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Comparison study of activators performance for MDEA solution of acid gases capturing from natural gas: Simulation-based on a real plant

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Abstract

Energy requirements and environmental regulations are the main limiting issues behind the continuous developments of amine absorption processes. Steady state simulation has been performed using the Aspen HYSYS program version 8.8 to determine the effects of adding various concentrations of activators up to 10% with maintaining the constancy of the entire amine strength of 45%. The present investigation addresses the performance of using piperazine/MDEA and sulfolane/MDEA on the absorption process in terms of energy consumption and acid gases loading. Four scenarios have been analyzed under the same operating conditions, 5% activator/ 40% MDEA has shown better performance superior to other scenarios regarding the balance between energy consumption and absorption capacity of acid gases. The results revealed that the addition of 5% piperazine improves the absorption of CO₂ and H₂S by 92.1% and 28.2% respectively. Correspondingly, 5% sulfolane enhances the absorption efficiency of CO₂ and H₂S by 80.48% and 48.18%. In terms of energy, the sulfolane system saved more reboiler energy compared to the piperazine system. Reboiler energy consumption was investigated by changing some effective parameters, namely sour gas temperature, lean amine temperature, reflux ratio, and rich amine temperature. Sulfolane promoter is more applicable

for the study plant conditions due to its high absorption capacity for H₂S and low reboiler duty requirements.

Keywords: CO₂, H₂S, Piperazine, Sulfolane, active-Methyldiethanolamine, Energy consumption.

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1. Introduction

Predominantly, natural gas has impurities such as H₂S, CO₂, and types of mercaptans. Owing to human health problems, environmental concerns, and corrosion issues, thus many restrictions introduced in which the specifications of sales gas are no more 3% carbon dioxide and 4 to 20 ppm hydrogen sulfide [1][2]. Carbon dioxide contributes by around 80% to global warming and reduces the heat value of natural gas and consequently the gas price, therefore it is important to minimize carbon dioxide content as low as possible before distribution [3][2]. Several technologies are available for removing acid gases from natural gas like using chemical and physical solvents, hybrid solvents, adsorption technology, and membrane technology [1]. Despite the significant improvements in technologies of sweetening of natural gas, the absorption by alkanolamine solvents is the most widespread commercial technology applies in many industries. Amines are chemical compounds known as regenerative solvents used widely in the natural gas sweetening plant. Alkanolamines react with acid gases via exothermic and reversible reactions. Three types of solvents proven to be of principal commercial interest for natural gas sweetening which are physical solvents, chemical solvents, and mixed solvents. Where, physical

solvents perform the removing of acid gases physically without chemical reaction, while chemical solvents perform the process with chemical reaction. Besides, the mixed solvents perform the process with both physical and chemical reactions. Many approaches presented to improve the capacity of the solvent and to tune the operational cost of the process. **Galindo et al. (2012)** examined the applying of DEA/MEA solution to absorb carbon dioxide, the results showed that mixed solvents offer the possibility to operate the regenerator column with lower temperature and minimizing energy requirements [4]. **Fouad and Berrouk (2013)** investigated the applying of mixed tertiary amines consist of MDEA and TEA, the results showed that 5% of TEA and 40% of MDEA mixture reduce the process cost by up to 3% considering the sales gas specifications [5]. Usually, mixed amines contain MDEA as the main solvent with adding one or more reactive amines like piperazine, TEA, sulfolane, and/or DEA which are known as a formulated solvent, and/or activated MDEA. The main concept behind mixing different amines is to combine the favorable characteristics of different solvents to improve the removing capacity of acid gases. **Al-Lagtah et al. (2015)** mentioned that MDEA as a tertiary amine has some advantages over primary and secondary amines [6]. The advantages involve low corrosion issues, comes with high resistance of degradation, lower heats of reactions, and low vapor pressure [7]. Another important advantage is the absorption selectivity of hydrogen sulfide preferentially to carbon dioxide [7]. Besides these advantages, the reaction of carbon dioxide does not react directly with MDEA, results in a slow absorption rate [8]. To combat this issue, **Suleman et al. (2018)** stated

that adding promoters such as piperazine or sulfolane to aqueous MDEA solvent improves the absorption rate [9]. Piperazine considers as an effective activator due to its ability to react with carbon dioxide to consist of carbonates. Piperazine comes with a high reaction rate toward carbon dioxide and low viscosity comparison to other modifiers [10]. **Bishnoi and Rochelle (2002)** mentioned that adding piperazine to MDEA absorbs carbon dioxide faster than adding MEA and/or DEA [11]. **Samanta and Bandyopadhyay (2011)** developed a comprehensive model to investigate the solubility of carbon dioxide into activated MDEA by piperazine to conclude that one mole of piperazine can theoretically absorb two moles of carbon dioxide [12]. Correspondingly, sulfolane is another activator developed by Shell company in a process called the Sulfinol process. The solvent in the Sulfinol process composed of base amine usually MDEA or DIPA, sulfolane, and water. Sulfolane activator uses in the absorption of acid gases due to its high stability, high physical absorption capacity, and low corrosivity [13] [14]. **Jalili et al. (2015)** studied the solubility of carbon dioxide and hydrogen sulfide in sulfolane to conclude that hydrogen sulfide solubility is higher by four times of that for carbon dioxide in sulfolane [15]. The using of mixed solvents has the benefits of deploying the physical and the chemical solvents together, besides the ability to manipulate the concentration of specific acid gas. Besides the alkanol amines, ionic liquid can be applied to absorb acid gas, also known as liquid organic salt and/or nonaqueous organic liquid. **Zhang et al. (2018)** study the applying of three different ionic liquid absorbents namely 1-butyl-3-methylimidazolium glycinate, 1-butyl-3 methylimidazolium lysinate and tetramethylammonium

glycinate to promote MDEA aqueous solvent [16]. Their results revealed that tetramethylammonium glycinate enhanced MDEA had the best performance regarding carbon dioxide absorption. **Tian et al. (2019)** measured the absorption performance of low-pressure hydrogen sulfide using activated MDEA by tetramethylammonium glycinate [17]. The formulated absorbent can remove hydrogen sulfide with an efficiency of up to 100%. However, the applicability of these kinds of modifiers still limited in the natural gas industry. Since the selection of solvent type and concentration is directly related to the energy required for regeneration, applying the optimum rate and solvent composition considers a crucial two factors to tune the process cost and sweet gas quality. Thus, this piece of work examines applying different scenarios of solvent composition with sulfolane and piperazine activators on the performance of the GASCO'S Habshan plant. Then, the best scenario will be chosen and compared with real plant specifications in addition to the effect of several parameters. These parameters include feed rich amine temperature to the stripper, lean amine temperature, sour feed gas temperature, and reflux ratio. Testing the mentioned parameters will help to reach the optimum operating conditions for the sweetening process based on the study of the GASCO'S Habshan plant.

2. Sour feed gas specifications

The sour feed natural gas stream that used in the simulation is reproduced from GASCO'S Habshan plant. It was specified to reduce carbon dioxide content in the sweet gas stream to a lesser extent than 2% and the hydrogen sulfide to less than 30 ppm. The rate of sour feed gas to the plant is 610 MMSCFD and the compositions used in the simulation is given by Table 1.

Table 1. Sour feed natural gas compositions.

Component	C ₁	C ₂	C ₃	N ₂	CO ₂	H ₂ S
Mole fraction	0.766	0.0643	0.0353	0.0913	0.03729	0.0055

The solvent used in the real plant is MDEA solvent with a concentration of 45%. The solvent will apply in this simulation is activated MDEA by piperazine or sulfolane activators with different compositions as shown in Table 2.

Table 2. Various concentrations of activated MDEA solvent.

Solvent concentration Mol (%)	Various scenarios of concentrations	Solvent Mixture		
		Sulfolane	MDEA	Water
	S-M-W-1	0.02	0.43	0.55
	S-M-W-2	0.05	0.4	0.55
	S-M-W-3	0.07	0.38	0.55
	S-M-W-4	0.1	0.35	0.55
		Piperazine	MDEA	Water
	P-M-W-1	0.02	0.43	0.55
	P-M-W-2	0.05	0.4	0.55
	P-M-W-3	0.07	0.38	0.55
	P-M-W-4	0.1	0.35	0.55

For the sake of simplicity, low amine concentration means low molecules that will contact acid gases resulting in a low absorption rate. The modifiers

concentrations in the blend solvent used up to 10 wt. % to avoid any chance of precipitation [18]. Therefore, in this simulation, the total activated MDEA solvent concentration keeps up to 45 % in total with various concentrations of activators up to 10 %.

3. Simulation validation

A case study was made to validate the reliability and accuracy of the simulation results with actual plant data. The simulation holds by the Aspen HYSYS version 8.8 program with the Acid gas fluid package which is recommended for natural gas treatment. Based on the results, 5% activator/40% MDEA chosen to be the best scenario for both activators regarding acid gases content in sweet gas and the energy requirements. According to Table 3, it is observed that piperazine and sulfolane activators enhance carbon dioxide removal efficiency by 92.1% and 80.48% respectively comparison to actual plant with the same operating conditions. Correspondingly, sulfolane and piperazine activators improve the hydrogen sulfide removal efficiency by 48.18% and 28.2% respectively. The results show that piperazine can be an efficient activator in case of high carbon dioxide contents. On the other hand, sulfolane shows excellent agreements regarding hydrogen sulfide removal.

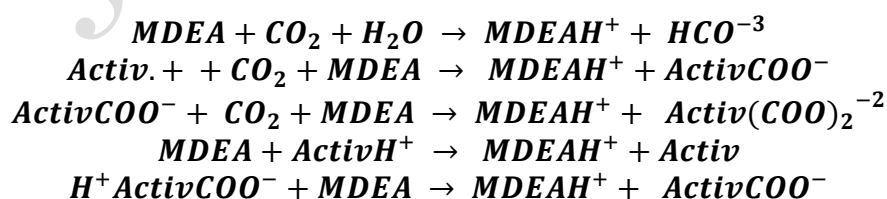
Table 3. Comparison of the simulation results and real plant data.

Parameter	Plant Data 45% MDEA	Simulation 5% Piperazine/40% MDEA	Simulation 5% Sulfolane/40% MDEA
Feed gas			
CO ₂	1133 kmol/h	1133 kmol/h	1133 kmol/h
H ₂ S	170.11 kmol/h	170.13 kmol/h	170.13 kmol/h
Temperature	54.5 C	54.5 C	54.5 C
Pressure	67.5 bar	67.5 bar	67.5 bar
Sweet gas			

CO ₂	676 kmol/h	55.396 kmol/h	485.2844 kmol/h
H ₂ S	0.60 kmol/h	0.3109 kmol/h	0.1171 kmol/h
Temperature	57 °C	58 °C	60 °C
Pressure	66.5 bar	66.5 bar	66.5 bar
Total flow	29835 kmol/h	29410 kmol/h	29706.1779 kmol/hr
Acid gas			
CO ₂	456.6 kmol/h	1021.4455 kmol/h	600.3818 kmol/h
H ₂ S	169.6 kmol/h	170.083 kmol/h	160.4959 kmol/h
Temperature	57 °C	51.43 °C	53
Pressure	2 bar	2 bar	2 bar
Total flow	686.66 kmol/h	1244 kmol/h	805.5 kmol/h

4. Chemical process description

Feed stream enters the absorber from the bottom which comes in countercurrent contact with lean amine solvent as shown by Fig. 1. The solvent captures the majority of the sour gas into the absorber column to leave the top of the absorber as clean gas. The rich amine leaves the bottom of the absorber to pass through a throttling valve to reduce the pressure and enters the flash drum. The flash drum removes dissolved hydrocarbons gas and some of the acid gases and helps in preventing foaming. Lean/Rich heat exchanger works as a preheater to increase the temperature of the feed stream to the stripper to meet the regeneration conditions. After that, the acid gases exist from the top of the stripper column, while the regenerated amine leaves the bottom of the stripper to pass through series of exchangers and pumps to restores the solvent to its initial conditions. **Samanta and Bandyopadhyay (2011)** represented the reactions between carbon dioxide and the activator/MDEA as follows [11]:



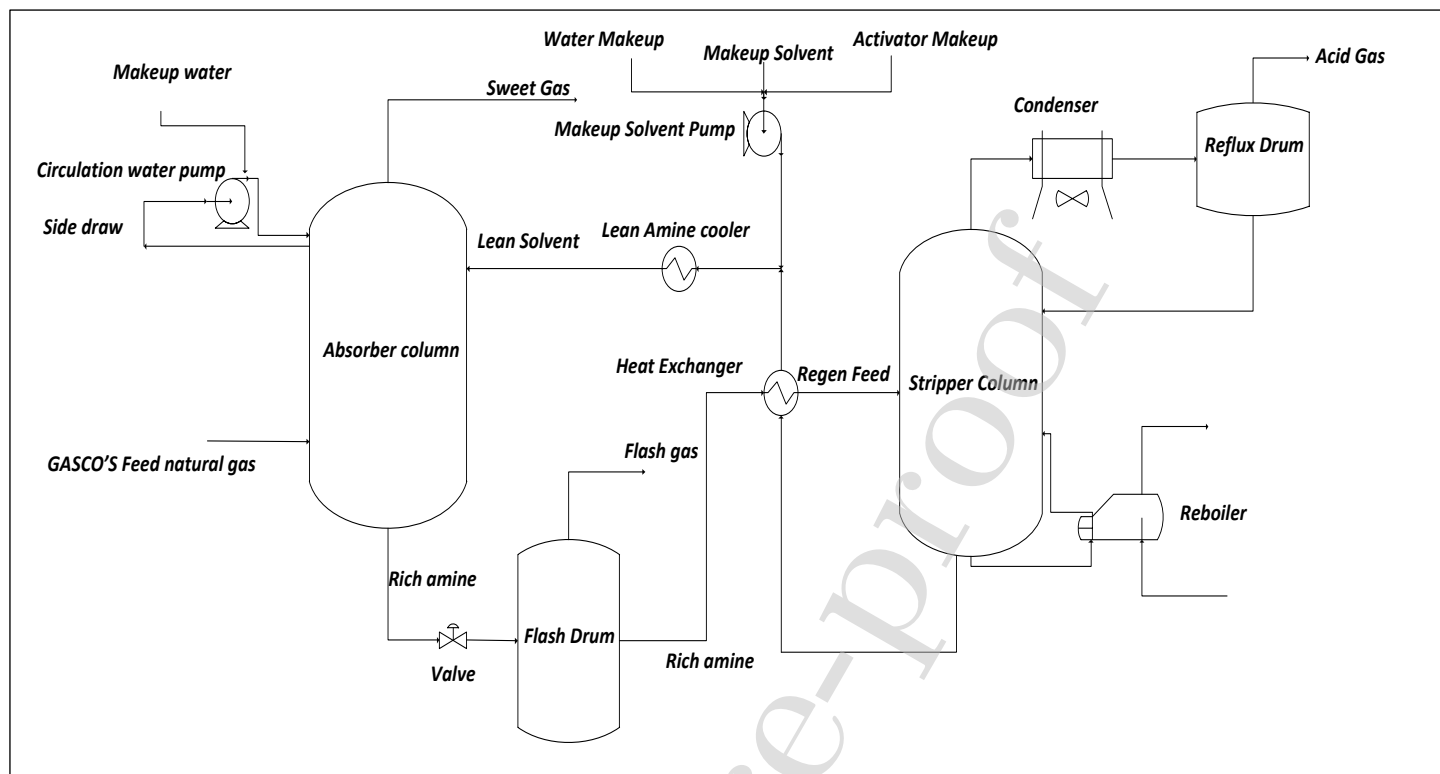


Fig. 1. Process flow diagram of a natural gas sweetening plant.

5. Results and discussion

5.1. Effect of activator concentration on the solvent MAKEUP

The amine losses in the natural gas sweetening plant stem from different sources like vaporization, foaming, and degradation. Amine vaporization process is a function of several factors such as temperature, amine solvent concentration, solvent volatility, and vapor pressure [19]. Amine losses due to volatility is a crucial problem causing environmental issues as the resulting byproduct will be potentially more toxic than the parent amine. Besides, high amine makeup flowrate requires to compensate for the losses in amine which increases the capital cost of the water wash process. Foaming is another factor causes amine losses which increases with using a high concentration of amine.

However, it can be controlled by using a spray of liquid, and water scrubber.

Sexton and Rochelle (2009) mentioned that degradation occurs by oxidation however most of the gas treatment plants using alkanolamine work without oxygen content [20]. To combat the issue of amine losses, the makeup stream applies to manage the amine strength in sweetening plants. According to Table 2 and Fig. 2, it is observed that for 2%, 5%, and 7% activators concentrations, piperazine recorded low amine makeup flow rate comparison to sulfolane. While, with a 10% activator, sulfolane requested low amine makeup flowrate. Modification of the reaction conditions and applying a proper solvent can mitigate the amine losses.

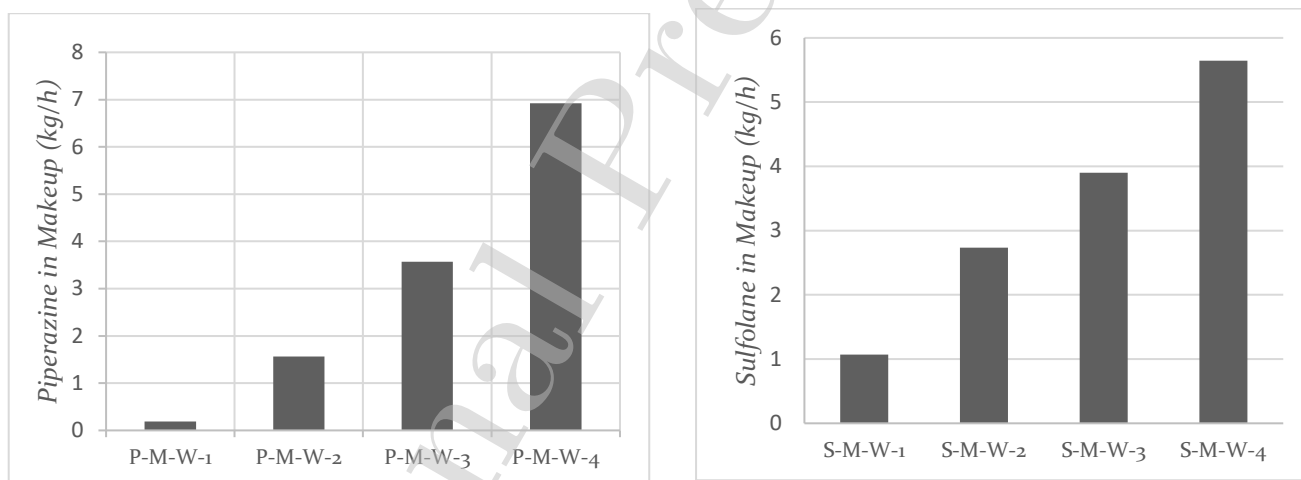


Fig. 2. Effect of using different activators concentrations on the makeup flow.

5.2. Effect of activator concentration on the CO₂ content in the sweet gas

Carbon dioxide flowrate in sweet gas requires to be as low as possible to meet the sales gas specifications and to avoid corrosion and solidification in the cold box during the liquefaction process. Many studies stated that deploy activators in an amine base solvent increase the acid gases loading. **Xia et al. (2003)**

studied the effect of adding piperazine modifier on the solubility of carbon dioxide in the mixed amine solvent [21]. They concluded that piperazine reacts with carbon dioxide to form three types of carbamate species which are PZ-carbamate, PZ-dicarbamate, protonated PZ-carbamate, previous studies also confirmed this trend [22] [23]. In the same vein, **Najibi and Maleki (2013)** stated that piperazine has a positive effect on the solubility of carbon dioxide in the piperazine/MDEA solution [24]. **Ghalib et al. (2017)** modeled the effect of adding piperazine to MDEA solvent on the CO₂ loading [25]. They conducted that carbon dioxide loading increases as the carbon dioxide partial pressure and piperazine concentration increases. On the other hand, **Dash et al. (2015)** studied the effect of using the sulfolane modifier on the carbon dioxide capturing to state that sulfolane improves the CO₂ loading in an efficient extent [26]. A simulation study has been performed to test the effect of applying various concentrations of activators to MDEA amine solvent on the performance of the sweetening plant. The concentration of carbon dioxide that fed to the sweetening plant is specified to be 3.73 mol.% which is the same as that of the actual plant. According to Table 2 and Fig. 3, it is observed that the piperazine activator shows high efficiency in capturing CO₂ with all scenarios. Where, 0.00262% CO₂ in the sweet gas stream is the best-recorded value with 10% piperazine/35% MDEA scenario. Correspondingly, increasing sulfolane concentration results in an increase in the CO₂ content in the sweet gas as shown in Fig. 3a. The possible reason is that the solubility of CO₂ in sulfolane is a weak comparison to MDEA and piperazine as found by Jalili, et al. (2015) [15], where increasing sulfolane concentration will reduce the MDEA percent which

turns in reducing the free molecules of MDEA that are more reactive with CO₂ molecules.

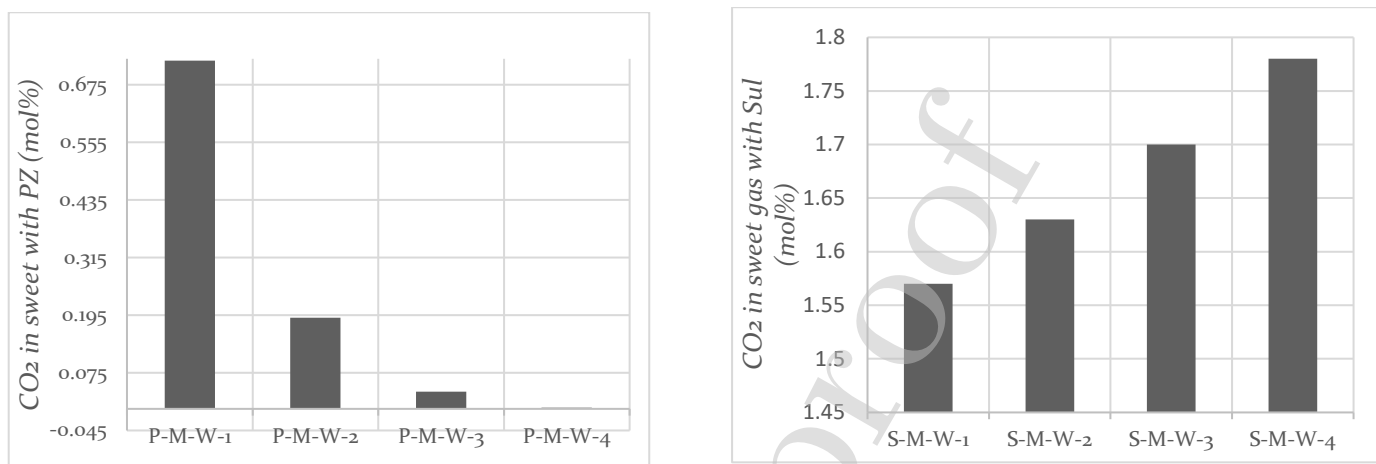


Fig. 3a. Carbon dioxide in sweet gas using Sulfolane and Piperazine with different concentrations.

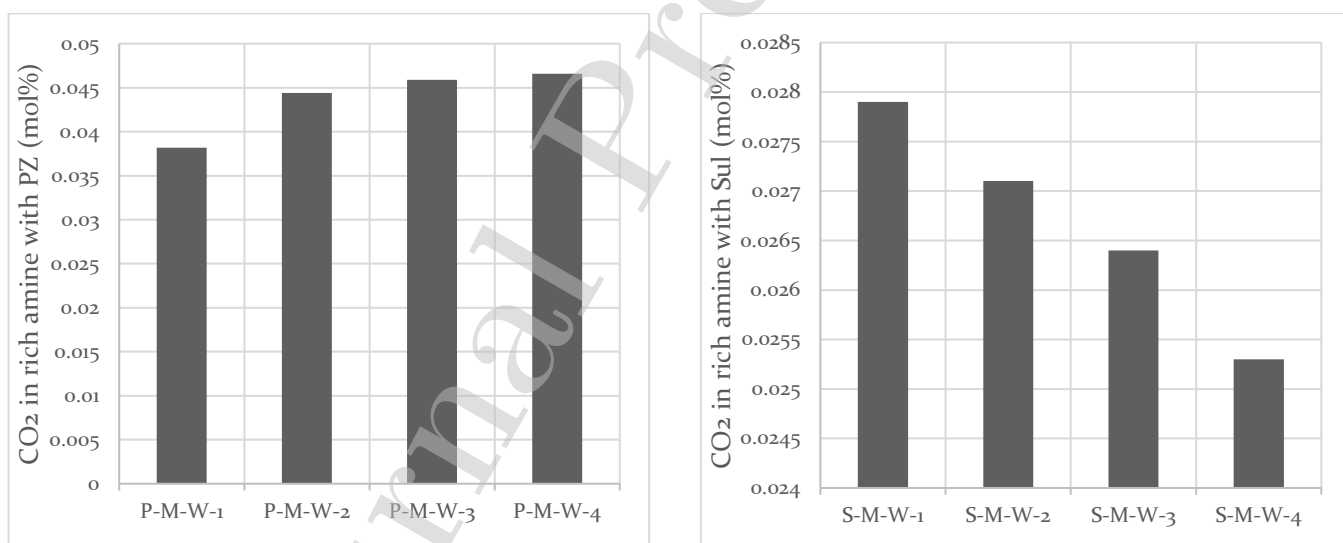
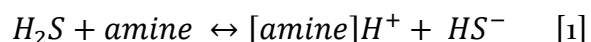


Fig. 3b. Carbon dioxide in rich amine stream using Sulfolane and Piperazine with different concentrations.

5.3. Effect of activator concentration on H₂S content in the sweet gas

Hydrogen sulfide concentration in sweet gas considers crucial matter based on the fact that H₂S considers as a strong corrosive and poisonous gas. It is thoughtful that hydrogen sulfide reacts immediately with amines by proton transfer.



Fouad and Berrouk (2013) assumed that H₂S reaction with the MDEA solvent is gas-phase limited while carbon dioxide reaction is liquid-phase limited [5].

Haghtalab and Izadi, (2014) studied the solubility of carbon dioxide and hydrogen sulfide in a mixed solvent to conclude that piperazine reduces the absorption of hydrogen sulfide in the presence of carbon dioxide [27]. On the other hand, **Jalili et al. (2015)** investigated the solubility of acid gases in the sulfolane to state that the solubility of hydrogen sulfide higher by four times than solubility of carbon dioxide [15]. The concentration of hydrogen sulfide that fed to the sweetening plant is specified to be 0.56 mol.% which is the same as that of the actual plant. According to Fig. 4, the results show good agreements with works in literature where sulfolane showed high efficiency to absorb hydrogen sulfide from sour feed gas.

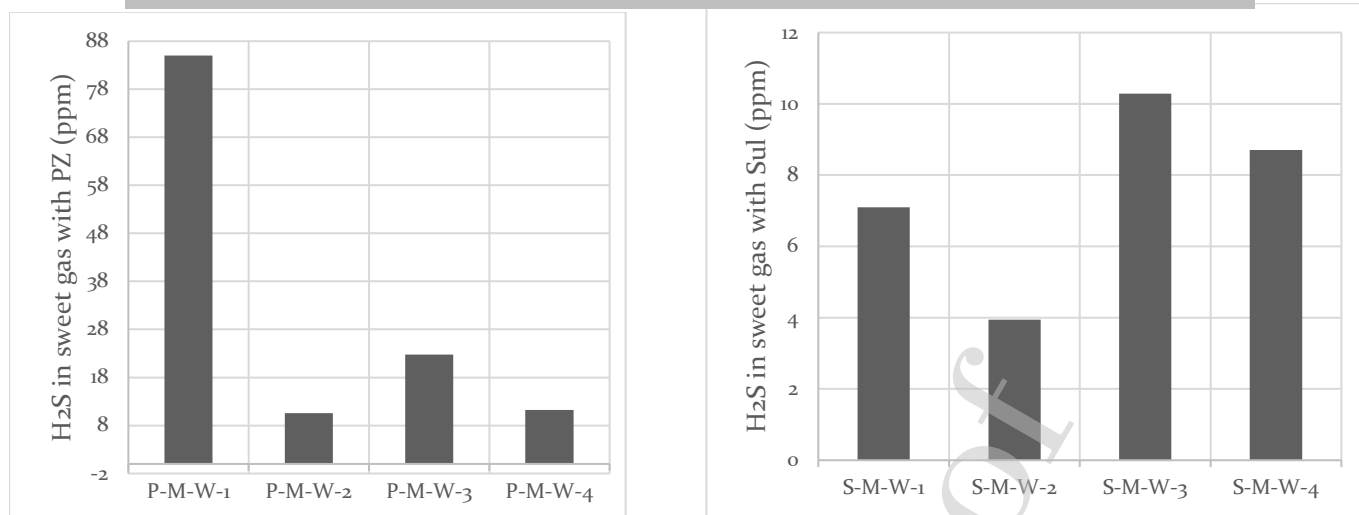


Fig. 4a. Hydrogen sulfide in sweet gas using Sulfolane and Piperazine with different concentrations.

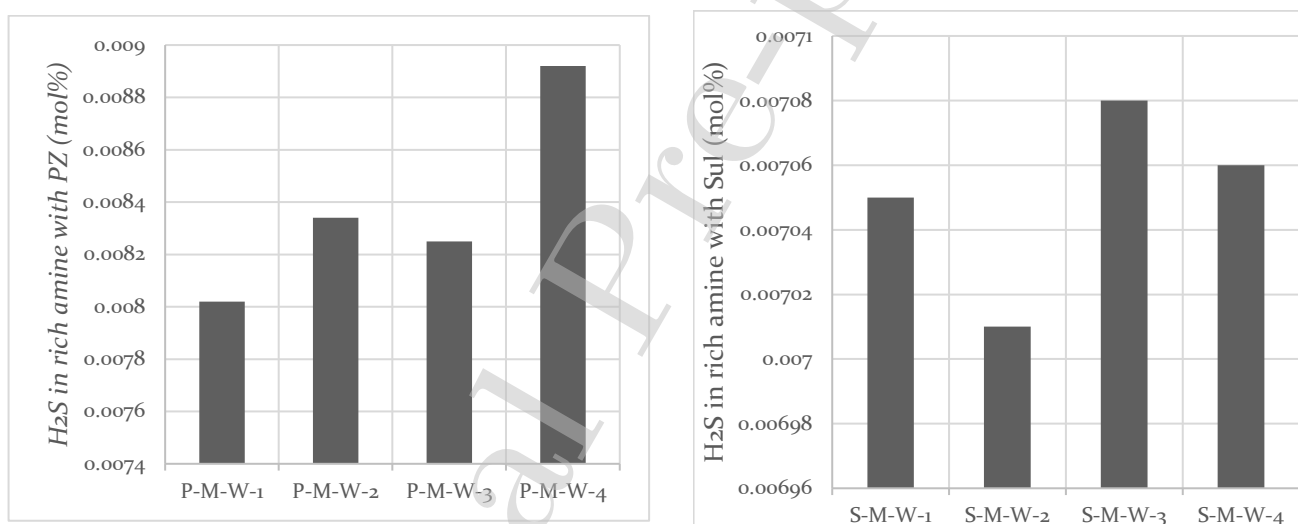


Fig. 4b. Hydrogen sulfide in rich amine stream using Piperazine and Sulfolane with different concentrations.

5.4. The effect of activators concentration on the total circulation of lean amine

Amine circulation rate plays a vital role in the economics of natural gas sweetening plants using chemical solvents. Circulation rate influences the pump size, energy for heat exchangers, energy for stripper column, and piping.

Tan and Chen (2006) stated that the mass flow rate coefficient increases by

increasing the circulation rate [28]. Greater circulation rate removes a greater amount of acid gases till reach the equilibrium, so it is possible to compensate for applying low amine concentration with a high circulation rate taking into account the economic aspect. **Abkhiz and Heydari (2014)** compared the using of single, mixed, and activated solvents to summarized that activated solvents need lower circulation rates to reach specifications for the same operation conditions [29].

According to Fig. 5, the total flow rate of lean amine feed to the absorber increases as the piperazine concentration increases. While generally, the total lean amine flow rate decreases with increasing sulfolane concentration. However, it is worthy to mention that water level in all scenarios kept constant at 55% to match the real plant feed data. Hydrogen sulfide/amine reaction needs no water, where the decreasing water level has no effects on the absorption process. On the other hand, carbon dioxide/amine reaction decreases as the water level decreases because the reaction should be in aqueous condition. Higher circulation solvent rate means an unstable system, more foaming tendency, and more amine required. While lower circulation solvent rate minimizes energy consumption and reducing the absorption rate as well. Therefore, it is important to reduce the amine circulation rate to the point that maintains the outlet gas specifications.

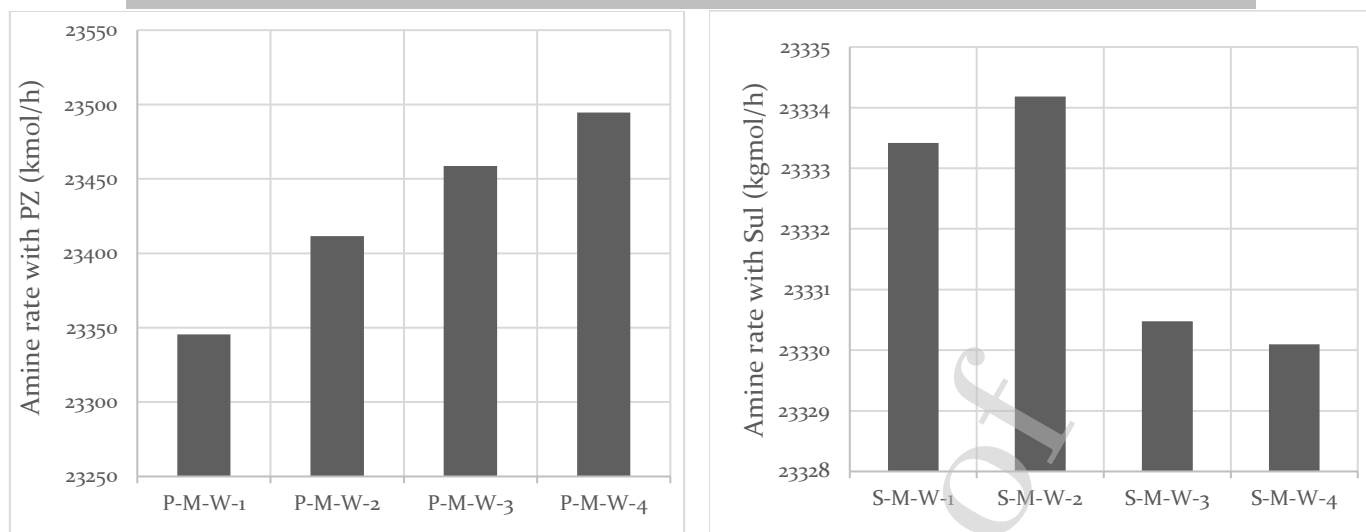


Fig. 5. Total circulation rate with different concentrations of activators.

5.5. The effect of activators concentration on the reboiler duty

The energy penalty is the main issue behind the continuous development of the acid gases capturing process. The desorption sector estimated to be responsible for more than 50% of the overall energy of capturing, primarily due to the high energy required for the regeneration process. **Oexmann and Kather (2010)** classified the required energy to regenerate the absorbent in the stripper column into the heat of reaction for desorption of acid gases, the reboiler duty, and sensible heat of the feed rich amine solution to the regenerator column [30]. **Warudkar et al. (2013)** described the reboiler energy as the difference between the enthalpy of feed vapor and enthalpy of leaving condensed liquid [31]. It is worthy to mention that increasing solvent concentration reduces the amine circulation rate and reduce energy consumption in the stripper. The selecting of activator concentration in solvents requires a detailed study on several parameters such as acid gases concentration in sweet gas, total cost relates to energy, solvent, and other operations conditions [32] [33].

Correspondingly, the addition of modifiers to the amine solvent will increase

the energy consumption because of the acid gases recovery would be high. The results in this study show that the best trade-off between acid gases recovery and the energy consumption is that 5% and beyond for sulfolane activator, and 5% of piperazine activator. While any solution strength beyond 5% piperazine comes with high energy requirements and little gain in carbon dioxide recovery. This means that if piperazine/MDEA and sulfolane/MDEA are compared at the same concentration, the reboiler energy of sulfolane/MDEA will be much more superior to that of piperazine/MDEA.

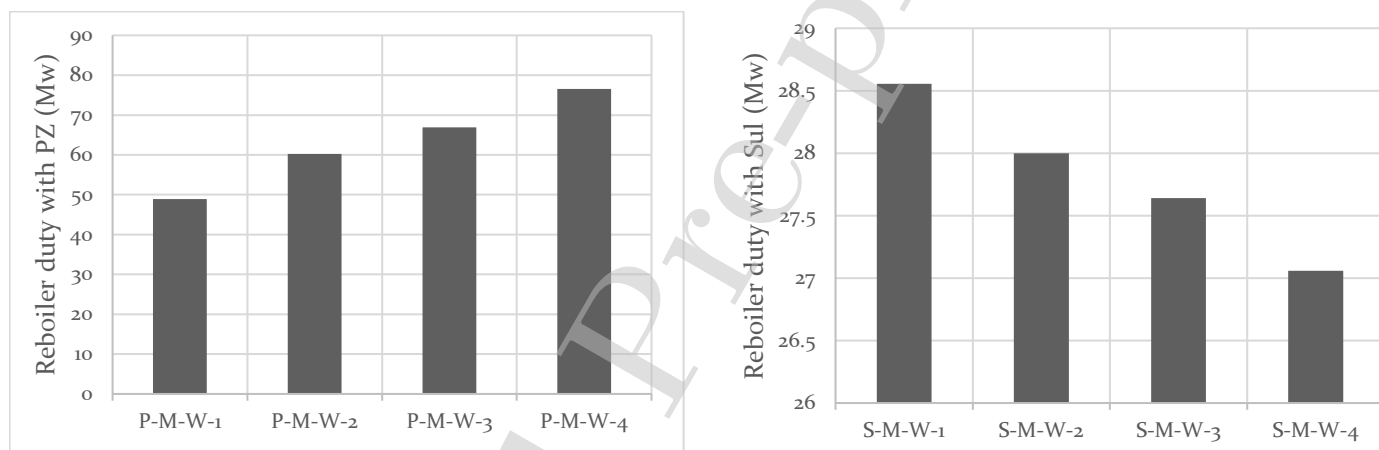


Fig. 6a. Reboiler duty with various concentrations of activators.

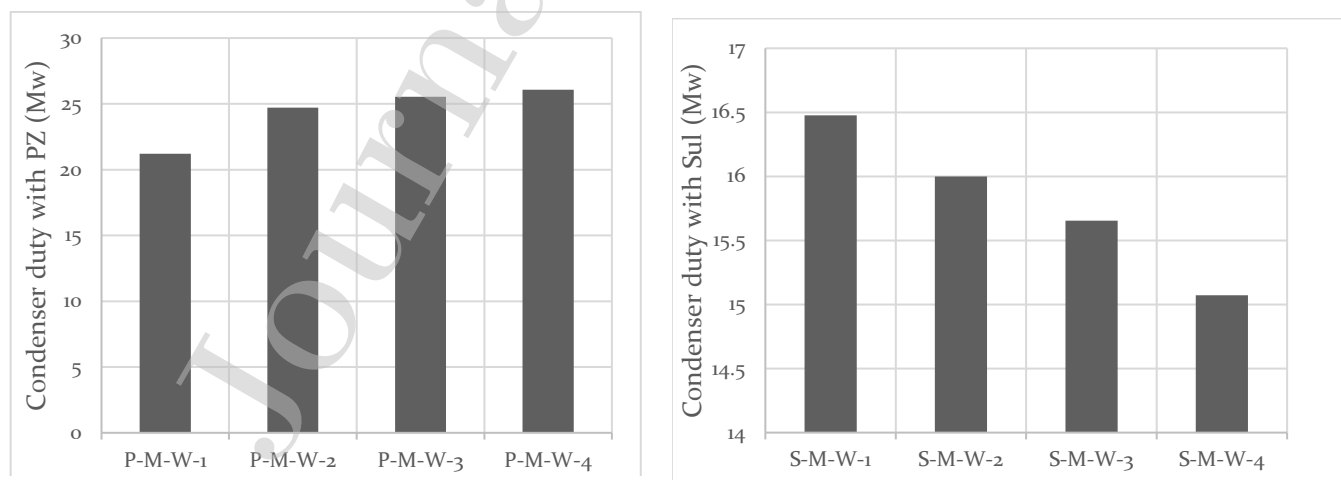


Fig. 6b. Condenser duty with various concentrations of activators.

6. Sensitivity analysis of some effective parameters

6.1. Effect of varying regenerator temperature

The reactions inside the stripper column are endothermic in nature, therefore the rich amine stream temperature will affect the reboiler duty to a great extent. The results revealed that good quality of clean gas is produced when rich amine temperature decreases for both activators, which turns in increasing the energy requirements for the regeneration process. According to Fig. 7, it is observed that reboiler energy decreases as the rich amine temperature increases for both solvent systems. Consequently, increase the rich amine temperature affects the LEAN/RICH amine exchanger energy to a great extent. Therefore, it is important to keep the temperature of the rich amine as high as possible taking into account the energy of the heat exchanger.

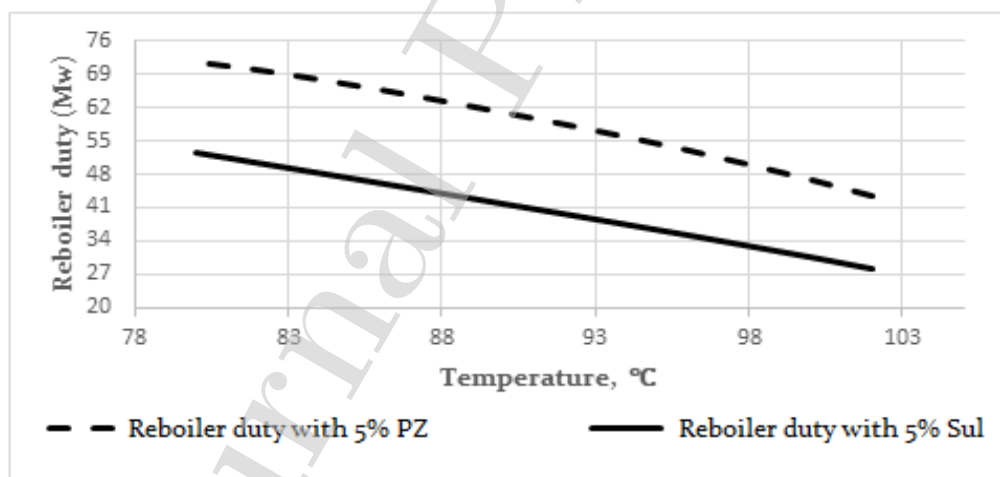


Fig. 7. Reboiler duty against regeneration feed temperature.

6.2. Effect of reflux ratio

Reflux is the process of feed some of the distillate back to the stripper column, the reflux ratio for this simulation specified to be 1.1. Varying the reflux ratio in the stripper column has a direct effect on the reboiler energy requirements. The results showed that increasing the reflux ratio in the regenerator column results

in increment in reboiler duty and reduction in hydrogen sulfide content in sweet gas. Fig. 8 shows that increasing the reflux ratio leads to an increase in the load on the reboiler with a slight improvement in the reduction of acid gases in the sweet gas stream for both activators systems.

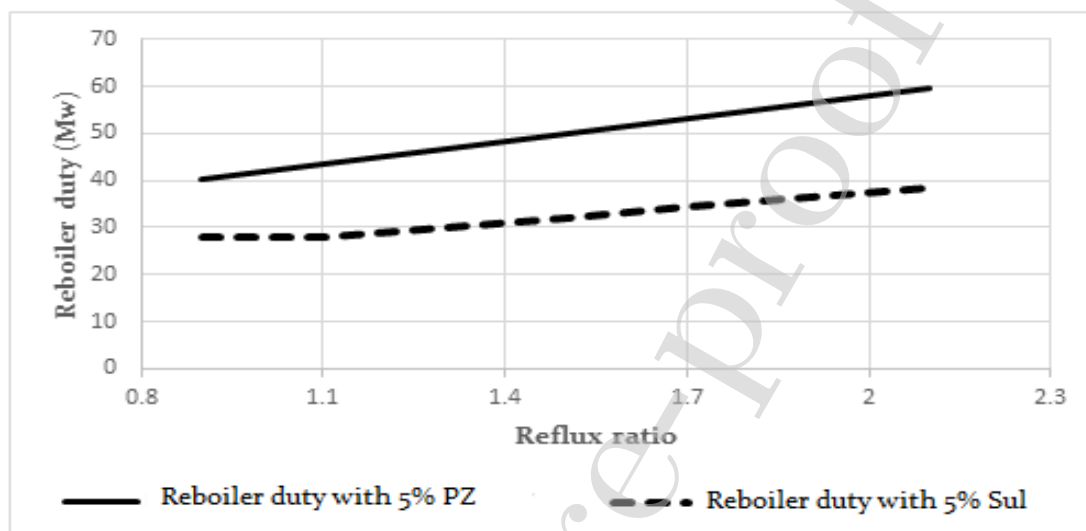


Fig. 8. Reboiler duty against reflux ratio.

6.3. Effect of sour gas feed temperature

The design temperature of the sour gas to the absorber column of the real plant is 55 °C, higher and lower temperatures were used to test the effect on the reboiler duty. Fig. 9 shows that at low feed temperature, the reboiler duty is high. The reboiler duty decreases as the sour gas feed temperature increases. The optimum feed temperature appears to lie between 45 °C and 55°C where for higher temperatures the solubility of acid gases decreases and the change in reboiler duty is almost constant for both activators. Among others, with the piperazine/MDEA solvent, reboiler duty changes with a rate higher than that with the sulfolane/MDEA system.

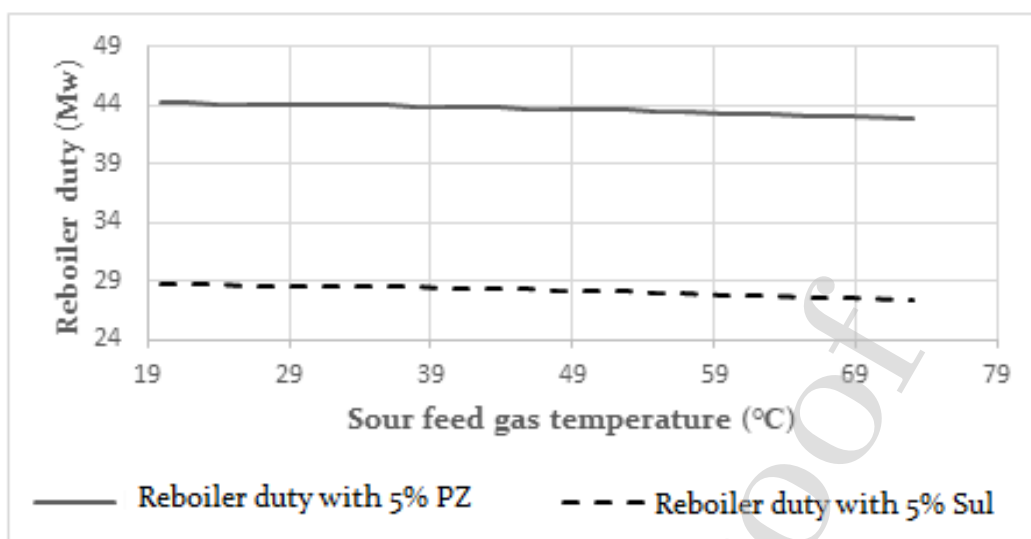


Fig. 9. Reboiler duty against sour feed gas temperature.

6.4. Effect of lean amine temperature

Amine temperature is the main factor that controls the absorber column temperature. Lean amine temperature manages using air cooler and lowers lean amine temperature leads to more air cooler duty. In regard to reboiler energy, it is observed by Fig. 10 that increasing lean amine temperature will reduce the reboiler duty for both activators. Another constraint is that to avoid condensation of heavy hydrocarbons, the lean amine temperature should be in range 5°C to 10 °C higher than sour feed gas temperature. Among others, lean amine temperature affects the amine losses from the absorption column in a great extent. According to Fig. 11, increasing amine temperature leads to an increasing in the amount of amine losses in sweet gas that saturated with water in higher temperatures. Besides, Fig. 11 shows that the piperazine/MDEA system has a low amine loss rate comparison to the sulfolane/MDEA system.

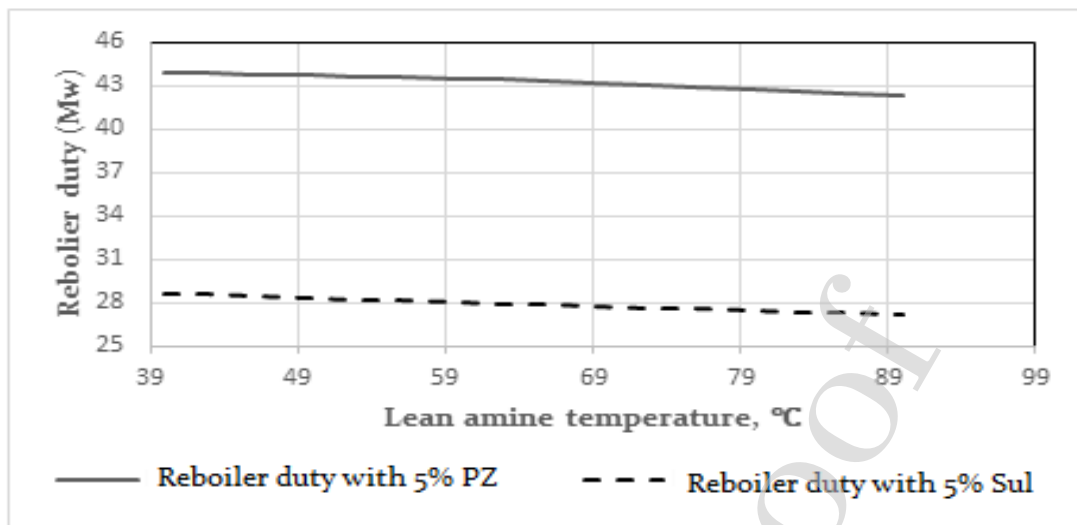


Fig. 10 Reboiler duty against amine temperature.

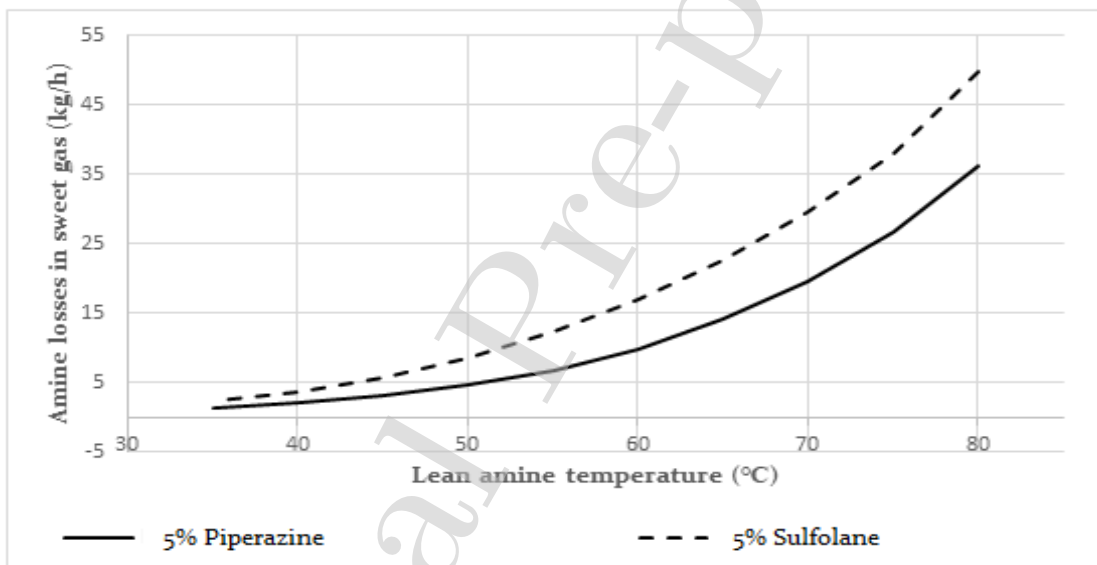


Fig. 11 Amine losses against lean amine temperature.

Conclusion

The simulation executes using the Aspen HYSYS simulator to evaluate the effect of adding promoter to MDEA solution for GASCO'S Habshan gas

sweetening plant. Besides, some of the effective parameters have been analyzed to nominate the optimum conditions that enhance the process for the best performance. The amine strength in the real plant was 45% of MDEA, while the simulation suggested using activated-MDEA with 2%, 5%, 7%, or 10% with keeping the total amine strength 45%. The results revealed that:

- 5% activator/40% MDEA solution chosen to be the best trade-off between acid gases recovery and energy consumption.
- The mixture of sulfolane/MDEA is more applicable due to the highest absorption capacity, energy penalty and low vaporization losses among the piperazine/MDEA solutions.
- Piperazine promoter would be the best choice for high carbon dioxide content, while sulfolane improves the capturing of hydrogen sulfide to a great extent.
- Sulfolane/MDEA mixture comes with low reboiler duty compared to the piperazine/MDEA system.
- Increasing the regenerator feed temperature resulted in decreasing the reboiler duty with both modifiers.
- Increasing the reflux ratio enhanced the absorption efficiency, which turned in an increase in the reboiler duty for both modifiers systems.
- Increasing of sour gas feed and lean amine temperatures reduced the reboiler duty for both modifiers systems.

- Amine vaporization is a function of lean amine temperature, where the piperazine/MDEA system showed lower amine losses compared to the sulfolane/MDEA system for the same range of lean amine temperatures.

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- 1- The performance of piperazine and sulfolane activators has been studied.
- 2- 5% sulfolane activator enhances CO₂ and H₂S absorption by 80.48% and 48.18%.
- 3- 5% piperazine activator promotes CO₂ and H₂S absorption by 92.1% and 28.2%.
- 4- Sulfolane is more applicable regarding the balance between energy consumption and H₂S loading.
- 5- Some effective parameters investigated to figure out the optimum operational conditions.

Conflict of Interest and Authorship Conformation Form

Please check the following as appropriate:

- All authors have participated in (a) conception and design, or analysis and interpretation of the data; (b) drafting the article or revising it critically for important intellectual content; and (c) approval of the final version.
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