Sulfur Capacity Expansion Options

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Overview

- Introduction
- Sulfur plant basics
- Hydrocarbon minimization
- Pressure drop minimization
- Ammonia recovery
- Oxygen addition
- Sulfur dioxide
- Tail gas compression
- Conclusions
Introduction

The refining world is never static.

- Higher economic returns are always sought.
- More stringent environmental regulations
- “Opportunity Crudes” mysteriously show up at the doorstep
- Changes from existing suppliers
An SRU is a mass-flow limited device

After the flow control valves sending acid gases and air to the burner, flow is based on natural pressure drop until it reaches the atmosphere.

More flow = higher required burner pressure
  - From Bernoulli, pressure drop is proportional to velocity$^2$
  - And therefore, the burner pressure will be proportional to velocity$^2$

Sulfur expansion methods focus on changing the composition, pressure, and sometimes temperature to get more flow.
Overall reactions

- Overall Sulfur Recovery Unit reaction:

\[ \text{H}_2\text{S} + 0.5 \text{O}_2 \rightarrow \text{S} + \text{H}_2\text{O} + \text{heat} \]

\[ \text{Mass flow} = 50 \text{ lb/hr} \]

- Including nitrogen and moisture in ambient air

\[ \text{H}_2\text{S} + 0.5 \text{O}_2 + 1.9 \text{N}_2 + 0.2 \text{H}_2\text{O} \rightarrow \text{S} + 1.2 \text{H}_2\text{O} + 1.9 \text{N}_2 + \text{heat} \]

\[ \text{Mass flow} = 105 \text{ lb/hr} \]

- The value of 105 lb/hr is a good reference number for future equations.
Impact of Hydrocarbons

- Hydrocarbons add mass flow to the SRU, taking up capacity:

- Assuming combustion to CO the destruction of butane proceeds as

  \[ \text{C}_4\text{H}_{10} + 4.5 \text{ O}_2 \rightarrow 4 \text{ CO} + 5 \text{ H}_2\text{O} + \text{heat} \]

  \[ \text{Mass flow} = 202 \text{ lb/hr} \]

- 1700 SCFH of oxygen consumption for every lb-mole/hr of butane.
- For Claus units using only combustion air:

  \[ \text{C}_4\text{H}_{10} + 4.5 \text{ O}_2 + 16.8 \text{ N}_2 + 1.5 \text{ H}_2\text{O} \rightarrow 4 \text{ CO} + 6.5 \text{ H}_2\text{O} + 16.8 \text{ N}_2 + \text{heat} \]

  \[ \text{Mass flow} = 700 \text{ lb/hr} \]

- Recall that 1 lb-mole/hr of H2S requires about 105 lb/hr of capacity.
Impact of Hydrocarbons

Additional problems with hydrocarbons

- Adds unnecessary heat to the Reaction Furnace
- Can create soot, which increases system pressure drop
- Can create COS and CS2, which are difficult to destroy and can make the environmental emissions go off-spec for SO2
- Aromatics (esp. xylene) can coke the catalyst
Hydrocarbon minimization

Sources of hydrocarbons:
- Undersized KO Drums or 3 phase separators
- Undersized or misoperated SWS Feed Preparation Tanks
- Lack of proper filtration and coalescing

Solutions
- Best answer is to right-size the upstream separators to separate amine or sour water from the hydrocarbon streams, but …
  - Perception is that right sizing is too expensive vs benefits
  - Requires shutdown of an operating unit

- Budget and schedule constraints may require:
  - Gas-liquid or liquid-liquid coalescer
  - Minimal capex
  - Minimal Plot space
  - Biggest benefits (ppb-ppm separation)
Pressure Drop Minimization

Because the Claus SRU is a mass-flow limited device, reducing pressure drop increases capacity.

- Use packing in amine regenerators
- Control Valves
- Flow Meters
- Acid Gas headers
- KO Drums (nozzles and internals)
Impact of Ammonia

Understanding Ammonia

- Sources: Hydrotreating / Coking
- Ends up in the wash water and takes H2S with it
- Nobody in the refinery wants it
- The SRU is the only place to send it
- But, the sulfur recovery unit is not an ammonia plant
  - It makes sulfur not ammonia
- Potential salt deposition problems
- Can destroy some using two-chambers in the Reaction Furnace
  - Front destroys ammonia
  - Rear completes the Claus reaction
Impact of Ammonia

- Simplified Chemistry
  \[ \text{NH}_3 + 0.75 \text{O}_2 \rightarrow 0.5 \text{N}_2 + 1.5 \text{H}_2\text{O} + \text{heat} \]
  \[ \text{Mass flow} = 41 \text{lb/hr} \]

- In SWSG, assuming equimolar NH3, H2S, and H2O, each mole of NH3 means an extra mole of water. Adding in air as well...
  \[ \text{NH}_3 + 0.75 \text{O}_2 + 2.8 \text{N}_2 + 1.2 \text{H}_2\text{O} \rightarrow 3.3 \text{N}_2 + 2.7 \text{H}_2\text{O} + \text{heat} \]
  \[ \text{Mass flow} = 142 \text{lb/hr} \]

- Recall that H2O drives the Claus reaction backwards
  \[ 2 \text{H}_2\text{S} + \text{SO}_2 \leftrightarrow 3/x \text{S}_x + 2 \text{H}_2\text{O} \]
Ammonia recovery - WWT

- Two-tower SWS developed by Chevron, now owned by Bechtel
- First tower at higher pressure gives nearly pure H2S
- Second tower at lower pressure gives nearly pure NH3
- Different degrees of purity available, up to Haber quality.
- What to do with several tons per day of ammonia?
  - The same thing you do with several tons of sulfur – call a broker.

Advantages
- Salable commodity
- Capex lower than a new SRU
- This sulfur expansion project can be self-funded
- Can solve ammonia salt deposition problems

Disadvantages
- Plot
- Capex higher than other options shown
- Steam consumption

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Ammonia removal

- Ammonium Thiosulfate (ATS)
- Sulfuric Acid
- Combustion to produce power
Oxygen Addition

Why it works:

- Recall the overall reaction:

  \[ \text{H}_2\text{S} + 0.5 \text{ O}_2 \rightarrow \text{S} + \text{H}_2\text{O} + \text{heat} \]
  
  **Mass flow = 50 lb/hr**

- Including nitrogen and moisture in ambient air

  \[ \text{H}_2\text{S} + 0.5 \text{ O}_2 + 1.9 \text{ N}_2 + 0.2 \text{ H}_2\text{O} \rightarrow \text{S} + 1.2 \text{ H}_2\text{O} + 1.9 \text{ N}_2 + \text{heat} \]
  
  **Mass flow = 105 lb/hr**

- Because the SRU is mass flow limited, removing N2 and H2O help increase capacity.
Oxygen addition attempts to alter the composition of the gases to achieve a higher throughput.

- Oxygen source is typically 95%+ O2 purity
  - with the balance being N2 and perhaps Argon

- Three “flavors” of oxygen addition:
  - <28% oxygen
  - 28-50% oxygen
  - 50-100% oxygen
  - The “flavors” are given numbers based on oxygen concentration as if all sources of oxygen are combined into one stream.

- Oxygen is used “on-demand”

- Capex varies
Oxygen considerations

- Amine Acid Gas (AAG) header sizing
- Controls
  - FE, CV for AAG, SWSG, Air, BFW, steam, reducing gas
- Burner Capacity
- Refractory
- Waste Heat Exchanger vapor lock
- Nozzle velocities in select locations
- 1st Reheater duty
- Check condenser outlet temperatures
- Update all reheater setpoints due to:
  - Changes in sulfur dewpoint
  - Increased reactor temperatures
Oxygen considerations outside the SRU

Tail Gas Treating Unit

- Reducing gas supply / RGG
  - Flow to TGTU is lower, but is at a higher % (H2S + SO2)
- Quench Tower cooling duty
  - Every mole of sulfur produces a mole of water … which must be condensed
- Amine performance
- Regenerator internals
- Regenerator overhead condenser
- Regenerator controls / AAG hydraulics
Oxygen flavor #1: <28%

- Oxygen is put into the combustion air piping
- Also called “simple enrichment”
- Lowest capex of oxygen options
- Above 28-30%, the oxygen reacts with the air blower’s CS piping
- Each incremental ton of oxygen ~ 1 ton of incremental sulfur capacity
Oxygen flavor #2: 28%-50%

- Requires a special oxygen “lance” put into the new burner
- Sometimes called “mid-level enrichment”
- Moderate capex among oxygen options
- More likely to require equipment replacement
  - Especially refractory and quench tower duties
- COPE™ recycles Reaction Furnace gas to modulate temperature
- The last incremental ton of oxygen ~ 0.8-0.9 tons of incremental sulfur capacity
Oxygen flavor #3: 50%-100%

- Uses two-stages due to high temperatures
  - Burner + Reaction Furnace + WHE
  - 2nd Burner + 2nd Reaction Furnace + 2nd WHE

- The highest level of enrichment possible
- Highest capex of the oxygen options
- Plot requirement is most awkward
- Most likely to require equipment replacement
- Most complex controls
- Diminishing returns: The last incremental ton of oxygen gives minimum return at highest oxygen concentrations
Sulfur dioxide addition

- SO2 is a required intermediate
  
  \[ H_2S + 1.5 \text{ O}_2 \rightarrow \text{SO}_2 + \text{H}_2\text{O} + \text{heat} \]
  
  *Mass Flow = 82 lb/hr*

- But the real story is more complex. If not using oxygen addition,
  
  \[ H_2S + 1.5 \text{ O}_2 + 5.6 \text{ N}_2 + 0.5 \text{ H}_2\text{O} \rightarrow \text{SO}_2 + 1.5 \text{ H}_2\text{O} + 5.6 \text{ N}_2 + \text{heat} \]
  
  *Mass Flow = 250 lb/hr*

- Because SO2 has MW=64, direct SO2 addition can be attractive.
Sulfur dioxide addition

- Remove SO2 from stack gases with a regenerable solution
- Such as Belco® (aka LABSORB™) or CANSOLV
- The regenerated gas is concentrated SO2
  - Feed to a Claus unit
Such as SO2Clean™

- Takes liquid sulfur from the SRU pit
- Oxidizes it in an OSBL facility
- Returns SO2 vapor to the refinery

- Removes heat from SRU’s Reaction Furnace
- On demand consumption
- Low capex
When to use Tail Gas Compression:

- Insufficient results from increasing AAG and SWSG pressure

- Increasing Combustion Air pressure is not normally simple
  - Might result in a new machine

- These will result in increasing the system operating pressure
  - New sulfur seal legs may be needed
  - Especially the burner
  - Not always desirable from a safety standpoint

- Oxygen addition was used during the last expansion or is unavailable
Tail Gas Compression

Use a compressor to add ~2.5-4.0 psi to the tail gas

- Locate after final SRU condenser or after the Quench tower
  - At the SRU condenser allows more flow because it is further upstream
  - Contains sulfur vapor and requires steam jacketing
  - Is hotter than the Quench tower overhead (more hp)
  - Still contains all the water, so it has more mass flow (more hp)

- Avoid partial vacuum situations
  - Atmospheric air may enter, causing problems in the TGTU reactor
  - Process gases may escape during turndown or shutdown

- Heat tracing considerations

- Metallurgy considerations

- Generally used as a last resort or niche situation.
Conclusions

Plenty of options are available:

- Simple pressure drop hardware changes
- Hydrocarbon minimization
- Pressure drop minimization
- Ammonia recovery
- Oxygen addition
- Sulfur dioxide
- Tail gas compression
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