

Renewed Challenges in Sulfur Processing

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ABSTRACT

The Rodeo Renewed Project fully converted the Phillips 66 San Francisco Refinery from petroleum to renewable feedstocks to generate low carbon-intensity transportation fuels. A crude-based diesel hydrotreating unit began to process renewable feedstocks in 2021. In 2024, as part of the complete refinery conversion, two hydrocracking units were modified to become renewable diesel processing units through hydrodeoxygenation (HDO) isomerization reactions. The Rodeo Renewable Energy Complex now processes up to 50,000 bpd of renewable feedstocks such as animal fats, vegetable oils, and greases. With the transition, sulfur production decreased from 210 Long Tons per day (LTPD) to 2.5 LTPD. Acid gas composition changed from a rich 90+% H_2S typical refinery feed to mostly CO_2 with nominally 6% H_2S .

To suit the new sulfur processing requirements, a new sulfur processing unit was constructed to be the primary sulfur treatment unit. Of the legacy sulfur plants, two Claus+Stretford (BSRP) systems were shut down while the remaining Claus/Amine-based tail gas unit (TGU) ran at 98.5% turndown. Primary amine solvent was swapped from digylcolamine (DGA) to methyldiethanolamine (MDEA) to maximize CO_2 slip. The continued presence of sour water stripper (SWS) gas from the hydrotreating units complicated the processing of the lean acid gas.

This paper will overview the challenges that were overcome during the transition to renewable fuels and some of the relevant design changes from the project. Neither the new sulfur treatment unit nor the existing MDEA-based SRU/TGU were available for use during the renewable conversion of the San Francisco Refinery, while the former diesel hydrotreating unit continued to process vegetable oils to produce renewable diesel. Compounding matters, the two Claus/BSRP units were near end-of-run. An alternative processing strategy was utilized to treat the waste gas from the existing renewable diesel unit while construction and commissioning of the new sulfur treatment unit and HDO units were being finished. Additional learnings were realized around the quality of the sulfur produced under extremely lean acid gas at the Claus/MDEA-based TGU.

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INTRODUCTION

The San Francisco Refinery in Rodeo, California previously operated three sulfur processing units; two Claus/BSRP plants that were originally constructed in 1954 and a Claus/MDEA-based TGU that was commissioned in 2009. In the years leading up to the conversion to renewable feedstocks, the San Francisco Refinery operated the Claus/MDEA-based TGU (U235) with 80-100% of the sulfur load and the larger of the two Claus/BSRP (U238) with the remainder or on hot-standby (HSB). The second BSRP (U236) was scheduled to shut-down due to expiring state boiler permits in October 2023. It had previously been idled for over a year due to suspected plugged TGU catalyst and the foreknowledge of the renewable fuels conversion. To manage the thiosulfate accumulation in U238, the Stretford was routinely purged to the U236 balance tank and evaporated there.

To execute the refinery conversion, the two Hydrocracker turnarounds were staggered into separate outages. Since U238 could not process the total sulfur load of one Hydrocracker still processing petroleum feedstock, U236 was started-up to run with U238 during routine maintenance on U235 and the construction of a new sulfur treatment unit (U237). Spent Stretford solution that was concentrated in thiosulfates was disposed of and fresh Vanadium and ADA were added.

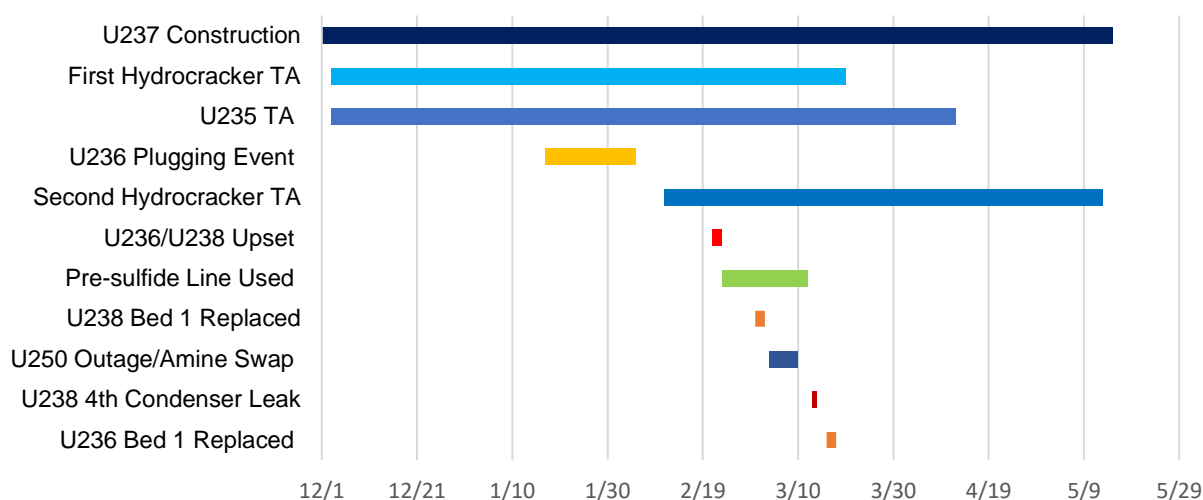
The U235 turnaround commenced in December 2023 with the shutdown of the heavy gas oil hydrocracker (Figure 1). In renewables service, U235 was modified to process H_2S and NH_3 by co-firing with either natural gas or hydrogen at 98.5% turndown when U237 is not in service. The turnaround scope included replacing the first Claus converter catalyst with titanium oxide catalyst, general maintenance, and adding co-firing controls.

In their remaining months of life, each BSRP plant underwent frequent sulfur washes on the first Claus converter to reduce dP. Several were executed during the first Hydrocracker turnaround, one of which plugged the first U236 auxiliary burner with sulfur. Due to this, U238 continued to operate as the primary sulfur plant through the shutdown of the Coker and second Hydrocracker in February. Afterward the only contributor to the refinery sulfur load was the former diesel hydrotreating unit (U250), which continued to process pretreated vegetable oils to produce renewable diesel. The renewable diesel unit was scheduled for a 1-week shutdown to perform electrical system work and to execute the primary amine swap from DGA to MDEA.

Two weeks before the U250 outage, an upset occurred which plugged both U236 and U238 first converter beds. This report will detail processing the amine acid gas via the pre-sulfide line, which kept the U250 outage on schedule and allowed it to start-up again before U235 and U237 were ready for start-up. The plugged first converter beds were replaced with spherical ceramic inert support, and later condenser leaks left each unit with one conversion stage. Additional learnings were realized from the co-processing of an extremely lean acid gas feed at 98.5% turndown.

Figure 1

Rodeo Renewed Turnaround Sequence of Events



END OF THE FOSSIL FUEL ERA

The two BSRP units were near end-of-run conditions at the start of the turnaround. Frequent sulfur washes were required, and thiosulfates were maintained at their concentration limits in the Stretford solutions. To best establish the impaired state of U236 in its final months, it is important to detail the upset that occurred in January 2024 in the middle of the first hydrocracker turnaround.

Both BSRP units have natural gas fired reheaters and underwent routine sulfur washes to remove soot on the first converter. Inline burner damage was suspected prior to the outage because of the frequency of washes. The upcoming shutdown of the second Hydrocracker would significantly reduce the refinery sulfur load and H₂S content of the feed gas, so a final sulfur wash was planned before the loss of H₂S-rich amine acid gas feed. During the U236 sulfur wash, the first auxiliary burner filled with sulfur. The second condenser leg had plugged, and sulfur filled the first reactor bed, the elevated piping between the first auxiliary and reactor, and the air lines to the burner. After noticing the pressure profile across the unit, operations attempted to light off the auxiliary burner and found sulfur in the ignitor port, Figure 2.

Figure 2

Auxiliary Burner Sulfur Plugging - U236 1/17/24 Sulfur Wash

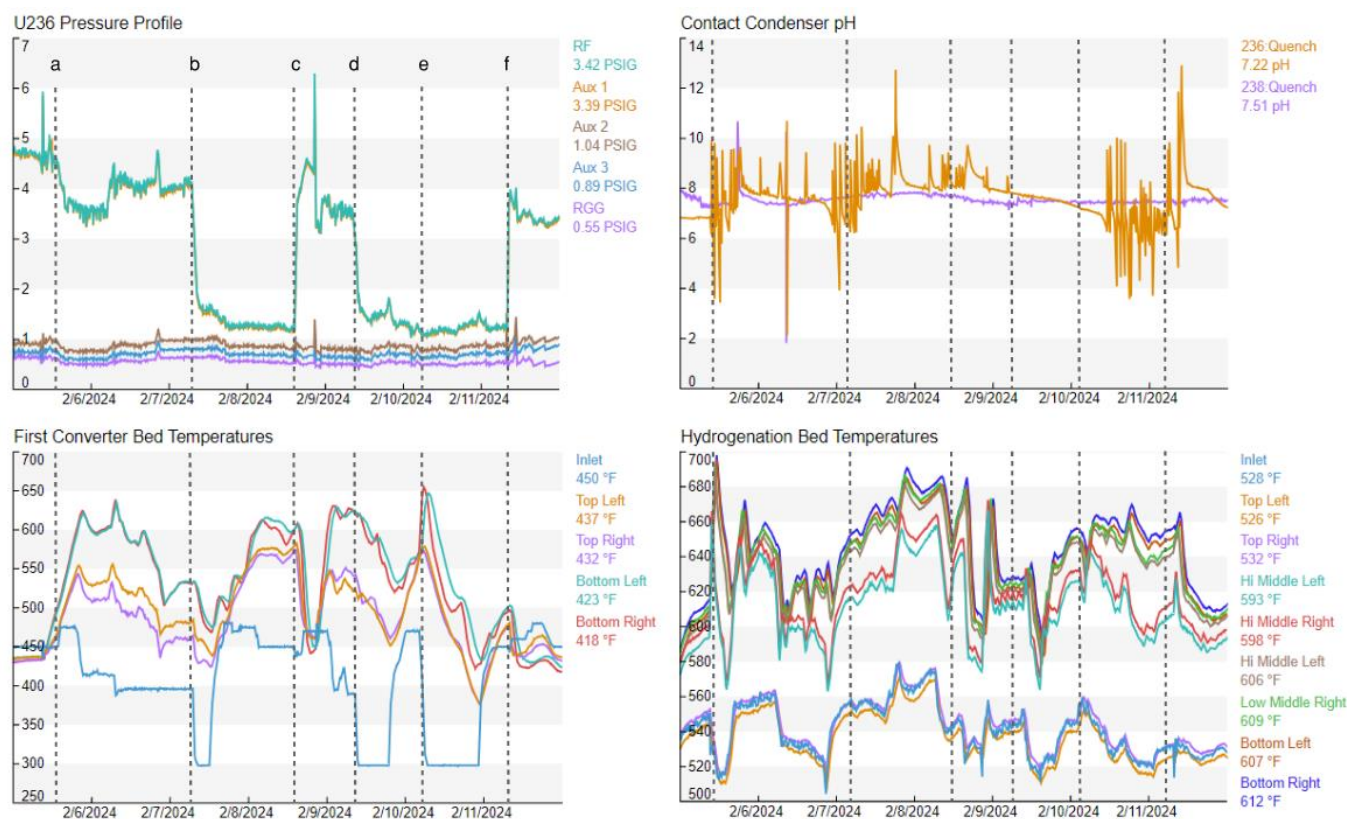


Troubleshooting involved draining and putting steam on the first and second condenser shells and steaming out the air line. It was only after heat-wrapping the air line to 650 °F that air flow was established, and the auxiliary burner was re-lit. The unit was then placed on hot-standby (HSB) but the pressure drop was worse than pre-sulfur wash dP at 3.7 psi. Gas was reintroduced to U236 to prepare for another sulfur wash. While starting up the unit, there was abnormally high tail gas reactor dT and the quench column pH would drop at air:AG ratios as low as 1.3:1 as compared to the normal air:AG ratio of 2:1. The first Claus bed also had abnormally high temperature rise, and the inlet temperature was reduced to 415 °F to avoid hitting the SOL of 650 °F. Reducing the reaction furnace air:AG ratios to 1.1:1 stabilized the tail gas unit but the front-end reaction furnace temperatures would drop to below 1700 °F due to too little air, which indicated that excess O₂ was being supplied by the first auxiliary burner.

After the first converter bed had cooled and the TGU was considered stable, another sulfur wash was initiated and the dP dropped to 0.36 psi. Due to low AAG rates between both U236 and U238, U236 was put back on hot standby. Once again, the dP across the first bed rapidly climbed. A final sulfur wash lowered the dP, but after pulling acid gas the dP immediately returned. The second Hydrocracker shutdown was scheduled for the following week, so U236 was left with suspected plugging across the first bed and the first auxiliary burner stayed shut down.

Figure 3

U236 Unit Conditions Before and After Sulfur Washes



- ^a Amine acid gas introduced.
- ^b First sulfur wash after burner unplugging incident.
- ^c U236 put on HSB.
- ^d Second (final) sulfur wash completed.
- ^e First aux shutdown due to high temperatures in first converter bed.
- ^f U236 put on HSB prior to shutdown of the second Hydrocracker.

First auxiliary burner damage was the most likely cause of both the catalyst plugging and off-ratio operation. Several light off attempts while the burner was plugged with sulfur could have damaged the burner ring. As of writing this paper the unit has yet to be opened to perform an autopsy.

Poor mixing in the first auxiliary burner sending excess O₂ and/or NG to the first Claus bed would cause soot formation and additional pressure drop. Excess O₂ would contribute to caustic consumption and high tail gas reactor dT. Compensating by lowering the air:gas ratio in the reaction furnace led to worse conversion and additional load on the tail gas unit. Contaminant destruction in the reaction furnace below 2150 °F is known to be questionable, likely complicating matters further.

The high observed activity in the bottom of the first bed was attributed to a combination of soot and sulfation and poor conversion in the reaction furnace. Sulfation is caused by excess O₂ whereby SO₂ builds

a layer on the catalyst as a thiosulfate and in the presence of excess O_2 converts SO_2 to sulfate, taking away an active site and shifting the reaction down the bed to available active sites. Additionally, reduced conversion in the reaction furnace would shift excess reactants to the first Claus bed and increase the DT and apparent activity of the catalyst. Reduced activity on the second and third beds due to running out of either reactant (H_2S or SO_2) was also observed. The sudden plugging off the bed after pulling acid gas was attributed to channeling in the catalyst. To operate without the first auxiliary reheat burner, the first condenser was drained and 50# steam was added to the shell side.

STRETFORD SURVIVAL MODE

While U236 and U238 were scheduled to be permanently shut down, and were being operated at significant turndown, they still played a critical role in processing acid gases from U250 and wastewater produced from unit chemical cleanings during the turnaround. After the January upset, U236 was considered operational only as needed and U238 processed 200-400 MSCFD of amine acid gas (AAG) and 300 MSCFD of sour water acid gas (SWAG) (83% turndown).

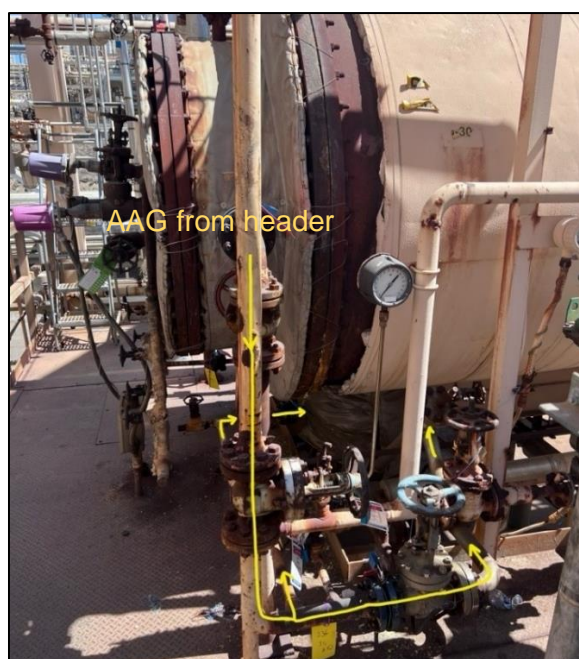
In late February a second upset occurred; the sequence of events was as follows:

- 1st Night Shift:
 - Operations shut down D-911 sour water stripper due to an external leak in the overhead condenser.
 - A surge of SWAG flow was experienced during the shutdown. The U238 reaction temperature dropped rapidly from 2400 °F to 1700 °F in <7 minutes and the front-end pressure rose to 8 psig.
 - Acid gas was shifted from U238 to U236. The temperature in the U236 hydrogenation reactor rapidly elevated and reached 1300 °F briefly.
 - The U236 reaction furnace (RF), all auxiliaries and reducing gas generator (RGG) were shut down and N_2 was added to cool the tail gas reactor.
- 1st Day Shift:
 - Acid gas was processed to the rear of U238 reaction furnace with only the sufficient air required to burn NG at a 10:1 ratio. Any additional air would cause the RF pressure to exceed the high-pressure trip of 9 psig.
 - Attempts were made to re-light U236, but the pressure would exceed the trip setpoint.
 - The U238 main air blower struggled to provide sufficient air due to the backpressure from the first converter. The first and second U238 condensers were drained and steamed to attempt to unplug any blockage.
 - All sour water strippers were shutdown.
- 2nd Night Shift:
 - Both sulfur plants could not process acid gas without exceeding the high-pressure trip, so AAG was routed to the flare gas recovery system. After several hours refinery fuel gas (RFG) sulfur exceeded 163 ppm H_2S . To ensure compliance with SO_2 emissions limits at the steam power plant gas turbines, the turbines were switched to natural gas and excess RFG was flared for 6hr 47mins. 21 lb of SO_2 was emitted, which did not exceed the 500 lb SO_2 reportable threshold.

- U236 temperatures stabilized, and the RF, 2nd and 3rd auxiliary reheat burners, and RGG were re-lit.
- 2nd Day Shift:
 - The refinery started processing acid gas via pre-sulfide line at U236 directly into the TGU to stop flaring. An attempt was made to split the flow between 236/238 pre-sulfide lines, but the line at U238 was plugged.
 - The pressure at U236 reaction furnace continued to climb towards the trip setpoint. The reaction furnace was shut down as well as the 2nd and 3rd auxiliaries. Only the RGG remained lit.

Figure 4

U236 Pre-sulfide Line



The last-ditch solution of processing acid gas via the pre-sulfide line worked. The unit was able to operate within its emissions limits (250 ppm SO₂, rolling 12-hour average) relying on the Stretford unit alone. However, this was not a long-term solution for the remainder of the outage. Thiosulfate concentrations were at typical concentrations for end-of-run conditions, the oxidizer mixers would frequently trip, and air would be lost to one or more cells. Additionally, the pressure was building slowly across the U236 tail gas reactor and only 400 MMSCFD of amine acid gas could be processed through the 2" pre-sulfide line.

The following week a soot test was completed at the inlet to the tail gas reactor. A 10-second filter test revealed significant amounts of soot at an air:gas ratio of 9:1 on the RGG, and there was also 0.4-0.5% O₂ in the flue gas. At a ratio of 9.5:1 no soot was formed, but the temperature at the inlet to the TGU reactor exceeded 650 °F with the NG valves nearly closed. During the following night shift, the bed temperatures exceeded the SOL of 830 °F and the RGG was shutdown. With no air (nitrogen) from the reaction furnace, the mass flow through the unit was so low that the RGG was unable to operate with a stable flame at low air:gas ratios. Higher air:gas ratios and excess O₂ caused the bed inlet temperatures to exceed 650 °F,

potentially due to trace hydrocarbons in the amine acid gas. Due to high temperatures, the RGG was shut down and relit every other shift to maintain temperatures above 350 °F in the hydrogenation bed.

While operating with the pre-sulfide line, the refinery had to decide what unit to fix first and what repairs to make quickly with the Claus/MDEA SRU maintenance two months away from being complete. The location and extent of the plugging in each unit was unknown, so operations performed a pressure survey and soot test where possible.

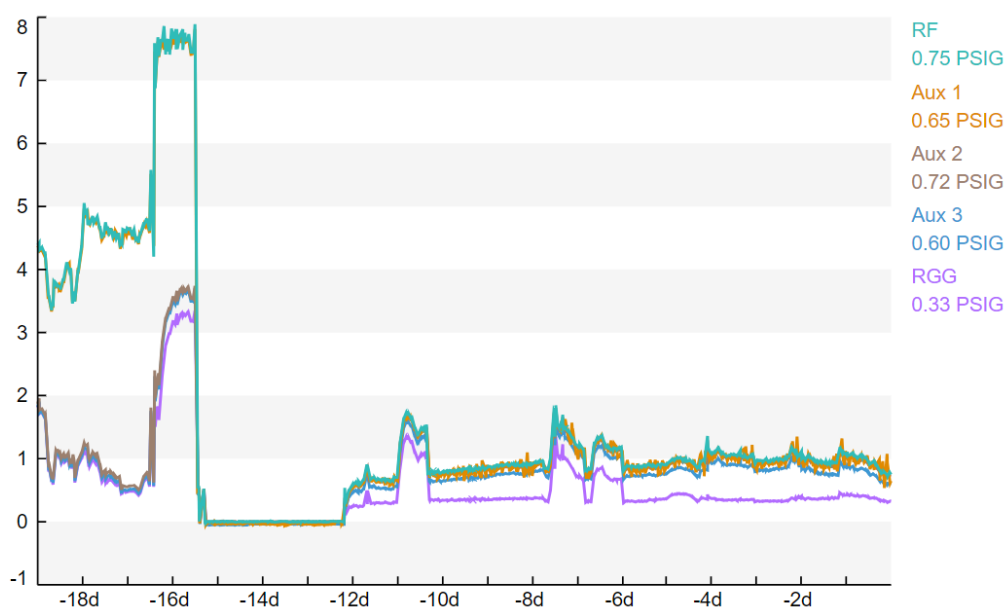
Upon inspection, it was confirmed that the first U238 reheater was generating significant amounts of soot, so the auxiliary burner was promptly turned off. During the soot test, the air to fuel gas ratio was at or above 9:1, suggesting sufficient air supply, whereby no soot should have been present. The auxiliary reheat burners do not have permanent steam supply for flame temperature moderation or soot mitigation. Time constraints prevented a definitive cause determination (poor metering vs. damaged burner).

To assess the U238 reaction furnace burner, O₂ concentration was measured at the first condenser inlet. A ratio of 9:1 in the reaction furnace resulted in an excess oxygen concentration of 0.5%, indicating that the meters were off by about 10%. Consequently, the observed 9:1 ratio was more likely closer to 10:1. Despite operating with excess oxygen, the reaction furnace burner was still generating some soot, indicating a possible mixing problem, likely due to a damaged burner.

The pressure tap at converter one outlet could not be unplugged, so it was not determined whether the first reactor or second condenser were causing the back pressure. We had confidence that the first reactor was the source of the plugging based on qualitative soot measurements. With the knowledge that U236 could operate with zero stages of conversion and the first U238 auxiliary reheat burner required repair, the refinery opted to replace the U238 converter bed with 1.5" spherical ceramic inert support and leave the first auxiliary down. This immediately improved the pressure drop across the unit, as shown in Figure 5.

Figure 5

U238 Pressure Profile Before and After Replacing Bed 1 with Inert Support Media



By operating on the pre-sulfide line, U250 was able to stay running until the scheduled shutdown date for electrical system work, at which time the refinery performed the amine swap from DGA to MDEA. After the amine swap and start-up of U250, acid gas was introduced to U238. With the RF at U236 shutdown, there was no way to perform a dP survey or soot test to determine the exact location of the plugging. After the success of replacing U238 first converter bed, the refinery repeated the replacement at U236 with 1.5” spherical ceramic support media. The U236 RGG was able to run reliably after establishing normal flowrates through the unit.

Each unit was now available for processing acid gas with one less conversion stage. At U238, pressure drop across the third bed continued to rise, and a few weeks after startup condenser leaks were discovered in the fourth condenser. The third auxiliary reheat burner was shut down and the fourth condenser was drained, leaving U238 with two sulfur condensers and one converter. See Figure 6 and 7 in the Appendix for an overview of out-of-service equipment. The refinery ran in this mode for three more weeks until the start-up of U235.

SRU OPERATION AT 98.5% TURNDOWN

With U236 and U238 operating with limited conversion stages and an increase in acid gas rate approaching at the end of the first hydrocracker maintenance period, the turnaround team accelerated the start-up of the U235 Claus/MDEA based TGU. U235 is intended to actively process sour gases at turndown in case Unit 237 is unavailable. U235 front-end feed metering and controls were configured for hydrogen or natural gas co-firing and combustion air pre-heating. These changes aim to give higher control fidelity at turndown and provide enough mass flow through the SRU (while avoiding soot formation) to prevent sulfur fogging and plugging. Additionally, the first Claus reactor bed was loaded with titania to maximize COS/CS₂ conversion. The H₂S and CO₂ in the AAG and SWAG feed were sampled after the startup of both Hydrocrackers.

Table 1

U235 Amine and Sour Water Acid Gas H₂S and CO₂ Content (Dry Basis)

Mol %	SWS	AAG
H ₂ S	28.147	5.714
CO ₂	37.908	90.873

Operating U235 with very lean acid gas feed presented several new constraints, the first was limited 600# steam production. The 600# steam produced from the reaction furnace waste heat boiler is used to supply the three Claus reheaters, the tail gas reactor preheater and the remainder is superheated by the incinerator waste heat boiler to run two turbines and support the refinery 600# header. Historically 15 MLb/hr of excess steam was exported, now no steam could be exported and only one of the boiler feed water pumps and incinerator blowers could be ran on the turbine without sagging the header. Operation of the incinerator waste heat boiler with limited steam throughput was a significant reliability concern. Since 2009, multiple tube failures had occurred in the secondary coil due to excess condensate addition to the

desuperheater. During turndown, the condensate addition was required to cool the outlet steam below the code piping limit of 800 °F, which led to flashing, steam hammering, and eventual tube failures in the secondary coil. A minimum amount of steam imported from the reaction furnace waste heat boiler is required to operate the superheater within its temperature limits, so Claus converter inlet temps were reduced to conserve steam:

- Bed 1 inlet – 475 °F
- Bed 2 inlet – 360 °F
- Bed 3 inlet – 345 °F

With the incredibly lean acid gas feeds, the dewpoint for sulfur in the catalytic converter beds is quite low, permitting the unconventionally low temperature operations in the converters. Process simulation confirmed these opportunities before they were tried.

One tail gas reactor preheater bundle was also removed from service, so the tail gas reactor inlet temperature could only be maintained at 435 °F. The minimum activation temperature for the hydrogenation catalyst is 430 °F. With lower activity and a CO₂ rich feed, stable emissions were near the 50 ppm SO₂ 1-hr average permit limit. The refinery opted to try H₂ co-firing, which immediately dropped the emissions, presumably by reducing CS₂ and COS formation in the reaction furnace.

For reference, ProTreat® simulator modeling showed that in natural gas firing mode, the carbon was forming COS and CS₂ with essentially zero sulfur recovery from the SRU thermal section. While co-firing with H₂, cumulative sulfur recovery was still only on-the-order of 50%. Despite these realities, the small load of sulfur to the TGU was well within levels that the TGU could process.

Table 2

U235 ProTreat® Simulated Sulfur Conversion and Recovery, H₂ Co-firing

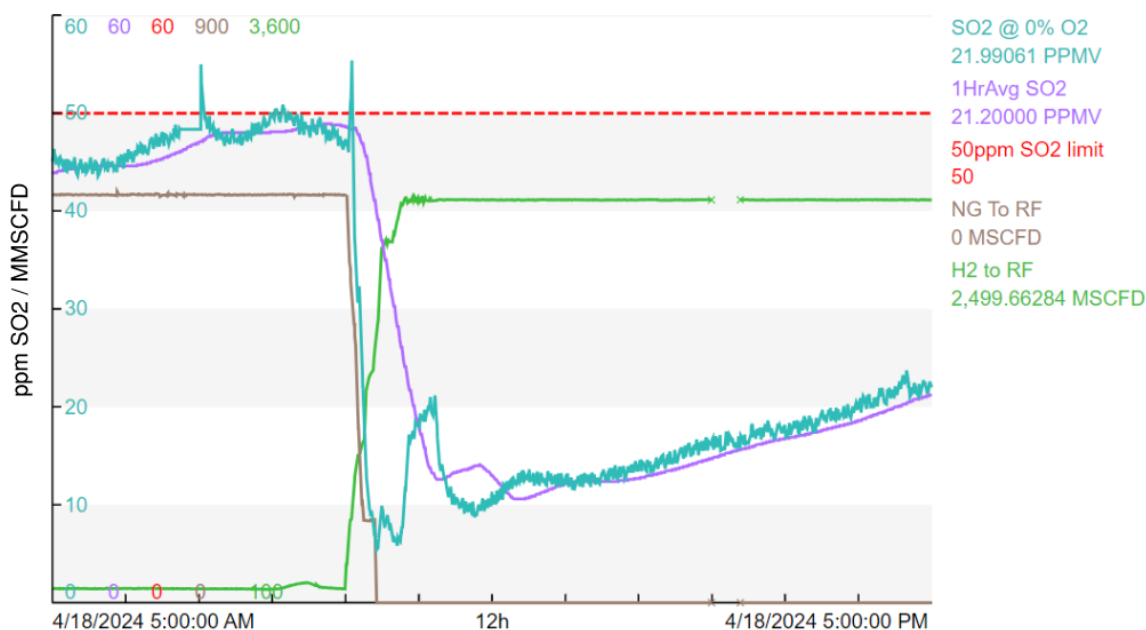
Sulfur Conversion				
Stage	Thermal Stage	Stage 1	Stage 2	Stage 3
Stage Conversion %	1.829	30.424	41.452	32.768
Cumulative Conversion %	1.829	31.697	60.010	73.114
Sulfur Recovery				
Stage	Thermal Stage	Stage 1	Stage 2	Stage 3
Stage Conversion %	0.000	16.762	33.887	22.081
Cumulative Conversion %	0.000	16.762	44.969	57.120 ^a

^a Cumulative sulfur recovery was modeled at only 57%.

ProTreat® simulator modeling with NG co-firing was unable to converge with the kinetic BTEX/hydrocarbon destruction kinetics enabled, so the effect of the formation of CS₂ in the reaction furnace was unable to be replicated for the lean acid gas. Emissions during the transition from NG to H₂ co-firing are shown below in Figure 8.

Figure 8

U235 SO₂ Emissions NG and H₂ co-firing



The other limitation was stable incinerator operation. While co-firing the reaction furnace with hydrogen, it was impossible to maintain a 2:1 H₂S to SO₂ ratio in the Claus tail gas without tripping the incinerator. H₂ which was normally added directly to the tail gas reactor was blocked in, and >10% excess H₂ in the quench column overhead was still maintained. Reducing air would slip H₂ through the unit as a free fuel source for the incinerator. Incinerator NG and air would reduce accordingly and would drive the incinerator toward the low air flow and low NG pressure trips. In the reaction furnace, air was added at 77% of H₂ stoichiometry and the tail gas analyzer H₂S to SO₂ ratio was set to 0.2:1 to maintain stable incinerator temperatures. This in turn helped the tail gas reactor bed temperatures; with higher activity from the SO₂ reactant, TGU catalyst would reach temperatures closer to 500 °F and improve COS and CS₂ conversion.

By optimizing steam consumption in the Claus section and operating off-ratio (0.2:1 instead of 2:1 H₂S to SO₂) we were able to run stably with emissions near 10-15 ppm SO₂. Meeting emissions requirements was the number one priority, but the unit was not yet producing sulfur. It took *three days* after introducing acid gas feed to see sulfur in the collection header, after that period sulfur production was on the order of 2.5 LTPD. A side benefit of the lean acid gas processing with co-firing under extreme turndown is that the sulfur produced by the Claus unit is nearly degassed. Modeling predicted 11-12 ppmw total H₂S in the rundown sulfur and the extra residence time in the rundown collection header is sufficient to allow well under 10 ppmw H₂S in the sulfur leaving the unit.

CONCLUSION

The years leading up to and execution of the Rodeo Refinery conversion to the Rodeo Renewable Energy Complex required creative processing strategies by the Sulfur Operations team. With the knowledge that the two BSRP plants would not operate post fuels conversion, maintenance work such as desalting the Stretford solution and replacing catalyst were deferred. Frequent sulfur washes and routine solution purges were executed to keep both units operational.

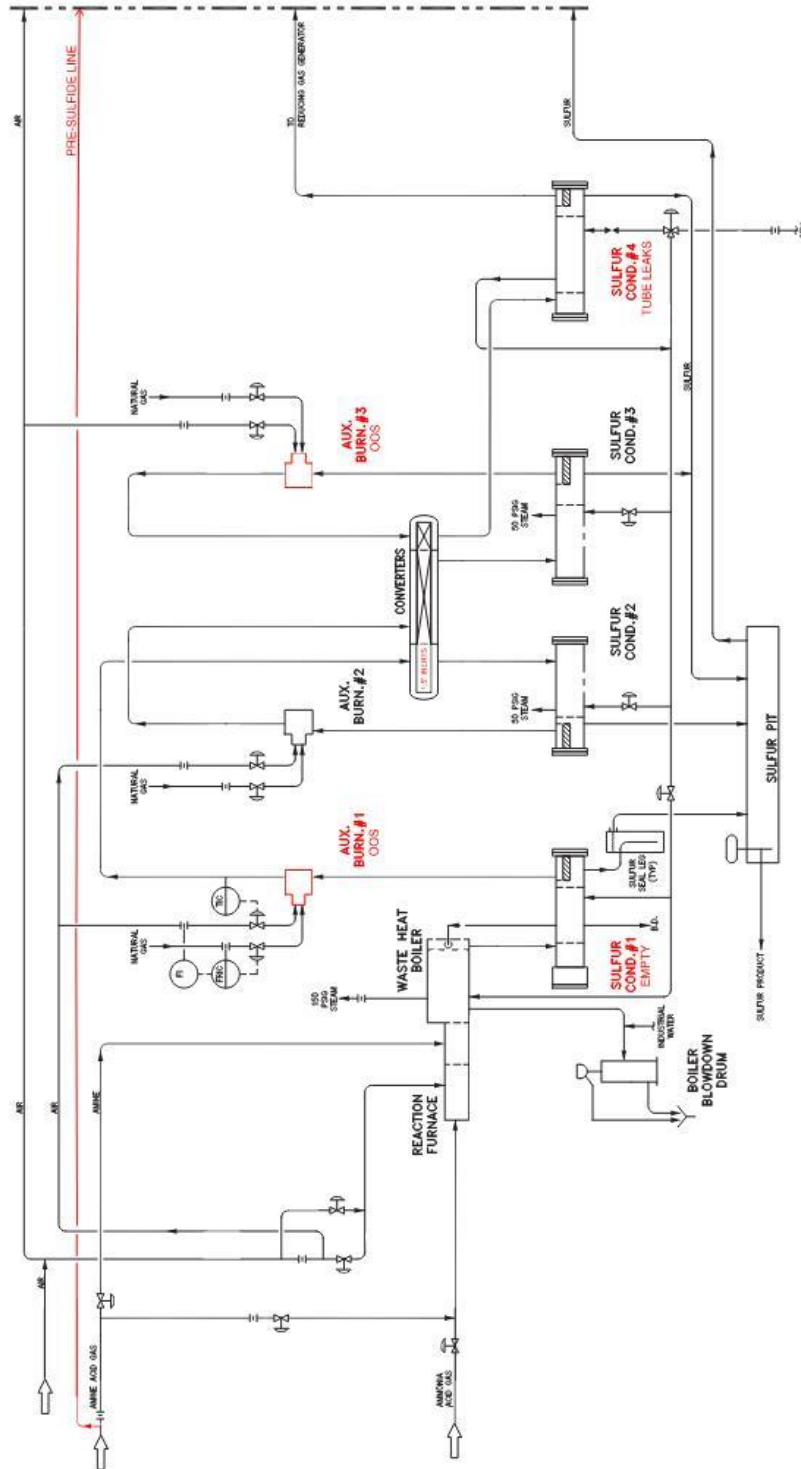
Unexpected upsets during the turnaround left each Claus plant with plugging across the first converter beds, so acid gas was routed directly to the TGU via the pre-sulfide line. With the deteriorated state of the Stretford solution and mixers, operating in this mode required a constant effort to restart mixers, purge, and make-up the Stretford solution with fresh chemicals. It also required careful monitoring of stack emissions, the TGU catalyst temperatures, and increasing pressure drop across the hydrogenation bed due to soot formation in the RGG. Even at end-of-run conditions in the Stretford solution, renewables sulfur processing was feasible while bypassing the Claus unit entirely. This knowledge enabled us to replace the first converter beds with support media instead of replacing the catalyst to serve as soot scavenging. Later sampling of the amine acid gas stream revealed nominally 6% H_2S and 91% CO_2 with all three renewable diesel units running. This lean H_2S stream eased the operation of processing via the pre-sulfide line (and later with fewer conversion stages) but complicated running the Claus/MDEA-based TGU at 98.5% turndown.

Operating a 200 LTPD unit at 2.5 LTPD required a different approach to the air-demand controls and new performance indicators. The lower unit rates placed unexpected constraints on the integrated 600# steam system. Co-firing with H_2 was unexpectedly necessary to reduce the formation of COS/CS_2 in the reaction furnace and meet SO_2 emissions limits. This required operating at 0.2:1 H_2S to SO_2 for stable incinerator controls. Finally, one of the few side-benefits of the lean acid gas processing at extreme turndown in a conventional Claus unit is that sulfur degassing may not be required to produce degassed sulfur.

APPENDIX

Figure 6

U236 and U238 Claus Plant



U236 and U238 TGU

