Claus Sulfur Recovery Units

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Outline

- Overview of the process
- "Tour of the flowsheet" – discussion of each piece of equipment

- Many creative variations exist for Claus Sulfur Recovery Units
- This presentation is a brief introduction to
  - Overall process objectives
  - Basic flowsheet
  - Main pieces of equipment
  - Major operating and design considerations

Claus Sulfur Recovery Units (SRUs)

- Purpose: Convert H_2S into elemental sulfur
  - H_2S is a highly toxic flammable gas
  - Sulfur (liquid or solid) can be safely transported and stored
  - After H_2S removal, whatever is left of the SRU feed is safe to emit to atmosphere – after further clean up in a Tail Gas Unit
  - Exothermic conversion: SRU is a net exporter of steam

- Process Inputs: Acid gas, air
- Process Outputs: Elemental sulfur w/ 100s ppmw H_2S, Tail gas

Claus Sulfur Recovery Units (SRUs)

- Applicability: Economics usually favor larger applications
  - CAPEX heavy / OPEX light
  - Sulfur content >15 LTPD
  - H_2S concentration > 30%

Claus Sulfur Recovery Units (SRUs)

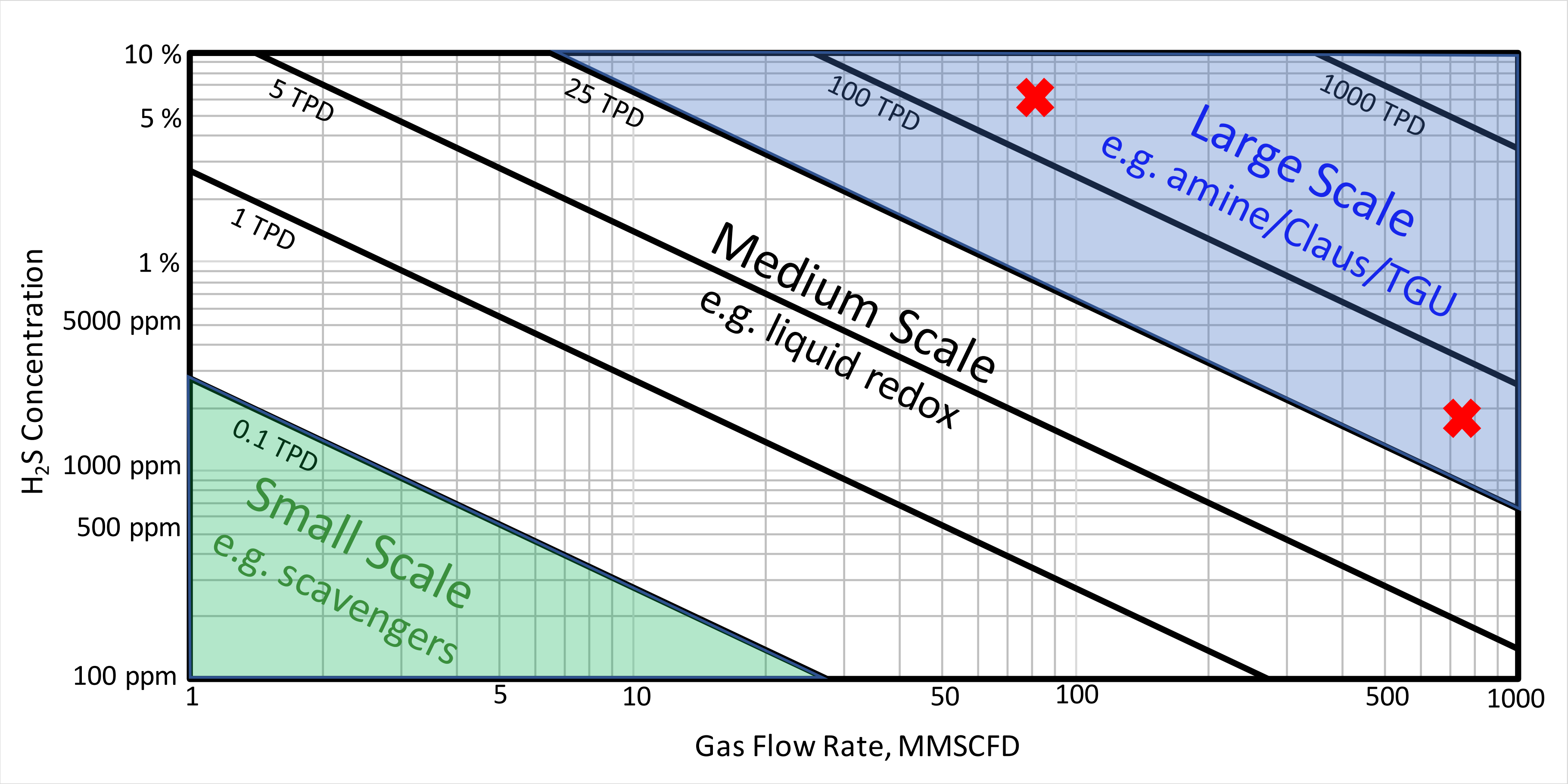


Image Source: "Alternatives to Flare Gas Recovery for Sour Gas", presented by Trimeric to AFPM 2016

Process Chemistry: Principal Reactions

- Overall Reaction

$$3\ H_2S\ +\ 1.5\ O_2\ \leftrightarrow\ \frac{3}{x}S_x\ +\ 3\ H_2O$$

Overall conversion is exothermic:
88,000 BTU/lbmole H_2S

- Step 1: Thermal Reaction

$$H_2S\ +\ 1.5\ O_2\ \rightarrow\ SO_2\ +\ H_2O$$

- Step 2: Conversion Reaction

$$2\ H_2S\ +\ SO_2\ \leftrightarrow\ \frac{3}{x}S_x\ +\ 2\ H_2O$$

Process Chemistry: Other Reactions

- NH3 destruction (simplified)

$$2\ NH_3 + 1.5\ O_2 \rightarrow N_2 + 3\ H_2O$$

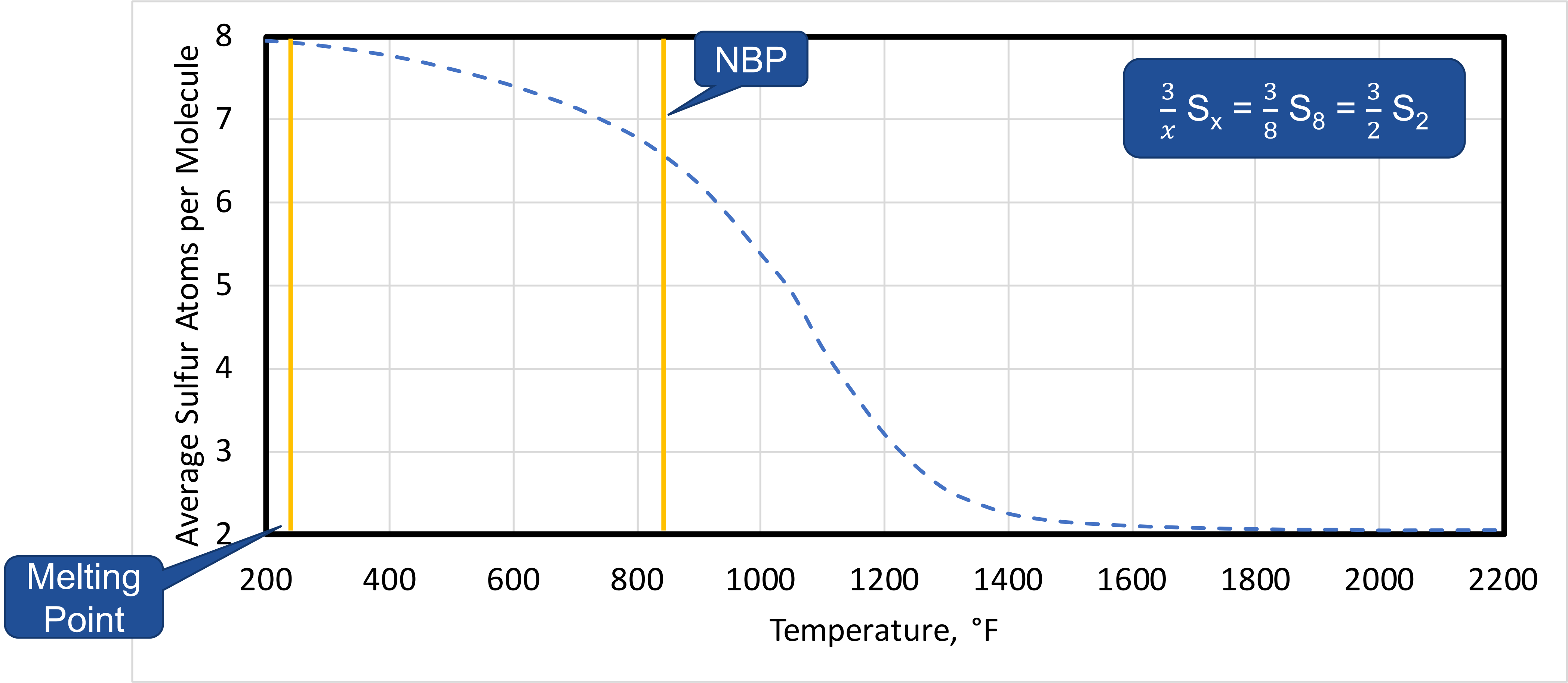
- COS destruction

$$COS + H_2O \leftrightarrow H_2S + CO_2$$

- CS_2 destruction

$$CS_2 + 2\ H_2O \leftrightarrow 2\ H_2S + CO_2$$

Sulfur Molecules



$$\frac{3}{x}S_x = \frac{3}{8}S_8 = \frac{3}{2}S_2$$

Data Source: GPSA Engineering Data Book, 13th ed., Fig 22-21.

Typical Claus SRU: Principal Reactions

$$2\,H_2S + SO_2 \leftrightarrow \frac{3}{8}S_8 + 2\,H_2O$$

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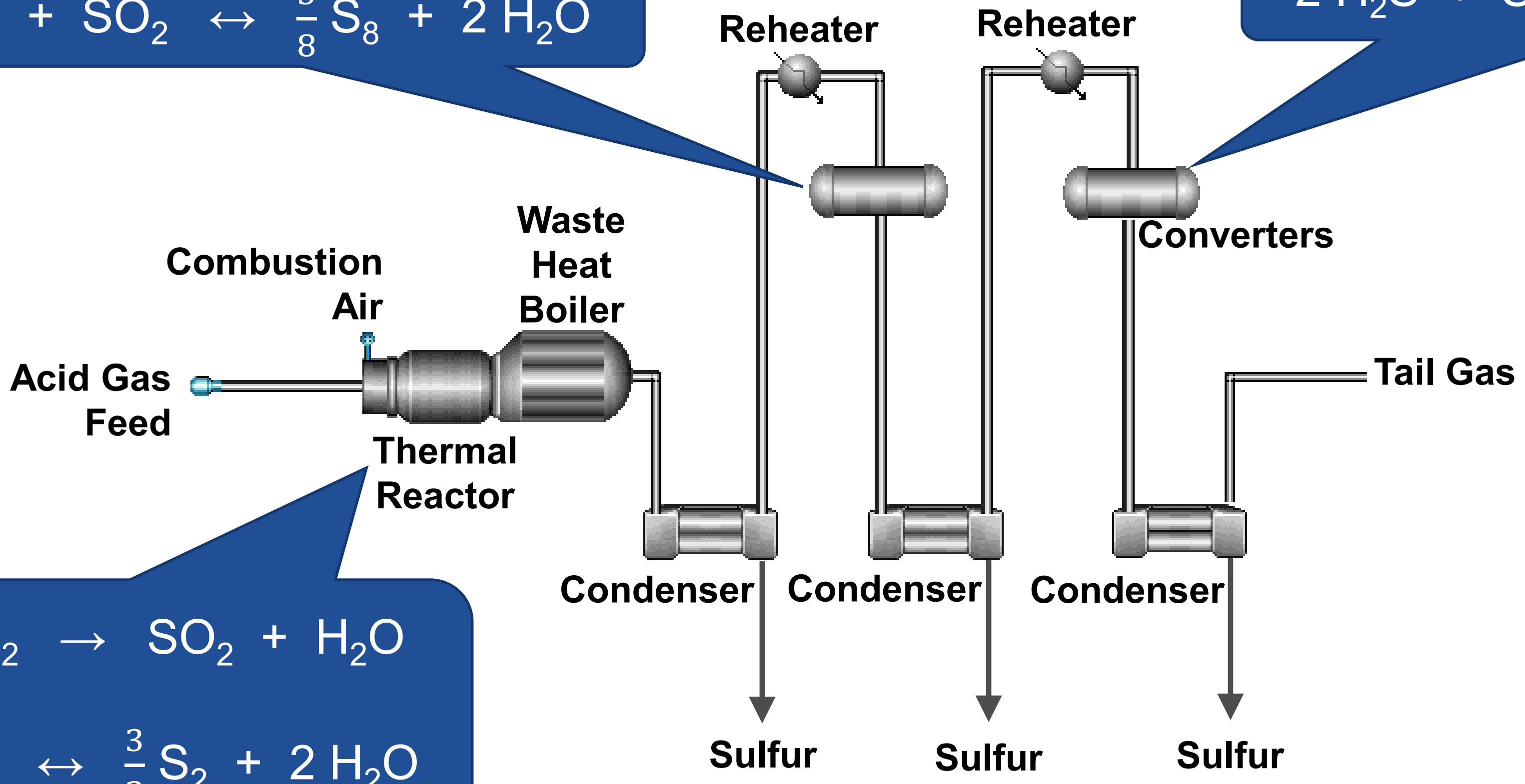
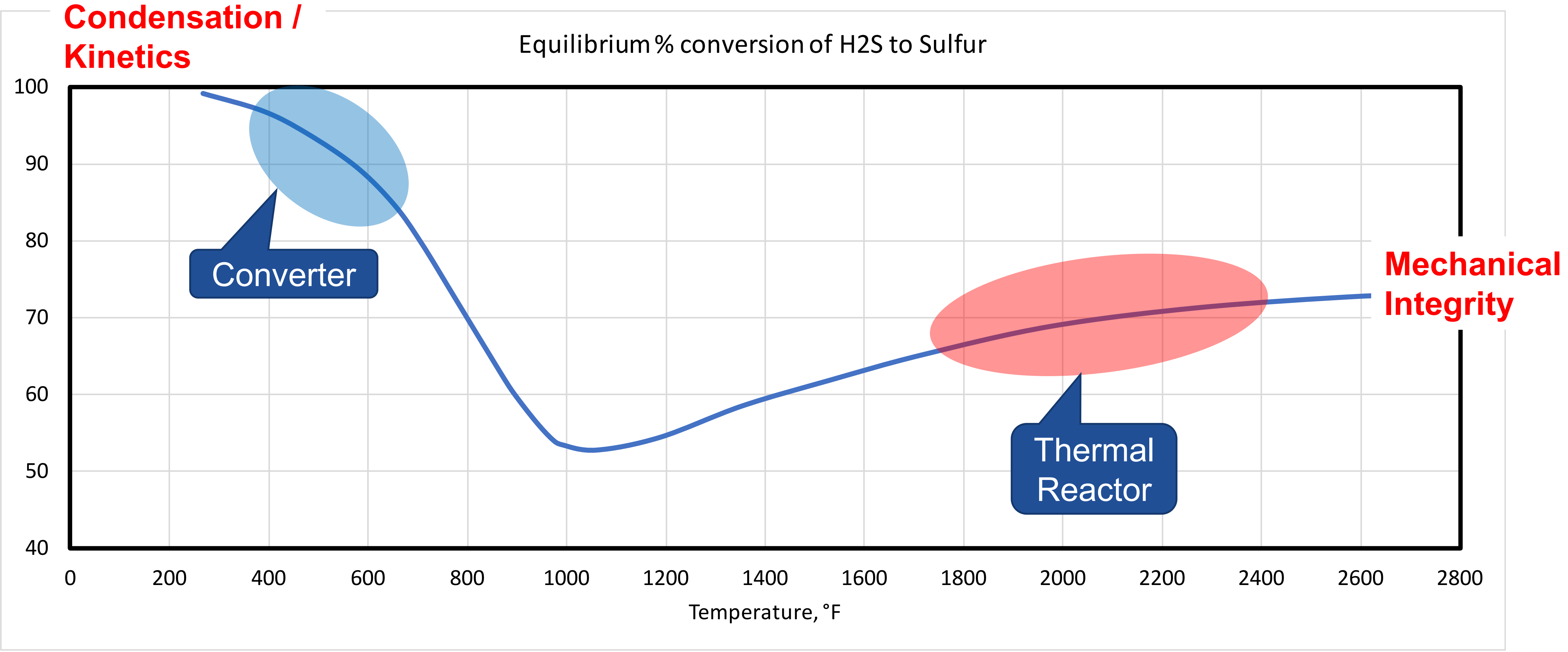


$$H_2S + 1.5\,O_2 \rightarrow SO_2 + H_2O$$

$$2\,H_2S + SO_2 \leftrightarrow \frac{3}{2}S_2 + 2\,H_2O$$

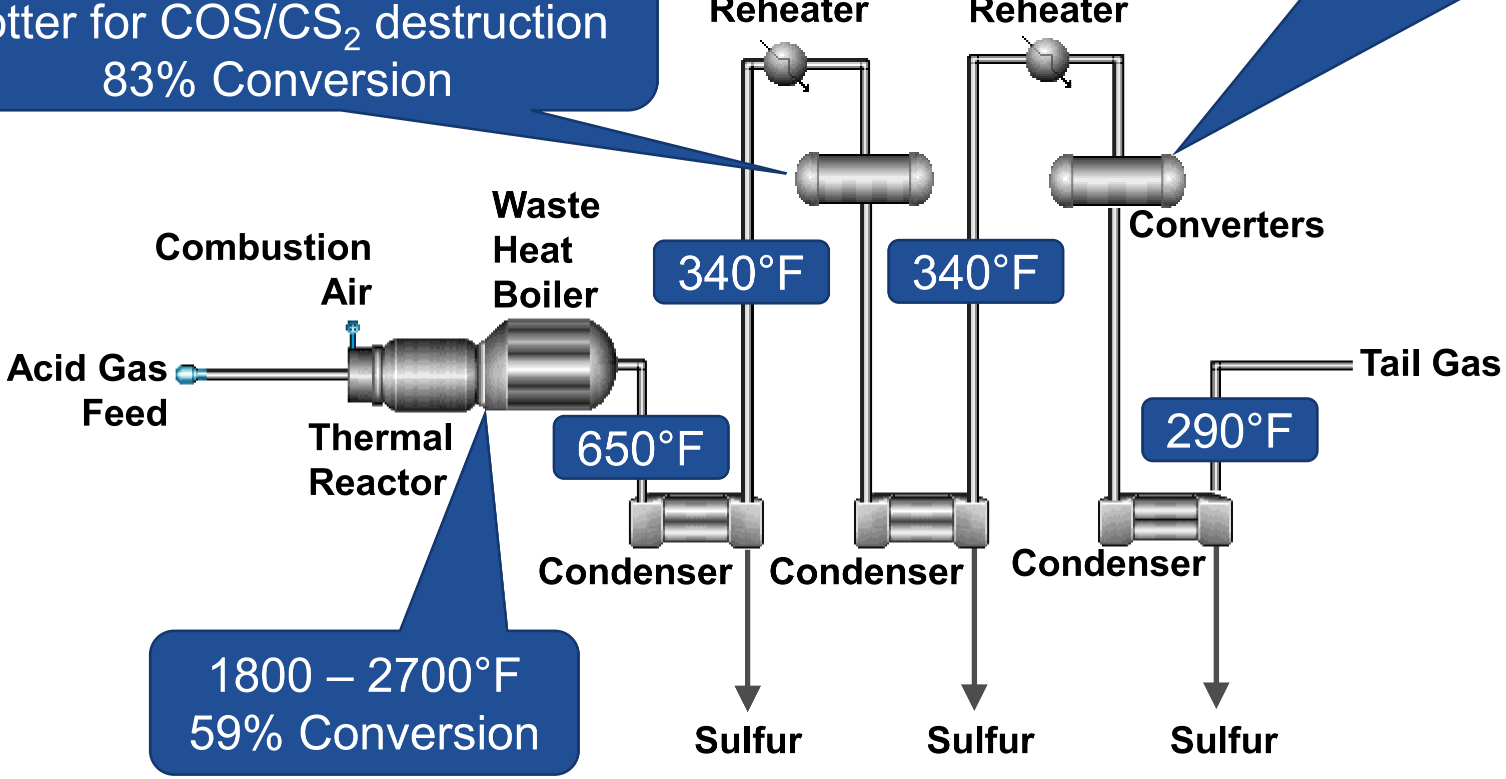
Image Source: Sour Gas and Sulfur Symposium 2017

Equilibrium Conversion of H_2S to Sulfur



Data Source: GPSA Engineering Data Book, 13th ed., Fig 22-2.

Typical Claus SRU: Temperature / Conversion



650°F outlet
Hotter for COS/CS_2 destruction
83% Conversion

400°F outlet
Cooler for Claus conversion
93% Conversion

1800 – 2700°F
59% Conversion

Temperatures are typical

Conversions are cumulative

Image Source: Sour Gas and Sulfur Symposium 2017

Conversion Stages

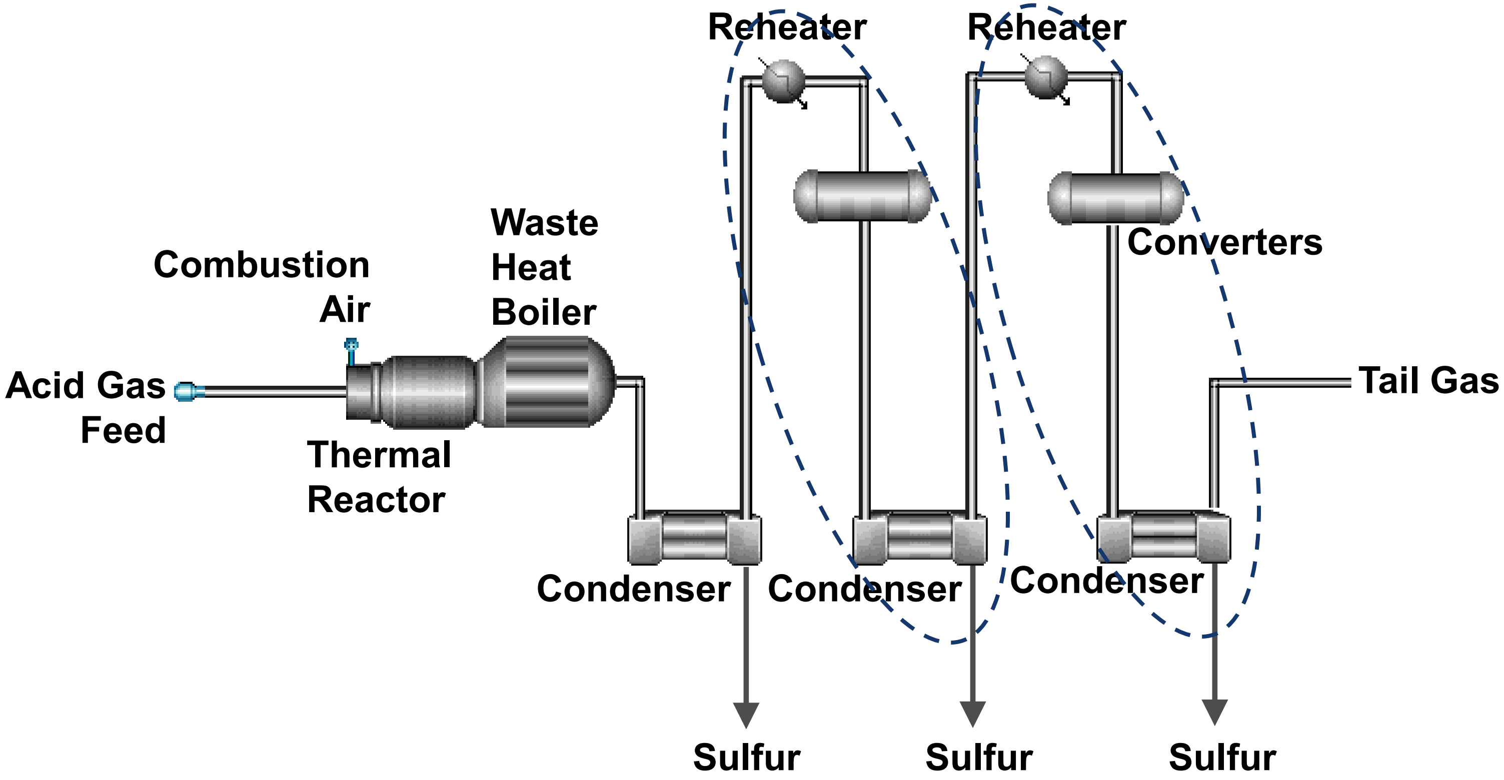
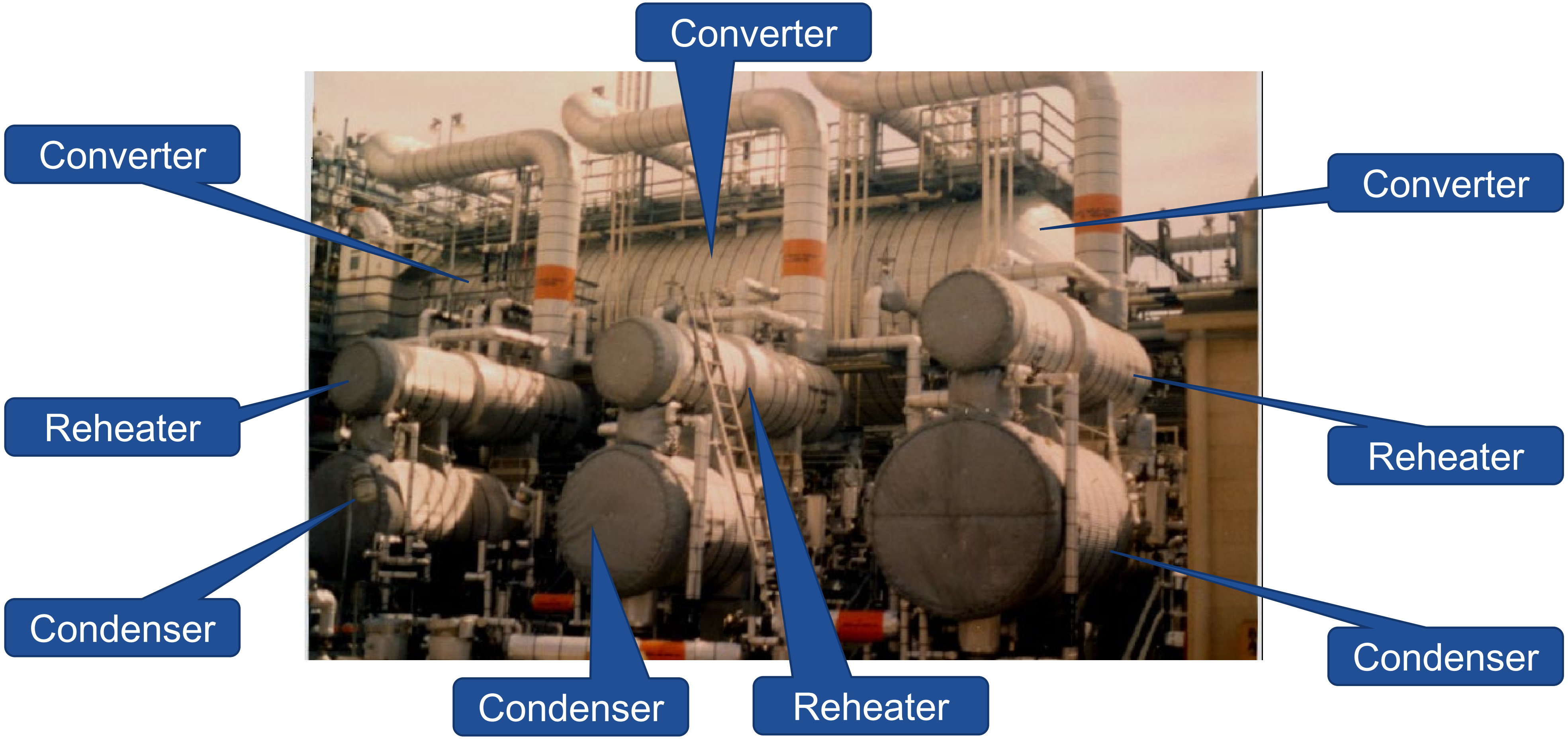


Image Source: Sour Gas and Sulfur Symposium 2017

Conversion Stages



Source: LRGCC 2007 Fundamentals

Pressure

- Claus SRUs are low pressure units (process side)
- Feeds come from regenerator / stripper tower overheads
- Products go thru TGU then to the atmosphere
- Pressure drop is at a premium
- Plugging is a serious operational concern

Tour of the flowsheet

- Acid Gas Feeds - including common contaminants NH_3 and HC
- Air Demand – “the most complex control scheme in the plant”
- Thermal Reactor
- WHB
- Sulfur Condenser
- Reheater
- Converter

Acid Gas Feeds

	Refineries	Gas Plants
Amine Acid Gas	70-95%H_2S Balance CO_2 Hydrocarbons <1% Water saturated	<5-80% H_2S Balance CO_2 Hydrocarbons <1% (more for physical solvent) Water saturated
Sour Water Stripper Acid Gas	Equal parts H_2S, NH_3, water Sometimes more hydrocarbon	N/A
Combined AG Feeds	5-25% NH_3	N/A

Feed Contaminants: NH_3

- Source: SWS Acid Gas
- Risk: Plugging with solid ammonium salts
- Mitigation: Thermal Reactor design / operation to destroy NH_3

Feed Contaminants: HC

- Source: Upstream units, esp. upsets and instrument malfunction
- Risks:
  - Very high Thermal Reactor temperatures, equipment damage
  - Formation of soot causing plugging
  - Formation of COS and CS_2 in Thermal Reactor causing increased emissions
- Mitigation:
  - Air Demand monitoring, Thermal Reactor temperature monitoring
  - Titania catalyst and high operating temperature in 1st converter

Air Demand

- Chemical Requirement for O_2
  - Oxidize 1/3 of H_2S to SO_2
  - Destroy all NH_3
  - Destroy all HC
- Complex control scheme
  - Main air
    - Bigger control valve on feed-forward control
    - Anticipate air needs based on acid gas feed rates
  - Trim air
    - Smaller control valve on feed-back control
    - Adjust air in real time based on measured H_2S / SO_2 ratio

Oxygen Demand of Acid Gas Components

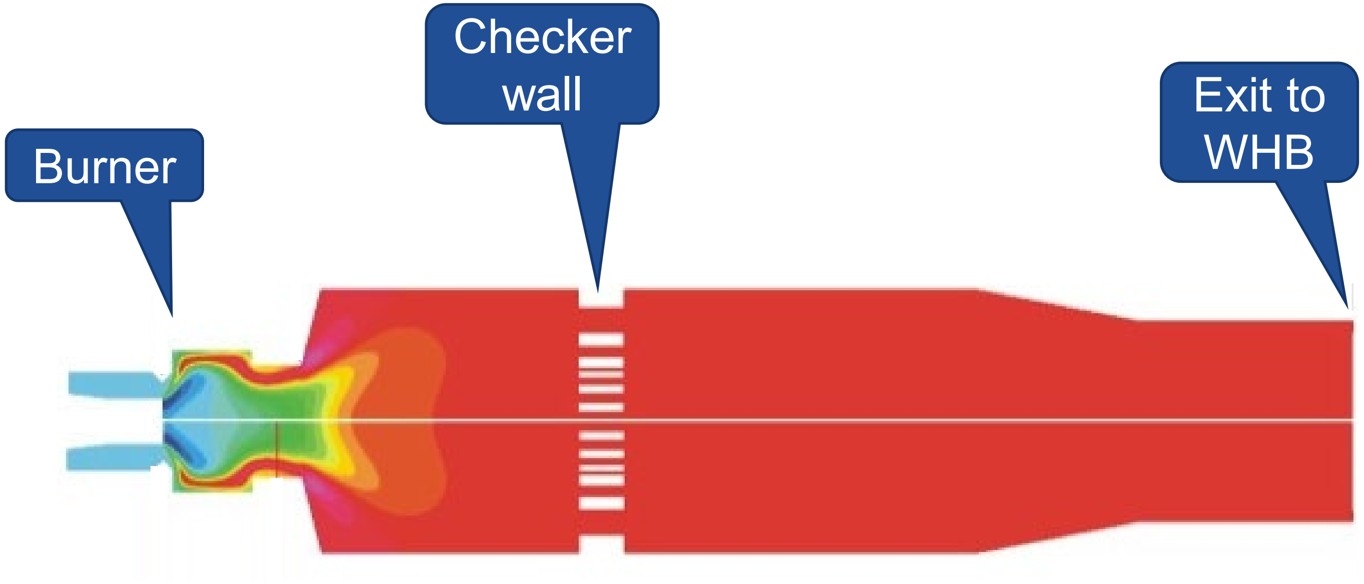
	Moles O_2 / Mole for oxidation	**Compare to H_2S**
H_2S	1.5 x 0.33 = 0.5	1.0
NH_3	0.75	1.5
CH_4	2.0	4
C_2H_6	3.5	7
C_3H_8	5.0	10
C_4H_{10}	6.5	13
C_5H_{12}	8.0	16
C_6H_{14}	9.5	19

Thermal Reactor

- Process objectives
  - Achieve maximum conversion of H_2S to Sulfur
  - Destroy feed impurities: NH_3, HC, BTEX
  - Provide long service life

- The Three T's
  - Temperature
  - Turbulence
  - Time

Thermal Reactor: Design Elements

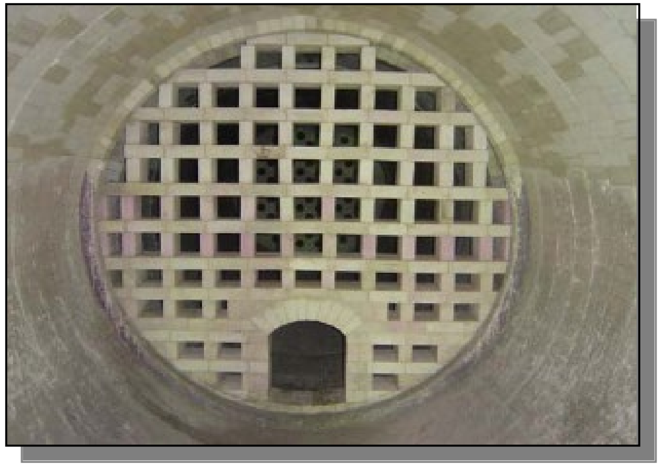


- Residence time 0.5-1.5 sec
- Complex heat shielding
  - Multiple layers of refractory
  - Rain shield
- Vessel wall temperature
  - Cool enough to avoid sulfidic corrosion
  - Warm enough to avoid acid dew point corrosion

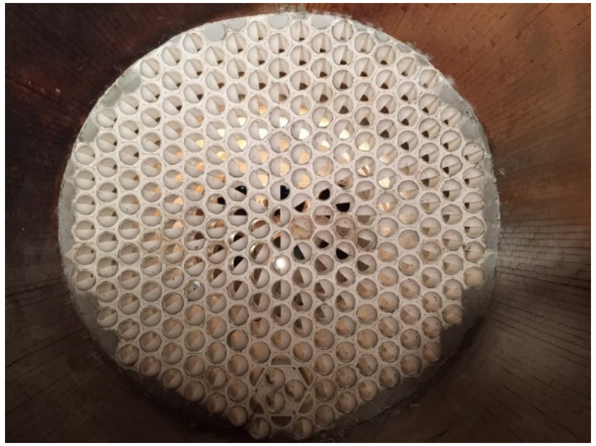
CFD Model Image Courtesy of HEC Technologies

Thermal Reactor: Design Elements

Choke Ring



Traditional
Checker Wall



VectorWall™

Courtesy Blasch
Precision Ceramics

Thermal Reactor

Source: LRGCC 2007 Fundamentals

Thermal Reactor

- Higher temperature is better for process chemistry
  - Higher conversion of H_2S
  - Better destruction of contaminants

- Strategies to increase temperature
  - Bypass part of the Acid Gas
  - Preheat the Combustion Air and / or Acid Gas
  - Fuel Gas Co-Firing
  - Oxygen Enrichment
  - Acid Gas Enrichment

WHB

- Process objectives
  - Cool process gas in preparation for conversion section (650°F)
  - Recover exothermic combustion heat as steam (350 – 600 psig)
  - Provide long service life

- Common failure point: WHB inlet tube sheet
  - Corrosive environment on process side: 2400°F with sulfur species
  - High pressure on utility side
  - Difficult to sufficiently cool the metal, especially at the tube-tube sheet joint

WHB Tubesheet with Ferrules

Source: LRGCC 2007 Fundamentals

Sulfur Condenser

- Process objectives
  - Cool the process stream to condense liquid sulfur (290 – 340°F)
  - Vapor / liquid separation in outlet channel head
  - Generates low pressure steam (50 psig)

- Operational limits with respect to vapor / liquid separation
  - > 5 lb / sec-ft^2 mass velocity in tubes can lead to droplet entrainment
  - < 1 lb / sec-ft^2 can lead to sulfur fog formation
  - Either of these conditions can impact sulfur recovery

Reheater

- Process objective
    - Increase process temperature to get desired reaction rates in converter
    - Target temperature set by converter outlet temperature

- Many heat sources can be used
    - Indirect reheat using steam (600 psig)
    - Hot gas bypass around condenser
    - Direct firing with acid gas or fuel gas

Converter

- Process objectives
  - Bring Claus reaction to equilibrium
  - Destroy COS and CS_2

- Converter design
  - Single bed of catalyst per converter vessel
  - 3 - 4’ bed depth
  - Gas Space Velocity
    - Alumina catalyst: 700 – 1000 hr^{-1}
    - Titania catalyst: 1200 – 1500 hr^{-1}

Converter catalysts

- Alumina
  - Least expensive: \$0.60 - \$0.80 / lb
  - Limited ability to destroy COS and CS_2
- Enhanced alumina
  - Moderate cost: \$1 - \$3 / lb
  - Intermediate performance between Alumina and Titania
- Titania
  - Most expensive: \$4 – \$5 / lb
  - More prone to BTEX degradation than Alumina
  - High conversion of COS and CS_2
  - Often installed as partial bed at the bottom of 1st converter

What’s left over

- Process gas leaving the last condenser is “Tail Gas”
- Typically requires further clean-up before emitting
- Representative composition of tail gas

58%	N_2
35%	H_2O
4%	CO_2 + CO
2%	H_2
0.4%	H_2S
0.2%	SO_2
0.1%	COS + CS_2
0.01%	Sulfur

Conclusion

- Claus Sulfur Recovery is a mature technology
- Many creative variations and improvements exist

- This presentation was an introduction to
  - Principal chemistry of the process
  - Major equipment common to most SRUs
  - Operating and Design considerations

- The next presentation will describe what can be done with the tail gas leaving the last sulfur condenser

Thank You

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