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Influence of Using Different Mixtures of Amines on the Performance of Natural Gas Sweetening Process at Iraqi North Gas Company

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Abstract

The study examines the effect of using mixed amines (MDEA) and (DEA) mixtures as a solvent on the process of gas treatment plant at the Northern Iraqi Gas Company. The results show that the mixtures MDEA\DEA (30\20wt%), MDEA\DEA (25/25wt%), and MDEA\DEA (15\35wt%) can remove H_2S concentration in sweet gas at 300 m^3/h to $1.1844x10^{-6}$, $1.7289x10^{-3}$, and 0.0200 ppm respectively. MDEA\DEA (40\10) wt% reduces H_2S to 0.0083 at the same circulation rate. MDEA\DEA (40\10) wt% has the lowest boiler duty at the circulation rate from 200 to1000 m^3/h, also when using this mixture; the energy requirement could be reduced by 15%.

Keywords: *Gas sweetening; Simulation; Amine mixtures; Natural gas.*

1. Introduction

Natural gas usually contains impurities including, H_2S, CO_2 and heavy hydrocarbons. These compounds are classified as the acid gases, natural gas that is H_2S-containing or any compound of sulphur such as CS_2-COS and are referred to as the acid gas, but when containing only CO_2, the acid gas is considered as sweet gas [13]. The specifications of the sales gas have been adopted so as to minimize the environmental impacts and safety of the conveying pipes of the natural gas from corrosion or the presence of water. Concentrations of gaseous gases in treated gas often do not exceed 4 parts per million for H_2S, and 0.2% of CO_2, depending on final consumer requirements [1].

Natural gas has to undergo several major and minor treatment processes before being sold to end users. Sweetening sour natural gas or removal of acidic components, i.e., CO_2 and H_2S from natural gas is the first major step. Acidic components can be removed by using amine solvents (single amine or blend of amines) and also by using solid bed desiccants like iron sponges. Absorption of solid beds allows total removal of H_2S at low concentrations and the following methods are used: iron sponge-molecular sieve, zinc oxide. these processes are appropriate when the gas flow is limited to remove a small amount of sulfur, the concentration of H_2S is low, or both. Chemical solvent methods use a strong base aqueous solution to chemically react with the acid gases and remove them from the natural gas stream. There are chemical processes that use the basic action of various amines. All amines can be classified as primary, secondary or tertiary amines.. The amine is able to react with both CO_2 and H_2S to form compounds that are more liquid-soluble than gas. Unwanted acid compounds are therefore removed from the gas stream [2]. The sweetening process selectivity depicts the preference with which it removes one element of acid gas over the other. There are therefore some possible scenarios for natural gas sweetening: removal of CO_2 from a gas containing no H_2S; H_2S removal from a gas containing no CO_2; simultaneous removal of both acid gases; Selective H_2S removal of the gas containing both acid gases The appropriate method is selected based on the amount of sulfur entering and the concentration of sulfur in the output gas stream. When sulfur extraction is not desired, indirect methods such as liquid-phase processes and dry-bed process methods may be selected if the concentration of sulfur is too low.

the liquid phase processes are used if you want to remove a large amount of H_2S, CO_2 or both. When the line entering contains H_2S or CO_2 and wishes to remove it, chemical solvents such as amines and carbonates should be used. The amine method is highly reactive and low cost in addition to high flexibility in design and operation. In any case, the choice of the appropriate method must be taken into account environmental and economic considerations [3].

Stronger-base mines react more with CO_2 and H_2S gas and form stronger chemical bonds. Therefore, primary amines such as monoethanolamine (MEA) are stronger bases than secondary amines, such as diethanolamine (DEA) which are stronger than tertiary amines methyldiethanolamine (MDEA). These amines are most three amines that have known to be of major industrial importance in gas sweetening process. By combining different amounts of amines to MDEA, mixed amines lead to increased absorption efficiency, removal rate of acid gases and cost savings for solvent regeneration [4].

Using mixed solvents such as MDEA and DEA, led to remove large amounts of H_2S and CO_2. however, is an increasing concept that can increase the concentration of amine solution without increasing corrosion problems. The MDEA solution added to the current DEA solution increased CO_2 absorption rate without significant corrosion increases [5]. MDEA is used primarily as fundamental amine whereas MEA and DEA are secondary amines. Adding MDEA increases rates of amine reaction with CO_2 and energy saving for the heating requirements for regeneration column [6]. In the combined amine blends, the concentration range of MDEA is 40%-55%, while the secondary amine is less than 20% in the molar basis. Because the MDEA solution enables too much absorbed CO_2 to flow across the outlet sweet gas. In fact, blended amines are concentrated in the raw natural gas sweetening, depends on the operating pressure, and the sweet gas concentration [7]. The MDEA with MEA or DEA is indeed beneficial for the required CO_2 removal for low pressure operation. In addition, mixed amines are useful when the concentration of CO_2 in the inlet sour gas increases over time as a consequence of aging in the oil field. However, in greater vapor pressure applications these combined amines have little or no benefits over the MDEA solution [8].

2. Gas sweetening process description

The process of sweeting of natural gas generally consists of two units, the first is the high-pressure gas absorption unit and the low-pressure stripping unit. The acid gas enters at the bottom of the absorption tower, while the amine solution flows from the top. During the absorption process, the acid gases are absorbed by a group of chemical reactions. These units used trays or packing, but high corrosion rates, stainless steel trays are used.

Figure 1 illustrates a typical amine sweeting, initially the natural gas enters to knock out vessel or gas separator to remove the associated water or heavy hydrocarbons dissolved in water.

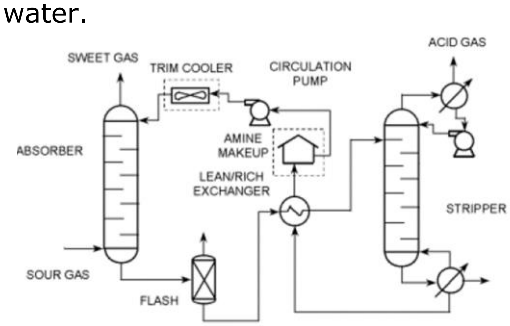

Figure 1. Amine sweetening process

The gas-free water enters at the bottom of absorber, while the amine solution flows down the column. The amine solution, which is rich with absorbed acid gases, is excreted from bottom at high pressure which is reduced later by using a throttle valve to a low pressure before entering the flash tank. The advantage of the flash tank is to get rid of heavy hydrocarbons associated with the rich amine solution.

The liquid stream exiting the flash tank contains acid gases and a low concentration of light hydrocarbons. The rich amine is passed through a heat exchanger that raises the temperature of rich amine by means of a heat exchange with the hot lean amine coming from the stripping column. Then the heated rich amine solution enters the middle of the stripping column, which removes acid gases from the amine by the reboiler. Due to higher heat rate, the amine solution is stripped from all hydrocarbon gases which leaves out from the top of the stripping tower, while the lean amine flows to the bottom of the tower contains very small amounts of CO_2 and H_2S. The lean amine solution entering the heat exchanger is reduced to about 5°C above the dew temperature of the hydrocarbons to prevent dissolving hydrocarbons from carry over. Before returning the amine solution to the absorption tower, it is cooled, and the process is repeated continuously between the two towers [9].

In order to increase the temperature of the reboiler for optimum stripping capacity, stripping columns should be operated at as high a pressure as possible. The degradation temperature should not be exceeded, but the lean amine is restored to its temperature by its rich and lean exchanger. A pump increases the pressure to be greater than the column of the absorber. Finally, before completing the sweetening loop back to the absorber, a heat exchanger can cool the lean solution. The natural gas sweetening unit amine process at north gas company Kirkuk, Iraq includes two main sections: the absorption section and the regeneration section. In absorption section the sour gas is routed to a knock out drum, where any liquids carry-over is removed. The scrubbed gas is fed to the amine absorber, where it is contacted counter currently with a 28.55% weight concentration DEA solution for absorption of acid gasses. The rich amine solution from the rich amine flash drum proceeds to the rich/lean exchangers. The acid gases absorbed in the amine solution are stripped from the rich solution in DEA regenerator by the steam generated in the amine reboiler. The lean DEA is drawn from the bottom of the regenerator and cooled down in the rich/lean exchangers and the lean amine cooler. The cooled lean amine is stored in the DEA surge tank which is sized to hold the total amine inventory. The composition and operating condition of sour natural gas are listed in Table 1 [10].

3. Formulated solvents and mixed amines

The recent method of sweetening involves combined or modified amines. For a specific task, in example selective removal of H_2S from light hydrocarbon in the presence of carbon dioxide, or separate large quantities of carbon dioxide, the formulated amine can be defined as an amine specifically made for a specific performance The mixed amines are produced from a solvent like methyl diethanolamine (MDEA), or a solvent mixture, such as an aqueous solution blend of MDEA and diethanolamine (DEA). Most solvents marketed by major solvent manufacturers depend on manufactured amines, and the main reason for using them is to reduce equipment size and reduce corrosion rates or reduce the solvent flow rate. In addition, the specifications of the local gas must be in accordance with the standards of sale and transportation, and the concentration of H_2S gas must be less than 4 ppm [11].

The use of amine mixtures is the most important development in formulated solvents. They are generally based on MDEA, but they contain additional amines and inhibitors of corrosion, foam depressants. These mixtures can be developed to selectively remove H_2S, partially or completely also carbon dioxide removal at high acid gas loading, remove COS and other unique properties. Several steps must be taken to screen the solvent mixtures accessible for optimum setup. Based on a case study strategy, every solvent test unit should check whether or not a solvent can comply with the design requirements [12-13].

4. Simulation of treating process

The natural gas sweetening plant at Iraqi north gas company is simulated with the use of acid gas package using Aspen software. Figure 2 illustrates the overall process flow diagram of the plant. The following parameters have not been modified or changed for all simulation cases. This includes the inlet gas flow rate, gas residence time in the absorber, the circulated amine flow rate, absorber and stripper pressure, and number of stages. In this study, the most appropriate concentrations of single amine were selected are 28.5wt percent, 30wt percent and 35wt%. The composition and operating condition of sour natural gas are listed in Table 1.The examined amine mixtures in this case study are:

- 25 wt% MDEA +25 wt% DEA; 30 wt% MDEA +20 wt% DEA
- 15 wt% MDEA +35 wt% DEA; 40 wt% MDEA +10 wt% DEA

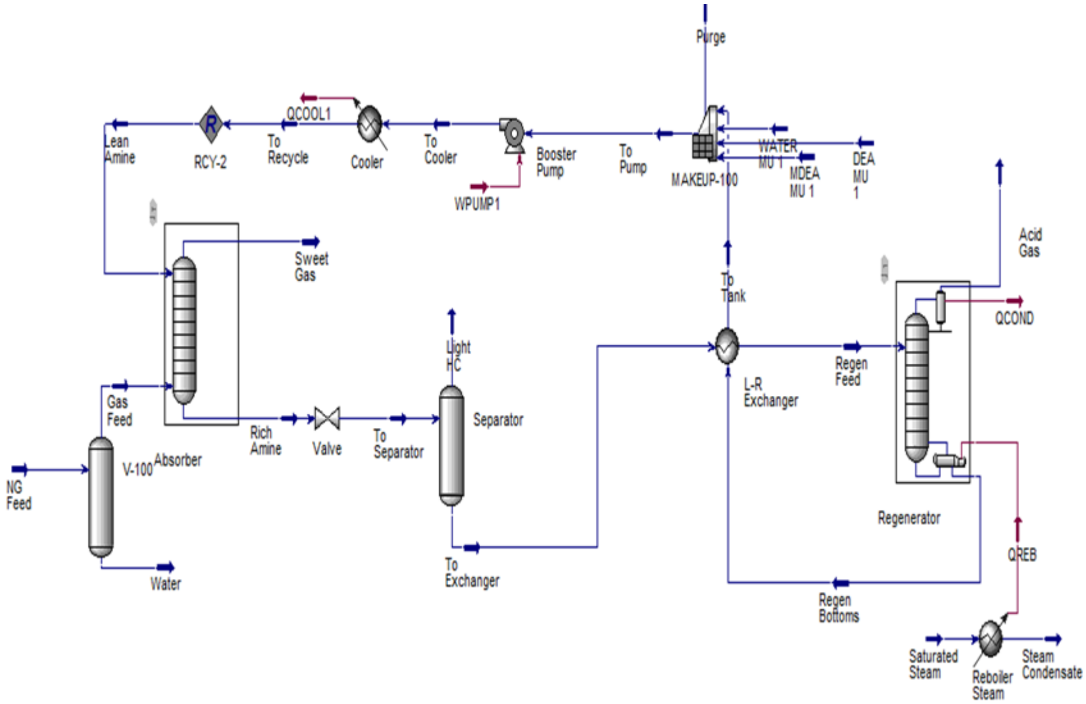

Figure 2. Flowsheet for the amine sweetening process

5. Results and discussions

A correct choice and monitoring of the operating conditions is an important factor for the good performance of gas sweetening plant. These conditions were analyzed using the simulation software and for each case the effects of these factors were reported below are variables that affect gas sweetening systems:

5.1. Temperature profile

Figure 3 shows the temperature profile across the absorption column when using different amine mixtures, it can be noticed that a temperature profile is almost similar to the pattern of temperature distribution. It is clear that when the lean liquid amine enters the tower bottom and absorbs the acid gases, the temperature begins to rise gradually. Because the absorption reactions are mostly exothermic reactions, the temperatures continue to rise until it reaches a maximum temperature at the bottom of the tower, then the temperature starts to drop near the feed plate when the hot amine contacts with the cold acid gas.

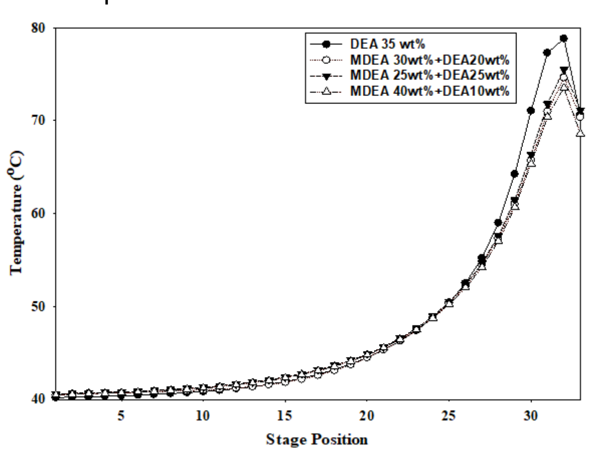

Fig. 3. Absorber temperature profile for different amines at 800 m^3/h circulation rate

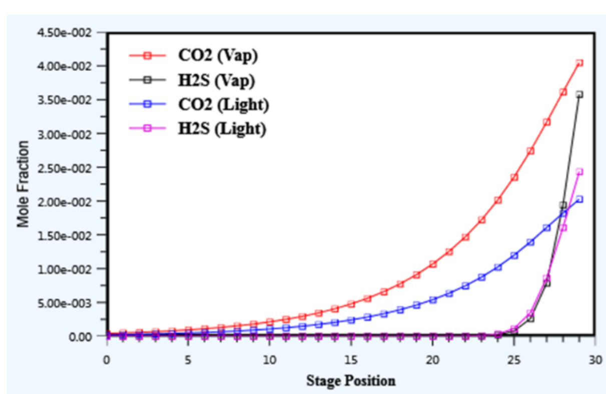

Fig.4. H_2S and CO_2 Composition vs. stage number when using MDEA

5.2. CO_2 and H_2S composition profiles

The composition of the two acid components, H_2S and CO_2, is shown in Figure 4 as a function of the number of stages when using DEA as solvent. At the top where the liquid lean amine is entered, the concentration of the two components is low in both phases. In the bottom where the gas enters, the concentration of the components is high due to the high concentration in natural gas, which allows the liquid to absorb more of the acid components also the reaction rate will be high at this section. On the other hand, raising the concentration for both H_2S and CO_2 is almost completely absorbed in the lower part of the column.

Figures 5 and 6 represent the simulation outputs for H_2S expressed as pmm and CO_2 mole fractions in the inlet gas stream vs the amine flow rate. All other parameters have been set constant and the amine flow rate only tried to changed. The concentration of H_2S and carbon dioxide decreases progressively as the amine circulation rate increases for all types of amine blends, and after 0,00025 mole fraction for CO_2, purification is no more occurring. Any increase in amine flow rate therefore increases the acid gas concentration. The fact that the increased amine flow rate allows more lean amine to remove the absorbed gasses from the rich amine solution, as the reboiler requirement is fixed in the simulation, and therefore the stripper does not conduct its normal conditions. The concentration of lean amine therefore exceeds the design value, and thus the driving force for mass transfer decreases in absorber column.

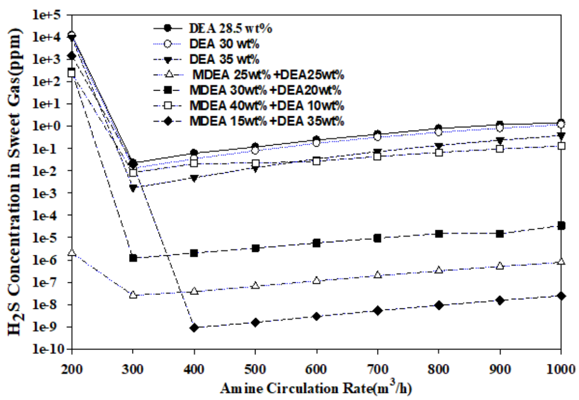

Fig. 5. The relationship between amine circulation rate (m^3/h) and H_2S composition in sweet gas stream for various amines

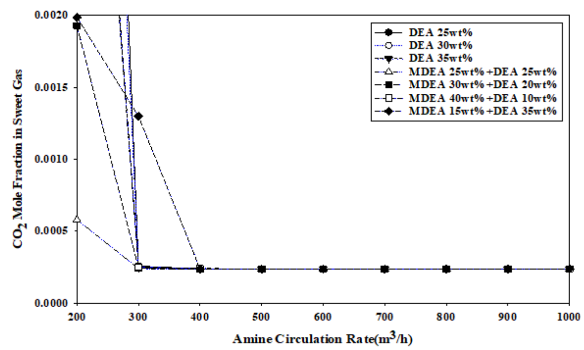

Fig. 6. The relationship between amine circulation rate (m^3/h) and CO_2 composition in sweet gas stream for various amines

All types of amines give acceptable concentration of H_2S for amine circulation rate above 300 m^3/h, below that flow rate the concentration is very high except when using MDEA 25wt%+ DEA25wt% which give 1^{-6} ppm. However, the using of MDEA and its mixtures may achieve more acceptable results at a low amine circulation rate. For MDEA, as illustrated in Figure 5, this amine has one of the best performance in the H_2S absorption among the different tested amines. In particular, the best results for purification of sour gas with significant CO_2 content and the absorption of both H_2S and CO_2 from natural gas with a lower circulation rate leading to a lower operating cost are the mixed amines (MDEA 25wt % + DEA25wt %, MDEA 15wt%+ DEA35Wt percent) and MDEA 30wt % + DeA20wt %.In figure 6 the CO_2 mole fraction is decreasing rapidly, and then when the circulation rate reaches 300 m^3/h and above, the CO_2 content reduced to the same level for all amines (0.00025 mole fraction) even when the flow is relatively high. It seems that MDEA mixtures is efficient for reducing the content of H_2S in the gas stream, but not at the higher circulation rate for removing CO_2.

5.3. Rich solution acid gas loading

The total quantity of acid gas absorbed by the amine solution (concentration of acid gas in the rich solution, leaving the absorber) per mole of pure amine. The normal loading range for sweeting processes as indicated by [14] is 0.40-0.73, which indicates that process efficiency can probably be enhanced, for example by reducing the amine flow rate making the most of its absorption capacity. Above this loading range, corrosion can occur.

The effect of the rates of amine circulation on rich amine loading is shown in Figure 7. DEA has the higher values for constant specified amine rate, and MDEA mixtures have the minimum loading values. Increasing the rich solution loading would allow less solvent to circulate, reducing the solubility of hydrocarbon in the rich amine solution, leaving the absorber bottom diminishing. Therefore, it is desirable to use as high a rich solution loading. Higher acid gas loading in the rich solution is limited by several factors such as, higher rates of corrosion. it can be seen that mixed amines have amine loading around 0.55 for amine flow rate 200 m^3/h and about 0.38 for 300 m^3/h, which is acceptable loading range for sweeting process since they have lower corrosion rate.

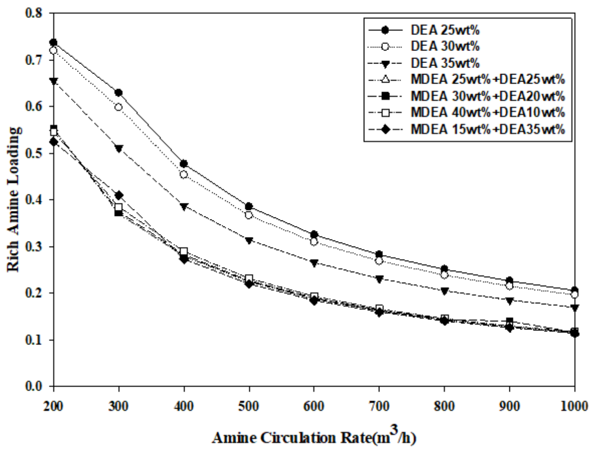

Fig. 7. Rich amine loading for different amine mixtures at different amine flow rates

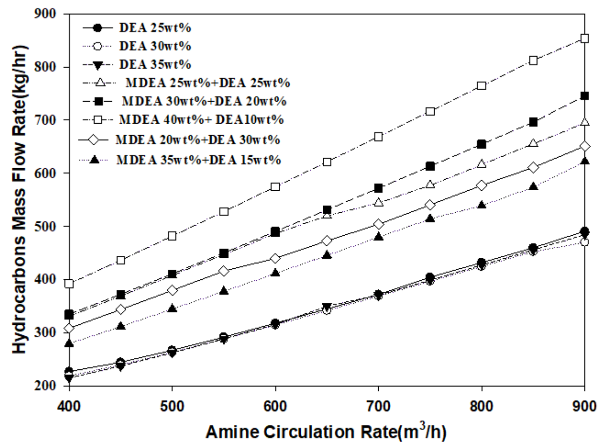

Fig.8. Effect of MDEA & DEA mixtures circulation rates on hydrocarbons mass flowrate in the rich amine stream

5.4. The hydrocarbons mass flow rate

The amine flow rate also has a significant impact on hydrocarbon compounds dissolved in the rich amine stream. The relation between the rate of amine circulation and the mass flow rate for hydrocarbon (kg/hr) in a rich amine stream is shown in Figure 8. With increasing amine circulation rate, the hydrocarbon mass flow rates are progressively rising. The DEA solutions (25, 30, 35wt%) have low hydrocarbon mass flow rates in the whole range of circulation rate.

The hydrocarbon compounds mass flow rate in the rich amine stream must be as low as possible to prevent foaming on regeneration columns due to the presence of methane (CH_4). From the figure, it can be concluded that the amine mixtures MDEA35wt%+DEA15wt% and MDEA20wt%+DEA30wt% gives acceptable results while the MDEA40wt%+DEA10 wt% gives the highest hydrocarbons flow rate.

5.5. Reboiler duty

Reboiler heat duty must be minimized to reduce the capital cost of the regenerator column. The regenerated solution from the reboiler at temperatures generally between 110°C and 120°C. The effect of circulation rate upon the reboiler duty for different amine mixtures is shown in Figure 9.

The reboiler duty required for amine mixtures at 400 m/h are 3.05×10^4, 3.01×10^4, and 3.91×10^4kW for MDEA25wt% + DEA25wt%, MDEA30wt%+DEA20wt%, and MDEA 40wt% + DEA10wt% respectively. From the Figure 9, the reboiler duty for regenerating column is slightly close to the duty needed when using amine mixtures 25, 30, and 35wt% DEA. The amine mixture MDEA40wt%+DEA10wt% has the lowest value of duty.

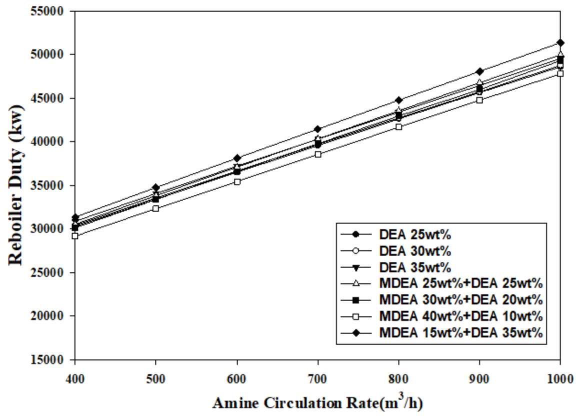

Fig.9. Effect of MDEA & DEA mixtures circulation rates on reboiler duty

6. Conclusions

The gas sweetening unit at the Northern Gas company has been simulated by Aspen HYSYS simulator V.9, comparing the results of different amine mixtures. Acid Gas Solvent Fluid Package was used to simulate the process with a 200 to1000 m^3/hr circulation rate. Based on this study, the results shows that the amine mixtures MDEA\DEA (30\20wt%), MDEA\DEA (25/25wt%), and MDEA\DEA (15\35wt%) can remove H_2S concentration in sweet gas at 300 m^3/h to $1.1844x10^{-6}$, $1.7289x10^{-3}$, and 0.0200 ppm respectively. The amine mixtures MDEA\DEA (40\10) wt% reduce H_2S to 0.0083 at the same circulation rate. At circulation rate 400 m^3/h these mixtures will reduce H_2S below $1x10^{-6}$ pmm, and meet the sales gas specifications (H_2S< 4 ppm). The concentration of CO_2 in sweet gas for DEA and MDEA\DEA mixtures for amine circulation rate above 400 m^3/h, has a mole fraction from 0.000236 to 0.000241.

However, the MDEA\DEA mixtures had several drawbacks over the DEA. Higher reboiler energy is required for amine regeneration, higher amine losses in the sweet gas stream and lower amine circulation rate. Only MDEA\DEA (40\10) wt% mixtures has the lowest boiler duty blend at the amine circulation rate from 200 to1000 m^3/h, also when using this amine mixture, the energy requirement could be reduced by 15% if it compared with the duty for DEA. DEA (25, 30, 35) wt% has the maximum rich amine loading and MDEA\DEA mixtures Has the minimum loading value of rich amine. The results of the simulation illustrated that mixed amines have amine loading around 0.55 for amine flow rate 200 m^3/h and about 0.38 for 300 m^3/h, which is acceptable loading range for sweeting process as they have lower rates of corrosion.

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