, the amount of rich loading is higher than 0.45 that causes corrosion and other operational problems. Consequently, the lower steam consumption and the lower lean loading of other cases in remaining rates determine the proper points that bring better condition. In the other hand, in operation we should consider some secure margins to ensure high quality and consistent production. Based on the results of this work that has been tested in an industrial scale, the simulation and plant performance were in a good consistency. Alternative mixtures including case 1 (MDEA 15 wt% and DEA 30 wt%), case 2 (MDEA 20 wt% and DEA 25 wt%) and case 3 (MDEA 25 wt% and DEA 20 wt%) will cause the reduction in amine circulation rate between 11.1% (v/v) and 19.4% (v/v) as compared to the original amine circulation rate. Likewise, steam consumption decreases between 24.4 %(wt/wt) and 27 %(wt/wt). Therefore, substitution of DEA solvent in the unit with the aqueous mixture of DEA and MDEA could be the suitable option.

The results of foaming test showed that in all solutions increasing industrial antifoam concentration decreases foam height; however the slight reduction was observed by increasing concentration from 5000 ppm to 10,000 ppm as compared from zero to 5000 ppm.

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Figure captions

Fig. 1- Schematic flow diagram of the gas sweetening plant.

Fig. 2- Simulated process flow diagram

Fig. 3- Effect of amine circulating rate on the H_2S concentration

Fig. 4- Effect of amine circulating rate on the CO_2 concentration

Fig. 5- Amount of used steam in the regeneration step

Fig. 6- Rich loading of aqueous mixtures of DEA and MDEA

Fig. 7 Lean loading of aqueous mixtures of DEA and MDEA

Fig. 8- The foaming height of aqueous mixtures of DEA and MDEA

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Table 5. Various solvents consiered in this study.

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