The Simulation of Removal Hydrogen Sulfide from Liquefied Petroleum Gas by Software ASPEN HYSYS V8.8

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Abstract:
The main aim of this study is to investigate the effect of the use of piperazine as an additive on the MDEA solutions which is already used to sweeten LPG from H2S & CO2. ASPEN HYSYS is used to simulate this case study. In this article many design criteria (MDEA concentration, piperazine concentration, amine solution flow rate etc) are studied. The composition and operating conditions of pressure and temperature of LPG to be treated is taken from literature (Hanan JQ et al) & slightly modified, in such situation the composition of our LPG Feed can be considered as theoretical, the flow and the other operating parameters of AGRU (Acid Gas Removal Unit) are also optimized.

1. Introduction

The Liquefied Petroleum Gas (LPG) plays an essential role in current human's life; LPG is used to minimize air pollution in comparison with classical fuel. The big demand of LPG makes its production increasing and the need to more efficient and economic treatment is also increasing. The common LPG's contaminants are CO_2, H_2S, mercaptans, COS, CS_2 and elemental sulfur. Since its vapor density is bigger than 1 [1-3], hydrogen sulfide gas tends to settle in low places and creates a toxicity hazard. The hydrogen sulfide cannot be released directly from regeneration tower to atmosphere.

To recuperate the elemental sulfur, firstly the LPG needs to be treated to liberate the hydrogen sulfide. This is usually achieved by dissolving the hydrogen sulfide in an aqueous amine solution. After regeneration of rich amine solution the hydrogen sulfide is released in the head of the regenerator. The atmospheric pollution caused by the released hydrogen sulfide could be mitigated by sending the released hydrogen

sulfide to flare or incinerator to be converted to less harmful/toxic gas after oxidation in form of SO_2. Even the directives control environment is less severe for SO_2 in comparison to H_2S, but both are harmful for the environment; the allowable amounts of pollutants to be released are also limited by environmental regulation [4, 5]. If contaminants' concentration is important, direct conversion of acid gas seems to be the most appropriate solution to eliminate hydrogen sulfide and produce the elemental sulfur.

In the earliest years, the industry of petrochemical process enhanced the removal of H_2S from LPG by using the solid catalysts such adsorbents; the sodalite zeolites being a successful adsorbent for removal of hydrogen sulfide, they have good sulfur loading capacity, good regenerability and stable structure. These are natural zeolites having high adsorption capacity compared to other zeolites and synthetic zeolites. These zeolites can be modified by metals or metal oxides in order to increase their adsorption capacity [6, 7]. Despite the fact that this technique is environmentally friendly, but from an economic point of view, this process is expensive, compared to the processes of amine solutions.

Formulated solvents composed of alkanolamines and physical solvents (such as *N*-formyl morpholine, *N*-methyl pyrrolidone, sulfolane and dimethyl sulfoxide) allow simultaneous removal of H_2S and mercaptans [8, 9, 10], whereas some of them have the disadvantage of higher solubility of hydrocarbons. Instead of monoethanolamine (MEA) or diethanolamine (DEA), currently methyldiethanolamine (MDEA) appears to be the most used solvent for hydrocarbon sweetening. Generally, MDEA is chosen for its appropriate qualities, such as its great resistant to chemical and thermal degradation, it's basically noncorrosive properties and its low specific heat and reaction heat with H_2S and CO_2 [11].

In such case, an activator as piperazine ($C_4H_{10}N_2$) will be used to enhance the efficiency of the global system to eliminate maximum hydrogen sulfide with minimum energy consumption. In this article, the effect of piperazine adding in small concentration will be studied for LPG treatment.

For small concentration of acid gas, caustic wash is widely used as treatment method. If high amount of contaminants are present, treatment with amine seems to be the most cost effective process. In this work an ordinary scheme for acid gas removal unit will be used when the extraction is done in liquid-liquid extractor, and then the regeneration of rich amine will be done in the regeneration column.

2. Materials and Methods

2.1. Amine Type

As illustrated in the table 1, The MDEA is considered as the most advantageous amine for hydrocarbon sweetening, because of its lower vapor pressure, lesser corrosive, its wide range of operating conditions, its lower reaction heat and its selectivity toward H2S when CO2.

2.2. Piperazine Use

In the last decades many formulations and blends of amine are provided to improve the capacity and the efficiency of sweetening operation within an activator. One of the most activator widely used is the piperazine.

The effect of varying piperazine concentrations (from 0 to 5 wt %) will be studied within three fixed MDEA concentrations: 20, 35, 45 wt %.

2.3. Amine Solution Concentration

Based on the equilibrium, a minimum flow rate will be calculated after choosing the appropriate concentration of MDEA within recommended interval of concentration. In our simulation, the combination of 35% weight of MDEA & 5% wt Pr was chosen [3,11,12], shown Table 1.

2.4. Operating Treatment Conditions

For maintaining the LPG at liquid state; its treatment will be done within an optimum interval of temperature and pressure conditions. The optimum operating temperature should be less than bubble point at the operating pressure (less than 80 ℃) and at the same time, it should be higher than certain value to minimize the amine and hydrocarbon entrainment. Generally, for keeping up the viscosity less than 2 centipoises at operating pressure of 40 bar, the temperature should be more than 37.5 ℃ [13]. While the LPG will penetrate the column at 40.21 bars and 45 ℃, the lean Amine will be feed the column at the same pressure but an additional of 12.5 ℃ temperature than that of LPG is recommended for good separation.

2.5. Process Simulation

The software ASPEN **HYSYS** V8.8 is used with new equation of state (EOS) to simulate the acid gas removal unit. Amine property package is replaced by Acid gas Property package. both of property packages cannot be used in our case study , The acid gas property package is limited to gas treating by using an ordinary absorber column as unit operation; whereas treating LPG by liquid-liquid extraction cannot be done by using this equation of state (EOS) which is our case.

At the same time, Amine package doesn't support the piperazine component which is also the case for our study. For these two reasons, the basis of our simulation will be based on DBR Amine package as equation of state (EOS), with this property package we can use liquid-liquid extractor and we can use normally piperazine component which can be supported by this property package.

Table 1. *Typical Operating Conditions and Data for Amines [12].*

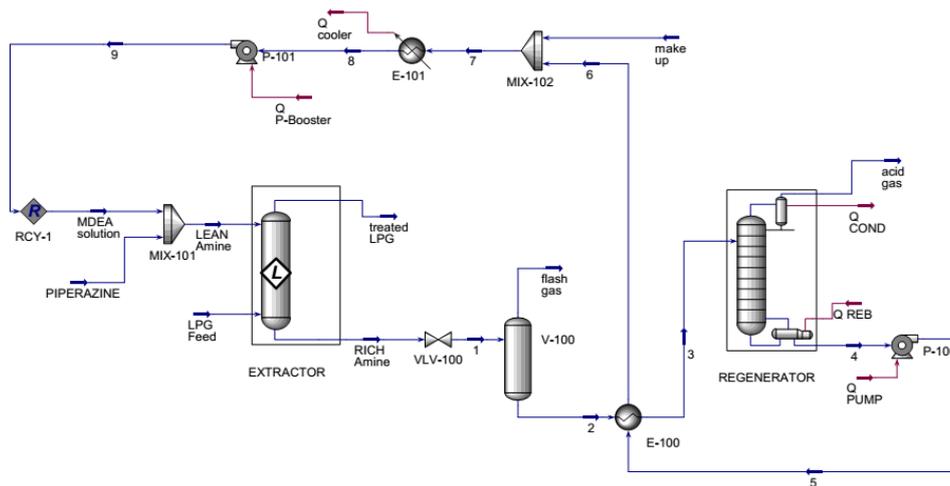| Amine	MEA	DEA	DGA	MDEA
Solution strength, wt.%	15-20	25-35	50-70	20-50
		0.3-0.35	0.3-0.35	unlimited
Acid gas loading, mole/mole (carbon steel)	0.3-035	under limited limited conditions	No	under limited conditions
Ability to selectively absorb H2S	No			

Figure 1. *Process flow sheet of AGRU for LPG.*

2.6. Design Basis - Feed Composition

The solvent is supposed to be delivered as a concentrated solution comprising MDEA and the activator. The activator in our case is piperazine.

In our study, an extractor with 10 stages, 100 % MURPHEE efficiency is considered. The flow of LPG to be treated is 13000 Kg/h at 45 °C and 40.21 bars; this stream will feed the lower side of the liquid-liquid extractor, the upper side will be fed with 4500 kg/h of lean amine solution (35 wt % of MDEA and 5 wt % of piperazine) at 50 °C and 40.21 bars. The temperature of lean amine solution should be well controlled to avoid LPG evaporation.

The rich amine loading (mole of H_2S/ mole of MDEA) considered in our case study is about 0.04511.

It has been taken such small rich amine loading parameter just for being able to vary the study's parameters to be capable to do case studies in large interval of each varying parameters (LPG Mass Flow, LPG Temperature, Lean Amine Mass Flow, Lean Amine Temperature etc).

In case of choosing a higher rich amine loading, for example 0.20 mole of acid gas/mole of MDEA the circulation rate will be about 1600kg/h. This flow of lean amine /piperazine solution can treat no more than the specified flow rate of LPG which is 13000 kg/h. So, in the case study of variation of LPG mass flow, we will face a problem that this amount of amine is limited to a maximum of 13000 kg/h for LPG. The same problem will emerge for the other parameters. The rich amine leaves the extractor to feed flash drum to eliminate some dissolved hydrocarbon and H_2S after leaving the expansion valve.

After the flash drum, the rich amine solution will be heated to attain 90 °C via shell & tube heat exchanger. The last is used to get the heat of hot lean amine leaving the bottom of regenerator. The rich amine solution is then feed the regenerator to be stripped to remove the hydrogen sulfide gas. (Figure 1)

H_2S removal efficiency and regenerator Reboiler duty were investigated by varying process parameters, namely MDEA concentration, piperazine addition, on account of water when MDEA is always fixed 35 wt %, weight % piperazine, lean amine solution and LPG feed temperature, amine circulation rate and the temperature of rich amine which feed the regenerator. The study will be based on some criteria, which

should be maintained for all case studies and only one parameter will be changed when the others are fixed as it is given in the heat and material balance table. See Table 2.

Table 2. Heat and material balance table for the AGRU.

Parameter	Unit	LEAN Amine	RICH Amine	treated LPG	LPG Feed
Temperature	℃	50	46	48	45
Pressure	kPa	4021	4000	3900	4021
Molar Flow	kgmole/h	166	166	259	259
Liquid Volume Flow	m³/h	5	5	24	24

3. Results and Discussions

3.1. The Effect of MDEA Concentration

In our study, the same approach has been followed for all cases studies, changing the MDEA content, while the other parameters are keeping up fixed. The increase of MDEA concentration will enhance the elimination of hydrogen sulfide, which means the increasing of hydrogen sulfide content in the sweet LPG. In the same time of increasing the MDEA's concentration, the duty needed to regenerate this more concentrate rich amine is also increasing (from 859 kw to 2251 kw). However with this case study, it is clear that after eliminate the big part of hydrogen sulfide, the effect of raising the MDEA's concentration is insignificant. Passing from 20 wt % to 45 wt % of MDEA will improve the elimination of hydrogen sulfide from LPG by 1.45 ppm (passing from 5.28 ppm to 3.84 ppm).
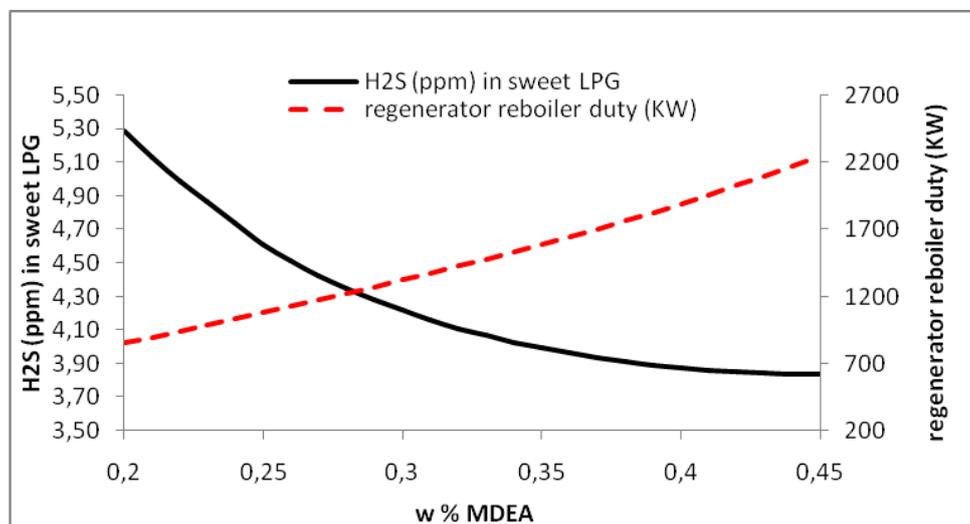

Figure 2. The effect of MDEA concentration.

3.2. The Effect of Piperazine Concentration

With this case study 20, 35, & 45 wt % aqueous MDEA solutions are used as basic cases, while the other process parameter are conserved constant, only the concentration of piperazine is changed from 0 to 5 wt %.

3.2.1. The Effect of Piperazine Concentration with 20 wt % MDEA

Within this case study, the MDEA concentration is fixed to 20 wt %, when the piperazine's concentration is varied from 0 to 5 wt %. Figure 3 shows that the increase in piperazine concentration enhances the hydrogen sulfide (H_2S) recovery, so the concentration of H_2S in treated LPG will decrease from 7.5 ppm to 2.1 ppm. In the same time the duty of regenerator reboiler is increasing from 250 kw to 1925 kw.

Passing from 0 wt % to 5 wt % of piperazine will improve considerably the elimination of hydrogen sulfide from LPG (more than 5 ppm) in comparison of effect of MDEA solution.
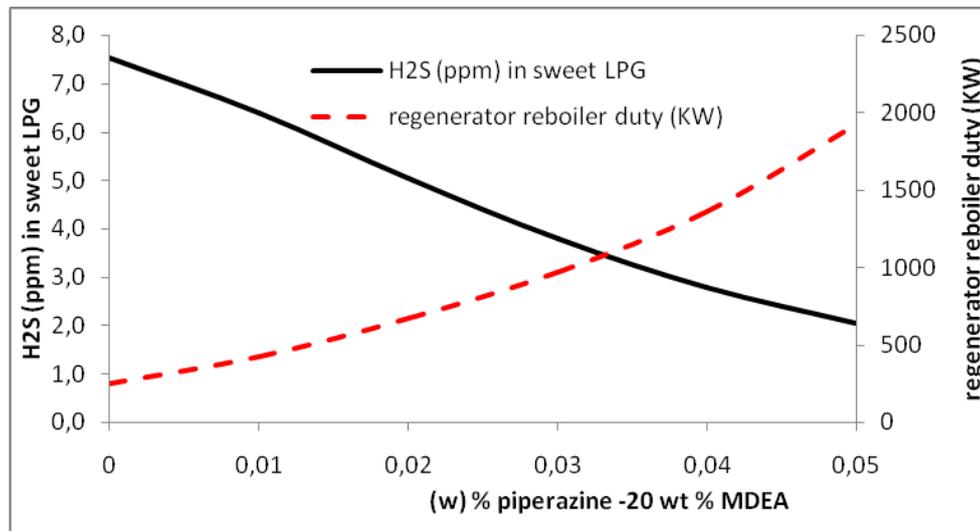
Figure 3. The effect of piperazine concentration-20 wt % MDEA.

3.2.2. The Effect of Piperazine Concentration with 35 wt % MDEA

As the precedent case study the effect of piperazine's concentration is studied within fixed MDEA concentration, in this case 35 wt % MDEA is considered. As well as seen in the previous case study the same behavior is remarked when increasing the piperazine's concentration. Figure 4 illustrates that the rise in piperazine concentration enhances the hydrogen sulfide (H_2S) recovery so the concentration of H_2S in treated LPG will decrease from 4.36 to 2.25 ppm. the duty consumed in regenerator's reboiler increases considerably when it passes from 382 kw to 1380 kw with the increasing of piperazine concentration from 0 to 5 wt %. Passing from 0 wt % to 5 wt % of piperazine will improve considerably the elimination of hydrogen sulfide from LPG (2.11 ppm) in comparison of effect of MDEA. In this case it has been seen that the efficiency (elimination of H_2S and energy consumption) of global system has improved in comparison with the case of 20 wt % MDEA.
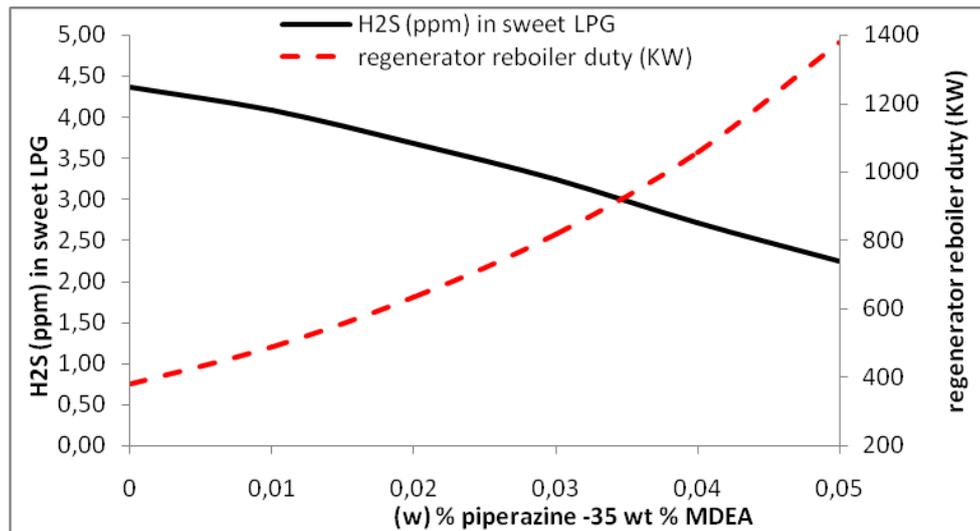
Figure 4. The effect of piperazine concentration-35 wt % MDEA.

3.2.3. The Effect of Piperazine Concentration with 45 wt % MDEA

Varying piperazine concentration when the MDEA concentration is fixed at 45 wt %, in this case also the use of piperazine pushes the global capacity of the amine solution to eliminate more hydrogen sulfide from LPG (from 3.45 ppm to 2.12 ppm), then within this case study the need for energy is less than the other two previous cases when MDEA weight concentrations are 20 and 35 wt % but with more consumption of MDEA (high concentration of MDEA solution). Figure5.
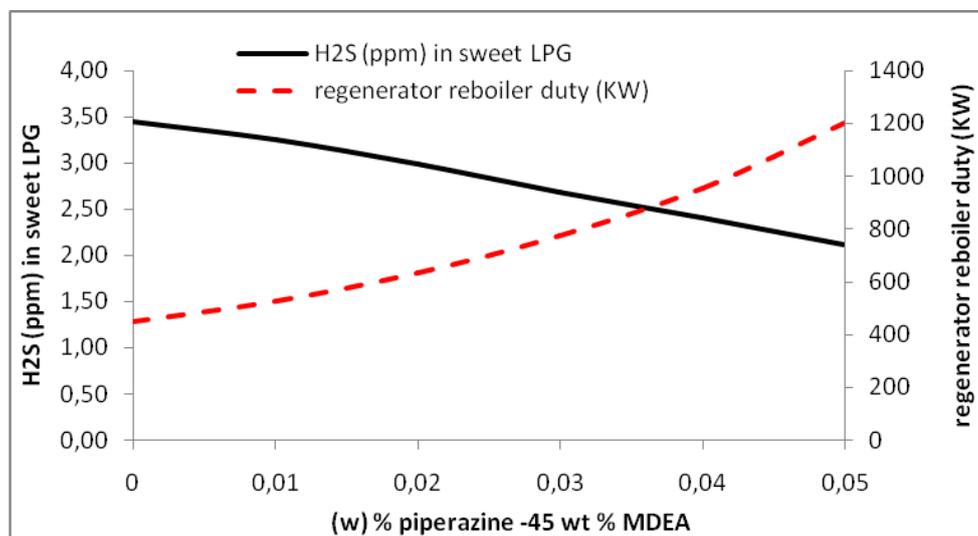

Figure 5. The effect of piperazine concentration 45 wt % MDEA.

3.3. The Effect of LPG Feed Mass Flow

The impact of increasing the mass flow of row LPG, more or less constant when looking to important increasing of row LPG mass flow (figure 6), this is due surely of extra-capacity design of the unit, The rich amine loading mole of acid gas/mole of MDEA considered in this design is very weak for the normal operating LPG mass flow (0.045), thus lead the sweetening unit is able to remove more acid gas from LPG.
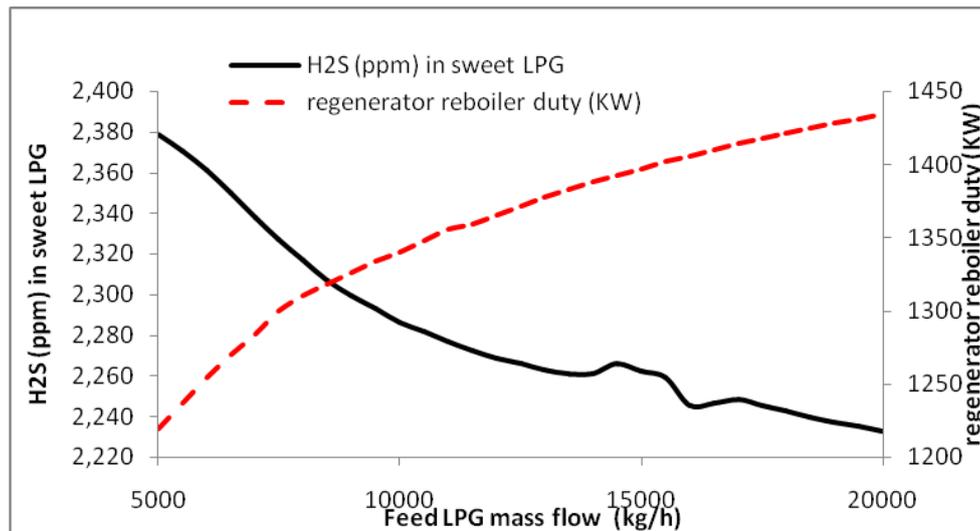
Figure 6. The effect of LPG Feed mass flow.

3.4. The Effect of LPG Feed Temperature

Within this case study, it has been remarked that the increase of LPG temperature increase the capacity of amine/piperazine solution to eliminate the acid gas, the H_2S content in sweet LPG drop from 3.26 ppm to 2.2 ppm, while increasing LPG temperature from 30°C to 42°C, it is shown in figure 7, that behavior changes drastically when LPG temperature is more than 42 °C, we can conclude that the heat enhances the release of H_2S from no treated LPG, however the duty in this case study has been decreased (from 1386 kw to 1376 kw).
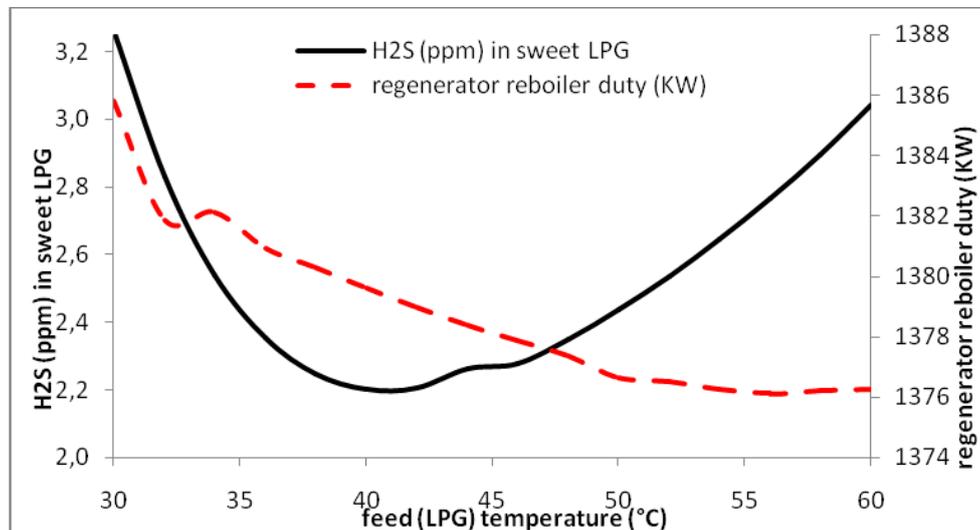

Figure 7. The effect of LPG feed temperature.

3.5. The Effect of Circulation Rate of Piperazine / MDEA Solution

In this case study the circulation rate of piperazine/MDEA solution is studied, the effect of rising of piperazine/MDEA solution circulation rate has a negative impact on the efficiency of the hydrogen sulfide elimination, so this increasing the circulation rate decreases the capacity to remove the acid gas from the LPG; the explanation of such situation is that the residence time is decreasing. Arise from 1.85 ppm to 1.90 ppm (figure 8), in our case study it is clear that the increase of circulation rate of the

MDEA/piperazine solution increases the demand on duty for the regenerator's reboiler passing from 1234 kw to 1513 kw.
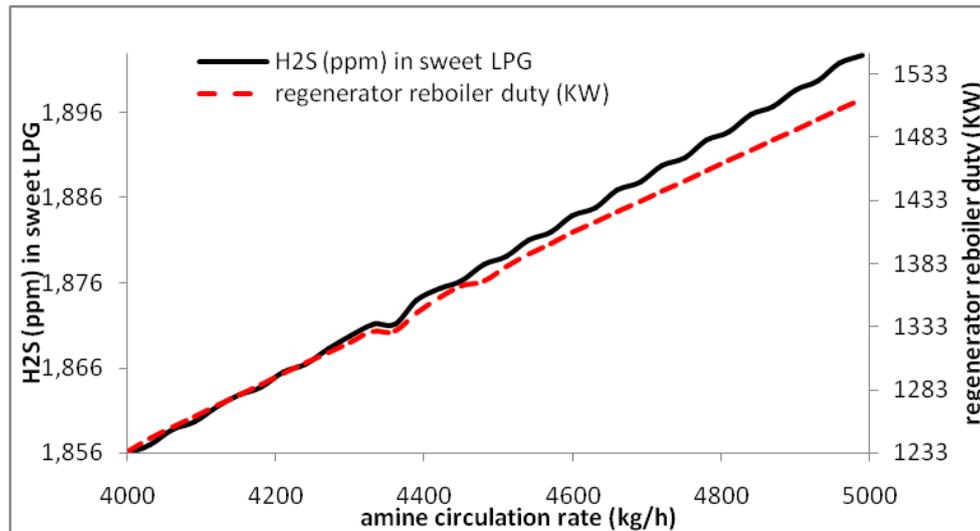

Figure 8. The effect of circulation rate of MDEA.

3.6. The Effect of Lean Piperazine/MDEA Solution Temperature

As the other parameters, temperature of lean amine is changed in order to discover its impact on the extraction of H_2S, in this case study, it has been noticed that the increase of temperature of lean amine/piperazine solution lead to increasing of the H_2S concentration on the treated LPG, this is due to the exothermic reaction of absorption, the H_2S content in sweet LPG raise from 2.1 ppm to 2.89 ppm. The last is of course favorable in low temperature. In the same time the increasing of lean amine/piperazine solution temperature affect very slightly the need on the reboiler duty of the regenerator. (Passed from 1344.30 kw to 1343.48 kw). See figure 9.
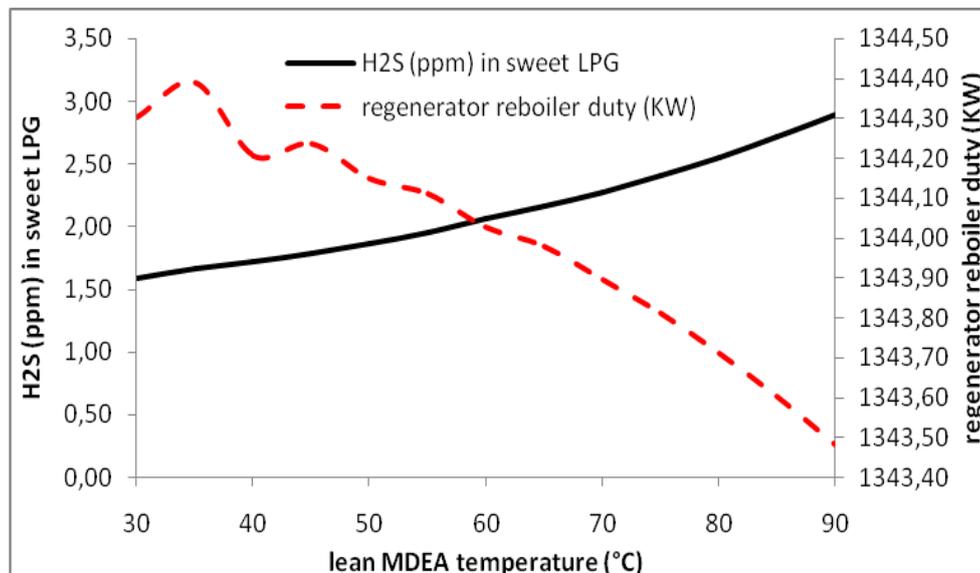

Figure 9. The effect of lean amine temperature.

3.7. The Effect of Rich Piperazine/MDEA Solution Temperature

In the figure 10, it seen that the increase of rich amine/piperazine solution temperature is an enhancing parameter of energy consumption (reduced from 1376 kw

to 1253 kw), while isn't for the content of rich amine/piperazine solution on hydrogen sulfide, so with this an optimum between saving energy and rich amine piperazine solution loading should be well specified and in our study case, the optimum is to operate between 90 ℃ and 95 ℃.
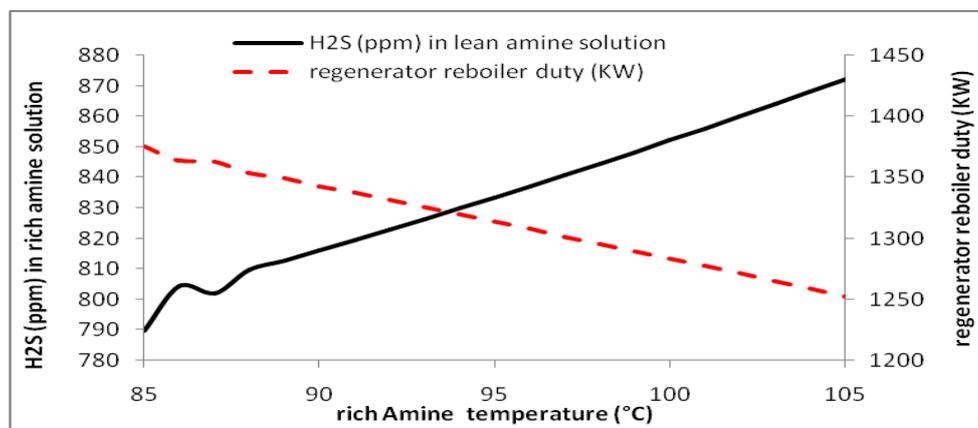

Figure 10. *The effect of rich amine temperature.*

4. Conclusions

After doing many case studies within the use the mixture of piperazine and MDEA, it has seen that the use of piperazine has enhanced considerably the capacity of the process to eliminate more hydrogen sulfide. The operating conditions and parameters affecting system performance of sulfur recovery from LPG were studied in this article.

The increase of MDEA concentrations from 20 to 45% leads to more removal of hydrogen sulfide , but in this same case the regeneration energy of rich amine solution increase by 2.5 times.

To improve the recovery of hydrogen sulfide from LPG, the piperazine was added to solution of MDEA by varying the concentration of MDEA from 20 to 45% and that of piperazine from 0 to 5%.

The best results were obtained for the following concentrations (45% of MDEA and 5% of piperazine), the maximum rate of H_2S removal from LPG was obtained with a lower consumption of regenerative energy of rich MDEA.

The effect of the temperature on the MDEA / piperazine couple absorption capacity of H_2S has been studied. We found that increasing the LPG temperature from 30 to 42 °C, leads to decreasing H_2S content in sweet LPG (from 3.26 ppm to 2.2 ppm). The temperature boost up the release of H_2S from LPG.

The effect of increasing the temperature of lean MDEA/ piperazine was controversy compared to the above case, then the rise of MDEA lean temperature conduct to reducing of the removal rate of H_2S from LPG. This is due in fact to exothermic character of this absorption reaction.

Finally, we conclude that even with weak addition of piperazine of 5 wt %, the global efficiency of the system is highly improved. The use of piperazine as an activator even within small amounts pushes highly the elimination of acid gas from the hydrocarbons to twice (getting 2.12 instead of 3.84 ppm). In the other hands it has been remarked that the addition of piperazine decrease also considerably the energy consumption in the reboiler of the regenerator to the half (consuming 1200 kw instead of 2251kw. For the same amounts of piperazine and MDEA, the piperazine is 8 times

more efficient then the MDEA in solution. However, the addition of piperazine has a positive impact on the behavior of process versus the energy consumption. There is an optimum to be respected between the limit of hydrogen sulfide in the LPG and the process energy consumption.

Conflicts of Interest

The authors declare that, we have no conflict of interest regarding the publication of our article entitled: *The Simulation of Leaked Hydrogen Sulfide from Petroleum Gas by ASPEN HYSYS Software V8.8* published in the International Technology and sciences ITS Journal.

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