Oil Refineries

Overview, Unit Interrelationships, & Some Unique Perspectives

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Bechtel Corporation – 02/28/2023


SHELL OIL COMPANY
WOOD RIVER, ILLINOIS
REFINERY
1972

My Background

- **Over 12 years experience –**
  Retrofit and grass roots projects
- **University Course – Co-taught**
  Both Seniors and Graduate Students
- **Corporate Seminars – Taught**
- **Trained to “Cut Coke” at age 19**

Short to Intermediate Term Perspective

“Oil Demand Seen Hitting (All Time) Record in 2023”

- Wall Street Journal Headline - January 19, 2023 (Page B-11)

“The News of My Demise has been Greatly Exaggerated”

- Mark Twain

Definitions

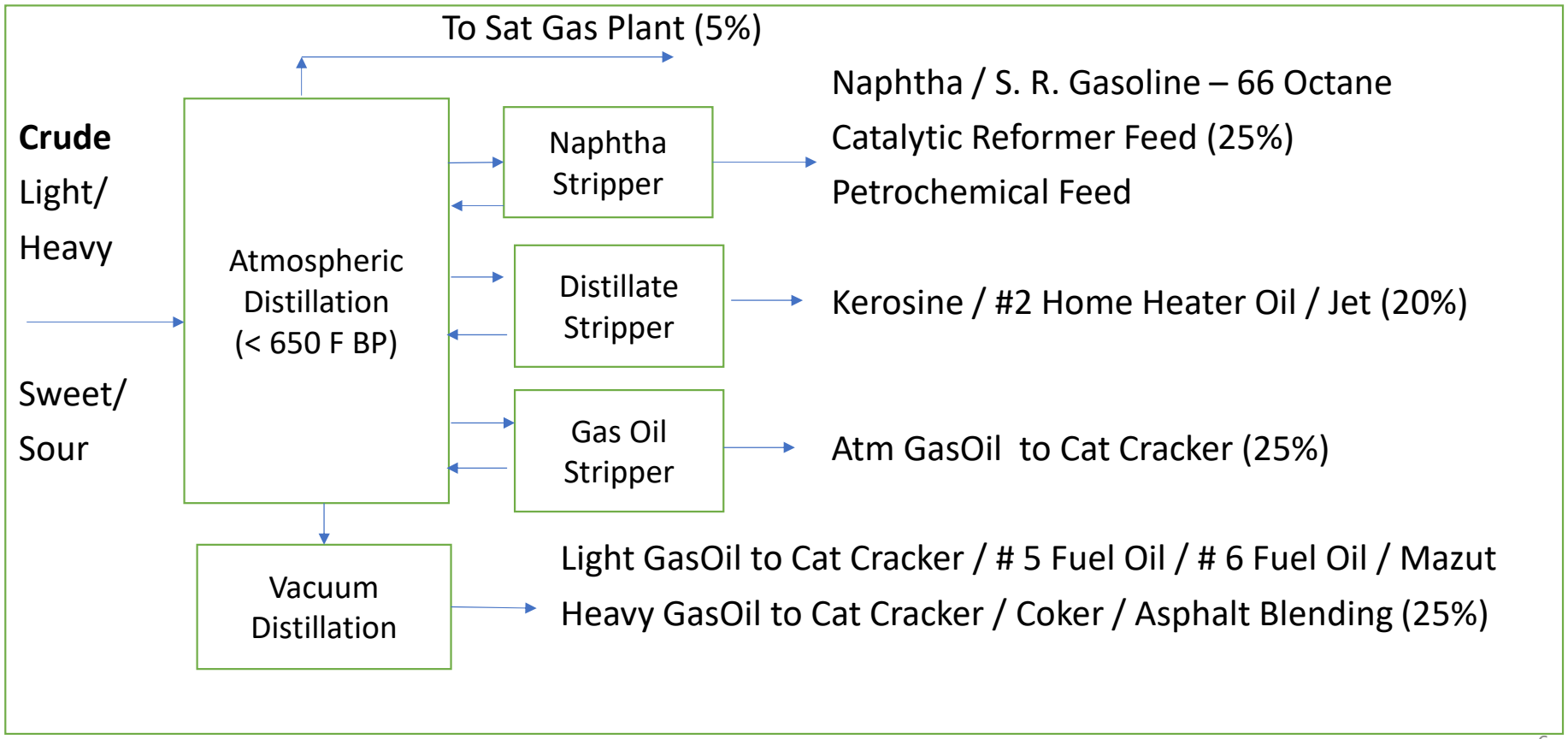
PONA ACRONYM

- P = Parafinic (Propane C-C)
- O = Olifinic (Propylene C=C)
- N = Napthinic (Cyclohexane – C6H12)
- A = Aromatic (Benzene – C6H6, BTX, etc.)

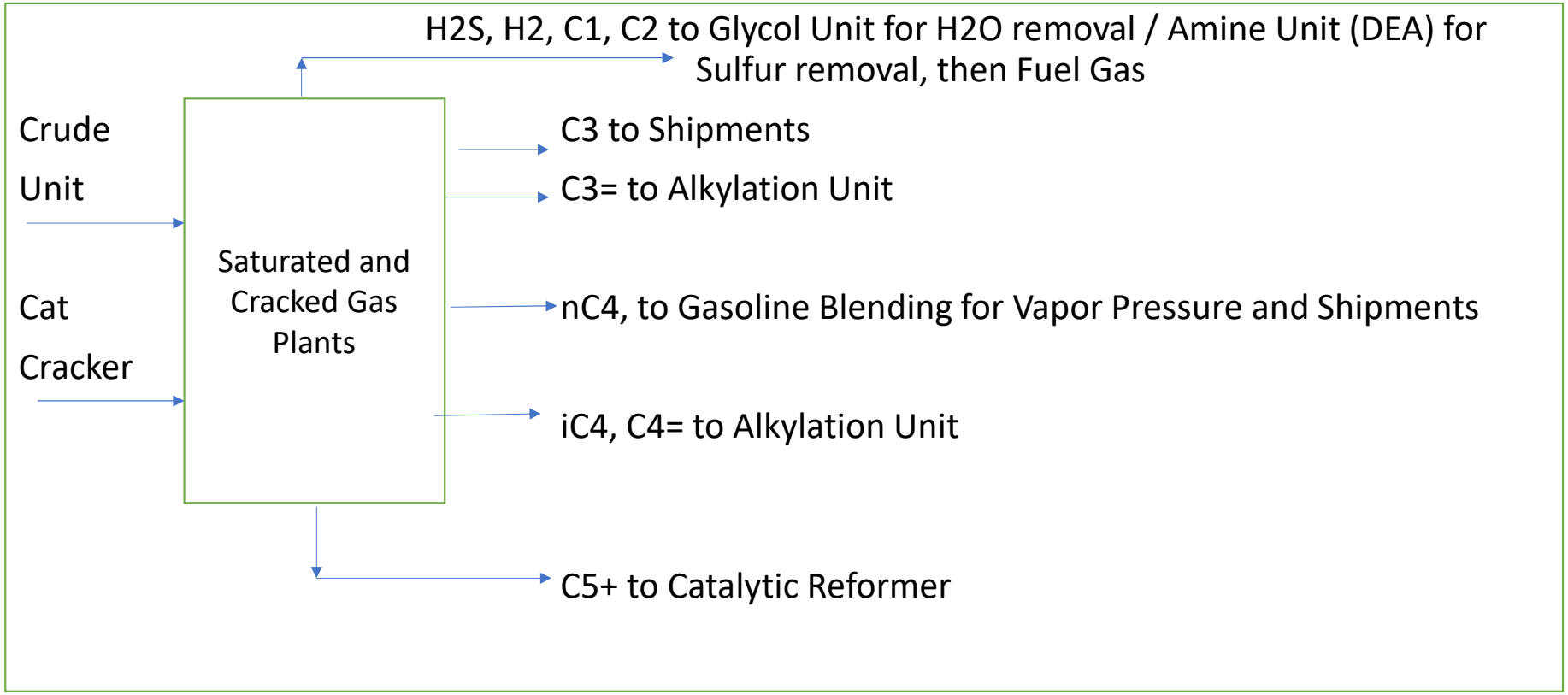
OCTANE DEFINITION

- 0 = n-Heptane 100 = i-Octane
- RON (Research Octane Number) - Highway
- MON (Motor Octane Number) – 900 RPM – City Streets

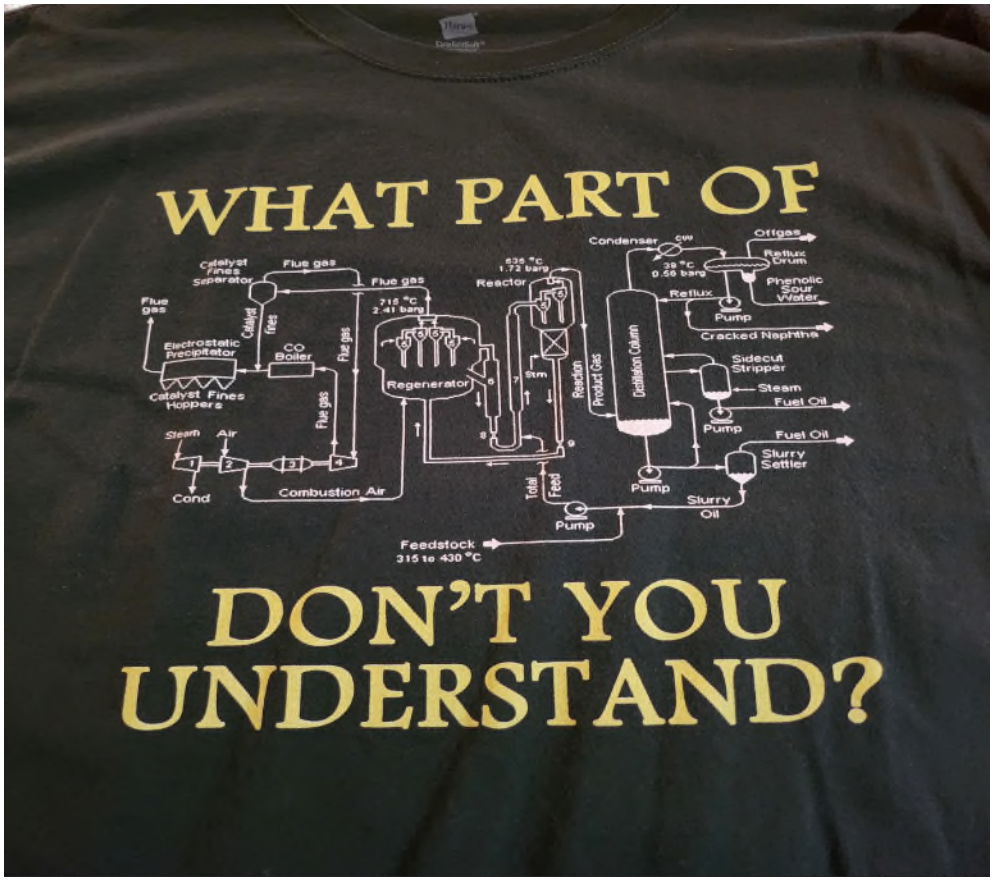
Units Block Diagram #1



Units Block Diagram #2

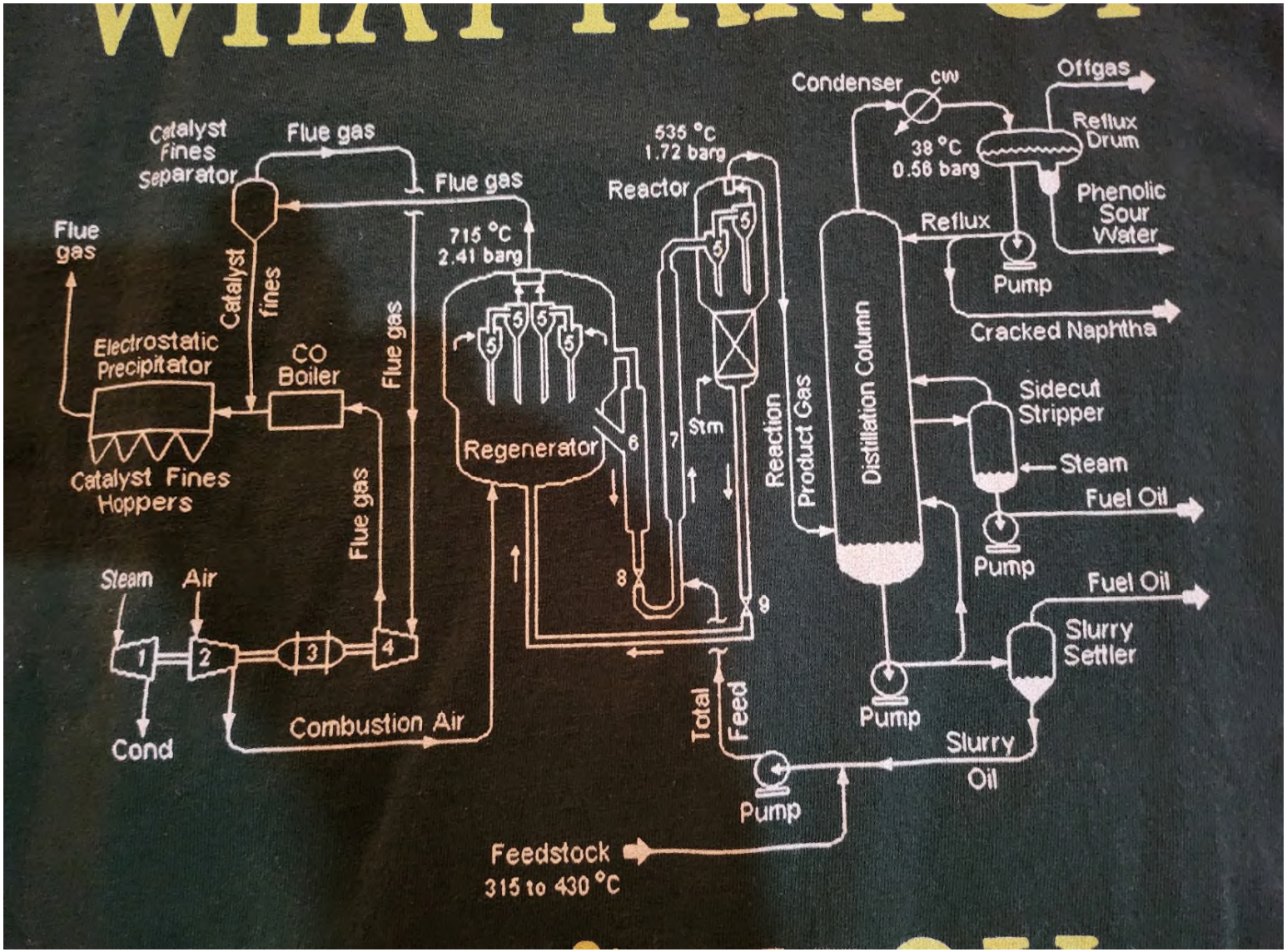


Fluid Catalytic Cracker



Fluid Cat Cracker

- Developed in WWII - Backbone of Profitability for an Oil Refinery
- GasOil Feed – Volume Gain 5 to 10%
- Fluidized Zeolite Silica-Alumnia Catalyst
- 1210 deg F – Gaseous Phase – Hexmetal and Troweled Refractory
- 70% Conversion to Gasoline – 87 Octane
- Reactor (Riser Now) and Regenerator
- Distillation
- Burn off Carbon Laydown on Catalyst in Regenerator
- Slide Gate Valve – Critical Wear / Reliability – Like Sand Blasting
- Cyclones – Critical Wear
- Electrostatic Precipitator


Catalyst Fines Separator
Flue gas
Flue gas
Flue gas
715 °C
2.41 barg
535 °C
1.72 barg
Reactor
Condenser
CW
Offgas
Reflux Drum
38 °C
0.56 barg
Phenolic Sour Water
Reflux
Pump
Cracked Naphtha
Catalyst fines
Electrostatic Precipitator
CO Boiler
Catalyst Fines Hoppers
Regenerator
Distillation Column
Sidecut Stripper
Steam
Fuel Oil
Pump
Fuel Oil
Slurry Settler
Steam
Air
Combustion Air
Cond
Total Feed
Pump
Slurry Oil
Pump
Feedstock
315 to 430 °C

Alkylation Unit

- IsoButane + Propylene -> IsoHeptane
- IsoButane + Butylene -> IsoOctane (Alkylate) (Most of it)

- Catalysts:
  - H2SO4 – Higher Capital Cost
  - HF – More Special Handling / Danger (Phillips Developed)

- Results in high octane: IsoOctane is 100 Octane
  - AvGas – Aviation Gasoline – WWII (Higher Compression Piston Engines)
  - MoGas – Motor Gasoline – Blending Component

Hydrotreaters

- NHT – Naphtha Hydrotreater
- DHT – Distillate Hydrotreater

- C=S + 2H2 → C=H2 + H2S
- Mostly all feeds from Atmosphere Distillation Unit
- Add H2, over a Nickel – Cobalt Catalyst


QANTAS
LONGREACH
THE SPIRIT OF AUSTRALIA

Catalytic Reformer

- Takes Paraffinic (Straight Run, Low Octane)
- Makes Cyclic – Naphthenic and Aromatic
- Platinum Catalyst (Until Catalytic Converters, was largest use in the world.)
- Gives up Hydrogen

- Increases Octane (harder to Pre-Combust)
- E.g. Toluene has a 121 Octane
- Overall, 92 Octane

Delayed Coker - #1

- “A 19 year old’s perspective”

- Bottom of the Barrel – Bottom of Vacuum Flasher
- Some Very Heavy GasOil

- Cracking Furnace – 1250 F – High Velocity to Delayed Coking
- Coke Drum – Deposit Coke
- Then, Liquid Products to Fractionation

Delayed Coker - #2

- The Coke Drums

- Two (or Four) Drums – one on stream, other being cut
  - Cool Down, Steam Out (Purge)
  - De-Head - If you do too fast before fully steamed out – **You become a torch**
  - Cut Coke with Drill String, then 5,000 psig water jet, spiraling up
  - Coke Drops into a sluiceway. Either Scooped out or into Rail Cars.
  - Coke used with Coal in Power Plants, etc.

  - Needle Coke - Electrodes

Hydrogen Plant (Steam Methane Reformer)

- Still Short of Hydrogen
- $CH_4 + H_2O \rightarrow 2H_2 + CO_2$

Glycol - Water Removal

- Removal of Water from Fuel Gas
- Absorber / Stripper
- Sour Water Stripper – NH3 from Water

Amine – H2S Removal from Fuel Gas

- Originally – MEA (Mono-Ethanol Amine)
    - Products of Degradation
- Today – Mostly DEA (Di-Ethanol Amine)
    - Absorber/ Stripper
- 70% H2S off the Stripper
- Sour Water Stripper – H2S Removal/ NH3 Removal

Sulfur Recovery #1

- Claus Process
  - 1883 – Dr. Claus Developed
  - $H_2S + 3/2\ O_2 \rightarrow SO_2 + H_2O$
  - Combust 1/3 of H_2S (O_2 feed controlled)
  - Bypass 2/3 of H_2S around burner
  - $2\ H_2S + SO_2 \rightarrow 3\ S$ (elemental) $+ 2\ H_2O$ (Alumina III catalyst)
  - Problem – COS, CS_2, and NH_3 left un-combusted

Sulfur Recovery #2

- Modified Claus (Most Popular)
  - All feed (usually 70% H_2S) through burner
  - $H_2S + 3/2\ O_2 \rightarrow SO_2 + H_2O$
  - Combust 1/3 of H_2S (based on analyzer after the burner)
  - $2\ H_2S + SO_2 \rightarrow 3\ S$ (elemental) $+ 2\ H_2O$ (Alumina III catalyst)

  - COS and CS_2 and NH_3 combusted with 1 sec. residence time in burner

  - THEN – Cooled to condense S (elemental) (65% conversion)
  - Stage 2 – Reheat, Catalyst Bed, Condense S (elemental) (90% conversion)
  - Stage 3 – Repeat (95% conversion)
  - Diminishing Return – Not Good enough for Environmental

Sulfur Recovery #3 – Tail Gas Unit

- SCOT (Shell Claus Offgas Treater)
  - The 1/3 Combusted SO2 Reduced over a Catalyst, with H2, to H2S
  - H2S absorbed in MDEA – Methyl Di Ethanol Amine
    - Methyl radical Sterically Hinders the CO2, now present, from Absorption
    - CO2 too big
    - H2S is smaller, okay
  - H2S Stripped, returned to head of Modified Claus
  - Gets H2S down to <10 ppm

- Tail Gas to incinerator, with fuel gas to get to SO2

Sulfur Recovery #4 - Issues

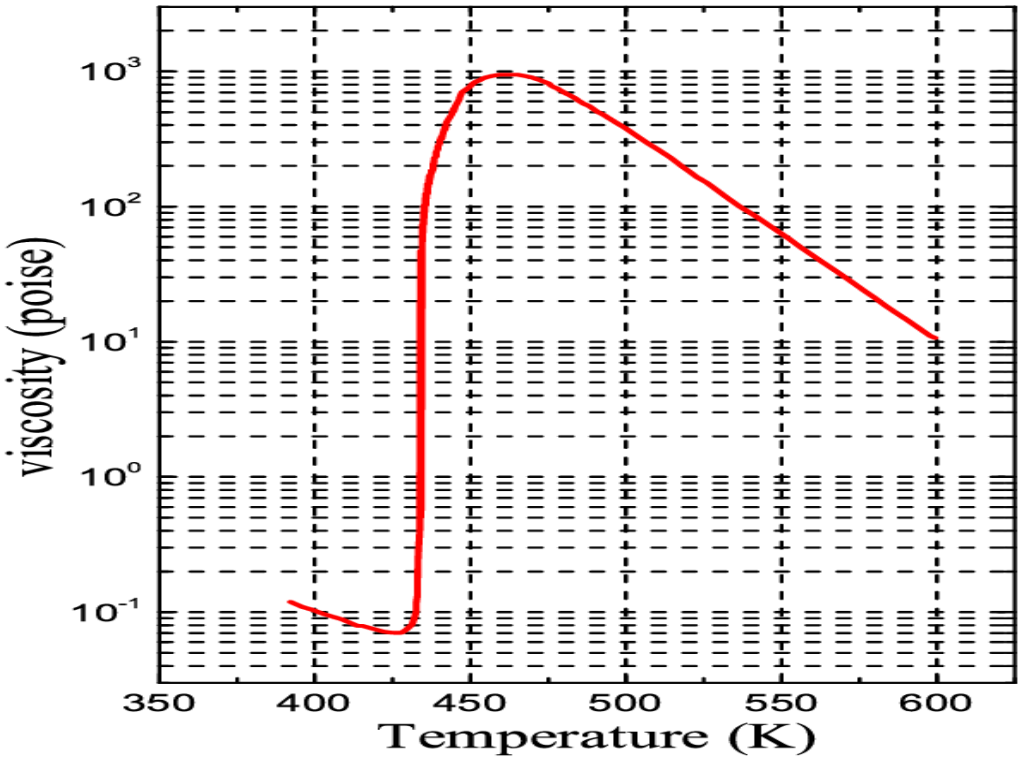
- H2S Concentrations in Air
  - Below 0.5 PPM not detectable
  - Above 10 PPM not detectable (cuts out sense of smell)
  - Above 25 PPM fatal

Sulfur Recovery #5 - Issues

- Liquid Sulfur Tight Temperature 50 F Window (Throughout)
  - Too Cool – Solid
  - Too Warm – Polymerizes “Sulfcrete”

- SO2 equilibrium with SO3
- With H2O present – H2SO4 in highly corrosive percentages
  - Eats through Carbon Steel
  - Eats through 304 Stainless Steel (3x cost of C.S.)
  - Eats through 316 Stainless Steel (5x cost of C.S.)
  - Alloy 20 (Carpenter Technologies) is Good (10x cost of C.S.)

Sulfur Viscosity vs. Temperature



Other Sulfur Recovery #6 - Technologies

- Stretford / Bevon Stretford
  - Vanadium Penta-Oxide
  - “Frothy Removal”
  - Oxidation / Reduction Process
  - Limited to smaller volumes
- Iron Sponge
  - “Rusty Wood Chips”
  - Non-regenerative – Dispose of Rusty Wood Chips
  - Limited to smaller volumes
- Cold Bed Adsorption (CBA)
  - Good for Gas, not Oil Refineries
  - Large Volumes
  - Not Used Much
- Others

Not Discussed

- Gasoline Blending
- Asphalt Blending
- Utilities
  - Power
  - Steam
  - Cooling Water
  - Process Water
- Waste Water Treatment
- Fire Protection
- Etc.