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Original Paper

Technical enhancement amine gas treating and cost reduction by assisting response surface methodology

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ABSTRACT

The process of amine sweetening of natural gas is crucial to purify it, meet environmental regulations, and boost its commercial value. This study proposes a novel hybrid optimization framework combining Response Surface Methodology (RSM) with process simulation, specifically addressing additive impacts on MDEA-based solvents, a combination not extensively explored in prior studies. The research recommends a new combination of response surface methodology (RSM) and process simulation to address this goal. Using RSM for optimization is a statistical technique applied to model the functional relationship between major input variables (like temperature, pressure, concentration of additives, and MDEA). Therefore, integrating RSM with process simulation helps assess scenarios that give reliable results. In particular, this study considers how additives affect indicators such as acid gas removal efficiencies (CO_2 and H_2S), energy consumption, percent of yield for solvent regeneration, and overall economy. A framework for optimizing acid gas removal efficiency has been developed by systematically varying the concentrations of additives across specific predefined ranges so that optimal operating conditions are determined that maximize both acid gas removal efficiency and yield of solvent regeneration while minimizing utility consumption, resulting in low total annual costs. The results show that incorporating additives into MDEA-based solvents significantly promotes acid gas removal efficiency at reduced energy consumption. Additionally, it has been noted that some additives have cooperative effects when used with MDEA, leading to enhanced solvent regeneration yield and lowered total annual cost. These findings underscore the significant economic benefits of our proposed methodology, which can lend valuable insights to plant operators and engineers who wish to optimize their amine-sweetening processes. The study's findings highlight the substantial financial benefits that can be derived from the addition of blending agents into MDEA-based solvents, thus enhancing processing efficiencies and making them economically viable in the natural gas industry.

1. Introduction

The global trend toward industrialization has led to increased energy demands. However, the regulations surrounding fossil fuels and the rise in energy prices pose challenges in meeting the diverse needs for power generation and transportation. Consequently, these factors have significantly contributed to environmental issues. Thus, it is imperative to explore alternative energy sources that are less polluting (Jaiswal et al., 2022). Among these alternatives, natural gas (NG) emerges as a lower carbon-intensity energy option. It emits 71% and 56% fewer greenhouse gases compared to oil and coal, respectively. Additionally, natural gas is economically viable, offering competitive pricing, good fuel efficiency, and relatively cleaner attributes when compared to

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other primary energy sources such as coal or oil (Lim et al., 2013). Notably, there has been a substantial increase in the demand for NG over the past decade (Darani et al., 2021). The importance of NG processing is as crucial as its necessity to comply with environmental standards and secure favorable market prices (Speight, 2017). There is a lot of contamination in the process of production of raw natural gases, which include hydrogen sulfide (H_2S) and carbon dioxide (CO_2) (Farooqi et al., 2024; Sadeghi et al., 2024). Thus, corrosion prevention is essential; environmental compliance standards can be achieved if these contaminants are removed safely (Abotaleb et al., 2022; Sadeghi et al., 2023). The removal or reduction of acid gases in industrial settings is typically accomplished through various methods, including the use of chemical amines, physical solvents, and their combinations (Esmaeili et al., 2023; Abotaleb et al., 2022). Among these methods, chemical absorption using amine solutions has been identified as the most economically viable method for large-scale acid gas removal, despite the existence of alternative processes such as membrane separation, cryogenic distillation, and hydrate formation (Mohamadi-Baghmolaei et al., 2021). The various case study illustrates that, on one hand, these resistances are necessary to improve the industrial process of sweetened natural gas, while on the other hand, the efficient removal of acid gas is a prerequisite for clean energy generation (Georgiadis et al., 2020; Karimi and Sadeghi, 2022). With the rise in demand comes the need to further emphasize the role of amine-based solvents in gas treating systems, particularly in their application to ensure continued cost-effectiveness and competitiveness of natural gas as an energy source (Gilassi et al., 2021; Sadeghi and Rahimpour, 2024). One of the challenges in chemistry today is how to enhance existing processes in amine gas sweetening, as the process removes carbon dioxide (CO_2) and hydrogen sulfide (H_2S), which are pollutants when purifying natural gas (Jassim, 2016; Vali et al., 2024). These technical and financial challenges are currently relevant to the industry. However, this approach can eliminate acid gases from gases like H_2S to prevent issues with natural gas and achieve the pipelining-level capability (Chew et al., 2022). This system requires higher absorption capacity to effectively and economically strip acid gases while minimizing energy use, especially on the regeneration tower's reboiler duty side (Long and Lee, 2017). Therefore, it is crucial to limit solvents and reduce energy consumption to enhance the economic effectiveness of inputs into natural gas use (Yagihara et al., 2024). As a result, innovation is becoming a significant aspect of the processing challenges for designing sustainable and economically viable gas processing systems in emerging energy markets (Meng et al., 2022). It aims at progressively advance gas treatment in the model to reach optimum functioning that complies with a high environmental standard and results in a significant reduction in operating costs (Hajilary et al., 2011).

As previously mentioned, the alkanolamines solvent process is vastly admitted within the oil and gas industry for treating natural gas containing sour gas (Tikadar et al., 2023). Among the various amines used in this process, mono-ethanolamine (MEA), di-ethanolamine (DEA), and methyl di-ethanolamine (MDEA) are frequently employed as absorbents for natural gas purification (Shi et al., 2016). It has been established that MDEA exhibits superior performance in natural gas sweetening compared to other amines due to its high selectivity for H_2S absorption over CO_2 absorption (Tikadar et al., 2020, 2023; Gonzalez et al., 2023). The utilization of solvents alone due to some challenges such as including limited carbon dioxide absorption due to the constraints imposed by chemical reactions, high energy requirements for amine regeneration, and substantial wastage of solvents and water. To mitigate these issues to some extent, hybrid solvents have been proposed. Notable examples include sulfinol and or sulfolane (tetramethylene sulfone) as physical-chemical solvents (Wang et al., 2020; Pereira et al., 2021). This research focuses on natural gas sweetening and its performance, and the economic implications of the results from this analysis are expected. The primary objective is to reduce the concentration of MDEA in the solvent to decrease the reboiler duty by up to five percent via additive. The nature of this reduction is equally crucial for conserving energy and reducing the carbon footprint of process operations. It also forecasted improved rates of solvent regeneration, leading to lower operating expenses and the added benefit of an extended solvent lifespan. Also, the use of physical and chemical solvent mixtures offers a more effective method for removing impurities from natural gas.

Moreover, the foaming ability of sulfolane when mixed with CO_2 is significantly lower than that of aqueous solvents, leading to increased downtime and maintenance costs due to the operational concern regarding foaming agents and other typical loss prevention measures. Thus, it becomes crucial to present this to an industry where any percentage increase in efficiency and cost reduction represents substantial annual savings, establishing an environmental connection and making a case for adopting this amine gas treatment technology. From here, Zou et al. (2020) commence their work. However, it is essential to note that this paper has demonstrated how mass transfer rates in amine-based physical solvent systems can be enhanced by blending hybrid MEA/sulfolane, thereby improving the CO_2 capture rates. On the other hand, Ejeh et al. (2020) propose an optimization strategy for amine solvent blends to optimize the temperature and pressure for the sweetening process. Moreover, Choi et al. (2021) assert that free of divalent cations, mono-cationic phosphate salts may protect amines and minimize solvent degradation while highlighting identified metal impurities associated with ion pairs. The last one is an article by Abd and Naji (2020); it focuses on various MDEA-enhancing agents and concludes that efficiency always comes at the price of energy, especially in reboiler energy consumption, where sulfolane outperforms others. Enhancing productivity across different units can be achieved through the optimization of processes, which can be implemented using various methods, such as simulation, genetic algorithm, or design of experiments (Tikadar et al., 2021; Shahbazi et al., 2023). Mathematical and statistical techniques, such as response surface methodology (RSM), provide a means to achieve optimal conditions with limited input data. RSM is a modeling and optimization method that allows for the anticipation of the relationship between variables and the prediction of optimal scenarios. Altogether, these groundbreaking readings would be a rational foundation for research applications and support investigations into potential solvent additives that may include sulfolane and phosphoric acid, possibly due to their cost benefits and enhancement of operations in amine gas treating processes.

2. Methodology

2.1. Process description

The procedure begins by allowing sour gas to flow into an absorber or contactor column. Sour gas usually contains high levels of H_2S and CO_2 that must be reinjected before undergoing further treatments. The absorber column includes trays to provide a large contact area between the sour gas and the amine solution. In the absorber column, sour gas is contacted counter-currently by a liquid amine solution (MDEA). The amine solution chemically interacts with H_2S and CO_2 in the gas stream, forming stable amine-acid gas complexes. The primary purpose of this unit is to

increase the contact time of the gas with the amine to improve the removal efficiency of the acid gas. When the sour gas exits the absorber column, it is referred to as sweet gas because the significant components of acid gas have been removed. The sweet gas is then separated from the absorber column, and depending on the intended application, it either be circulated and treated further or directly taken to the storage unit for later distribution. After absorption of the acidic gas, the rich amine solution is directed to the regeneration unit accompanied by any stripping column or equipment necessary for the regeneration of the rich amine solution. The regeneration unit is designed to heat the amine solution to a suitable level for removing the amine from the acid gas molecules. The acid gas may consist of a concentrated solution of H_2S and CO_2 at lower pressure and higher temperature (Jones, 2006; Godini and Mowla, 2008; Salem and Reyhani, 2015; Darani et al., 2021; Abotaleb et al., 2022) (see Fig. 1).

2.2. Techno-economic optimization

To optimize the conventional natural gas sweetening process, the described process is simulated based on the industrial real data in HYSYS. The acid gas equation was selected as the fluid property package. Subsequently, a validation using industrial data was conducted to assess the reliability of the simulation. Next, the effect of objective changes on the performance and efficiency of the process was analyzed. By understanding the influence of selected variables on the technical performance of the process, their economic effects were then examined. The study focuses on the technical-economic optimization of the process by identifying the effective parameters in the technical performance in the previous step. The experimental design was performed, and the simulated results were utilized to derive the outcomes of the designed experiments. Finally, by analyzing the results obtained from the experimental design, the optimal points of the variables are determined both technically and economically. All stages of this study, from the beginning namely, the simulation work to the economic evaluation is presented in the flowchart in Fig. 2.

2.3. Cost calculation

The redesign and renovation of many chemical processes can enhance energy efficiency and boost the unit's productivity. However, the implemented changes may have positive or negative effects on the process's economy. Thus, it is necessary to evaluate any modifications in a commercialized process from an economic point of view (Alipour et al., 2022). Therefore, the capital investment and operating cost must be assessed. According to the method briefly outlined by Sinnott and Towler (2019), the cost of each purchased equipment will be estimated using Eq. (1), where C_e represents the purchased equipment cost on a U.S. Gulf Coast basis, Jan. 2007 (chemical engineering price cost index (CEPCI) for 2007 was 509.7). The variables a, b and n are cost constants and exponent for that type of equipment, as referenced from Table 6.6 of Sinnott and Towler textbook, and S is size parameter of equipment.

$$C_e = a + b \times S^n \tag{1}$$

Each obtained C_e should be updated before use in continuous calculations. For this purpose, purchased equipment costs are indexed to 2022 through Eq. (2) (CEPCI for 2022 was 797.6).

$$\text{Cost}_{2022} = \text{Cost}_{2007} \times \frac{\text{CEPCI}_{2022}}{\text{CEPCI}_{2007}} \tag{2}$$

The Total Annual Cost (TAC) is a method of converting the cost

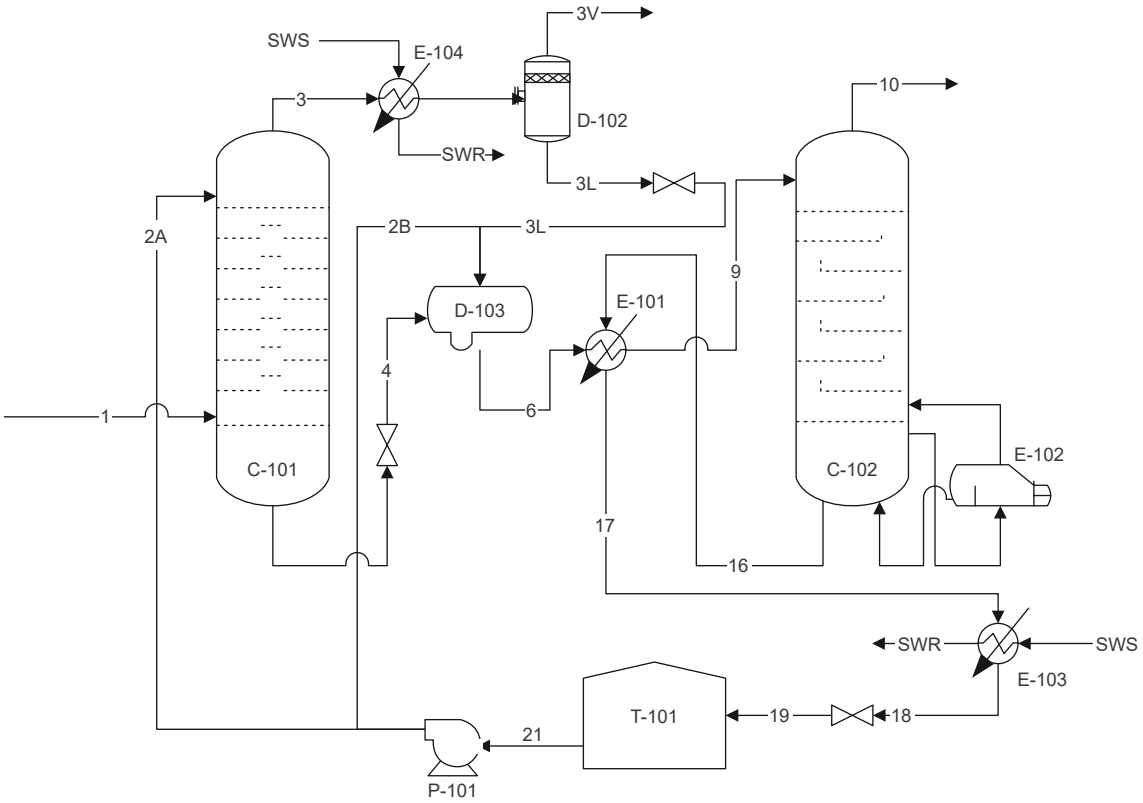

Fig. 1. Process flow diagram of natural gas sweetening plant.

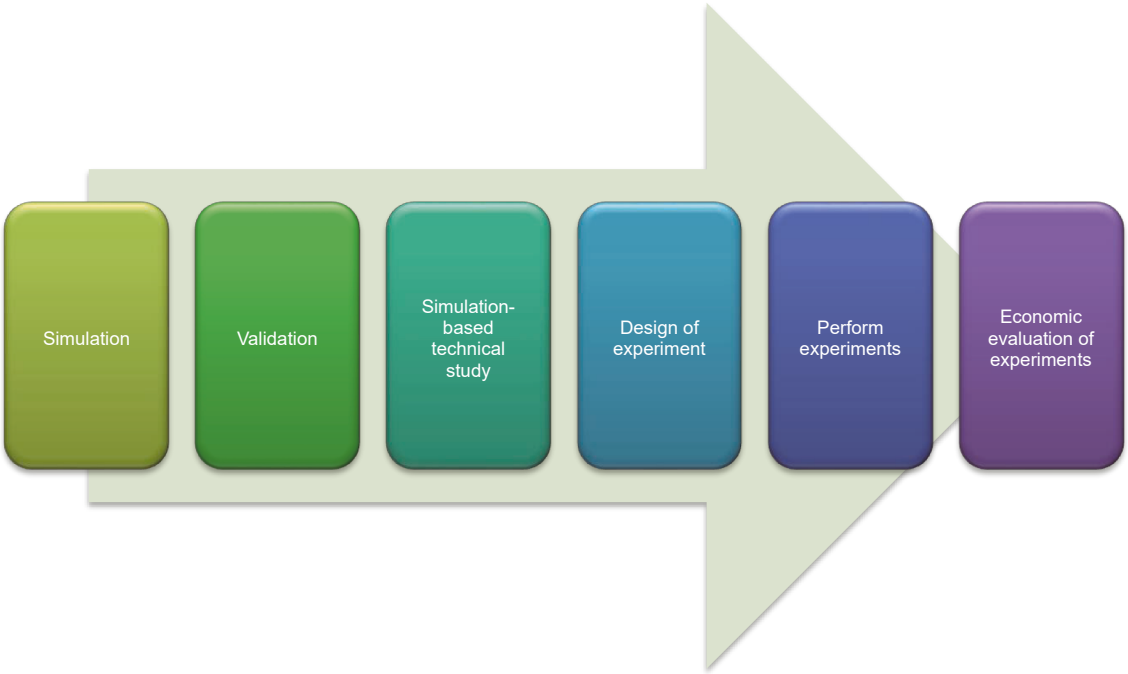

Fig. 2. The flowchart of techno-economic.

of capital into a future Annual Capital Cost (ACC) by comparing the current capital investment to future income sources. TAC, also called total cost of production (TCOP), is calculated by Eq. (3), where ACCR is the annual cost of capital ratio (assumed 0.205). For this goal, total operating costs primarily encompass raw material costs, total annual utility costs, labor (based on three shift position), maintenance (0.02 of fixed capital investment), taxes (0.01 of fixed capital investment), and insurance costs (0.004 of fixed capital investment) according to method described by Peters and Sinnott (Peters et al., 2003; Sinnott and Towler, 2019).

$$\text{Total Annual Cost} = (\text{Capital cost} \times \text{ACCR}) + \text{Operating cost} \quad (3)$$

2.4. Response surface methodology (RSM)

The Design of Experiments (DoE) considers the impact of interactions of input factors on the output responses. DoE aims to reduce experiment time and costs, determine essential variables, and achieve optimal conditions. DoE methods involve factorial, Taguchi, RSM, etc. (Karimi et al., 2022). RSM is categorized into four subordinate methods, i.e., Box-Behnken design (BBD), central composite design (CCD), circumscribed central composite, and inscribed central composite. As mentioned, the RSM method provides a reliable technique for improving process variables. This study applied a BBD to reach an appropriate operating condition. BBD requires fewer design points in experiment design compared to other methods (Shahbazi et al., 2023). In various studies, Response Surface Methodology was employed for multi-objective optimizations in conjunction with aspen plus and was also implemented to obtain optimal treatment conditions (Singh and Tirkey, 2021; Karimi et al., 2022). The influential variables of work are MDEA Concentration (X_1), Sulfolane (X_2), phosphoric Acid (X_3), Temperature (X_4), and pressure (X_5) as categorical factors. Table 1 demonstrates experimental ranges and levels of the independent variables. It should be noted that the range of operating conditions, i.e., temperature, pressure and solvent concentration, has been selected based on the range of real conditions of the petrochemical complex. As is clear, an arbitrary selection of the range could lead to a complete collapse of the hydraulic conditions of the tower. Additionally, the range of additives was determined based on previous work (Pereira et al., 2021).

3. Results and discussion

3.1. Simulation validity

Verifying and validating the simulation model is a crucial step to ensure its reliability. Typically, deviations below 10% between simulated and actual operational data are considered acceptable. Table 2 presents a comparison of simulation results and plant data for key process variables. The close agreement between values confirms that the simulation model is well-calibrated and suitable for optimization studies.

3.2. Technical optimization

To date, the amine gas treatment process is the most common technology used to sweeten natural gas on an industrial scale. Solvents such as MEA, DGA, DEA, DIPA, and MDEA are among the most common alkanoamine-based solvents used in the amine gas treatment process (Seidi et al., 2019; Ellaf et al., 2023). In this

Table 1
Experimental ranges and levels of the independent test variables.

Name	Type	Changes	Std. Dev.	Low	High
MDEA Conc., wt%	Factor	Easy	0	35	45
Sulfolane, wt%	Factor	Easy	0	0.5	2
Phosphoric acid, wt%	Factor	Easy	0	0.5	2.5
Temperature, °C	Factor	Easy	0	40	50
Pressure, Bar	Factor	Easy	0	60	70

study, MDEA is used as a solvent that has recently received much attention. One of the notable features of MDEA is its ability to selectively absorb CO_2 with reduced energy requirements during regeneration, owing to its lower heat of reaction (less energy consumption in the regeneration section) (Mudhasakul et al., 2013; Cao et al., 2021; Nie et al., 2023).

The temperature and pressure profile significantly influence the performance and stability of the absorption and regeneration columns (Madeddu et al., 2018; Hemmati et al., 2019). In particular, in the natural gas sweetening process, absorption occurs at low temperatures and high pressure (Van Roij, 2021). Therefore, increasing the temperature helps achieve ideal operating conditions. This temperature rise is mainly caused by the heat released from the reaction between the solvent and the acid gases (Abotaleb et al., 2022). In addition, sudden change in pressure parameters in the absorption and reduction columns can cause foaming (Thitakamol and Veawab, 2008; Leuner et al., 2022). Conversely, a sudden decrease in pressure changes in both columns can lead to fouling or plugging (Rix and Olujic, 2008). Therefore, maintaining a uniform pressure load is essential to prevent such undesirable phenomena. Consequently, the temperature and pressure profiles of the absorption and regeneration columns are significant factors. Smooth and gradual profiles, as shown in Fig. 3, help mitigate issues such as foaming or fouling, without any unexpected changes. Therefore, the risk of foaming in the absorption column or fouling/plugging in the regeneration column is improbable. This study's simulated temperature and pressure trajectories were free from sudden fluctuations, indicating stable operation. Literature review has shown that adding non-aqueous solvents such as sulfones to an amine solution helps prevent this reaction (Rayer et al., 2018; Pereira et al., 2021).

The case study's operational MDEA concentration was 46 wt%, and at CO_2 to H_2S feed ratios exceeding 2.0, such as the observed ratio of 2.6. This third type, alkanoamine, shows a good efficiency compared to other solvents in conditions where the CO_2 to H_2S feed ratio is less than one and the amount of loading of more minor acid gases is equal to 0.2. Under these conditions, energy consumption is 40% lower than in other processes using different solvents. Also, regardless of the licensing process type, the acid gas loading for MDEA solvent should not exceed 0.45, because as higher levels may cause corrosion in process equipment. Outside this range (the CO_2 to H_2S feed ratio is greater than one, and the acid gas loading exceeds 0.2), selectivity is lessened. In addition, with the development of oil and gas extraction, the CO_2 content in refinery feed has increased in recent years (Pereira et al., 2021). Eqs. (4) and (5), provide the CO_2 to H_2S feed ratio and the acid gas loading, respectively.

$$\text{Ratio of } CO_2 \Big/ H_2S = \frac{\text{The content of } CO_2}{\text{The content of } H_2S} \tag{4}$$

$$\textit{Acid gas loading } (\text{mol} / \text{mol}) = \frac{\text{Total molar flow of acid gas}}{\text{Molar flow of amine}} \tag{5}$$

As mentioned above, because the ratio of CO_2 to H_2S in the inlet stream is 2.5 times more than the standard limit, energy consumption efficiency in the unit is inadequate. Furthermore, the amount of amine loading is slightly above the allowable critical

Table 2
Validation of the simulation results with the actual value.

Parameters	Operating data	Simulation data	R.E., %
Sweet gas temperature, °C	48	43	9.9
Sweet gas pressure, bar	66	66	0.0
Sweet gas flow, m^3/d	629,010	632,932	0.6
Rich amine pressure, bar	66	66	0.0
Rich amine temperature, °C	35	29	15.6
Acid gas flow, m^3/d	13,433	13,433	0.0
Rich amine to exchanger temperature, °C	36	31	14.4
Stripper bottom temperature, °C	132	131	0.8
Stripper bottom pressure, bar	3	3	0.0
Lean amine pressure, bar	3	3	0.0
Lean amine temperature, °C	131.4	131.1	0.2

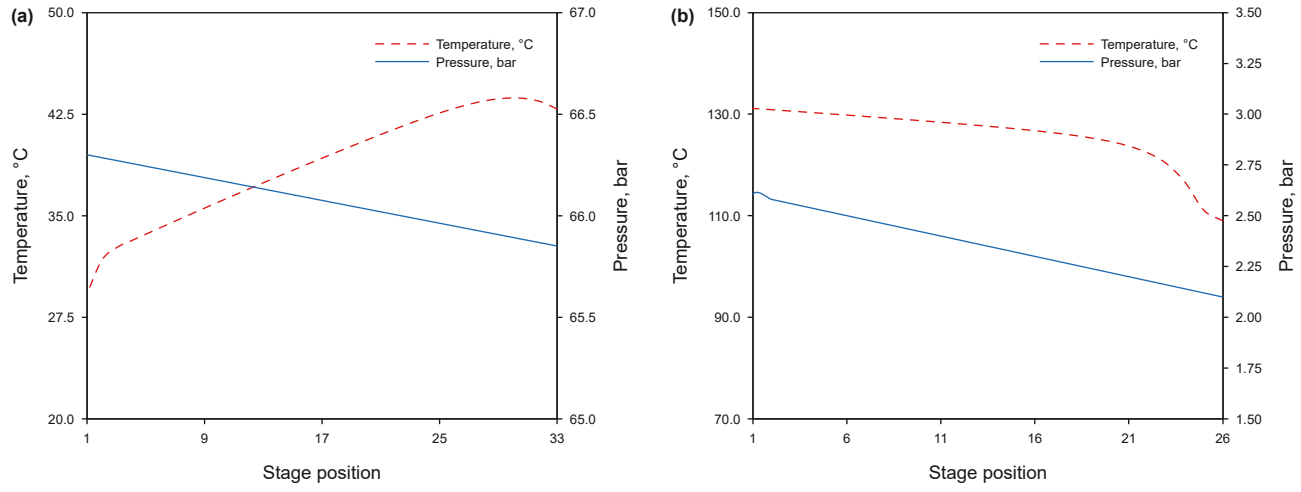

Fig. 3. The temperature and pressure profile of (**a**) absorber and (**b**) stripper column at the case study.

level, leading to severe unforeseen corrosion (Pereira et al., 2021). With these interpretations, it should be done in such a way that the corrosion rate of the solvent must be reduced. One logical approach to do this is to add catalytic promoters, also known as activators. Various catalytic promoters such as piperazine, sulfolane, or phosphoric acid are proposed. Sulfolane is known to reduce solvent foaming, improve CO_2 absorption, and lower solvent pH, thereby reducing corrosion. Phosphoric acid, based on literature and industrial patents, reduces reboiler duty, improves solvent regeneration, and ultimately lowers total annual cost (Ejeh et al., 2020; Wang et al., 2020; Cheng et al., 2021).

The molar composition of these two components was studied in two columns absorption and regeneration, shown in Fig. 4. As can be seen, the hydrogen sulfide reaches tray number 4, and the absorption of carbon dioxide continues to the top of the tower. Also, in the regeneration column, the excretion of carbon dioxide and hydrogen sulfide continues until the bottom of the column and the solvent is almost regenerated.

After reviewing patents for natural gas sweetening, it is recommended that a small amount of phosphoric acid be added to the solvent. As mentioned before, this can reduce the reboiler's energy consumption, which, in a broader sense, reduces the operating costs and the total annual cost. Also, the addition of phosphoric acid helps regenerate the solvent better, which reduces the solvent makeup flow and consequently improves operating costs. However, no explanation has been given for the cause of this behavior (Pereira et al., 2021). Fig. 5 illustrate the profiles of gas absorption and the energy-saving potential of phosphoric acid addition.

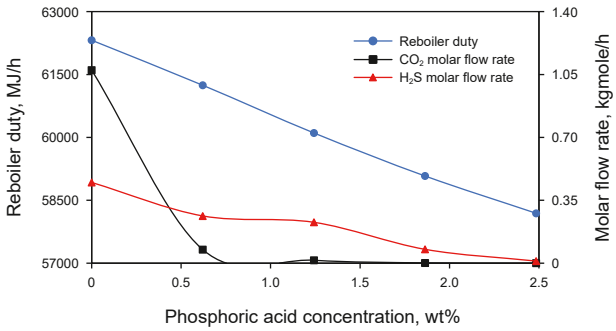

Fig. 5. The effect of phosphoric acid on the reboiler duty.

3.3. RSM evaluation and ANOVA analysis

The experimental design employed a Box-Behnken Design (BBD) with five variables affecting TAC (Total Annual Cost). Table 3 summarizes all experimental runs. This table shows that TAC consequences are achieved differently based on various runs.

Experiment No. 13 yielded the lowest TAC value of 27.077 M$/year, achieved through optimal combinations of MDEA, sulfolane, and phosphoric acid levels. According to Table 3, the MDEA concentration was reduced compared to the design data. Also, according to Table 3, the amount of sulfolane is rational as it is in the middle of the selected range. This consequence will make the process's costs reasonable (Pereira et al., 2021). Fig. 6 compares the obtained results through the simulation with the predicted values by the DoE method. It also indicates the distribution of model errors. If points are distributed around the reference line, confirm that the model error follows the normal distribution. Otherwise, it can be assumed that the model error follows the inefficiency indicators. A strong correlation between predicted and actual simulation results is demonstrated in Fig. 6, confirming model validity. Therefore, the achieved model can anticipate the process efficiently (Karimi et al., 2022).

Analysis of variance was employed to evaluate statistical models and analyze the differences among group means. Also, variance analysis was utilized to survey factors that influence the outcome. ANOVA tables consist of the degree of freedom, the sum of squares, the F-value, and the P-value for each factor. Table 4 demonstrates the ANOVA report for model adequacy checking. According to Table 4, the effects of multiple levels of multiple factors are compared. Therefore, the influence interaction of the F-value will be better when the amount of P-value must be less than 0.05 (for validation of the results). Also, the P-values less than 0.05 indicate that the model terms are significant.

Table 4 presents that the quantity P-value of the model (almost wholly) is less than 0.0001; the achieved amounts prove that the influence of all parameters is prominent and cannot be ignored. As well as the obtained model could be an appropriate model for anticipating experimental values. Also, the high F-value was another cause to confirm the model's adequacy. The model's F-value was obtained at 2390.52, which implies that the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise. The correlation coefficient values of TAC are illustrated in Table 5. The correlation coefficient values include R^2, adjusted R^2, and predicted R^2 values above 99.9% (for total annual cost). If the difference between adjusted R^2 and predicted R^2 is less than 20%, it shows the reliability of the model prediction.

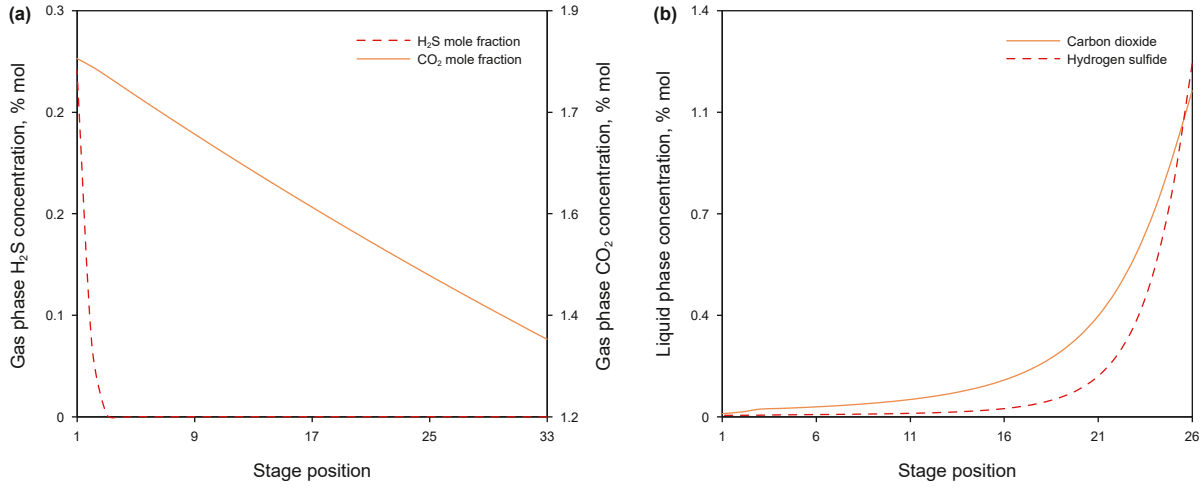

Fig. 4. The hydrogen sulfide and carbon dioxide mole fraction profile trough (**a**) absorber and (**b**) stripper column at the case study.

Table 3
The 5-factors BBD, together with the observed response of TAC.

Order of running experiment	The level value of each variable in the experimental run					Target, M$/year
	X_1	X_2	X_3	X_4	X_5	TAC
8	40	2	1.5	45	60	27.136
20	40	2	0.5	45	65	27.155
27	40	1.25	0.5	45	60	27.154
9	40	0.5	1.5	45	70	27.142
35	40	0.5	1.5	40	65	27.139
29	40	1.25	0.5	45	70	27.159
12	45	1.25	0.5	45	65	27.199
31	35	1.25	1.5	45	60	27.085
39	40	1.25	1.5	45	65	27.138
6	40	1.25	2.5	50	65	27.127
3	40	1.25	0.5	40	65	27.156
37	40	0.5	1.5	50	65	27.136
17	40	1.25	1.5	40	70	27.144
30	40	1.25	2.5	45	70	27.133
21	40	0.5	2.5	45	65	27.127
25	35	1.25	1.5	50	65	27.088
32	45	1.25	1.5	45	60	27.177
4	40	1.25	2.5	40	65	27.13
13	35	1.25	2.5	45	65	27.077
23	35	1.25	1.5	40	65	27.091
24	45	1.25	1.5	40	65	27.183
1	35	2	1.5	45	65	27.091
34	45	1.25	1.5	45	70	27.186
5	40	1.25	0.5	50	65	27.154
14	45	1.25	2.5	45	65	27.174
2	45	2	1.5	45	65	27.184
10	40	2	1.5	45	70	27.143
38	40	2	1.5	50	65	27.138
19	40	0.5	0.5	45	65	27.155
33	35	1.25	1.5	45	70	27.095
18	40	1.25	1.5	50	70	27.14
28	40	1.25	2.5	45	60	27.122
26	45	1.25	1.5	50	65	27.181
11	45	0.5	1.5	45	65	27.183
16	40	1.25	1.5	50	60	27.134
7	40	0.5	1.5	45	60	27.132
15	40	1.25	1.5	40	60	27.135
36	40	2	1.5	40	65	27.141
22	40	2	2.5	45	65	27.13

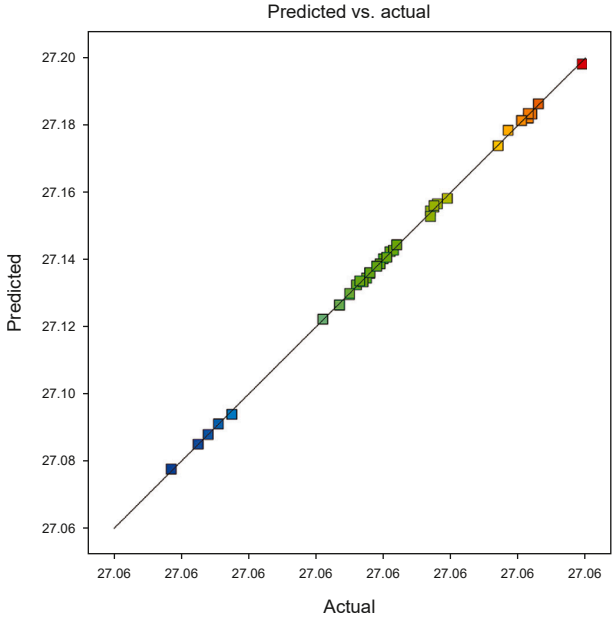

Fig. 6. The comparison of actual values from the simulation.

Table 4
ANOVA results for quadratic model.

Source	Sum of squares	DF	Mean square	F-value	P-value
X_1	0.0262	1	0.0262	36349.42	<0.0001
X_2	0.0000	1	0.0000	18.51	0.0004
X_3	0.0027	1	0.0027	3729.27	<0.0001
X_4	0.0000	1	0.0000	38.21	<0.0001
X_5	0.0003	1	0.0003	388.97	<0.0001
Quadratic model	0.0345	20	0.0017	2390.52	<0.0001
Residual	0.0000	18	7.213×10^{-7}		
Cor total	0.0345	38			

Table 5
Correlation coefficient values for total annual cost.

	R^2 values		
	R^2	R^2_{adj}	R^2_{perd}
TAC	99.96%	99.92%	99.13%

According to those above, the statistical results confirm that the predicted model is rational (for fitting data). As well as this result confirms Fig. 6, adequate precision measures the signal-to-noise ratio. If this ratio is more significant than 4, it is desirable. Adequate precision of the model is 193.262 (Gomravi et al., 2021).

The quadratic polynomial equation will be achieved based on experimental results. Eq. (6) declares an empirical relationship between the independent variables (MDEA Concentration (X_1), sulfolane (X_2), phosphoric acid (X_3), temperature (X_4), and pressure (X_5)) and response (TAC).

$$\begin{aligned}TAC = {} & 27.138 + 0.0464342 \times X_1 + 0.000971416 \times X_2 \\ & - 0.0137872 \times X_3 - 0.0013125 \times X_4 + 0.0041875 \times X_5 \\ & - 0.000385662 \times X_1 \times X_2 + 0.00164882 \times X_1 \times X_3 \\ & + 0.00025 \times X_1 \times X_4 - 0.00025 \times X_1 \times X_5 + 0.00075 \\ & \times X_2 \times X_3 + 8.88332 \times 10^{-16} \times X_2 \times X_4 - 0.00075 \times X_2 \\ & \times X_5 - 0.00025 \times X_3 \times X_4 + 0.0015 \times X_3 \times X_5 \\ & - 0.00075 \times X_4 \times X_5 - 0.00210088 \times X_1^2 \\ & + 0.000349516 \times X_2^2 + 0.00369434 \times X_3^2 + 6.14035 \\ & \times 10^{-5} \times X_4^2 + 6.14035 \times 10^{-5} \times X_5^2 \end{aligned} \quad (6)$$

Due to Eq. (6), the negative and positive signs before the coefficient exhibit antagonistic and synergistic effects, respectively (Gomravi et al., 2021). Based on Eq. (6), phosphoric acid (X_3) and temperature (X_4) have antagonistic effects in the quadratic polynomial, while MDEA concentration (X_1), sulfolane (X_2), and pressure (X_5) illustrate synergistic effects.

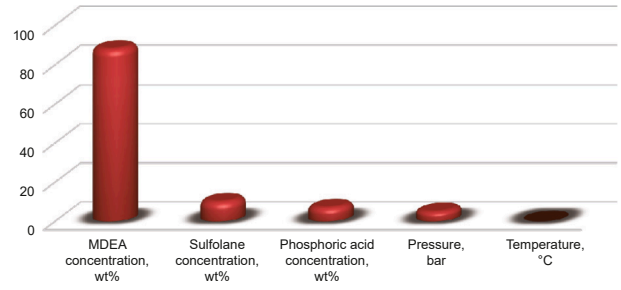

Fig. 7. Pareto bar chart analysis.

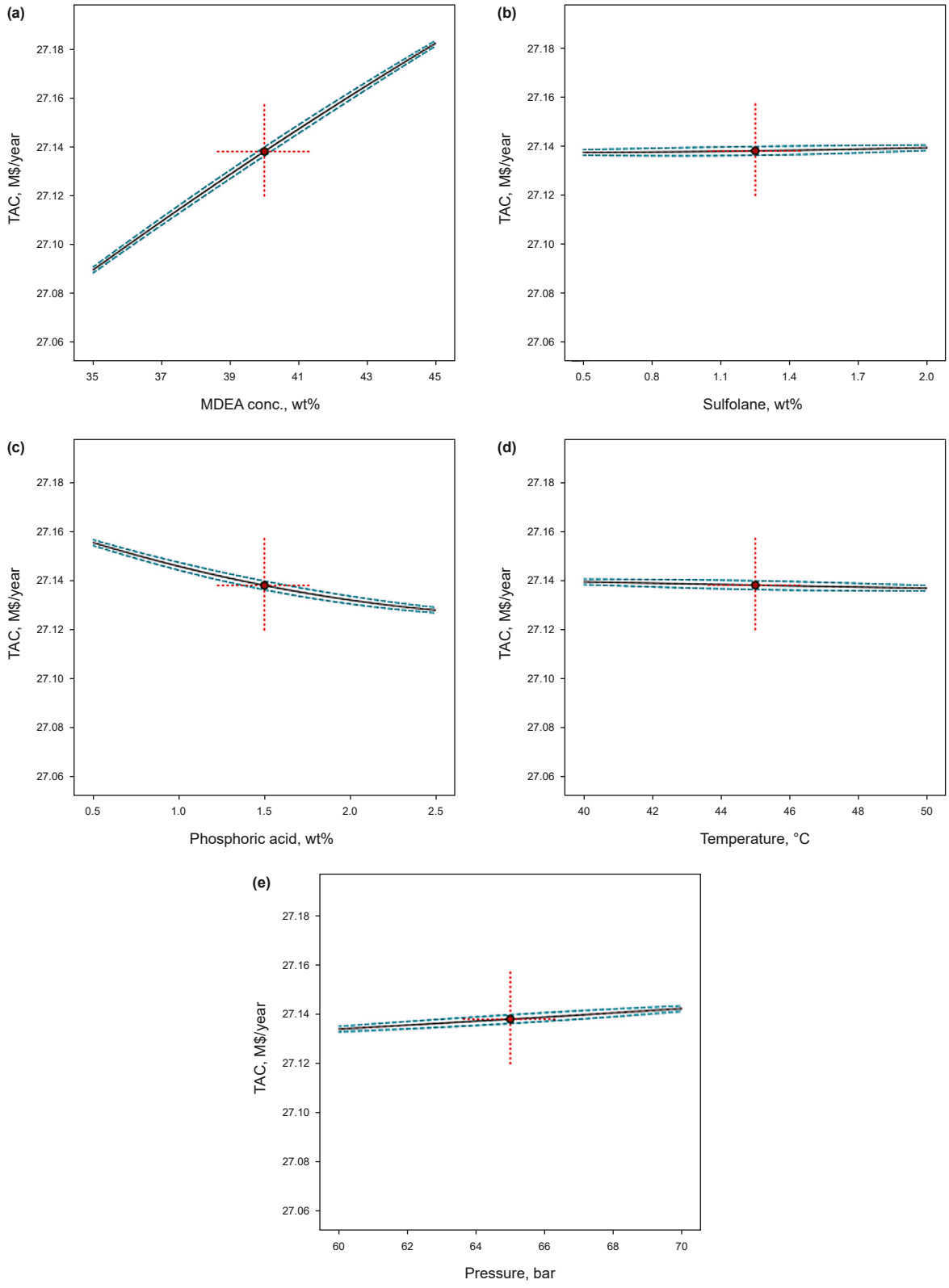

Fig. 8. Plot of the factors that affect the results.

3.4. Effect of variables

A Pareto graph (specialized bar chart) is a vital tool that applies to the DoE method while displaying the most significant consequences. Fig. 7 illustrates the Pareto bar chart. It's utilized to show the 80–20 principle; as seen in this bar chart, all four independent variables (except the temperature parameter) influence the efficiency process. A Pareto chart (Fig. 7) indicates MDEA concentration as the most influential factor on TAC, followed by phosphoric acid. Temperature had the least effect.

Fig. 8 shows the effect of each independent variable on cost (response TAC). As shown in Fig. 8, the impact of three parameters on total annual cost is approximately uniform. Generally, the response will change in a short range with the alteration in sulfolane amount, temperature, and pressure. MDEA concentration commonly has the highest effect on TAC, and the phosphoric acid amount has the second degree of impact on TAC. MDEA concentration is an essential factor in designing a low-cost process system. Due to the achieved result, the maximum cost of TAC is observed at 27.186 M$/year, and with the change of MDEA concentration, the total annual cost is decreased. Also, it should be noted that other independent variables affect response with low influence.

4. Limitations and future work

Despite the promising results achieved through simulation and RSM-based optimization, several limitations remain that must be considered when translating this framework to full industrial applications. First, the current study is based on steady-state simulation data under ideal conditions. Real plant environments often involve dynamic disturbances, feedstock variability, and operational upsets that were not modeled in this study. Second, scale-up from simulation to industrial implementation presents challenges related to equipment sizing, process control integration, corrosion management, and heat transfer limitations. Additionally, economic assessments are based on average utility and material prices, which may fluctuate regionally or seasonally. Real-world constraints, including operator training, regulatory approval, and solvent degradation rates, also influence long-term feasibility. For future research, pilot-scale testing is recommended to validate the optimized conditions under real gas compositions. Integration of real-time process analytics, advanced control strategies, and machine learning models could further improve predictive accuracy and adaptability across different natural gas fields.

5. Conclusions

The conclusion of the natural gas simulation and optimization can be as follows.

(1) The simulation of the amine sweetening process, incorporating phosphoric acid and sulfolane (as additives) into the MDEA-based solvent, was successfully implemented. Additionally, a techno-economic approach was utilized to develop a cost model for sour gas sweetening. The aim of using additives was to assess acid gas removal efficiency, energy consumption, solvent regeneration yield, and overall process economics.
(2) RSM methodology (BBD) was employed to simulation optimization and modeling. MDEA Concentration, Sulfolane, phosphoric Acid, Temperature, and Pressure were chosen as independent variables affecting amine sweetening performance.
(3) ANOVA results indicated a high correlation coefficient for this purpose, with the correlation coefficient reaching $R^2 = 0.9996$, $R^2_{adj} = 0.9992$. Based on the results from the ANOVA analysis and Pareto chart, MDEA concentration significantly impacts the independent variables.
(4) The RSM optimization result demonstrates that the total annual cost of the amine sweetening process can reduced by up to 27.077 million US dollars per year at 35 wt%. It is important to note that the typical MDEA solvent concentration in petrochemical complexes is approximately 40%. This significant consequence of the MDEA concentration occurs when the sulfolane amount is 1.25 wt%, the phosphoric acid amount is 2.5 wt%, at 45 °C and 65 bar.
(5) The addition of phosphoric acid and sulfolane enhanced acid gas removal efficiency and energy consumption. Furthermore, certain additives can lead to improved solvent regeneration yield and reduced total annual costs. Overall, it is evident that the selected solution provides valuable insights for the unit designer to optimize their sour gas sweetening processes.

CRediT authorship contribution statement

Asadollah Karimi: Project administration, Writing – original draft, Data curation, Software, Conceptualization, Methodology, Investigation. **Arash Sadeghi:** Investigation, Resources, Methodology, Data curation, Writing – original draft, Conceptualization. **Mohammad Shamsi:** Investigation. **Mohammadreza Rahimpour:** Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Nomenclature

H_2S	Hydrogen sulfide
CO_2	Carbon dioxide
MDEA	Methyl-diethanolamine
DoE	Design of Experiment
X	Independent variables in DoE
R^2	Coefficient of determination
RSM	Response Surface Methodology
BBD	Box-Behnken Design
DGA	Diglycolamine
DIPA	Diisopropylamine
DEA	Diethanolamine
MEA	Ethanolamine
wt	Weight
C_e	Purchased equipment cost
TAC	Total Annual Cost
M$	Million doller
DF	Degree of freedom

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