Iranian Journal of Chemical Engineering

Journal Homepage: www.ijche.com

pISSN: 1735-5397
eISSN: 2008-2355

Regular Article

Screening Gas Sweetening Process and Optimizing its Parameters with MDEA-PZ Solvent using Plackett-Burman Approach

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ARTICLE INFO

Article history:
Received: 2023-06-15
Accepted: 2023-12-27
Available online: 2023-12-27

Keywords:
Gas sweetening,
Plackett-Burman approach,
Methyl Diethanol Amine,
Optimization,

ABSTRACT

Amine gas sweetening is a process in which acidic gases including hydrogen sulfide (H_2S) and carbon dioxide (CO_2) are removed by a solution of water and amines. Many parameters influence the sweetening process. Knowledge about the important parameters and their degree of importance is of great interest to achieve the optimum condition. Nine effective parameters including the CO_2 and H_2S contents of the feed, the temperature and pressure of the feed, the tray number and pressure of the absorber, the lean amine temperature, and the concentrations of Methyl Diethanol Amine (MDEA), and Piperazine (PZ) have been chosen as effective variables, while CO_2/H_2S recovery and total process energy have been considered as response variables. After the verification of the present study with real plant data, the experimental layout was designed by the Plackett-Burman approach, and the model validation has been confirmed by ANOVA. The results of the present study showed that the most effective parameters in the CO_2 recovery are the absorber tray number and PZ concentration, while in the H_2S recovery, the absorber tray number is the most important variable. Regarding the total energy of the proces, feed temperature, PZ concentration, absorber tray number, lean amine temperature, and feed pressure are obtained as important variables. The optimum condition has been obtained in the feed and absorber pressures of 5758.9, and 1458.9 kPa respectively, with the feed and lean amine temperature of 0.11 and 50 °C respectively, the concentrations of 17.57 and 3.8 wt.% of MDEA and PZ respectively, the absorber tray number of 20 and the mass flow rates of 792 and 103.6 kg/h of CO_2 and H_2S respectively. Under the mentioned conditions, the CO_2 and H_2S recovery were achieved at 99.99 % while the total energy of the process was 3.56 Mw.

DOI: 10.22034/ijche.2023.402335.1494 URL: https://www.ijche.com/article_186138.html

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1. Introduction

Electricity, heat generation, and transportation, which are heavily dependent on coal and the most carbon-intensive fossil fuel, are responsible for two-thirds of the global CO_2 emissions [1]. The flue gas from a typical fossil-fueled power generation unit contains N_2 (a major component) followed by CO_2, H_2O, O_2, and small amounts of NO_x, SO_x, and other compounds[1]. CO_2 is the main source of corrosion and reduces the heating value of natural gas. Besides, the contribution of CO_2 to global warming is around 80%. Therefore, it is required to remove CO_2 before the downstream processing or distribution of natural gas [2]. On the other side, the removal of H_2S from natural gas eliminates corrosion problems that destroy pipelines and equipment [3]. Therefore, global attention is focused on reducing CO_2 emissions to improve the global climate and eliminate H_2S[1].

A wide range of CO_2 capture technologies, including physical absorption, chemical absorption, membranes, and hybrid applications, have been developed in recent years in the face of climate change [4]. The most common method for removing CO_2 and H_2S from natural gas is absorption in an amine solvent, which can be pure or mixed [3]. Amine solutions are weak organic bases. They absorb acid gases at normal temperatures and desorb them at higher temperatures [5]. MDEA and MEA (Mono Ethanol Amine) are the most common amines used to separate acid gases. MDEA has many advantages over other amines, but the reaction rate of this solvent with CO_2 is low. Therefore, the PZ solvent is used to increase the reaction rate [3]. The favorable application of the MDEA+PZ system may be due to the higher reaction rate of PZ and the lower heat of the reaction of MDEA with CO_2, which results in higher absorption rates and lower energy requirements [6].

Up to now several sweetening processes with amine solvents have been reported including PZ activators. CO_2 removal by MDEA+PZ has been studied by A.Y. Ibrahim et al.[7]. Their study showed that the addition of PZ to the MDEA solution enhances the CO_2 absorption until the reaction is not limited by mass transfer. They have reported that with the addition of 5 wt.% of PZ, the amount of CO_2 in the sweetened gas reduces from 1 to 0.3 % by mole. They have also reported the lean amine pressure increase has no significant effect on absorption while the increase in feed pressure has an enhanced effect [7]. Ali Khan et al.[8] have studied the CO_2 capture technique through the post-combustion process in a packed column using an experimentation method with the MDEA+PZ solvent. They have concluded that MDEA+PZ acts as a superior absorber to MDEA and enhances many features of MDEA including the lower CO_2 loading capacity, higher process energy, and solvent degradation. The highest specific rate of absorption equaling $30.16*10^{-6}$ kmol m^2 s^{-1} and maximum CO_2 loading of 0.78 mol were attained in 10 wt. % PZ. Abd and Naji[9] have compared the performance of PZ and sulfolane activators in MDEA solutions. Their results showed that the addition of 5% of PZ to MDEA, enhances the CO_2 and H_2S absorption by 92.1 and 28.2% respectively, while the addition of 5% sulfolane increases the absorption efficiency by 80.48 and 48.18% for CO_2 and H_2S respectively. Rao K and Ponnusami A[10] have studied the gas sweetening process using the PZ solution and reported that with the concentration of 30 wt.% of PZ, the CO_2 and H_2S contents in the sweetened gas reach the 1.51×10^{-4} mole % and 0.0198 ppm respectively. They have also reported that the increase in feed temperature has a slight effect on the reboiler duty [10]. Laribi et al.[11] studied CO_2 capture from flue gas containing a high content of CO_2 (20-60 mol %) using MEA, PZ, and DEA+PZ solvents and reported a reduction in the regenerator energy with the increase of the CO_2 content in the feed gas. This reduction was about 15% in the case of PZ when CO_2 concentration in the feed gas increases from 20.4 to 62 mol%.

As it was reviewed, many parameters influence the CO_2/ H_2S capture process. Hence in the present study, the screening of parameters has been accomplished by DOE (design of experiments), in which all parameter variations are considered simultaneously to find the most effective parameters in the process. In this way, the Plackett-Burman design method (PBD), has been used which is well-known for acting well in the screening of many effective parameters [12-15]. As shown in the literature review, there is no numerical/experimental study in which the effects of numerous parameters have been considered simultaneously or the optimized values for many independent variables have been proposed to achieve the best process condition. In the present study, the effects of nine independent parameters have been studied with the three response variables of CO_2 and H_2S recovery and energy consumption using the PBD method, and at the final stage, the optimized condition has been presented. This study is organized as: in the first section, the simulation method has been described. Second, the experimental layout has been prepared and presented by the PBD. In the results section, firstly, the verification study was given, and then ANOVA was used to approve the DOE model accuracy. Then DOE results have been discussed with HYSYS simulations, and finally, the optimized condition has been proposed.

2. Methodology

2.1. HYSYS simulations

In this work, the gas sweetening process is simulated using the Aspen-HYSYS V11.0 software. The process PFD has been shown in Fig. 1 using the MDEA+PZ solvent. The sour gas enters from the bottom of the absorber as the feed and sweet gas leaves the top of the column. The remaining of the process refers to solvent regeneration. Simulations aim at maximizing CO_2 and H_2S recovery (Eqs. 1 and 2) and minimizing the process net energy (Eq. 3).

In Eq. 3 the process total energy (ε) is the sum of the absolute values of each term on the right side. Equations 1-3 have been considered as three objective functions in the optimization of the process optimization in the next sections. The HYSYS inputs for the simulation of the base case have been shown in Table 1.

$$\eta_{CO_2} = \frac{CO_2Feed(kg/h) - CO_2sweetened\ Gas(kg/h)}{CO_2Feed(kg/h)} \times 100 \quad (1)$$

$$\eta_{H_2S} = \frac{H_2S\ Feed(kg/h) - H_2S\ Sweetened\ Gas(kg/h)}{H_2S\ Feed(kg/h)} \times 100 \quad (2)$$

$$\varepsilon = \text{pump energy} + \text{Reboiler energy} + \text{condenser energy} + \text{cooler energy} \quad (3)$$

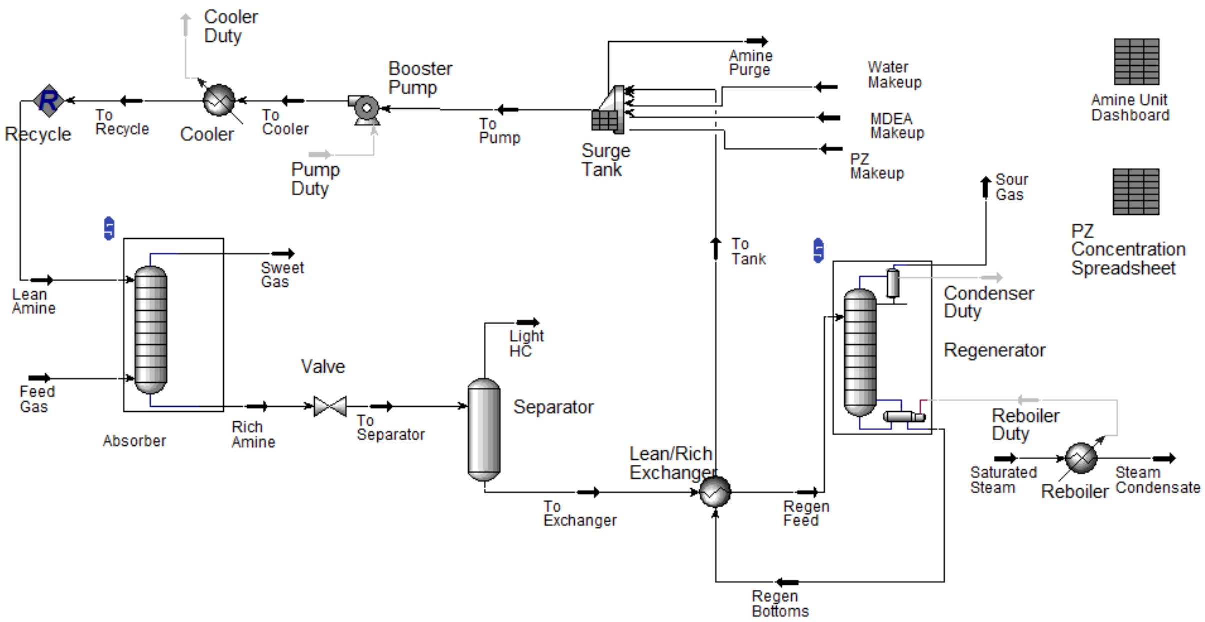


Figure 1. Process flow diagram of the gas sweetening unit using the MDEA+PZ solvent

Table 1
Base parameters in HYSYS

parameter	The original value
Feed P (kPa)	1618
Absorber P (kPa)	1618
Regenerator P(kPa)	232.4
Feed T (°C)	8.889
Lean amine T (°C)	35
CO_2 in feed (kg/h)	797.09
H_2S in feed(kg/h)	102.88
MDEA concentration (wt. %)	42%
PZ concentration (wt. %)	2.5%
Number of absorber trays	20

2.2. Design of experiments

To achieve the goals of the present study, the effects of several parameters have been examined through simulations. In this regard, feed temperature and pressure, CO_2 and H_2S contents in the feed, absorber pressure and tray numbers, lean amine temperature, and the weight percents of MDEA and PZ in the solvent have been selected as the independent variables. The ranges of these parameters have been given in Table 2. As it can be seen, there are numerous parameters, hence the PBD screen method has been applied to recognize the most effective of them and their degree of importance. Nine independent variables have been changed in two levels namely a low level (-1) and a high level (+1) including the ranges of Table 2.

Regarding CO_2 and H_2S contents of the feed, they have been considered in the ranges of 5.9-6.1(mol %) and 1-2(mol.%) respectively. To the best of the authors' knowledge, the effects of these variables have not been studied before in the sweetening process. In previous studies, the feed pressure range was 1400 - 9000 (kPa)[7, 16], and in the present study it was determined as 1618- 6000(kPa). The absorber pressure should be lower than the feed pressure to prevent the reverse flow from the absorber, hence in the present study, it was specified in the range of 1400-1618 (kPa) which matches the same in previous studies [17]. Low feed temperature is the favor for the process since in high temperatures, the volatility of CO_2 and H_2S increases and consequently the absorption efficiency decreases. This parameter range was 20-60 (°C) in previous literatures [10, 16, 18], and in the present study whereas it is 0 - 300 (°C) in the present study for analytical purposes. Regarding lean amine temperature, it was in the range of 38 -80 (°C) [7, 19], and in the present study, it was specified in the range of 10- 60(°C). Regarding MDEA and PZ concentrations, the concentrations of both amine types varied simultaneously along with other parameters. The MDEA is the base amine while PZ is the activator, hence their concentrations have varied in the ranges of 15-60 and 0-4 (wt.%) respectively[7, 9]. Regarding the absorber tray number, the considered range was 2-30.

The experimental matrix layout by PBD has been given in Table 3 with nine independent variables and three response parameters which have been specified in Eqs.1-3. The values for the three response variables agree well with the literatures [20, 21]. In PBD, the interactions between variables are ignored; therefore, a first-order equation explains the model:

$$Y = a_0 + \sum_{i=1}^{k} a_i\, x_i \tag{4}$$

Where Y is the response parameter which includes CO_2/H_2S recovery, and net energy. $a0$ is the constant value, and $a_i$is the regression slope. The regression analysis on response data has been done to find the coefficients of independent variables (a_i in Eq. 4), and their statistical importance. The analysis of variance (ANOVA) has been used to determine the statistical significance of the regression model obtained by the PBD. All calculations were accomplished by the Design Expert 11.0 software.

Table 2

Ranges of arameters in simulated experiments

Name	Low	High
CO_2 in Feed (kg/h)	770	800
H_2S in Feed (kg/h)	102.8	120
Feed T (°C)	0	300
Feed P (kPa)	1618	6000
Absorber P (kPa)	1400	1618
Absorber tray numbers	2	30
Lean amine T (C)	10	60
PZ concentration (wt. %)	0	4
MDEA concentration (wt. %)	15	60

Table 3.

Layout of simulated experiments by PBD

	Factors									Responses		
Run	**CO_2 in Feed (kg/h)**	**H_2S in Feed (kg/h)**	**Feed T** (°C)	**Feed P (kPa)**	**P absorber (kPa)**	**Absorber tray NO.**	**Amine T (°C)**	**PZ (wt. %)**	**MDEA (wt. %)**	**CO_2 Removal (%)**	**H_2S Removal (%)**	**Energy (MW)**
1	770	102.8	0	6000	1400	30	60	0	60	30.61	98.93	2.42
2	770	102.8	300	1618	1618	30	10	4	60	99.79	99.99	4.93
3	770	120	300	6000	1400	2	10	4	15	41.34	67.36	3.97
4	800	120	0	6000	1618	30	10	0	15	33.09	99.97	2.69
5	800	102.8	0	1618	1618	2	60	4	15	51.96	67.84	2.85
6	800	120	0	1618	1400	30	10	4	60	99.64	99.99	3.87
7	770	120	300	1618	1618	30	60	0	15	55.47	99.88	3.97
8	770	102.8	0	1618	1400	2	10	0	15	2.11	71.67	2.31
9	800	102.8	300	6000	1400	30	60	4	15	99.99	99.95	4.72
10	800	102.8	300	6000	1618	2	10	0	60	2.02	56.44	3.36
11	800	120	300	1618	1400	2	60	0	60	4.991	48.07	3.19

12	770	120	0	6000	1618	2	60	4	60	1.95	63.64	1.91

3. Results and discussion

3.1. Verification

Before simulation experiments, the simulated results of the present study have been compared with real plant data [20] and the results have been given in Table 4 showing good agreement with the average relative error of about 6%.

Table 4

Verification of simulation results with real plant data[20]

Parameter	Operating Data	Simulation Data
Sweet gas T(℃)	40	41
Rich amine to heat exchanger T(℃)	50	43.24
Stripper bottom T(℃)	110	106.4
Lean amine T(℃)	48	40
CO_2 in Sweet Gas (mol %)	2	2.07
Sweet gas P (kPa)	6000	5884
Rich amine P (kPa)	6000	6080
Lean amine P (kPa)	9800	9611
Stripper bottom P (kPa)	132	120

3.2. Analysis of variance

In this section, the ANOVA results have been demonstrated for the response variables of CO_2/H_2S and the total process energy in Tables 5-7. The p-value of the CO_2 / H_2S recovery and energy models demonstrate that the models are significant. In the ANOVA analysis, the effects of independent variables can be completely determined by ANOVA if the difference between “Pred. R^{2}” and “Adj. R^{2}” is lesser than 0.2[22]. According to Tables 5-7, these values justify well this category. The ANOVA second criterion for the regression model correctness is” Adeq Precision”, which measures the signal-to-noise ratio, and a ratio greater than 4 is preferred[22]. Tables 5-7 show that the models justify this requirement well. Finally, the p values less than 0.05 show the significant terms in the models which have been shown with ‘**’ in Tables 5-7.

Table 5 results show that among the nine parameters of Table 2, only two parameters have a significant effect on CO_2 absorption including the absorber tray numbers and PZ concentration in the solvent. Regarding H_2S recovery, the results in Table 6 show that, only the absorber tray number is of great importance. Table 7 results demonstrate that various variables are of great importance in the total energy (Eq. 3), including feed temperature, absorber tray number, PZ concentration, feed pressure, and lean Amine temperature. In Section.3, in Tables 5-7, conclusions are discussed in more detail by the HYSYS simulation. The ANOVA prediction results in comparison with the HYSYS simulation data have been shown in Fig. 2 showing good agreement.

Table 5
ANOVA and quality of the model for CO_2 recovery

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	26493.13	9	2943.68	35.59	0.0276	significant
A-CO_2 in Feed(kg/h)	504.10	1	504.10	6.09	0.1323	
B-H_2S in Feed (kg/h)	358.05	1	358.05	4.33	0.1730	
C-Feed T (°C)	970.82	1	970.82	11.74	0.0757	
D- Feed P (kPa)	1500.78	1	1500.78	18.14	0.0509	
E- Absorber P (kPa)	167.04	1	167.04	2.02	0.2912	
F-absorber trays	13045.27	1	13045.27	157.71	0.0063	**
G-Lean amine T (°C)	159.68	1	159.68	1.93	0.2992	
H- PZ (wt.%)	9566.02	1	9566.02	115.65	0.0085	**
J-MDEA (wt.%)	221.38	1	221.38	2.68	0.2435	
Residual	165.43	2	82.71			
Cor Total	26658.56	11				
Adjusted R^2	0.96					
Predicted R^2	0.79		Adeq Precision	15.88		

Table 6.
ANOVA and quality of the model for H_2S recovery

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	50.69	9	5.63	64.01	0.0155	significant
A-CO_2 in Feed(kg/h)	0.9893	1	0.9893	11.24	0.0786	
B-H_2S in Feed (kg/h)	0.2966	1	0.2966	3.37	0.2078	
C-Feed T (°C)	1.06	1	1.06	12.07	0.0738	
D- Feed P (kPa)	8.677E-06	1	8.677E-06	0.0001	0.9930	
E- Absorber P (kPa)	0.0067	1	0.0067	0.0767	0.8078	
F-absorber trays	45.59	1	45.59	518.15	0.0019	**
G- Lean amine T (°C)	0.3287	1	0.3287	3.74	0.1930	
H- PZ (wt.%)	0.6633	1	0.6633	7.54	0.1110	
J-MDEA (wt.%)	1.75	1	1.75	19.89	0.0500	
Residual	0.1760	2	0.0880			
Cor Total	50.86	11				
Adjusted R^2	0.98					
Predicted R^2	0.89		Adeq Precision	20.81		

Table 7
ANOVA and quality of the model for the total energy

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	23.67	9	2.63	93.27	0.0107	significant
A-CO_2 in Feed(kg/h)	0.2083	1	0.2083	7.39	0.1129	
B-H_2S in Feed (kg/h)	0.2155	1	0.2155	7.64	0.1097	
C-Feed T (°C)	12.64	1	12.64	448.20	0.0022	**
D- Feed P (kPa)	0.7821	1	0.7821	27.73	0.0342	**
E- Absorber P (kPa)	0.1059	1	0.1059	3.76	0.1922	
F-absorber trays	4.96	1	4.96	175.95	0.0056	**
G- Lean amine T (°C)	0.8215	1	0.8215	29.13	0.0327	**
H- PZ (wt.%)	3.82	1	3.82	135.44	0.0073	**
J-MDEA (wt.%)	0.1187	1	0.1187	4.21	0.1766	
Residual	0.0564	2	0.0282			

Cor Total	23.73	11		
Adjusted R^2	0.99			
Predicted R^2	0.91		Adeq Precision	30.27

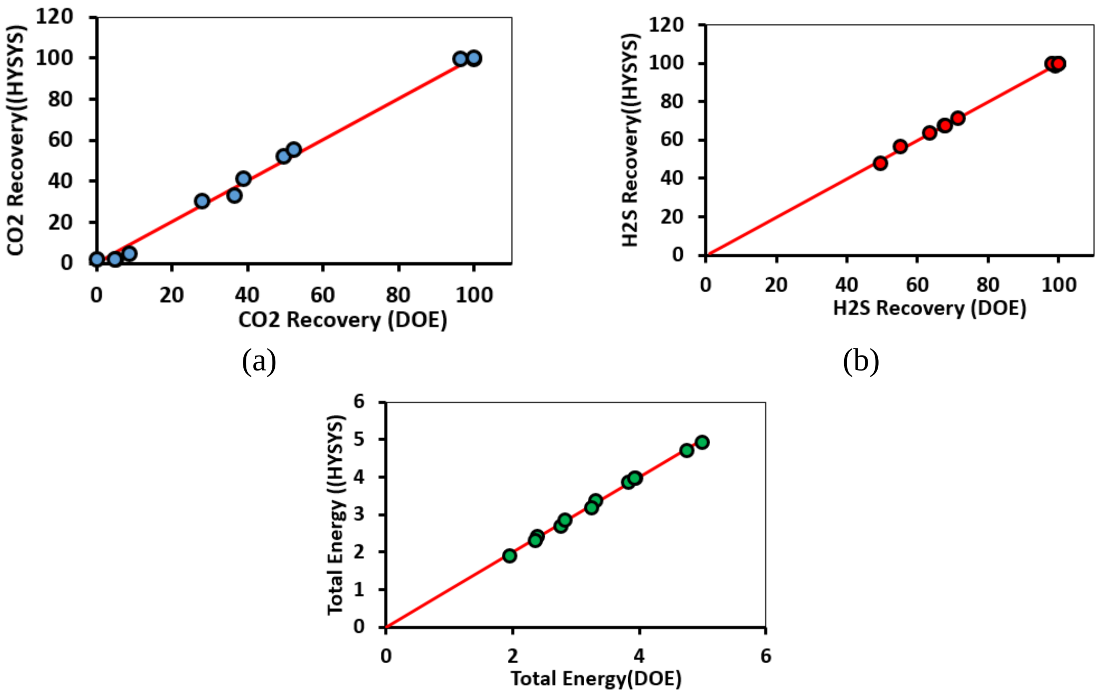


Figure 2. Comparison of HYSYS simulation results with DOE predictions for a) the absorption of CO_2, b) the absorption of H_2S, and c) total energy of the process

3.3. Discussion of ANOVA results with HYSYS simulations regarding absorption

In this section, the results in Tables 5 and 6 have been discussed with the HYSYS simulation.

3.3.1. Discussion of different factors effects on CO_2 and H_2S absorption

Tables 5 and 6 show that, in CO_2 and H_2S removal, among nine independent factors, only a limited number of them have significant effects. To show how these variables affect the process, the effects of all variables on CO_2 and H_2S removal have been shown in Figs. 3 and 4 using HYSYS simulations.

It can be seen from Fig. 3 that, although all variables influence CO_2 removal, the effects of many of them are negligible, except the concentration of PZ and tray numbers which have been pointed out as main factors using the ANOVA analysis (Table 5). Regarding H_2S removal (Fig. 4), similar to that of CO_2, slight changes are almost observed by all variables except the absorber tray number which was previously reported in Table 6.

It can be seen from Figs. 3a and b that, with the increase of CO_2 and H_2S concentration in the feed gas, CO_2 absorption decreases. In fixed solvent flow rates, with the increase of CO_2 and H_2S in contents in the feed, the amine ability to absorb more concentrations of CO_2 and H_2S reduces. Similar conclusions have been reported in previous studies[10, 23].

Referring to Fig. 3c, it can be seen that, with the increase in the feed temperature (sour gas), the absorption efficiency decreases. It was due to an increase in volatility and more tendency of CO_2 to remain in the gas phase as it has been reported in previous studies [16, 23], hence amine solution cannot easily absorb the CO_2 from the gas phase, consequently, the absorption efficiency decreases.

With the increase in the feed pressure (Fig.3d), CO_2 absorption reduces, as reported in previous studies[16]. Regarding the absorber pressure (Fig. 3e), it can be seen that, with the increase in the absorber pressure, CO_2 absorption increases[19, 24]. It was due to an increase in the solubility of gas components inside the liquid phase at elevated pressures according to Henry's law.

The increase in the lean amine temperature has an enhanced effect on CO_2 absorption [19], since it increases CO_2 partial pressure, and consequently, CO_2 solubility in the amine solution improves[24] (Fig.3f).

The absorber tray number and PZ concentration have enhanced effects on CO_2 absorption (Fig. 3g and h) due to the high separation efficiency with large tray numbers and fast reaction opportunity in the presence of PZ which will be discussed in more detail in the Section. 3.3.2.

Regarding MDEA concentration, Fig. 3i shows that, with the increase in the concentration of MDEA in the amine solution, CO_2 absorption deteriorates, as reported in previous studies[23]. It may be due to the reduction of water as one of the main reactants in an amine solution.

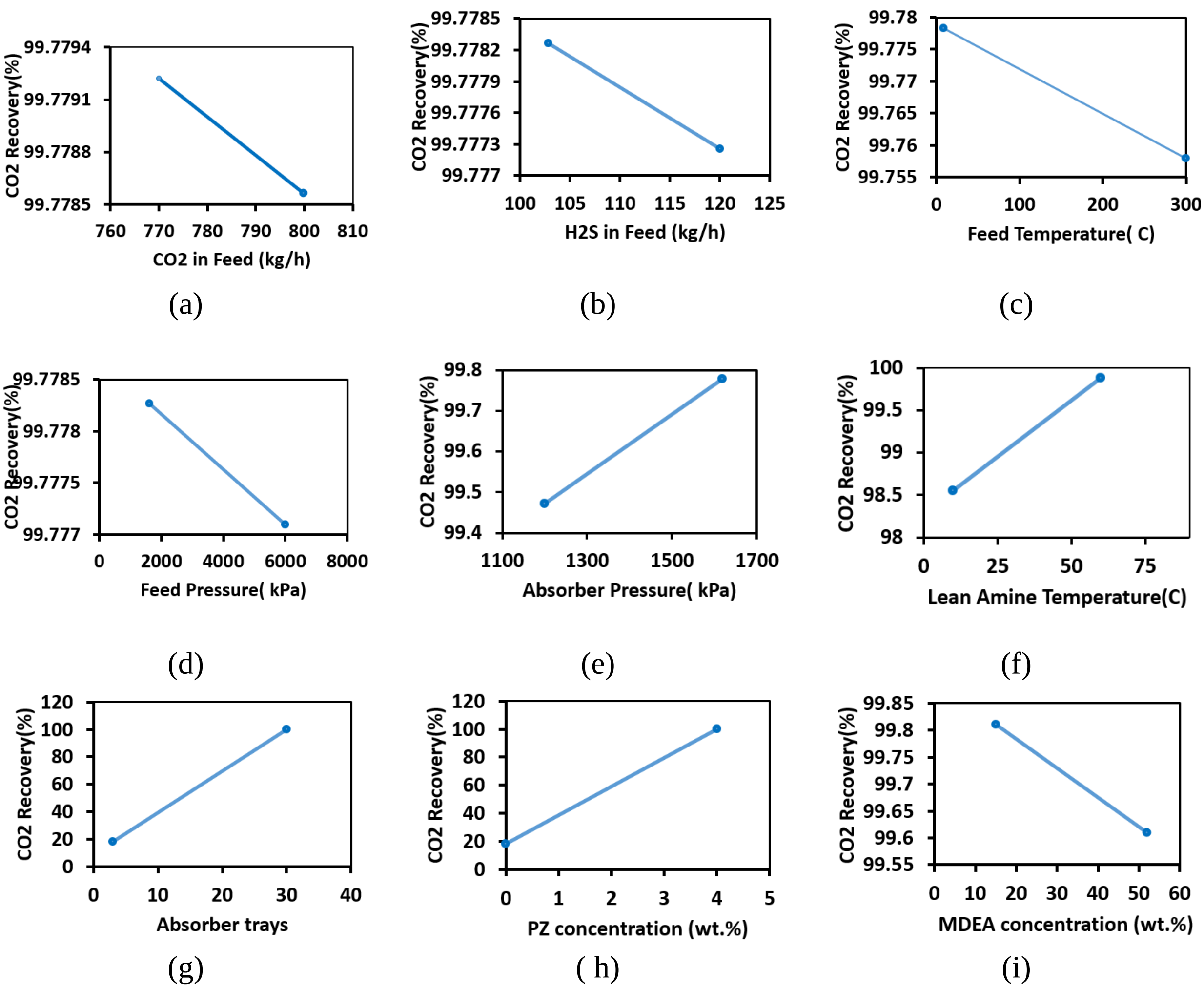


Figure 3. Effect of nine independent variables on CO_2 recovery

Regarding H_2S, the results in Figs. 4a and b show that, with the increase in the concentration of CO_2 and H_2S in the feed, the absorption of H_2S reduces for the same reason as shown in Figs. 3a and b. Similar to that of CO_2 (Fig. 3c), H_2S absorption reduces with the increase in the feed temperature (Fig. 4c).

With the increase in the feed pressure, H_2S absorption improves due to the increase in the partial pressure of H_2S and increase in the absorption reaction rate (Fig. 4d). Fig. 4.e shows that with the increase in the absorber pressure, H_2S absorption improves as it has been previously explained in Fig. 3e about CO_2. The increase in the lean amine temperature has a deteriorating effect on H_2S absorption (Fig. 4f)[19]. It was due to the deteriorating effects of increasing the temperature on exothermic absorption reactions and also the reduction of the solubility of gases in high temperatures[24].

As expected, with the increase in the tray numbers, H_2S absorption improves (Fig. 4g). It can also be seen in Fig. 4h that, PZ concentration has also enhancing effects on H_2S absorption[10]. MDEA concentration effects on H_2S removal have been shown in Fig. 4i, demonstrating deteriorating effects as it has been explained in Fig. 3i.

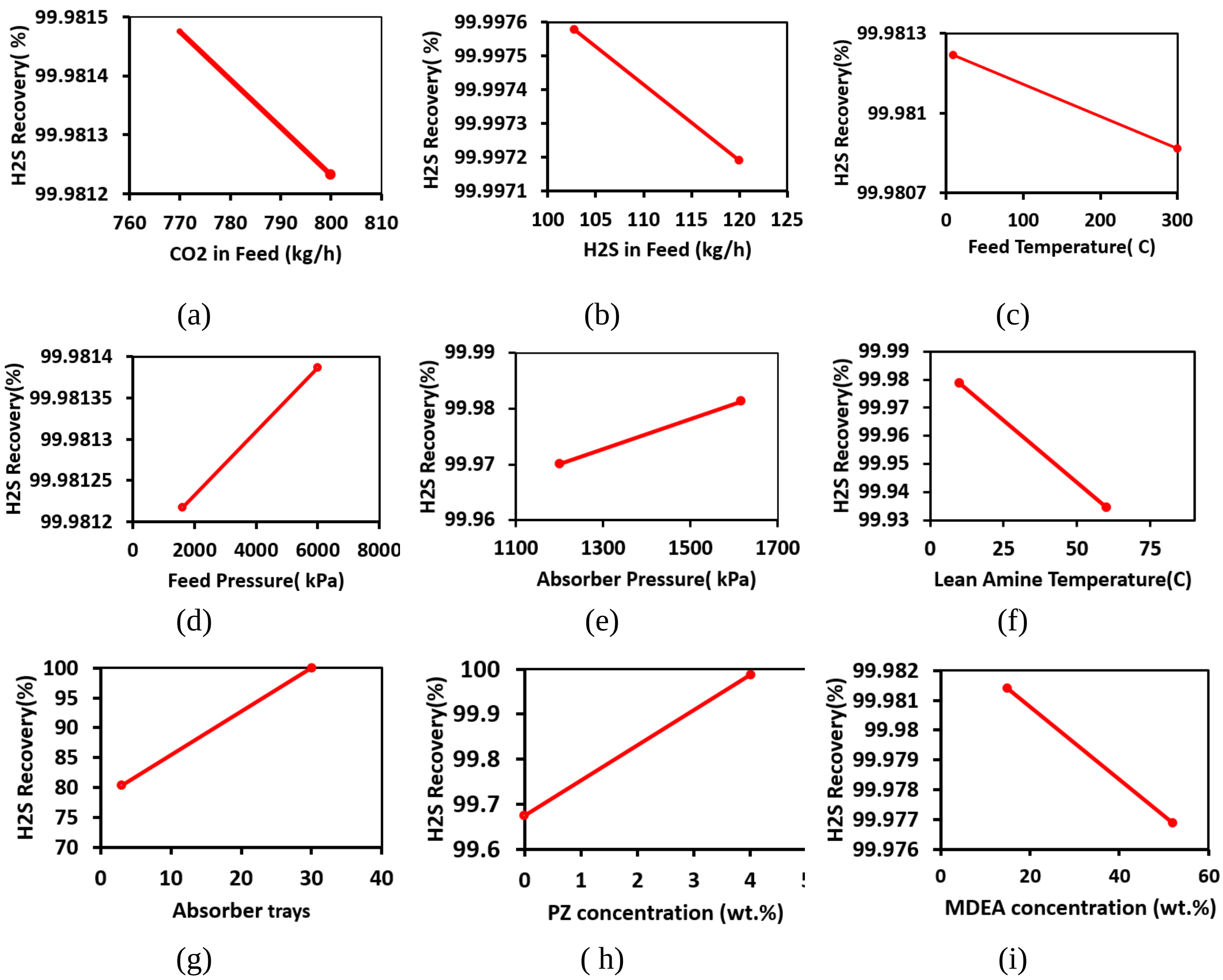


Figure 4. Effects of nine independent variables on the recovery of H_2S.

3.3.2. Effects of MDEA/PZ concentrations, and absorber tray numbers on absorption

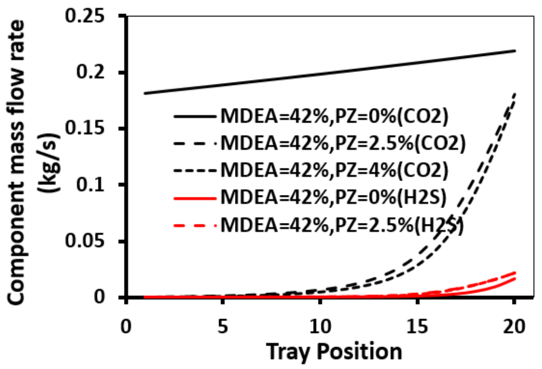
Tables 5 and 6 show that the PZ concentration has the dominant effect on CO_2 removal while its effect on H_2S removal is negligible. To show this effect, PZ concentration has been varied from 0 to 4% wt.% and CO_2 and H_2S profiles have been plotted in Fig. 5 in the absorber in terms of mass flow rate.

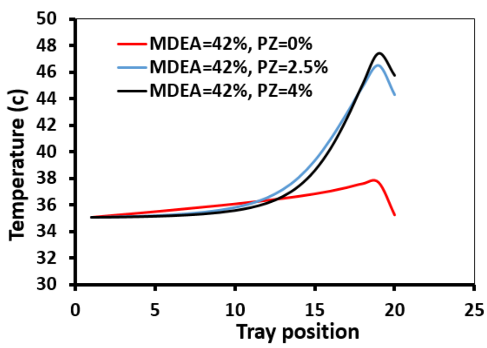
It can be seen from Fig. 5a that in the pure MDEA (zero PZ concentration), the considerable amount of CO_2 remains in the sweet gas at the top of the column in tray 1 and leaves the absorber, but with the increase in the concentration of PZ to 2.5%, almost all of CO_2 has been removed. The effects of the concentration of PZ on H_2S removal are insignificant (Fig. 5a) as previously shown in Table 6. The reason is that tertiary amines like MDEA, due to instantaneous and fast reactions by proton transfer with H_2S, separate it from sour gas with high selectivity from streams containing H_2S, CO_2, and hydrocarbons[7]. Regarding CO_2, the absorption reaction is limited due to the slow bicarbonate reaction and it is improved in the presence of PZ as an additive. PZ reaction with CO_2 is quick and reduces the mass transfer resistance against CO_2 transfer into the liquid phase, consequently, it improves the reaction rate with MDEA [7].

The effect of the concentration of PZ on the temperature profiles of the absorber has been shown in Fig. 5b. The comparison of Figs. 5a and 5b shows that almost all of the absorption reaction takes place at the bottom of the absorber, around the trays of 15-20. In this section, the absorption reaction releases more energy in high PZ concentration, consequently, it increases the temperature of the bottom trays. This plot clarifies the important effect of PZ on the total process energy as previously stated in Table 7.

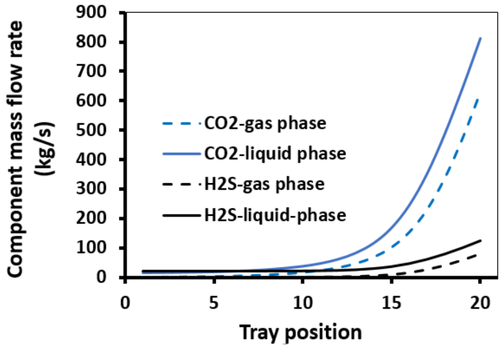
It can be seen from Fig. 5c that, in the bottom of the absorber (tray 20), CO_2 and H_2S mass flow rates are high in both liquid (solvent) and gas phases. This is because the sour gas inlet and rich amine exit are located in the column bottom with a high content of CO_2 and H_2S. To the top of the column, the mass flow rate of both components reduces and reaches almost zero around the 10^{Th} tray. This is because the lean amine inlet and sweetened gas exist are in top of the absorber (first tray). The large variations in the mass flow from the top to the column bottom exist only for the transferred components, while for the other components, the mass flow rates are constant in any section of the absorber (Fig. 5d).

The MDEA concentration effects on the H_2S and CO_2 profiles have been shown in Fig. 5e. As it can be seen, H_2S and CO_2 profiles have not changed significantly in different MDEA concentrations as observable in the results in Tables 5 and 6 with larger p-values.

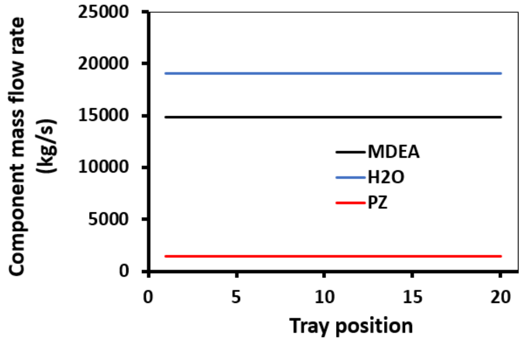




(a)

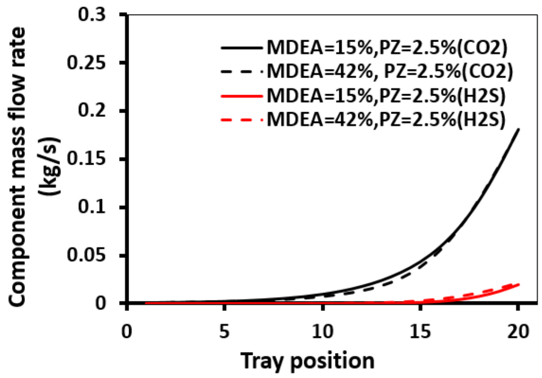


(b)



(c)

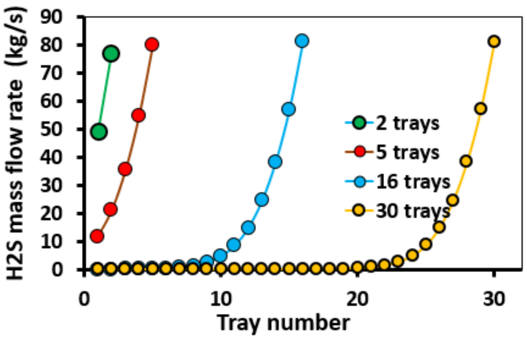
(d)

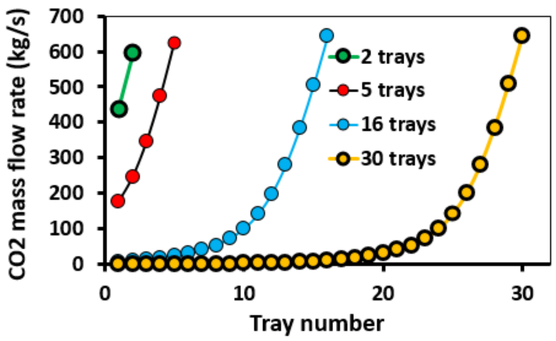


(e)

Figure 5. PZ concentration effect on a) CO_2 and H_2S profiles in the absorber, b) The temperature profile of absorber, c) the mass flow rates of CO_2 and H_2S in gas and liquid phases inside the absorber, d) the mass flow rate of MDEA, PZ, and H_2O in the liquid phase inside the absorber, and e) the effects of MDEA concentration on CO_2 and H_2S profiles

Tables 5 and 6 results show that the effects of the absorber tray number are significant on the both CO_2 and H_2S removal. To show this effect, CO_2 and H_2S mass flow rates have been shown in Fig. 6 in the absorber. It can be seen that at small tray numbers (2 to 6 trays), significant values of CO_2 and H_2S leave the column and cause the incomplete sour gas removal at the PZ concentration of 2% and MDEA concentration of 40%.





(a)

(b)

Figure 6. Mass flow Profiles in the absorber in different tray numbers for a) H_2S, b) CO_2

3.4. Discussion of ANOVA results with HYSYS simulations regarding energy

In this section, the results in Table 7 have been discussed with HYSYS simulations.

3.4.1. Effects of nine independent factors on the total process energy

In this section, firstly, the effect of three variables with the smallest p-values n Table 7 has been discussed and results have been shown in Fig. 7. Then the effects of other six parameters are discussed in Fig. 8.

To show how the feed temperature affects the total process energy, all energy terms of Eq. 3 have been plotted against the feed temperature in Figs. 7a and b. An increase in the feed temperature increases the 'Rich Amine' temperature as shown in in Fig.1, while the temperature of 'Regen Feed' and 'Regen Bottoms' have been assumed constant in the present study. Referring to Fig. 1, it can be seen that, the four streams exchange energy with each other. The temperature of two of them is constant and not changed with the feed temperature, while the temperature of 'To Exchanger' increases and leads to the increase of 'To Tank' and then 'To Pump' temperature. With the increase in the temperature of the 'To Pump', the gas temperature inside the pump increases, consequently the pump duty increases (Fig. 7a). The temperature increase in 'To Pump' increases the 'To Cooler' temperature, while the temperature of 'Lean Amine' is assumed constant, hence the cooler duty increases (Fig. 7b). Due to the insignificant effect of the feed temperature on absorption (Tables 5 and 6), the reboiler and condenser duties remain almost constant as shown in Fig. 7b[9, 10, 18]. Consequently with the increase in the feed temperature and subsequent increase in the cooler and pump duties, the total energy increases. It can be seen from Figs. 7a and b that the contribution of pump energy among other terms of total energy is the smallest as pointed out in previous studies[18, 25].

The absorber tray number effects on the energy terms of Eq.3 have been plotted in Figs. 7c and d. It can be seen that, with the increase in the tray number in the absorber, 'Rich Amine' loading from CO_2 and H_2S increases as demonstrated in Tables 5 and 6. Consequently, the reboiler and condenser duties in the regenerator should be increased to desorb higher contents of CO_2 and H_2S from the 'Regen Feed' and recycle the 'Regen Bottom" with low contents of CO_2 and H_2S into the process (Fig. 7d). It can also be seen from Fig. 7d that, after the tray number of 20, the changes are not significant in energy terms (Figs. 7c and d), because after certain tray number, its effect on CO_2 and H_2S removal is insignificant (Fig. 6). On the other hand, with the increase in the tray number in the absorber and the increase in the absorption efficiency, the energy released from the exothermic reaction increases and leads to the increase in the 'Rich Amine' and 'To Exchanger' temperatures. Hence the cooler and pump duties increases with the similar reason as demonstrated in Figs. 7a and b, consequently with the increase in all energy terms of Eq. 3, the total process energy increases.

It can be seen from Table 7 that, the PZ concentration is the other important factor in total energy estimation. To show how it affects the estimation, all variations in the energy terms with PZ concentration have been plotted in Figs. 7e and f. Referring to Figs. 7c.and d, it can be seen that the trend of variations is similar to the same in Figs 7. e and f. This is because PZ plays a similar role as the tray number in total energy and energy terms. Hence similar to the absorber tray, with the increase in the concentration of PZ, the 'Rich Amine' loading increases, consequently, the duties of the reboiler and condenser in the regenerator increase (Fig. 7f). Similarly, with the increase in the 'Rich Amine' temperature, the cooler and pump duties increase (Figs. 7e and f), as a result, the total process energy consumption increases (Fig. 7f).

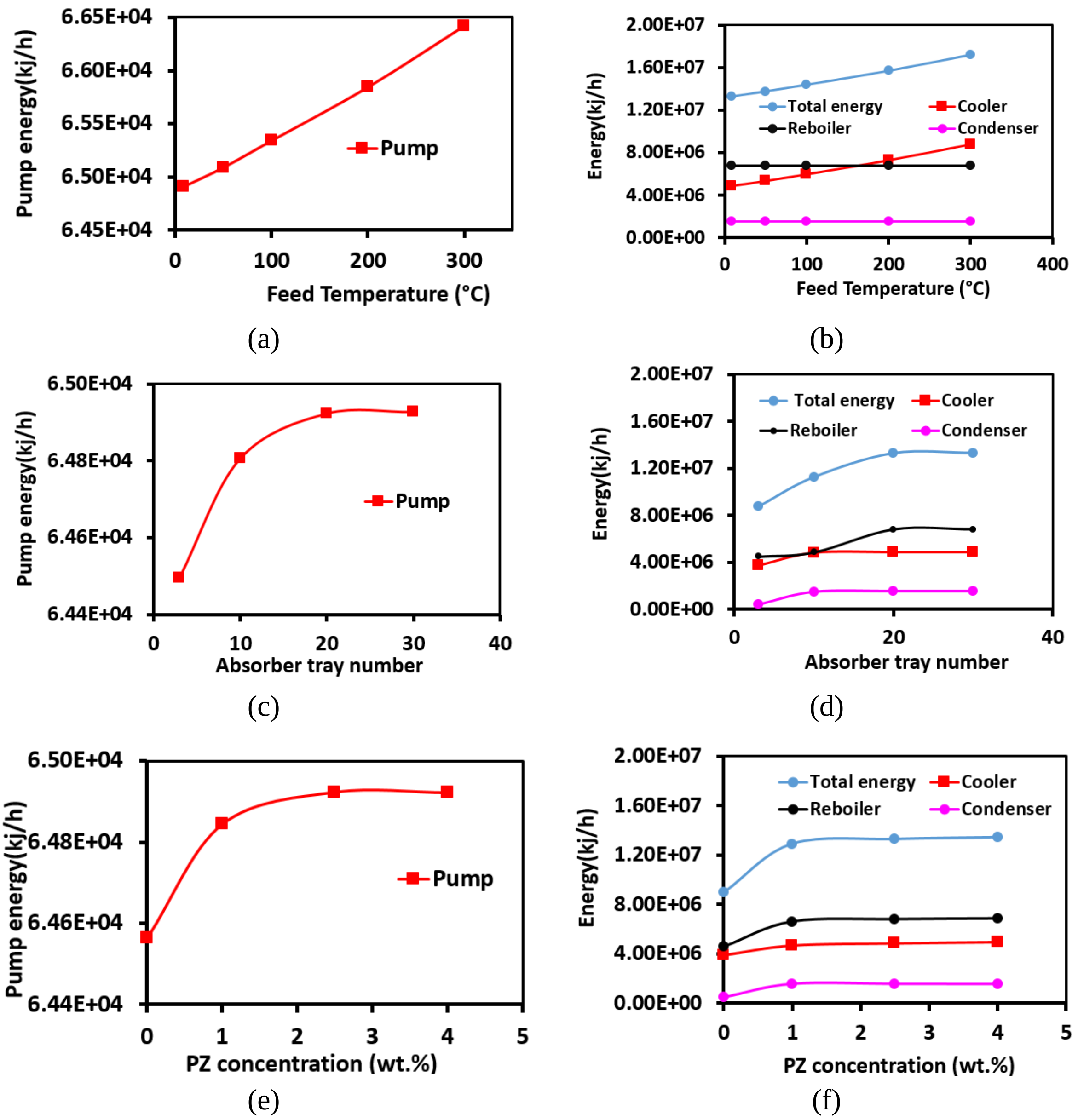


Figure 7. Variation of energy terms with a) the feed temperature, b) the absorber tray number, and c) the concentration of PZ.

Table 7 results showed that several parameters affect the total process energy. To show how variables influence the process energy, the total energy changes with nine factors have been plotted in Fig. 8. The changes with the feed temperature, PZ concentration, and tray number have been reported again in Fig. 8 for compatibility with Figs. 3 and 4.

It can be seen from Fig. 8 that, all variables influence the total energy, but the effect of some of them, is most emphasized including the feed temperature, tray number, PZ concentration, lean amine temperature, and feed pressure (Figs. 8c, d f, g, and h). They have the p-values less than 0.05, as shown in in Table 7, so, their effects are more significant than other parameters (Fig. 8).

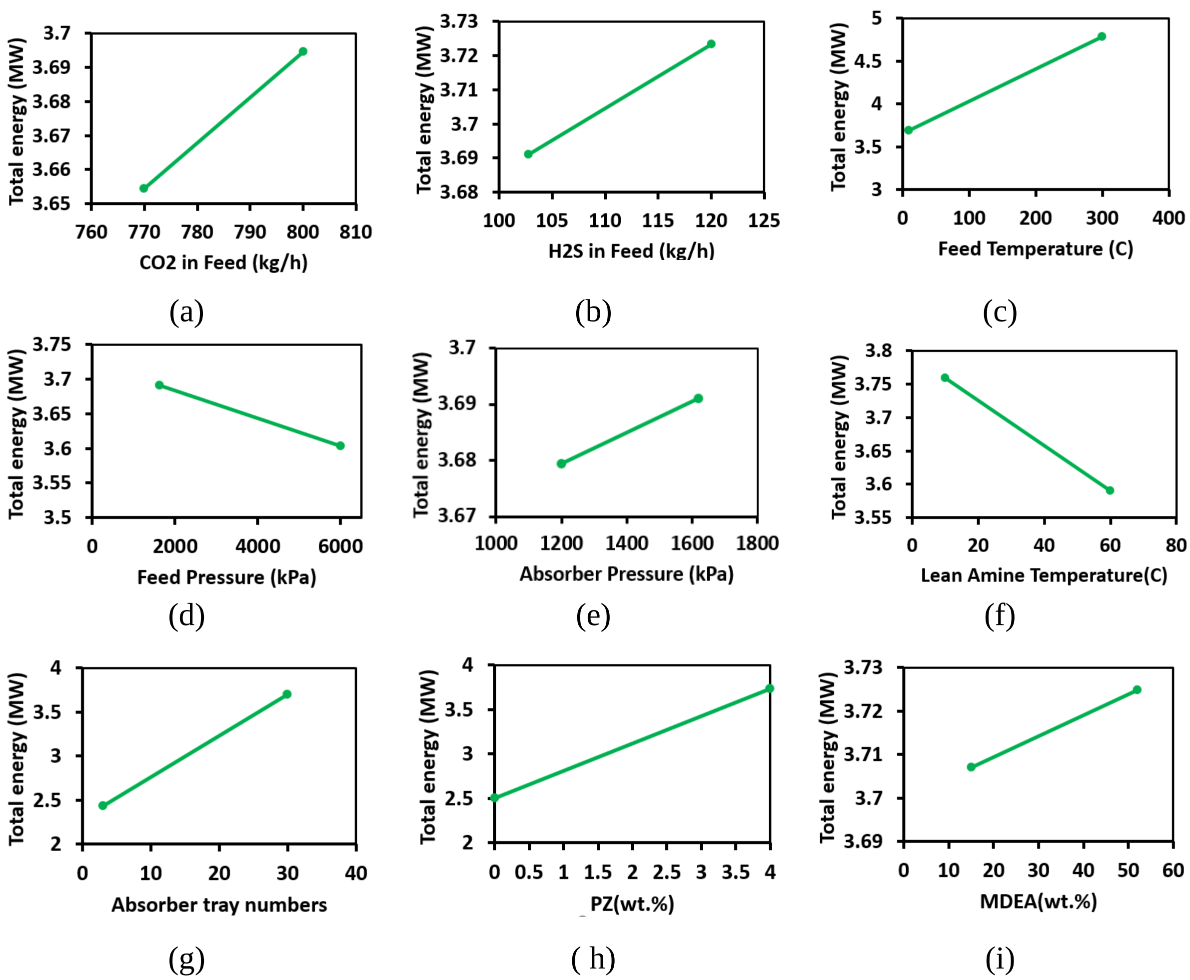


Figure 8. Effects of nine independent variables on the total process energy.

Referring to Fig. 8a, it can be seen that with the increase in CO_2 content in the feed, the total energy consumption increases. With the increase in CO_2 content in the feed from 770 to 800 kg/h, the CO_2 mass fraction in ‘Rich Amine’ increases from 2.1 to 2.2 wt.%, while the ‘Rich Amine’ temperature remains almost constant. Hence, with the increase in CO_2 mass fraction, reboiler and condenser duties increase by 1.38 and 3.2 percent respectively, but due to the almost constant temperature of ‘To Pump’, the changes in cooler and pump duties are insignificant. Hence with the increase in the content of CO_2 in the feed, the total process energy increases[17] (Fig. 8a). Regarding H_2S (Fig. 8b), with the increase in the amount of H_2S in the feed from 102.8 to 120 kg/h, H_2S mass fraction in ‘Rich Amine’ increases from 0.32 to 0.38 wt.%, but, no significant change was observed in the ‘Rich Amine’ temperature, hence variations in pump and cooler duties were insignificant. So, with the increase in reboiler and condenser duties, the total energy increases (Fig. 8b).

It can be seen in Fig. 8d that, with the increase in the feed pressure, the total process energy reduces. Referring to Figs. 3d and 4d, it can be seen that, with the increase in the feed pressure, CO_2 loading in ‘Rich Amine’ decreases while H_2S loading increases and the changes in CO_2 loading are more than that in H_2S loading in the ‘Rich Amine’ (Figs. 3d and 4d). Hence, by weakening the absorption, the heat release of the exothermic absorption reaction decreases and it reduces the ‘Rich Amine’ temperature. In the feed pressure of

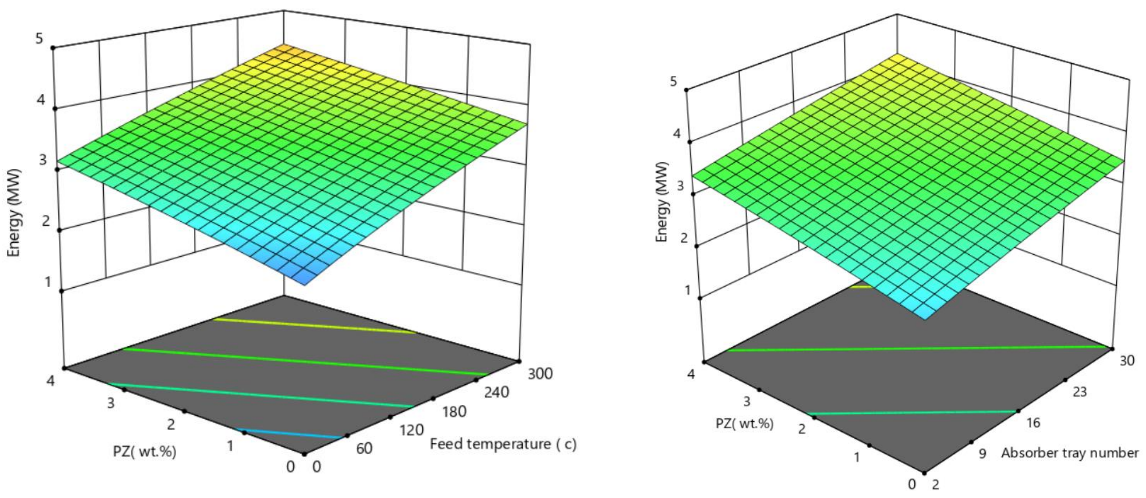
1618-6000 (kPa), the ‘Rich Amine’ temperature varied from 44.28 to 41.59 (°C). Hence, for a similar reason as in Figs. 7a and b, with the reduction of ‘Rich Amine’ temperature, the temperature of the ‘To Pump’ stream reduces, and consequently, the cooler and pump duties and consequently, the total process energy reduce as reported in previous studies[16]. Due to slight changes in the compositions of the ‘Regen Feed’ with the increase in the feed pressure, the changes in reboiler and condenser duties are insignificant. Referring to Fig. 8e, it can be seen that with the increase in the absorber pressure, the total process energy increases. It can be seen in Fig. 3e and Fig. 4e that, with the increase in the absorber pressure, the amounts of CO_2 and H_2S in the sweet gas reduces, ‘Rich Amine’ loading from CO_2 and H_2S increases, consequently reboiler and condenser duties increase, hence, the total energy increases (Fig. 8e). Similar findings have also been reported in previous studies[17, 19, 24]. The increase in the absorber pressure does not significantly change the ‘Rich Amine’ temperature, hence the temperature of the ‘To Pump’ stream remains almost constant, and the changes in cooler and pump duties become insignificant.

With the increase in the lean amine temperature, the total energy reduces (Fig. 8f) as observed in previous findings[19]. Referring to Fig. 3f and Fig. 4f, it can be seen that, with the increase in the lean amine temperature, the CO_2 is enhanced by 1.35 percent, while the H_2S removal deteriorates by 0.04 percent, hence, rich amine loading increases and the reboiler and condenser duties increase. On the other hand, with the lean amine temperature changing from 10 to 60 (°C), the ‘Rich Amine’ temperature increases from 22.23 to 65.94 (°C). Hence with the increase in the ‘To Pump ‘temperature, the pump duty increases. On the other hand, with the increase in the lean amine temperature from 10 to 60 (°C), the temperature difference between ‘To cooler’ and ‘To recycle’ streams reduces from 44.8 to 36.18 (°C) (Fig. 1), consequently, the cooler duty reduces. Because of the high contribution of the cooler duty in the total energy, the process total energy is reduced [25] (Fig. 8f)

Fig. 8i shows that, with the increase in MDEA concentration, the total process energy increases, similar findings have also been reported in previous studies[17]. With the increase in MDEA concentration from 15 to 52 percent, the ‘Rich Amine’ temperature increases from 42.71 to 45.27 (°C), and consequently the ‘To Pump’ temperature increases from 72.73c to 77.24 (°C), and pump and cooler duties increase. On the other hand, as it can be seen in Figs. 3i and 4i, the CO_2 and H_2S mass fractions reduce in ‘Rich Amin’, consequently reboiler and condenser duties decrease but these reductions are weaker than the increase in the duties of the pump and cooler, hence the process total energy increases with the increase in the concentration of MDEA.

3.5. The simultaneous effects of parameters in the gas sweetening process

The simultaneous effects of PZ concentration and the feed temperature on the total energy have been presented in Fig. 9a. It can be seen that with the increase in the feed temperature and PZ concentration, the total energy consumption increases as explained in section 3.4.1. The effects of PZ concentration and absorber tray number have been shown in Fig. 9b reporting the increase in the total energy with the increase of both factors.



a b

Figure 9. Simultaneous effects of a) PZ concentration and feed temperature on the total energy, b) the PZ concentration and absorber tray number on the total energy.

3.6. Multi-objective optimization of the process

After process modeling with DOE, the gas sweetening process was optimized. The mathematical description of the optimization method has been given below:

$$\text{Object (1)} = \eta_{CO_2} \quad (5)$$

$$\text{Object (2)} = \eta_{H_2S} \quad (6)$$

$$\text{Object (3)} = \varepsilon \quad (7)$$

In this way, object (1) and object (2) are maximized while object (3) is minimized. According to Table 2, the decision variables are confined as below:

$$770 < CO_2 \text{ in Feed (kg/h)} < 800 \quad (8)$$

$$102.8 < H_2S \text{ in Feed(kg/h)} < 120 \quad (9)$$

$$0 < \text{ Feed T(°C)} < 300 \quad (10)$$

$$1618 < \text{ Feed P(kPa)} < 6000 \quad (11)$$

$$1400 < \text{ Absorber P(kPa)} < 1618 \quad (12)$$

$$2 < \text{Absorber tray number} < 30 \quad (13)$$

$$10 < \text{ Lean Amine T(°C)} < 60 \quad (14)$$

$$0 < \text{PZ Concentration (wt.\%)} < 4 \quad (15)$$

$$15 < \text{MDEA Concentration (wt.\%)} < 60 \quad (16)$$

In the DOE, the values of nine parameters have varied in the range of Eqs. 8-16 and the values of three objective functions (Eqs.5-7) have been calculated from Eqs. 1-3. Among the results, one set of independent variables has been selected that satisfies Eqs.5-7 conditions in maximize or minimization. The independent variables and the values of related objective functions under the optimized condition have been reported in Table 8.

Table 8
The values of independent variables and objective functions in optimized condition

Independent variables	**values**
Feed P (kPa)	5758.86
Absorber P (kPa)	1458.89
Feed T (°C)	0.11
Amine T(°C)	50
MDEA concentration (wt. %)	17.57
PZ concentration (wt. %)	3.8
Absorber tray number	20
CO_2 in Feed (kg/h)	792
H_2S in Feed (kg/h)	103.69
Objective functions	values
η_{CO_2}	99.99
η_{H_2S}	99.99
ε(MW)	3.56

It can be seen that, under the proposed condition in Table 8, the CO_2 and H_2S contents have been fully removed from the sour gas, while the process total energy consumption has reached the minimum value with respect to the values in Table 3. Additionally, under the optimized condition, the absorber tray number is 20 and the amine concentration reached a small value which is one of the main causes of the costs of the process.

4. Conclusion

In the present study, the effects of various parameters on the gas sweetening process have been studied using the HYSYS simulation coupled with the design of experiments (DOE). Nine parameters have been selected as independent variables including feed CO_2 and H_2S contents, feed temperature and pressure, absorber tray number and pressure, lean amine temperature, MDEA, and PZ concentrations. The effects of chosen variables on the three response variables of CO_2 and H_2S recovery and the total energy have been examined. In the first step, simulations were verified by actual plant data, and good agreement was achieved with an average relative error of about 6%. In the next step, the experimental layout by PBD has been simulated by HYSYS and the validity of the PBD regression model has been approved by ANOVA. In the next step, the ANOVA results were discussed for three response variables with HYSYS simulations and the simulation results confirmed the ANOVA conclusions regarding the important variables and their degree of importance. The main results of the present study are summarized below:

1- The present study results showed that the most effective parameters in CO_2 recovery are the absorber tray number and PZ concentration among nine selected variables.
2- Regarding H_2S recovery, the absorber tray number was determined as the most effective variable. In small tray numbers, only a low percent of H_2S can be removed from the sour gas, even in high MDEA concentrations.
3- Regarding the process energy, the most important variables are the feed temperature, absorber tray number, PZ concentration, lean amine temperature, and feed pressure.
4- In the optimization process, nine effective parameters have been set to give optimum conditions using the PBD-ANOVA approach. Results showed that even with low amine concentration (MDEA 17.57 and PZ 3.56 wt.%) and the absorber tray number of 20, the CO_2 and H_2S recovery of about 99.99 % is achievable along with the minimum process energy of 3.56 MW.

Nomenclature

P	Pressure (kPa)
T	Temperature (°C)

Abbreviations

MDEA	Methyl Diethanol Amine
MEA	Mono Ethanol Amine
PZ	Piperazine
PBD	Plakett-Burman Design
DOE	Design of Experiments
ANOV A	Analysis of Variance

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