



# Effect of acidic products from degradation of *N*-methyldiethanolamine amine on CO<sub>2</sub>/H<sub>2</sub>S capturing from natural gas

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## Abstract

To evaluate the impact of heat-stable salts on the CO<sub>2</sub>/H<sub>2</sub>S separation from natural gas using 45 wt% of MDEA amine, we comprehensively and systematically examined essential parameters, such as acid gas loading, solvent makeup flowrate, and reboiler duty, in the presence of various acidic oxidative products with Aspen Hysys version 9. We also investigated the pH of an acid/solvent amine aqueous solution at feed amine conditions. Acidic products from the MDEA oxidation considered were glycolic, oxalic, formic, acetic, thiosulfuric, sulfuric, phosphoric, and thiocyanic products. The simulation results showed that the presence of acids with different chemical structures can minimize both the pH of the solution and acid gas loading. However, the energy demand in the reboiler was reduced. Some of these acids, namely thiosulfuric, formic, and thiocyanic acids, worked as promoters in the desorption process and reduced the solvent makeup flowrate by – 51.71%, – 62.24%, and – 86.39%, respectively, compared with fresh 45 wt% MDEA. Furthermore, a countermeasure for exploiting the reduced reboiler energy demand and promoting the desorption rate in the presence of these acids was proposed. The study outputs can serve as a guide for classifying acid impact and developing a countermeasure for using MDEA amine in managing the formation of heat-stable salts during the absorption of acid gases.

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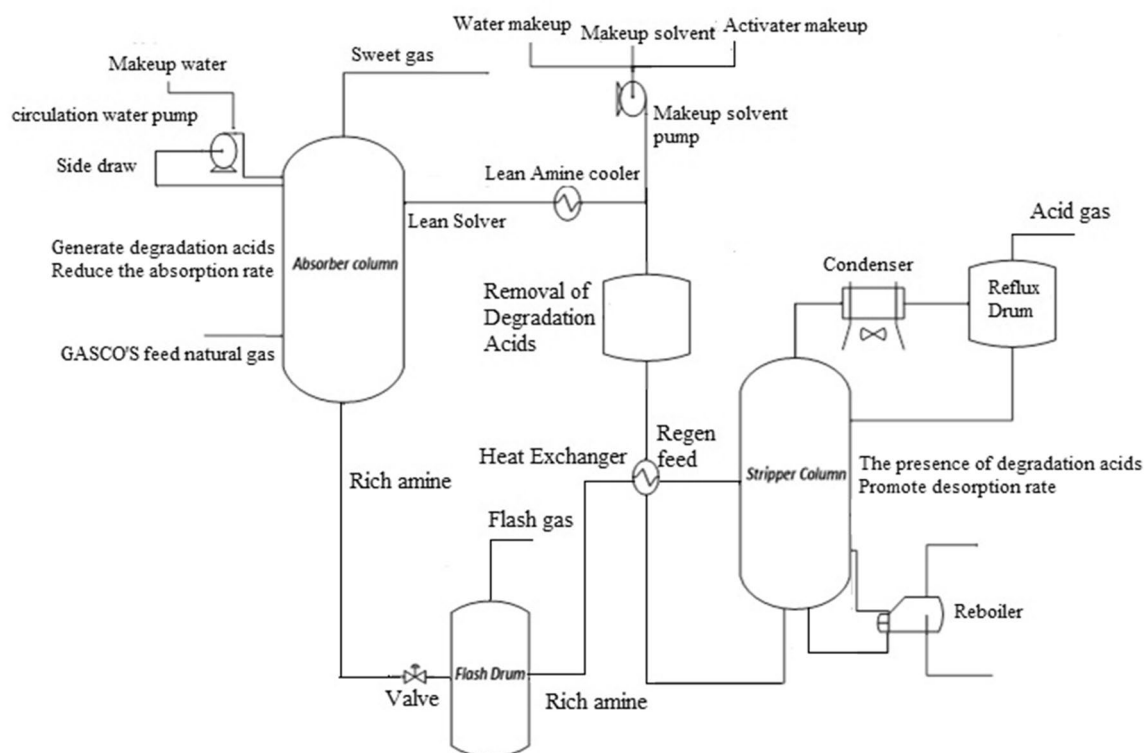
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## Graphic abstract



**Keywords** Amine degradation · CO<sub>2</sub> capture · H<sub>2</sub>S removal · Heat-stable salts · Energy control · MDEA acidic oxidation products

## Introduction

### Overview

Reduction in greenhouse gasses is a major issue posing a considerable challenge the environmental health. Carbon dioxide, a main component of greenhouse gases, is mainly produced by anthropogenic activities (Caravaggio et al. 2019). According to the World Energy Outlook, total CO<sub>2</sub> emissions will increase up to 37.2 Gt by 2035 because of fuel combustion facilities (Sharif et al. 2020). Thus, a method for capturing CO<sub>2</sub> from fossil-based fuels and storing it is attracting considerable interest worldwide. Such method offers the possibility of continuously using fossil-based fuels by reducing their contribution to environment warming. Besides, this sweetening method would result in a complete departure from classic thinking about climate security that would need elimination or severely limiting the application of fossil fuels. Fossil fuel combustion has a clear relationship with elevated greenhouse gases emission levels (Braungardt et al. 2019). CO<sub>2</sub> emissions associated with the burning of fossil fuels constitute up to 78% of the

total emissions between 1970 and 2010. Specifically, Olajire (2010) stated that the total acid gas emissions from the combustion of three main fossil fuel types, namely natural gas, oil, and coal, are 117,140, 165,687.007, and 214,000.016 lb/billion BTU of energy input, respectively (Olajire 2010). Natural gas, as a fossil-based fuel, comprises various types of acid gases, such as CO<sub>2</sub>, H<sub>2</sub>S, and some mercaptans, and the removal of these gases is essential to addressing environmental concerns and operating issues, such as corrosion, caused by acidic gases (Huttenhuis et al. 2007; Abd et al. 2019b).

### Technology options for removal of acid gases

Various technologies using absorption (Fang et al. 2020), adsorption (Abd et al. 2020), membrane (Lei et al. 2020), and cryogenic processes (Song et al. 2019) for capturing acid gases, mainly CO<sub>2</sub>, have been proposed. The selection of a capturing technology depends on different parameters, such as the composition of feed gas and processing capacity. Chemical absorption using amines solvents is the most common method for removing acid

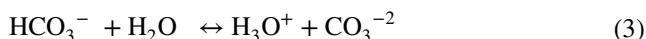
gases from natural gas (Kuramochi et al. 2012). The main advantages of amine absorption technology are its capability to treatment large amounts of feed gas and to remove high concentrations of acid gases. Conversely, the main drawbacks are its high energy requirements during the regeneration process, corrosion issues in plant facilities, and amine loss due to degradation (Olajire 2010; Gouedard et al. 2012). The amine degradation issue is inevitable when acid gases and amine degradation products are present in three various pathways, namely (1) carbamate polymerization, (2) thermal degradation, and (3) oxidative degradation (Chi and Rochelle 2002). In a same approach, carbamate polymerization and thermal degradation occur under a high operating temperature of approximately 205 °C in the regenerator column (Rochelle 2012). By contrast, oxidative degradation occurs because of the reaction between amine with O<sub>2</sub> and acid gases at the absorber column and results in the formation of acidic oxidative products. The products from the oxidative degradation of amine significantly govern corrosion and foaming because these products are easily generated and accumulate through the absorption of acid gases (Fredriksen and Jens 2013). Thus, the impact of these acidic products on process performance should be evaluated.

### Scope of the study

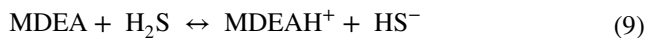
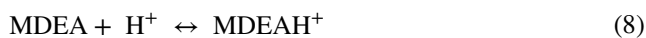
This work is motivated by a desire to understand the impact of various types of acidic oxidative products on the performance of acid gas removal. Given that the subject is fairly intricate, some critical issues should be addressed, such as (1) the reaction pathways for formation of the heat-stable salts (HSSs) in MDEA aqueous solution, (2) the impact of acidic oxidative products on the performance of capturing process, (3) the chance that these acids can serve as promoters for the process, and (4) countermeasures for controlling and reducing the impact of acidic oxidative products. Thus, in the present study, the effects of nine different types of oxidative degradation acids, namely glycolic, oxalic, sulfuric, thiosulfuric, thiocyanic, acetic, hydrochloric, formic, and phosphoric acids, which can react with MDEA solvents and form a wide range of HSSs, on acid gas removal performance have been evaluated. The inputs of GASCO'S Habshan plant were used in highlighting the impacts of these amine oxidative acidic products on solution pH, the absorption rates of CO<sub>2</sub> and H<sub>2</sub>S, reboiler energy, and MDEA makeup flowrate. Moreover, the impacts of these acids were graded on the basis of the tested parameters. The results can be helpful in categorizing the common oxidative MDEA products and investigating their impacts.

### Reaction of CO<sub>2</sub>/H<sub>2</sub>S absorption in aqueous MDEA

The absorption of CO<sub>2</sub> and H<sub>2</sub>S is through the reaction of these acid gases with an amine solution. The following reactions may occur during CO<sub>2</sub> and H<sub>2</sub>S removal with MDEA solvent (Abd et al. 2019a; Feyzi et al. 2017):



The reaction between CO<sub>2</sub> and an MDEA solvent is a base-catalyzed hydrolysis reaction, which enhances hydrolysis reaction and results in the production of bicarbonates. Reactions 1, 2, and 3 show the process of ionization of the aqueous solution. Various approaches have been mentioned that the reaction of CO<sub>2</sub> and MDEA has low rate because it forms HCO<sub>3</sub><sup>-</sup> instead of MDEACOO<sup>-</sup>, as shown by Reactions 4 and 5 (Feyzi et al. 2017). This effect can be attributed to the absence of hydrogen atoms that can attach to nitrogen atoms in tertiary amines. Moreover, H<sub>2</sub>S reacts with an MDEA solvent instantaneously, involves proton transfer, and results in the formation of amine salt.



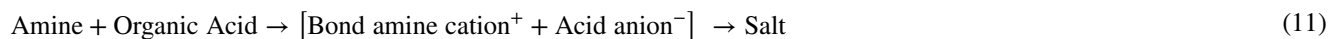
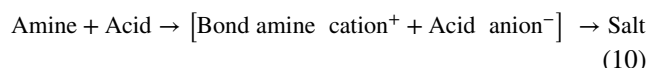
where Reactions 6 and 7 induce the ionization of water and Reaction 8 is the protonation of MDEA.

### Heat-stable salts formation in *n*-methyldiethanolamine solution

The pollutants of the amine aqueous solution are mainly HSSs and amine degradation products. These contaminants are produced from (1) reaction of amine and feed gas

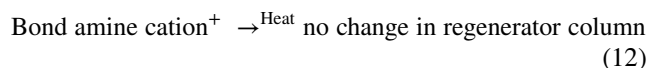
compositions (acid gases, impurities) and/or (2) physical or chemical degradation of amine. The amine oxidation is a major challenge in the amine scrubber process that can cause solvent loss and HSSs production. Through acid gases absorption, amine solution is subjected to moderate operation temperature of approximately 50 °C and oxidative conditions. Along with CO<sub>2</sub>, H<sub>2</sub>S, and O<sub>2</sub>, different

stronger than the reaction between an amine solvent and CO<sub>2</sub>/H<sub>2</sub>S, which forms HSSs, heat-stable amine salts, or organic HSSs (Verma and Verma 2009). The general reactions pathways involved in the formation the HSSs are as follows:

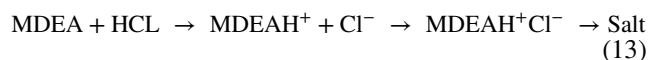


types of impurities are transferred to the amine solution through the absorption process. Amine oxidation and formation of HSSs are the most rapid amine degradation reactions in the acid gases removal (Goff and Rochelle 2004). A considerable amount of work is introduced on the oxidation of different types of amines (Gouedard et al. 2012; Mazari et al. 2015; Dickinson et al. 2016; Karnwiboon et al. 2017). The formation reactions of HSSs were deduced from (1) peroxide and chlorine oxide free-radical oxygen attack on aqueous amines; (2) measurement of products formed during long-term, high-temperature or pressure reactions; and (3) measurement of products formed during the medium term and high O<sub>2</sub> mass transfer conditions (Mazari et al. 2015). In a major advance in 2009, Lepaumier and co-authors reported that primary (MEA) and secondary (DEA) amines are more vulnerable to degradation than tertiary (MDEA) and hindered (AMP) amines (Lepaumier et al. 2009). They attributed this finding to the differences in reaction's pathways of the oxidation among types. For example, the first stage of the oxidation of primary and secondary amines commonly occurs in the formation of imine (Richard Keene 1999; Thiel 2003). By contrast, the lack of a labile proton at the  $\alpha$  position in the hindered amines impedes the production of stable imine. The first stage in the oxidation of tertiary amines is the production of cationic radical that is eventually rearranged during the production of iminium ion (Thiel 2003). In the presence of water, nonaryl imines and iminium ions rapidly hydrolyze to carbonyls (aldehydes or ketones) and amines or ammonia. Aldehydes oxidation occurs swiftly at moderate aqueous conditions and results in the production of organic acids, which accumulate under capturing conditions and is involved in the formation of the heat-stable salt.

Verma et al. (2009) determined the HSSs anionic as nitrate (NO<sub>3</sub><sup>-2</sup>), nitrite (NO<sub>2</sub><sup>-2</sup>), sulfate (SO<sub>4</sub><sup>-2</sup>), sulfite (SO<sub>3</sub><sup>-2</sup>), phosphate (PO<sub>4</sub><sup>-3</sup>), thiosulfate (S<sub>2</sub>O<sub>3</sub><sup>-2</sup>), thiocyanate (SCN<sup>-</sup>), formate (HCOO<sup>-</sup>), acetate (CH<sub>3</sub>COO<sup>-</sup>), and oxalate (C<sub>2</sub>O<sub>4</sub><sup>-2</sup>) (Verma and Verma 2009); this finding is supported by another study (Kadnar and Rieder 1995). Reactions between amine solvents and acidic products are

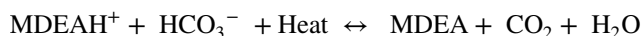


In Reactions 10 and 11, organic/non-organic acids react irreversibly with the solvent and generate bond amine cations. In Reaction 12, these compounds cannot be regenerated using heat and accumulates in the stripper as HSSs. For example, Reactions 13–19 demonstrate some possible reaction's pathways for HSSs formation from the reaction of MDEA and acids, such as formic, acetic, glycolic, oxalic, thiosulfuric, sulfuric, phosphoric, and thiocyanic. The production pathways of these acids were introduced as similar oxidative processes in accordance with radical induced oxidation of MDEA (Tavan et al. 2020; Reynolds et al. 2016). A peroxide radical was firstly generated, and it further reacted MDEA and oxygen, produced hydroperoxide, and was decomposed to form corresponding acids.



## Absorption of CO<sub>2</sub>/H<sub>2</sub>S reactions

Acid gases desorption in the regeneration column was a reverse reaction of absorption process and did not completely separated under normal operative conditions (Choi et al. 2010). Firstly, at a high loading rate, a part of  $\text{HCO}_3^-/\text{CO}_3^{2-}$  was heated to a certain temperature at which CO<sub>2</sub>/H<sub>2</sub>S release, while some of  $\text{HCO}_3^-$  will react with  $\text{MDEAH}^+$  to produce CO<sub>2</sub> and H<sub>2</sub>S. At low loading rate,  $\text{HCO}_3^-/\text{CO}_3^{2-}$  was completely decomposed and CO<sub>2</sub> and MDEA were generate under regeneration conditions.



## Simulation strategy

In the present work, the simulation inputs were obtained from the Acid Gases Removal (AGR) plant of GASCO'S Habshan, United Arab Emirates (Younas and Banat 2014; Alkasem et al. 2015). The operating conditions, streams compositions, and feed/product flowrates were determined according to the measures of GASCO'S Habshan plant. Aspen Hysys version 9, provided by Aspen Technology Inc, was deployed for the modeling of the process. The outputs of the simulation were obtained using the Acid Gas fluid package. The Acid Gas fluid package includes the eNRTL model variables and other transport property model factors established from a regression of huge thermodynamic and physical property data for aqueous amine solutions. This fluid package comprises the system of amines reactions pathways without the need to define them into the simulator (Song and Chen 2009; Zhang and Chen 2011; Zhang et al. 2011b). Once the definition of the feed components and the fluid package is completed, next is to insert the operating

units. The logical operator 'recycle' was presented for the purpose of correctly running the simulation. The absorption column had 24 internal trays and tray numbering from top to bottom. Natural gas was fed to the absorption column at the bottom and the MDEA aqueous solution stream at the top of the column. Tray spacing was specified to be 0.6096 m as recommended by Aboudheir and Elmoudir (2013) and Warudkar et al. (2013). In Table 1, the authors reproduced the other input specifications for our base study plant. The simulation products should be with CO<sub>2</sub> content around 2% and 20 ppm of H<sub>2</sub>S following environmental regulations and sales specifications. According to Aboudheir and Elmoudir (2013), the system factor was chosen to be 0.8 for both absorption and regeneration columns to avoid/minimize the foaming (Aboudheir and Elmoudir 2013). The main simulation assumptions are summarized and illustrated below:

1. The simulation works under steady-state conditions.
2. The operation mode of the absorber tower is adiabatic.
3. The heat exchangers are in counter-current flow.
4. Vapor/liquid move out the tray in equilibrium.
5. No chemical reaction in the gas phase.
6. The specific wetted area is the same for both heat and mass transfer.
7. Flow is one-dimensional in the z-direction.
8. H<sub>2</sub>S, CO<sub>2</sub>, and H<sub>2</sub>O are the only species transferred across the interface.

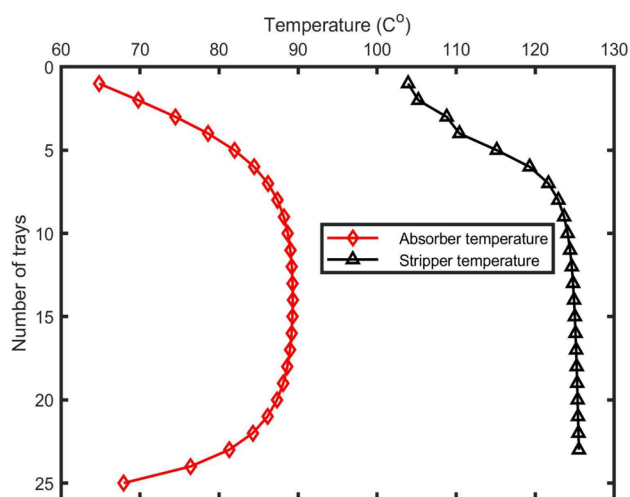
## Simulation validation

Validating simulation outputs is necessary to ensuring that the simulation accurately assesses the plant specifications. In conformity with (Nwaoha et al. 2017), the temperature profile of absorption and regeneration columns is the best course of action for validating the process on the basis of the reference plant specifications. CO<sub>2</sub>/MDEA reaction is exothermic nature, and the released heat increases with the loading rate (Kvamsdal and Rochelle 2008). The temperature profile of the absorption column with a high loading of MDEA solvent (> 30 wt%) generally increases initially and then decreases to the outlet temperature at the bottom of the column (Moioli et al. 2013; Borhani et al. 2016; Shahsavand and Garmroodi 2010). By contrast, the temperature profile of a regeneration column is generally high at the bottom of the column owing to the reboiler action and continuously linear to the center of the column (Zahid et al. 2017; Gutierrez et al. 2016). The outputs of this simulation closely resemble previous findings concerning the temperature profile of absorption and regeneration columns using MDEA solvent as shown in Fig. 1.

**Table 1** Input specifications for the simulator from reference plant (Younas and Banat 2014)

Parameter	Value
Feed gas flowrate	610 MMSCFD
Feed gas temperature	54.5 °C
Feed gas pressure	67.5 bars
CO <sub>2</sub> content in feed gas	0.032
H <sub>2</sub> S content in feed gas	0.005
MDEA flowrate	360 m <sup>3</sup> /h
MDEA temperature	60 °C
MDEA pressure	67.5 bars
MDEA loading	45 wt%





**Fig. 1** Temperature profile of both absorption and regeneration columns with MDEA solvent

To build confidence, the authors present a comprehensive comparison between the simulation results and the measured outputs of the reference plant as shown in Table 2. Now, we can declare that the model accurately reproduced the separation process, and it is capable to exhibit the investigation under the scope of this paper.

## Results and discussion

### Initial pH values

To investigate acid impacts, we estimated the pH of the aqueous amine solution at feed temperature. The result illustrated in Fig. 2 show that (1) the presence of individual acid considerably influenced the solution pH in comparison to fresh 45 wt% MDEA, (2) the presence of all the types of acids reduced the pH of the solution, (3) different types of acids offer different rates of reduction in

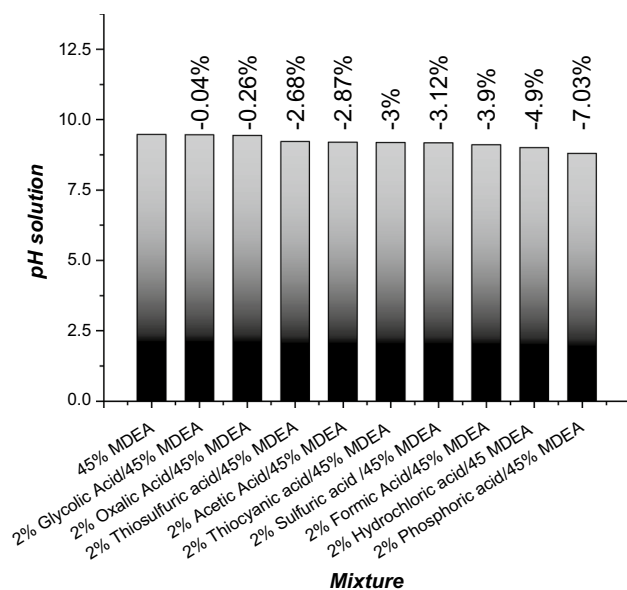
the pH of 45 wt% MDEA/ 2% acids, and the order of pH values for the mentioned acids was 45 wt% MDEA/ 2% glycolic acid, followed by oxalic acid, hydrochloric acid, formic acid, sulfuric acid, thiocyanic, acetic acid, thiosulfuric acid, and phosphoric acid at the same concentration.. The clear reduction in the solution pH of 45 wt% MDEA and 2% acids can be attributed to the reactions between the acids and MDEA. The reduction in turn decreased the amount of free active MDEA molecules and the acid gases capacity of the solvent solution. Some of the acids, particularly carboxylic acids, are partly dissociated into  $H^+$  cations and  $RCOO^-$  anions in neutral solution, since the molecular structure and number of carboxylic groups significantly determined their acidity. Based on the inductive impact of molecular structure, the acidity of dicarboxylic acid (e.g., oxalic) is broadly higher than the acidity of monocarboxylic acid (e.g., formic and acetic) and hydroxy monocarboxylic acid (e.g., glycolic) with same number of carbons atoms. The acidity of hydroxy monocarboxylic acid is greater than the acidity of monocarboxylic acid and increase in the number of carbons can result in reduction of the acidity of carboxylic acid. Therefore, the pH of 45 wt% MDEA/ 2% acids can be regulated using the acidity order of the tested acids.

### Absorption rate of acid gases

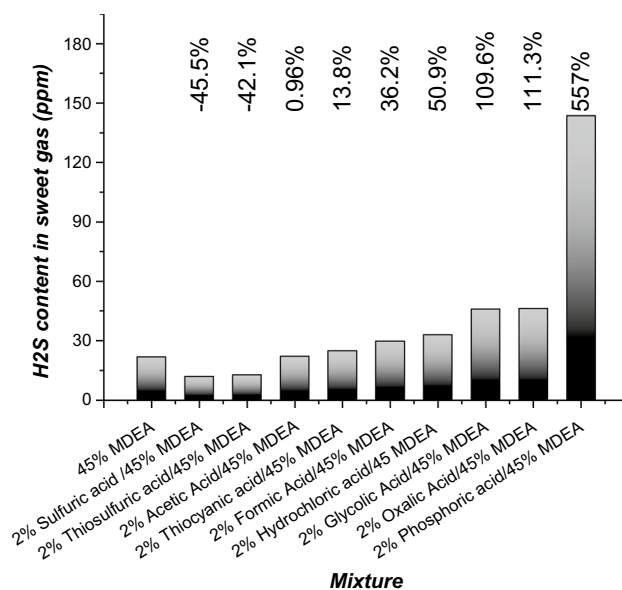
The sweet gas specifications of the reference plant under this study are 3%  $CO_2$  and 20 ppm  $H_2S$ . A simulation study was used assessing the effects of various acids presence in the MDEA solution on the acid gases absorption capacity. As shown in Fig. 3, these tests highlighted that the presence of all the acids reduced the MDEA capturing efficiency for acid gases with different extents. The reduction can be attributed to that these acids, which reduced the solution pH and the number of free active MDEA molecules through reactions pathways of 4–13. This process can reduce the intermolecular effective collision between  $CO_2/H_2S$  and MDEA solvent.

**Table 2** Comparison of real plant outputs and simulation outputs (Younas and Banat 2014)

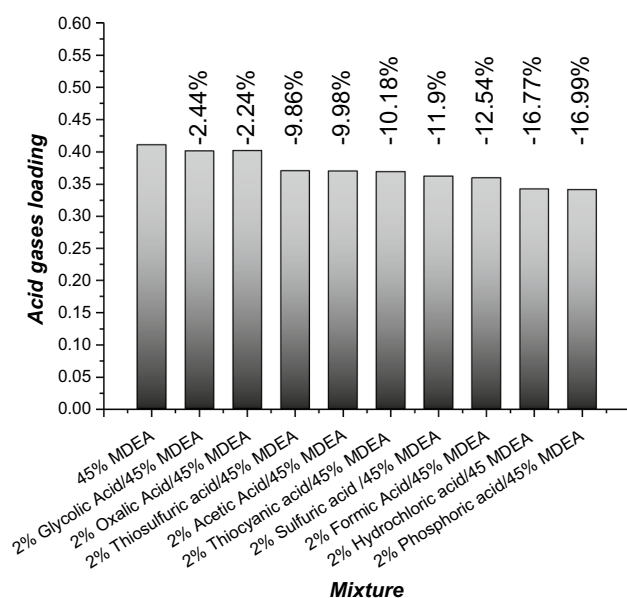
Parameters	Base plant outputs	Simulation outputs
Clean gas flowrate (Kmol/h)	29,835	29,944.39
$CO_2$ content in clean gas	676	569.6
$H_2S$ content in clean gas	0.6	0.6547
clean gas stream pressure (bars)	66.5	66.5
clean gas stream pressure ( $^{\circ}C$ )	60	64
Acid gas flowrate (Kmol/h)	686.66	601.2084
$CO_2$ content in acid gas stream (Kmol/h)	456.6	419.856
$H_2S$ content in acid gas stream (Kmol/h)	169.6	134.42
Acid gas stream pressure (bars)	2	2
Acid gas stream temperature ( $^{\circ}C$ )	57	54



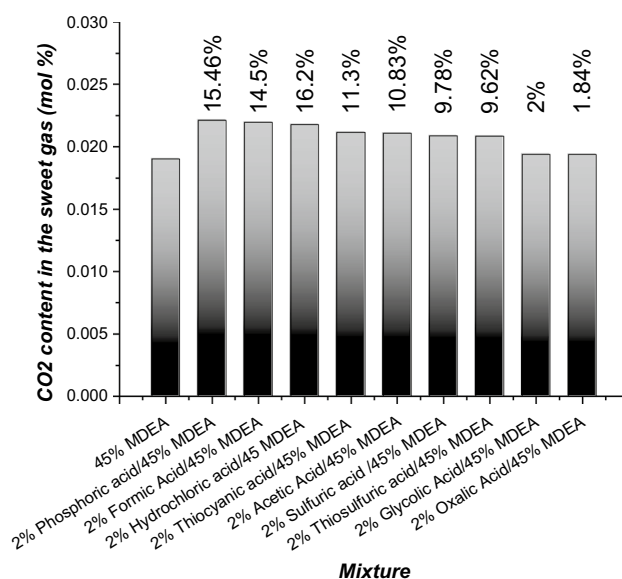
**Fig. 2** The impact of tested acids presence on the solution pH of 45 wt% and various acids



**Fig. 4** Impact of tested acid presence on the H<sub>2</sub>S content in the sweet gas stream



**Fig. 3** Impact of tested acid presence on the total acid gases loading in the rich amine stream



**Fig. 5** Impact of tested acid presence on the CO<sub>2</sub> content in the sweet gas stream

Besides, the level of impact can be categorized based on the reaction between an acid and MDEA solvent which form different types of HSSs with various characterizations and effects on the plant performance. For example, the presence of 2% phosphoric acid elevates the H<sub>2</sub>S content in the sweet gas to 143 ppm, as shown in Fig. 4; one of the possible reasons is that this acid reacts with MDEA and form DEA (mechanism proposed by (Gross 2000))

which has a low affinity toward H<sub>2</sub>S. The single most striking result to emerge from the results is that the presence of sulfuric and thiosulfuric acids promoted the removal of H<sub>2</sub>S by – 45.5% and – 42.11%, respectively, in comparison with fresh 45 wt% MDEA. Phosphoric and formic acids showed the lowest acid gases absorption rate among the tested acids. However, all the tested acids presented same behavior regarding the absorption of CO<sub>2</sub> in which all the acids reduced the CO<sub>2</sub> loading as shown in Fig. 5.

A 15.46% reduction in CO<sub>2</sub> loading was caused by 2% phosphoric acid followed by 14.5% with 2% formic acid. A plausible explanation for this phenomenon is that the mass transfer behavior can be improved by the turbulence of gas and liquid phases caused by foaming during the acid gases absorption into MDEA/acid solution. Hence, foaming plays a considerable role in the absorption of acid gases than the solution pH.

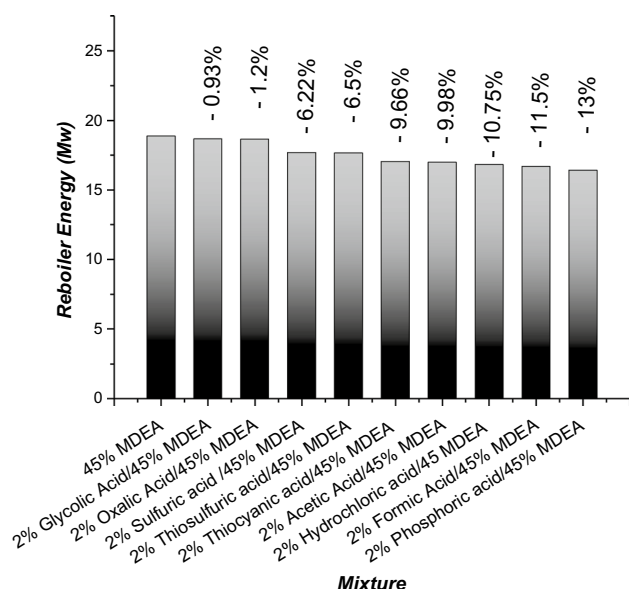
### Reboiler energy

One of the main drawbacks of using amine technology is the high energy requirements, particularly for the desorption section. The regeneration process is responsible for approximately 50% of the total energy owing to the high heat required to separate acid gases from amine solutions (Abd and Naji 2019). Desorption energy can be categorized into three main elements, namely absorption heat, sensible heat, and vaporization heat (Abd and Naji 2019; Abd et al. 2019a). Generally, the reaction between acid gases and amine is exothermic and depends on change in enthalpy. Warudkar et al. (2013), an authority on regenerator performance, also affirmed that the reboiler energy is the difference in enthalpies between feed vapor and condensed liquid (Warudkar et al. 2013). A simulation study was performed for the evaluation of the presence of various acids on reboiler energy demand in the regenerator column. The results revealed that the presence of acids reduced the required reboiler energy of the regeneration column, as shown in Fig. 6. Notably, 2% of phosphoric acid had the highest reduction percentage of—13%, whereas 2% glycolic acid had the lowest reduction

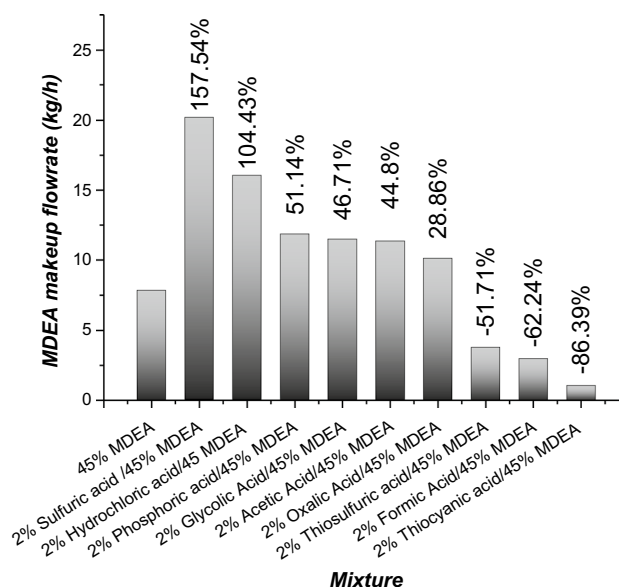
rate of—0.92% in reboiler energy. These results can be explained by the formation of HSSs, reduced the amine circulation rate and the energy demand in the reboiler to generate steam. The formation of HSSs obviously offered an advantage of minimizing the steam consumption, and some acids maintained the sweet gas specifications constant. Thus, a certain concentration of HSSs can be used in balancing the energy demand and the sweet gas specifications.

### Methyldiethanolamine solvent makeup flowrate

Amine loss is a serious issue in the removal of acid gases plants and stems from various sources, such as vaporization, foaming, and degradation. The amine makeup process in some plants contributes to up to 10% of the total operation cost (Mazari et al. 2015). Amine vaporization is a common issue that causes amine loss in the natural gas sweetening plants. Vaporization is highly dependent on the operating conditions such as temperature, pressure, and amine type and concentration (Zhang et al. 2011a). Volatility generally causes serious environmental problems because it generates highly toxic emerging gases compared with CO<sub>2</sub> and H<sub>2</sub>S. Foaming is induced via several pollutants such as liquid hydrocarbons and organic acids; it reduces the absorption efficiency and minimizes the mass transfer area (Chen et al. 2011). Degradation inevitability occurs through the absorption of acid gases when amine solvents are used and is considered a major expense in cost evaluation (Mazari et al. 2015). Therefore, attention must be devoted to the management and reduction of the products of amine degradation. A simulation study was performed for the evaluation



**Fig. 6** Impact of tested acid presence on the reboiler duty of the stripper column



**Fig. 7** Impact of tested acid presence on the MDEA makeup flowrate



of the impact of the presence of different acids on MDEA makeup flowrate. Figure 7 depicts the impact of tested acids on the desorption rate on the basis of the MDEA makeup flowrate. The results indicated that (1) the tested acids influenced the MDEA makeup flowrate, (2) sulfuric acid had the highest increase in MDEA makeup flowrate (157.53%) than fresh 45 wt% MDEA solution, and (3) the presence of thiocyanic, formic, and thiosulfuric acids minimized the MDEA makeup flowrate by – 86.38%, – 62.23%, – 51.71%, respectively. The conceivable reason for these differences in makeup flowrate can be explained by the acids ability to generate H<sup>+</sup> in the amine aqueous solution. Some of the acid types presented a lot of H<sup>+</sup> that can enhance the desorption process and reduce the MDEA makeup flowrate. Thus, the presence of thiocyanic, formic, and thiosulfuric acids in the MDEA solution for capturing CO<sub>2</sub> and H<sub>2</sub>S can improve the desorption rate and minimize the solvent makeup flowrate.

### Grading of the impact of tested acids

All the tested acids reduced the volume of MDEA in the aqueous solution by reacting with a portion of the MDEA. The grading was allocated in order of highest impact percent (left to right) to the lowest impact percent on the MDEA aqueous solution on the basis of pH solution, reboiler duty, CO<sub>2</sub>/H<sub>2</sub>S loading, and solvent makeup flowrate. It is important to mention that some acids may have a positive impact at a concentration lower than 2%. Table 3 summarizes the percentage changes from fresh 45 wt% MDEA solution resulting via each acid.

*pH* Glycolic acid, oxalic acid, thiosulfuric acid, acetic acid, thiocyanic acid, sulfuric acid, formic acid, hydrochloric acid, phosphoric acid.

*Reboiler energy* Phosphoric acid, formic acid, hydrochloric acid, acetic acid, thiocyanic acid, thiosulfuric acid, sulfuric acid, oxalic acid, glycolic acid.

*CO<sub>2</sub> in sweet gas* Oxalic acid, glycolic acid, thiosulfuric acid, sulfuric acid, acetic acid, thiocyanic acid, hydrochloric acid, formic acid, phosphoric acid.

*H<sub>2</sub>S in sweet gas* Sulfuric acid, thiosulfuric acid, acetic acid, thiocyanic acid, formic acid, hydrochloric acid, glycolic acid, oxalic acid, phosphoric acid.

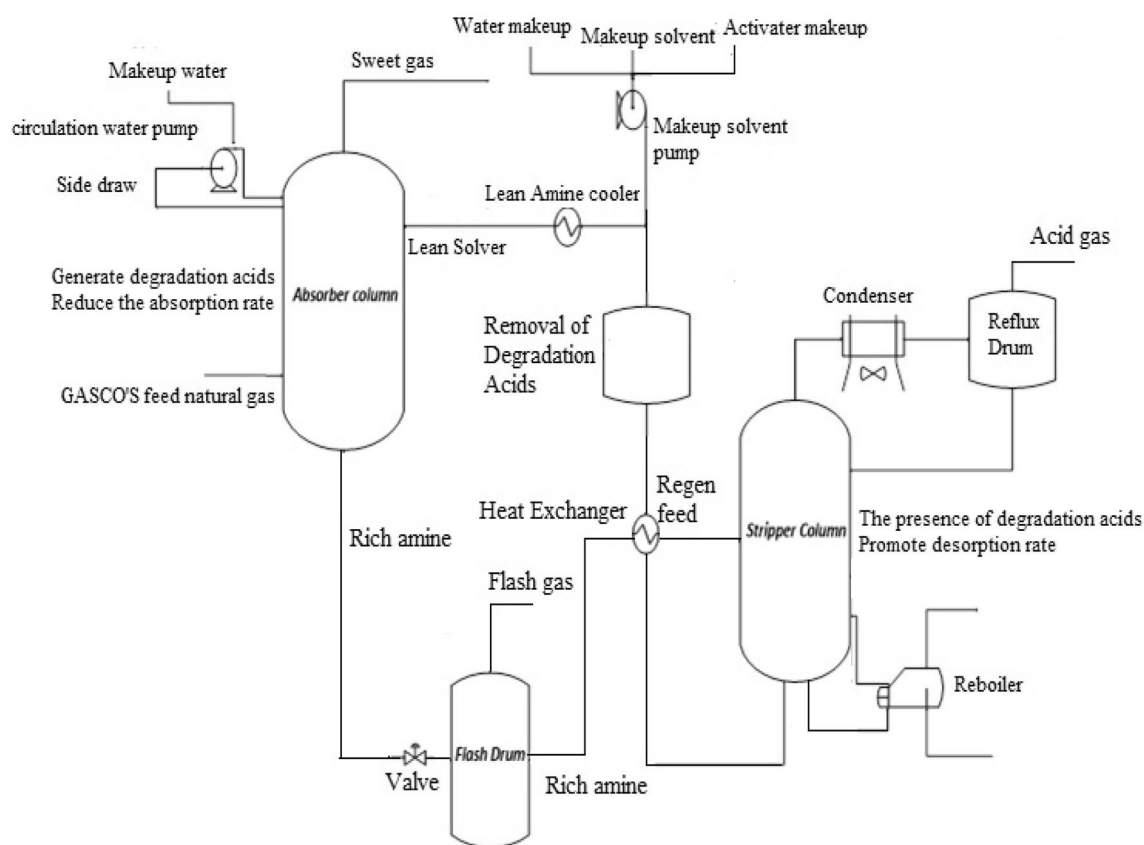
*MDEA makeup flowrate* Sulfuric acid, hydrochloric acid, phosphoric acid, glycolic acid, acetic acid, oxalic acid, thiosulfuric acid, formic acid, thiocyanic acid.

### Countermeasures for reducing formation of HSSs

The simulation results show that the presence of acids at 2% concentration in the 45 wt% MDEA solution generally minimized reboiler duty and enhanced the desorption rate but reduced the absorption capacity. The mechanisms of the standard MDEA amine absorption technology are that feed gas enters the absorption column at the bottom and reacts with the lean amine solution that feeds from the top of the column. The rich amine in the bottom of the absorption column travels to the regenerator column and releases acid gases under high operating temperature conditions. Finally, amine is recycled in a heat exchanger, and its temperature is minimized before it is fed again to the absorber. Since the amine oxidation reaction is unavoidable, the acidic products will be accumulated in the action of increasing the absorption cycles. For the maintenance of amine solvent performance and minimization of reboiler duty, countermeasures are essential. As it has been revealed during the study that the presence of acids improved the desorption process and minimized the reboiler duty, however the absorption rate reduced. Thus, introducing the acidic products at the top of the regeneration column to reduce the energy demand and remove the acids before the absorption column to avoid the reduction in absorption rate. Figure 8 describes the proposed process of absorption/regeneration with the application of acids as energy promoter. This approach can improve the absorption capacity for both CO<sub>2</sub> and H<sub>2</sub>S. Technologies of

**Table 3** Deviation percentage of the study parameters in the presence of acid

Acid	pH	Reboiler duty	CO <sub>2</sub> loading	H <sub>2</sub> S loading	MDA makeup
Sulfuric	– 3.12	6.2207	9.7792	– 45.496	157.5389
Hydrochloric	– 4.895	10.7515	14.511	50.89	104.427
Phosphoric	– 7.0327	13.008	13.937	557.064	51.139
Glycolic	– 1.1	0.925	2.0505	109.6	46.7088
Acetic	– 2.872	9.983	10.8307	0.96	44.8054
Oxalic	– 1.3165	1.18353	1.84017	111.248	28.86
Thiosulfuric	– 2.6753	6.476	9.62145	– 42.11	– 51.71
Formic	– 3.88	11.495	7.83386	36.2	– 62.238
Thiocyanic	– 3	9.661	11.25	13.8	– 86.3889



**Fig. 8** The proposed process flow diagram of deployment the tested acids as modifiers for the reboiler duty and desorption efficiency

removing these acids from the amine solution are essential investigated in the future.

## Conclusion

Some acidic products from MDEA amine degradation were investigated for understanding the impact of HSSs on the process of removing acid gases from the natural gas. We proposed a simulation strategy using the inputs measures of GASCO'S Habshan Acid Gases Removal plant. The pH of amine aqueous solution was estimated at amine feed conditions. Our conclusions were as follows:

1. The pH of amine solution decreases in the presence of the tested acids in the MDEA amine solution compared with fresh MDEA solution. The order of amine solution pH is glycolic, oxalic, thiosulfuric, acetic, thiocyanic, sulfuric, formic, hydrochloric, and phosphoric.
2. The presence of the tested acids in the MDEA amine solution reduces acid gas loading rate, and the order according to impact is glycolic, oxalic, thiosulfuric, acetic, thiocyanic, sulfuric, formic, hydrochloric, and phosphoric acids. Interestingly, sulfuric and thiosulfuric acids promote the absorption rate of  $H_2S$  by  $-45.5\%$  and  $-42.1\%$ , respectively. Foaming impact is higher than the impacts of low free active molecules of amine and the role of pH in the reduction of acid gas loading.
3. The presence of the tested acids in the MDEA amine solvent minimizes the energy demand for the reboiler in the stripper. The highest reduction was obtained in the presence of phosphoric acid ( $-13\%$ ), followed by formic acid ( $-11.5\%$ ).
4. The MDEA makeup flowrate influences by the presence of tested acids with different rates depending on the level of degradation. The high increase in solvent amine makeup flowrate is attributed to the presence of sulfuric, followed by hydrochloric, phosphoric, glycolic, acetic, and oxalic acids. The presence of thiocyanic, formic, and thiosulfuric acids reduces the solvent makeup flowrate by  $-86.39\%$ ,  $-62.24\%$ , and  $-51.71\%$ , respectively.
5. Countermeasure has been proposed for maintaining acid gas loading rate and exploiting the effects of these acids on reboiler energy by eliminating these acids before re-entering the absorption column.

This study is the first step toward enhancing our understanding of control and removal of the acidic degradation products of MDEA amine in the natural gas sweetening plant.

## References

- Abd AA, Naji SZ (2019) Comparison study of activators performance for MDEA solution of acid gases capturing from natural gas: Simulation-based on a real plant. *Environ Technol Innov*. <https://doi.org/10.1016/j.eti.2019.100562>
- Abd AA, Naji SZ, Barifcani A (2019a) Comprehensive evaluation and sensitivity analysis of regeneration energy for acid gas removal plant using single and activated-methyl diethanolamine solvents. *Chin J Chem Eng*. <https://doi.org/10.1016/j.cjche.2019.12.004>
- Abd AA, Naji SZ, Hashim AS (2019b) Failure analysis of carbon dioxide corrosion through wet natural gas gathering pipelines. *Eng Fail Anal* 105:638–646. <https://doi.org/10.1016/j.engfailanal.2019.07.026>
- Abd AA, Naji SZ, Hashim AS, Othman MR (2020) Carbon dioxide removal through physical adsorption using carbonaceous and non-carbonaceous adsorbents: a review. *J Environ Chem Eng*. <https://doi.org/10.1016/j.jece.2020.104142>
- Aboudheir A, Elmoudir W (2013) Optimization of an existing 130 tonne per day CO<sub>2</sub> capture plant from a flue gas slipstream of a coal power plant. In: *Energy Procedia*. Elsevier Ltd, pp 1509–1516
- Alkasem A, Al Zarouni YA, Slagle JC, et al (2015) Optimization of an existing Habshan II Amine sweetening unit at variable throughputs. In: *Society of Petroleum Engineers: Abu Dhabi International Petroleum Exhibition and Conference, ADIPEC 2015*. Society of Petroleum Engineers
- Borhani TNG, Afkhamipour M, Azarpour A et al (2016) Modeling study on CO<sub>2</sub> and H<sub>2</sub>S simultaneous removal using MDEA solution. *J Ind Eng Chem* 34:344–355. <https://doi.org/10.1016/j.jiec.2015.12.003>
- Braungardt S, van den Bergh J, Dunlop T (2019) Fossil fuel divestment and climate change: Reviewing contested arguments. *Energy Res Soc Sci* 50:191–200
- Caravaggio N, Caravella S, Ishizaka A, Resce G (2019) Beyond CO<sub>2</sub>: a multi-criteria analysis of air pollution in Europe. *J Clean Prod* 219:576–586. <https://doi.org/10.1016/j.jclepro.2019.02.115>
- Chen X, Freeman SA, Rochelle GT (2011) Foaming of aqueous piperazine and monoethanolamine for CO<sub>2</sub> capture. *Int J Greenh Gas Control* 5:381–386. <https://doi.org/10.1016/j.ijggc.2010.09.006>
- Chi S, Rochelle GT (2002) Oxidative degradation of monoethanolamine. *Ind Eng Chem Res* 41:4178–4186. <https://doi.org/10.1021/ie010697c>
- Choi YS, Duan D, Nešić S et al (2010) Effect of oxygen and heat stable salts on the corrosion of carbon steel in MDEA-based CO<sub>2</sub> capture process. *Corrosion*. <https://doi.org/10.5006/1.3524834>
- Dickinson J, Percy A, Puxty G, Verheyen TV (2016) Oxidative degradation of amine absorbents in carbon capture systems: a dynamic modelling approach. *Int J Greenh Gas Control* 53:391–400. <https://doi.org/10.1016/j.ijggc.2016.08.001>
- Fang M, Yi N, Di W et al (2020) Emission and control of flue gas pollutants in CO<sub>2</sub> chemical absorption system: a review. *Int J Greenh Gas Control* 93:102904
- Feyzi V, Beheshti M, GharibiKharaji A (2017) Exergy analysis: A CO<sub>2</sub> removal plant using a-MDEA as the solvent. *Energy* 118:77–84. <https://doi.org/10.1016/j.energy.2016.12.020>
- Fredriksen SB, Jens KJ (2013) Oxidative degradation of aqueous amine solutions of MEA, AMP, MDEA, Pz: A review. In: *Energy Procedia*. Elsevier Ltd, pp 1770–1777
- Goff GS, Rochelle GT (2004) Monoethanolamine degradation: O<sub>2</sub> mass transfer effects under CO<sub>2</sub> capture conditions. *Ind Eng Chem Res* 43:6400–6408. <https://doi.org/10.1021/ie0400245>
- Gouedard C, Picq D, Launay F, Carrette PL (2012) Amine degradation in CO<sub>2</sub> capture. I. A review. *Int J Greenh Gas Control* 10:244–270
- Gross ML (2000) Charge-remote fragmentation: an account of research on mechanisms and applications. *Int J Mass Spectrom* 200:611–624. [https://doi.org/10.1016/S1387-3806\(00\)00372-9](https://doi.org/10.1016/S1387-3806(00)00372-9)
- Gutierrez JP, Benitez LA, Ale Ruiz EL, Erdmann E (2016) A sensitivity analysis and a comparison of two simulators performance for the process of natural gas sweetening. *J Nat Gas Sci Eng* 31:800–807. <https://doi.org/10.1016/j.jngse.2016.04.015>
- Huttenhuis PJG, Agrawal NJ, Hogendoorn JA, Versteeg GF (2007) Gas solubility of H<sub>2</sub>S and CO<sub>2</sub> in aqueous solutions of *N*-methyldiethanolamine. *J Pet Sci Eng* 55:122–134. <https://doi.org/10.1016/j.petrol.2006.04.018>
- Kadnar R, Rieder J (1995) Determination of anions in amine solutions for sour gas treatment. *J Chromatogr A* 706:339–343. [https://doi.org/10.1016/0021-9673\(94\)01210-6](https://doi.org/10.1016/0021-9673(94)01210-6)
- Karnwiboon K, Saiwan C, Idem R, et al (2017) Solvent extraction of degradation products in amine absorption solution for CO<sub>2</sub> capture in flue gases from coal combustion: effect of amines. In: *Energy Procedia*. Elsevier Ltd, pp 1980–1985
- Kuramochi T, Ramírez A, Turkenburg W, Faaij A (2012) Comparative assessment of CO<sub>2</sub> capture technologies for carbon-intensive industrial processes. *Prog Energy Combust Sci* 38:87–112
- Kvamsdal HM, Rochelle GT (2008) Effects of the temperature bulge in CO<sub>2</sub> absorption from flue gas by aqueous monoethanolamine. *Ind Eng Chem Res* 47:867–875. <https://doi.org/10.1021/ie061651s>
- Lei L, Bai L, Lindbråthen A et al (2020) Carbon membranes for CO<sub>2</sub> removal: status and perspectives from materials to processes. *Chem Eng J* 401:126084
- Lepaumier H, Picq D, Carrette PL (2009) Degradation study of new solvents for CO<sub>2</sub> capture in post-combustion. In: *Energy Procedia*. Elsevier, pp 893–900
- Mazari SA, Si Ali B, Jan BM et al (2015) An overview of solvent management and emissions of amine-based CO<sub>2</sub> capture technology. *Int J Greenh Gas Control* 34:129–140. <https://doi.org/10.1016/j.ijggc.2014.12.017>
- Moioli S, Pellegrini LA, Picutti B, Vergani P (2013) Improved rate-based modeling of H<sub>2</sub>S and CO<sub>2</sub> removal by methyldiethanolamine scrubbing. *Ind Eng Chem Res* 52:2056–2065. <https://doi.org/10.1021/ie301967t>
- Nwaoha C, Odoh K, Ikpat E et al (2017) Process simulation, parametric sensitivity analysis and ANFIS modeling of CO<sub>2</sub> capture from natural gas using aqueous MDEA-PZ blend solution. *J Environ Chem Eng* 5:5588–5598. <https://doi.org/10.1016/j.jece.2017.10.038>
- Olajire AA (2010) CO<sub>2</sub> capture and separation technologies for end-of-pipe applications: a review. *Energy* 35:2610–2628
- Reynolds AJ, Verheyen T V., Meuleman E (2016) Degradation of amine-based solvents. In: *Absorption-Based Post-Combustion Capture of Carbon Dioxide*. Elsevier Inc., pp 399–423
- Richard Keene F (1999) Metal-ion promotion of the oxidative dehydrogenation of coordinated amines and alcohols. *Coord Chem Rev* 187:121–149
- Rochelle GT (2012) Thermal degradation of amines for CO<sub>2</sub> capture. *Curr Opin Chem Eng* 1:183–190
- Shahsavand A, Garmroodi A (2010) Simulation of Khangiran gas treating units for various cooling scenarios. *J Nat Gas Sci Eng* 2:277–283. <https://doi.org/10.1016/j.jngse.2010.08.006>

- Sharif M, Zhang T, Wu X et al (2020) Evaluation of CO<sub>2</sub> absorption performance by molecular dynamic simulation for mixed secondary and tertiary amines. *Int J Greenh Gas Control* 97:103059. <https://doi.org/10.1016/j.ijggc.2020.103059>
- Song C, Liu Q, Deng S et al (2019) Cryogenic-based CO<sub>2</sub> capture technologies: state-of-the-art developments and current challenges. *Renew Sustain Energy Rev* 101:265–278
- Song Y, Chen CC (2009) Symmetric electrolyte nonrandom two-liquid activity coefficient model. *Ind Eng Chem Res* 48:7788–7797. <https://doi.org/10.1021/ie9004578>
- Tavan Y, Moradi M, Rostami A, Azizpour H (2020) Theoretical and industrial aspects of amine reclaiming unit to separate heat stable salts. *Sep Purif Technol* 237:116314. <https://doi.org/10.1016/j.seppur.2019.116314>
- Thiel WR (2003) Transition metal mediated oxygen transfer to organo nitrogen compounds. In: *Coordination chemistry reviews*. Elsevier, pp 95–106
- Verma N, Verma A (2009) Amine system problems arising from heat stable salts and solutions to improve system performance. *Fuel Process Technol* 90:483–489. <https://doi.org/10.1016/j.fuproc.2009.02.002>
- Warudkar SS, Cox KR, Wong MS, Hirasaki GJ (2013) Influence of stripper operating parameters on the performance of amine absorption systems for post-combustion carbon capture: Part I. High pressure strippers. *Int J Greenh Gas Control* 16:342–350. <https://doi.org/10.1016/j.ijggc.2013.01.050>
- Younas O, Banat F (2014) Parametric sensitivity analysis on a GAS-CO's acid gas removal plant using ProMax simulator. *J Nat Gas Sci Eng* 18:247–253. <https://doi.org/10.1016/j.jngse.2014.03.007>
- Zahid U, Al Rowaili FN, Ayodeji MK, Ahmed U (2017) Simulation and parametric analysis of CO<sub>2</sub> capture from natural gas using diglycolamine. *Int J Greenh Gas Control* 57:42–51. <https://doi.org/10.1016/j.ijggc.2016.12.016>
- Zhang J, Nwani O, Tan Y, Agar DW (2011a) Carbon dioxide absorption into biphasic amine solvent with solvent loss reduction. *Chem Eng Res Des* 89:1190–1196. <https://doi.org/10.1016/j.cherd.2011.02.005>
- Zhang Y, Chen CC (2011) Thermodynamic modeling for CO<sub>2</sub> absorption in aqueous MDEA solution with electrolyte NRTL model. *Ind Eng Chem Res* 50:163–175. <https://doi.org/10.1021/ie1006855>
- Zhang Y, Que H, Chen CC (2011b) Thermodynamic modeling for CO<sub>2</sub> absorption in aqueous MEA solution with electrolyte NRTL model. *Fluid Phase Equilib* 311:67–75. <https://doi.org/10.1016/j.fluid.2011.08.025>

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