

Hot and Humid Claus

A New Perspective on Optimizing Claus Process

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Outline

- Claus reactor chemistry
- Humidity and adsorption
- Relationship: inhibition of reaction pathway
- Competing forces: equilibrium and activity
- Equilibrium: temperature and conversion
- Comprehensive kinetic expression
 - Higher temperature favors higher activity, higher conversion
 - Computational model
- Impact of temperature and water content:
 - Picking optimum temperatures for Claus reactors

Humidity



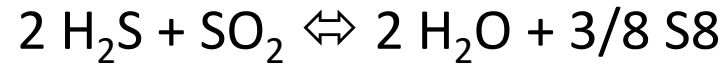
Relative Humidity – $\frac{\text{Partial pressure of water in atmosphere}}{\text{vapor pressure of water}} = P/P_o$

ratio of the partial pressure of water vapor to the equilibrium vapor pressure of water at a given temperature.

Relative humidity depends on temperature and the pressure of the system of interest. The same amount (concentration) of water vapor results in higher relative humidity in cool air than warm air.

Claus Reactor Chemistry

Reactions



Equilibrium

$$K_p = \frac{[\text{H}_2\text{O}]^2 * [\text{S}_8]^{3/8}}{[\text{H}_2\text{S}]^2 * [\text{SO}_2]}$$

Equilibrium Constraints:

Gamson and Elkins, McGregor – McBride,
Bennett & Meisen - Kellogg

Reaction kinetics:

Dalla Lana, George, McGregor

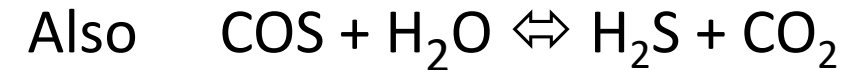
$$\text{Rate} = -k_o * P_{\text{H}_2\text{S}} * P_{\text{SO}_2}^{0.5} / (1 + K_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}})$$

k_o = Arrhenius function, $A \exp(-E_a/RT)$



Equilibrium

$$K_p = \frac{[\text{H}_2\text{O}]^2 * [\text{S}_6]^{3/6}}{[\text{H}_2\text{S}]^2 * [\text{SO}_2]}$$



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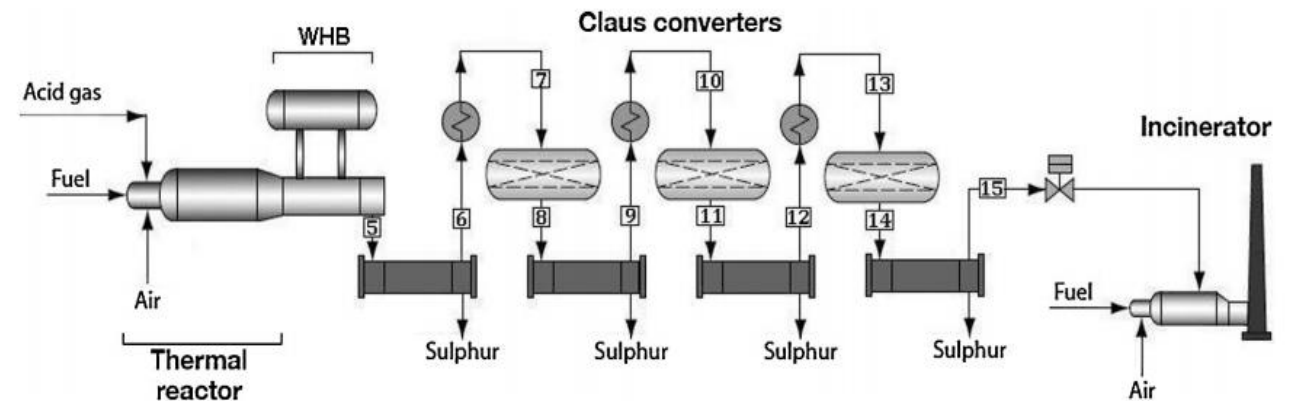


Fig. 1. PFD of a typical Claus straight through configuration sulfur recovery unit [40].

Alumina

Alumina: Al_2O_3 : versatile, varied

from high surface area to refractory to dense abrasive to jewel stone

- Activated Alumina:
- 250 – 350 m²/g surface area, porous with basic sites –
- attractive to water and acids

Uses: Dessicant Catalyst Absorbate
properties are similar

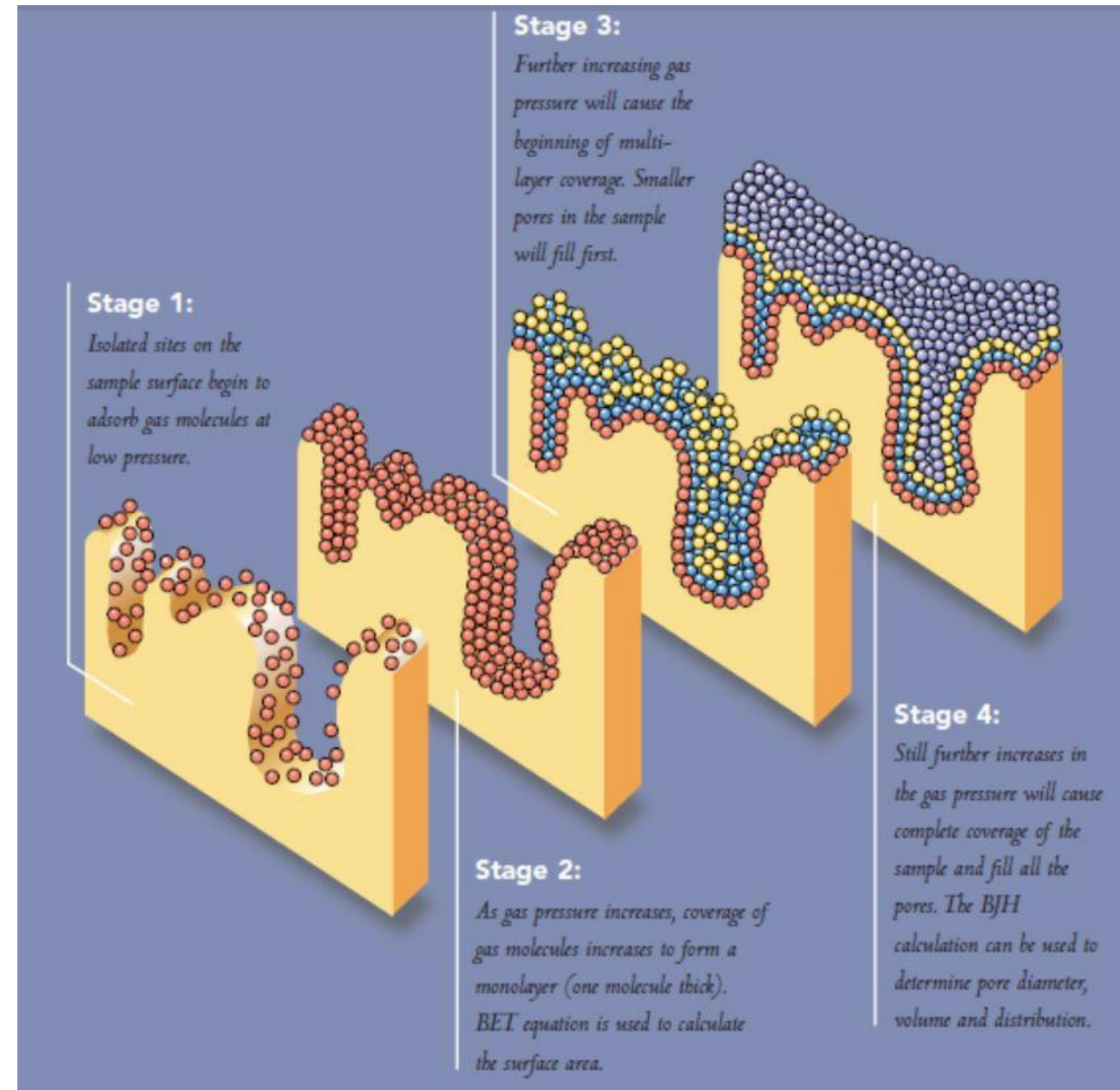
- Our interest: Claus catalyst

Activated Alumina - active basic sites
adsorption of water and acidic process gases



Water Adsorption on Alumina

- Water adsorption on alumina is in several stages and mechanisms:
 - **Chemisorption**
Strongest held, chemical bonds
 - **Physisorption**
Van der Waals forces, less strong, heat of condensation
 - **Pore filling/capillary trapping**
- Increasing partial pressure of water vapor increases adsorption
- Lower temperatures favor adsorption,
- Higher temperature for desorption



Equilibrium data plotted versus the relative humidity are essentially independent of temperature.

Adsorption and Humidity

Loading:

Function of partial pressure or Relative Humidity, typically expressed as
weight fraction of adsorbent or
fraction of total loading (or mono layer)

$$\text{Relative Humidity} = P/P_o$$

P = component partial pressure in system

P_o = vapor pressure component at system temperature

Operation:

Adsorption at higher humidity, ie, lower temperature, higher partial pressure

Regeneration at lower humidity, ie, higher temperature, but chemisorbed often remains

Claus conditions at higher temperatures but humidity in the chemisorption loading range

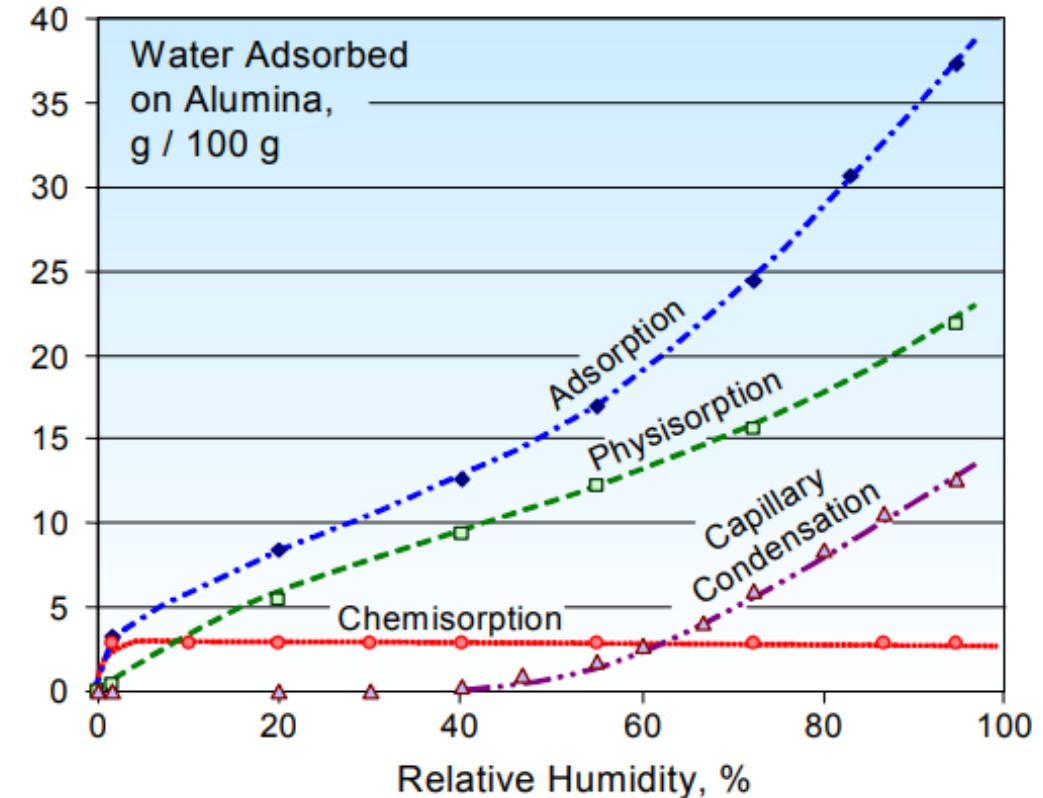


Figure 3. Relative participation of components making up the total water adsorption isotherm on activated alumina: chemisorption, physisorption and capillary condensation.

Representative of 300 m²/gram alumina; H₂O = 12.5 A² mono layer 7% wt , chemisorption ~ 3.5% wt
Chemisorption sites 50% mono layer

Adsorption

water concentration, pressure and temperature

Adsorption Equations:

Langmuir adsorption – mono layer

$$v/v_m = KP/(1+KP)$$

Brunauer–Emmett–Teller (BET)– multi-layer, physical

$$v = v_m * c * P / [(P - P_o) * (1 + (c - 1) * (P / P_o))]$$

v = vol adsorbed; v_m = volume mono layer

K = Adsorption Equil Coefficient (k/k_r)^{*}

P = partial pressure = $[H_2O] * \text{Pressure}$

P_o = Vapor Pressure, $f(\text{Temperature})$

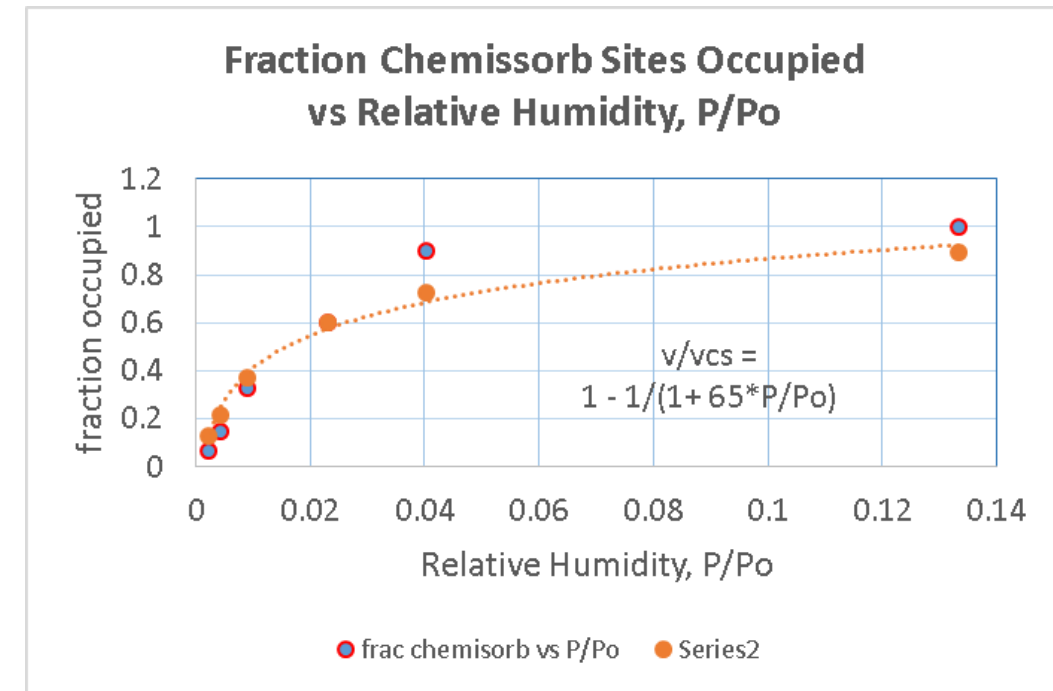
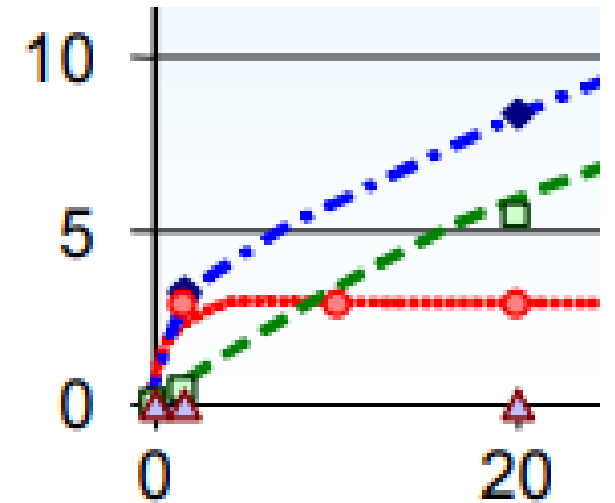
Proposing using $K = B/\text{Vapor Pressure}$: $KP = B * P/P_o$

Can this be applied to the chemisorb layer?

$$v/v_{\text{chemi}} = B * P/P_o / (1 + B * P/P_o)$$

$$\text{active site vacancy} = (1 - v/v_{\text{chemi}}) = 1 / (1 + B * P/P_o)$$

^{*}for water and active sites, K varies as adsorption energy is a function of loading and temperature.



Humidity in Claus Process

Water Partial Pressures in Process

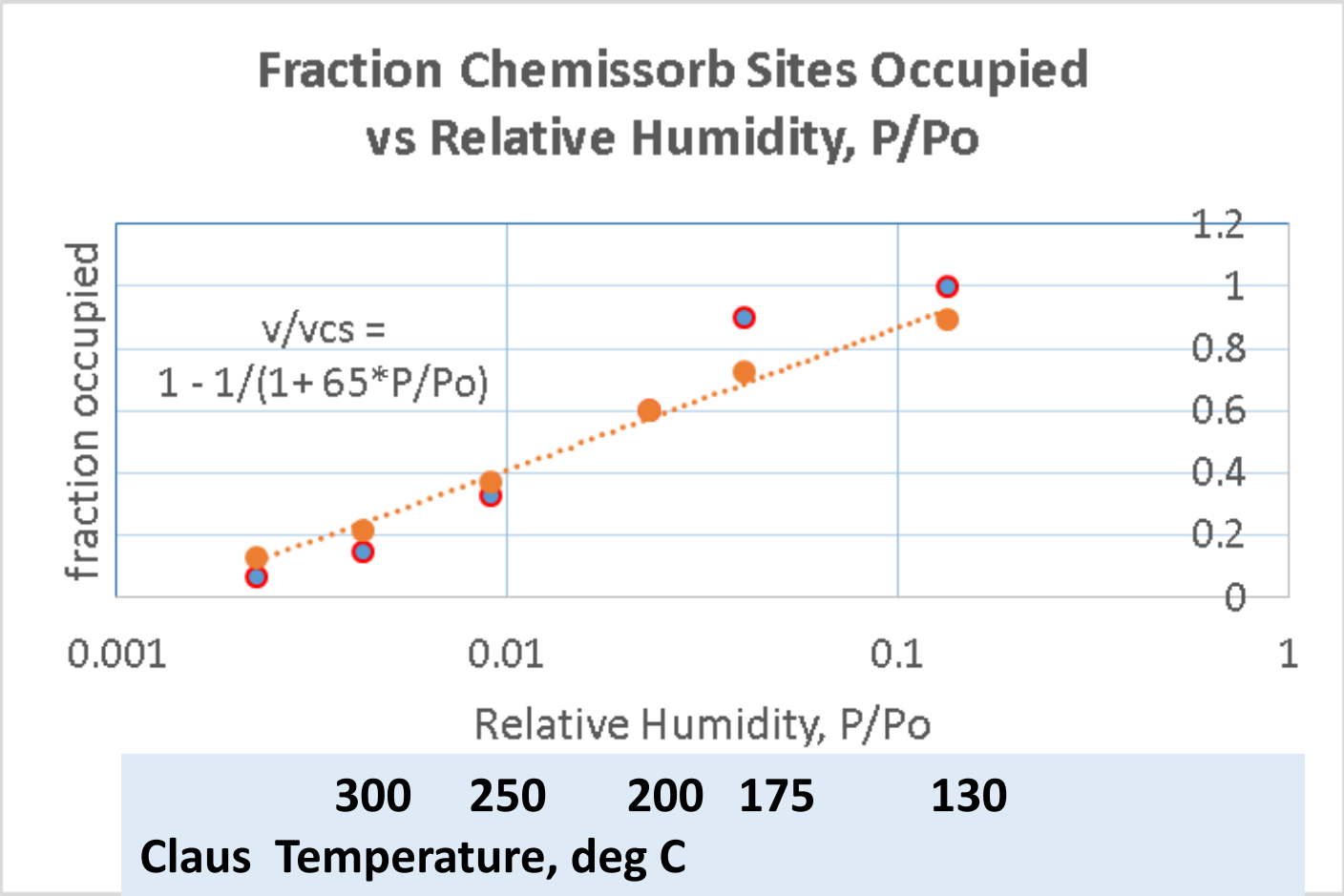
Bed	1	2	3	TG	CBA
H2O.%	22	30	33	34	34
Bara	1.6	1.4	1.2	1.1	1
P, bara	0.37	0.42	0.41	0.37	0.34

Water Vapor Pressure

T, °C	300	250	200	220	130
Po bara	86	39	15	23	2.7

Humidity

P/Po	0.004	0.01	0.026	0.016	0.13
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Claus Reaction Kinetics

- Hougen-Hinselwood adsorption:

impact on kinetics, rate = - $k_o K_a P_a / (1 + K_a P_a + K_r K_r + \dots)$

vacancy = $1 / (1 + K_a P_a + K_r K_r + \dots) = 1 / (1 + K P_{H_2O})$;

$K P_{H_2O} \gg K P_{SO_2}, K P_{H_2S}, \text{ etc } \dots \text{ or } \dots K P_{H_2O} \sim K P_{H_2O} + K P_{SO_2}$

- Claus kinetic expression (McGregor/Dalla Lana/George) is similar form

rate $H_2S = - k_o * P_{H_2S} * P_{SO_2}^{0.5} / (1 + 0.004 * P_{H_2O})$

and using humidity concept:

$$\text{rate}_{[H_2S]} = - \frac{k_o * [H_2S - H_2S_{eq}] * [SO_2 - SO_2_{eq}]^{0.5} * P^{1.5}}{(1 + 65 * [H_2O] * P/P_o)^{1.5}}$$

$k_o = A * \exp(-E_a / R T)$ $A = 6500$; $E_a / R = 30770 / 8.314 = 3700 \text{ K}$

with equilibrium offset: $[H_2S - H_2S_{eq}]$

or

$$\text{rate}_{[H_2S]} = \{k_o [H_2S] * [SO_2]^{0.5} * P^{1.5} - k_o / K_p^{0.5} * [H_2O] * [S_8]^{3/16} * P^{1.19}\} / (1 + 65 * [H_2O] * P/P_o)^{1.5}$$

concentration is raised to 1.5 power, so pressure and vacancy also to 1.5 power

Equilibrium

Gamson and Elkins -Kelly

McGregor – McBride,

Bennett & Meisen - Kellogg

Reaction completion is temperature dependent,
full conversion at melting point of elemental sulfur

S8 and S6 equilibrium distinct and differ

Lowest temperature in final stage (third bed) but
humidity inhibition strongest

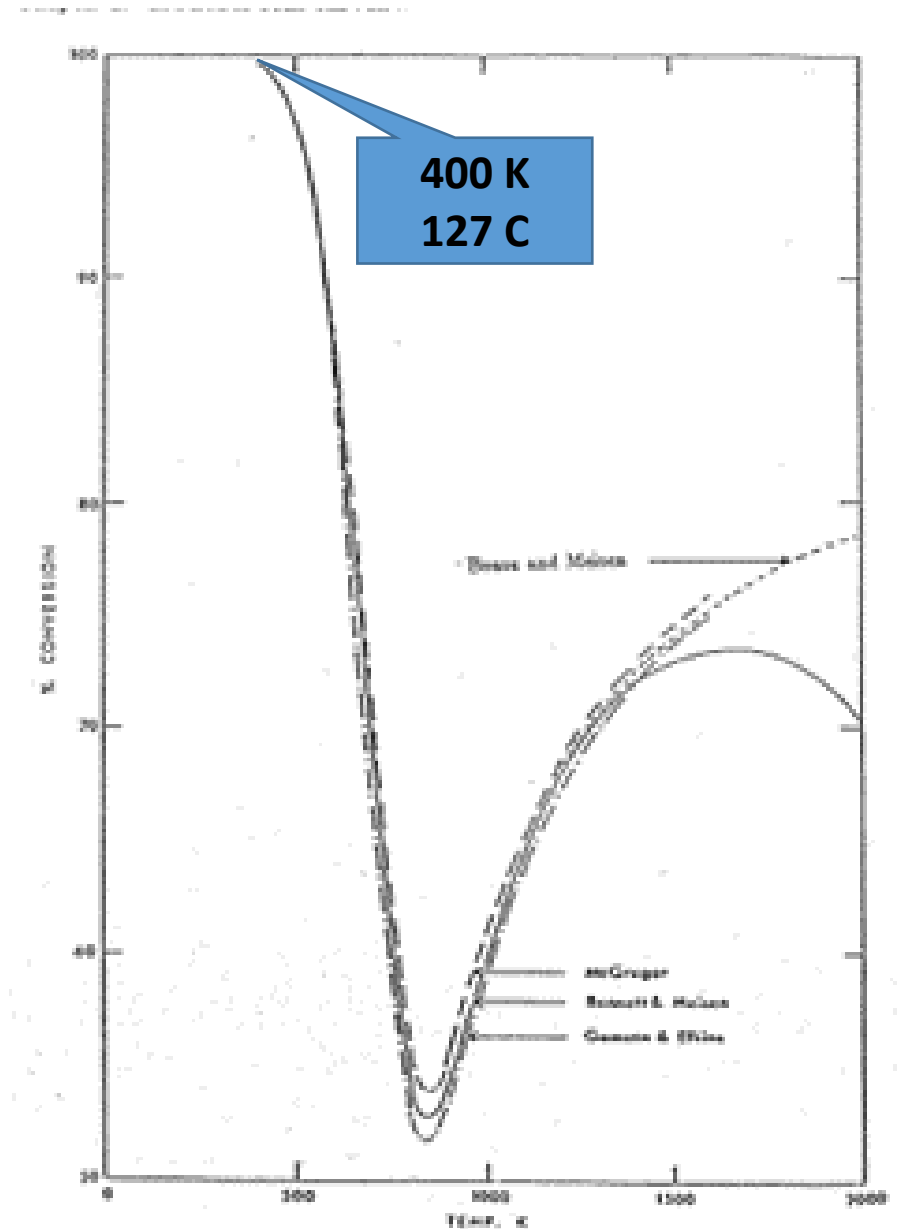


Figure 2.1: Claus reaction equilibrium conversion versus temperature (basis: 1 mole H_2S with stoichiometric air)

Process Considerations

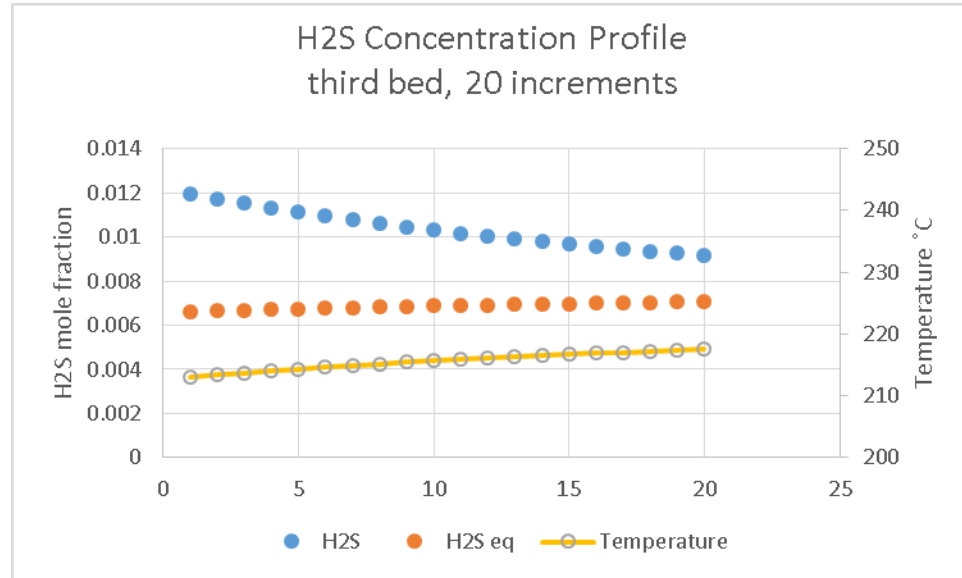
Traditional

- First bed: temperature set for COS and CS₂ conversion
- Activity vs temperature
- Second bed: sulfur dewpoint
- Third bed: minimum temperature (equilibrium)
heat loss/sulfur dewpoint
- New perspective for third bed:
activity and inhibition vs equilibrium

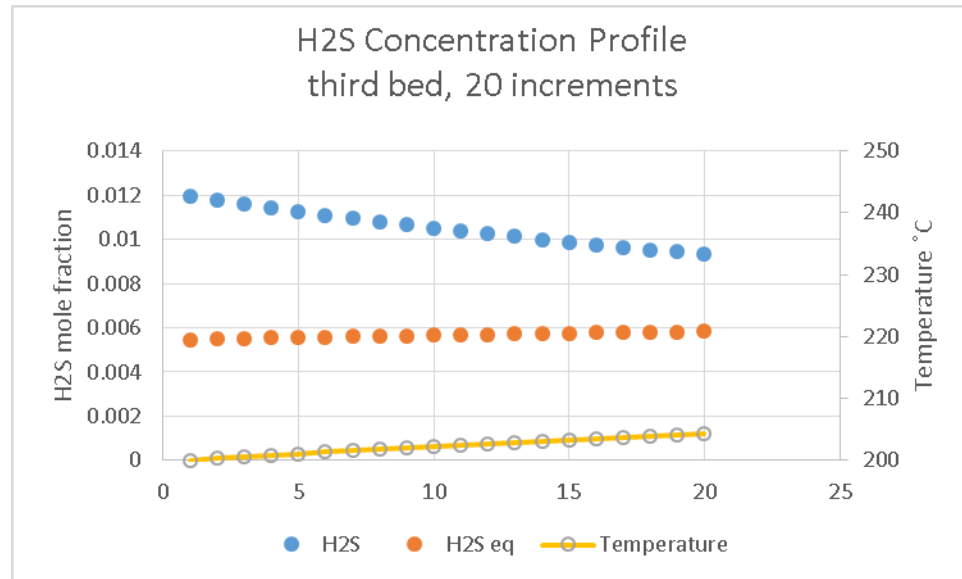
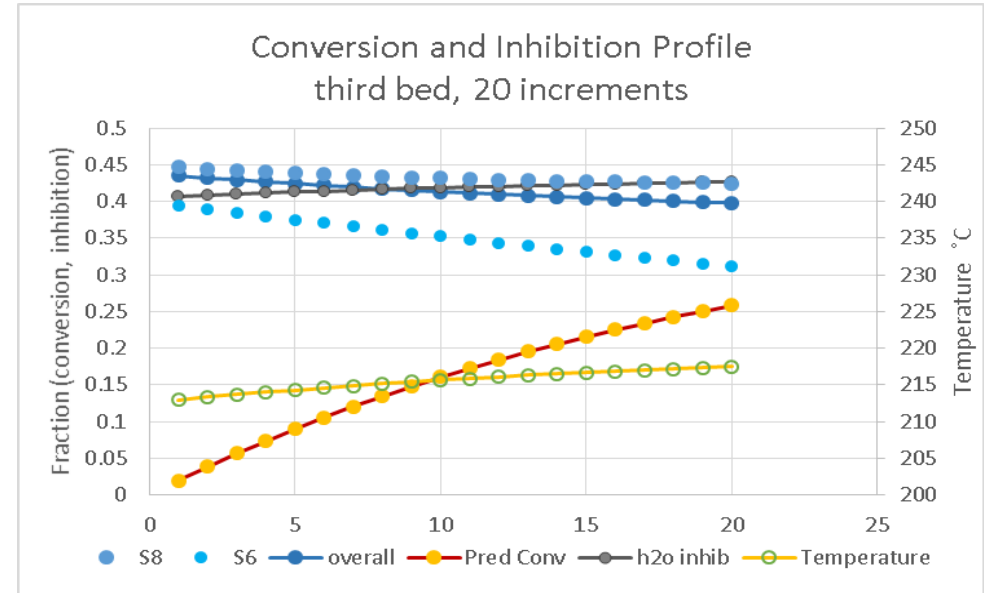
Third bed

- Classic low temperature, sulfur condensation
 - Typically observe low conversion
 - Could this be due to inhibited activity of catalyst?
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- Catalyst amounts in first and second beds achieve close approach to equilibrium, but temperatures are higher with humidity effects lower
 - Examine third bed profile, inhibition, conversion => kinetic limitation

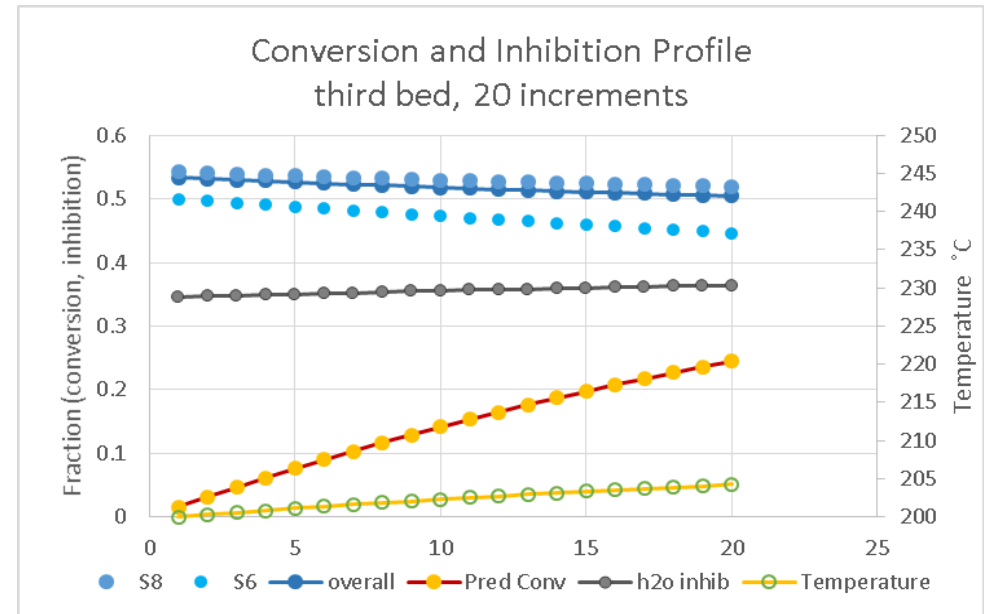
Inhibition and Conversion



213 C

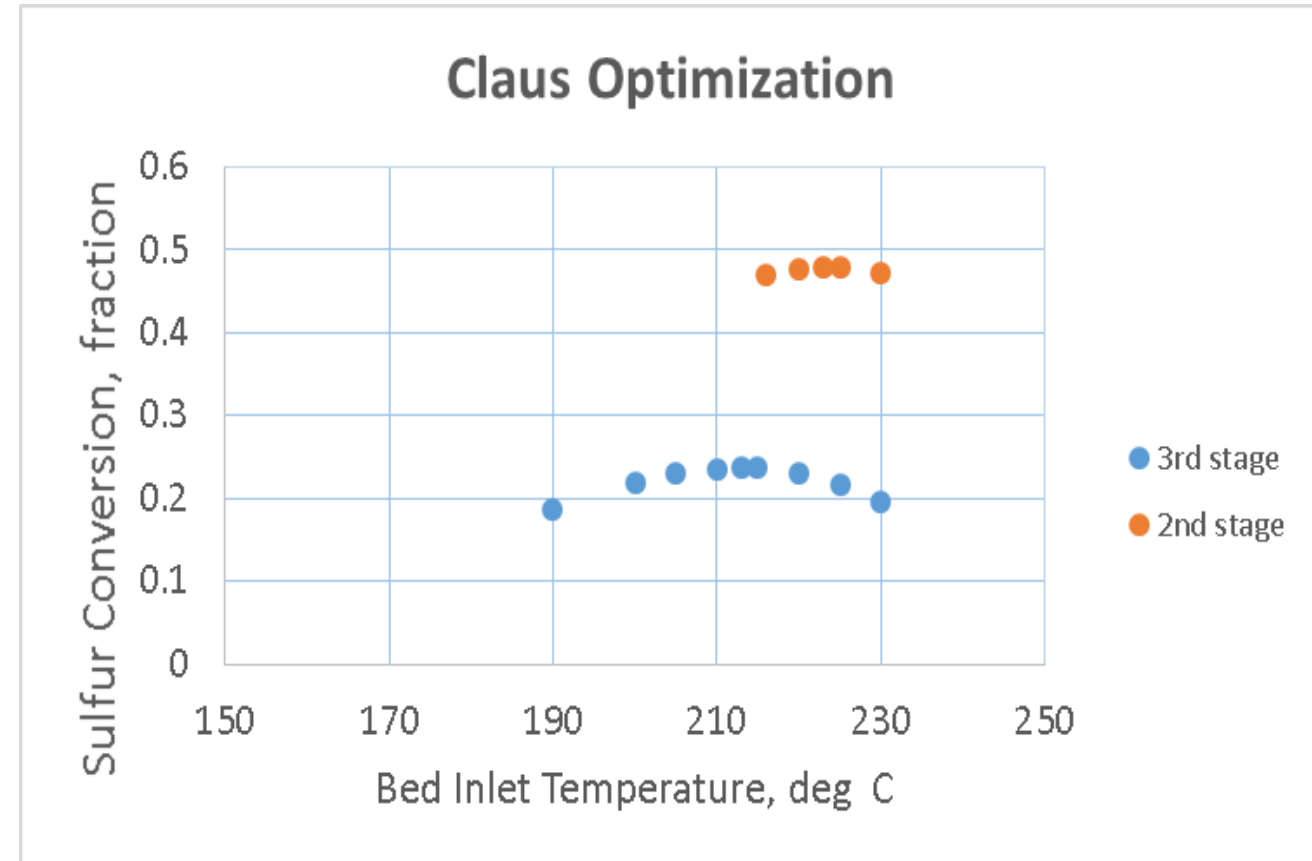


200 C



Optimizing Sulfur Recovery

- Assessing impact of temperature
- Activity vs temperature – Arrhenius relationship;
 - stronger activity at higher temperature
 - Activity expectation
- Equilibrium effect – favors lower temperature
- Conversion expression- limited by equilibrium
 - Conversion at equilibrium limit
 - Consideration of S6 and S8; tables, expression, solution of
- Impact of humidity
- Plot shows optimization: conversion vs temperature 213°C vs 200 °C



Additional benefit: improved ease and quality of operation increase + 15 to 20°C

To Summarize.....

- Assess impact of temperature
- Activity vs temperature vs humidity –
 - Arrhenius relationship
 - stronger activity at higher temperature
 - humidity inhibition - activity expectation reduced further at lower temperature
- Equilibrium effect – reference Gamson and Elkins
- Conversion expression- limited by equilibrium
 - Conversion at equilibrium limit
 - Consideration of S6 and S8
- Optimum conversion: activity and inhibition vs temperature and
- improved quality of operation

Conclusions

- Humidity adversely impact Claus kinetics
- Hotter is less humid
- Hotter impacts equilibrium, a profound constraint but not absolute
- Competing effects, so optimization opportunity
- Raising third bed temperature has benefits
 - Target 210 C– 220 C inlet vs 200 C typical
 - Somewhat increased sulfur conversion
 - Enhanced point of operation – moving away from heat loss/sulfur dewpoint

Remember: hotter is a less humid Claus

Further Assessment

- Next steps = in plant evaluation
- Examples or low conversion situations which humidity helps explain
- Sulfur dew point impacts
- Evaluation of SO₂ co-adsorption
- Chemisorption loading refinement