CHEMICAL ENGINEERING TRANSACTIONS

VOL. 86, 2021

A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.cetjournal.it

Guest Editors: Sauro Pierucci, Jiří Jaromír Klemeš

ISBN 978-88-95608-84-6; **ISSN** 2283-9216

Performance Improvement of Gas Sweetening Units by Using a Blend of MDEA/PZ

Asma E. Etoumi[a], Mohamed R. Alhansh[a], Marwan M. Almabrouk [a], Mansour M. Emtir [a,*]

[a]Libyan Petroleum Institute, Gergarish Km7, P.O. Box 6432, Tripoli, Libya
m.emtir@lpilibya.com

This work investigates three gas sweetening units in Libya; particularly, Mellitah complex, Alestiklal, and Sahel gas plant. These units are designed mainly to use Methyl diethanolamine (MDEA) as a solvent for the removal of H_2S and CO_2 from the raw gas. Thus, the handling of higher gas production rates for the forthcoming years is a bottleneck without being upgraded. This work aims to increase throughput and reduce operating costs while maintaining the product quality of these units. HYSYS simulation was used to simulate the processes, assess the potential advantages of using a blend of MDEA and Piperazine (PZ), and investigate important parameters in the process. Results show that the MDEA/PZ blend provides high-performance as a gas treating solvent. The raw gas flow rate can be increased from 16,208 kmol/h to 18,820 kmol/h in the Mellitah complex with specs of 1.98 vol % CO_2 and 0.9915 ppm H_2S. In the Alestiklal gas plant, the flow rate can be increased from 8,012.79 kmol/h to 8,750 with specs of 0.975 Mole % CO_2. But Sahel gas plant had a different behaviour, where the addition of Piperazine led to deviation of H_2S from the required specification. The value of H_2S reached 25.944 ppm, and the percent of CO_2 was 1.347 Mole %. However, the decrease of the amine temperature reduces H_2S to 13.76 ppm and CO_2 to 1.276 Mole %. These results demonstrate the potential for significant improvements in increasing throughput via the use of PZ as an activator to the MDEA.

1.Introduction

Acid gas removal from natural gas is a crucial treatment process that is required to obtain a sweet gas with the required specifications of the sales gas. Many types of cleaning processes have been developed and tested for gas sweetening (Mokhatab et al., 2019). The most common method for removing CO_2 and H_2S from natural gas is by absorption into a mixed or pure amine solvent like monoethanolamine (MEA) and MDEA (Al-Lagtah et al., 2015). MDEA has several distinct advantages over primary and secondary amines. It has a lower vapor pressure, which allows the use of a higher concentration of MDEA in the absorber column that results in a lower circulation rate and consequently smaller plant size and lower plant cost (Islam and Habib, 2018). The lower miscibility of MDEA with hydrocarbons results in a negligible loss of the hydrocarbons. It also has a lower heat of reaction, higher resistance to degradation, fewer corrosion problems, and selectivity toward H_2S in the presence of CO_2. Although MDEA alone can be used for bulk CO_2 removal at high pressure, its reaction rate with CO_2 is slow. Activated MDEA in aqueous solutions are quite often used as solvents (Schultes, 2018). An activator such as PZ used to enhance the kinetic reaction rate between CO_2 and MDEA. The thermal degradation rates for MDEA and PZ are negligible, and PZ, unlike other metals, protects MDEA from oxidative degradation. This increased stability of the MDEA/PZ blends over MDEA and other amine solvents (Alvis et al., 2012).
Improving the performance of the sweetening units by the use of selective amines, and MDEA has been reported in the literature. Jassim (2016) performs sensitivity analysis and optimization of a gas sweetening plant for H_2S and CO_2 capture using MDEA solutions. The sensitivity analysis results showed that the circulation rate and the MDEA concentration are the two main factors improving process performance. Kheirinik et al. (2018) evaluate the efficiency of the MDEA and DEA at various mass concentrations. Abotaleb et al. (2018) evaluate the

performance parameters for acid gas removal systems in terms of energy and utility consumptions for single amines and MDEA/PZ amine blend with different concentrations. The reliability and robustness of Aspen Hysys software have been reported for MDEA gas sweetening plant that selectively captures H_2S in the presence of CO_2 (Jassim, 2016), and for CO_2 removal from natural gas using Di-glycol amine and PZ (El-Maghraby et al., 2019). This study explores the possibility of improving the performance of the amine treating plant in Libya by adding PZ to the MDEA. Three Libyan gas sweetening units in the Mellitah complex, Alestiklal, and Sahel gas plants are investigated and simulated using Aspen HYSYS.

2. Industrial Case Studies

2.1. Mellitah complex sweetening unit

The gas sweetening unit has been designed for removing H_2S and CO_2 from the raw gas using MDEA as a solvent. It consists of three parallel identical absorption trains, in addition to the amine storage and recovery unit. In this case, it is desired to increase the inlet gas flow rate from 48,624 to 54,788 kmol/h, where each train will carry 18,263 kmol/h. The feed condition and its composition is shown in Tables 1 and 2. The required specifications of the sweet gas stream are 2 vol % of CO_2 and 5 ppm of H_2S.

Table 1: Sweetening unit conditions of Mellitah plant

Stream Name	Raw Gas	Lean Amine
Flow rate/ train, kmol/h	16,208	39,848
Pressure, bar	40	41
Temperature, ˚C	27	49.35
MDEA (wt %)	-	50

Table 2: Raw gas composition data – Mellitah plant

Component	Mole %	Component	Mole %
H_2O	0.017	n-Butane	0.799
Nitrogen	5.000	i-Pentane	0.296
CO_2	13.255	n-Pentane	0.254
H_2S	1.159	n-Hexane	0.079
Methane	71.355	n-Heptane	0.110
Ethane	4.724	n-Octane	0.030
Propane	2.475	n-Nonane	0.005
i-Butane	0.442	MDEA	0.000

2.1.1. Simulation and results–Mellitah plant

In this work, the sweetening unit was simulated using Aspen HYSYS. The fluid package which is selected and used for all the simulations and calculations reported in this paper is acid gas -chemical solvent. Figure 1 shows the process flow diagram of the sweetening unit. In the first scenario, the case was simulated for a total gas flow rate of 48,624 kmol/h without and with the addition of PZ to MDEA. Simulation results show that by adding 0.2 % PZ to 49.8 % MDEA, the absorption efficiency increased, and the reboiler duty slightly decreased in the base case. This finding is consistent with Islam and Habib, 2018. However, when the raw gas flow rate per train increased from 16,208 to 18,263 kmol/h, the CO_2 content in the sweet gas increased to 2.14 vol %.

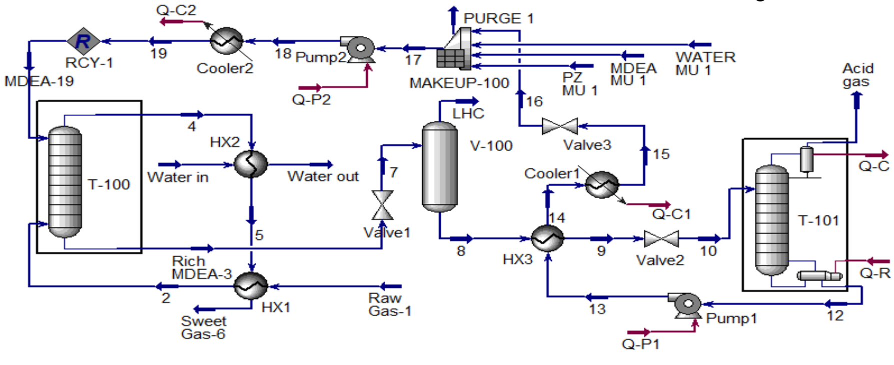


Figure 1: Process flow diagram for Mellitah sweetening unit by Aspen HYSYS software

To solve the problem of deviating from the required specifications, two scenarios are implemented; the first was adding PZ to the amine solution with a concentration of 0.2 wt % PZ, 49.8 wt % MDEA and 50 wt % H_2O. This concentration was chosen to allow more CO_2 to be absorbed and offset the amine degradation over time (Islam and Habib, 2018). The second scenario was to add a fourth absorption train so that the new flow rate is divided into four trains, each train carrying about 13,697 kmol/h. The maximum value of the raw gas flow rate that can be reached within the required specifications for different scenarios is also calculated as shown in Figure 2. The results of the second scenario, which illustrated in Table 3, show that the CO_2 and H_2S content in the sweet gas decreased by adding the PZ to the MDEA and the reboiler duty slightly decreased.

Table 3: Sweet gas compositions and plant duties – Mellitah plant

Scenarios	Base case -3 trains		Upgrade flow -3 trains		Upgrade flow -4 trains	
Solvent	MDEA	MDEA + PZ	MDEA	MDEA + PZ	MDEA	MDEA + PZ
H_2O, Mole %	0.398	0.393	0.401	0.422	0.395	0.391
Nitrogen, Mole %	5.763	5.847	5.715	5.749	5.797	5.856
CO_2, Mole %	1.516	0.091	2.283	1.685	1.007	0.006
H_2S, ppm	0.108	0.0437	0.147	1.244	0.0807	0.026
Methane, Mole %	82.03	83.23	81.36	81.85	82.48	83.32
Ethane, Mole %	5.417	5.496	5.374	5.406	5.444	5.499
Propane, Mole %	2.839	2.880	2.817	2.833	2.853	2.882
i-Butane, Mole %	0.508	0.515	0.503	0.507	0.510	0.516
n-Butane, Mole %	0.915	0.928	0.908	0.913	0.920	0.929
i-Pentane, Mole %	0.295	0.299	0.297	0.298	0.291	0.294
n-Pentane, Mole %	0.243	0.246	0.246	0.247	0.239	0.240
n-Hexane, Mole %	0.060	0.061	0.063	0.063	0.055	0.056
n-Heptane, Mole %	0.012	0.014	0.025	0.026	0.001	0.001
n-Octane, Mole %	0.000	0.000	0.000	0.000	0.000	0.000
n-Nonane, Mole %	0.000	0.000	0.000	0.000	0.000	0.000
Flow rate kmol/h	14,052	13,851	15,970	15,876	11,803	11,684
Reboiler duty, 10^8 kJ/h	6.528	6.490	6.473	6.476	6.551	6.629
Condenser, 10^8 kJ/h	3.482	3.493	3.490	3.496	3.479	3.473
Cooler1 duty, 10^8 kJ/h	1.272	1.312	1.255	1.278	1.292	1.355
Cooler2 duty, 10^7 kJ/h	8.715	8.136	8.381	8.060	8.851	8.964
Pump1 10^5 kJ/h	8.617	8.642	8.634	8.646	8.610	8.604
Pump2 10^6 kJ/h	6.553	6.546	6.549	6.545	6.554	6.555

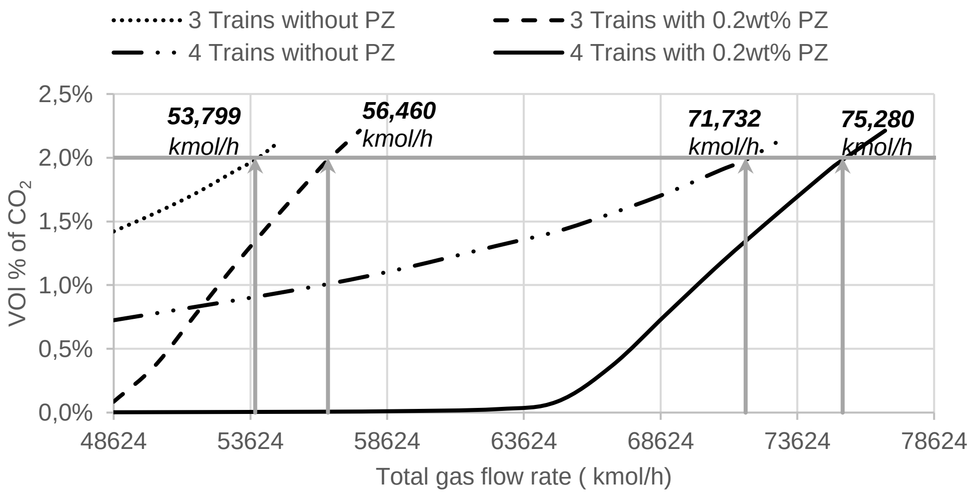


Figure 2: Raw gas flow rate vs. CO_2 concentration (vol %) in the sweet gas stream for different scenarios

2.2. Alestiklal sweetening unit

The sweetening unit in the Alestiklal plant has been simulated in Aspen HYSYS with the specifications given in Tables 4 and 5. The Aspen HYSYS process flow diagram is shown in Figure 3. This case aims to investigate the effect of the use of PZ as an additive on the MDEA solution, which is already used to sweeten the raw gas. The effect of the inlet gas flow rate on acid gas concentration in sweet gas was also investigated. The required specifications in the Alestiklal sweetening unit are 1 Mol % of CO_2 and 5 ppm of H_2S in the sweet gas.

Table 4: Conditions of Alestiklal sweetening unit streams

Stream Name	Raw Gas	Lean Amine Solution	Sweet Gas
Flow rate, kmol/h	8,013	20,284.25	7,107.53
Pressure, bar	56.12	60.47	55.16
Temperature, ˚C	59.72	65.94	66.45
MDEA (wt %)	0.0	50	0.0

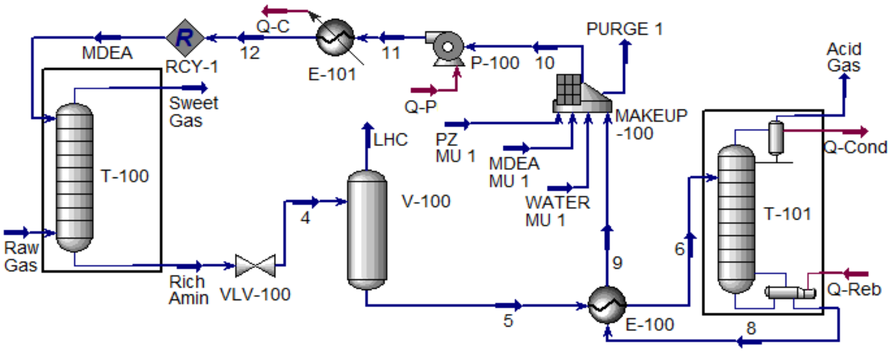


Figure 3: Process flow diagram for Alestiklal sweetening unit by Aspen HYSYS software.

Table 5: Raw gas composition – Alestiklal plant

Component	Mole %	Component	Mole %
Nitrogen	0.200	n-Butane	0.800
CO_2	11.00	i-Pentane	0.500
H_2S	0.000	n-Pentane	0.300
Methane	74.20	n-Hexane	0.400
Ethane	8.100	n-Heptane	0.300
Propane	2.700	n-Nonane	0.200
i-Butane	0.800	H_2O	0.500

2.2.1. Simulation and results–Alestiklal plant

Table 6 shows the simulation results for the Alestiklal case before and after adding PZ to the lean amine. It is clear that adding PZ to MDEA with 0.2 wt % PZ to 49.8 wt % MDEA reduces the CO_2 concentration in the outlet gas stream from the absorption tower. On the other hand, it increases the regenerator duties requirements by 4 %. The effect of changing the raw gas flow rate on the molar composition of CO_2 in the sweet gas was also investigated. The maximum value of the gas flow rate under the required specifications is 8,765 kmol/h.

Table 6: Sweet gas composition and duties requirement- Alestiklal plant.

Scenarios	1	2
Solvent	MDEA	MDEA + PZ
CO_2 concentration, Mole %	0.695	0.047
H_2S concentration, Mole %	0.000	0.000
Reboiler duty 10^8 kJ/h	1.420	1.480
Condenser duty 10^7 kJ/h	6.723	7.000
Pump duty 10^6 kJ/h	5.039	5.040
Cooler duty 10^7 kJ/h	7.213	7.500

2.3. Sahel complex sweetening unit

Figure 4 shows the process flow diagram for the Sahel treating unit. The raw gas stream, which fed to two trains, is contacted counter- currently with three streams of an aqueous amine solution in a trayed absorber. Acid gases are absorbed into the solvent that is flashed, heated and then fed to the top of the regeneration tower. Stripping steam produced by the reboiler causes the acid gases to desorb from the amine solution as it passes down the column. Lean amine solution is cooled and recycled back to the absorber. The required specifications in the Sahel sweetening unit were 1.8 Mole % of CO_2 and 5 ppm of H_2S in the sweet gas. The objective of this case was to establish the feasibility of utilizing a blend of MDEA/PZ to replace the MDEA in the gas sweetening unit when the inlet gas stream has a low concentration of CO_2.

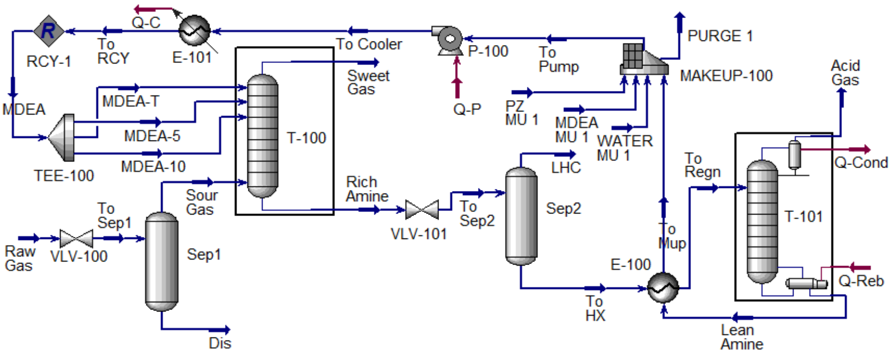


Figure 4: Process flow diagram for Sahel sweetening unit by Aspen HYSYS software.

Table 7: Molar composition of Sahel raw gas stream

Component	Mole %	Component	Mole %
Nitrogen	0.100	n-Butane	0.560
CO_2	2.420	i-Pentane	0.000
H_2S	0.630	n-Pentane	0.560
Methane	52.850	n-Hexane	0.260
Ethane	3.260	n-Heptane	0.790
Propane	1.420	n-Nonane	0.000
i-Butane	0.420	H_2O	36.730

Table 8: Conditions of Sahel sweetening unit streams

Stream Name	Raw Gas	Lean Amine	Sweet Gas
Flow rate, kmol/h	5,900	2,534.019	3,608.51
Pressure, bar	69.98	54.44	46.19
Temperature, ˚C	37.77	47.7	64.85
MDEA (wt %)	0.0	50	0.0

2.3.1. Simulation and results–Sahel plant

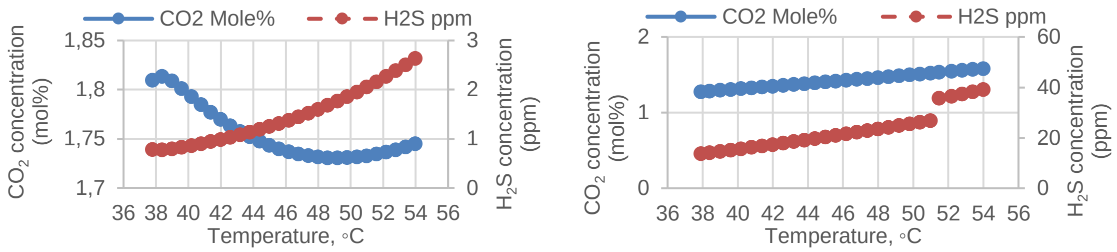
Table 9 shows the simulation results for the sweetening unit in the Sahel gas plant before and after adding the PZ to MDEA solution in a concentration of 0.2 wt % PZ, 49.8 wt % MDEA, and 50 wt % H_2O. When the MDEA/PZ amine blend was used, the concentration of CO_2 in sweet gas was reduced by 22 %, the concentration of H_2S increased from 2.739 to 25.944 ppm, and the reboiler duty increased by 6 %. Adding PZ to MDEA allows more CO_2 to be absorbed which tends to displace the H_2S.

Table 9: Sweet gas composition and duties requirement- Sahel plant

Scenarios	1	2	3	4
Solvent	MDEA	MDEA + PZ	MDEA	MDEA + PZ
Lean amine temperature, ˚C	53.89	53.89	42.78	42.78
CO_2 concentration, Mole %	1.745	1.347	1.755	1.129
H_2S concentration, ppm	2.739	25.945	1.0976	14.481
Recirculation rate m^3/h	78.024	78.085	78.024	78.085
Reboiler duty 10^7 kJ/h	2.830	2.990	2.84	3.08
Condenser duty 10^7 kJ/h	1.070	1.190	1.08	1.26
Pump duty 10^5 kJ/h	4.910	4.909	4.90	4.90

To increase the absorber performance and reduce the concentration of H_2S in the sweet gas, the lean-solvent temperature was reduced and tested for 49.8 MDEA + 0.2 % PZ solvent blend and 50 wt % MDEA alone. Figure

5(a) shows reducing the lean-solvent temperature to 37.89 °C causes a decrease in sweet gas compositions of H_2S and an increase in CO_2 Mole %. Results in Figure 5(b) show that the sweet gas H_2S and CO_2 contents decrease with the decrease in lean-amine temperature. It can be seen that although the lean-solvent temperature reduced, the H_2S content in the sweet gas still crossed the limit of 5 ppm. Therefore, when the target is sweetening, MDEA alone should be the first choice (Abotaleb et al., 2018).



(a) Before adding Piperazine (b) After adding Piperazine

Figure 5: Effect of lean solvent temperature on sweet gas composition.

3. Conclusions

CO_2 absorption in the gas-sweetening units of Mellitah complex, Alestiklal, and Sahel gas plants using aqueous solutions containing MDEA and PZ as blends components have been investigated and compared to the absorption in standalone MDEA solutions at similar concentrations. Results show that MDEA/PZ blend with 49.8 wt % / 0.2 wt % has a better absorption capacity than MDEA. The mass of the absorbed CO_2 in PZ and MDEA aqueous solution is much higher than that in MDEA aqueous solution. The concentration of H_2S in the sweet gas was within the required specifications in the Mellitah complex and the Alestiklal gas plant. In the Sahel case, the performance of the MDEA solvent alone was better than that of the MDEA/PZ amine blend. Results show that although adding PZ to MDEA improves CO_2 absorption efficiency, H_2S concentration in the sweet gas crossed the specification limit of 5 ppm, and the reboiler duty increased by 8 %. H_2S concentration in sweet gas reduced by decreasing the lean amine temperature (MDEA/PZ amine blend) from 25.9 to 14.5 ppm. Other operational parameters and process modifications that could help in enhancing recovery of acid gas and saving energy will be investigated in future work.

References

Abotaleb A., El-Naas M. H., Amhamed A., 2018, Enhancing gas loading and reducing energy consumption in acid gas removal systems: A simulation study based on real NGL plant data, Journal of Natural Gas Science and Engineering, 565-574.

Al-Lagtah N. M.A., Al-Habsi S., Onaizi S. A., 2015, Optimization and performance improvement of Lekhwair natural gas sweetening plant using Aspen HYSYS, Journal of Natural Gas Science and Engineering, 376-381.

Alvis R. S., Hatcher N. A., Weiland R. H., 2012, CO_2 removal from syngas using piperazine-activated MDEA and potassium dimethyl glycinate, Nitrogen+Synagas 2012, 20-23 February 2012, Athens, Greece.

El-Maghraby R. M., Salah A. A., Shoaib A. M., 2019, Carbon dioxide capturing from natural gas using di-glycol amine and piperazine – A new solvent mixture, International Journal of Recent Technology and Engineering (IJRTE), 11378-11383.

Islam N., and Habib M., 2018, Comparative study on the effect of acid gas cleaning by MDEA vs. Methyl diethanolamine + Piperazine as a solvent using Aspen Hysys, International Journal of Science, Engineering and Technology Research (IJSETR), 147-153.

Jassim M. S., 2016, Sensitivity analyses and optimization of a gas sweetening plant for hydrogen sulfide and carbon dioxide capture using methyl diethanolamine solutions, Journal of Natural Gas Science and Engineering, 175-183.

Kheirinik M., Rahmanian N., Farsi M., Garmsiri M., 2018, Revamping of an acid gas absorption unit: an industrial case study, Journal of Natural Gas Science and Engineering, 534-541.

Saeid M., William A. Poe W. A., John M., 2019, Handbook of natural gas transmission and processing- Principles and Practices, 4th Edition, Elsevier.

Schultes M., 2018, Designing CO_2 absorption columns with activated amine solutions, Chemical Engineering Transactions, 69, 133-138.