Simulation and Optimization of Gas Sweetening Process at Mellitah Gas Plant Using Different Blends of Amines

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Abstract:

Mellitah gas plant uses the MDEA solution as a solvent for gas sweetening process. Selectivity of MDEA over MEA and DEA leads to saving energy for amine regeneration and solution circulation rate. However, the MDEA does not react directly with CO2 particularly as an extensive amount of CO2 is required to be removed. At Mellitah gas plant the concentration of CO2 is high (14.5% vol.) and H2S concentration is 1.2 % vol. To overcome this disadvantage, Mellitah gas plant uses the MDEA *solution with absorber plate weir height of 100 mm to increase the holdup time up to 3.6 seconds instead of standard plate weir height of 50 mm. The absorption column with plate weir height of 100 mm requires design of a special column which costs more. To avoid paying extra money for design of a special column, secondary amines such as MEA or DEA have to be added to MDEA solution as activators to increase the reaction rate of MDEA solution with CO2. Gas sweetening process at Mellitah gas plant was placed under investigation with the use Aspen HYSYS software v.8 as a simulator. In addition, optimization by two blends of amines (a 40% wt MDEA with 10% wt DEA blend, and a 40% wt MDEA with 10% wt MEA blend) using standard plate weir height of 50 mm. This study showed that the two blends of the amine can remove the acid gasses from the raw natural gas to required specifications. In contrast, 40% MDEA with 10% DEA blend was the optimum because of its lower reboiler duty for amine regeneration, lower losses of amines in the sweet gas stream but requires more amines circulation rate. Moreover, the specification of the sweet gas stream was 0.492 ppm H2S and 0.055% CO2 at amine circulation rate of 1200 m3/h and lean amine temperature of 35°C. In addition, the optimization work illustrated that the CO2 absorption rate in the 40% MDEA with 10% DEA blend was 2.5 times greater than that for CO2 absorption in the 50% MDEA solution at amine circulation rate of 1200 m3/h. The 40% MDEA & 10% DEA blend is the recommended one for optimization the gas sweetening process at Mellitah gas plant.*

1.Introduction:

Natural gas has recently become a key source for supplying energy around the world. The demand for natural gas has increased extremely through the past few years because of its varied uses as a fuel. To utilize natural gas as a fuel and receiving maximum energy capacity, several impurities like water, CO_2, H_2S, COS, N_2, Mercury, mercaptans (methanethiol and ethanethiol) and other sulfide compounds have to be completely or partially removed. These impurities in presence of water can cause corrosion, freezing, plugging, and environmental pollution [1]. Various processes are employed to remove acid gases from natural gas, for instance, membranes, chemical absorption, and physical adsorption. Chemical absorption processes using aqueous solutions of amines are the widest processes for removal acid gases from natural gas at moderate pressures. The most common types of amines used for acid gases removal processes are monoethanolamine (MEA), diethanolamine (DEA) and methyldiethanolamine (MDEA). The MDEA process was developed in the mid-1970s, and it is essentially for the processes that do not need complete CO_2 removal [2]. MDEA has several advantages over MEA and DEA amines, for example, lower energy requirements, lower vapour pressure, lower heat of reaction, excellent stability and fewer corrosion problems [3]. However, the importance of a MDEA solution is quickly increasing as a non-selective solvent that absorbs H_2S in the presence of high concentration of CO_2 due to its minimal reaction rate for CO_2. To increase the reaction rate of MDEA with CO_2, the primary or secondary amines such as MEA and DEA has to be added to MDEA solution to form mixtures of amines [4]. Blends of MDEA and DEA have been investigated by Mshewa and Rochelle (1994) [5]. The absorption rate of CO_2 in a 50 %

wt. MDEA solution and in a 40% MDEA with 10% DEA blend has been measured over a varied range of temperatures and partial pressures. The results illustrated that the absorption rate in a 40% MDEA with 10% DEA blend is 1.7 to 3.4 times greater than that for CO_2 absorption in a 50% wt MDEA solution under typical absorption column conditions. Mixed amines containing MDEA are now offered by several licensors such as the BASF. Activated MDEA process uses a 2.5 to 4.5 molar MDEA solutions containing 0.1 to 0.4 molal MEA or up to 0.8 molal piperazine as absorption activators [6]. MDEA solution is used as a main amine solution for removal H_2S and CO_2 at Mellitah gas plant with plate weir height of 100 mm into the absorption column. Mellitah Oil & Gas Company is built and operated by the Libyan government in western Libya. The scope of the plant is to treat the raw natural gas coming from the Wafa field and Sabratha Offshore platform before to be transported to the customer (Italy). The raw natural gas coming from off-shore platform is constantly rich in H_2S (1.2% vol.) and CO_2 (14.5% vol.) that should be removed to meet sales gas specifications. Sales gas specifications at Mellitah gas plant are $H_2S < 5$ ppm, $CO_2 < 2\%$ vol., and the total sulfur content < 100 mg/Sm^3 at typical operating conditions of 30°C and 3950 kpa [7].

This paper aims firstly to simulate Mellitah gas sweetening process using a 50% wt% MDEA solution by Aspen Hysys software v.8 as a simulator. Secondly, optimization of the gas sweetening process using a 40% MDEA and 10% DEA blend and a 40% MDEA and 10% MEA blend with standard plate weir height of 50 mm. Finally, identify the optimum blend of amine to optimize the performance of the gas sweetening process at Mellitah gas plant.

2. Gas Sweetening Process Description:

Various types of processes are provided to remove acid gases from natural gas. The most common processes used are adsorption, and absorption [8]. The adsorption process is a physical-chemical phenomenon in which the gas is concentrated on the surface of a solid or liquid to remove impurities. Absorption process is a chemical phenomenon (by reaction) or a physical phenomenon [9]. Absorption processes are considered as the best and common processes to remove acid gases from natural gas streams. Moreover, amine processes are considered the most successful processes in natural gas industries due to its high ability to absorb acid gases. Indeed, there are several parameters need to be taken into consideration at the removal of acid gases from the raw natural gas: first, types and concentrations of impurities in the raw natural gas. Second, the number of impurities needed to remove. Third, the ratio required to achieve carbon dioxide to hydrogen sulphide in the sweet gas. Four, operating conditions of the natural gas to be treated [9].

Figure (1) illustrates the typical gas sweetening process. Throughout the process, the lean amine solution (50 % wt. MDEA) enters at the top side of the absorber and flows down. The sour gas enters at the bottom side of the absorber and flows up in counter-current flow with the lean amine solution. A chemical reaction takes place between MDEA solution and H_2S and CO_2. The MDEA solution absorbs H_2S and CO_2 and leaves from the bottom of the tower as a rich solution, while the sweetened gas leaves from the top of the absorber and goes through an outlet separator and then flows to a dehydration unit. The rich amine solution coming from the high-pressure tower (absorber) enters to a throttling valve to decrease the pressure before flowing into a flash tank. The flash tank removes free liquid and liquid droplets in the gas. Subsequently, the left rich amine from the bottom of the flash tank is preheated by an amine-amine heat exchanger before feeding to amine regeneration column (low-pressure column). Indeed, amine regeneration column stripes MDEA from acid gases, dissolved hydrocarbon, and water. Finally, regenerated MDEA leaves from the bottom of regeneration column and is cooled by the amine-amine heat exchanger before recycling back to the absorption tower for reuse.

The reaction of MDEA with H_2S is the following:

$H_2S + R_2\text{-}N\text{-}CH_3 \leftrightarrow R_2NCH_4^+ + HS^-$ Fast

The reaction of MDEA with CO_2 is the following:

$CO_2 + H_2O \leftrightarrow HCO_3^- + H$ Slow

$HCO_3^- + H^+ + R_2\text{-}N\text{-}CH_3 \leftrightarrow R_2NCH_4^+ + HCO_3^-$ Fast

(Where, R: MDEA)

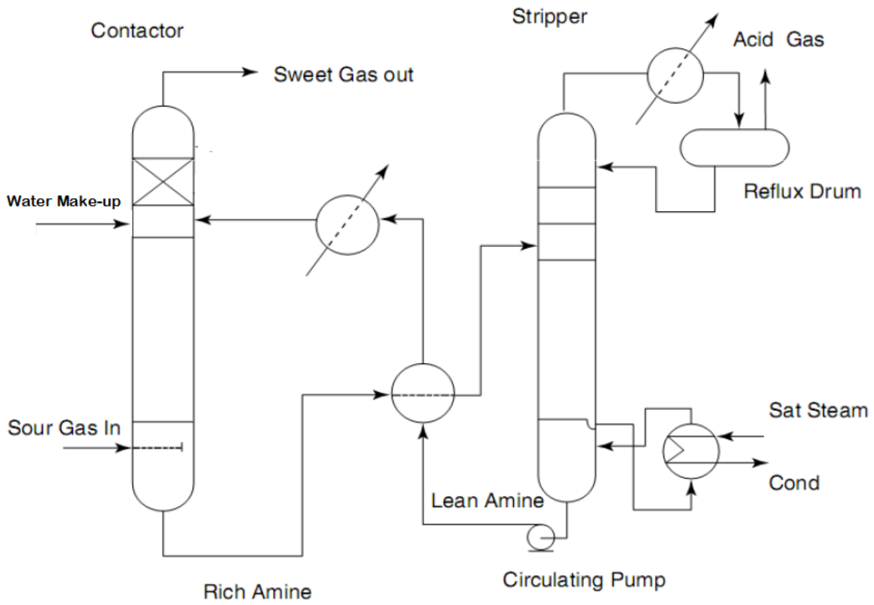

Figure 1: Typical gas sweetening process diagram

3. Blended amines :

According to Polasek et. al (1992) blended amines are defined as blends of MDEA and MEA or MDEA and DEA. The MDEA is essentially used as a basic amine, whereas the MEA and DEA as secondary amines. Adding the secondary amines to MDEA leads to increase amine reaction rate with CO_2 and saving energy for the regeneration column [10]. Ordinary, the concentration of MDEA is 40 – 55% in the total amine mixture, while the secondary amines concentration is less than 20% on molar bases. The importance of using blended amines is a result of that MDEA solution is allowing too much CO_2 to slip overhead with the sweet gas. Typically, MDEA blends are utilized to increase the CO_2 pickup from the raw natural gas as the concentration of CO_2 is high, as well as enhance the performance of gas sweetening processes by MDEA. Indeed, the concentration of blended amines relies on the concentration of the acid gases (H_2S and CO_2) in the raw natural gas, operating pressures and sweet gas required specifications. Consequently, the MDEA with MEA or DEA is often advantageous to accomplish the required CO_2 pickup for lower pressure applications. Moreover, blended amines are beneficial when the CO_2 concentration in the raw natural gas is increasing over time as a result of field aging. Nevertheless, these blended amines have little or no advantages in higher vapour pressure applications over the MDEA solution[11].

4. Mellitah raw gas composition and operating conditions :

Mellitah raw natural gas stream composition and operating conditions that completed by Aspen Hysys simulator are presented in table (1). The raw natural gas stream composition is based on a wet basis. Aspen Hysys simulator v.8 with amine property package was used to achieve all the calculations for the gas sweetening process.

Table (1): Raw natural gas composition and operation conditions at Mellitah gas plant

Compounds	Mole %	Molar flow rate (kgmol/h)
H_2O	0.02	**2.42**
Nitrogen	4.59	**660.63**
CO_2	15.71	**2260.45**
H_2S	1.29	**185.46**
Methane	70.12	**10088.95**
Ethane	4.46	**641.94**
Propane	1.80	**259.23**
i-Butane	0.40	**56.97**
n-Butane	0.66	**95.43**
i-Pentane	0.29	**41.83**
n-Pentane	0.28	**40.79**
n-Hexane	0.25	**35.56**
n-Heptane	0.13	**18.16**
Operating Conditions		
Temperature, °C	**30**	
Pressure, Kpa	**3950**	
Molar Flow, kgmole/h	**14388**	

5. Methodology :

Aspen Hysys Software v.8 is used to simulate and optimize the Mellitah gas sweetening process at steady state conditions. The following specifications and assumptions are carried out for the steady-state process simulation:

1. Absorption Column:

Feedstock is sour gas with water
Temperature (°C) = 30 °C
Pressure (kpa) = 3950
Number of theoretical plates = 30
Column pressure drop = 3.5 kpa
Temperature of lean amine solution = 50°C
Lean amine solution flow rate = 2.5 of sour gas flow rate

2. Regeneration Column:

Number of theoretical plates = 18
Feed is rich amine solution
Feed temperature = 103 °C
Feed pressure = 637 kpa
Bottom pressure = 210 kpa
Column pressure drop = 2 kpa

3. Heat Exchange:

Rich side delta T = 37 °C
Lean side delta T = -50 °C
Shell-side pressure drop = 67 kPa
Tube-side pressure drop = 59 kPa

4. Cooler:

Cooler pressure drop = 30 kPa

5. Pump:

Discharge Pressure = feed gas pressure + 35 kPa

Efficiency = 70 %

6. Valves:

Pressure drop of rich solution in the first expansion valve (VLV-100) = 3145 kPa

Pressure drop of rich solution in the second expansion valve (VLV-101) = 100 kPa

6. Results and Discussion :

6.1. Mellitah gas plant data validation :

Mellitah gas plant is simulated by Aspen HYSYS software v.8 using amine package and a 50% MDEA as a solvent. The specifications of the sweet gas stream resulted from the simulation were compared to the actual Mellitah gas plant data, and summarized in Table 2. The comparison of results demonstrated that the obtained results from the simulation were very close to the actual data of Mellitah gas plant and the degree of the absolute error between the actual and simulated data was less than 1% for hydrocarbon compounds. However, the concentration of H_2S and CO_2 in the sweet gas stream resulted from the simulation looks overestimating the actual concentrations. The actual concentrations are usually verified by laboratory tests or sensors.

Table 2: Simulation results for sweet gas stream specifications using Aspen HYSYS compared to the actual data of Mellitah gas plant.

Compounds	Mellitah gas plant data Molar flow (kgmol/ h)	Simulation results Molar flow (kgmol/ h)	Error (%)
Nitrogen	660.63	660.05	0.088
Methane	10088.95	10073.30	0.155
Ethane	641.94	641.12	0.128
Propane	259.23	258.99	0.092
i-Butane	56.97	56.97	0.000
n-Butane	95.44	95.43	0.010
i-Pentane	41.83	41.83	0.000
n-Pentane	40.79	40.79	0.000
H_2S	3.29×10^{-6}	6.94×10^{-7}	-
CO_2	0.0139	0.00142	-
Total (wet basis)	11885.78		
Temperature (°C)	30	30	
Pressure (kPa)	3950	3950	

6.2. Mellitah gas plant process optimization :

The optimization process for Mellitah gas plant studied first, optimization of operating parameters for the gas sweetening process. Second, effect of the amine circulation rate on the acid gases concentrations (H_2S and CO_2) in the sweet gas stream. Third, effect of amine circulation rates on the flow rate of hydrocarbon compounds in rich amine stream and reboiler duty requirements. Last, the effect of lean amine temperatures on losses of amines in the sweet gas stream. The optimization process has taken place at the same operating conditions of Mellitah gas plant with fixing the number of plates in the distillation and absorption columns.

The optimization process showed that using 40 % of MDEA reduces the concentration of CO_2 in the sweet gas stream to around 1.0 ppm for each 5 % wt. of MDEA. In contrast, the concentrations of H_2S stayed relatively unchanged with increasing MDEA concentrations. According to Addington and Ness (2013), the rule of thumb says that lean amine temperature should be 5 °C higher than the feed gas temperature to avoid any phase change and light hydrocarbon compounds condensation in the rich stream. This rule of thumb will be applied for this study. Since, the feed gas temperature is 30 °C, and then the lean amine temperature will be fixed at 35 °C. Table 3 summarizes the optimized operating parameters.

Table 3: Optimized operating parameters for the gas sweetening process

Parameter	Current plant data (MDEA)	Optimized value by MDEA&DEA blend	Optimized value by MDEA&MEA blend
Circulation rate (m^3/hr)	1160	1166	1150
Lean solvent temperature (°C)	50	35	35
MDEA concentration (wt. %)	50	40 & 10 DEA	40 & 10 MEA

Lean amine circulation rate is one of the most important parameters that should be taken into consideration. The amine circulation rate has to be adjusted using the lean amine booster pump. The optimum efficiency of the lean amine booster pump should be from 60 to 75% to maintain the entered amount of the lean amine into the absorber in the acceptable range and meet the required specifications for the sweet gas stream

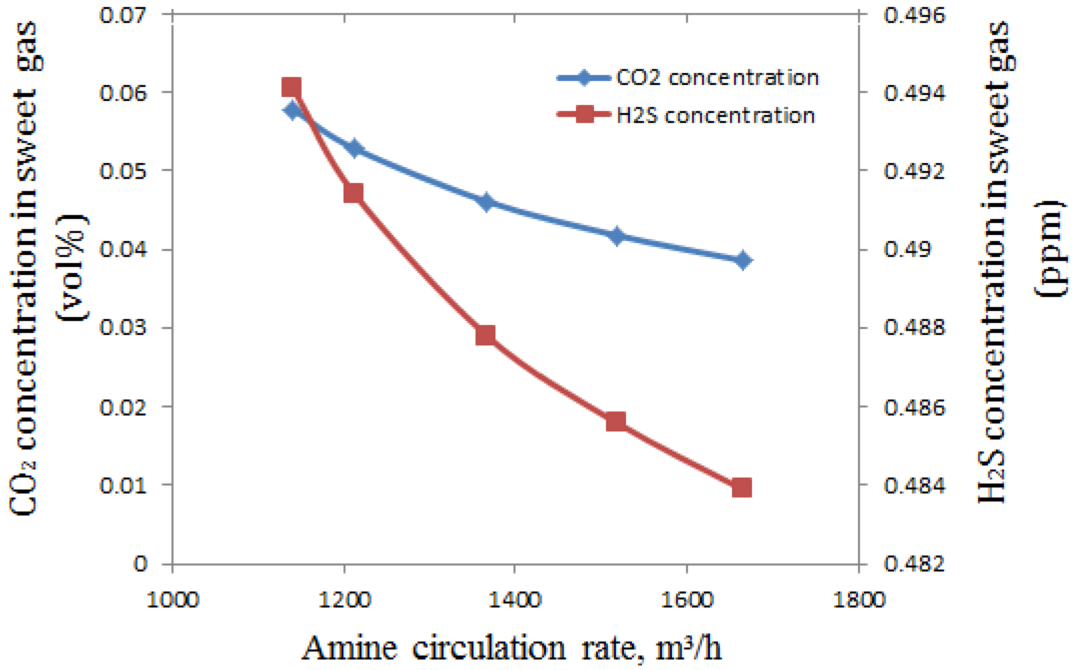

Figure 6. Effect of MDEA & DEA blend circulation rates on acid gases concentration in the sweet gas stream

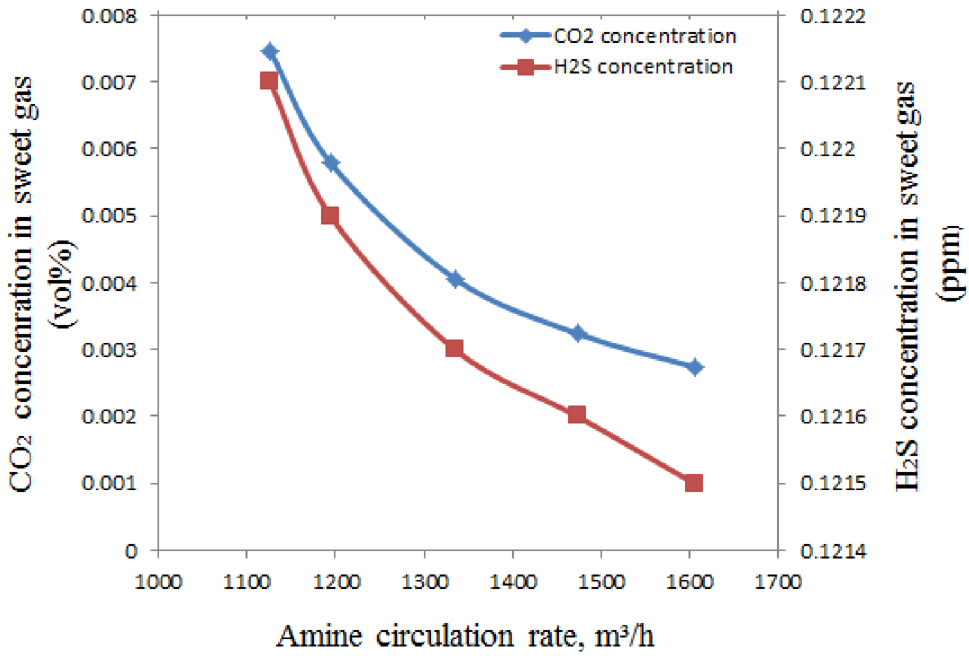

Figure 7. Effect of MDEA & MEA blend circulation rates on acid gases concentration in the sweet gas stream

Figure 6 and 7 illustrate how amines circulation rates can affect the acid gases concentration in the sweet gas. From figure 6 and 7 it can be seen that the concentration of H_2S and CO_2 decreases gradually with increased the amine circulation rate. Figure 6 shows that as amine circulation rate is 1200 m^3/h the concentration of H_2S decreases to about 0.492 ppm, while the concentration of CO_2 is about 0.055 % at amine circulation. As can be seen also that amine flow rate below 1200 m^3/h results in large amount of CO_2 to split overhead in the sweet gas stream. In contrast, the concentration of both H_2S and CO_2 in figure 7 decreases rapidly to 0.1219 ppm and 0.006 % respectively at amine circulation rate of 1200 m^3/h. The minimum amine flow rate for the MDEA & MEA blend should be at least 1110 m^3/h to achieve the acceptable removal for H_2S and

CO_2 in the sweet gas stream. Obviously, the amount of H_2S and CO_2 absorbed by an MDEA & MEA blend is higher than that absorbed by an MDEA & DEA blend. Adding MEA solvent to MDEA solution provides the advantage of the removal of all quantities of CO_2 and H_2S in the raw natural gas.

The amine circulation rate also has an important effect on the amount of hydrocarbon compounds absorbed by blended amines in the rich amine stream as well as the reboiler duty required for regeneration. Figure 8 and 9 illustrate the effect of amine circulation rates on the reboiler duty (kW) and hydrocarbons mass flow rate (kg/h) in the rich amine stream.

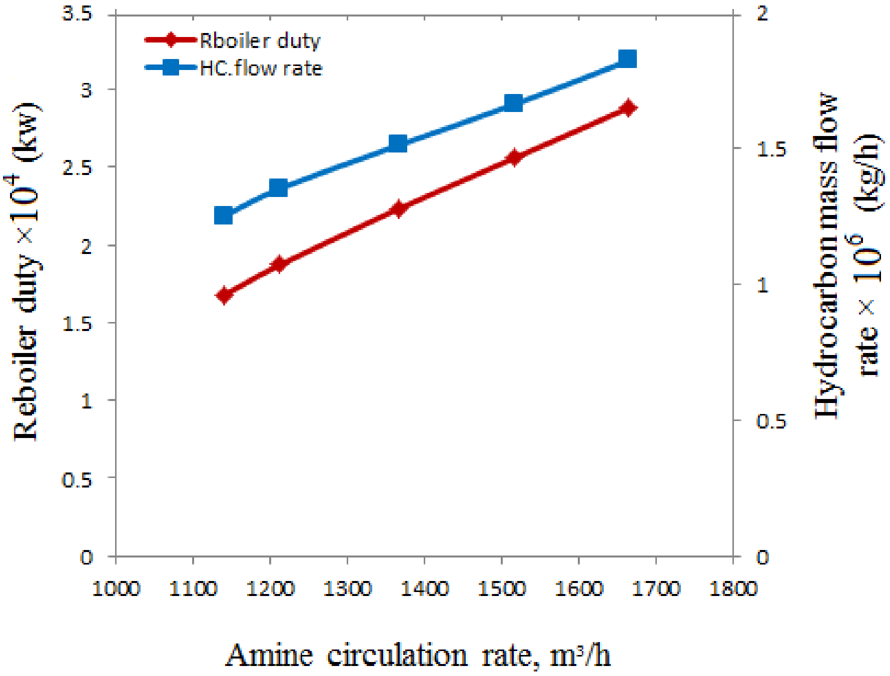

Figure 8. Effect of MDEA & DEA blend circulation rates on hydrocarbons mass flowrate in the rich amine stream and reboiler duty

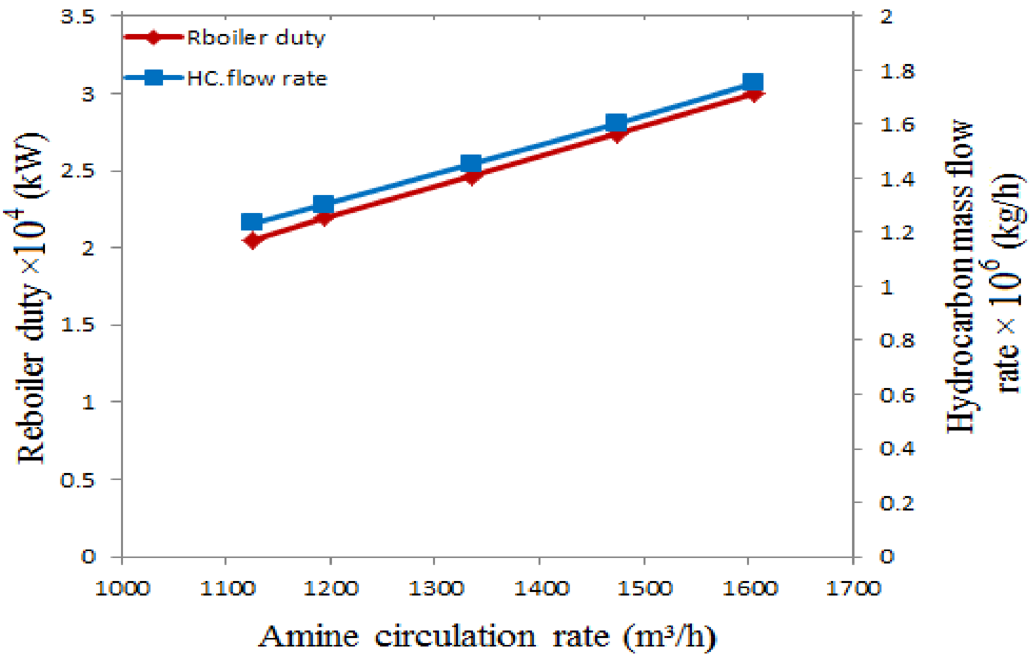

Figure 9. Effect of MDEA&MEA blend circulation rates on hydrocarbons mass flow rate in the rich amine stream and reboiler duty required

Figure 8 and 9 show that hydrocarbon compounds in the rich amine stream and reboiler required duty for regeneration increase gradually with increasing amine circulation rates. Moreover, the reboiler required duty rise due to increased hydrocarbon compounds mass flowrate in the rich amine stream. The hydrocarbon compounds mass flowrate and the reboiler duty required by the MDEA & DEA blend are 1.4×10^6 kg/h and 1.55×10^4 kW respectively at amine circulation rate of 1200 m^3/h, whereas by the MDEA & MEA blend are 1.3×10^6 kg/h and 2.3×10^4 kW respectively at the amine circulation rate of 1200 m^3/h. The hydrocarbon compounds mass flowrate have to be as low as possible in the rich amine stream to avoid foaming in these regeneration column due to presence of methane (CH_4) [12]. In addition, high reboiler duty results in high temperatures in the regeneration column that may cause MDEA thermal degradation. From these two figures, it can be concluded that the reboiler duty required for regeneration the MDEA & MEA blend is higher than that required for the MDEA & DEA blend.

The last part of the discussion includes the effect of lean amine temperatures on losses of amines in the sweet gas stream. The lean amine temperature has an essential effect in controlling the concentration of the acid gases (H_2S and CO_2). The maximum removal of acid gases can be made at the adjusted absorption column temperature by the lean amine temperature. Ordinary, the controlling of the lean amine temperature is carried out by a fan cooler before entering the recycled lean amine into the absorption column.

The effect of lean amine temperature on losses of amines in the sweet gas stream is shown in figure 10.

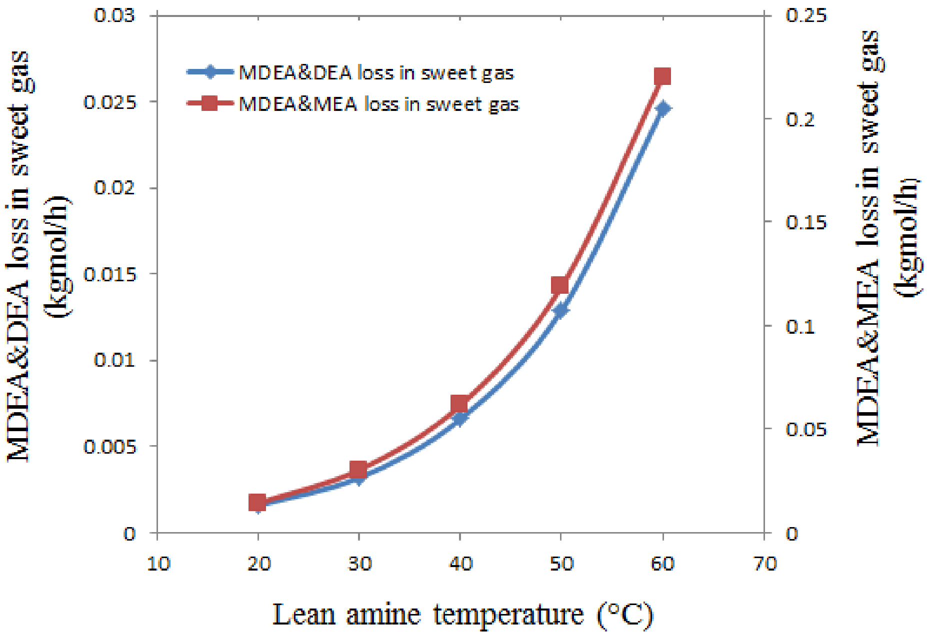

Figure 10. Effect of lean amine temperatures on the losses of amines in the sweet gas stream

Figure 10 shows the effect of lean amine temperatures on the performance of the absorption column to acid gases removal. From this figure, it can be seen that losses of amines clearly rise with increasing the lean amine temperatures. Furthermore, raising the lean amine temperatures bring about increase losses of amines and water in the sweet gas stream. Lower absorption column temperatures raise the absorption of light hydrocarbon compounds in amine rich stream and reboiler required duty. In addition, lost water in the sweet gas stream brings about saturation the sweet gas with water at high temperatures. The lean amine temperatures should be between 35 - 60°C to avoid phase change. Amine temperatures greater than 60°C cause spliting overhead the lean amine and water in the sweet gas stream. On the other hand, amine temperatures lower than 35°C may cause condensation of light hydrocarbon compounds in the rich amine stream, in addition to high reboiler duty requirements for regeneration. At lean amine temperature of 35°C, the losses of amines by the MDEA&DEA blend is 0.004 kgmol/h, and by the MDEA&MEA blend is 0.05 kgmol/h at the amine circulation rate of 1200 m^3/h. Evidently, losses of amines from the MDEA&MEA blend are significantly higher than that lost from the MDEA&DEA blend. Furthermore, amine losses may take place as a result of entrainment, leaks, vaporisation and degradation.

Conclusion & Recommendation:

In summary, this case study was performed for simulation of Mellitah gas plant (Libya) using Aspen HYSYS simulator v.8 and optimized by two blends of amines (a 40% MDEA with 10% DEA blend and a 40% MDEA with 10% MEA blend). Amine fluid package was used to simulate the plant with 50% of MDEA as a solvent. The results of simulation process were virtually equal to the actual data of Mellitah plant with an absolute error less than 1%. The results of the optimisation process illustrated that the two blends of amines can remove the acid gases and meet the sales gas specifications (CO_2< 2% vol. & H_2S< 5 ppm). However, the MDEA&MEA blend had several disadvantages over the MDEA&DEA blend. It required higher reboiler energy for amine regeneration, higher losses of amines in the sweet gas stream and lower amine circulation rate. The MDEA&DEA blend at the amine circulation rate of 1200 m^3/h and the lean amine temperature of 35°C can complete acceptable results for removal of acid gases. The specifications of the sweet gas stream by the MDEA& DEA blend at amine circulation rate of 1200 m^3/h were 0. 492 ppm H_2S and 0.055% CO_2 . The lean amine temperature should be 35°C to avoid any problems might take place due to the phase change in lean amine blends or the raw natural gas. On the other hand, the high circulation rate over 1300 m^3/h may cause rising the process operation cost and amine solution losses. Furthermore, the absorption rate of CO_2 by the 40% MDEA with 10% DEA blend was 2.5 times more than that for CO_2 absorption by the 50% MDEA solution. In contrast, the absorption rate of CO_2 by the 40% MDEA with 10% MEA blend was 5 times higher than that for CO_2 absorption by the 40% MDEA with 10% DEA. The optimization work found that the most recommended blending is the 40% MDEA with 10% DEA blend.

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