INFRASTRUCTURE

MINING & METALS

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OIL, GAS & CHEMICALS

Sulfur Capacity Expansion Options

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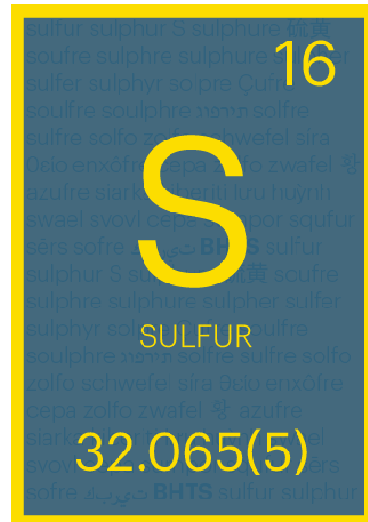
Overview

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



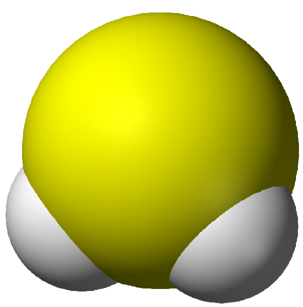
Introduction

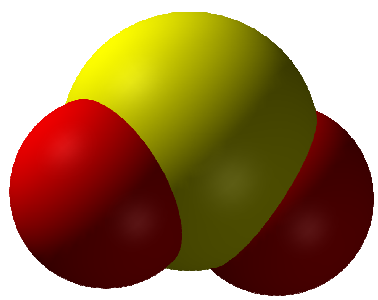
The refining world is never static.

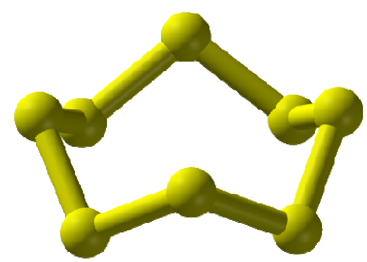
- Higher economic returns are always sought.
- More stringent environmental regulations
- “Opportunity Crudes” mysteriously show up at the doorstep
- Changes from existing suppliers

Sulfur Plant Basics

- 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







Drawing Credits: Ben Mills

Overall reactions

- Overall Sulfur Recovery Unit reaction:

$$H_2S + 0.5\ O_2 \rightarrow S + H_2O + \text{heat}$$

Mass flow = 50 lb/hr

- Including nitrogen and moisture in ambient air

$$H_2S + 0.5\ O_2 + 1.9\ N_2 + 0.2\ H_2O \rightarrow S + 1.2\ H_2O + 1.9\ N_2 + \text{heat}$$

Mass flow = 105 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

$$C_4H_{10} + 4.5\ O_2 \rightarrow 4\ CO + 5\ H_2O + \text{heat}$$

Mass flow = 202 lb/hr

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

$$C_4H_{10} + 4.5\ O_2 + 16.8\ N_2 + 1.5\ H_2O \rightarrow 4\ CO + 6.5\ H_2O + 16.8\ N_2 + \text{heat}$$

Mass flow = 700 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

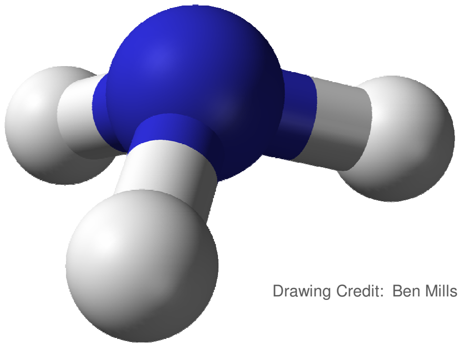
Because the Claus SRU is a mass-flow limited device, reducing pressure drop increases capacity.

- 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



Drawing Credit: Ben Mills

Impact of Ammonia

- Simplified Chemistry

$$NH_3 + 0.75\ O_2 \rightarrow 0.5\ N_2 + 1.5\ H_2O + \text{heat}$$

Mass flow = 41 lb/hr

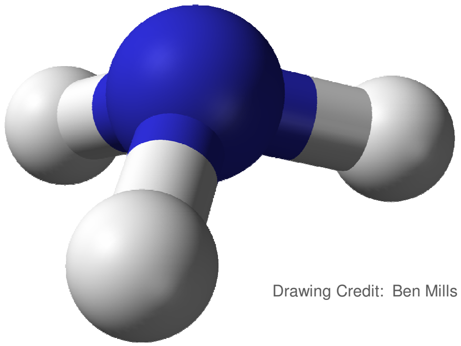
- In SWSG, assuming equimolar NH_3, H_2S, and H_2O, each mole of NH_3 means an extra mole of water. Adding in air as well…

$$NH_3 + 0.75\ O_2 + 2.8\ N_2 + 1.2\ H_2O \rightarrow 3.3\ N_2 + 2.7\ H_2O + \text{heat}$$

Mass flow = 142 lb/hr

- Recall that H_2O drives the Claus reaction backwards

$$2\ H_2S + SO_2 \leftrightarrow 3/x\ S_x + 2\ H_2O$$



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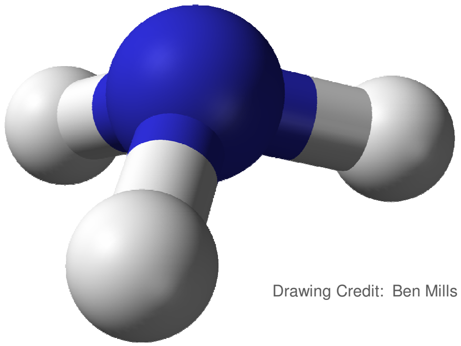
Ammonia recovery - WWT

- 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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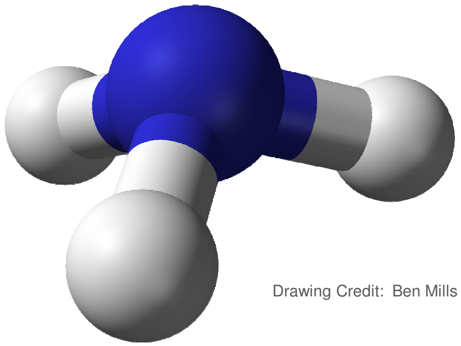
Ammonia removal

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



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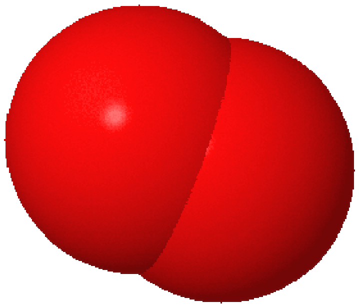
Oxygen Addition



Drawing Credit: Ulflund

Why it works:

- Recall the overall reaction:

$$H_2S + 0.5\ O_2 \rightarrow S + H_2O + \text{heat}$$

Mass flow = 50 lb/hr

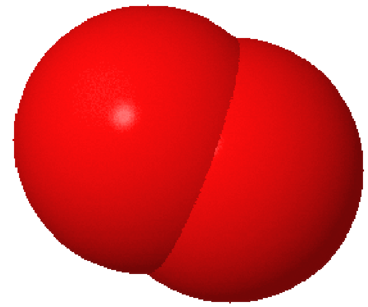
- Including nitrogen and moisture in ambient air

$$H_2S + 0.5\ O_2 + 1.9\ N_2 + 0.2\ H_2O \rightarrow S + 1.2\ H_2O + 1.9\ N_2 + \text{heat}$$

Mass flow = 105 lb/hr

- Because the SRU is mass flow limited, removing N_2 and H_2O help increase capacity.

Oxygen Addition



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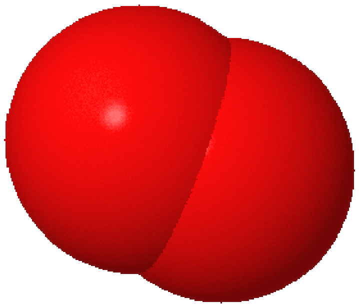
Oxygen addition attempts to alter the composition of the gases to achieve a higher throughput.

- Oxygen source is typically 95%+ O_2 purity
  - with the balance being N_2 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

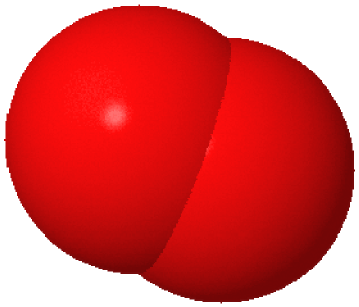
Oxygen considerations



Drawing Credit: Ulflund

- 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

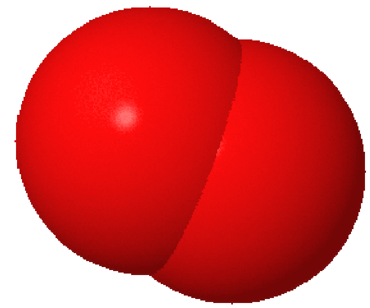


Drawing Credit: Ulflund

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%



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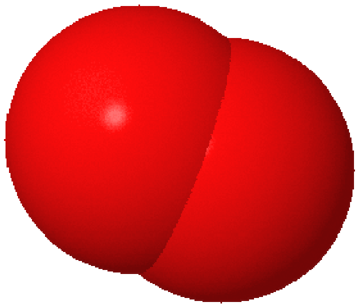
- Oxygen is put into the combustion air piping

- 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%



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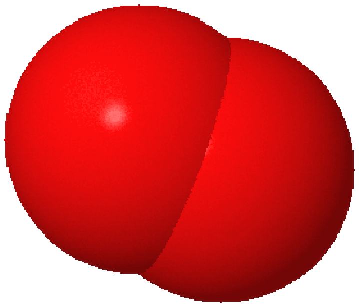
- Requires a special oxygen “lance” put into the new burner
- Sometimes called “mid-level enrichment”
- Moderate capex among oxygen options
- More likely to require equipment replacement
  - Especially refractory and quench tower duties
- COPE™ recycles Reaction Furnace gas to modulate temperature
-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

Oxygen flavor #3: 50%-100%



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- 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

- SO_2 is a required intermediate

$$H_2S + 1.5\ O_2 \rightarrow SO_2 + H_2O + \text{heat}$$

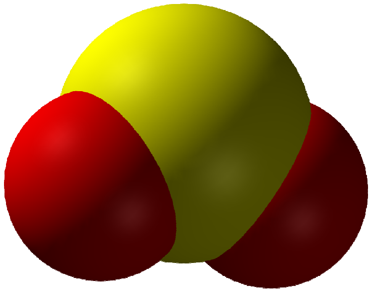
Mass Flow = 82 lb/hr

- But the real story is more complex. If not using oxygen addition,

$$H_2S + 1.5\ O_2 + 5.6\ N_2 + 0.5\ H_2O \rightarrow SO_2 + 1.5\ H_2O + 5.6\ N_2 + \text{heat}$$

Mass Flow = 250 lb/hr

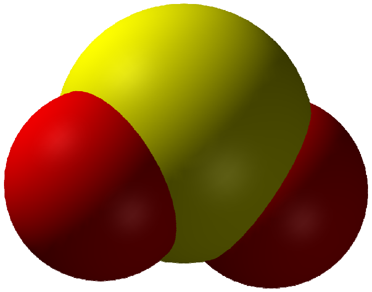
- Because SO_2 has MW=64, direct SO_2 addition can be attractive.



Drawing Credit: Ben Mills

Sulfur dioxide addition

- Remove SO_2 from stack gases with a regenerable solution
- Such as Belco® (aka LABSORB™) or CANSOLV
- The regenerated gas is concentrated SO_2
  - Feed to a Claus unit



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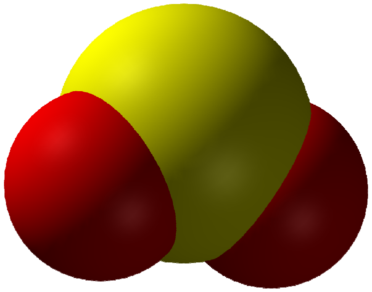
Sulfur dioxide – Offsite utility

- Such as SO2Clean™

- Takes liquid sulfur from the SRU pit
- Oxidizes it in an OSBL facility
- Returns SO_2 vapor to the refinery

- Removes heat from SRU's Reaction Furnace
- On demand consumption
- Low capex



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Tail Gas Compression

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 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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