Sulfur Recovery

Chapter 16

Based on presentation by Prof. Art Kidnay
Plant Block Schematic

Adapted from Figure 7.1, *Fundamentals of Natural Gas Processing*, 2nd ed. Kidnay, Parrish, & McCartney
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)
World Consumption of Sulfur

Primary usage of sulfur to make sulfuric acid (90 – 95%)

- Other major uses are rubber processing, cosmetics, & pharmaceutical applications

China primary market

Report published December 2017
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 December 24, 2018
U.S. sulfur production
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 as a function of temperature. The graph plots mol fraction of species on the y-axis and temperature in °F on the x-axis. Three species are labeled: S_8, S_6, and S_2.]
Viscosity of Molten Sulfur

Viscosity, cp

Temperature, °C

Pure Sulfur
Viscosity of Molten Sulfur

- Temperature, °C
- Viscosity, cp
- H₂S Partial Pressure, psia

- 0.0015
- 0.015
- 0.15
- 1.5
- 14.7

Pure Sulfur

Updated: January 4, 2019
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Viscosity of liquid sulfur

- Heavy machine oil at 60°F = 660 cP
- Water at 60°F = 1.12 cP
Sulfur recovery processes
Sulfur Recovery

Typically a modified Claus process

- H$_2$S rich stream burned with 1/3 stoichiometric air. Hot gases are then passed over alumina catalyst to produce free sulfur
  
  **Combustion:**  \[ H_2S + 1.5\cdot O_2 \rightarrow H_2O + SO_2 \]
  
  **Claus Reaction:**  \[ 2\cdot H_2S + SO_2 \rightleftharpoons 2\cdot H_2O + 3\cdot S \]

- 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

![Diagram of Claus Process]

**FIGURE 13.7** Once-through Claus sulfur process.

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

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

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

- **Converters 400 – 700°F**
- **Burner & Reactor above 1800°F**
  - 2300-2700°F for NH₃ destruction

**NOTE:**
BFW = BOILER FEED WATER
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

**Graphs:**
- % Conversion vs. Temperature
- Catalytic Converters
- Reaction Furnace
- Catalytic Region (Exothermic)
- Thermal Region (Endothermic)
Straight-through Claus Process

- Waste heat boiler
- Gas reheat HP steam
- Acid gas
- Boiler feed water (BFW)
- Reaction furnace
- 110°F, 8 psig
- Air
- 1700 - 2400°F

- Claus #1
  - 450°F gas reheat
  - 600°F steam
  - 375°F LP steam
  - 590°F
  - 450°F sulfur
  - BFW

- Claus #2
  - 420°F gas reheat
  - 453°F steam
  - 350°F LP steam
  - 420°F
  - 453°F sulfur
  - BFW

- Claus #3
  - 400°F gas reheat
  - 300°F steam
  - 407°F LP steam
  - 400°F
  - 407°F sulfur
  - BFW

Tail gas

Temperature values:
- 110°F
- 8 psig
- 600°F
- 375°F
- 590°F
- 450°F
- 420°F
- 453°F
- 350°F
- 400°F
- 407°F
- 270°F
- 1700 - 2400°F
Equilibrium Conversion of $\text{H}_2\text{S}$ to $\text{S}$

% Conversion of $\text{H}_2\text{S}$ to Sulfur

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>204</th>
<th>427</th>
<th>649</th>
<th>871</th>
<th>1093</th>
<th>1316</th>
<th>1538</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature, °F</td>
<td>393</td>
<td>799</td>
<td>1192</td>
<td>1484</td>
<td>1776</td>
<td>2068</td>
<td>2360</td>
</tr>
</tbody>
</table>

- Boiling point
- Melting point
Equilibrium Conversion of H\textsubscript{2}S to S

![Graph showing equilibrium conversion of H\textsubscript{2}S to S. The graph plots percent conversion of H\textsubscript{2}S to sulfur against temperature in °F. Key points include:
- Claus #1
- Claus #2
- Claus #3
- Furnace & waste heat boiler: 1700 - 2400°F
- Melting point
- Boiling point

Temperature, °F

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

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Hydrocarbons in the Claus Process

HYDROCARBONS AND THEIR DESTRUCTION

Oxidation/Combustion

CH₄ + 2 O₂ → 2 H₂O + CO₂ + Heat

Partial Oxidation/Combustion

CH₄ + 3/2 O₂ → CO + 2H₂O + Heat

Undesirable Side Reactions

2CO ↔ CO₂ + C
CH₄ → 2H₂ + C
C + S₂ → CS₂

H₂S + CO₂ + heat ↔ H₂O + COS

Thermal Reaction Kinetics: H₂S >> CH₄ > NH₃
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 $\text{H}_2\text{S}$ feed concentrations (5 to 30 mol% $\text{H}_2\text{S}$)
- Sulfur recycle < 5% H2S
- Direct oxidation < 5% H2S
Claus Process

Claus unit feed usually contains H$_2$S and CO$_2$

High concentrations of noncombustible components (CO$_2$, N$_2$)

- 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
- Air
- Boiler feed water (BFW)
- Reaction furnace
- Gas reheat
- LP steam
- HP steam
- Claus #1
- Claus #2
- Claus #3
- Condenser
- BFW
- 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 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 $\text{H}_2$ and CO and heat in inline burner

Catalytically convert all sulfur compounds to $\text{H}_2\text{S}$

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 $\sim 570^\circ\text{F}$) in waste heat exchanger and water wash to complete cooling.

Strip $\text{H}_2\text{S}$ from gas & recycle to Claus

Typically use MDEA – can get to low $\text{H}_2\text{S}$ levels in Stack Gas & slip $\text{CO}_2$ 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