Towards zero carbon dioxide concentration in sweet natural gas product from amine sweetening plant

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Abstract. This work presents a two-step method to reduce CO2 concentration of sweet natural gas product from amine sweetening plant via amine blending (Step 1) followed by minor process modification (Step 2). In Step 1, an industrial natural gas sweetening plant was simulated using Aspen HYSYS and the simulation results were validated against the plant data. Afterwards, different blends of methyl diethanolamine and monoethanolamine (MDEA-MEA) and methyl diethanolamine and diethanolamine (MDEA-DEA) were investigated. Then the optimum amine blend of 28 wt.% MDEA and 10 wt.% MEA was reported. The optimum amine blend achieved a significant reduction in CO2 concentration of sweet natural gas of 99.9% compared to the base case (plant data). In Step 2, two types of amine stream splits, i.e., lean amine stream split and semi-lean amine stream split were studied. The study covered split stream amount, absorber recycle stage, and regenerator stage withdrawal. Both types of stream splits attained a significant reduction in CO2 concentration of sweet natural gas product and amine circulation rate compared to Step 1. However, the semi-lean amine stream split was superior to lean amine split with 69.1% and 63.6% reduction in CO2 concentration of sweet natural gas and lean amine circulation rate, respectively.

1. Introduction

Natural gas has an immense impact on today’s economy given its much-increased demand over the last decade [1]. In comparison to other conventional fossil fuels such as coal and oil, natural gas provides cleaner combustion as it produces 71% and 56% less carbon dioxide (CO2) emissions, respectively [2]. Nonetheless, raw natural gas usually contains unwanted inorganic gas components that are often referred to as sour gases given their acidic characteristics [3]. Such inorganic components particularly CO2 and hydrogen sulphide (H2S) are to be removed from natural gas to meet the allowable limit for gas pipelines regulations, which is 2 mol.% and 4 ppm, respectively [4]. Carbon dioxide is responsible for the corrosion of transmission pipelines and other equipment including pumps, turbines, and compressors by its reaction with water vapour to form carbonic acid. Moreover, the presence of CO2 reduces natural gas heating value [5]. Many methods have been used to remove acid gases from natural gas including absorption, adsorption, membrane separation, cryogenic distillation, and chemical conversion [6]. From these methods, absorption-based gas sweetening technology attracts considerable attention due to its high acid gas removal percentage [7]. Absorption can be achieved by means of chemical solvents,
physical solvents, and their mixtures [8]. However, the commercialized absorption technology adopts aqueous alkanolamines solutions to remove the acid gas components, i.e., amine gas sweetening due to their low operating cost and flexibility of modifying the solvent composition to fit the sour gas properties [9]. Alkanolamines are organic bases formed from ammonia (NH3) where one, two, or three alkyl groups substitute ammonia’s hydrogen resulting in primary, secondary, and tertiary amines [10]. Monoethanolamine (MEA) and diethanolamine (DEA), which are examples of primary and secondary amines, respectively, have a high absorption rate due to their highly reactive behaviour whereas tertiary amine such as methyl diethanolamine (MDEA) has a relatively slower absorption rate given its lower reactivity. However, this attribute of MDEA translates to a lower regeneration energy requirement compared to DEA and MEA, with MEA having the highest regeneration requirements [11]. Thus, to achieve higher removal of acid components whilst maintaining low regeneration cost, amine blending has become an attractive option. Amine blending involves the combination of a tertiary amine (such as MDEA) with a primary or secondary amine (MEA and DEA, respectively). Other techniques to reduce stripper regeneration energy including alternative configurations like stream-split, vapour recompression, and their combinations have been recently investigated. Results approved the possibility of decreasing the stripper reboiler duty significantly with the different configurations [12]. To this end, this work aims to reduce CO2 concentration in a sweet gas product far beyond the standard pipeline specification (2 mol.%), i.e., towards zero concentration of CO2 in sweet gas product to maintain the sustainable operation of natural gas facilities by eliminating pipeline and equipment corrosion as well as maintaining higher heating value of natural gas. Hence, it is proposed to achieve this aim via employing amine blends followed by a stream splitting technique.

2. Amine Sweetening Process Description

Figure 1 shows a conventional amine sweetening process flow diagram [13]. A sour gas feed is introduced directly into the bottom of the absorption column (absorber) where it is counter-currently contacted with the CO2-lean alkanolamines solution (lean amine), which flows into the column from the top stage of the absorber. The lean amine solution reacts with CO2 in the feed gas on the column trays in an exothermic reaction, which causes the absorption of CO2 into the lean amine solution. The CO2-deprived gas (sweet gas product) exits overhead from the column while the remaining CO2-rich amine solution (rich amine) exits the bottom of the absorber entering a flash separator, where it is throttled and flashed to remove the light hydrocarbons. The rich amine solution is then heated as it flows through a lean/rich amine heat exchanger to attain the required stripping column (stripper) temperature. The stripper receives hot rich amine flowing downwards from the top stage contacting rising steam, which is supplied by a reboiler, in a counter-current manner. The cross-counter between the rich amine and steam strips the CO2 from the rich amine, with the remaining CO2-rich gas leaving at the top of the column while the stripped-amine solution comes out at the bottom as lean amine. The lean amine solution’s flow rate and concentration are maintained by mixing it with a makeup stream to compensate for any solvent loss throughout the process. Finally, the lean amine solution is pumped and cooled by an air cooler before being recycled back to the top of the absorber.

3. Methodology

3.1. Base case

An amine-based sweetening process for the removal of CO2 from natural gas was simulated in Aspen HYSYS version 11 (figure 2). The sour natural gas composition, process parameters, and process design specification are adopted from a real plant located in Argentina (figure 1) [14]. The thermodynamic fluid package used for the simulation was Acid Gas package designed by Aspen Technology for amine gas sweetening process. The accuracy of the findings and the reliability of the base case simulation model are essential factors to carry out parametric studies. Thus, to verify the reliability of the model, the simulation results were validated against the plant data where the percentage error was found to be less than 10% (table 2). This minor discrepancy validates the accuracy of the simulation. It is worth
noting that the presented simulation results in table 2 have been accomplished at a lean amine circulation rate of 15.4 m$^3$ hr$^{-1}$, reboiler duty of 0.8309 MW, and sweet gas product CO$_2$ concentration of 0.3418 mol.%. 

Figure 1. A basic amine sweetening process flow diagram [13].

Figure 2. Base case aspen HYSYS v11 configuration (Note: HX – Heat Exchanger, RCY – Recycle).
3.2. Parametric Analysis

In this work, the parametric analysis was carried out in a two-step method with the aim of achieving the lowest CO2 concentration in sweet gas product at the minimum levels of lean amine circulation rate and stripper reboiler duty, which are considered as indicators for minimising operating cost. In Step 1, different blends of MDEA-MEA and MDEA-DEA were studied to find the best blending ratio, while in Step 2, two types of amine stream split configurations; lean amine split stream configuration (figure 3) and semi-lean split stream configuration (figure 4) were investigated to further improve the process performance in terms of stripper reboiler duty and CO2 concentration in sweet gas product. In the lean amine split stream configuration (figure 3), the lean amine leaving the stripper is split into two portions where one portion is recycled back into some tray below the top of the absorber and the remaining is recycled to the top tray. In the semi-lean split stream configuration (figure 4), however, a partly

Table 1. Input data for Aspen HYSYS v11 base case simulation.

| Parameters                          | Operating Data | Simulation Data | Error (%) |
|-------------------------------------|----------------|-----------------|-----------|
| Sweet Gas Temperature (°C)          | 40             | 41.3            | 3.25      |
| Sweet Gas Pressure (kPa)            | 6000           | 6000            | 0         |
| Sweet Gas Molar Flow (m³/d)         | 240000         | 239470          | 0.22      |
| Sweet Gas CO2 (mol.%)               | 0.35           | 0.3418          | 2.31      |
| Rich Amine Pressure (kPa)           | 6000           | 6000            | 0         |
| Acid Gas Mole Flow (m³/d)           | 9755           | 10320           | 5.79      |
| Acid Gas Pressure (Pa)              | 112            | 112             | 0         |
| Rich Amine to Exchanger Temperature (°C) | 50         | 54.79           | 9.58      |
| Stripper Bottoms Temperature        | 110            | 109.4           | 0.55      |
| Stripper Bottoms Pressure (kPa)     | 132            | 132             | 0         |

Table 2. Plant data validation.

| Parameter                        | Value         |
|----------------------------------|---------------|
| Feed Gas Temperature             | 40 °C         |
| Feed Gas Pressure                | 6000 kPa      |
| Feed Gas Flow                    | 250 Mm³/d     |
| CO2 in Feed Gas                  | 4 mol.%       |
| CH4 in Feed Gas                  | 93 mol.%      |
| Lean Amine Temperature           | 42 °C         |
| Lean Amine Pressure              | 9610 kPa      |
| MDEA in Lean Amine               | 38 wt.%       |
| Number of stages in Absorber     | 24            |
| Number of stages in Stripper Tower | 20         |
| Stripper Feed Temperature        | 90 °C         |
| Top of the Stripper Temperature  | 87.78 °C      |
| Reflux Ratio                     | 1.1           |

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regenerated (semi-lean) amine solution drawn from a certain stage in the stripper is recycled back into some tray below the top of the absorber, while the completely regenerated (ultra-lean) amine is recycled to the top. The partly regenerated amine draw from the stripper contains residual CO₂, which allows for bulk CO₂ capture in the absorption column without extra regeneration costs [12,15–17]. Apart from the base case parameters that affect the process performance, the amount recycled (lean amine split-ratio for figure 3 and stripper semi-lean side draw amount for figure 4) to the absorption column along with its feed stage-number as well as the stripper draw stage-number (for figure 4) need to be adjusted to enhance the overall performance of the plant [17].

![Figure 3. Lean amine split stream configuration (Note: HX – Heat Exchanger, RCY – Recycle).](image1)

![Figure 4. Semi-lean amine split stream configuration (Note: HX – Heat Exchanger, RCY – Recycle).](image2)
Figure 5 shows the parametric study framework proposed in this work. The first section focuses on selecting the best amine blend between (28 wt.% MDEA & 10 wt.% MDEA) and (28 wt.% MDEA & 10 wt.% DEA), which were benchmarked against the base case (38 wt.% MDEA). The chosen weight percentage for MEA and DEA are both 10 wt. % as the secondary amine is generally less than 25% of the total amine on a molar basis [8]. To this end, the chosen amine blend was subjected to further investigation in Section 2 to select the best blending ratio with five different ratios of secondary amine A (which is either MEA or DEA) ranging from 0 wt.% to 20 wt.% with the remaining MDEA, respectively. In Section 3, a minor process modification through two different types of split streams is carried out (lean amine and semi-lean amine split stream configuration).

**Figure 5.** Parametric study framework.
4. Results & Discussion

The parametric study framework depicted in figure 5 is demonstrated section by section as follow.

4.1. Section 1

The effect of the lean amine circulation rate on the reboiler duty and the sweet gas product CO₂ concentration for different amine blends is demonstrated in figure 6. The trends in figure 6 indicate that as the lean amine circulation increases, the CO₂ concentration in sweet gas product decreases for all the different blends. On the other hand, the reboiler duty increases with increasing lean amine circulation rate due to the increased rich amine fed to the stripper. Figure 6 also shows a significant decrease in the sweet gas product CO₂ concentration for the MDEA-DEA and MDEA-MEA blends compared to MDEA alone. Nonetheless, MDEA provides the lowest reboiler duty compared to the amine blends given its lower heat of reaction. However, the minimum sweet gas product CO₂ concentration is achieved at 11 m³ hr⁻¹ in the case of MDEA-MEA blend followed by the 12 m³ hr⁻¹ for the MDEA-DEA blend. There is a negligible decrease in CO₂ concentration after this point for both blends, but a constant increase in reboiler duty. Thus, MDEA-MEA blend is viewed as the best amine blend and will be subjected to further analysis to determine the best blending ratio that leads to better process performance.

Figure 6. Effect of lean amine circulation rate on sweet gas product CO₂ concentration and reboiler duty at different amine blends.

4.2. Section 2

Figure 7 and 8 show the effect of the lean amine circulation rate on the reboiler duty and the sweet gas product CO₂ concentration for different MDEA-MEA blend ratios. The sweet gas product CO₂ concentration decreases with increasing lean amine’s circulation rate (figure 7). However, the lowest
sweet product CO$_2$ gas concentration is achieved at blended amine of 28 wt.% MDEA and 10 wt.% MEA. Figure 8, on the other hand, reveals a different trend as sweet product CO$_2$ gas concentration increases with the lean amine circulation rate due to the mass transfer limitations that occur at MEA ratios of 15 wt. % and higher. As expected, the reboiler duty is shown to increase as the lean amine circulation rate increases for amine blends (figure 7 and figure 8). Out of the 5 MDEA-MEA blends presented in figure 7 and 8, the 28 wt.% MDEA and 10 wt.% MEA achieved the lowest sweet gas product CO$_2$ concentration at a lean amine circulation rate of 11 m$^3$ hr$^{-1}$. However, increasing lean amine circulation rate beyond 11 m$^3$ hr$^{-1}$ provides a negligible improvement in sweet gas product CO$_2$ concentration while adversely increases the reboiler duty.

4.3. Section 3
The effect of different split lean amine ratio on the sweet gas product CO$_2$ concentration and the reboiler duty is depicted in figure 9. The sweet gas product CO$_2$ concentration decreases with increasing split lean amine ratio due to extra lean amine flow to some trays below the top of the absorber, allowing for better mass transfer between the amine and the contacting sour gas. This enhances the absorption of CO$_2$, which is in agreement with semi-lean amine technique that picks up CO$_2$ when fed into some tray below the top of the absorber [15, 16]. As anticipated, the reboiler duty increases as the split lean amine ratio is increased because of a greater regeneration requirement to account for a larger CO$_2$ loading. The best split lean amine ratio is 0.5 as any further increase provides no significant improvement in the sweet gas product CO$_2$ concentration but increases the reboiler duty (figure 9).

![Figure 7](image1.png)

**Figure 7.** The effect of lean amine circulation rate on sweet gas product CO$_2$ concentration and the reboiler duty at different MEA blend ratios.
Figure 8. The effect of lean amine circulation rate on sweet gas product CO₂ concentration and the reboiler duty at different MEA blend ratios (2).

Figure 9. The effect of different split lean amine ratio on the sweet gas product CO₂ concentration and the reboiler duty.
Figure 10 shows the effect of the absorber feed stage-number for the split lean amine on the sweet gas product CO\(_2\) concentration and the reboiler duty. The results show an increase in sweet gas product CO\(_2\) concentration with an increase in feed stage-number (from top to bottom). At the same time, the reboiler duty tends to decrease between stage 6 and 10, then increases between stage 10 and 14 followed by another slight decrease in stage 16. Stage 10 is chosen as the best split lean amine feed stage for its minimum reboiler duty compared to the other stages. Figure 11 shows the effect of the semi-lean amine molar flow rate fed to the absorber on the sweet gas product CO\(_2\) concentration and reboiler duty. The results display an overall decrease in the sweet gas product CO\(_2\) concentration as the semi-lean amine flow rate increases, facing a significant decrease between 630 kgmol hr\(^{-1}\) and 650 kgmol hr\(^{-1}\), which gives the minimum concentration. On the other hand, the reboiler duty is shown to increase linearly as the semi-lean flow rate is increased. Therefore the best semi-lean amine flow rate is 650 kgmol hr\(^{-1}\) drawn from stage 10 (from top to bottom) of the stripper (figure 11). Figure 12 shows the effect of the absorber feed stage-number for semi-lean amine on the sweet gas product CO\(_2\) concentration and the reboiler duty. The sweet gas product CO\(_2\) concentration increases with the number of absorber semi-lean amine feed stages (from top to bottom) up to stage 16, where it faces a significant decrease till its minimum at stage 19 with a slight increase at stage 20. It appears that from stages 16 to 19, the semi-lean is enabled for efficient contact with sour gas improving absorption performance, while it is limited after stage 19. As for the reboiler duty, it shows a minimal increase as the number of semi-lean absorber feed stage is increased. Therefore, the best absorber stage for semi-lean feed is stage 19, which achieves the best sweet gas product CO\(_2\) concentration.
Figure 11. The effect of the semi-lean amine molar flow rate fed to the absorber on the sweet gas product CO$_2$ concentration and reboiler duty.

Figure 12. The effect of the absorber feed stage-number for semi-lean amine on the sweet gas product CO$_2$ concentration and the reboiler duty.
Figure 13 shows the effect of the stage-number of semi-lean amine drawn from the stripper on the sweet gas product CO₂ concentration and reboiler duty. The sweet gas product CO₂ concentration decreases with stage-number of semi-lean amine drawn from the stripper until stage 10 (from top to bottom) followed by significant increase in the sweet gas product CO₂ concentration after stage 10. In contrast, the reboiler duty increases with the stage-number of semi-lean amine drawn from the stripper (from top to bottom). Thus, the stage-number 10 from the top of the stripper is the best stage as it possesses the minimum sweet gas product CO₂ concentration.

![Figure 13. The effect of the stage-number of semi-lean amine drawn from the stripper on the sweet gas product CO₂ concentration and reboiler duty.](image-url)

Table 3 summarises the overall results of the proposed methodology, which comprises two steps; Step 1 (amine blending) followed by Step 2 (lean/semi-lean amine split). The results reveal that both steps of the proposed methodology achieved significant reduction in sweet gas CO₂ concentration and amine circulation rate at the expense of increase in the reboiler duty compared to the base case. Thus, since both the lean amine split and the semi-lean amine split configurations are combined with Step 1’s outcomes (choosing the best amine blend type and ratio), it is obvious that the semi-lean amine split configuration is the best option for its lower CO₂ sweet gas product concentration and lean amine circulation rate compared to lean amine split configuration.
Table 3. Overall results summary.

| Process configuration       | Lean amine circulation rate (m³ hr⁻¹) | Sweet gas CO₂ conc. (mol.%) | Reboiler duty (MW) |
|-----------------------------|--------------------------------------|-----------------------------|--------------------|
| Base case                   | 15.4                                 | 0.3418                      | 0.8309             |
| Step 1                      | 11                                   | 1.26 x 10⁻⁴                | 0.8730             |
| Step 2 (Lean amine split)   | 5.5                                  | 1.204 x 10⁻⁴               | 0.8692             |
| Step 2 (Semi-lean amine split) | 2                                   | 3.721 x 10⁻⁵               | 0.9093             |

5. Conclusion

In this work, a two-step method consist of amine blending (Step 1) followed by minor process modification (Step 2) has been presented. In Step 1, different blends of MDEA-MEA and MDEA-DEA were examined and the best amine blend of 28 wt.% MDEA and 10 wt.% MEA was selected. The best amine blend achieved a sweet gas CO₂ concentration of 1.26 x 10⁻⁴ mol.% with a lean amine circulation rate of 11 m³ hr⁻¹ and a reboiler duty of 0.8730 MW. This translates into a significant reduction of 99.9% in CO₂ concentration of sweet natural gas compared to the base case (plant data). In Step 2, two types of amine stream split, namely lean amine stream split and semi-lean amine stream split were considered. Several process parameters including the split stream’s ratio and amount, absorber’s recycle stage-number and stripper’s draw stage-number were studied. Compared to the lean amine configuration, the semi-lean amine configuration achieved a lower CO₂ concentration of sweet natural gas and a lean amine circulation rate of 69.1% and 63.6%, respectively. The application of semi-lean amine technique can be extended to Benfield process to investigate the effect of recycling semi-lean potassium carbonate on the performance of natural gas sweetening process.

References

[1] Abdulrahman R K and Sebastine I M 2013 Natural gas sweetening process simulation optimization: A case study of khurmala field in Iraqi Kurdistan region J. Nat. Gas Sci. Eng. 14 116–20
[2] Zahid U 2020 Simulation of an acid gas removal unit using a DGA and MDEA blend instead of a single amine Chem. Prod. Process Model. 15 20190044
[3] Mokhatab S, Poe W and Mak J 2018 Handbook of Natural Gas Transmission and Processing, 4th ed
[4] Stewart M and Arnold K 2011 Gas Sweetening and Processing Field Manual (Amsterdam: Gulf Professional)
[5] El-Maghraby R, Salah A and Shoaib A 2019 Carbon dioxide capturing from natural gas using di-glycol amine and piperazine — A new solvent mixture Int. J. Recent Technol. Eng. 8 11378–83.
[6] Ngu L, Mahmoud A and Sunarso J 2020 Aspen Plus simulation-based parametric study of benfield process using hot potassium carbonate promoted by diethanolamine IOP Conf. Ser.:Mater. Sci. Eng. 778 012058
[7] Shoukat U and Knuutila H 2020 Effect of various parameters on the thermal stability and corrosion of CO₂-loaded tertiary amine blends Energies 13 2626
[8] Yusuf M 2017 Anisotropic selection of amine in natural gas sweetening process for acid gases removal: A review of recent studies Pet. Petro. Chem. Eng. J. 1 000114
[9] Abbas T, Ghauri M, Shahid Z and Rashid M 2011 Dynamic simulation of sweetening process of natural gas Can. J. Chem. Eng. Technol. 2 156–61
[10] Gutierrez J, Benitez L, Ale Ruiz E and 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. 31 800–7
[11] Reza M, Hamlehder O, Boor H, Monnavar A and Rostami S 2011 Mixed amines application in
gas sweetening plants Chem. Eng. Trans. 24 265–70

[12] Øi L, Bråthen T, Berg C, Brekne S, Flatin M, Johnsen R, Moen I and Thomassen E 2014 Optimization of configurations for amine based CO₂ absorption using aspen hysys Energy Procedia 51 224–33

[13] Khalaf A 2020 Influence of using different mixtures of amines on the performance of natural gas sweetening process at Iraqi north gas company Pet. Coal 62 735–42

[14] Gutierrez J, Ale Ruiz E and Erdmann E 2017 Energy requirements, GHG emissions and investment costs in natural gas sweetening processes J. Nat. Gas Sci. Eng. 38 187–94

[15] Bae H, Kim S and Lee B 2011 Simulation of CO₂ removal in a split-flow gas sweetening process Korean J. Chem. Eng. 28 643–48

[16] Polasek J, Bullin J and Donnelly S T 2006 Alternative flow schemes to reduce capital and operating costs of amine sweetening units Bryan Research and Engineering, Inc.

[17] Al-Lagtah N, Al-Habsi S and Onaizi S 2015 Optimization and performance improvement of Lekhwair natural gas sweetening plant using aspen hysys J. Nat. Gas Sci. Eng. 26 367–81