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Technical enhancement amine gas treating and cost reduction 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 lower total annual costs. The results show that incorporating additives into MDEA-based solvents significantly promotes acid gas removal efficiency and reduce energy consumption. Additionally, it has been noted that some additives have cooperative effects when used with MDEA, leading to enhanced solvent regeneration and lower total annual cost. These findings underscore the significant economic benefits of our proposed methodology, which can deliver 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 increase other primary energy sources such as coal and oil (Lim et al., 2013). Notably there has been a substantial increase in the demand for NG over the past decade (Darabi 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 (Mohammadi-Baghmolaei et al., 2021). The various case study illustrates that on one hand these resistances are necessary to improve the industrial process of sweetening 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 delivery capability (Chew et al., 2022). This system requires high absorption capacity to effectively and economically strip acid gases while minimizing energy use especially on the regeneration towers 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 (Yaghnaha 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 progressive advanced 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 (Tirana et al., 2023). Among the various amines used in this process monoethanolamine (MEA), diethanolamine (DEA) and methyldiethanolamine (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 (Tirana et al., 2020, 2023; Gonzalez et al., 2023). The utilization of solvents alone leads 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 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 flow time and maintenance costs due to the operational concerns regarding foaming agents and other typical loss prevention measures. Thus it becomes crucial to present this to an industry where even a small 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 in MEA/sulfolane thereby improving the CO_2 capture rates. On the other hand Ejeh et al. (2020) proposed 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 (Tirana 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 relationships between variables and the prediction of optimal scenarios. Altogether these groundbreaking learnings would lay a foundation for research applications and support investigations into potential solvent alternatives 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 with 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 recirculated and treated further or injected/taken to the storage unit for later distribution. After absorption of the acidic gas, the rich amine solution is injected to the regeneration unit accompanied by and 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 high temperature (Jones 2006; Godini and Mowla, 2008; Salem and Rehani 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

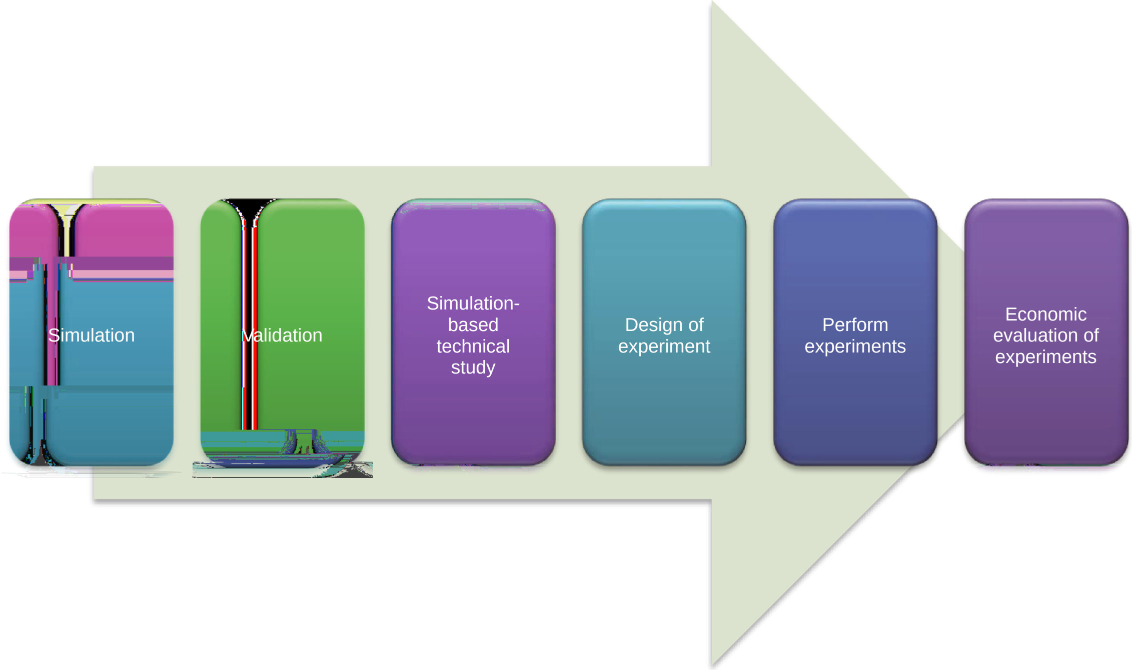

Fig. 2. The flowchart of techno-economic.

of capital to a future Annual Capital Cost (ACC) 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 (assume 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 (0.007 of fixed capital investment) according to methods described by Peters and Sinnott (Peters et al., 2003; Sinnott and Towler, 2019).

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

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 Ti e, 2021; Karimi et al., 2022). The influential variables of who 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 works (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 operation data are considered acceptable. Table 2 presents a comparison of simulation results and plant data for the process variables. The close agreement between values confirms that the simulation model is well-validated 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 alkanolamine-based solvents used in the amine gas treatment process (Seiri et al., 2019; E al 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 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 profiles significantly influence the performance and stability of the absorption and regeneration columns (Ma e u et al., 2018; Hemmati et al., 2019). In particular, in the natural gas sweetening process, absorption occurs at low temperatures and high pressure (Van Rooij, 2021). Therefore, increasing the temperature helps achieve ideal operating conditions. This temperature rise is mainly caused by the heat release from the reaction between the solvent and the acid gases (Abotaleb et al., 2022). In addition, sudden changes in pressure parameters in the absorption and reduction columns can cause foaming (Thitakamol and Veawab, 2008; Leu e et al., 2022). Conversely, a sudden decrease in pressure changes in hot columns can lead to fouling or pulsing (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/pulsing in the regeneration column is important. 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 sulfolanes to amine solution helps prevent this reaction (Ra e et al., 2018; Pe ei a et al., 2021).

The case study's operational MDEA concentration was 46 wt%, and that CO_2 to H_2S feed ratios exceeding 2.0 such as the observed ratio of 2.6. This third type alkanolamines 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 solvents 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 (Pe ei a et al., 2021). Eqs. (4) and (5) provide the CO_2 to H_2S feed ratio and the acid gas loading respectively.

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

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

As mentioned above, because the ratio of CO_2 to H_2S in the inlet feed 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
Variation 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/h	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/h	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

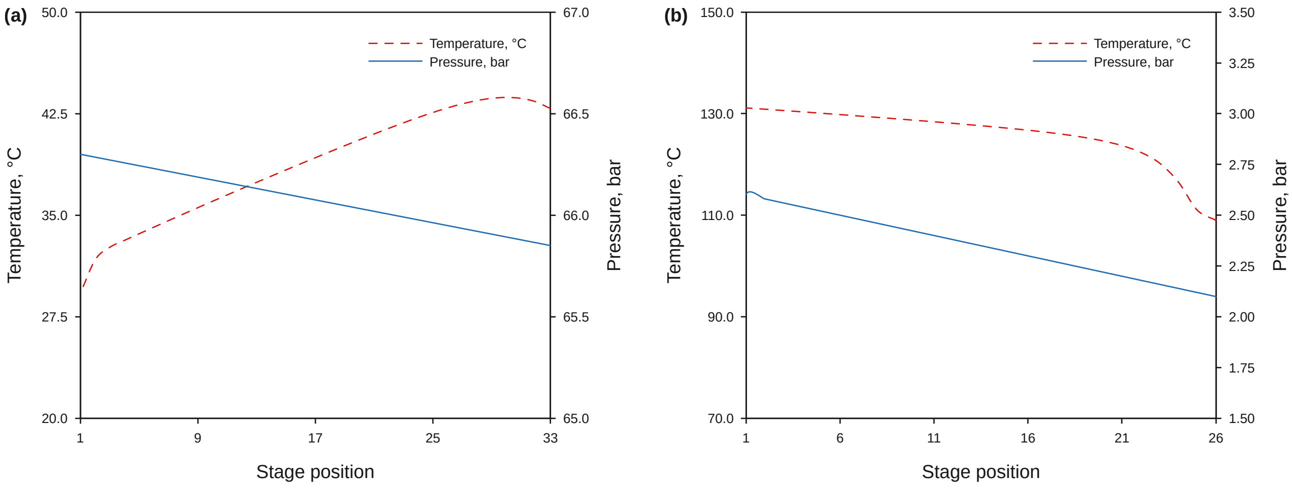

Fig. 3. The temperature and pressure profile of (**a**) absorber and (**b**) stripper column at the case study.

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 and 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 illustrates the profiles of gas absorption and the energy-saving potential of phosphoric acid addition.

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 minimize the process 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 efficiency (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 whole) 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 the

According to those above the statistical results confirm that the predicted model is rational (for fitting data). As we had this result confirms Fig 6 adequate precision measures the signal-to-noise ratio. If this ratio is more significant

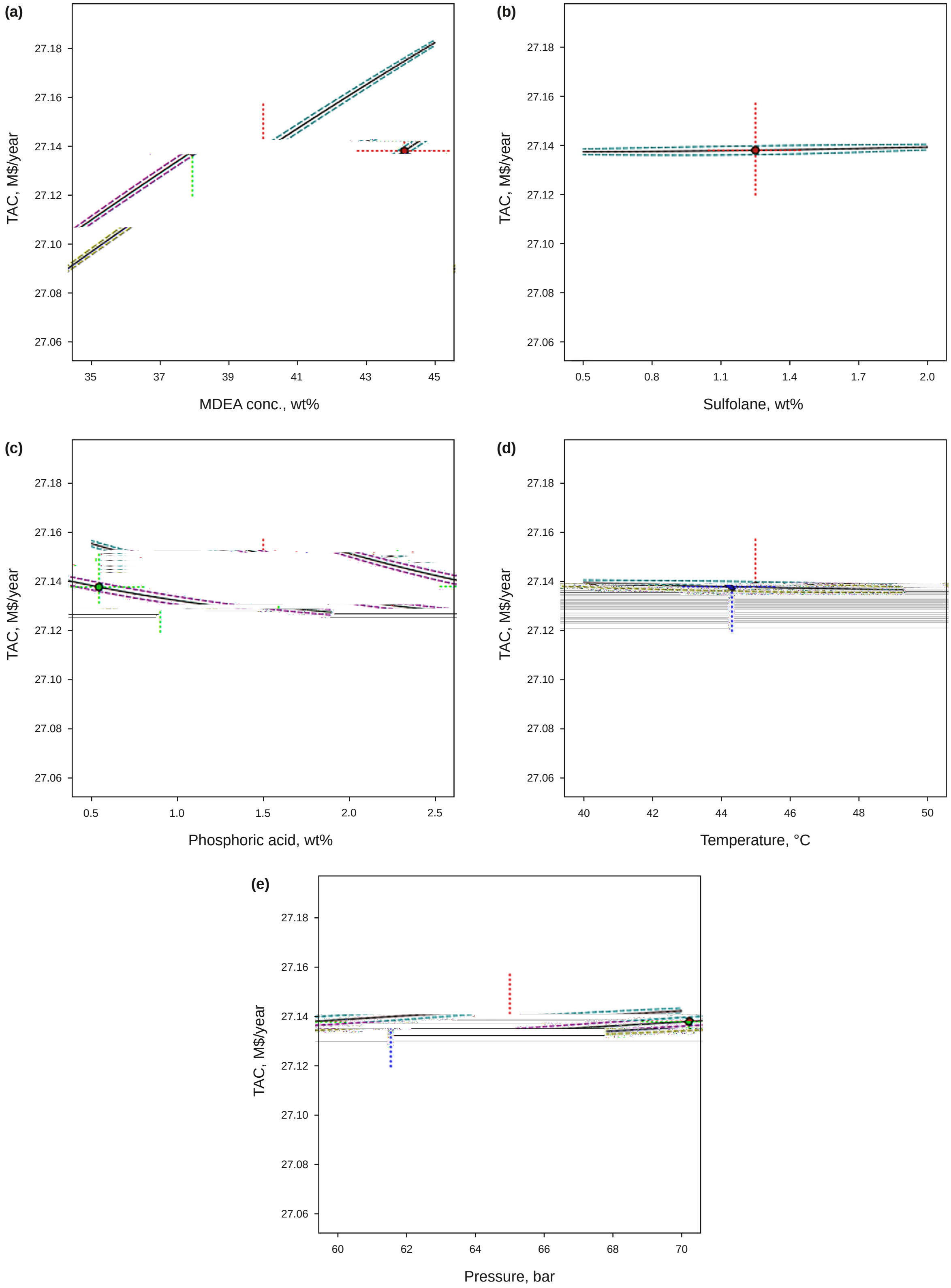

Fig. 8. Plot of the factors that affect the results.

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 chart. It's utilized to show the 80–20 principle, as seen in this 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

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