Unlocking Additional Capacity in the Tail Gas Unit (TGTU)

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Abstract

The Tail Gas Treatment Unit (TGTU) is critical for ensuring regulatory compliance by removing H_2S from Sulfur Recovery Unit (SRU) tail gas in gas plants and refineries. Selective amines aim to optimize H_2S selectivity for specific applications.

This paper focuses on a TGTU at a refinery on the US Gulf Coast which faced TGTU performance limitations with direct impacts on its operational efficiency and the overall production of the facility.

The Gulf coast refinery initially designed and operated its two TGTU's with absorbers utilizing trays and a generic MDEA (methyl diethanolamine) solvent. These units functioned efficiently without any complications at the initial production rates. In an effort to enhance SRU production capacity, one of the changes that the refinery made was to replace the trays with packing in the absorbers. However, soon after install, the new packing material began exhibiting signs of fouling-related performance degradation issues leading to loss of theoretical stages in the absorber. The generic MDEA solution was inadequate for the new conditions and resulted in increased emissions from the SRU. As a result, the refinery faced restricted capacity in its TGTUs and in turn overall refinery production.

This paper demonstrates enhanced refinery performance and productivity through a solvent swap. By comparing the new amine technology BASF OASE® yellow with existing generic MDEA, it has been determined through process model simulations and through actual performance data that the new solvent can optimize performance, meet specifications, and improve efficiency, even in these scenarios where absorber towers are not functioning properly. By evaluating the results of this solvent swap, the study provides valuable insights and practical data that can inform future decision-making for more efficient SRU operations leading to increasing refinery throughout.

Introduction

The Sulfur Recovery facilities primarily serve the purpose of pollution control. Crude oil and natural gas streams often contain sulfur compounds, which, when combusted, result in the formation of sulfur dioxide (SO_2) and small amounts of sulfur trioxide (SO_3). These compounds then react with atmospheric moisture to create acids. Due to legal requirements in most jurisdictions, minimizing sulfur dioxide (SO_2) and other sulfur emissions into the environment is imperative. Therefore, sulfur recovery plays a crucial role in many hydrocarbon processing facilities. Non-compliance with local and national government regulations frequently leads to significant fines or the mandatory shutdown of the processing facility.

In sulfur recovery units (SRU) or Claus sections, the reaction equilibrium restricts the complete conversion of sulfur species in the feed gas to elemental sulfur. Typically, a SRU with two to three Claus reactors is only able to achieve 93 to 98% sulfur recovery efficiency. However, higher recoveries of 99.8% and above are achievable if remaining sulfur compounds in the SRU tail gas are either hydrogenated or converted by hydrolysis to H_2S, which is then consequently removed in a selective amine section of the Tail Gas Treating Unit (TGTU).

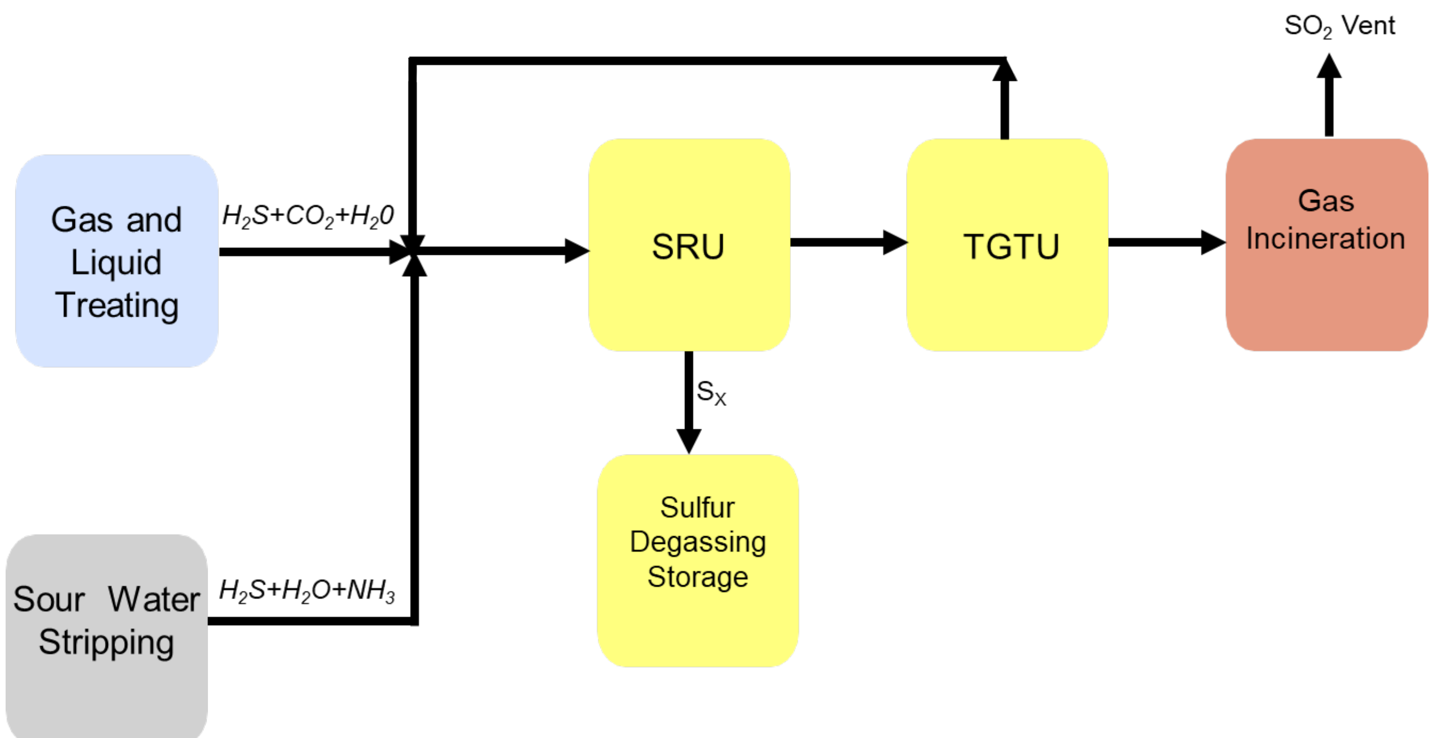


Figure 1. – Sulfur Recovery Facilities

The Sulfur Recovery Unit (SRU) processes acid gas from the gas and/or liquid treating unit(s) and Sour Water Stripper (SWS) unit(s), using the modified Claus process (Figure 1).; the selective amine removal of H_2S has become an important topic over the last two decades. Selective amine unit designs are tailored either on maximum or controlled H_2S selectivity depending on the application.

TGTU can significantly increase the complexity of the facility. They also increase both the OPEX (operating expenses) and CAPEX (capital expenses) of a sulfur recovery plant by 30-100%. Their main purpose is to meet the requirement of achieving higher recoveries and lower SO_2 emissions.

Selective Sulfur Treatment

The removal of H_2S in the presence of CO_2 is affected by various factors. Proper adjustment of these parameters plays a critical role in optimizing the amine unit throughout the various stages of design, commissioning, start-up, and operation.

Type of Amine

MDEA (methyl diethanolamine) a tertiary amine, has traditionally been a popular choice for H_2S selective applications in the industry. However, the implementation of more stringent SO_2 emission targets (Table 1) has necessitated the use of additional chemistry to improve the performance of MDEA and other amines. This is crucial in order to meet the stringent specifications for H_2S levels in treated gas. Besides performance-related characteristics, properties like volatility, stability, acid gas loading capacity, and commercial considerations also play a significant role in selecting the appropriate amine.

	Industry	**SO_2 Concentration**	**Basis**
World Bank	Refining[1]	50 ppmv (150 mg/Nm³)	dry 3% O_2
U.S.	Refining	250 ppmv (715 mg/Nm³)	dry, no excess air

1. International Fiannce Corporation - Wordl Bank Group "Enviromental, Health, and Safety Guideline for Petroleum Refining"www.ifc.org/ifcext/enviro.nsf/Content/Enviromental Guidelines, 2007

Table 1 Maximum Emission Requirements

Lean Amine Temperature.

The H_2S selectivity of generic amine solvent rapidly deteriorates once the lean amine temperature exceeds 120°F (>45°C). Ideal amine solvent should be able to maintain the H_2S selectivity even in high ambient temperature environments and subsequent high lean amine temperatures. This would eliminate the need for expensive chiller installations or operation for solvent cooling, resulting in a reliable, robust and flexible design suitable for various operational scenarios.

Selective treatment with the amine-based solvents generally takes advantage of the rapid reaction of H_2S compared to the kinetically hindered reaction of CO_2. CO_2 first must react with water to form carbonic acid before the solvent can absorb the CO_2. Thus, tertiary amines such as MDEA are often used for selective applications as they are not able to form carbamates

The following reactions of tertiary amines take place in aqueous solutions:

Reaction of water and amine (fast)

$R1R2R3N + H_2O \rightleftarrows R1R2R3NH^+ + OH^-$

$2\ H_2O \rightleftarrows H_3O^+ + OH^-$

H_2S Reaction (fast)

$H_2S + H_2O \rightleftarrows HS^- + H_3O+$

CO_2 Reactions (overall reaction: slow):

$CO_2 + 2H_2O \rightleftarrows HCO_3^- + H_3O+$ (slow)

$HCO_3^- + OH^- \rightleftarrows H_2O + CO_3^{2-}$ (fast)

The co-absorption of CO_2 and its impact on H_2S selectivity in this reaction system is greatly influenced by the reaction conditions. Higher pressure and temperature, along with a higher CO_2/H_2S ratio in the feed gas, tend to increase CO_2 co-absorption and decrease H_2S selectivity, particularly in geographic regions where ambient temperature is high.

Mass Transfer

In addition to lean amine temperature and feed gas pressure (partial acid gas pressure), several other factors significantly impact the overall mass transfer of individual components from the gas phase into the liquid phase in the absorption process. These factors include the lean amine loading, design of absorber internals, column height, and the liquid-to-gas ratio (solvent-to-feed gas ratio).

While the mass transfer of H_2S is primarily driven by the gas phase, the reaction kinetics of CO_2 are mainly influenced by resistance in the liquid phase. Absorber height and available surface area play a crucial role in facilitating vapor-liquid contact and directly affects the selectivity of the reaction. Moreover, the liquid-to-gas ratio not only influences mass transfer but also impacts the temperature profile within the absorber, which also affects reaction kinetics.

Solvent Selection

Selecting the appropriate amine technology for the TGTU is essential in ensuring the economic and environmental viability of these projects. The benefits of optimizing capital investments, reducing operating costs and enhancing the performance of the TGTU are realized by utilizing highly H_2S selective solvents. Higher H_2S selectivity over MDEA allows for reduced amine circulation rate, greater tolerance for higher lean amine temperature, decreased recycling of CO_2 to the sulfur recovery unit (SRU) and reduced reboiler duty.

OASE® yellow, specifically designed for selective H_2S removal, offers capabilities in both high-pressure applications, such as natural gas treatment, and low-pressure scenarios like acid gas enrichment (AGE) or tail gas treatment (TGTU). Its proprietary blend system enhances H_2S capture capacity, enabling lower H_2S specifications to meet stricter SO_2 emission targets as above outlined. A key benefit is that it maintains H_2S selectivity at high lean amine temperatures (>130°F or +50°C), making designs without an expensive chiller unit possible. Additionally, OASE® yellow exhibits low reboiler duty in the regenerator, resulting in reduced energy demands.

On the contrary, generic amines would require significantly higher overall operating costs from both higher amine flow and lower lean amine temperatures to achieve the required H_2S selectivity.

BASF utilizes a proprietary simulation software, OASE Connect, that which incorporates both thermodynamic and kinetic modeling of the process.   This software helps us obtain precise results.

Gulf Coast Refinery

The Refinery is situated on the US Gulf Coast and has the capacity to produce over 1,000 tonnes of sulfur per day. It operates two tail gas treatment units (TGTU), each capable of a maximum circulation rate of 900 gallons per minute (GPM). The residual tail gas from these units typically contains 1.1 - 1.5% H_2S. The maximum rate capacity of the Quench Column outlet tail gas flow is 1,900 MSCFH (thousands of standard cubic feet per hour) through each amine contactor tower.

The two Tail Gas Treating Units (TGTU #1 and TGTU #2) were originally designed with tray contactors and utilized standard Methyldiethanolamine (MDEA); initial models showed that MDEA met the Refinery SRU demands. Later, the refinery opted to increase its capacity by replacing the trays in the absorbers with structured packing material. This modification led to performance degradation issues caused by fouling in the new packing, reducing available and HETP making the generic MDEA solution less effective. Consequently, the refinery faced limitations in the treating capacity of its TGTUs, which had significant consequences for the performance of the Sulfur Recovery Unit (SRU) and resulted in cutback of refinery production.

Initial Results

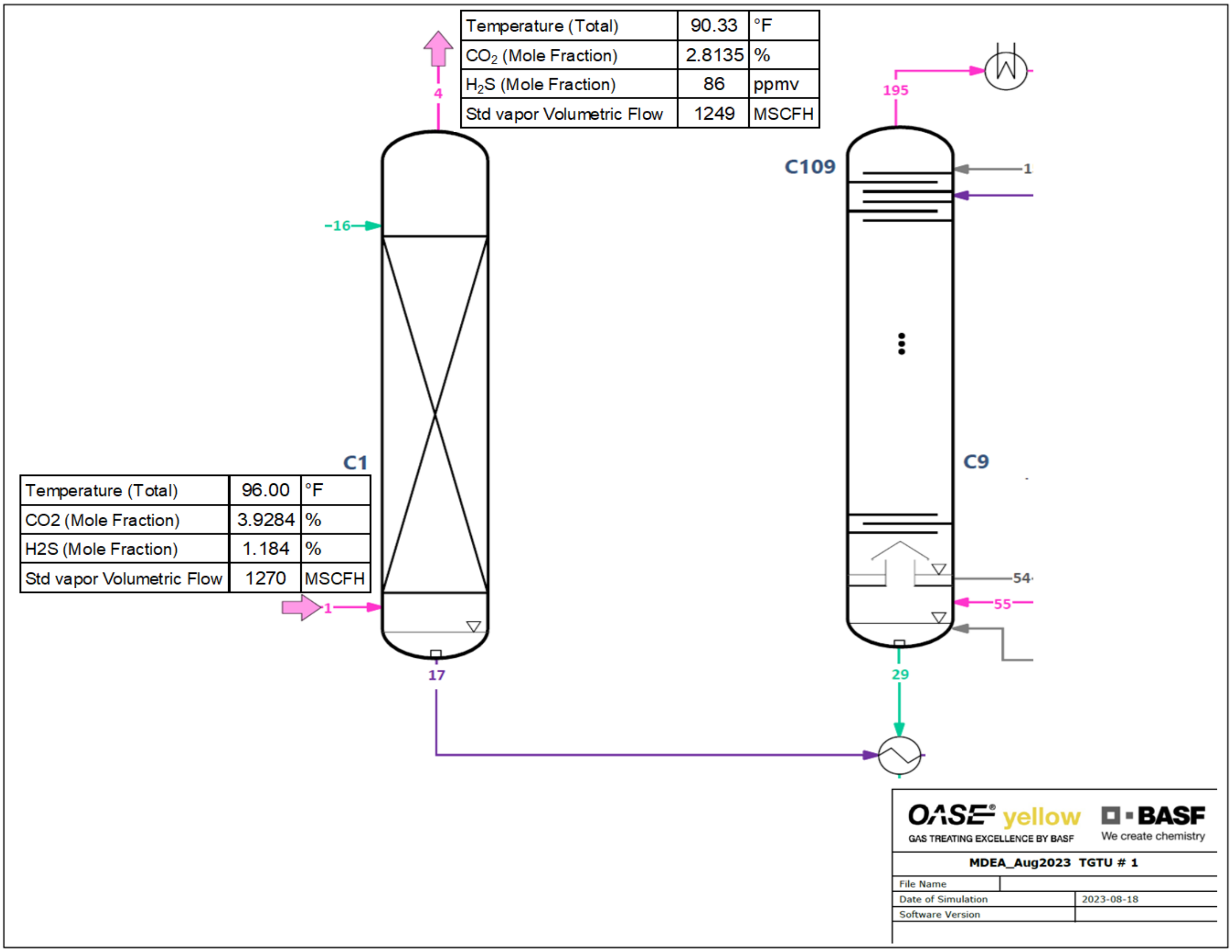
In August 2023, the Refinery reached out to the BASF Gas Treatment Team with a short-term objective of finding a drop-in solution to reduce the H_2S content in the treated tail gas. The Refinery placed a strong emphasis on identifying an online solution that could be implemented without causing any interruptions to plant. They wanted to avoid the expenses associated with shutdowns and decommissioning of TGTUs. Their main objective was to quickly recover their production rates and return to smooth operation.

BASF conducted process model simulations and explored various potential solutions, including a solvent conversion to further decrease the H_2S content in the treated gas and/or reduce reboiler duty requirements. The option to implement a swap "on the fly" approach was provided enabling a seamless transition to the new OASE® yellow technology. This approach involves adding the formulation package to the current amine solvent, allowing the conversion to take place while the TGTU continues fully operational. This ensures that production remains uninterrupted throughout the conversion process.

The primary objective of this paper is to assess the challenges encountered by the refinery and to discuss the key parameters for these selective designs followed by a real operational start-up data from swap to OASE® yellow solvent.

The following are the outcomes of the preliminary process model simulations conducted after our visit to the plant and gathering data from both TGTUs.

TGTU # 1: Process Model with MDEA

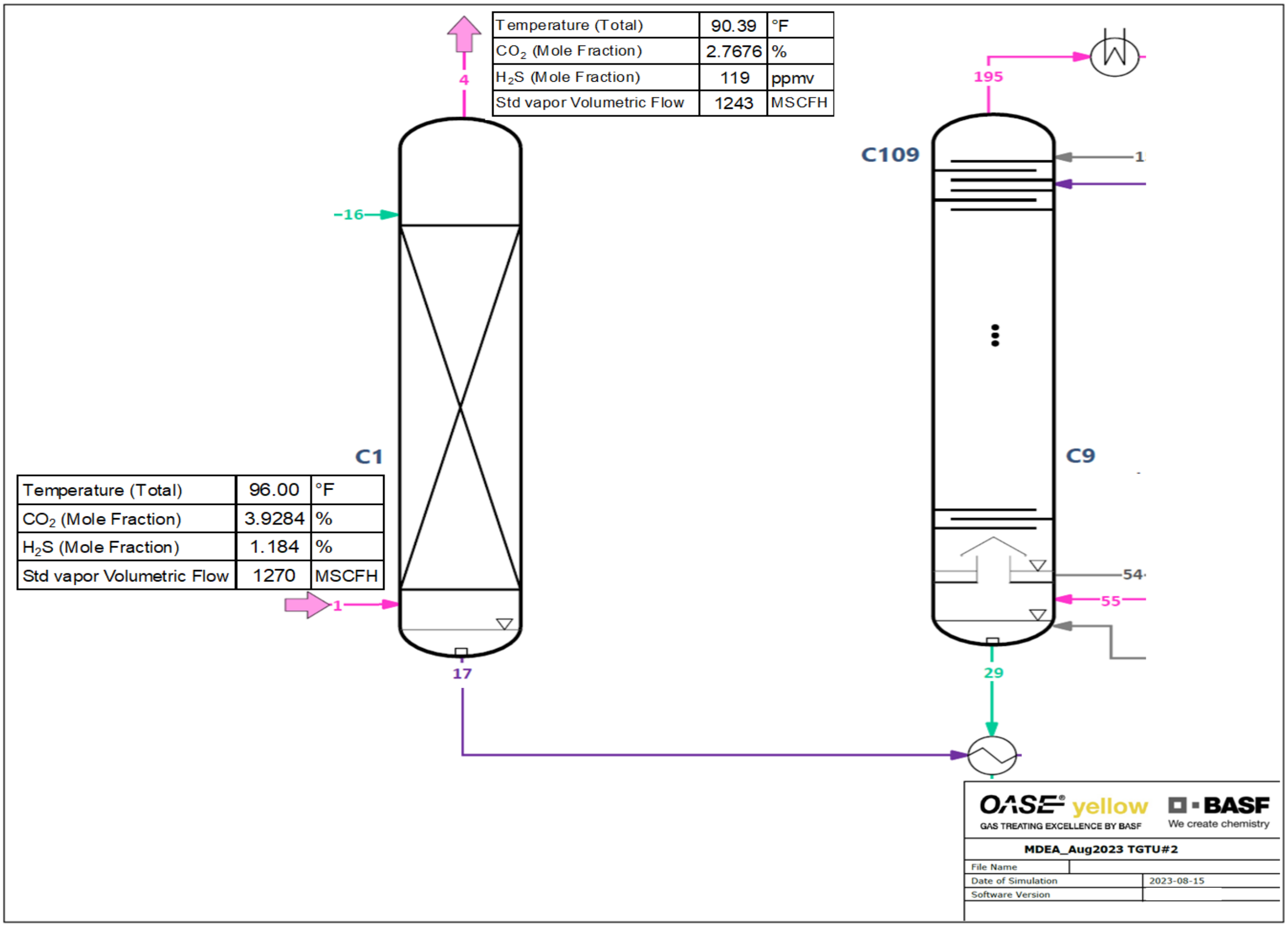


Gas streams

Stream		1 feed gas	4 treated gas
Mole composition (dry)			
CO2	mole%	3.9284	2.8135
H2S	mole%	1.1840	0.0086
N2	mole%	90.8270	92.3569
COS	mole%	3.0000E-04	3.0469E-04
AR	mole%	1.0032	1.0201
H2	mole%	3.0528	3.1041
CO	mole%	0.0043	0.0044
Properties			
Molar flow (dry)	SCF/hr	1.2700E+06	1.2489E+06
Temperature	°F	96.00	90.33
Pressure	psig	3.0	2.8

Figure 2. TGTU # 1 MDEA Flowsheet

TGTU # 2: Process Model with MDEA



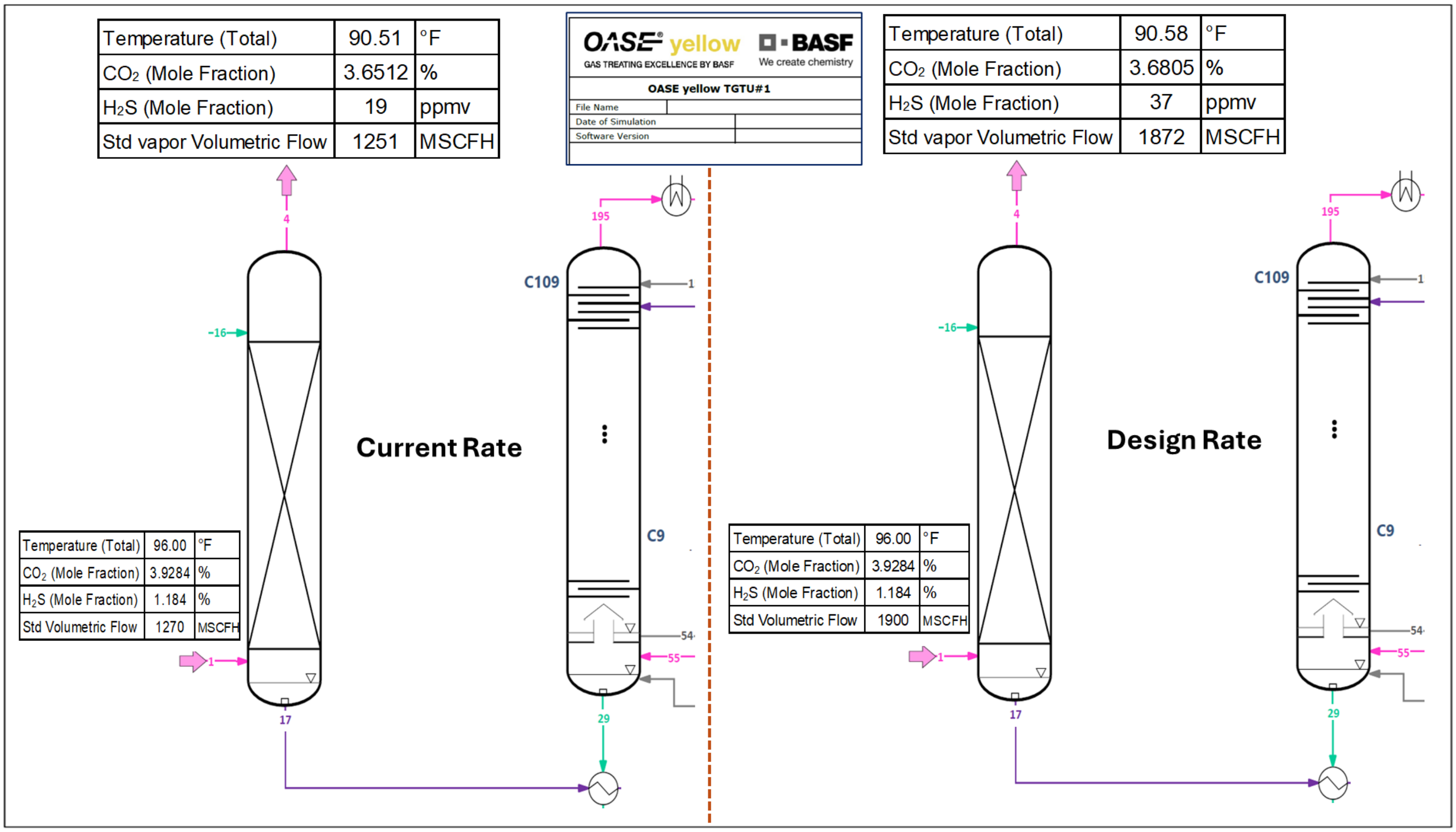
Gas streams

Stream		1 feed gas	4 treated gas
Mole composition (dry)			
CO2	mole%	3.9284	2.7676
H2S	mole%	1.1840	0.0119
N2	mole%	90.8270	93.0601
COS	mole%	3.0000E-04	3.0699E-04
AR	mole%	1.0032	1.0278
H2	mole%	3.0528	3.1278
CO	mole%	0.0043	0.0044
Properties			
Molar flow (dry)	SCF/hr	1.2700E+06	1.2436E+06
Temperature	°F	96.00	90.39
Pressure	psig	3.0	2.8

Figure 3. TGTU# 2 MDEA Flowsheet

The treated gas in both TGTU plants had reached a point where the rates needed to be reduced due to an increase in H_2S levels. In particular, TGTU #2 exhibited a significant rise in H_2S levels when the rates exceeded 1,300 MSCFH (68% of design capacity).

TGTU # 1: Process Model with OASE® yellow



Gas streams (Current Rate)

Stream		1 feed gas	4 treated gas
Mole composition (dry)			
CO2	mole%	3.9284	3.6512
H2S	mole%	1.1840	0.0019
N2	mole%	90.8270	92.2236
COS	mole%	3.0000E-04	3.0424E-04
AR	mole%	1.0032	1.0186
H2	mole%	3.0528	3.0997
CO	mole%	0.0043	0.0044
Properties			
Molar flow (dry)	SCF/hr	1.2700E+06	1.2507E+06
Temperature	°F	100.00	90.51
Pressure	psig	3.0	2.8

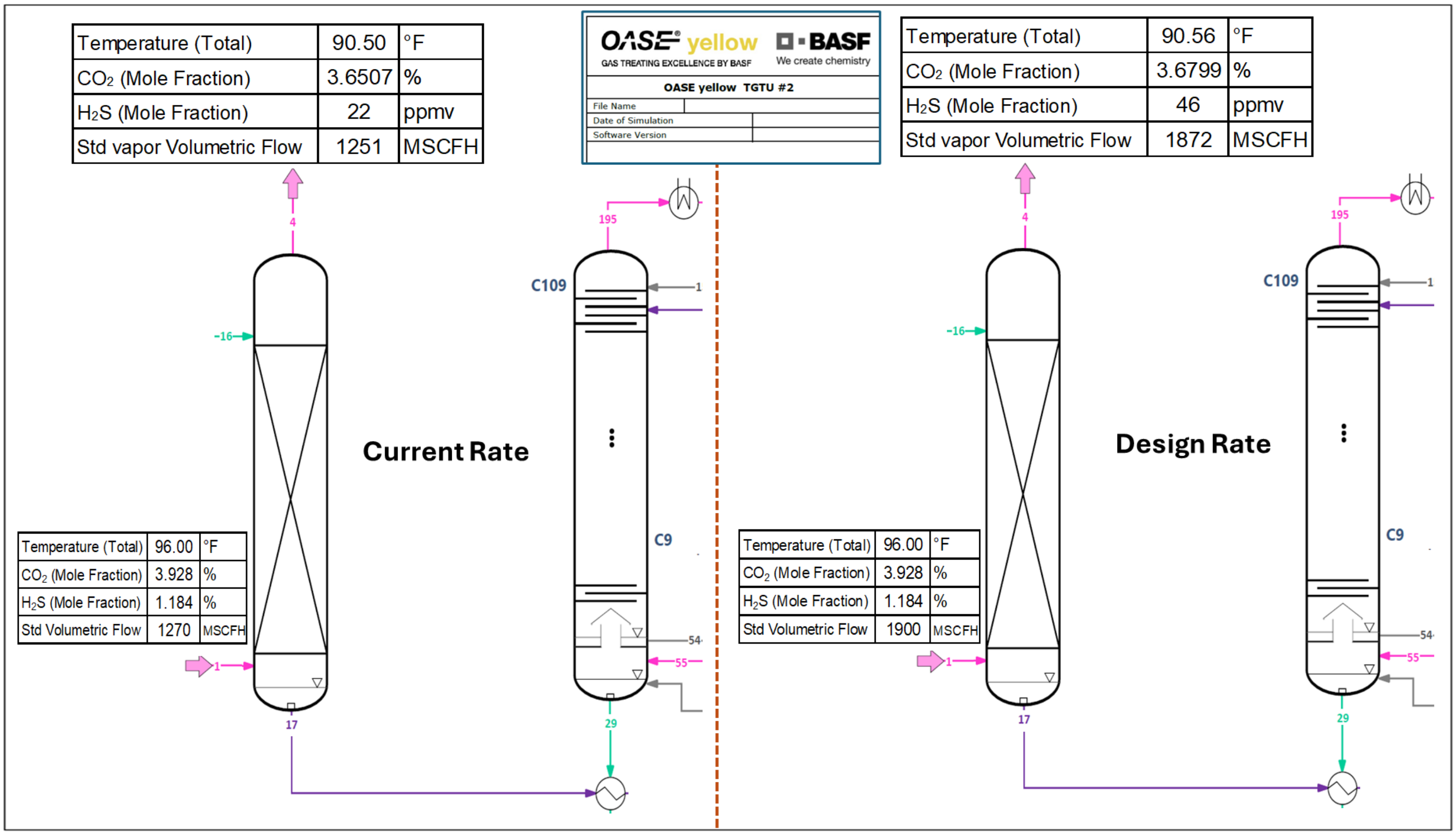
Gas streams (Design Rate)

Stream		1 feed gas	4 treated gas
Mole composition (dry)			
CO2	mole%	3.9284	3.6805
H2S	mole%	1.1840	0.0037
N2	mole%	90.8270	92.1961
COS	mole%	3.0000E-04	3.0428E-04
AR	mole%	1.0032	1.0183
H2	mole%	3.0528	3.0988
CO	mole%	0.0043	0.0044
Properties			
Molar flow (dry)	SCF/hr	1.9000E+06	1.8717E+06
Temperature	°F	90.00	90.58
Pressure	psig	3.0	2.8

Figure 4. TGTU #1 OASE® yellow results

Multiple runs were conducted on TGTU #1 to assess its performance with the new solvent technology OASE® yellow, and Figure 4 displays results from these models at both current and design rates. The expected outcome for TGTU#1 is a reduction in H_2S levels in the treated tail gas to below 20 ppmv at the current rates, and below 40 ppmv at the design flowrate.

TGTU # 2: Process Model with OASE® yellow



Gas streams

Stream		1 feed gas	4 treated gas
Mole composition (dry)			
CO2	mole%	3.9284	3.6507
H2S	mole%	1.1840	0.0022
N2	mole%	90.8270	92.1852
COS	mole%	3.0000E-04	3.0414E-04
AR	mole%	1.0032	1.0182
H2	mole%	3.0528	3.0984
CO	mole%	0.0043	0.0044
Properties			
Molar flow (dry)	SCF/hr	1.2700E+06	1.2512E+06
Temperature	°F	100.00	90.50
Pressure	psig	3.0	2.8

Gas streams

Stream		1 feed gas	4 treated gas
Mole composition (dry)			
CO2	mole%	3.9284	3.6799
H2S	mole%	1.1840	0.0046
N2	mole%	90.8270	92.1118
COS	mole%	3.0000E-04	3.0401E-04
AR	mole%	1.0032	1.0174
H2	mole%	3.0528	3.0959
CO	mole%	0.0043	0.0044
Properties			
Molar flow (dry)	SCF/hr	1.9000E+06	1.8724E+06
Temperature	°F	100.00	90.56
Pressure	psig	3.0	2.8

Figure 5. TGTU #2 OASE® yellow results

Based on the simulations above, OASE® yellow is expected to reduce H_2S levels in treated tail gas from 119 ppmv to less than 25 ppmv at a flowrate of 1,270 MSCFH. Additionally, at the maximum flowrate of 1,900 MSCFH, the solvent will maintain H_2S levels below 50 ppmv

TGTU #2 Conversion Process

As a result, the Refinery accepted the findings and made the decision to convert TGTU #2 first. The outcome of the conversion process will be evaluated once the tail gas conversion is fully implemented. The conversion process for TGTU #2 to OASE® yellow started on October 2023, with the final addition completed a few days later. Figure 5 shows the results achieved during the conversion process.

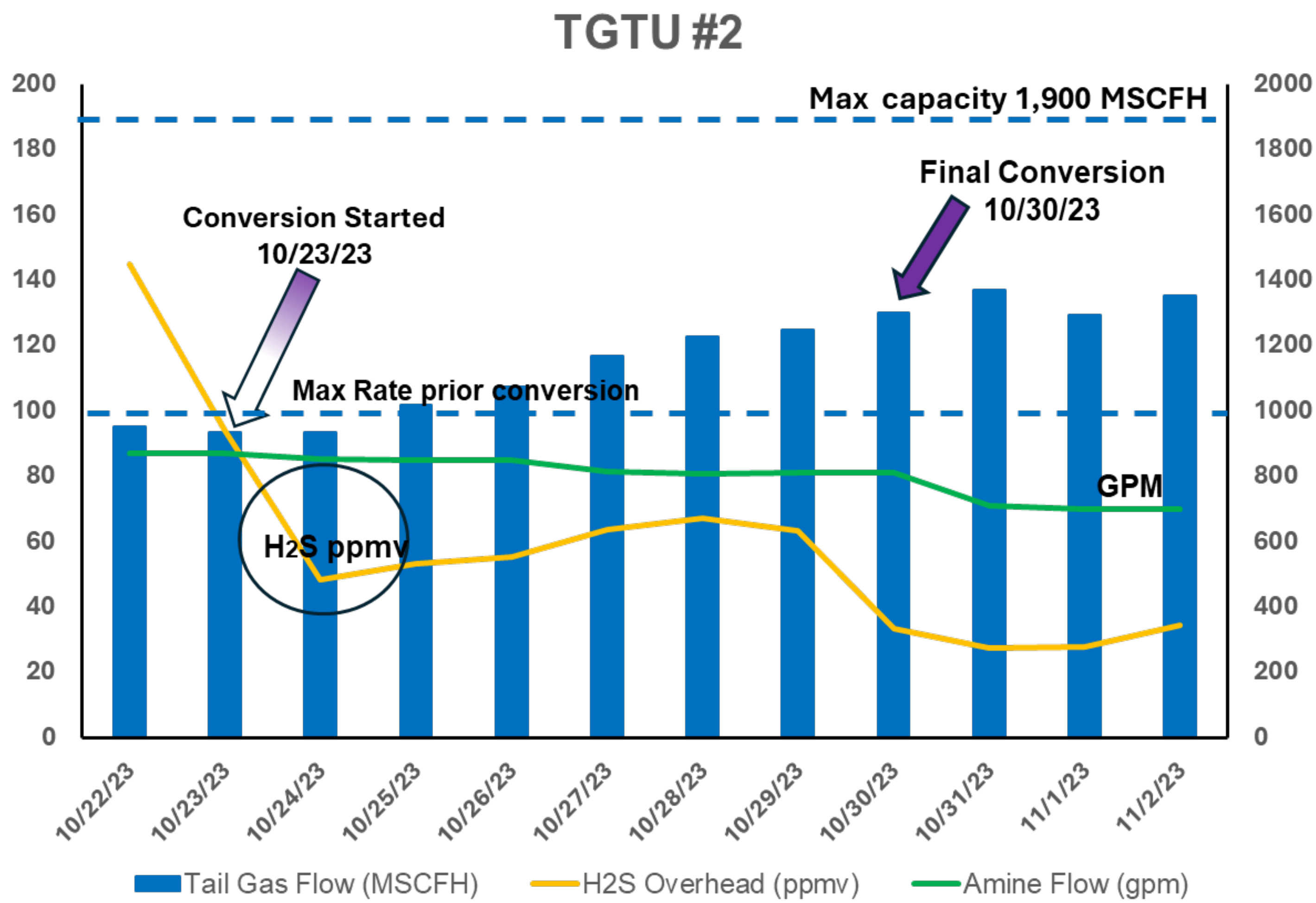


Figure 6. TGTU #2 OASE® yellow Conversion results

During the conversion process, the H_2S concentration in the treated acid gas significantly decreased from 140 ppmv to below 50 ppmv just after 24 hours, reaching a level below 30 ppmv once the plant was fully converted. Additionally, the tail gas flow was increased from 950MSCFH to 1,300MSCFH. Moreover, the solvent circulation rate was reduced from 880GPM to 700GPM. (a 20% reduction in amine circulation rate, therefore, a 20% in energy usage)

The following graph illustrates the sulfur load progression of TGTU#2 throughout the conversion process. Initially, the sulfur load was kept below 450 LTPD (long tons per day). However, after the conversion, the sulfur load in TGTU increased to a maximum of 600 LTPD, reflecting a 35% increase.

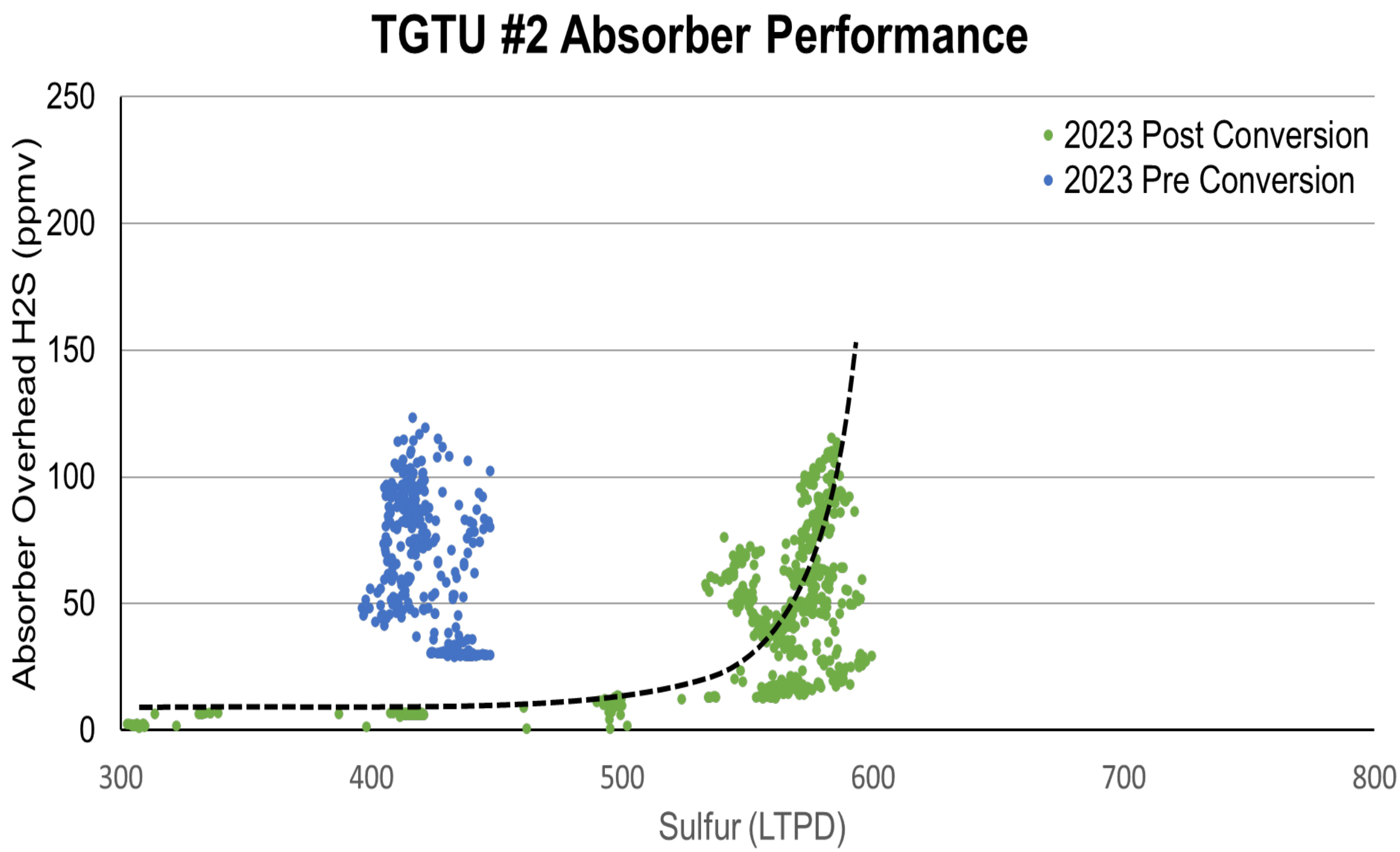


Figure 7. TGTU #2 Sulfur Load

The Refinery made the decision to proceed with the conversion of TGTU#1 after positive outcome from the conversion on TGTU#2, which will be further discussed in subsequent sections of this paper.

TGTU # 2 Performance After Conversion

The conversion to TGTU #2 was successfully completed in October 2023, allowing the plant to increase Tail gas rates by 30-40% and H_2S levels in the treated gas below 30ppmv, as depicted in Figure 8., in February 2024, the refinery decided to bring down TGTU#2 for repair work. During this maintenance activity, the internals in the absorber were completely replaced. This decision was made based on a previous tower scan that had identified the need to change the packing in both TGTUs. To ensure optimal performance of the unit, the refinery prioritized the replacement of the packing in the TGTU with the most severe fouling.

After the packing replacement, the refinery optimized the amine circulation in TGTU#2, leading to a reduction of over 30% or 1/3 less compared to when the plant was using MDEA.

Currently the TGTU#2 is processing 1,400 MSCFH with amine circulation set at 600GPM and the H_2S in treated tail gas is ~ 20ppmv

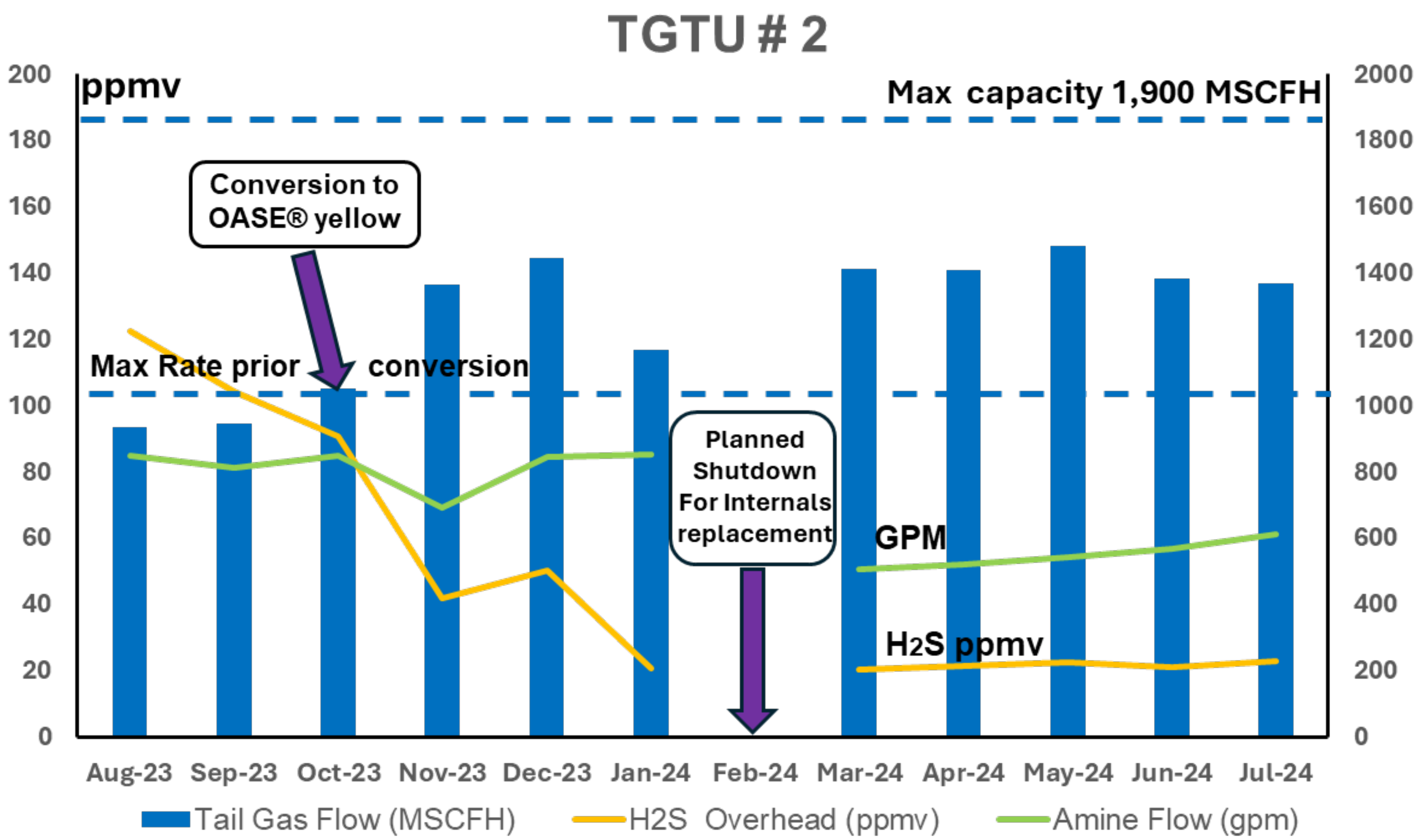


Figure 8. TGTU #2 Results Aug 23 – Jul 24

TGTU #1 Conversion Process

As per operational feedback, it was observed that the absorber TGTU#1 had relatively less fouled packing material. The conversion of TGTU #1 to OASE® yellow started in late December 2023 and was completed in early January 2024. The results achieved during the conversion process are below illustrated.

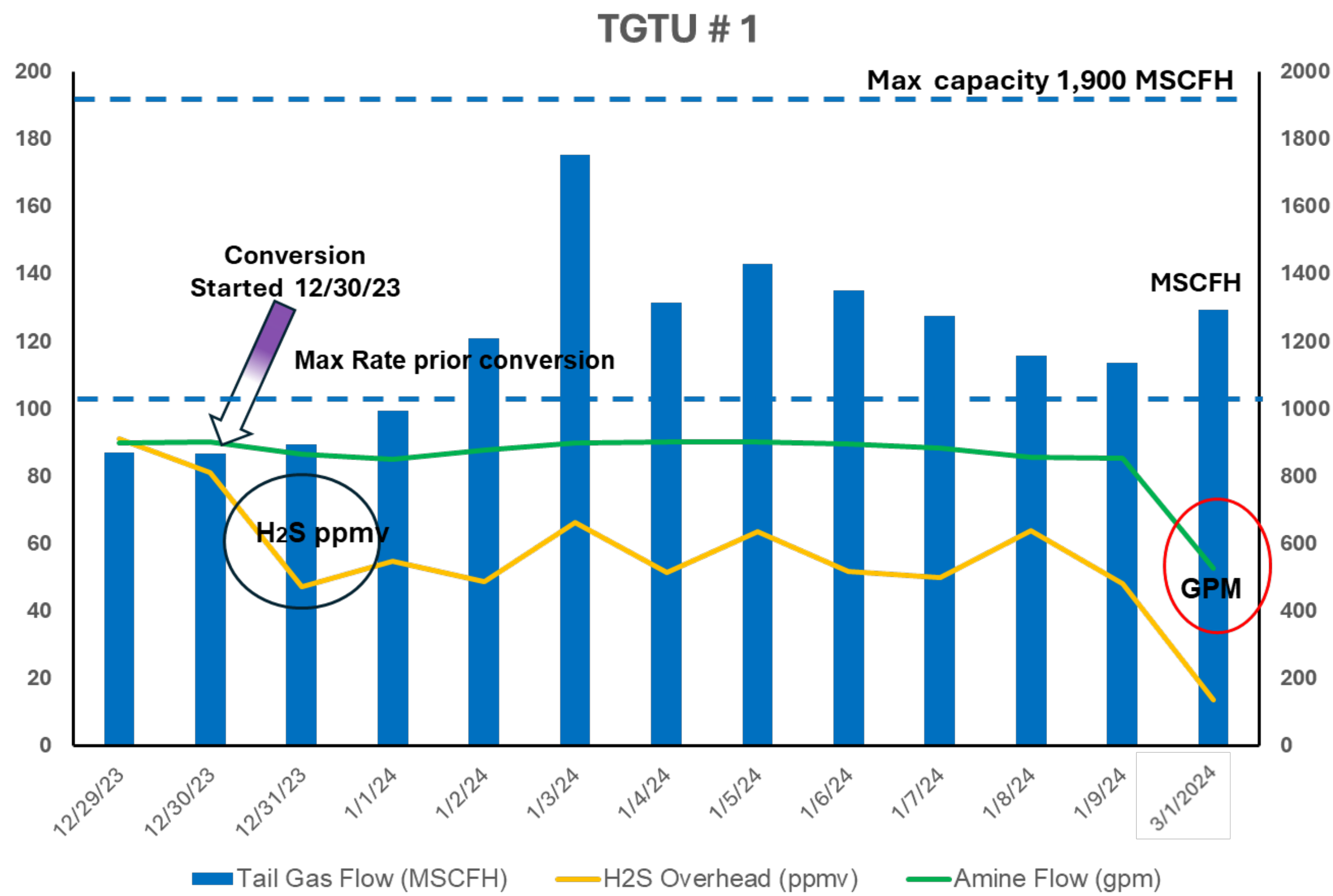


Figure 9. TGTU #1 OASE® yellow Conversion results

Throughout the conversion process of TGTU #1, the concentration of H_2S in the treated acid gas decreased from 90ppmv to below 50ppmv. During this conversion, the plant maintained a circulation range of 850-900 GPM until late February, while the tail gas flow rate was increased to an average of 1,300 MSCFH. In March, the refinery began reducing amine circulation while keeping the tail gas rate constant, resulting in amine circulation being set close to 600 GPM (a 30% reduction in circulation rate and energy use). By this time, the treated tail gas had reached levels below 30ppmv

The performance of TGTU#1 during the conversion process is illustrated in the graph below. Initially, the sulfur load was just under 500 LTPD. However, after switching to OASE® yellow, the new maximum sulfur load in TGTU#1 increased to 750 LTPD; a 50% increase over the prior level.

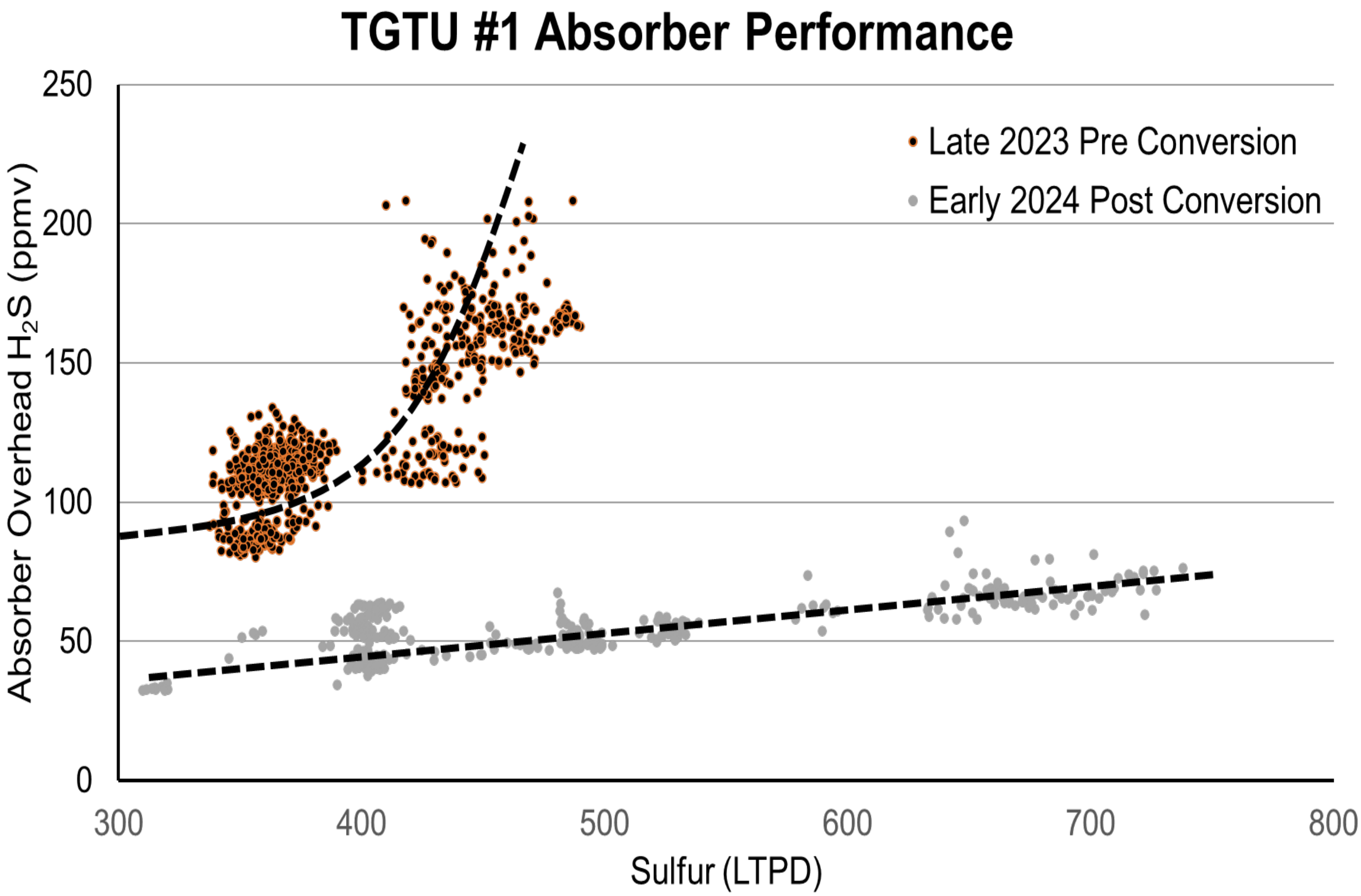


Figure 10. TGTU #1 Sulfur Load

TGTU # 1 Performance After Conversion

The conversion process for TGTU #1 began in late December 2023 and final addition was completed in the first week of January 2024. During this time, the plant maintained the same feed rates and amine circulation rate of 800 GPM in preparation for the shutdown of TGTU #2.

The H_2S levels in the treated gas showed significant improvement, decreasing from over 100 ppmv to below 60 ppmv. This downward trend continued in the following weeks, with H_2S levels dropping below 30 ppmv. By March 2024, the H_2S levels stabilized below 20 ppmv

Following the completion of the internal changeout on TGTU #2, the refinery optimized the amine circulation rate in TGTU#1, adjusting it to just under 600 GPM. This further contributed to the stabilization of H_2S levels below 20 ppmv.

Figure 9 provides a visual representation of TGTU #1's performance prior to the solvent swap and subsequent changeout.

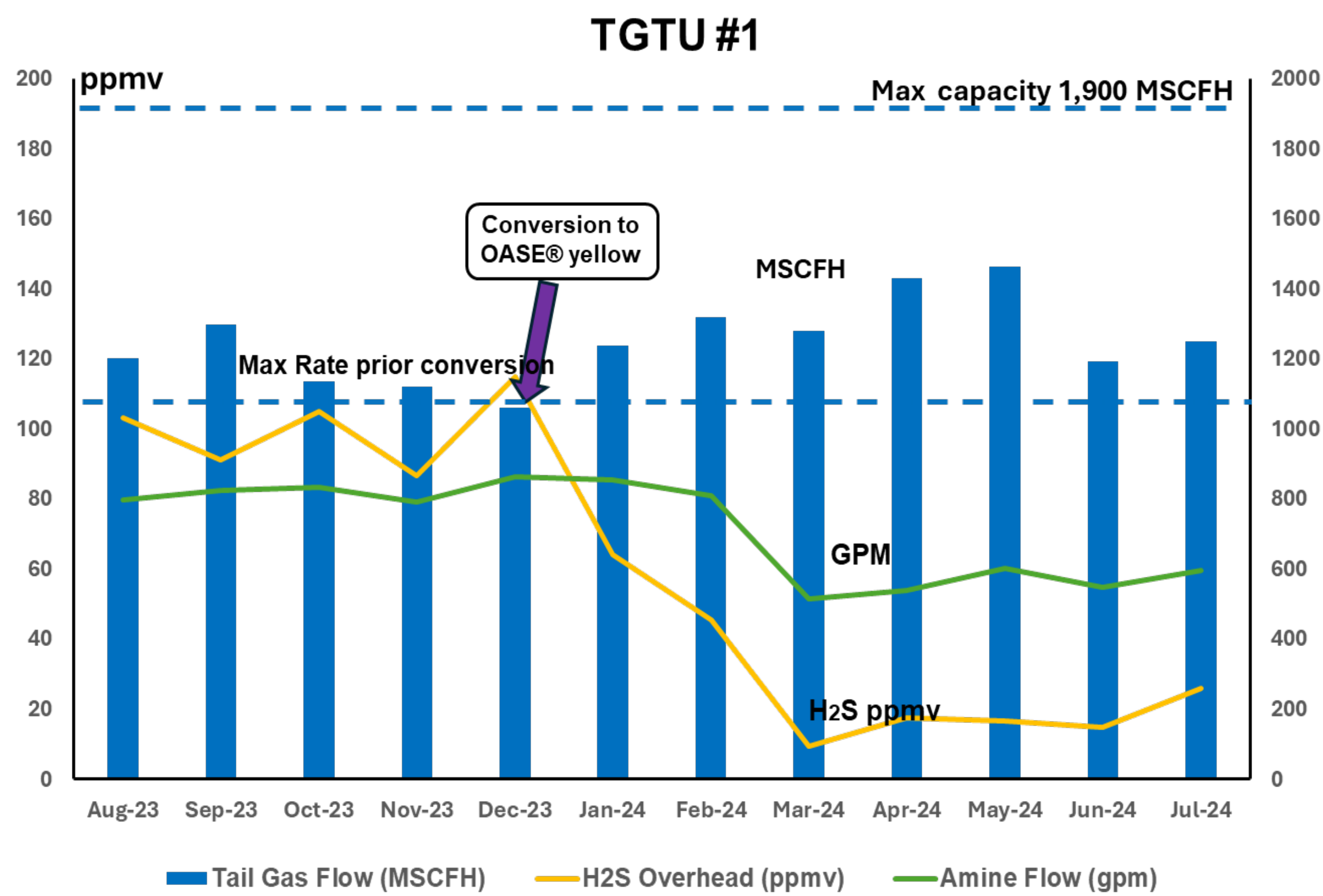


Figure 11. TGTU #1 Results Aug 23 – Jul 24

TGTUs Performance After Conversion

The Gulf coast refinery has successfully converted its TGTUs to OASE® yellow and has been operating with the new amine solvent since October 2023 for TGTU#2 and January 2024 for TGTU#1. Figure 12 below shows a comparison of the sulfur loads between the two TGTUs in the year 2023 (before conversion) and the year 2024 (after conversion).

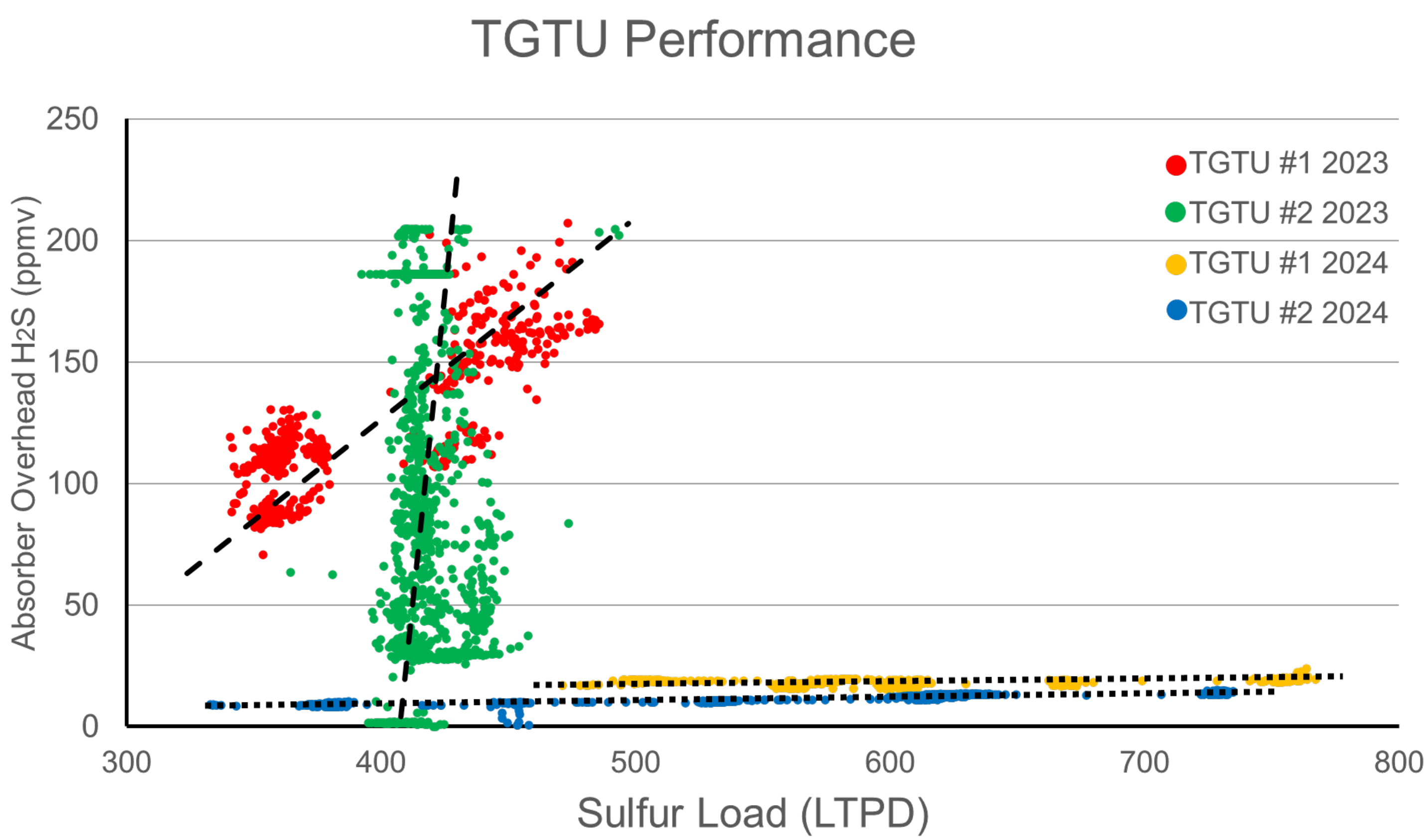


Figure 12. TGTUs Sulfur Load 2023 vs 2024

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Conclusions:

In recent decades, the selective amine removal of H_2S has emerged as a significant topic. Advanced H_2S selective tail gas removal can be accomplished using various types of amines, accompanied by carefully designed measures to guarantee reliable operation. Modern plants must possess a high degree of flexibility to accommodate changes in turndown rates, feed gas specifications, and operating conditions. Furthermore, they must meet stringent requirements for very low levels of sulphur in the treated gas, in the range of parts per million by volume (ppmv).

The Enhanced H_2S selective treatment provided by OASE® yellow technology offers several advantages. It allows refineries to increase production even if they are absorption limited, without the need for equipment additions or modifications. Additionally, it can restore capacity without causing any shutdowns. This technology optimizes equipment usage, resulting in substantial energy and circulation rate savings, ultimately reducing operating expenses (OPEX). Furthermore, these technologies enable projects to achieve both operational flexibility and robust performance, particularly in warm climates.

The Gulf Coast Refinery faced challenges with fouling in its Tail Gas Treatment Units (TGTUs) after switching from trays to packing material. To address this issue, BASF offered the utilization of OASE® yellow solvent for both TGTUs. The conversion process for both TGTUs involved a Swap “On the Fly” process not requiring an outage from generic MDEA and was accomplished smoothly. The conversion process has resulted in positive outcomes, as both TGTUs have exhibited improved performance and Refinery was able to increase back its production rates.

TGTU #1 has successfully achieved a 25% reduction in amine circulation, leading to at least 25% decrease in energy demand. Additionally, the H_2S levels have decreased from over 100 ppmv to 20 ppmv. Furthermore, the conversion to OASE® yellow has led to an increased sulfur load of up to 40%.

TGTU #2, on the other hand, has experienced a 40% increase in tail gas flow rate and achieved H_2S levels below 25 ppmv. This has been accompanied by a 33% reduction in energy demand due to the reduction in amine circulation. Moreover, the sulfur load was able to be raised up to 50% after the conversion process.

Additional analysis will be conducted to accurately determine the total energy savings achieved. However, it is evident that both TGTUs possess the capability to optimize their capacity in accordance with the refinery's requirements.

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