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Carbon Dioxide Capturing from Natural Gas using Di-glycol Amine and Piperazine – A New Solvent Mixture

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Abstract*: The effect of adding Piperazine to di-glycol amine (DGA) to reduce the CO_2 content in natural gas from 10% to 1% by mole was studied. Aspen HYSYS was used to simulate the process. Different concentrations of DGA (45, 50 and 55%) and Piperazine (3, 5, 7, 9 and 11%) were investigated. The effect of circulation rates variation from 1000 kg_{mol}/hr. to 5000 kg_{mol}/hr. were examined. Moreover, temperature ranges from 38 oC to 80 oC and pressure ranges from 45 kg/cm^2 to 80 kg/cm^2 were studied for 55% DGA without and with the addition of Piperazine. It was found that adding 9% Piperazine to 55% DGA achieved the best absorption efficiency. By using Piperazine, the circulation rate required to reach the 1% CO_2 level was reduced to 3250 kg_{mol}/hr. The amount of captured CO_2 was found to increase with the decrease in the lean gas temperature and the increase in absorber pressure.

Keywords*: Amine based solvents; Carbon dioxide; Gas sweetening; CO_2 capture; Piperazine (PZ); di-glycol amine (DGA).

I. INTRODUCTION

Natural gas demand in recent decades has dramatically increased. Natural gas plays an important role in world's economy and industrial developments. In most cases, natural gas contains carbon dioxide that needs to be extracted in order to meet the gas pipelines specifications [1]. Carbon dioxide (CO_2) caused corrosion of gas transportation pipelines [2], turbine, compressors and other equipment; as carbon dioxide will react with water vapor, and carbonic acid will be formed. In addition, carbon dioxide decreases the natural gas heating value. Moreover, carbon dioxide is one of the greenhouse gases that contributes to global warming [3]-[5] by more than 60% [6]. Raw natural gas containing acid gases such as hydrogen sulfide (H_2S) and CO_2 is referred to as sour gas [3]-[7]. Two major treatments can be carried on sour gas streams; the first is sweetening where CO_2 and H_2S are extracted by using appropriate solvents such as amine or amine mixtures. The second process is dehydration through which water content in natural gas is eliminated. Maximum allowable limit for H_2S and CO_2 in natural gas stream is 4-ppm and 2% respectively [8]. In this research, we will focus on CO_2 capturing from sour gas. There are several available solvents that can be used for CO_2 removal from natural gases [9]-[10]; amine-based solvents [11], hot potassium carbonate [12]-[13] and many physical solvents [14]. The most common solvent is the amine-based solvent, it is a chemical based solvent that has high affinity toward acid gases. Different amine types can be used as solvent for acid gases such as Monoethanolamide (MEA), Diethanolamine (DEA) and Methyl Diethanolamine (MDEA) [1]. The main drawback when using single amine is its relatively low reaction rate with CO_2 which affects the rate of absorption of CO_2, while adding a small amount of accelerator such as Piperazine to the amine-based solvent was found to increase the CO_2 reaction rate [15]. Very few researches studied CO_2 removal from natural gas by using Piperazine as an activator [5]-[7]. Moreover, no previous studies could be found in the literature that tested the effects of adding Piperazine to aqueous di-glycol amine (DGA) on carbon dioxide removal from natural gas. In this work different PZ and DGA blends were investigated and various operating condition such as temperature, pressure and circulation rate were tested to study their effect on the amount of carbon dioxide removed from natural gas.

II. PROCESS DESCRIPTION

The process flow diagram (PFD) of an actual natural gas sweetening plant in Egypt was used for our simulation study, as illustrated in Fig. 1. The feed gas containing 10% by mole CO_2 enters an inlet separator to remove of any liquid. After which, the sour gas enters the absorber counter-current to the lean solvent. In the case of the plant under investigation, the lean solvent is Methyl Diethanolamine (MDEA). In a flash vessel, carbon dioxide and hydrocarbons are first removed from the rich MDEA solvent. In this step the pressure is reduced to 5-10 bar. The temperature of the rich solvent is increased to the required regeneration temperature through exchanging heat with the lean solvent produced from the regeneration column. In the regeneration section, carbon dioxide is removed from the rich solvent. The lean solvent is then sent to the absorber after reducing its temperature. In this process, the selection of solvent used for CO_2 removal from natural gas depends on several factors such as capability of removing CO_2, pickup rate of hydrocarbons, energy consumption during regeneration, foaming, thermal stability, corrosivity, cost and availability [11]-[16].

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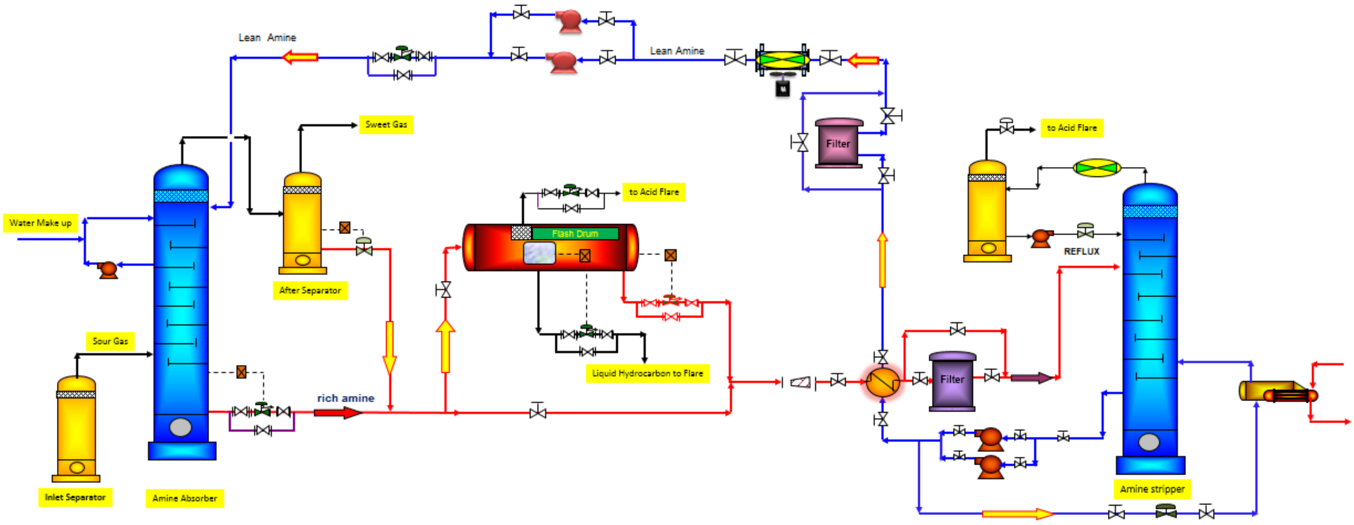

Fig.1. Process flow scheme of natural gas sweetening process in Egypt.

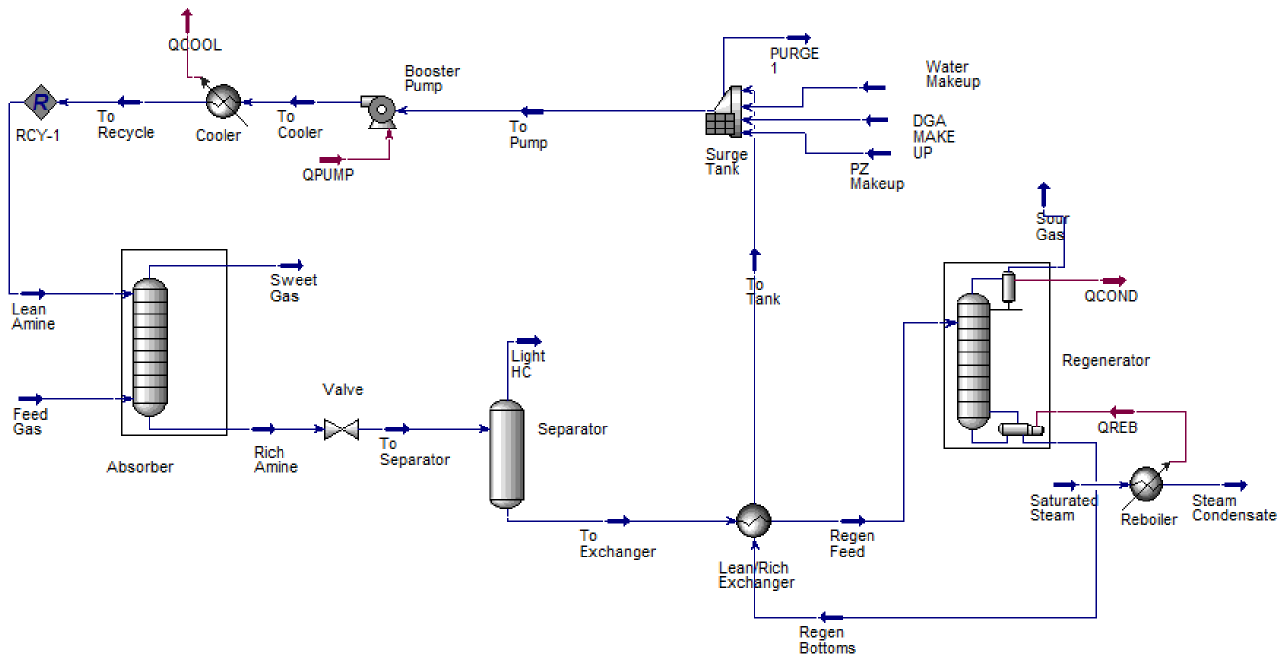

Fig. 2. Natural gas sweetening process from an actual plant in Egypt developed using Aspen Hysys.

In this research we will study replacing MDEA with PZ and DGA blend in the gas sweetening plant under investigation. The performance of the sweetening plant will be investigated using DGA as a stand-alone solvent and PZ as a blend with DGA. The amount of CO_2 captured using these new solvent combinations will be looked at. According to the literature, reaction **(1)** represent the absorption of CO_2 by DGA [11];

$$RNH_2 + H_2O + CO_2 \rightarrow RNH_3HCO_3 \qquad \textbf{(1)}$$

While the reaction occurring between Piperazine (PZ) and CO_2 can be represented as following [17];

According to Table I, piperazine has the highest reaction rate constant, this means that it reacts readily with CO_2 and the driving force for mass transfer is kept at minimum, hence, CO_2 can be easily absorbed by the solvent. According to the literature, two moles of carbon dioxide can be absorbed by

$$CO_2 + PZ + B \leftrightarrow (PZCOO)^- + (BH)^+ \qquad \textbf{(2)}$$

$$CO_2 + (PZCOO)^- + B \leftrightarrow PZ(COO^-)_2 + (BH)^+ \qquad \textbf{(3)}$$

The reaction rate constants of carbon dioxide absorption for different amine-based solvents is illustrated in Table I. Solvents with high reaction rate will require less packing or trays in the absorber, in the same time they can remove similar amount of CO_2. Hence, the associated capital cost of the plant will decrease.

In addition, solvents with high reaction rate will have low driving force toward the transfer of CO_2 from the gas phase (natural gas) to the liquid phase (solvent). In addition, the overall irreversibility of the process [18]-[19] will decrease; hence, the energy cost will be less.

one mole of PZ [20]. This make PZ an interesting additive that needs more investigation.

Table–I: Reaction rate constants of carbon dioxide absorption for different amine-based solvents [21].

Amine	Reaction rate constant (L $mol^{-1}s^{-1}$)
MEA	6000
DGA	4500
DEA	1300
DIPA	100
Piperazine	59000
MDEA	4

III. PROCESS SIMULATION

This study was performed using Aspen Hysys as shown in Fig. 2. Acid gas fluid package was used for MDEA and DGA solvent, while Non-random two-liquid (NRTL) fluid package was used in the case of PZ-DGA blend. Egyptian natural gas stream containing 10% CO_2 is used in this study. The developed simulation model was first validated with actual plant data using MDEA solvent. This step is essential to make sure that our developed model can predict the plant performance at different operating conditions. Actual plant data and simulated data are presented in Table II. The gas chromatograph analysis of natural gas stream composition entering the absorption section and exiting the separator is listed in Table II against simulation results for the exit gas from the separator. It is clear that the developed simulation results are in great match with the real data. The composition of the natural gas feed to the process and operating conditions in the actual gas sweetening plant is listed in Table II and Table III respectively. Our main target is to test the ability of solvents under investigation to decrease the CO_2 content in natural gas to less than 1 mol%.

Table-II: Actual plant data versus simulated data for model validation.

Component	Actual feed gas composition [mole fraction]	Actual sweet gas composition [mole fraction]	Simulated sweet gas composition [mole fraction]
Methane	0.8380	0.8688	0.8695
Ethane	0.0340	0.0352	0.0338
Propane	0.0090	0.0093	0.0095
I-Butane	0.0020	0.0021	0.0020
N-Butane	0.0020	0.0021	0.0023
I-Pentane	0.0020	0.0021	0.0020
Hexane	0.0040	0.0040	0.0036
Heptane	0.0020	0.0019	0.0021
Toluene	0.0020	0.0016	0.0016
H_2O	0.0040	0.0084	0.0081
CO_2	0.1000	0.0633	0.0646
N_2	0.0010	0.0010	0.0010

Table-III: Actual gas sweetening plant-operating conditions.

Conditions	Lean solvent	Feed gas
Pressure [kg/cm^2]	58	58
Temperature [^oC]	45	38
Flow rate [kg_{mole}/hr]	661	500

IV. RESULTS AND DISCUSSION

It is known that there are many parameters [22] than can affect CO_2 removal efficiency from natural gas. The most important parameters that we will focus on during this study are; type of solvent used, solvent concentration, solvent circulation rate, absorber pressure and lean solvent temperature.

A. Solvent Concentration *and Circulation Rate*

The effect of variation in circulation rate of both DGA and DGA+PZ blend on the amount of captured CO_2 from natural gas stream is shown in Fig. 3 and 4 respectively.

Different concentrations of DGA were investigated; 45%, 50% and 55% at different circulation rates as low as 1000 kg_{mole}/hr. up to 4500 kg_{mole}/hr. According to Fig 3, the amount of captured CO_2 increases with the increase in the circulation rate. Moreover, at constant circulation rate, the purity of natural gas increases as the concentration of DGA increases. It was found that 3750 kg_{mole}/hr. is the minimum circulation rate required to achieve CO_2 content of less than 1% in natural gas. This was reached at DGA concentration of 55%. A further increase in the circulation rate above such limit will increase the cost without any gain in the specification of the produced natural gas.

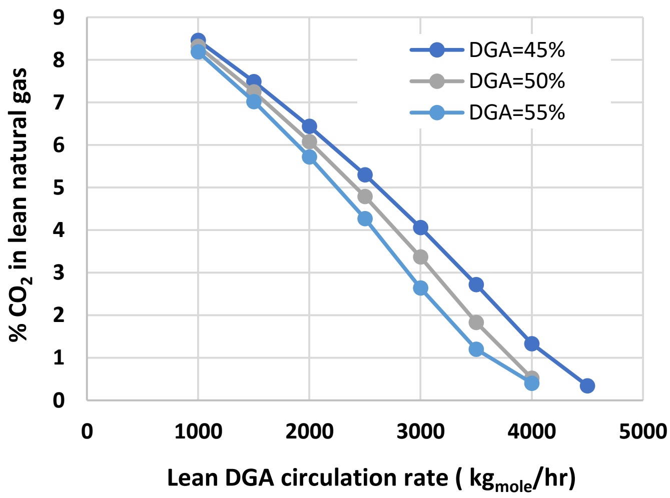

Fig. 3. The effect of DGA concentration variation at different circulation rate on the amount of CO_2 in natural gas (lean gas)

The addition of additives such as piperazine to amine-based solvents is believed to enhance the removal efficiency of CO_2 from natural gas streams. The variation of piperazine concentration (3, 5, 7, 9 and 11%) at constant DGA concentration of 55% was studied, see Fig. 4.

It was found that at constant circulation rate, the amount of absorbed CO_2 increases with the increase in the amount of added piperazine till 9% PZ concentration; above which no improvement in the purity of the natural gas could be found. Hence, the addition of PZ improves the CO_2 absorption efficiency until the reaction is no longer mass transfer limited, which is reached at solvent blend of 55% DGA and 9% PZ. The equilibrium partial pressure of CO_2 [22] is reduced by adding piperazine to the 55% DGA solvent.

According to Fig. 4, the amount of captured CO_2 increases with the increase in circulation rate. It was found that the minimum circulation rate obtained at 9% PZ + 55% DGA blend was 3250 kg_{mole}/h. At this circulation rate, the 1% CO_2 content limit was fulfilled at lower circulation rate compared to that reached when using 55% DGA solvent alone.

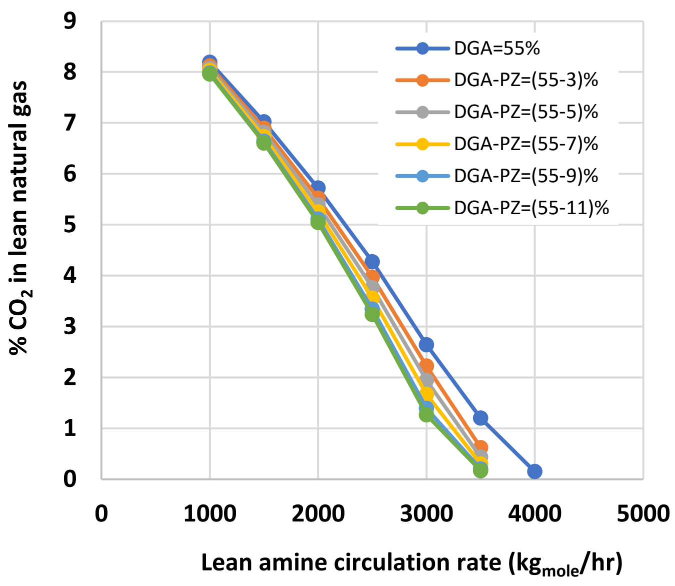

Fig. 4. The effect of PZ concentration variation in its solvent blend with 55% DGA at different circulation rate on the amount of CO_2 in natural gas (lean gas).

The greater the solvent circulation rate, the greater the amount of CO_2 that can be captured. However, there is a limit, as the circulation rate of lean amine is one of the important factors in the choice of chemical solvents. It influences the size of piping, pumps, regeneration tower and heat exchangers. The energy requirement for solvent regeneration depends on circulation rate as the reboiler heat duty increases with the increase in circulation rate [23]. So, circulation rate has great effect on the capital cost of the gas sweetening plant.

B. Lean Solvent Temperature

Both lean amine temperature and natural gas temperature are used to control the absorber temperature. In general, as the temperature in the absorber decreases, the absorber performance can be enhanced. In this study the effect of lean solvent temperature on the amount of CO_2 captured from natural gas is investigated. Different temperature ranges (38 ^oC to 80 ^oC) were tested for 55% DGA + 9% PZ solvent blend and 55% DGA alone at optimum circulation rate and constant pressure as shown on Fig. 5. Results show that, the sweet gas CO_2 content increases with the increase in lean amine temperature; this attributes to CO_2 solubility limitation. The CO_2 content crossed the limit of 1% CO_2 content in the sweet gas with the increase in temperature above 45 ^oC for both solvents under investigation. According to Fig. 5, at constant temperature, the performance of the PZ and DGA solvent blend is better than that of DGA alone. Lower CO_2 content was reached when using 9% PZ as an activator with 55% DGA compared to using 55% DGA solvent only at the same temperature. This makes adding PZ to DGA an attractive option. So, according to Fig. 5, 45^oC is the optimum temperature to conduct solvent extraction.

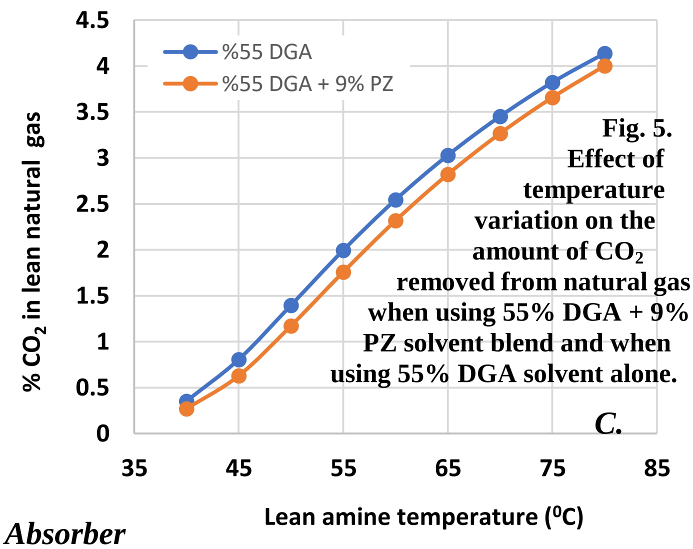

Fig. 5. Effect of temperature variation on the amount of CO_2 removed from natural gas when using 55% DGA + 9% PZ solvent blend and when using 55% DGA solvent alone.

C. Absorber Pressure

The absorber pressure was varied in the range from 45 kg/cm^2 to 80 kg/cm^2 for 9% PZ and 55% DGA solvent blend and for 55% DGA solvent alone. Results are shown in Fig. 6, in general, increasing the absorber pressure will slightly affect the carbon dioxide absorption efficiency. The higher the absorber pressure the lower the amount of CO_2 content in the sweet gas.

Pressure variation has a dual effect on CO_2 removal efficiency from sour gases. Reduction in column pressure will affect solvent volatility and as a result solvent loss to the gas phase will increase. In addition, the partial pressure of CO_2 will decrease with the decrease in the absorber pressure, hence, the reaction rate will be affected and the removal efficiency of CO_2 will decrease. In addition,

On the other hand, as the reaction rate decrease, the heat liberated from the reaction of CO_2 with the DGA/PZ solvent [21] will decrease causing the top temperature of the tower to decrease. This reduction in temperature is expected to compensate the effect of reducing pressure on solvent volatility.

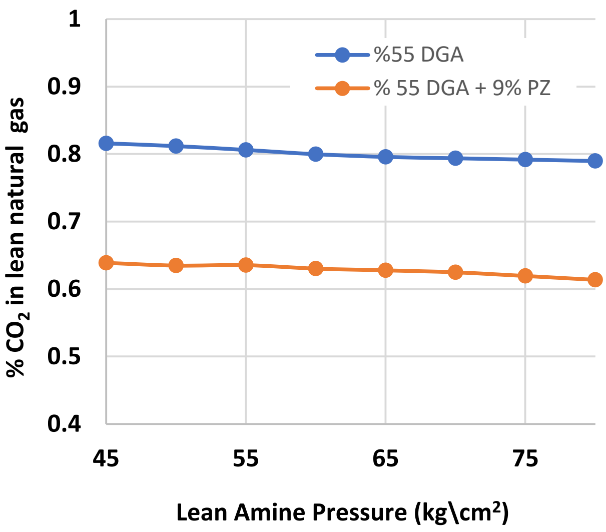

Fig. 6. Effect of pressure variation on the amount of CO_2 removed from natural gas using 55% DGA + 9% PZ solvent blend and when using 55% DGA solvent alone.

V. CONCLUSIONS

Amine absorption process for CO_2 removal can be enhanced by using piperazine as an additive to the diglycol amine (DGA) solvent. DGA and (DGA-PZ) mixture effects on removal of CO_2 have been studied and simulated using Hysys Simulation software. It is aimed at reducing the CO_2 content in natural gas from 10% to 1% by mole through solvent extraction. The effect of the solvent concentration variation and addition of PZ were studied. In addition, the effect of operating conditions variation such as circulation rate, solvent pressure and temperature on the amount of captured CO_2 were investigated. It was found that:

- At constant circulation rate, the amount of absorbed CO_2 increases with the increase in the amount of added piperazine to the 55% DGA solvent till 9% PZ concentration; above which, no improvement in the purity of the natural gas could be found.
- Increasing the circulation rate will increase the amount of captured CO_2. The optimum circulation rate at which the 1% CO_2 content limit was fulfilled are; 3750 kg_{mole}/hr in the case of using 55% DGA only and 3250 kg_{mole}/h in the case of 9% PZ + 55% DGA blend, which is lower than that of the 55% DGA solvent used without PZ.
- The carbon dioxide content in the sweet gas will increase with the increase in solvent temperature for both 9% PZ + 55% DGA solvent blend and 55% DGA alone. The maximum working temperature to achieve CO_2 content of less than 1% is 45 ^{o}C for both solvents. Any further increase in the temperature will increase the CO_2 content to more than 1% in the sweet gas.
- Adding 9% PZ to the 55% DGA solvent blend reduced the amount of CO_2 in the sweet gas compared to using 55% DGA solvent only at the same temperature. This makes adding PZ to DGA an attractive option.
- Increasing the absorber pressure will slightly affect the carbon dioxide absorption efficiency from natural gas. The higher the absorber pressure, the lower the amount of CO_2 content in the sweet gas.

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