Optimization and Throughput Opportunities at PTT PLC's Amine Plant

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Abstract

Removal of CO_2 from natural gas is a necessary treating step before cryogenic processing. At the PTT Public Limited Company Gas Processing Plant 5, the wellhead gas has CO_2 concentrations ranging from 19 to 23 mol%. This gas feeds an amine sweetening unit where most of the CO_2 is removed. The sweet gas product is dried before entering a cryogenic demethanizer where ethane and heavier natural gas liquids are recovered. The demethanizer overhead reaches temperatures as low as -100 to -120 C. Thus to prevent CO_2 freeze-out, the CO_2 concentration in the sweet gas must be less than 900 ppm. This study focuses on optimization of the amine sweetening unit to increase throughput, provide adequate cold protection, and avoid corrosive operating conditions in the amine regenerator.

Introduction

Carbon Dioxide (CO_2) is a major impurity in natural gas wells that causes corrosion in transportation pipelines, may form a solid "hydrate" when in the presence of water, and can freeze by itself (forming "dry ice") at cryogenic gas plant conditions. The required CO_2 level to prevent solids formation in the cryogenic NGL recovery process is in the hundreds of ppm range.

In the past, primary and secondary amines were used to sweeten natural gas to such low CO_2 levels. Lately, MDEA has become a popular solvent because it is less corrosive and needs less heat for regeneration. However, MDEA by itself is slow to absorb CO_2 [1]. Within typical amine absorbers, there is insufficient contact time for the gaseous CO_2 to complex with the aqueous MDEA cations. Thus, MDEA is usually incapable of sweetening gas to the ppm levels demanded by cryogenic gas processing. However, blends of MDEA with certain activating agents has been found to hasten CO_2 absorption so that gas can be suitably treated for subsequent cryogenic processing. These activators are added in small amounts to the MDEA solution to enhance the CO_2 absorption while mostly maintaining the desirable qualities of MDEA [2-3]. The primary reactions for an amine process are

$$H_2O \leftrightarrow H^+ + OH^- \qquad \text{Rxn 1}$$

$$CO_2 + OH^- \leftrightarrow HCO_3^- \qquad \text{Rxn 2}$$

$$MDEA + H^+ \leftrightarrow MDEAH^+ \qquad \text{Rxn 3}$$

The second equation represents the hydrolysis of CO_2. The reactions for the activator are [4]

$$AM + CO_2 \leftrightarrow AM(CO_2) \qquad \text{Rxn 4}$$

$$AM(CO_2) + H_2O \leftrightarrow AMH^+ + HCO_3^- \qquad \text{Rxn 5}$$

$$AMH^+ + MDEA \leftrightarrow MDEAH^+ + AM \qquad \text{Rxn 6}$$

AM represents different activators available on the market such as DGA, MEA, DEA, and Piperazine. The reactions show the activator cation reacts directly and quickly with CO_2. Then another very fast reaction occurs where the CO_2 flips from the activator cation to the MDEA cation. This combination of two very fast reactions replaces the slow reaction sequence occurring when CO_2 is absorbed by MDEA alone. The activating agent does have its own small amount of absorption capacity which comes with a high regeneration energy comparable to other primary or secondary amines [1]. The activated MDEA blend's activating energy increases proportionally to the amount of activating agent in the blend. Since the activating agent is present in small amounts, the low regeneration energy benefits of MDEA are largely achieved.

PTT PLC, a public owned company in Thailand, has such an activated MDEA sweetening unit. Our study of the sweetening unit was undertaken to maximize plant throughput, minimize operating expenses, reduce corrosion, and maintain adequate CO_2 removal. The study was accomplished by first creating a model in the ProMax [5] process simulation program and comparing it to plant operating data to ensure a good match. Then scenarios covering several key operating parameters were run to examine alternatives and find optimum operating conditions.

Current Plant Operation

Plant configuration

The process flow diagram for the PTT Gas Separation Plant (GSP) no. 5 amine sweetening unit is shown in Figure 1. GSP#5 consists of two identical amine trains of which one is shown in the figure. Sour gas is split equally by flow controllers to each packed bed absorber where it contacts the amine solution. The sweet gas is then dried before entering the Ethane Recovery Unit. Rich amine solution leaves the absorber bottom and proceeds to a high pressure flash tank where most light hydrocarbons and some acid gas are flashed. The rich amine from the high pressure tank proceeds to a lower pressure column where it contacts regenerator acid gas to scrub and recover any residual amines. The rich amine is then regenerated in a hot oil reboiled stripper. Figure 1 shows the current plant configuration of the Amine Unit.

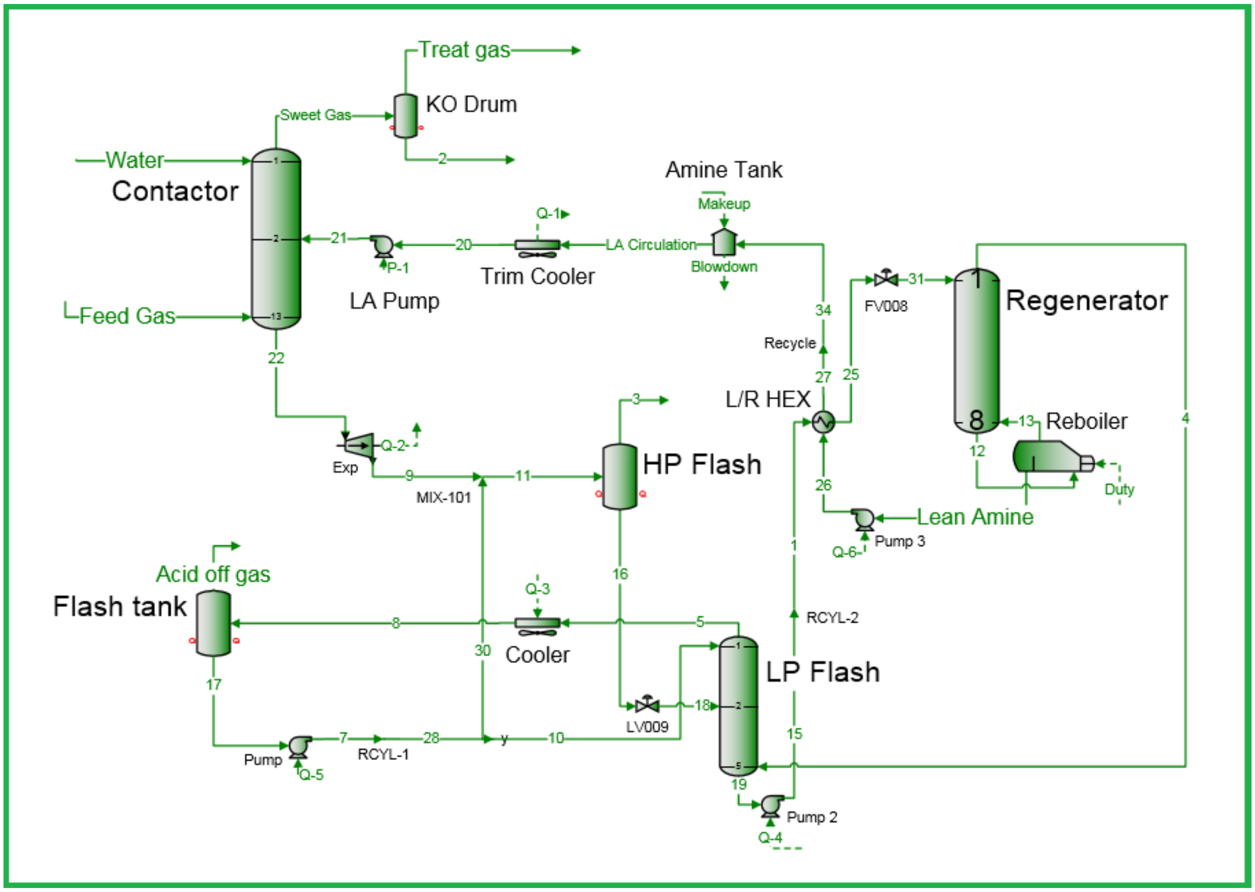

Figure 1: Process Flow Diagram for PTT GSP#5 Amine Sweetening Unit.

Comparing ProMax to Plant Operating Data

Operating data for the unit from July 1st to August 19th 2014 were used in ProMax to calculate plant performance. The average operating conditions are shown in table 1 below.

Average Plant Operating Conditions	
Combined Plant Feed Gas (MMSCFD)	550
Feed Gas CO_2 (%)	20.18
Feed Gas CH4 (%)	65.99
Lean Amine Temperature (°C)	46
Feed Gas Temperature (°C)	19
Feed Gas Pressure (Barg)	43
Regenerator Overhead Pressure (Barg)	0.60
Temperature LP Flash amine outlet E01 (°C)	101

Table 1: GSP#5 Amine Unit Operating Conditions.

The absorber and regenerator are modelled using the proprietary Electrolytic Property packaged developed by Bryan Research & Engineering, Inc. The excellent agreement between ProMax predictions and plant measurements of sweet gas CO_2 are shown in Figure 2 for several typical days.

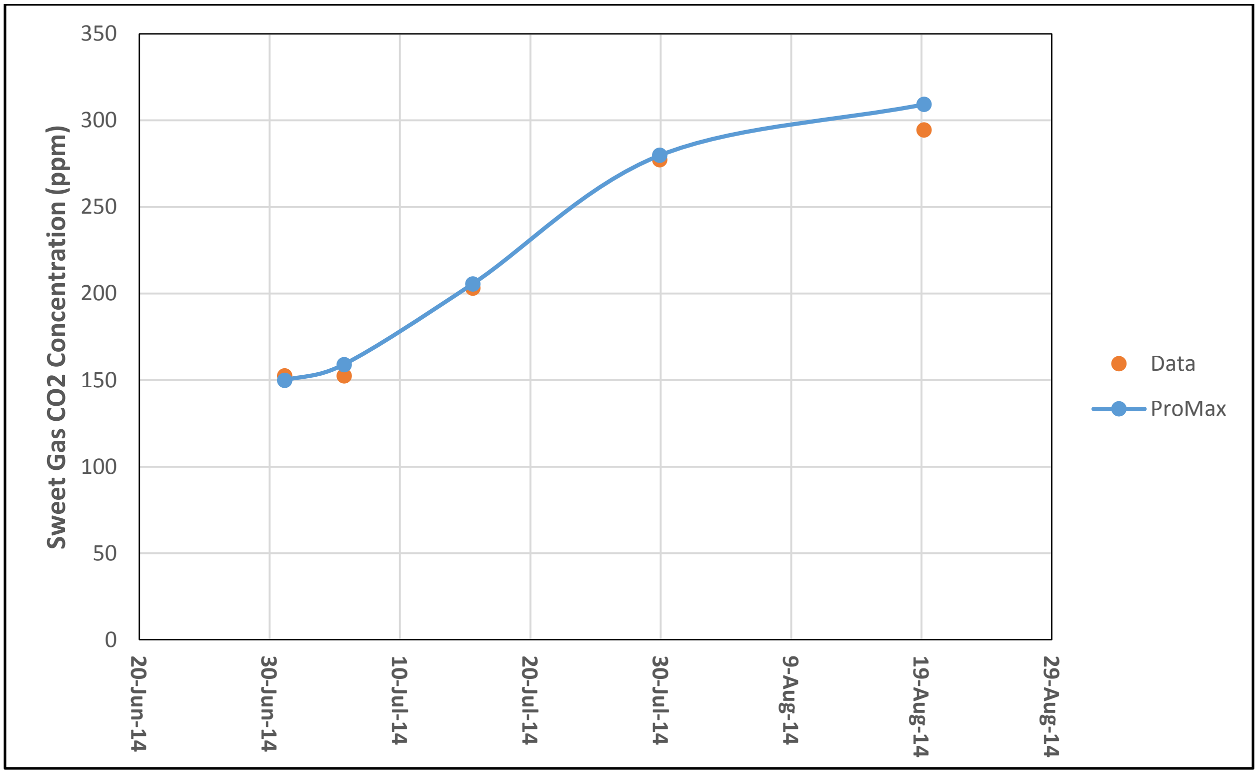

Figure 2: ProMax versus Operating Data

Process Optimization

Since ProMax accurately represents the plant performance, it can be used to carry out plant optimization. During the optimization study, the desire is to most profitably utilize the process equipment without violating any of the product quality, reliability, or equipment constraints. One requirement is to keep the treated gas below the 900 ppm CO_2 spec while reliably operating the amine unit. Optimization will consider opportunities to reduce reboiler duty. Also, avoidance of corrosive conditions in the reboiler will be monitored within the ProMax simulation strategy.

Optimization Input Variables

The following adjustable input parameters (or manipulated variables) are considered in this study.

Reboiler Duty: The reboiler duty will be optimized primarily to avoid corrosion in the regenerator and assure constraint variables are within limits. If there is additional flexibility, reboiler duty will be reduced to save energy.

Amine Ratio (mass rate of activator / mass rate of MDEA): The amine ratio describes the proportion of activator relative to base amine, MDEA, in the custom amine blend. Too low of a ratio may reduce the effectiveness of the solvent in absorbing CO_2 while too high of a ratio will increase the required duty for regeneration. The optimization will determine the optimal amine ratio for meeting CO_2 spec at minimum reboiler duty.

Amine Circulation Rate: The circulation rate will be optimized to keep the treated gas below the CO_2 spec while not exceeding a Rich Loading limit. Rich Loading must stay below a certain limit to prevent corrosion.

Plant Throughput: Plant operating conditions are optimized at various throughputs. There is generally more gas available than this plant can process. The ultimate goal is to find the highest possible throughput for the Amine unit.

Constrained variables

The optimization of the adjustable inputs are subject to the following constraints.

Sweet gas CO2 concentration: The maximum limit for the sweet gas CO2 concentration is 900 ppm. However, a target of 300 ppm is used in the study to accommodate any sudden acid gas spikes in the feed.

Reboiler vapor CO_2 *concentration*: As discussed in literature, high concentrations of CO_2 in the presence of water causes corrosion in the reboiler tube bundle [6]. The recommended maximum CO_2 concentration in the reboiler vapor is 1% when carbon steel is the reboiler material of construction.

Rich Loading: A maximum of 0.53 mole/mole rich loading was used to avoid corrosion.

Lean amine pump capacity: The maximum capacity of the existing amine circulation pump is 1200 m^3/h. Part of the throughput optimization study will consider opportunities available if this pump capacity is increased.

Column flood: ProMax calculations for flooding in the amine contactor will be limited to 85%. The throughput study will be limited to opportunities this maximum flood limit. Major column capacity expansions are quite expensive so we will assume no throughput opportunities are available that lead to flooding in this existing absorber.

Reboiler duty: The maximum available reboiler duty is 65 MW. Part of the throughput optimization study will consider opportunities available if the reboiler bundle and hot oil system capacity are enhanced.

Phase 1: Process optimization at current inlet gas rate

This section aims to establish the best operating conditions for the current plant. The amine ratio and reboiler duty are varied for the present throughput (275 MMSCFD) to determine the operating conditions having lowest operating cost within the plant constraints. It should be noted that at 275 MMSCFD, amine absorber and regenerator flooding are well below the limits and are omitted from Phase 1 constraint analysis.

Adjusting Amine Ratio at Various Reboiler Duties

The amine unit reboiler was designed to operate at 60 MW and an amine ratio of 0.12 while treating 265 MMSCFD of sour gas. Currently, the feed rate is 275 MMSCFD, the amine ratio fluctuates from 0.04 to 0.12 due to amine make up and losses, and the reboiler duty averages 55 MW. As discussed previously, changes in activator concentration affect both the sweet gas CO_2 concentration and required regeneration duty. Figure 3 shows the sweet gas CO2 concentration versus amine ratio for several duties.

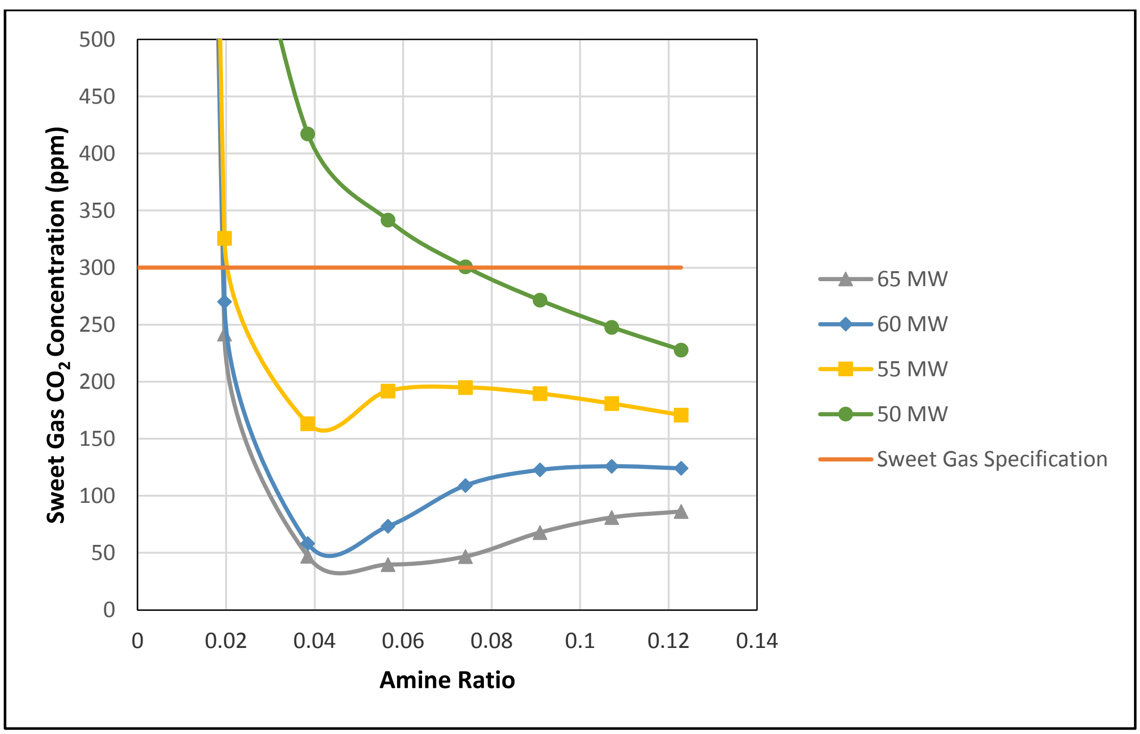

Figure 3: Absorber Performance for Various Amine Ratios

The graph shows that amine ratios below 0.04 show drastic increases in sweet gas CO2 concentration. Therefore, ratios below 0.04 will not be considered for future analysis. For the range of 0.04 to 0.12, the amine ratio does not have a major impact on the CO_2 in the sweet gas, which is always well below the 300 ppm target (except for the 50 MW case). At current operation, the amine ratio can be reduced below the design value without detrimental effect. Figure 3 also shows that it is possible to reduce the reboiler duty by at least 23% without going over the 300 ppm CO_2 target. However, other constraints must also be considered before the optimal amine ratio duty can be determined.

Optimizing Reboiler Duty

As previously observed, the reboiler duty above 55 MW has a relatively minor effect on the CO_2 sweet gas concentration for the current plant. However, to ensure reliable plant operation, a study is conducted to observe the rich amine loading and the reboiler vapor CO_2 concentration at various duties to determine the minimum duty requirements. Both of these variables can lead to corrosion when exceeding their recommended limits. Figure 4 below represents the regenerator performance for various operating points discussed in Figure 3.

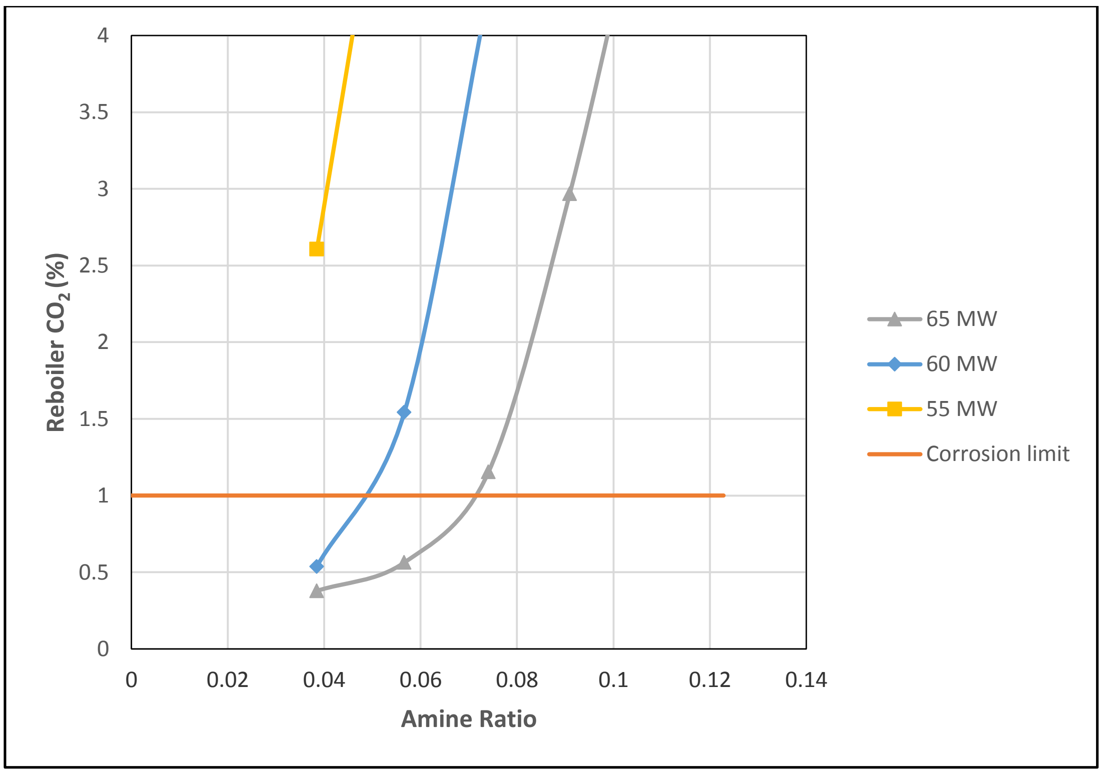

Figure 4: Reboiler Vapor CO_2 Concentration versus Amine Ratio

The graph shows a drastic increase in reboiler vapor CO_2 concentration as the amine ratio increases. At the maximum ratio (0.12), the CO_2 concentration in the reboiler vapor is 7% for maximum capacity (65 MW). At 50 MW, the CO_2 concentration in the reboiler vapor is well above 5% for a 0.04 amine ratio (not shown on graph). Carbon steel is highly susceptible to corrosion at these conditions. Concentrations above 1% can cause corrosion issues in the reboiler and above 5%, exotic material (stainless steel) is required to avoid corrosion.

High CO_2 in the reboiler vapor indicates insufficient stripping in the lower section of the regenerator which can lead to corrosion on the reboiler tube bundle. Cavitation damage of the tubes, caused by the formation and collapse of vapor bubbles near the tube surfaces, leaves the metal susceptible to oxidation by bicarbonate in the liquid solution [7]**.** As a result, rapid corrosion occurs in localized areas of the tube where this phase change occurs. This is known as pitting corrosion. In the past several years, PTT has experienced leakage of hot oil into the amine solution due to tube bundle corrosion. It can be observed in Figure 4 that over-concentration of activator drastically increases CO_2 concentration in the reboiler vapor. Activators require more energy to regenerate a unit amount of CO_2 than MDEA. Therefore, over-concentrating activator for a system with fixed duty results in less stripping capability which leads to corrosion issues.

The graph shows that lowering the amine ratio reduced corrosion potential in the reboiler. The rich loadings for all amine ratios studied were below 0.53. Thus, the optimal amine ratio for the current plant is 0.04 as shown in Figures 3 and 4. Due to the corrosion constraint, the minimum duty required for the amine unit is 58 MW at the optimal amine ratio. Here, the plant is able to minimize energy consumption while satisfying all constraints. Therefore, 0.04 amine ratio will be used as the basis in the unlimited feed process optimization study that follows.

Phase 2: Process Optimization with Unlimited Feed Availability

With the acquisition of new gas sources, PTT PLC hopes to increase the capacity of GSP#5. This next optimization study relaxes the limit on inlet gas rate which was set to 275 MMSCFD in the prior case. Again, amine circulation, amine ratio, and duty are adjusted to find optimal operating conditions. Another factor to consider is that the amine circulation rate and reboiler duty limits could be increased through reasonable equipment upgrades. Potential gas treating capacity increases subject to these equipment upgrades are presented.

Column Flood

The capacity of the contactor determines the ultimate throughput of the plant because it isprohibitively expensive to add hydraulic capacity to major distillation columns. The correct response to this is building additional gas treating and processing trains. Also, absorber hydraulic capacity is largely dependent on vapor traffic. Therefore this graph of the inlet feed rate versus column flooding in Figure 5 shows an ultimate throughput of 370 MMSCFD at 85% flood. This study assumes constant inlet gas and absorber pressure 43 barg. If inlet gas pressure were to change, then this optimization would need to be re-evaluated as absorber flood is also a strong function of column pressure. Finally, the regenerator is well below its flood limit and is not considered a constraint in this study.

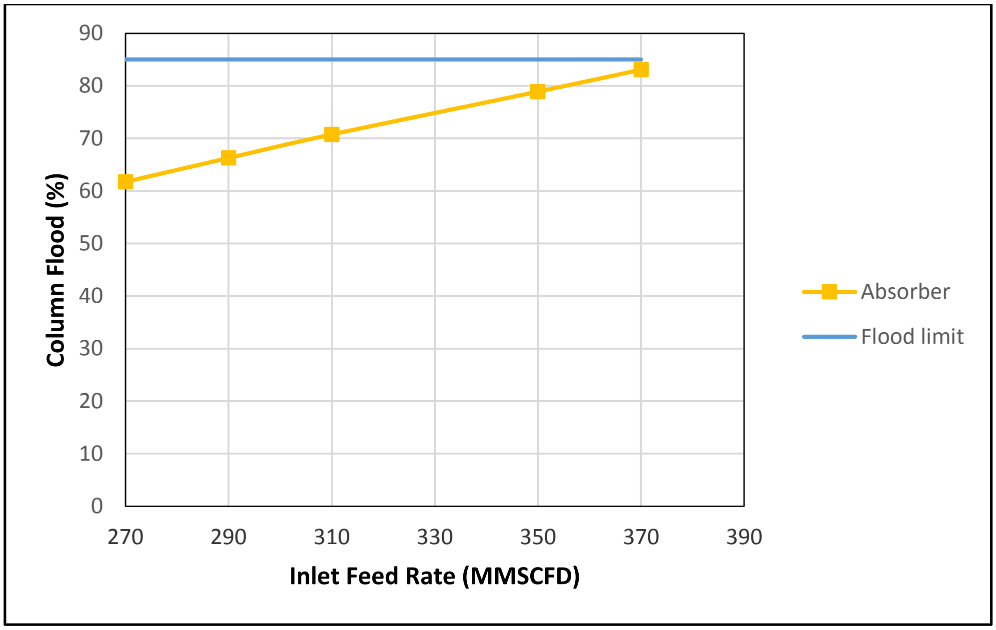

Figure 5: Amine Absorber Capacity

It should be note that the ultimate throughput assumes unlimited amine circulation and reboiler availability to meet plant constraints stated previously. The rest of the paper discusses the potential investment needed to achieve the ultimate throughput.

Circulation Rate

Scenarios are run with various inlet gas rates from 270 to 370 MMSCFD at maximum reboiler duty (65 MW) and maximum circulation rate (1200 m3/h). A graph of inlet feed rate versus sweet gas CO_2 concentration and rich amine loading is shown in Figure 6. As previously mentioned, the Amine Ratio is set to 0.04.

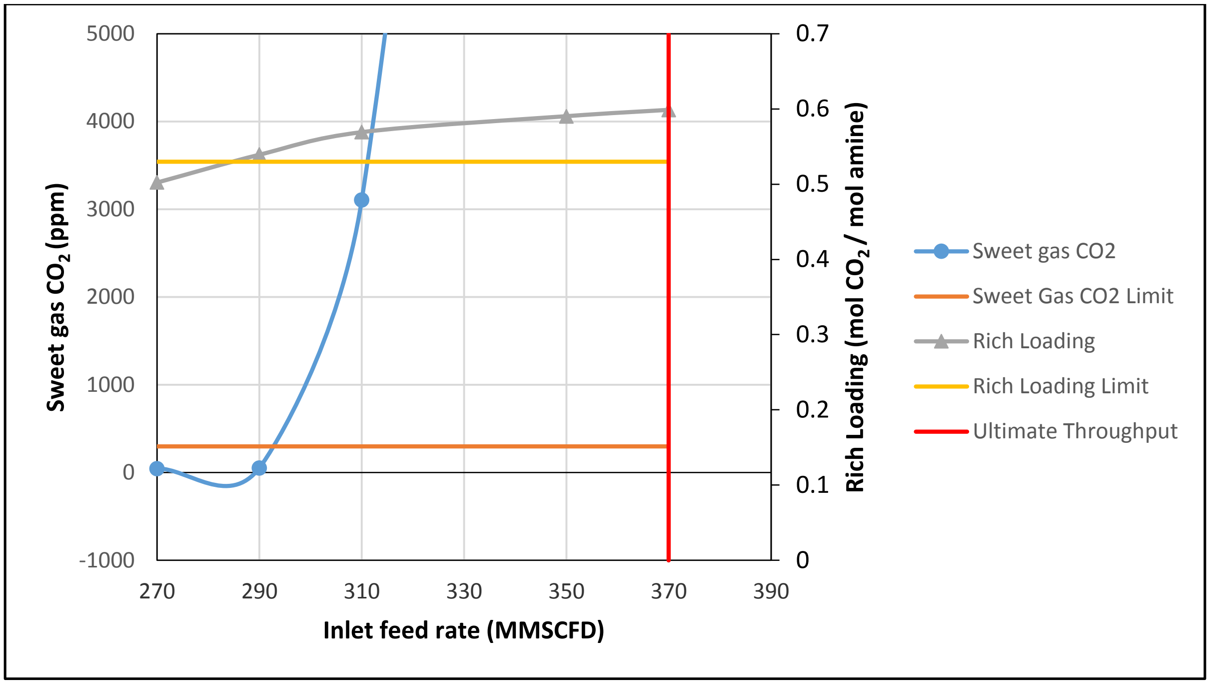

Figure 6: GSP#5 Absorber Performance at Maximum Pump Capacity

Figure 6 shows that the sweet gas CO_2 concentration increases quite rapidly for throughputs beyond 290 MMSCFD. At 300 MMSCFD, the CO_2 concentration in the sweet gas is well above the 300 ppm target. An inspection of the absorber's CO_2 Rich Approach shows it is rich-end pinched and slips CO_2 into the Sweet Gas as shown by the drastic CO_2 increased in Figure 6. The Sweet gas CO_2 limit shows that the column can handle a maximum of 293 MMSCFD. However, above 285 MMSCFD, rich loading increases beyond 0.53 for a fixed amine circulation. A side-by-side comparison of the Rich Loading and Sweet Gas CO_2 limit shows the Rich Loading as the limiting factor when amine circulation is limited. The reboiler vapor CO_2 is found to be well below 1% for all cases studied in figure 6. Therefore, the maximum achievable throughput with the current pump capacity is 285 MMSCFD. This is a 3.5% increase in inlet gas capacity without any equipment upgrades.

A second study is repeated with the amine circulation rate controlled in the simulation to always maintain a rich amine loading of 0.53. Cases here often exceed the previous amine rate upper limit of 1200 m3/hr. To achieve these conditions, additional amine circulation capacity is required. A graph of inlet feed rate versus sweet gas CO_2 concentration and reboiler vapor CO_2 concentration is shown below.

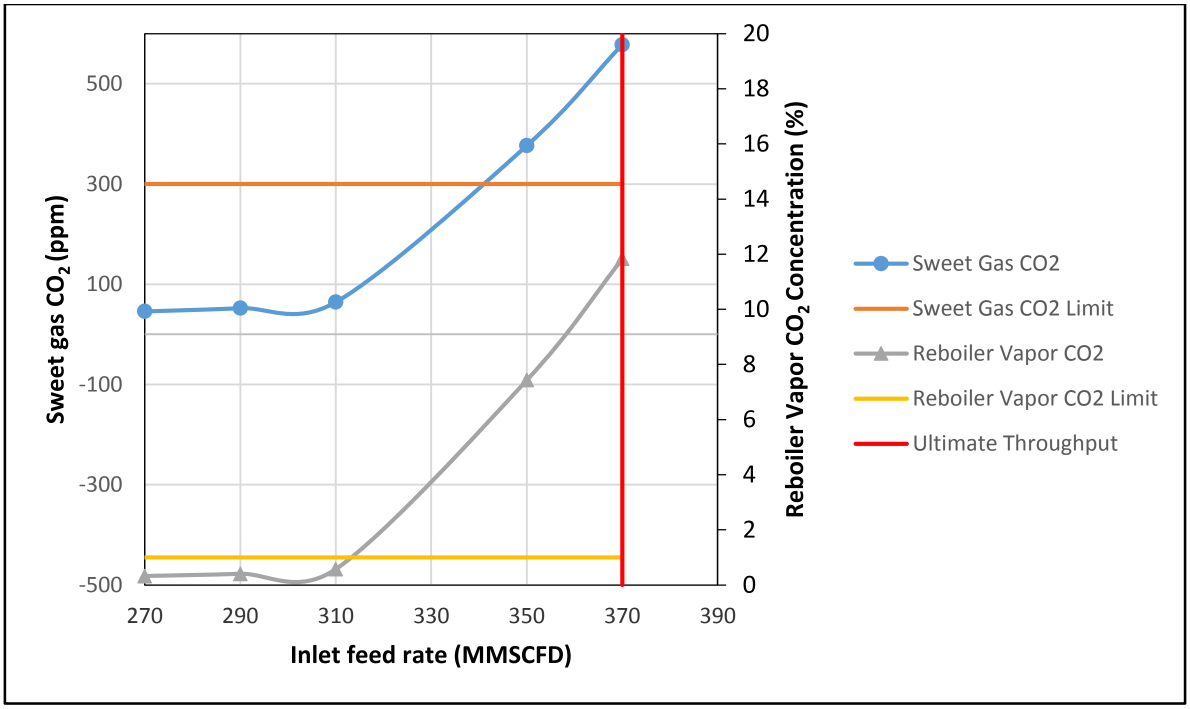

Figure 7: GSP#5 Amine Absorber Performance at 65 MW and 0.53 Rich Loading

Increasing the circulation rate resolves the absorber rich end pinch issue and permits higher throughput. Figure 7 shows the absorber and regenerator performance side-by-side for increasing feed rate. The graph shows how the absorber can 340 MMSCFD without exceeding the sweet gas CO_2 limit. However, above 315 MMSCFD, the system exceeds its reboiler vapor CO_2 concentration limit. With additional circulation capacity, the reboiler vapor CO_2 becomes the limiting factor. Results from figure 7 indicate that investing in an additional lean amine pump can raise potential throughput to 315 MMSCFD (8% increase from the previous maximum).*Reboiler Duty*

After increasing amine circulation capability, corrosion due to insufficient reboiler duty is the next limitation. In this section, the reboiler duty is increased to 75 MW. The amine circulation is controlled to meet 0.53 rich loading and the amine ratio is 0.04.

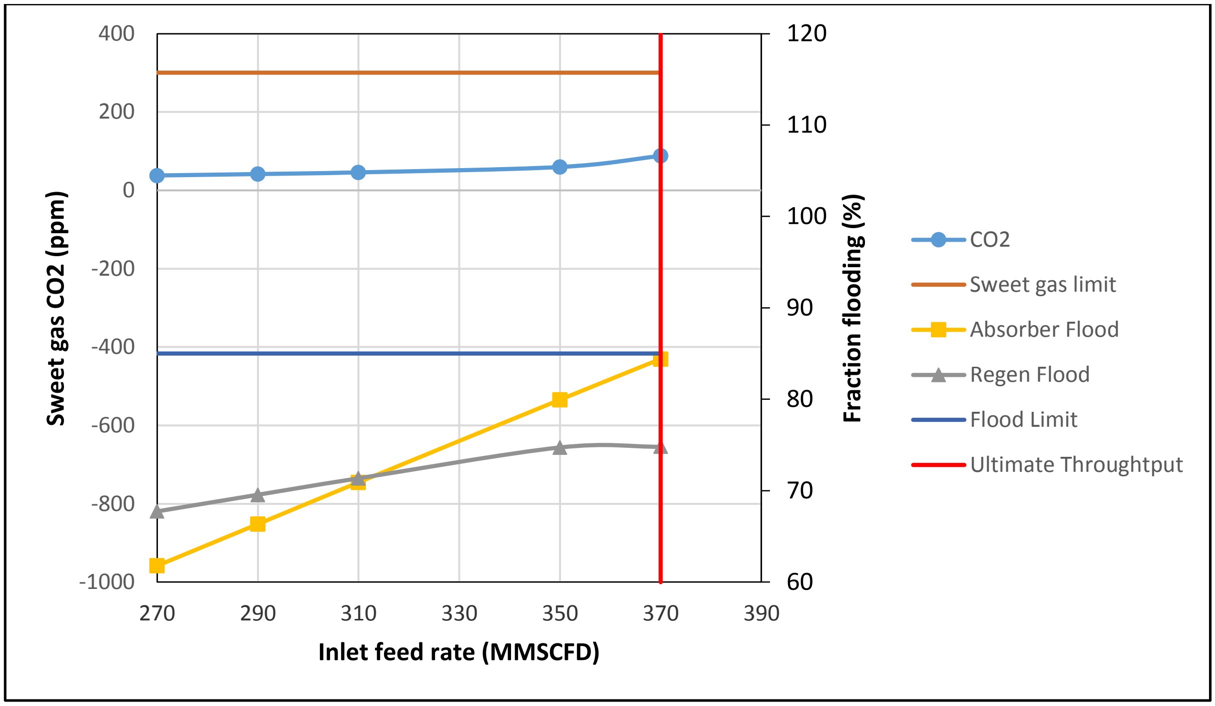

Figure 8: GSP#5 Amine Absorber Performance at 75 MW

Figure 8 shows drastic increase in the absorber performance while only slight increase in the regenerator vapor traffic. An additional 10 MW in duty allows the amine unit to meet its CO_2 sweet gas specification at the ultimate throughput (370 MMSCFD). Furthermore, the reboiler performance is drastically improved as seen below.

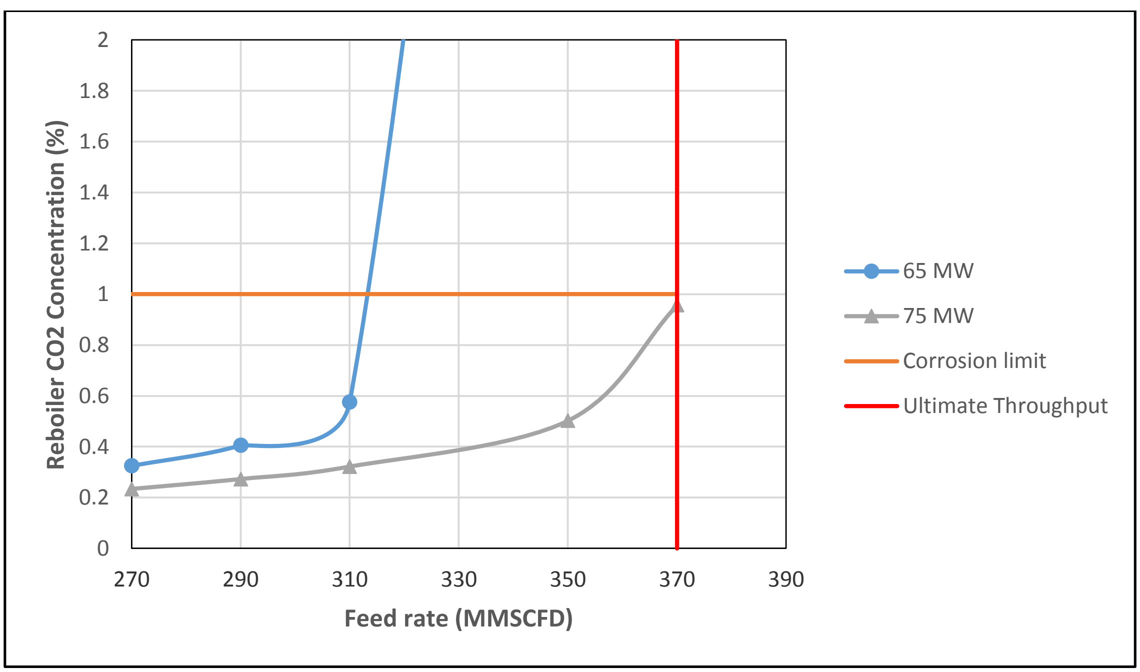

Figure 9: Effect of Reboiler Duty on Reboiler Vapor CO_2 Concentration

Results from Figure 9 show the plant reaches maximum potential gas feed of 370 MMSCFD (17% increase from previous maximum) with 75 MW reboiler duty and 1570 m3/h of amine circulation system.

Optimization Guidelines

The thorough investigation of plant operating parameters allowed us to identify two important limitations or bottlenecks: circulation rate and reboiler duty. Investing in additional equipment to overcome these limitations substantially improves plant performance.

Feed	Potential increase	Capacity increase	Investment
MMSCFD	**MMSCFD**	**%**	
275	0	0	None
285	10	+3.6%	None
315	40	+14.5%	Additional pump
370	95	+34.5%	Additional pump Additional heat exchange

Table 2: Plant performance guideline

The current amine unit can be optimized to achieve 285 MMSCFD (3.6% total increase) without additional investment. Investing in an additional pump raises capacity to 315 MMSCFD (14.5% total increase). Finally, investing in an additional reboiler allows the plant to achieve its ultimate capacity of 370 MMSCFD (34.5% total increase).

Conclusion

In an effort to maxmize plant profit, an overall analysis is performed on the CO_2 removal unit of GSP#5 to determine its ultimate throughput. The existing plant performance was evaluated and optimized to establish best practices at normal gas feed rate. Finally, amine circuation,reboiler duty, and absorber hydraulic bottlenecks were studied to determine ultimate throughput conditions. A step-by-step analysis of benefits versus each stage of investment can be carried out to determine the potential plant profit. A maximum increase of 35% in plant throughput can be achieved with investment in new equipment. It should be noted that this optimization method can be applied to other gas processing plants.

Furthermore, this step-by-step approach to gas treating facility optimization is fairly simple and straightforward. Generally, when feed rate is limited, the only optimization opportunity is energy consumption. Then when additional inlet gas becomes available, the hydraulic limits of one of the main columns can be determined early to place an upper bound on inlet gas capacity. After that, one can perform studies of the other manipulated variables at their initial maximum supply limits. As each variable becomes the limiting property, its limit is relaxed to show the additional throughput opportunities available until the next manipulated variable reaches a limit. Eventually, all manipulated variables which can be upgraded at reasonable cost are studied resulting in sets of optimum operating conditions at each manipulated variable limit.

This step-by-step optimization approach is applicable to many other absorber-driven gas processing units for determing capacity upgrade benefits and corresponding equipment upgrades that may be required.

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