Sulfur Recovery

Chapter 16

Based on presentation by Prof. Art Kidnay
Plant Block Schematic
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

Thousand metric tons

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

Temperature, °F

Mol Fraction of Species

$S_8$

$S_6$

$S_2$
Viscosity of Molten Sulfur

Viscosity, cp

Temperature, °C
Viscosity of Molten Sulfur

H₂S Partial Pressure, psia

Viscosity, cp

Temperature, °C

Updated: June 3, 2017
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Viscosity of liquid sulfur

![Graph showing the viscosity of liquid sulfur as a function of temperature. The graph compares water at 60°F (1.12 cP) and a heavy machine oil at 60°F (660 cP).]
Properties of sulfur
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: \( 2\cdot H_2S + SO_2 \Leftrightarrow 2\cdot H_2O + 3\cdot S \)

- 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

**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

*Burner & Reactor above 1800°F*

*2300-2700°F for NH₃ destruction*

**Theoretical Equilibrium Percent Conversion of Hydrogen Sulfide to Sulfur¹**

1. ACID GAS FROM WELLHEAD FACILITIES
2. ACID GAS FROM REFINERY TREATER
3. PURE H₂S

1. **Converters 400 – 700°F**
2. **Burner & Reactor above 1800°F**
3. **2300-2700°F for NH₃ destruction**
Straight-through Claus Process

110°F, 8 psig

1700 - 2400°F

waste heat boiler

acid gas

1700 - 2400°F

reaction furnace

boiler feed water (BFW)

110°F, 8 psig

air

gas reheat

HP steam

600°F

steam

condenser

sulfur

BFW

Claus #1

450°F

gas reheat

375°F

Claus #2

420°F

gas reheat

350°F

Claus #3

400°F

gas reheat

300°F

sulfur

BFW

sulfur

tail gas

1700 - 2400°F
Temperature Regimes for the Claus Process

THE CLAUS REACTION

2 H₂S + SO₂ ⇌ 3/n Sₙ + 2 H₂O

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

% Conversion

Catalytic Converters
Reaction Furnace

Catalytic Region (Exothermic)
Thermal Region (Endothermic)

Temperature, °F

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Equilibrium Conversion of $\text{H}_2\text{S}$ to $\text{S}$
Equilibrium Conversion of $\text{H}_2\text{S}$ to $\text{S}$

![Graph showing the equilibrium conversion of $\text{H}_2\text{S}$ to $\text{S}$ as a function of temperature. The graph includes labels for melting point, boiling point, and the operating temperatures of Claus plants and a furnace & waste heat boiler.]

Temperature, °F

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

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

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Hydrocarbons in the Claus Process

**HYDROCARBONS AND THEIR DESTRUCTION**

**Oxidation/Combustion**

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

**Partial Oxidation/Combustion**

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

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

<table>
<thead>
<tr>
<th>Approximate concentration of H₂S 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, O₂ enrichment, or with acid gas and air preheat</td>
</tr>
</tbody>
</table>
Tail Gas Clean Up

Three process categories:

Direct oxidation of H$_2$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)

SO$_2$ reduction and recovery of H$_2$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