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A NEW APPROACH IN THE SIMULATION AND CALIBRATION OF THE AMINE REGENERATOR COLUMNS

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Abstract

The sour gases coming from gas reservoir or oil refinery units contain acidic non-hydrocarbon components, such as hydrogen sulfide and carbon dioxide which can increase the problems caused by corrosion, hydrate formation, SO_2 emission and environmental pollution in the oil and gas refineries to reduce the amounts of CO_2 and H_2S below the technical and environmental standards. Amine process is considered as the most common process in the oil and gas refineries. Performing a reliable simulation of the regenerator column is a key point for improving the design and optimization of amine sweetening units. In this paper, the regenerator column of an industrial Amine sweetening unit is simulated by ProMax software. Then, the accuracy of the results is checked by industrial data, and a new method is presented to calibrate the simulation. The achieved results reveal the capability of this method for accurate simulation of the amine sweetening units.

Keywords: *Amine sweetening unit, Regenerator column, Simulation, Calibration, Hydrogen sulfid.*

1. Introduction

Natural gas is considered as the most important and attractive fossil fuel in terms of lower emission compared to the other fossil fuels and ease of use. However, the sour gas coming from the well usually contains some non-hydrocarbon components, such as hydrogen sulfide and carbon dioxide which can arise several problems, e.g. corrosion, hydrate formation, and environmental pollution [1-2]. Moreover, the sour gases in the oil refineries usually contain considerable amounts of hydrogen sulfide which burning such gas as fuel will increase the emission of SO_2 to the atmosphere and rise environmental problems. Therefore, the gas treatment for removing impurities, such as CO_2 and H_2S, is one of the main parts of gas and oil refineries [3]. The concentration of H_2S and CO_2 in the natural gas stream must be kept below 4 ppm and 2 mol%, respectively [4-5]. There are several processes to remove acid gases from sour gases, for instance, solid bed process, and chemical solvent process. Among them, Amine process is considered as the most common process in the oil and gas refineries. Alkanamines such as monoethanolamine (MEA) and diethanolamine (DEA) and methyl-diethanolamine (MDEA) possess a high affinity to chemically absorb acid gases [6].

In a conventional amine sweetening unit, firstly CO_2 and H_2S of sour gas coming from the gas reservoir or oil refinery units are absorbed by amine solution in the absorber column (see Figure 1). The rich amine leaves the bottom of the absorber column and sent to the flash drum to release trapped hydrocarbons in lower pressure. Then, the rich amine after passing through the lean/rich heat exchanger enters the regenerator column in which the absorbed CO_2 and H_2S gases are released and leave the top of the regenerator column. The lean amine leaves the bottom of the regenerator column and then cooled in the lean/rich heat exchanger and Amine cooler and pumped and recycled to the top of the absorber column. The sweet gas leaves the top of the absorber column and sent to downstream units for more treatment if needed [7].

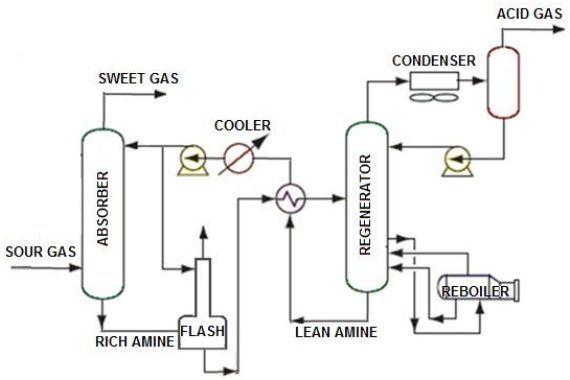

Figure 1. Schematic diagram of a typical amine sweetening unit

Since as described above, the absorber and regenerator columns are the most important equipment in the amine sweetening unit, the simulation, and modeling of amine absorption/desorption columns for natural gas sweetening process have been studied for decades [8]. As a result, two main methods, i.e., equilibrium and mass transfer, are developed to simulate the amine sweetening columns which identified by their accuracy and fast calculations, respectively [9]. These models are applied in the commercial simulation software such as Aspen, ProMax, etc. and used for design and optimization of the amine units. However, the results achieved from the commercial software usually include some deviations from actual data and need to be tuned and calibrated [10-15]. In the next section, a regenerator column of a typical Amine sweetening unit is simulated by ProMax software, and the accuracy of the results is checked by industrial data. Then, the achieved results are corrected by means of a new approach for calibration of the amine regenerator column.

2. Regenerator column simulation and calibration

In order to investigate the ability of the ProMax software for simulation of the regenerator column, a typical regenerator column in an industrial amine sweetening unit is considered. The specifications of the rich amine, which is considered as the regenerator column feed, are given in table 1. Moreover, Table 1 shows the specifications of acid gas leaves the top of the column, and lean amine leaves the bottom of the column. The considered regenerator column has 23 valve trays, and the duty of reboiler is equal to 22.12 MW. By means of this duty, the amounts of residual CO_2 and H_2S in the lean Amine are decreased to 0.01 mole% (188.6 mg/L) and 0.03 mole% (141.6 mg/L), respectively.

Table 1. Specifications of the input and output streams of regenerator column

	Rich amine	Acid gas	Lean amine
Temperature, °C	377	328	406
Pressure, kPa	340	210	260
Molar flow, kmole/h	11 000	471	10 529
Composition			
CO_2	2.34	54.49	0.01
H_2S	1.63	37.42	0.03
H_2O	85.27	7.63	88.74
MDEA	10.74	0.00	11.22
CH_4	0.02	0.47	0.00

The simulation of the amine regenerator column has been performed by ProMax software developed by BR&E company, which is a proper software for simulation of the Amine sweetening units [16]. In the simulation of a separation column, a solution is reached when all equations used to describe the steady state condition of that column, i.e., MESH equations, are solved and converged. These equations involve [17]: Material balance equations; Equilibrium equations; Summation equations; Heat balance equations.

The rigorous computational methods presented to solve these equations can be divided into four major groups:

1. The bubble-point methods (BP)
2. The sum-rates methods (SR)
3. The 2N Newton methods
4. The global Newton or simultaneous correction (SC) methods

Further classifications include:

5. Inside-out methods
6. Relaxation methods
7. Homotopy-continuation methods
8. Non-equilibrium models

Among them, items 5, 6, and 7 are modified forms of the first four methods in order to solve difficult systems. The non-equilibrium models are rate-based methods that instead of efficiencies, applying mass transfer correlations [17].

In the BP methods, the stage temperatures are found directly from solving the bubble-point equation. While, in the SR methods, the energy balances are used to adjust the stage temperatures. In the 2N Newton's methods, the temperatures and total flow rates are solved with each other, but compositions are calculated separately. Contrary to these three methods, in the SC method, the MESH equations and variables are solved simultaneously. Ishii and Otto method is considered as SC methods and has been used by ProMax software to solve the tower equations [17].

There are two general approaches for design and simulation of separation columns [15-19], (1) Applying overall efficiency to convert the theoretical stage numbers to real required tray numbers. The following relation can be considered:

$$Teoritical\ Stage\ Numbers = Overal\ Efficiency \times Real\ Tray\ Numbers \quad (1)$$

(2) Using real required tray numbers and applying component efficiencies for each tray. The Murphree efficiency of the tray j is defined as below:

$$E_i = \frac{y_{i,j} - y_{i,j-1}}{y^*_{i,j} - y_{i,j-1}} \quad (2)$$

wherein, $y_{i,j}$ is the mole fraction of component i in the vapor leaving the tray j. The star sign indicates the equilibrium condition.

Some commercial softwares such as Aspen-Hysys suppose component efficiencies for CO_2 and H_2S, while the others such as ProMax suppose component efficiencies equal to 100% and suggest using overall efficiency for simulation of separation columns. The conventional overall efficiency for Amine regenerator column is supposed to be equal to 50 percent [15-17].

Since this study is performed using the ProMax software, the simulation of the considered Amine regenerator column is performed firstly by considering an overall efficiency equal to 50 percent for this column. Therefore, the number of theoretical stages set equal to 12 ($23 \times 0.5 \approx 12$). "TSWEET Alternate Stripper" model is used as a distillation calculation procedure which does not take column hydraulic into consideration. The degree of freedom for running the regenerator column is equal to 2. As mentioned above, by setting the condenser temperature equal to 50°C and reboiler duty equal to 22.12 MW, the simulation can be executed. The achieved results presented in Table 2 shows that there is not a significant error in the predicted values for compositions of CO_2 and H_2S in the acid gas stream. On the other hand, the calculated values of the residual CO_2 and H_2S in the lean Amine have considerable errors.

Table 2. The composition of acid gas and lean amine streams in the first simulation

Stream		CO_2	H_2S
Acid gas composition, %mol	Actual	54.04	37.51
	Simulation	54.49	37.42
	Error %	0.52	0.66
Lean amine composition (mg/L)	Actual	183.96	143.61
	Simulation	111.28	326.07
	Error %	39.51	127.05

Since the amounts of residual CO_2 and H_2S in the lean amine can affect on the performance of the amine absorbers, a good prediction of them will be an important factor in the simulation of amine sweetening units [20]. Therefore, in the next step, a mixed approach is used by applying

both mentioned efficiencies, i.e., overall efficiency together with component tray efficiency. According to the information presented in Table 2, the predicted value for the residual CO_2 gas in the lean amine is less than its actual value (111.28 compared to 183.96). Conversely, the predicted value for the residual H_2S gas in the lean amine is more than its actual value (326.07 compared to 143.61). More release of H_2S from amine solution and therefore, a decrease of the residual H_2S in the lean amine stream can be expected by increasing the efficiency of CO_2 in the regenerator column. For this purpose, a case study is performed in which the influence of decreasing the CO_2 efficiency on the concentration of the CO_2 and H_2S in the acid gas and lean amine streams leaving the regenerator column was studied. The results of this case study are summarized in Table 3. Moreover, the changes in residual H_2S and CO_2 in the lean amine vs. CO_2 efficiency is presented in Figure 2. As is shown in this figure, the decrease of the CO_2 efficiency decreases the residual H_2S and increases residual CO_2, simultaneously. In accordance with the information presented in Table 3, when the efficiency of CO_2 is equal to 70%, the amount of residual H_2S reaches to 144.07 mg/L which is near to its actual value, i.e., 143.61 mg/L.

Table 3. The influence of decreasing the CO_2 efficiency on the concentration of the CO_2 and H_2S

Efficiency (%)		Acid gas (mol %)		Lean amine (mg/L)	
CO_2	H_2S	CO_2	H_2S	CO_2	H_2S
100	100	54.49	37.42	111.28	326.07
85	100	54.32	37.58	194.12	233.35
70	100	54.14	37.77	318.22	144.07
55	100	53.94	37.96	487.73	71.34
40	100	53.75	38.15	704.02	26.35

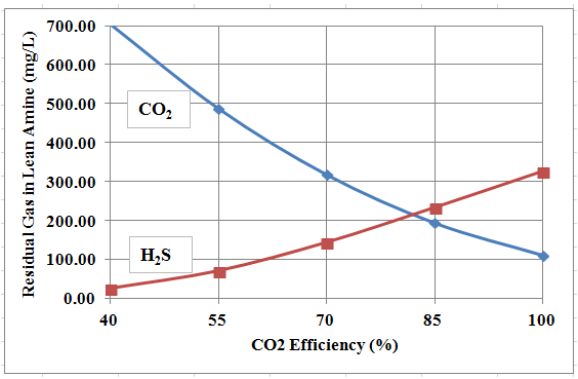

Figure 2. The changes of residual H_2S and CO_2 in the lean amine vs. CO_2 efficiency

The results of the second simulation in which the CO_2 efficiency is supposed to be equal to 70%, are presented in Table 4. As indicated in this table, the absolute error of CO_2 composition in the acid gas stream is decreased from 0.52% in the first simulation to 0.12% in the second simulation. Furthermore, the error of H_2S is decreased from 0.66% to 0.26%. On the other hand, although the absolute error of H_2S composition in the lean amine stream is decreased considerably from 127% in the first simulation to 0.32% in the second simulation, the difference between calculated and actual values of residual CO_2 in the lean amine stream is increased in the second simulation rather than the first run. This increase is due to the assumption of an efficiency lower than 100% for CO_2 in the regenerator column, which causes less CO_2 to be released.

Table 4. The composition of acid gas and lean amine streams in the second simulation

Stream		CO_2	H_2S
Acid gas composition, %mol	Actual	54.04	37.51
	Simulation	54.14	37.77
	Error %	0.12	0.26
Lean amine composition (mg/L)	Actual	183.96	143.61
	Simulation	318.22	144.07
	Error %	72.98	0.32

By increasing the number of stages in the regenerator column, disengaging of the CO_2 will be enhanced. Therefore, the effect of changing tray numbers or overall efficiency on residual CO_2 in the lean Amine is investigated in the next step of this work. The results of this case

study are presented in table 5. Moreover, the changes of residual H_2S and CO_2 in the lean amine vs. tray numbers (overall efficiency) has been shown in Figure 3.

Figure 3 reveals that desorption of H_2S occurs mostly thermodynamically and has not affected by adding the number of trays. On the other hand, desorption of CO_2 occurs kinetically and is increased by adding the number of trays in the regenerator column (the residual CO_2 is decreased by increasing the number of trays). According to the information presented in table 5, when regenerator column has 16 trays in the simulation (i.e., overall efficiency is equal to 16/23 ≈ 70%), the amount of residual CO_2 reaches to 180.04 mg/L which is near to its actual value, i.e., 183.96 mg/L.

Table 5. The influence of changes in overall efficiency on the concentration of the CO_2 and H_2S

Overall efficiency	Equilibrium tray No	Acid gas (mol%)		Lean amine (mg/L)	
		CO_2	H_2S	CO_2	H_2S
43	10	54.09	37.81	420.42	160.84
52	12	54.14	37.77	318.22	144.07
61	14	45.19	37.72	239.25	140.69
70	16	54.22	37.68	180.04	141.36
78	18	54.25	37.65	136.32	142.79

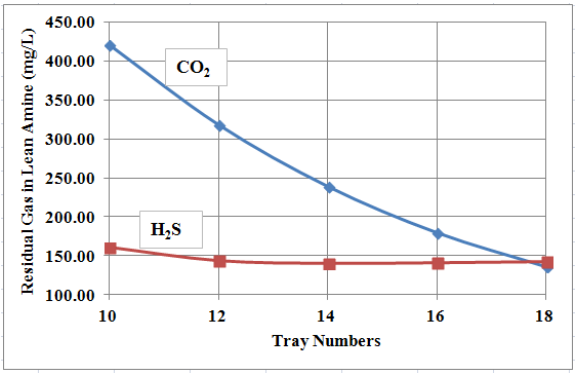

Figure 3. The changes of residual H_2S and CO_2 in the lean amine vs. tray numbers

The results of the third simulation in which both of the CO_2 efficiency and overall efficiency are supposed to be equal to 70%, are presented in table 6. As indicated in this table, the absolute errors of CO_2 and H_2S composition in the acid gas stream have more improvement in the third simulation rather than the second one. The absolute error of CO_2 composition in the lean amine stream is decreased from 39% in the first simulation and 73% in the second simulation to 2% in the third simulation which is in good agreement with industrial data can be considered as a satisfactory result. Although the error of calculated H_2S has a bit increase in the third simulation rather than the second simulation, since the total errors of the simulation are significantly decreased, it can be ignored.

Table 6. The composition of acid gas and lean amine streams in the third simulation

Stream		CO_2	H_2S
Acid gas composition, %mol	Actual	54.04	37.51
	Simulation	54.22	04
	Error %	0.03	0.26
Lean amine composition (mg/L)	Actual	183.96	143.61
	Simulation	180.04	141.36
	Error %	2.13	1.56

3. Conclusions

Amine process is considered as a common process in the oil and gas refineries to reduce the amounts of the acid gases from natural and fuel gases to overcome operational as well as environmental problems. Performing a reliable simulation of the regenerator column is a key point for improving the design and optimization of Amine sweetening units. Therefore, an industrial regenerator column was considered and simulated by ProMax software. Checking the simulation results with industrial data shows significant errors in the residual CO_2 and H_2S of lean Amine stream. A new approach was presented to adjust and calibrate the achieved

results by means of applying overall efficiency and component efficiency concepts simultaneously. By considering the overall efficiency of the regenerator column equal to 70% and also, component efficiency of CO_2 equal to 70%, the total error of simulation was minimized, and the satisfactory results were achieved.

References

[1] Mohamadbigy Kh, Bazmi M, Behradi R, Binesh R. Amine absorption column design using mass transfer rate simulation. Petroleum & Coal, 2005; 47(2): 39-46.

[2] Hafizi A, Koolivand-Salooki M, Janghorbani A, Ahmadpour A, and Moradi MH. An Investigation of Artificial Intelligence Methodologies in the Prediction of the Dirty Amine Flow Rate of a Gas Sweetening Absorption Column. Petroleum Science and Technology, 2014; 32: 527-534.

[3] Mandal BP, and Bandyopadhyay SS. Simultaneous absorption of carbon dioxide and hydrogen sulfide into aqueous blends of 2-amino-2-methyl-1-propanol and diethanolamine. Chemical Engineering Science, 2005; 60(22): 6438-6451.

[4] Stewart M, and Arnold K. Gas Sweetening and Processing Field Manual, Gulf Professional Publishing, Waltham, 2011.

[5] Nourmohamadi Taemeh A, Shariati A, and Khosravi Nikou MR. Analysis of energy demand for natural gas sweetening process using a new energy balance technique, Petroleum Science and Technology, 2018; 36(12): 827-834.

[6] Saghatoleslami S, Salooki M K, and Mohamad N., Auto-Design of Neural Network–Based GAs for Manipulating the Khangiran Gas Rfinery Sweetening Absorption Column Outputs. Petroleum Science and Technology, 2011; 29: 1437-1448.

[7] Anonymous. Gas Processors Suppliers Association (GPSA). Engineering Data Book, GPSA, Tulsa, Chapter 22, 1987.

[8] Kohl AL, and Nielsen RB. Gas purification. 5th. Ed. Gulf Publishing Company, Houston, 1997.

[9] Danckwerts PV. Gas absorption accompanied by chemical reaction. AIChE Journal, 1995; 1(4): 456–463.

[10] Øi LE, and Kvam SHP. Comparison of energy consumption for different CO_2 absorption configurations using different simulation tools. Energy Procedia, 2014; 63: 1186-1195.

[11] Øi LE. Comparison of Aspen HYSYS and Aspen Plus simulation of CO_2 absorption into MEA from atmospheric gas. Energy Procedia, 2012; 23: 360-369.

[12] Garciaa M, Knuutilab HK, Gu K. ASPEN PLUS simulation model for CO_2 removal with MEA: Validation of desorption model with experimental data. Journal of Environmental Chemical Engineering, 2017; 5: 4693-4701.

[13] Gervasi J, Dubois L, Thomas D. Simulation of the post-combustion CO_2 capture with Aspen HysysTM software: study of different configurations of an absorption regeneration process for the application to cement flue gases. Energy Procedia, 2014; 63: 1018-1028.

[14] Alkatheri M, Grandas R, Betancourt-Torcat A, Almansoori A. Tapping Singular Middle Eastern Ultrasour Gas Resources Combining Membrane and Absorption Systems: Potential for Energy Intensity Reduction. Ind. Eng. Chem. Res., 2018; 57(17::5748-5763

[15] Mahdipoor HR, Dehghani A. Feasibility study of a sulfur recovery unit containing mercaptans in lean acid gas feed. Journal of Natural Gas Science and Engineering, 2016; 31: 585e588.

[16] Mahdipoor HR, Ghorbani A, Hamidnia M Kh. Technical Investigation of Integrated Gas Sweetening and Enrichment Process. Petroleum Research, under publication, 2018.

[17] Kister HZ. Distillation Design, McGraw-Hill, New York, 1992.

[18] Mahdipoor HR, Shirvani M, Jafari Nasr MR, Shakiba S. Rigorous dynamic simulation of an industrial tray column, considered liquid flow regime and efficiency of trays. Chemical Engineering Research and Design, 2007; 85(8): 1101–1111.

[19] Manning FS, Thompson RE. Oil field processing of petroleum, Volume One: Natural gas, Pennwell Publishing Company, Tulsa, Oklahoma, 1991.
[20] Mahdipoor HR. The influence of acid gas loading on the performance of acid gas enrichment (AGE) absorber column. IJCPS, 2015; 4(1): 1-7.

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