Simulation and Optimization of Amine Sweetening Process

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Abstract

Amine sweetening is the most vital segment of the gas processing plant, which contributes to the removal of H\textsubscript{2}S, CO\textsubscript{2} and other minor contaminants such as COS and mercaptans. The work attempts to improve the efficiency of the gas processing process through a process simulation exercise towards which ProMax was utilized. A base case simulation mimicking a real operational amine sweetening plant was developed using process parameters and flow rates currently being in practice. Based on a thorough literature search, it was understood that parameters such as the pH, heat stable salts, regenerator pressure, and absorption column intercooling were found to influence the plant efficiency. The present work attempts to assess the effect of the above said parameters on the base case simulation and identify optimal conditions to enhance the overall efficiency. A decrease in the pH was attempted through the addition of different acids, and it was not found to improve the efficiency of the operation as stated in the literature pertaining to MEA solvent. In other words, the regenerator energy consumption was found to increase with the increase in the acid concentration. An increase in the regenerator pressure was found to decrease the regenerator energy requirement contributing to better energy efficiency, with the optimal operating pressure being 2.5 bar. An increase in the heat stable salts at a controlled concentration was found to improve the absorption efficiency of the H\textsubscript{2}S while had no significant effect on CO\textsubscript{2} absorption. The application of intercooler improved the absorption efficiency of both H\textsubscript{2}S and CO\textsubscript{2} as well as reduced the reboiler heat duty. The combination of optimal conditions revealed that the plant processing capacity could be increased to about 4.2% with an energy reduction of 81,000 tons of steam per year.

Keywords: gas sweetening; amine solvent; acid gases, simulation; ProMax; MDEA; gas processing; Heat stable salts.

1. Introduction

Natural gas that comes from an underground reservoir is predominantly a mixture of hydrocarbons mainly methane along with other hydrocarbons like ethane, propane, and butane. The gas can also carry an appreciable amount of non-hydrocarbons such as hydrogen sulfide, nitrogen, carbon dioxide and other minor contaminants such as mercury, water, and other inorganic compounds. They are widely utilized for industrial, commercial and residential purposes as it is the most preferred fuel for the generation of heat and electricity. Natural gas accounts for 23.7% of the global primary energy consumption (BP Statistical Review of World Energy, 2015). The growth is expected to be 1.9% per annum mainly due to the demand from the power and other industrial sectors [1-2].

The natural gas processing plants typically include a number of stages to remove the contaminants such as dusting stage, acid gases removal, dehydration and Hg removal, nitrogen rejection, so as to meet the product specification. The dusting stage is a gas filtration stage to remove small solid particles. In the acid gas removal, operation separates acid gases hydrogen sulfide (H\textsubscript{2}S) and carbon dioxide (CO\textsubscript{2}) from the natural gas directing it to the sulfur recovery process [3]. In dehydration stage, water is removed, while in the mercury removal stage separates extremely toxic mercury. The nitrogen rejection stage separates nitrogen so as to improve the heating value methane [4-5].
Sour gas contains different concentrations of H$_2$S and CO$_2$; these gases have certain threshold values and a specific standard for their concentration as products of a sweetening process. The selection of the appropriate sweetening process to achieve certain gas specification is dependent on many factors like the limits of concentration of both the sour and the sweet gas, the maximum design flowrate, the pressure of the inlet gas, the requirements for sulfur recovery and propose an acceptable method to dispose of waste products [6].

There are many different processes for sour gas sweetening, but one of the most popular and the one that is discussed in this work is the liquid-phase absorption by chemical solvents. In chemical solvent processes, absorption of the acid gases is achieved mainly by use of alkanol amines that can absorb H$_2$S, CO$_2$, and to some extent COS. Chemical solvents are specifically suitable when contaminants at relatively low partial pressure have to be removed to very low concentrations [7]. In natural gas sweetening industry, the removal of carbon dioxide and hydrogen sulfide by alkanol amines is essential and maybe the most popular. This technology depends mainly on absorption/desorption reactions between the acid gases and alkanol amines. This treatment step is critical in any gas processing industry because the presence of such contaminants can cause corrosion to pipelines and equipment, can also affect the human health and deteriorate the surrounding environment [8].

2. Methodology

2.1. Base case simulation

The base case simulation model involving absorption and desorption columns mimicking the operation conditions of a typical gas processing plant was built using ProMax simulation tool. The details of the process parameters utilized in developing the simulation are provided in Table 1. The process simulator utilized Peng-Robinson Amine Sweetening property method to perform the simulations. The process flow diagram adopted for simulation is shown in Fig. 1.

![Figure 1. Base Case Process Flow Diagram](image)

Since the design data and process flow for each stream were available, it was much easier to build the model block by block with the correct state of phases, compositions, and flowrates. The feed stream contains mostly hydrocarbons (C$_1$-C$_3$) along with Hydrogen Sulfide (H$_2$S) at 4.8% and Carbon Dioxide (CO$_2$) at 5.5%. The feed stream saturated with water will enter a 9 stages absorber, while the solvent is flowing downward the column noted as rich amine stream.
goes to a flash drum that flashes any gases still in the vapor phase out from the loop. Then the stream exchange heat with the lean amine wherein the temperature increase to 104 °C, and enters a stripping section wherein all the dissolved acid gases were stripped out and sent to sulfur recovery units. The stripper is operated by a steam driven reboiler that provides enough energy for stripping and recovery of the solvent that is recycled back to the absorber.

### Table 1. The Base Case Specifications along with simulation results

<table>
<thead>
<tr>
<th>Specification</th>
<th>Value</th>
<th>Specification</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plant capacity (MMSCFD)</td>
<td>379</td>
<td>Solvent rate (m³/hr)</td>
<td>790</td>
</tr>
<tr>
<td>Acid H₂S (mol. %)</td>
<td>4.8</td>
<td>Solvent concentration (wt. %)</td>
<td>45</td>
</tr>
<tr>
<td>Acid CO₂ (mol. %)</td>
<td>5.5</td>
<td>Regenerator pressure (bar)</td>
<td>2</td>
</tr>
<tr>
<td>Sweet H₂S (ppm)</td>
<td>19.98</td>
<td>HSS content (mol. %)</td>
<td>0.041</td>
</tr>
<tr>
<td>Sweet CO₂ (mol. %)</td>
<td>1.95</td>
<td>Rich amine loading</td>
<td>0.568</td>
</tr>
<tr>
<td>Steam rate (Kg/min)</td>
<td>2060</td>
<td>Lean amine loading</td>
<td>0.003</td>
</tr>
<tr>
<td>Steam pressure (bar)</td>
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<td>Property method</td>
<td>PR-Amine</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Sweetening</td>
</tr>
</tbody>
</table>

#### 2.2. Acid injection case (pH swing)

The effect of acid injection for an MDEA sweetening plant has not been reported in the open literature, and hence an attempt has been made to assess its effect. Three weak acids were tested with the model to lower the pH. Adipic, phthalic and suberic acids were added to the MDEA solvent at 1-5 wt.%

#### 2.3. Regenerator pressure elevation

In the base case model, the regenerator operating pressure was 2 bars; with the corresponding reboiler temperature of 127 °C. The effect of regenerator pressure was assessed covering the pressure in the range of 2 to 3 bars, while all the other parameters were held constant corresponding to the base case. These reboiler temperatures were acceptable as they were lower than the amine degradation temperature. The effect of regenerator pressure on the energy consumption was assessed along with a check on the reboiler temperature.

#### 2.4. Inter-cooled absorber (ICA)

The effect of the addition of an inter cooler to the MDEA process has not been reported in the open literature and hence attempt to assess its effect was made. Towards this the hot MDEA solution was withdrawn from stage 5 and was cooled using an air-cooled heat exchanger and reinjected back From the total volumetric flowrate 20% was withdrawn from stage 5, cooled by -4 °C, before being injected back to the column in stage 6. All other parameters were held constant at the base case level.

#### 2.5. Heat stable salts (HSS)

The presence of HSS in the amine system is well established. In order to quantify their presence, a weak acid like Phosphoric Acid (H₃PO₄) was added to the amine solvent by very small percentages in the range 0.1-0.5 mol. %. This range was acceptable because small addition of acid showed a significant effect on the sweet gas specification. To follow up the concentration of the protonated form of the amine (MDEAH⁺) an ionic info analysis was used in the model to keep track of the concentration buildup of HSS.

### 3. Results and discussion

#### 3.1. Addition of weak acids

Figures 2&3 show the simulation results on the effect of adipic, phthalic and suberic acid on the CO₂ as well as the H₂S mole % leaving the absorption column. The data clearly indicate an increase in the concentration of the CO₂ in the sweet gas with an increase in the acid concentration, while the concentration of the H₂S was almost constant. Among the three acids,
Adipic acid seem to have a far higher effect on the CO\textsubscript{2} exit concentration compared to the other two acids. Considering the permissible sweet CO\textsubscript{2} specification of only 2 \%, any increase in the pH.

![Figure 2. Effect of acids addition on sweet CO\textsubscript{2} concentration](image)

![Figure 3. Effect of acids addition on H\textsubscript{2}S concentration](image)

Figure 4 shows that all acids had a negative effect on the regenerator performance. The reboiler duty increased with increase in the acid concentration. However, the effect of adipic & phthalic acids on the steam rate was marginal as compared to suberic acid. In the regeneration section, it was noticed that the increased percentage of acid had a negative effect on desorption energy requirement. As the percentage of acid is increased, the pH value decreased, and the steam supply to the regenerator increased in proportion.

![Figure 4. Effect of acids addition on reboiler duty](image)

![Figure 5. Effect of acids addition on the latent heat of vaporization](image)

Since the steam supply is one of the key contributors to operating cost of the process, a detailed assessment of the regenerator was performed in order to understand the increase in regeneration energy. The below figure summarizes the effect of each acid based on the latent heat of vaporization of the solvent in the reboiler.

It can be seen that an increase in the percentage of acid, so as to lower the pH increases the latent heat of vaporization of the solvent entering the regeneration stage while maintaining other terms relatively constant. An increase in the acid concentration contributed to the increase in boiling point of the regenerator solvent which in turn demands higher desorbing energy to strip the acid gases.
The details of the various contributors affecting desorption energy can be summarized as follows:

\[
Q_{reg} = Q_{des, CO_2} + Q_{sens} + Q_{vap, H_2O} \\
Q_{reg} = \Delta H_{abs, CO_2} + \rho_{solvent} \cdot C_p \cdot (T_{reb} - T_{feed}) + \dot{m}_{H_2O} \times \Delta H_{2O, vap}
\]

where, \( \Delta H_{abs, CO_2} \) is heat of reaction; \( C_p \) is the heat capacity of the rich solvent; \( T_{reb} \) and \( T_{feed} \) are reboiler temperature and feed solvent temperature, respectively; \( \dot{m}_{H_2O} \) is the mass flow rate of water vaporized from stripper and \( \Delta H_{2O, vap} \) is the latent heat of vaporization.

The addition of acids was claimed to be beneficial for the gas sweetening process having MEA as the solvent [11]. Hence simulations were performed to cross verify the claims with the MEA solvent. The results of the simulation are presented in the section below.

### 3.1.1. Reboiler duty for absorber with MEA solvent

Figure 6 presents the results of the simulation specific to Adipic acid addition for an absorber with MEA as a solvent. An increase in the acid concentration was found to decrease the reboiler due to the reduction in the latent heat of vaporization. The results clearly authenticate that the addition of acid to MEA solvent system is beneficial while with the MDEA solvent it contributes to an increase in the regenerator energy.

![Figure 5 Effect of acid addition on MEA systems](image)

### 3.2. Effect of stripper operating pressure

Figure 7 shows the effect of regenerator operating pressure with the sweet gas specifications of H\(_2\)S and CO\(_2\).

![Figure 6. Effect of increased stripper pressure on sweet gas specs](image)

![Figure 7. Regenerator pressure effect on temperature](image)
An increase in the regenerator pressure is found to decrease the sweet gas \( \text{H}_2\text{S} \) concentration favorably while the concentration of \( \text{CO}_2 \) was not affected. This could be attributed to the better performance of regenerator due to decreased lean loadings. The effect of acid addition on the absorption section was not very much noticed.

Figure 8 captures the effect of stripper temperature with increase in the regenerator pressure. An increase in the regenerator pressure was found to increase the regenerator temperature thus rendering an effective stripping. Although the increase in pressure was found to be beneficial, the optimal pressure was chosen to be 2.5 bars based on the amine degradation temperature of 140°C. A temperature safety margin of 5°C was chosen to select the optimal regenerator pressure.

The major effect was observed in the steam supply with increased regenerator pressure. Elevating regenerator pressure helped in increasing regeneration temperature, which led to better performance and more efficient stripping of gases.

The figure 9. summarizes the effect of increased pressure on the regeneration energy requirement. It can be noticed that as the pressure is increased, the latent heat of vaporization of the solvent mixture decreases which eventually contributes to a reduction in the steam requirement for regeneration.

### 3.3. Effect of the addition of intercooler to the absorber

The effect of the addition of an intercooler on the overall performance of the amine sweetening process is assessed by reducing the absorber temperature to a maximum of -4°C. The simulation results are captured in Figure 9. It can be seen that an increase in the degree of cooling showed a positive impact on the sweet gas specs, especially for \( \text{CO}_2 \). A temperature reduction of 4°C has contributed to a reduction in the concentration of \( \text{CO}_2 \) from 1.95 % to 1.88 %, also evident from the increased rich loading of the absorber. In the regeneration section, intercooling helped in stripping more acid gases as with decreasing lean loadings of the amine.

In any amine absorption process, reactions of the amine with \( \text{CO}_2 \) and \( \text{H}_2\text{S} \) are as follows:

\[
\begin{align*}
\text{H}_2\text{O} + R_3\text{N} & \leftrightarrow \text{OH}^- + R_3\text{NH}^+ \\
\text{OH}^- + \text{CO}_2 & \leftrightarrow \text{HCO}_3^- \\
\text{H}_2\text{S} + R_3\text{N} & \leftrightarrow R_3\text{NH}^+ + \text{HS}^- 
\end{align*}
\]

As the solubility increase with a decrease in temperature, provision of an intercooling would increase the mass transfer rate thus absorbing more \( \text{CO}_2 \) lowering its concentration in the sweet gas stream. From the above reaction between \( \text{CO}_2 \) and amine, it can be seen that as more absorption of \( \text{CO}_2 \) occurs, the reaction shifts toward consuming more \( \text{CO}_2 \) while decreasing the equilibrium concentration of \( \text{OH}^- \).
This would shift the first reaction towards making more OH\(^-\) increasing absorption of CO\(_2\). On the other hand, and for the absorption of H\(_2\)S, the instantaneous reaction of an amine with water will increase the equilibrium concentration of R\(_3\)NH\(^+\) rendering reaction (3) to proceed towards keeping H\(_2\)S concentration in the dissolved phase at the relatively constant magnitude.

It was also noted that an increase in cooling duty contributed to higher degrees Fig.10 re summarizes effects on regeneration energy with intercooling. It can be seen that as the cooling degree is increased, the reboiler demand less energy for stripping, reflecting less steam supply. Since the plant specs are at 20 ppm H\(_2\)S and 2\% CO\(_2\), it is possible to increase the processing capacity of the plant with the presence of side cooler or to reduce the steam supply to the reboiler.

3.4. Effect of heat stable salts (HSS)

![Figure 11. Effect of H\(_3\)PO\(_4\) concentration on sweet gas specs](image)

Reactions governing the absorption and desorption reactions with the presence of HSS are as follows:

\[
\begin{align*}
H_2S &\rightleftharpoons H^+ + HS^- & \text{Rxn 1} \\
H_2CO_3 &\rightleftharpoons H^+ + HCO_3^- & \text{Rxn 2} \\
H_3PO_4 &\rightarrow H^+ + H_2PO_4^- & \text{Rxn 3} \\
MD\text{EA} + H^+ &\rightarrow MD\text{EAH}^+ & \text{Rxn 4} \\
CO_2 + H_2O &\leftrightarrow H_2CO_3 & \text{Rxn 5}
\end{align*}
\]

It can be clearly seen that as the concentration of H\(_3\)PO\(_4\) is increased, more H\(^+\) ions are present increasing the concentration of the heat stable salts. The concentration of H\(_2\)S is sharply decreased by the addition of the acid to very low values, and this can be explained from Rxn 1, as the concentration of H\(^+\) ions is increased from the acid, the equilibrium concentration of HS\(^-\) is decreased shifting the reaction towards consuming more H\(_2\)S. For CO\(_2\) it can be seen from both Rxn 2 and Rxn 3 that as the amount of H\(^+\) is increased this shifts the Rxn towards producing more H\(_2\)CO\(_3\) and from Rxn 5 as the concentration of H\(_2\)CO\(_3\) is...
increased, this shifts the Rxn toward making more CO₂ and that’s why the effect is reversed from H₂S.

When H₃PO₄ is added to the mixture, it increases the amount of H⁺ present. This shifts the amount of MDEA and MDEAH⁺ present in this basic system of water, amine, and acid from that observed when just the water and amine are present. It is this additional amount of MDEAH⁺ that can represent heat stable salts [11].

The effect and concentration of HSS were tracked in the absorber and in the regenerator as well as whenever there is a pressure or temperature variations in the process.

In the amine absorber, H₂S and CO₂ dissolve into the aqueous solution. These dissolved gases can then undergo Rxn 1 and Rxn 5. If the aqueous solution did not contain anything to react with the dissolved gases or the resulting ions, the capacity of the solvent would be very limited on the amount of acid gas that it can absorb [12]. To explain the opposite effect of adding acid, adding a base to the solvent increases its capacity. The increase in capacity is due to the removal of H⁺ on the product side of Rxn 1, 2, and H₂CO₃ in Rxn 5. This can progress until Rxn 4 reaches equilibrium, at which point the solvent reaches maximum capacity [13].

In the regenerator, the temperature and pressure are drastically changed from the absorption column. The increased temperature and decreased pressure greatly reduce the amount of dissolved acid gas in the liquid solvent [14]. By reducing these, the reactions shift away from the ions and towards the production of dissolved gas. As the solvent travels down the column, more acid gas is removed resulting in less MDEAH⁺ being present as the reactions shift.

Since the H₃PO₄ remains in solution, the amount of H⁺ present is slightly higher than if it were not present. This increase in pH assists in stripping the acid gasses from the solvent. However, if more H₃PO₄ is added, eventually enough MDEA remains the MDEAH⁺ state that the amine no longer picks up enough H⁺ produced by the dissolved acid gas species and the capacity of the solvent diminishes. It is usually when this happens that reclamation is brought online so as to reduce the amount of MDEAH⁺ that is in solution by removing the salts and freeing up the amine base.

As the temperature of an aqueous solution of H₂S, CO₂, and MDEA is increased, the solubility of the dissolved gasses decreases. This results in H₂S and CO₂ leaving the solution [15]. This reduces the concentration of reactants for Rxn 1 and Rxn 5. Based on Le Chatelier’s principle, Rxn 1 and Rxn 5 will shift in the direction of making dissolved gas molecules. This reduces the amount of H⁺, as directly observable in Rxn 1, and observable through a combination of Rxn 5 and Rxn 2. Reducing the amount of H⁺ thus affects Rxn 4 such that less MDEAH⁺ is present [16].

A decrease in temperature increases the solubility of the gasses in the liquid solvent. Assuming that equilibrium is reached, and reaction kinetics is ignored, the increase in the dissolved gasses will cause the Rxn 1 and reactions Rxn 5 and Rxn 2 to shift to creating a larger amount of H⁺. The increase in H⁺ will increase the amount of MDEAH⁺ in the system as Rxn 4 shows.

Changes in pressure have a similar effect on the system. As pressure is lowered, the solubility of the dissolved gasses is reduced. This causes Rxn 1 and Rxn 5 to shift to the reactant side, causing a decrease in H⁺ and a resulting shift in Rxn 4 so that less MDEAH⁺ is present in the system.

An increase in pressure increases the solubility of the gasses in the liquid solvent. The increase in dissolved gasses will again increase the amount of MDEAH⁺, as discussed for the case where the temperature was decreased.

3.5. Limits for the dominance of corrosion and fouling

The total amount of acceptable HSS depends on kinds of ions present, and its corrosion characteristics, its effect on the performance of the system [17]. The simulation results indicate complete consumption of free amine at 1.2% addition of H₃PO₄, beyond which the H₂S concentration started to raise and present in its protonated form. It doesn't necessary mean that the acid can be added up to this point because the negative effects start to appear at
much lower concentrations. The solution to retrieve the free amine is either to flush fresh solvent to the system or by solvent reclamation techniques like Ion Exchange, Electro dialysis, etc. [18].

4. Conclusion

In summary, optimal conditions to enhance the overall efficiency of the sweetening process were discussed. Although the decrease in the pH was not found to improve the efficiency of the operation as stated in the literature pertaining to MEA solvent and the reason can be explained from kinetics point of view and reactions governing the desorption process. However, an increase in the regenerator pressure was found to decrease the regenerator energy requirement contributing to better energy efficiency, with the optimal operating pressure being 2.5 bar. An increase in the heat stable salts at a controlled concentration of 0.2 mol.% was found to improve the absorption efficiency of the H2S while had no significant effect on CO2 absorption. The application of intercooler improved the absorption efficiency of both H2S and CO2 as well as reduced the reboiler heat duty by achieving higher mass transfer driving force as the temperature is brought down. The combination of optimal conditions revealed that the plant capacity could be increased to about 4.2 % process capacity with an energy reduction of 81,000 tons of steam per year.

References


