Plant Block Schematic

Gas & liquids from wells
- Field liquids removal
  - Field acid gas removal
  - Field dehydration
  - Field compression

Inlet receiving
- Water & solids
- Inlet compression
- Gas Treating
  - Dehydration
    - Helium recovery
    - Nitrogen rejection
      - Hydrocarbon recovery
        - Sulfur recovery
          - CO₂
            - Elemental Sulfur

- Liquids processing
  - Natural gasoline
  - NGLs
  - LNG
  - Sales gas

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Topics

Introduction

Properties of sulfur

Sulfur recovery processes
  - Claus Process
  - Claus Tail Gas Cleanup

Sulfur storage

Safety and environmental considerations
Introduction & Properties of Sulfur
Sulfur Crystals

http://www.irocks.com/minerals/specimen/34046

http://www.mccullagh.org/image/10d-5/sulfur.html
Molten Sulfur

http://www.kamgroupltd.com/En/Post/7/Basic-info-on-elemental-Sulfur(HSE)
Sulfur Usage & Prices

Natural gas & petroleum production accounts for the majority of sulfur production.

Primary consumption is agriculture & industry:
- 65% for farm fertilizer:
  - sulfur → sulfuric acid → phosphoric acid → fertilizer
- $50 per ton essentially disposal cost
- Chinese demand caused run-up in 2007-2008

“Cleaning up their act”, Gordon Cope, Hydrocarbon Engineering, pp 24-27, March 2011

Ref: http://ictulsa.com/energy/
Updated April 9, 2017
U.S. sulfur production

Recovered from natural gas, petroleum refining, and coking operations

Frasch process
**Sulfur Chemical Structure**

Pure sulfur exists as $S_X$ where $X = 1$ to 8

The dominant species are $S_2$, $S_6$, & $S_8$

May be in ring structure or open chain

Species determined by temperature

This composition greatly affects its properties!

Octasulfur, $S_8$
Sulfur Vapor Species

![Graph showing the mol fraction of sulfur vapor species vs. temperature in °F. The graph includes curves for S_8, S_6, and S_2.](image-url)
Viscosity of Molten Sulfur

![Graph showing the viscosity of molten sulfur as a function of temperature. The x-axis represents temperature in °C, ranging from 300 to 800. The y-axis represents viscosity in cp, ranging from $10^0$ to $10^5$. The graph includes a curve for pure sulfur.]
Viscosity of Molten Sulfur

![Graph showing viscosity of molten sulfur vs. temperature and H₂S partial pressure.](Image)

**Temperature, °C**

300 400 500 600 700 800

**Viscosity, cp**

10^0 10^1 10^2 10^3 10^4 10^5

**H₂S Partial Pressure, psia**

- 14.7
- 1.5
- 0.15
- 0.015
- 0.0015
- 0.001

**Pure Sulfur**
Viscosity of liquid sulfur

![Graph showing the viscosity of liquid sulfur as a function of temperature. The graph includes data for water at 60°F = 1.12 cP and heavy machine oil at 60°F = 660 cP.](image)
Properties of sulfur
Sulfur Recovery

Typically a modified Claus process

- $\text{H}_2\text{S}$ rich stream burned with 1/3 stoichiometric air. Hot gases are then passed over alumina catalyst to produce free sulfur

  Combustion: $\text{H}_2\text{S} + 1.5\cdot\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{SO}_2$

  Claus Reaction: $2\cdot\text{H}_2\text{S} + \text{SO}_2 \leftrightarrow 2\cdot\text{H}_2\text{O} + 3\cdot\text{S}$

- Sulfur formation reaction mildly exothermic

- Sulfur conversion reactors kept above 400°F (sulfur dew point)

The Claus reaction is reversible – therefore, 100% conversion can never be achieved

- Practically, Claus units are limited to about 96% recovery

- Tail gas units are used to provide improved conversion
## Modified Claus Process

**Petroleum Refining Technology & Economics – 5th Ed.**
by James Gary, Glenn Handwerk, & Mark Kaiser, CRC Press, 2007

**GPSA Engineering Data Book**, 13th ed., Fig. 22-2, 2012

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**Theoretical Equilibrium Percent Conversion of Hydrogen Sulfide to Sulfur**

1. Acid gas from wellhead facilities
2. Acid gas from refinery treaters
3. Pure H₂S

Converters: 400 – 700°F

Burner & Reactor above 1800°F

2300-2700°F for NH₃ destruction

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**FIGURE 13.7** Once-through Claus sulfur process.
Temperature Regimes for the Claus Process

THE CLAUS REACTION

\[ 2 \text{H}_2\text{S} + \text{SO}_2 \leftrightarrow \frac{3}{n} \text{S}_n + 2 \text{H}_2\text{O} \]

What Limits the Reaction?
- Reaction Products
- Water and sulfur
- Operating Temperature
- Reactant Stoichiometry

Catalytic Converters

Reaction Furnace

Catalytic Region (Exothermic)

Thermal Region (Endothermic)

% Conversion

Temperature, °F
Equilibrium Conversion of H\textsubscript{2}S to S

Temperature, °C

Percent Conversion of H\textsubscript{2}S to Sulfur

melting point

boiling point

Temperature, °F
Equilibrium Conversion of H$_2$S to S

Temperature, °F

Percent Conversion of H$_2$S to Sulfur

Claus #1
Claus #2
Claus #3
Furnace & waste heat boiler 1700 - 2400°F

boiling point
melting point
Hydrocarbons in the Claus Process

Oxidation/Combustion

\[ \text{CH}_4 + 2 \text{O}_2 \rightarrow 2 \text{H}_2\text{O} + \text{CO}_2 + \text{Heat} \]

Partial Oxidation/Combustion

\[ \text{CH}_4 + \frac{3}{2} \text{O}_2 \rightarrow \text{CO} + 2\text{H}_2\text{O} + \text{Heat} \]

Undesirable Side Reactions

\[ 2\text{CO} \Leftrightarrow \text{CO}_2 + \text{C} \]
\[ \text{CH}_4 \rightarrow 2\text{H}_2 + \text{C} \]
\[ \text{C} + \text{S}_2 \rightarrow \text{CS}_2 \]
\[ \text{H}_2\text{S} + \text{CO}_2 + \text{heat} \Leftrightarrow \text{H}_2\text{O} + \text{COS} \]

Thermal Reaction Kinetics: \( \text{H}_2\text{S} \gg \text{CH}_4 > \text{NH}_3 \)
Claus Process

Use multiple stages to obtain highest conversion
  - Typically three

Various flow patterns
  - Straight-through – best, used whenever possible
  - Split flow – best at low H₂S feed concentrations (5 to 30 mol% H₂S)
  - Sulfur recycle < 5% H2S
  - Direct oxidation < 5% H2S
Claus Process

Claus unit feed usually contains H₂S and CO₂

High concentrations of noncombustible components (CO₂, N₂)
  ▪ Lower flame temperature
  ▪ Difficult to maintain stable combustion furnace flame temperatures below 1700°F

Solutions include
  ▪ Preheating air
  ▪ Preheating acid gas feed
  ▪ Enriching oxygen in air
  ▪ Using split-flow process
Split-flow Claus Process

- Acid gas
- LP steam
- Gas reheater
- HP steam
- Claus #1
- Claus #2
- Claus #3
- Condenser
- Boiler feed water (BFW)
- Reaction furnace
- Air
- Sulfur
- Tail gas
## Typical Claus Configurations

<table>
<thead>
<tr>
<th>Approximate concentration of $\text{H}_2\text{S}$ in feed (mol%)</th>
<th>Process variation</th>
</tr>
</thead>
<tbody>
<tr>
<td>55 - 100</td>
<td>Straight-through</td>
</tr>
<tr>
<td>30 - 55</td>
<td>Straight-through + acid gas and/or air preheat</td>
</tr>
<tr>
<td>15 - 30</td>
<td>Split-flow or acid gas and/or air preheat</td>
</tr>
<tr>
<td>10 - 15</td>
<td>Split-flow with acid gas and/or air preheat</td>
</tr>
<tr>
<td>5 - 10</td>
<td>Split-flow with fuel added, $\text{O}_2$ enrichment, or with acid gas and air preheat</td>
</tr>
</tbody>
</table>
Tail Gas Clean Up

Three process categories:

Direct oxidation of $\text{H}_2\text{S}$ to sulfur   (Superclaus)

$$2 \text{H}_2\text{S} + \text{O}_2 \rightarrow 2 \text{S} + 2 \text{H}_2\text{O}$$

Sub-dew point Claus processes   (Cold Bed Adsorption)

$\text{SO}_2$ reduction and recovery of $\text{H}_2\text{S}$   (SCOT)
Claus Tail Gas Cleanup

Conventional 3-stage Claus units recover 96 to 97.5% of sulfur

- Remainder was burned to $\text{SO}_2$ and vented
- Adding fourth stage results in 97 to 98.5% recovery

Regulations now require 99.8 to 99.9% recovery

Meeting regulations requires modified technology
Shell Claus Offgas Treating (SCOT)

Four step process:
- Mix feed with reducing gas (H₂ and CO)
- Convert all sulfur compounds to H₂S
- Cool the reactor gas
- Strip H₂S using amine
**SCOT Process**

Mix Claus tail gas with H₂ and CO and heat in inline burner

Catalytically convert all sulfur compounds to H₂S

Reactions:
- \( \text{SO}_2 + 3\text{H}_2 \rightarrow \text{H}_2\text{S} + 2\text{H}_2\text{O} \)
- \( \text{S}_2 + 2\text{H}_2 \rightarrow 2\text{H}_2\text{S} \)
- \( \text{COS} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2\text{S} \)
- \( \text{CS}_2 + 2\text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2\text{S} \)

Cool reactor gas (exiting at ~570°F) in waste heat exchanger and water wash to complete cooling.

Strip H₂S from gas & recycle to Claus

Typically use MDEA – can get to low H₂S levels in Stack Gas & slip CO₂ so it doesn’t build up in the recycle gas
Alternate Conversion & Sulfur Removal Processes

Selectox™
- Proprietary catalyst removes need for furnace

CrystaSulf
- Uses modified liquid-phase Claus reaction
- Elemental sulfur removed by filtration
- Mid-range process to handle sulfur amounts between 0.1 and 20 tons per day
Sulfur storage
Sulfur Piles

Sulfur pile at North Vancouver, B.C., Canada, brought by rail from the province of Alberta

Ref: Wikimedia Commons
Sulfur “Blocking”
Summary
Summary

Natural gas & petroleum production accounts for the majority of sulfur production
- Primary consumption is agriculture & industry, 65% for farm fertilizer.
- $50 per ton essentially disposal cost

Sulfur properties depends upon which sulfur species are present
- Dominant species are S$_2$, S$_6$, & S$_8$

Dominant sulfur recovery process is modified Claus
- Extent controlled by chemical equilibrium, so can only get 96% conversion
- Tail Gas Cleanup process required for very low sulfur emissions

Sulfur storage
- Temporary storage as hot liquid
- Shipping in pellets & long-term bulk storage as blocks