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Simulation studies on natural gas sweetening using Piperazine amine

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Abstract
This work aims at studying acid gas removal from natural gas with piperazine (PZ) amine by using Aspen HYSYS V9.0. Design of acid gas removal process is explained using sensitivity analysis. Plant capacity enhancement studies are performed by considering the crucial parameters like sour gas feed rate, amine recirculation rate and regenerator reboiler duty etc. The optimum feed temperature is identified as 31^0C. Optimum concentration and flow rate of amine is 30 wt% and 350 m^3/hr respectively. Rigorous hydraulic studies are performed for absorber to know the operational issues like flooding and weeping in the column. Arranging the packing in the absorber solved the operational issues and improved the CO_2 and H_2S removal efficiencies by 58% and 20% respectively. By arranging packing revenue losses are minimized by 2.1%. The techno-economic analysis results of this study are useful for process engineers working in gas plants to take reasonable decisions in operating the gas plant.

Keywords: *Acid gas; Gas plant; Hydraulic studies; Natural gas; Sensitivity analysis; Process Simulation; Gas Sweetening.*

1. Introduction

The worldwide market for liquefied petroleum gas (LPG) and natural gas liquids (NGL) is continuously increasing [1]. Presence of H_2S, CO_2, mercaptans, CS, elemental sulfur and contaminated water decreases the quality of sales gas and their presence is not acceptable, since they corrodes the equipment, pipelines and release in to atmosphere leads to acid rains [2]. Chemical solvents, physical solvents, adsorption processes, hybrid solvents and physical separations especially membranes are the available acid gas removal techniques [3]. According to the environmental regulations the acceptable limits for H_2S and CO_2 are 4 ppm and 2 mole % respectively.

Aspen HYSYS V9.0 acid gas removal model supports various amines in its data base [4]. Continuous investigations are going on to invent the new efficient amines and their blends for efficient removal of CO_2 from gas mixtures. Piperazine is one of the amine [5]. Bishnoi *et al.* [6] conducted modelling experiments and revealed that the carbon dioxide removal rate is more for PZ amine compared to the other amines like MDEA, MEA, DEA and their blends. Kinetic studies by [7], VLE studies by [8], absorption studies by [9-11], high pressure absorption studies by [12] concluded that piperazine in alone and in combination with methyldiethanolamine has reported improved absorption rates of CO_2 from aqueous solutions. Aqueous solutions containing piperazine is used as washing agent for removing H_2S, CO_2 and COS present in natural gas, coke-oven gases, and synthesis gases [13]. Configurations and methods of acid gas removal to meet the pipe line requirements are explained by [14]. A process for removal of H_2S and CO_2 from an acid gas stream is explained by [15-16] using various amines.

Silhavy *et al.* [17] provided simulation based operational data base for acid gas removal plant. The author [18-20] conducted numerical simulation and optimization studies using process simulators like Aspen HYSYS. In their studies they used diethanol amine for acid gas removal. Similarly, the autors [21-22] used MEA. Pellegrini *et al.* [23] used diethanolamine (DEA) and methyldiethanolamine (MDEA), Kazemi *et al.* [24] used mixed amines and checked the feasibility of the process by improving the acid gas removal efficiency.The authors [25-26] tested impact of operating conditions like absorption temperature, pressure, number of absorber trays and solvent recirculation rate on acid gas removal are tested to identify the optimum conditions. The authors [27-28] identified optimum conditions from the steady state and dynamic studies and these observations are useful for safety and economy of the processes. Øi *et al.* [29] tested alternative flow sheet arrangements in improving the acid gas removal rates. Zare Aliabad *et al.* [30] used MDEA and DEA amines in combined form and studied the effect of major operating parameters like operating pressure of the absorber column, temperature of the amine, sour gas feed rate and morpheme efficiency, on the rate of absorption and on energy point of view [31]. Optimization studies are conducted by [32] for optimum absorber working pressure to get 99% purity of the methane.

The above studies motivated the present research to do acid gas removal using piperazine (PZ) amine from natural gas. Objective of this work is to analyse the effect of process parameters like amine temperature, feed gas flow rate on acid gas removal and to check the role of column hydraulic studies in improving the acid gas removal efficiency and feasibility. This work is useful for process engineers to optimize their gas processing units and to take decisions on retrofit studies.

2. Process description

Equipment involved in the Aspen HYSYS V 9.0 acid gas cleaning simulation model are: extractor, absorber, separator, rich amine heater, regenerator, lean amine cooler, booster pump and makeup operation. Process flow sheet is shown in figure 1. In the extractor contaminants are removed by passing the acid gas through the amine solution. In the absorber sour gas is passed through the bottom and the lean amine enters from the top of the absorber as a result of absorption, sweet gas comes out from the top of the absorption column and the rich amine comes out from the bottom part of the absorber. Rich amine obtained from the absorber column bottom, is send to the separator. In the separator low hydrocarbons are removed and the remaining rich amine is send to the regenerator. In the regenerator, sufficient heat is provided by the reboiler for the separation of impurities present in the amine solution. Separated hydrogen sulfide (H_2S) and carbon dioxide (CO_2) are sent for processing. Losses in amine quantities are makeup using the make-up block.

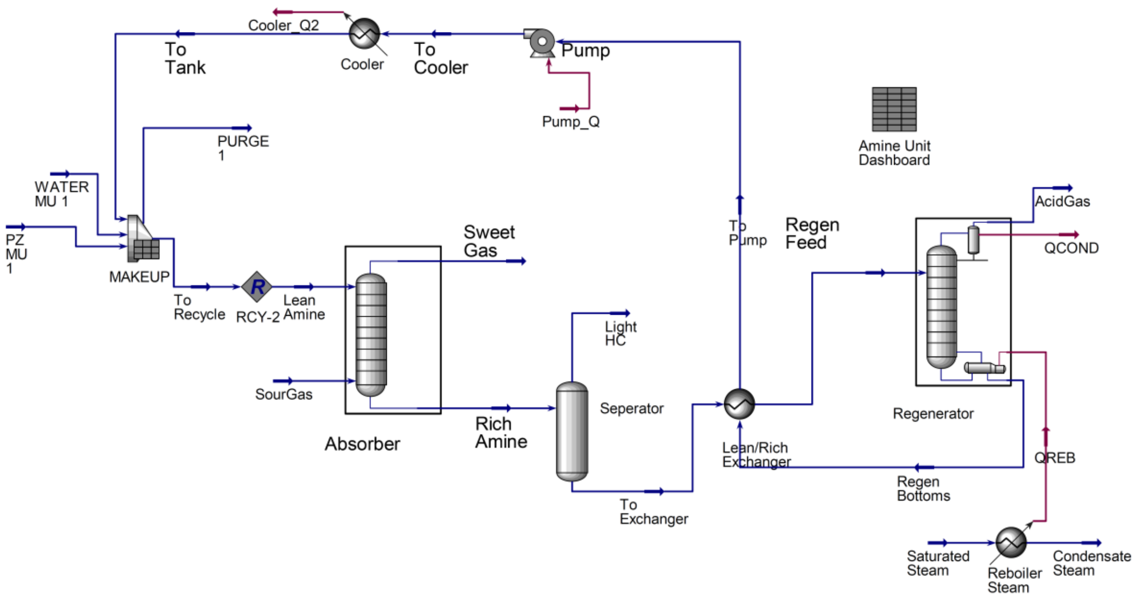

Figure 1. Aspen HYSYS acid gas cleaning flow sheet

3. Process simulation

The flow sheet for natural gas sweetening using PZ was developed in Aspen HSYS V9.0. The fluid package used in this study is acid gas cleaning package. The composition of the sour gas is given in table 1. The design capacity of this process plant is 1128 m^3/hr or 1.703×10^5 barrel/day. Sour gas feed enters at 40^0C and 20 bar pressure is feed to the bottom of the absorber.

Absorber contains 20 number of stages. Lean amine is entering the top of the absorber and its concentration is 30 wt% and temperature 42^0C. Lean amine temperature is higher than the sour gas temperature. When the sweetening process is completed and the regenerated piperazine (PZ) is recycled back to the absorber, Aspen HYSYS recalculates the actual operating composition. In makeup block aspen HYSYS, ADJUST operation is the inbuilt operation and it adjusts the circulation rate of lean amine.

Table 1. Feed gas composition of sour gas

Component	Mole fraction	Component	Mole fraction
CO_2	0.0202	Ethane	0.0707
H_2S	0.0202	Nitrogen	0.0303
Methane	0.8656		

Sensitivity analysis studies are conducted using various process parameters like feed gas flow rate, feed gas temperature, amine recirculation rate to calculate the composition of the acid gases in sweet gas. Desirable concentrations of CO_2 and H_2S in sweet gas will be maintained by optimizing the reboiler duty and the recirculation rate of the amine in the surge tank. Hydraulic studies for the absorber are conducted to improve the performance of absorber. Packing material is used as a substitute for trays to avoid the hydraulic problems in the column. Acid gas removal and the economic study values of the both tray column and packed column are compared.

4. Results and discussion

4.1. Effect of PZ amine concentration

Increasing concentrations of PZ amine in lean amine stream positively affected the acid gas removal. Figure 1 illustrates the effect of varying concentrations of PZ on extraction of CO_2 and H_2S. From 10 to 30 wt% of PZ amine concentration, acid gas removal is good. It indicates the desired concentration of PZ is 30 wt%. At 30 wt% of PZ concentration, acid gas concentration in sweet gas is 1.51×10^{-4} mole% for CO_2 and 0.0198 ppm for H_2S.

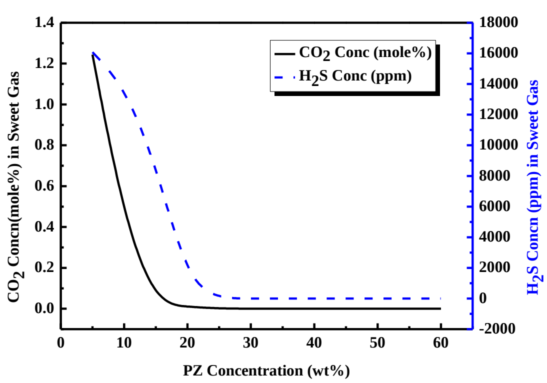

Figure 1. Effect of PZ concentration on acid gas concentration in sweet gas

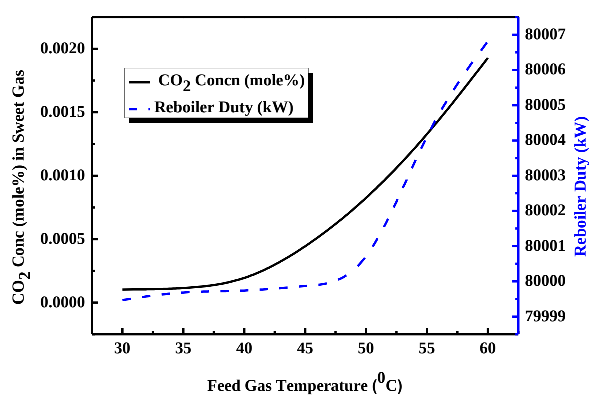

Figure 2. Effect of feed gas temperature on CO_2 concentration in sweet gas

4.2. Effect of feed gas temperature

Plant behaviour is predicted for various temperatures of the feed gas. Temperature is varied from 30⁰C to 60⁰C. Observed parameters are CO_2 and H_2S concentrations in sweet gas. As the feed gas temperature is increased from 30⁰C to 60⁰C, CO_2 and H_2S concentrations are increased in sweet gas and the reboiler duty also increased.

Reboiler duty remains constant between 35⁰C to 40⁰C. Beyond 40⁰C reboiler duty increased to higher values, it shows that acid gas cleaning demands more reboiler duties. From figure 2 and from figure 3 the optimum temperature range for acid gas cleaning is in between 35⁰C to 40⁰C.

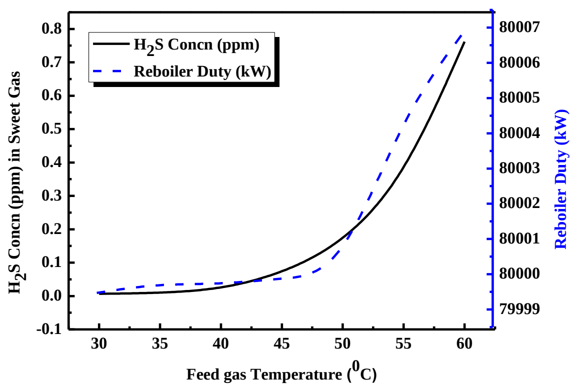

Figure 3. Effect of feed gas temperature on H_2S concentration in sweet gas

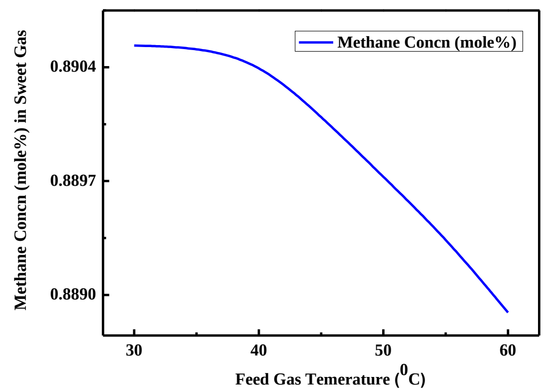

Figure 4. Effect of feed Gas temperature on methane concentration in sweet gas

Increasing temperatures decreased the concentrations of methane in sweet gas. Figure 4 illustrates that methane concentration is constant with temperature of the feed gas in between 30⁰C and 35⁰C. Maximum concentration of methane i.e 89 mole% is observed at 30⁰C.

4.3. Effect of feed gas flow rate

Effect of feed gas rate on acid gas concentration in sweet gas is illustrated in figure 5. CO_2 concentration in sweet gas increased 3.8×10^{-6} mole % to 6.87×10^{-5} mole %. It is evident that CO_2 concentration is increased nearly ten times. At the same time H_2S concentration decreesed from 0.93 ppm to 0.41 ppm. For feed gas flow rate of 35000 kg/hr, H_2S and CO_2 concentrations are optimum and their values are: CO_2 concentration is 4.32×10^{-5} mole% and the H_2S concentration is 1 ppm.

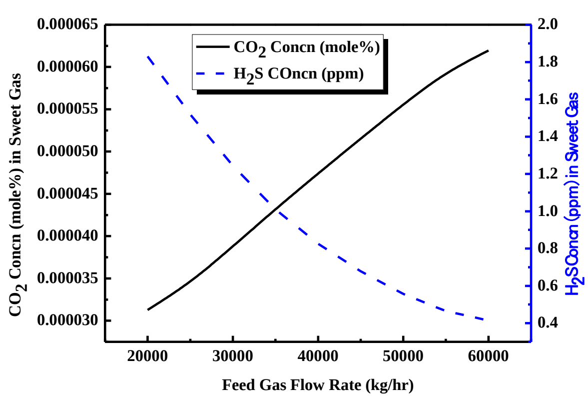

Figure 5. Effect of feed gas flow rate on acid gas concentration in sweet gas

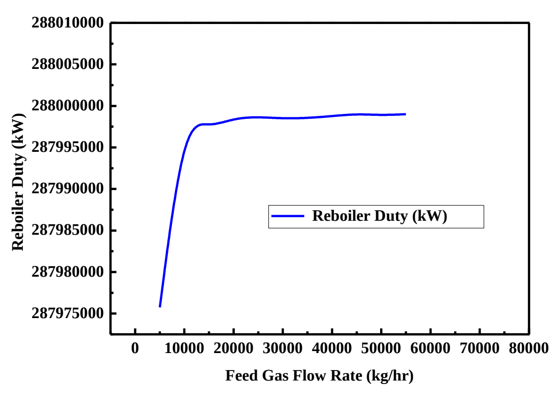

Figure 6. Effect of feed gas flow rate on reboiler duty (kW)

Effect of feed gas rate on reboiler duty is given in figure 6. For feed gas flow rate of 5000 kg/hr reboiler duty is 2.879×10^8 kW and it is the minimum reboiler duty recorded. Reboiler duty is constant from the 20000 kg/hr to 55000 kg/hr. In this region CO_2 concentration is from 3.13×10^{-5} mole% to 5.94×10^{-5} mole% and the H_2S concentration is from 1.83 ppm to 0.46 ppm.

4.4. Effect of lean amine recirculation rate

Lean amine recirculation rate is changed from 284.65 m^3/hr to 641.18 m^3/hr and it is shown in figure 7. Increased amine recirculation rates decreased the concentration of H_2S in sweet gas. Increased amine recirculation rates increased the reboiler duties. Minimum reboiler duty observed is 2.878×10^8 kW.

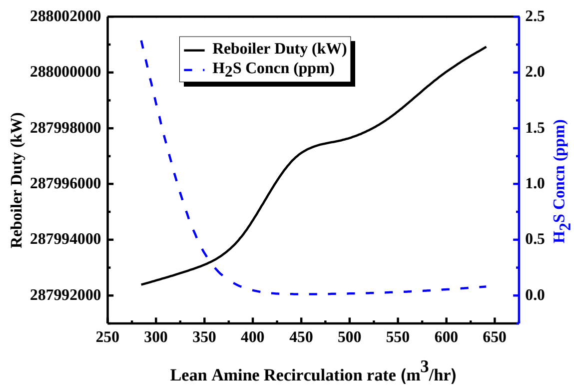

Figure 7. Effect of amine recirculation rate on reboiler duty

4.5 Absorber hydraulic studies

Hydraulic studies of absorber are performed for two cases. First case is absorber fitted with trays and the second case is absorber fitted with packing material. Absorber fitted with trays is considered as the base case. Base case hydraulic plots are illustrated in figure 9.

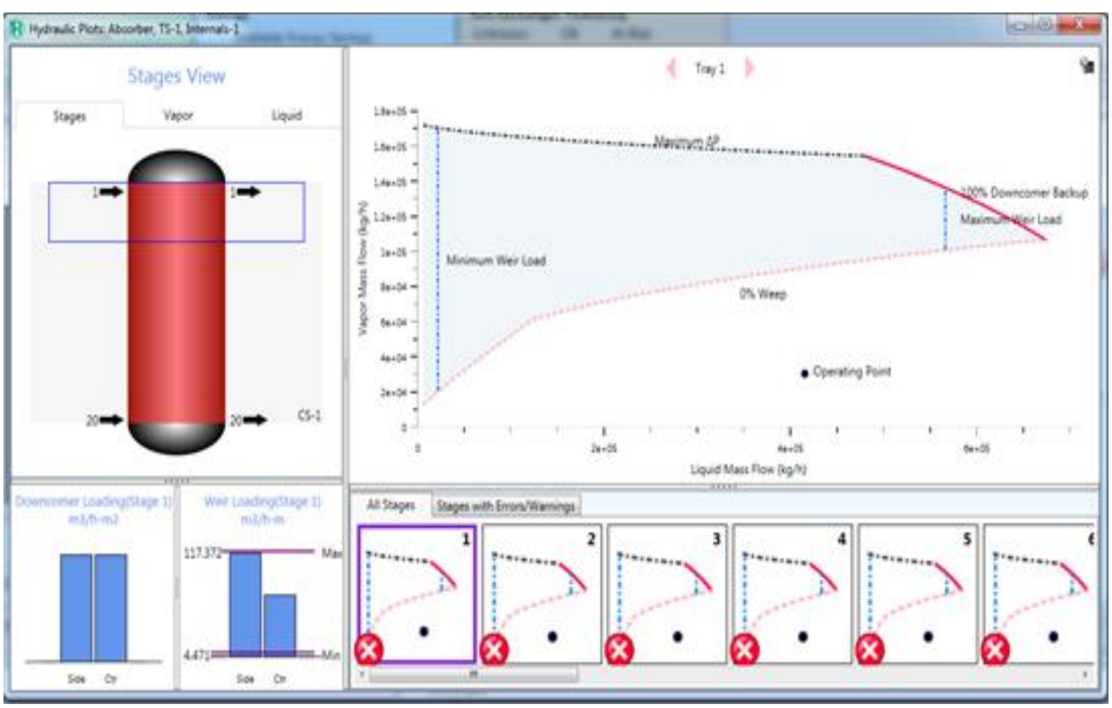

Figure 9. Hydraulic profile of absorber fitted with trays

Area under the plot gives the operating area of the tray column and it shows operating issues existing in the column. General operating issues are flooding and weeping. For stage 1 of the absorber hydraulic plot is shown in figure 10. The upper limit curve indicates the maximum pressure drop allowable in the column. The minimum limit curve indicates the minimum pressure drop allowable in the column. Area between the upper limit curve and the lower limit curves gives the absorber operation area.

Operation conditions reaching the upper point indicates the increased pressure drop in the column, it shows flooding in the column. Operation conditions reaching the minimum point in the plot indicates the weeping in the column.

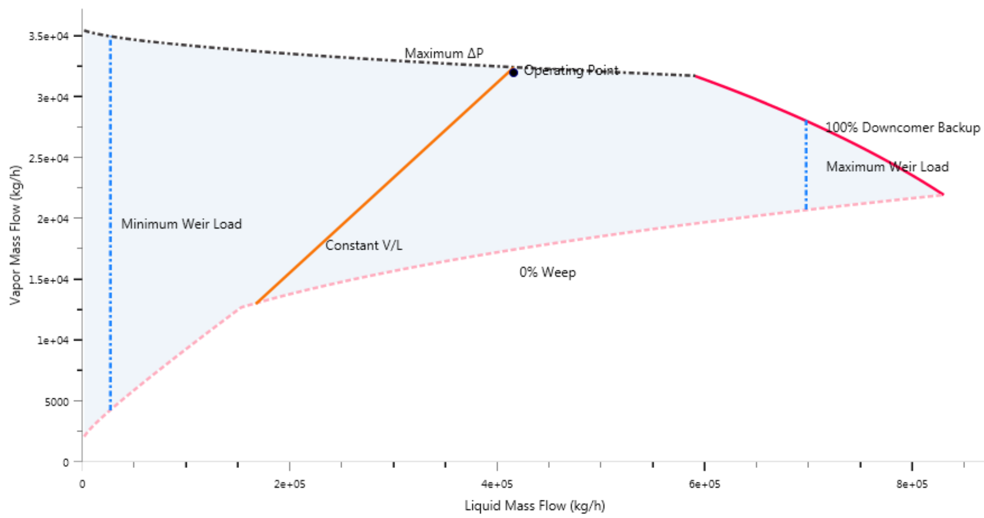

Figure 10. Hydraulic plot for stage 1 of the absorber fitted with trays

In figure 10, operating point reached the upper curve. It indicates flooding is present in the column and it reduces the efficiency of the column. Flooding should be avoided and this operating issue is solved by arranging packing material in the absorber. Trays are replaced with packing material of type raching ring made up of ceramic material. Size of the raching ring is 1 inch. Hydraulics of absorber filled with packing material is shown in figure 11.

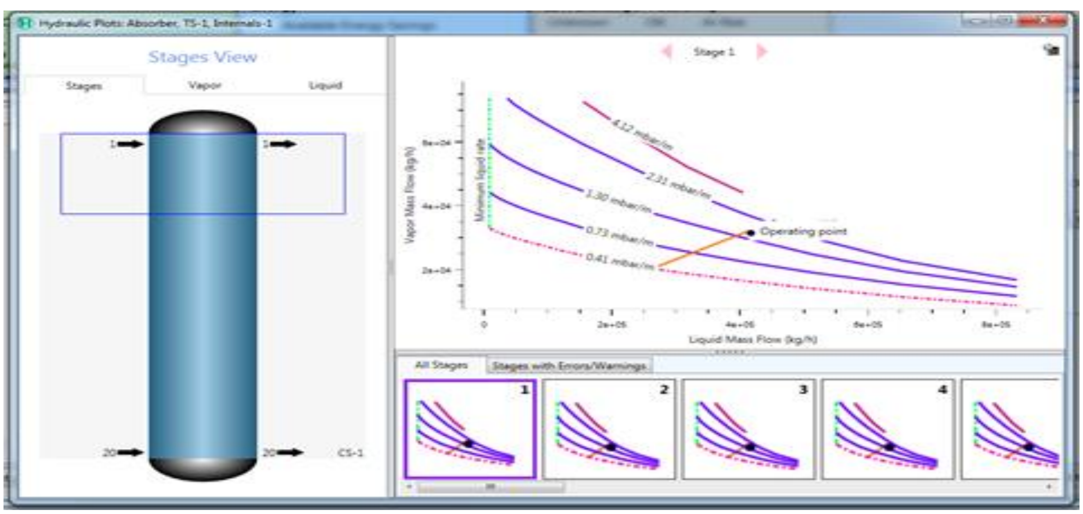

Figure 11. Hydraulics of packed column

It is observed that there are no operational issues for absorber filled with packing material. Absorber filled with packing material eliminated the operation issues of all stages in the column. Figure 12 shows the hydraulic plot of first stage of the absorber with packing material.

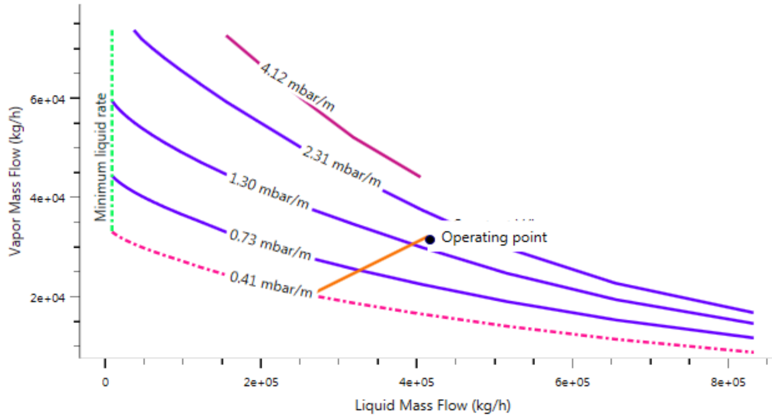

Figure 12. Hydraulic plot for packing column

Operating point is present in between the maximum pressure drop of 4.12 mbar/m and lower operating pressure of 0.41 mbar/m for the first stage of the column. Similarly the same pattern is observed for the remaining stages. The reason for improved operation is packing material provided more contact area for Vapour-Liquid contacting simultaneously it decreased the re-boiler duty demands. Results of the absorber column without operating issues are used for design calculations of the absorber. Absorber design data for rigorous rating calculations is given in Table 2.

Table 2. Absorber design data for rating calculations

Parameter	Values
Section Starting Stage	1
Section Ending Stage	20
Column diameter [m]	2.496
Packed Height Per Stage [m]	0.5
Section Height [m]	10.0
Maximum % Capacity (Constant L/V) [%]	80
Maximum Capacity Factor [m/s]	0.01645
Section Pressure Drop [mbar]	84.2
Average Pressure Drop / Height [mbar/m]	8.4
Average Pressure Drop / Height (Frictional) [mbar/m]	7
Maximum Stage Liquid Holdup [m^3]	0.49
Maximum Liquid Superficial Velocity [m^3/h-m^2]	84.37
Surface area [m^2/m^3]	190
Void Fraction	0.74
1st Stichlmair Constant	2.24
2nd Stichlmair Constant	3.24
3rd Stichlmair Constant	2.728

In table 3, acid gas removal and economics results of both base cases i.e tray column and packed column are given. CO_2 concentration is reduced from 1.56×10^{-4} mole% to 6.192×10^{-5} mole%, which shows 58% improvement in CO_2 recovery. H_2S concentration is reduced from 0.3868ppm to 0.3094 ppm indicates 20% improvement in H_2S removal from the natural gas. Arranging packing in the column reduced the total cost by 2.1%.

Table 3. Absorber comparison table

	Tray column	Packed column
Capital cost (USD)	98 323 200	96 183 500
Operating Cost(USD)	28 368 600	27 772 859
CO_2 (mole%)	1.56×10^{-4}	6.192×10^{-5}
H_2S (ppm)	0.3868	0.3094

5. Conclusions

Acid gas removal of natural gas using piperazine (PZ) amine is studied. Effect of feed gas flow rate, temperature, amine concentration and effect of amine recirculation rate on acid gas removal are studied. Effect of amine recirculation rate on reboiler duty is observed. Rigorous hydraulic studies are performed and the packed column design data is tabulated. Absorber operational efficiency is improved by improving the acid gas removal rates. CO_2 removal enhanced by 58% and the H_2S removal enhanced by 20%. Economic performance improved by 2.1%. The methodology and the results of this study are useful for process engineers those who are using piperazine (PZ) amine or other amines for the acid gas removal in their acid gas cleaning plants.

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References

[1] Kumar S, Kwon H. T, Choi K. H, Cho J. H, Lim W, Moon I. Current status and future projections of LNG demand and supplies: A global prospective, Energy Policy, 2011; 39(7): 4097-4104.
[2] Moore CW, Zielinska B, Petron G, Jackson R. B. Air impacts of increased natural gas acquisition, processing, and use: a critical review, Environmental science & technology, 2014; 48(15): 8349-8359.
[3] Ebenezer SA, Gudmunsson JS. Removal of carbon dioxide from natural gas for LNG production, Semester project work, 2005.
[4] AspenTech Knowledge base
[5] Munoz DM, Portugal AF, Lozano AE, José G, de Abajo J. New liquid absorbents for the removal of CO_2 from gas mixtures, Energy & Environmental Science, 2009; 2(8): 883-891.
[6] Bishnoi S, Rochelle GT. Absorption of carbon dioxide in aqueous piperazine/methyldiethanolamine, AIChE Journal, 2002; 48(12): 2788-2799.
[7] Zhang X, Zhang CF, Qin SJ, Zheng ZS. A kinetics study on the absorption of carbon dioxide into a mixed aqueous solution of methyldiethanolamine and piperazine, Industrial & engineering chemistry research, 2001; 40(17): 3785-3791.
[8] Xu G. W, Zhang CF, Qin SJ, Gao WH, Liu HB. Gas– Liquid Equilibrium in a CO_2 - MDEA-H_2O System and the Effect of Piperazine on it, Industrial & engineering Chemistry research, 1998; 37(4): 1473-1477.
[9] Samanta A, Bandyopadhyay SS. Absorption of carbon dioxide into piperazine activated aqueous N-methyldiethanolamine. Chemical engineering journal, 2011; 171(3), 734-741.
[10] Samanta A, Bandyopadhyay SS. Kinetics and modeling of carbon dioxide absorption into aqueous solutions of piperazine. Chemical Engineering Science, 2007; 62(24), 7312-7319.
[11] Bishnoi S, Rochelle GT. Absorption of carbon dioxide into aqueous piperazine: reaction kinetics, mass transfer and solubility, Chemical Engineering Science, 2000; 55(22): 5531-5543.
[12] Kadiwala S, Rayer AV, Henni A. High pressure solubility of carbon dioxide (CO_2) in aqueous piperazine solutions, Fluid Phase Equilibria, 2010;292(1): 20-28.
[13] Appl M, Wagner U, Henrici HJ, Kuessner K, Volkamer K, Fuerst E. Method for neutralizing a stream of fluid, and washing liquid for use in one such method, U.S. Patent No. 4,336,233, 1982.
[14] Mak J. Configurations and methods of acid gas removal, U.S. Patent No. 7,637,987, 2009.
[15] Brok TJ, van der Zwet GP. Process for removal of hydrogen sulphide and carbon dioxide from an acid gas stream, U.S. Patent No. 8,765,086, 2014.
[16] Schubert CN, Frank TC. Regeneration of acid gas-containing treatment fluids, U.S. Patent No. 8,303,685, 2012.
[17] Silhavy B, Erdos L, Mizsey P, Koczka K, Szanyi A, Mika L, Benko T. Generation of Simulation Based Operational Database for an Acid Gas Removal Plant with Automatic Calculations, Periodica Polytechnica. Chemical Engineering, 2016; 60(1):24-28.
[18] Gutierrez JP, Benitez LA, Ruiz ELA, Erdmann EA. sensitivity analysis and a comparison of two simulators performance for the process of natural gas sweetening, Journal of Natural Gas Science and Engineering, 2016; 31: 800-807.

[19] Abdulrahman R, Sebastine IM. Natural gas sweetening process simulation and optimization: a case study of the Khurmala field in Iraqi Kurdistan, WIT Transactions on Engineering Sciences, 2012; 81: 37-46.

[20] Elfattah STA, Eldrainy YA, Attia A. Numerical Simulation to Optimize Di-Ethanol-Amine (DEA) Strength for Achieving the Highest Methane Purity from Biogas, Int. J. Adv. Sci. Tech. Res, 2015; 4(5):742-751.

[21] Sanggie FW. Process Modeling And Comparison Study Of Acid Gas Removal Unit by Using Different Aqueous Amines, Doctoral dissertation, UMP, 2011.

[22] Qiu, K, Shang JF, Ozturk M, Li TF, Chen SK, Zhang LY, Gu XH. Studies of methyldiethanol-amine process simulation and parameters optimization for high-sulfur gas sweetening, Journal of Natural Gas Science and Engineering, 2014; 21: 379-385.

[23] Pellegrini LA, Moioli S, Picutti B, Vergani P, Gamba S. Design of an acidic natural gas purification plant by means of a process simulator, Chemical Engineering Transactions, 2011; 24: 271-276.

[24] Kazemi A, Malayeri M, Shariati A. Feasibility study, simulation and economical evaluation of natural gas sweetening processes–Part 1: A case study on a low capacity plant in Iran, Journal of Natural Gas Science and Engineering, 2014;20:16-22.

[25] Qiu K, Zhu L, Bagajewicz M, Kim SY, Ozturk M. A simulation study on the impact of operating conditions on desulphurisation selectivity in high-sulphur gassweetening, International Journal of Oil, Gas and Coal Technology, 2013; 6(3): 348- 366.

[26] Abdulrahman R, Sebastine I. Effect of lean amine temperature on amine gas sweetening: case study and simulation, Chemistry and Technology of Fuels and oils, 2013; 49(4): 293-297.

[27] Pouladi B, Hassankiadeh MN, Behroozshad F. Dynamic simulation and optimization of an industrial-scale absorption tower for CO_2 capturing from ethanegas, Energy Reports, 2016; 2:54-61.

[28] Al-Lagtah NM, Al-Habsi S, Onaizi SA. Optimization and performance improvement of Lekhwair natural gas sweetening plant using AspenHYSYS, Journal of Natural Gas Science and Engineering, 2015; 26: 367-381.

[29] Øi L. E, Brathen T, Berg C, Brekne S. K, Flatin M, Johnsen R, Thomassen E. Optimization of configurations for amine based CO_2 absorption using Aspen HYSYS, Energy Procedia, 2014; 51: 224-233.

[30] Zare Aliabad H, Mirzaei S. Removal of CO_2 and H_2S using aqueous alkanolamine solutions, World Academy of Science, Engineering and Technology, 2009; 49(1):194-203.

[31] Angaji MT, Ghanbarabadi H, Khodabandehlo H. Study and examining the processing parameters on function of MDEA and DEA solvents for measuring removal units of CO_2 and H_2S, European Journal of Experimental Biology,2013; 3(3):609-616.

[32] Elfattah STA, Eldrainy YA, Attia A. Utilization of Aspen HYSYS simulation to determine the optimum absorber working pressure needed to achieve more than 0.99 methane purity from Egyptian biogas, International Journal of Information Research and Review, 2016; 3:1739-1744.

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