

Claus Thermal Stage Yields: A Question of Equilibrium, Kinetics, or Heat Transfer?

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ABSTRACT

Data from laboratory work for the development of the SPOC™ Sulfur Partial Oxidation Catalysis process was analyzed for controlling factors determining the observed sulfur and hydrogen yields. Gas chromatograph data, and flow data were used to make detailed mass balances to determine which paths the key elements in the process, oxygen, hydrogen, and sulfur took to form the Claus unit products.

Graphs for distribution of products were examined by normalizing the amount of oxygen used per Claus sulfur produced. Feed rates to the lab reactor were also used to compare yields. H₂S feed rate appeared to have a significant effect on hydrogen yields which would not be anticipated in an equilibrium-controlled yield environment.

Further analysis of equilibrium from the mass balances and a comparison to equilibrium computations for adiabatic conditions by free energy minimization (FEM) demonstrated that significant heat loss moved the final equilibrium distributions dependent on both oxygen uptake and H₂S feed rate.

When this method was used to examine plant data, a similar shift from adiabatic flame temperature (AFT) equilibrium to a lower temperature equilibrium distribution likely resulted from rapid heat losses in the first part of the WHE.

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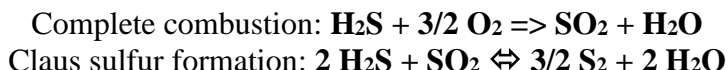
Introduction

Almost as long as the Claus Sulfur Recovery process has been in operation, there have been many different ideas about modeling the burner and thermal reactor section of the process. The simplest model of course was built similarly to the well-known adiabatic flame temperature (AFT) computation used for combustion processes. In the simplest terms:

$$H_{\text{reactants}} = H_{\text{products}}$$

H is the enthalpy of all the species computed using the same temperature basis. The typical furnace combustion computation though differs from the Claus burner-thermal reactor as the combustion of hydrocarbon fuels is assumed to go to completion, and there is usually oxygen in excess of the amount required to fully combust the fuel. One only need know the amount of excess O₂, the O₂ required to convert all carbon to CO₂ and all hydrogen to H₂O, and the nitrogen associated with the oxygen from the air to compute the temperature of the products based on the equation above.

In the Claus burner-thermal reactor we have quite a difference in the operation compared to a furnace. The first consideration is the Claus combustion is done with deficient oxygen. The rudimentary Claus combustion and reaction is depicted by:



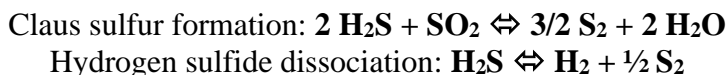
Only 1/3 of the fuel undergoes complete combustion, while the remaining 2/3 of the H₂S reacts with the SO₂ from complete combustion. Secondly, contrary to the furnace situation, the combustion is not complete and an equilibrium-controlled reaction is introduced.

In the Claus system, H₂S streams coming from amine regenerators or sour water strippers contain other fuel components such as NH₃, hydrocarbons, and hydrogen. A wide variety of reactions can take place forming a wide variety of reaction products. Some of these reactions may result in partial combustion products and in equilibrium reactions as well. This adds further complication to the development of Claus burner-thermal reactor models.

Gamson and Elkins¹ aided the industry in a quantum leap understanding of the Claus burner-thermal reactor in a model considering the effects of many simultaneous equilibria. Their model allowed for more robust predictions of yields and thermal reactor temperature allowing the industry to design more efficient units with significant operating uptime. As the quality of thermodynamic data and computational capabilities increased, newer models based on Free Energy Minimization became more commonly available. This allowed for more accurate prediction of AFT conditions in a burner-thermal reactor, **BUT**...

Claus Thermal Stage Yield Discrepancies

...Even though the computational methods and thermodynamic correlations have greatly improved, there have been many studies and papers² that have been done to explore the differences in the AFT predictions and actual plant yields. Companies offering Claus simulation capabilities have developed correlations using various factors to account for the discrepancies. Generally, these correlations are used for adjusting the amount of hydrogen, COS, and CS₂ in the models to match the actual values from lab and plant data. In this review, we will be focusing on the progress of two major equilibrium-controlled reactions:



COS and CS₂ formation and destruction and ammonia destruction are also key parts of the Claus thermal stage puzzle, but these will not be addressed in this context.

By using equilibrium computations to determine the performance of the Claus burner-thermal reactor, we must build in the assumptions of adiabatic conditions, perfect mixing, and no kinetic limitations on either forward or reverse reactions to make the computation work.

Computational Fluid Dynamics (CFD) modeling work on Claus burner-thermal reactors has been very useful in proving the assumptions of adiabatic operation and perfect mixing to be less than accurate. Even then, in order to make CFD modeling affordable, the assumption about reaction rates must remain. Adding classical kinetics increases the computational complexity due to the number of intermediate species that must be accounted for.

Deciding which factor(s) decide the yield structure from the Claus burner-thermal reactor is fraught with difficulties. For the two reactions in question, does equilibrium alone account for the discrepancy between AFT and actual yields? At what condition (temperature) do we pick for computing the equilibrium? Is there a particular reaction and its kinetics that control the yield? Is it the rate of heat transfer from the reaction mixture that controls yield?

Data Sources

Two sets of data were examined to see which factors contributed to the yield discrepancy. The first data set was generated in the laboratory at Conoco/ConocoPhillips research facility in Ponca City, Oklahoma between 2001 and 2004. Known as the SPOCTM process for Sulfur Partial Oxidation Catalysis, the research sought to reduce the size of the Claus thermal stage by employing a catalyst to do what the burner and thermal reactor accomplish. Residence times in the catalyst were less than 1/10th of the normal residence time for an operating Claus unit.

Figures 1 and 2 show the lab configuration as designed along with the actual apparatus as depicted in a presentation at this Symposium in 2004³.

Figure 1 Lab Reactor Flow Sheet

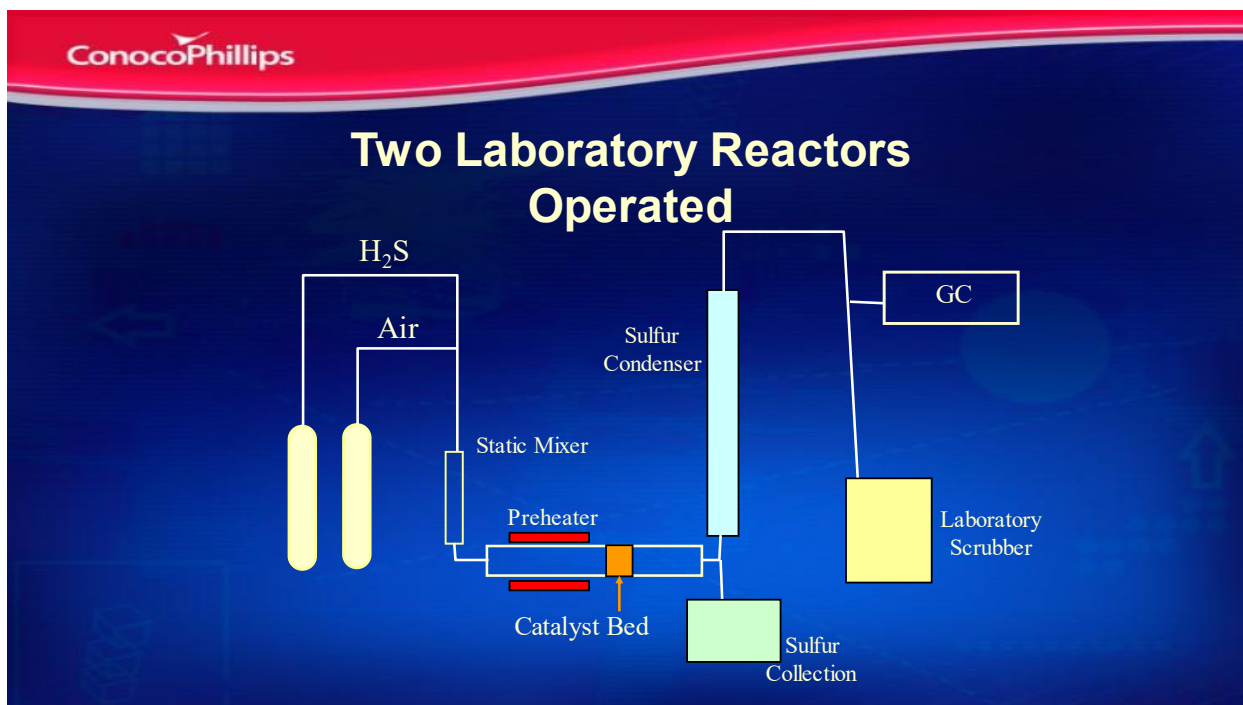
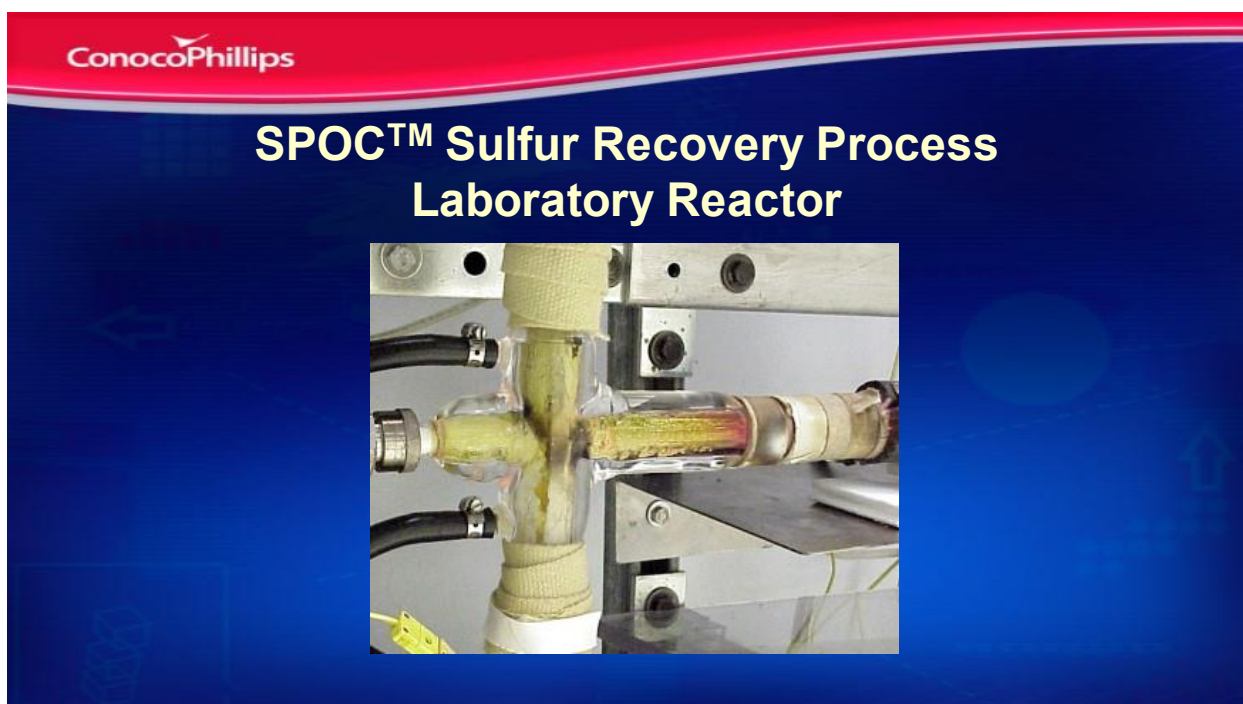


Figure 2 SPOC™ Reactor in Operation



The second set of data came from plant tests conducted by Brimstone Sulfur Testing Services for a variety of anonymous clients and from plant tests conducted on what are now Phillips 66 facilities by Brimstone and other testing providers.

Molecular Bookkeeping

Since there are multiple pathways the reactions in the catalytic or burner-thermal reactor, and since detailed kinetic models are still in an evolutionary stage, it becomes necessary to find an ordered way to classify the key reactions in the system and hone in on a system to isolate the two equilibrium reactions from the remainder of the mix.

There are numerous classification systems used to deal with complex sets of reactants and reactions. A couple of well-known methods are:

- Oxidation-Reduction
- Acids-Bases⁴
 - **Aqueous Bronsted-Lowry** – proton donors and acceptors
 - **Lewis** – electron acceptors and donors
 - **Non-aqueous solvent system** – similar to Bronsted only using solvent species
 - **Lux-Flood** – oxide ion donors and acceptors

Most of the sulfur processing literature concentrates on oxidation-reduction due to using combustion. While it is helpful for the electron bookkeeping in reactions, it does not seem to be helpful in the goal of isolating the key reactions.

Acid-Base classification is applied to systems with complex equilibria involving many reactions. Outside of the Lux-Flood system used for solid reactions, the other systems are more suited to liquid environments, especially aqueous ones. However, this does not limit the use of an analogy in the case of Claus thermal stage gas system.

In order to use the analogy, there must be a definition of what is an acid in the system and what is a base. The properties of the acid and base must be such that the products of an acid-base reaction form a new acid-base pair. For the SPOCTM catalyst reactor and the conventional Claus burner-thermal reactor these definitions are:

Acid-a hydrogen atom donor
Base-a hydrogen atom acceptor

With the definitions in place, we classify the major components in the system.

Acids: H₂S, NH₃, C_mH_n, H₂O and H₂
Bases: O₂, SO₂, S₂, CO, CO₂, COS, CS₂, and N₂

With the definition and classification of materials in place we can order the reactions according to an acid-base system as shown below in Figure 3.

Figure 3 SPOC™ and Claus Burner-Thermal Reactor Acid Base Reaction Classification

Strong Acid + Strong Base => Weak Acid + Weak Base

- | | |
|---|--|
| <ul style="list-style-type: none"> • Reactants • $\text{H}_2\text{S} + \text{O}_2$ • $\text{H}_2\text{S} + \text{SO}_2$ • H_2S • $\text{NH}_3 + \text{O}_2$ • $\text{C}_m\text{H}_n + \text{O}_2$ • $\text{C}_m\text{H}_n + \text{H}_2\text{S} + \text{O}_2$ | <ul style="list-style-type: none"> • Products • $\text{H}_2\text{O} + \text{SO}_2$ (full oxidation) • $\text{H}_2\text{O} + \text{S}_2$ (Claus) • $\text{H}_2 + \text{S}_2$ (dissociation) • $\text{H}_2\text{O} + \text{N}_2$ (full oxidation) • $\text{H}_2 + \text{CO}$ (partial oxidation) • $\text{H}_2\text{O} + \text{CO}_2$ (full oxidation) • $\text{H}_2\text{O} + \text{COS}$ • $\text{H}_2\text{O} + \text{CS}_2$ |
|---|--|

Now that the reaction classification basis has been set, we can set the criteria for doing the mole balancing necessary to isolate the desired equilibria from the other reactions. Table 1 gives a rundown of the reaction bookkeeping incorporating the data available in the lab and plant tests.

Table 1 Incorporation of Lab and Plant Test Data into Mole Balancing Model

Chem. E. 101 Mole Balancing

In	- depletion	+ generation	= Out
N_2 metered air			N_2 (GC)
O_2 metered air	O_2 by combustion	S_2 , SO_2 , H_2O , H_2 from full combustion of H_2S and Claus reaction	SO_2 , CO , CO_2 , COS , H_2 (GC)
H_2O metered streams, simulations		N_2 and H_2O from full combustion of NH_3	H_2O in + H_2O generation
H_2S metered acid gases, analysis	H_2S by full and partial combustion	CO , CO_2 , H_2 and H_2O from full and partial combustion of C_mH_n	H_2S (GC)
NH_3 metered acid gases, analysis	NH_3 by combustion	COS , CS_2 , and H_2O from mixed combustion of H_2S and C_mH_n	NH_3 (SRU test method)
CO_2 metered acid gases, analysis	CO_2 and H_2 by reverse WGS reaction	CO and H_2O from reverse WGS reaction	S_2 from Claus and H_2S dissociation reactions
C_mH_n metered acid gases, analysis	C_mH_n by full and partial combustion		$\text{C}_1\text{-C}_6$ (GC)

The acid-base classification of reactions and assignment of where atoms go in the various molecules are assigned by the following set of rules.

- No metering adjustments
- Hydrogen, oxygen, sulfur, and carbon assigned to molecules in metered streams and GC measured tail gas first
- Reaction priority is acid plus the strongest base (O_2) first, then equilibrium of weak acids and weak bases (Claus reaction, H_2S dissociation)
- Measured H_2 in tail gas assigned to C_mH_n partial oxidation first; then reverse water gas shift (When CO_2 in $> CO_2$ out); remaining is assigned to H_2S dissociation
- H_2O formation from NH_3 and C_mH_n reactions assigned first; H_2O from SO_2 formation second, Claus reaction the remainder
- S_2 from both Claus and dissociation are computed

By this method of molecule bookkeeping, we can associate the reactants necessary to make the measured amount of products for minor components such as CO , CO_2 , COS , and CS_2 without introducing well known equilibrium reactions involving these species, hydrogen, and water. This method bypasses kinetic and mechanistic considerations since we are looking only at end results. We are left at the end with hydrogen from H_2S dissociation (computed from H_2 measured in outlet- H_2 generated from C_mH_n partial oxidation), sulfur from Claus reaction and dissociation (computed from dissociation hydrogen), and water (computed from inlet plus all water forming/consuming reactions).

Equilibrium Yield Comparison Method

The results from the mole balancing were used to determine what fractions of sulfur, hydrogen, and oxygen in the feeds went to each of the measured and computed components in question. The fractions computed from the mole balancing were compared to FEM generated fractions at AFT conditions and at temperatures below AFT conditions that encompassed the range of the actual results.

Nominally, a plant operation would try to achieve an air flow to the process in accordance with the guidance provided by the air demand analyzer at the back end of the Claus portion of the process. The air necessary to operate the plant in this manner would not only be subject to the optimization of Claus sulfur recovery, but also the need to complete the destruction of ammonia and hydrocarbon as well. On the other hand, the lab set up tested catalyst operations not with the intent of operating at optimum sulfur recovery conditions, but by trying varying air to H_2S ratios over a wide range to see if any process advantages were available to exploit.

Since the fractions of each atom in each product component varied significantly with the amount of O_2 that reacted with the H_2S in the lab, it was decided to make the O_2 going to SO_2 and water in the Claus chemistry per S in the H_2S in the feed the normalization factor to bypass the O_2 used by the competing fuels in the process. This factor was used to set up the FEM yield computations for comparison.

Figure 4 gives the distribution of hydrogen from feed H_2S to unreacted H_2S , H_2O , and dissociation H_2 . Figure 5 shows how sulfur from feed H_2S distributed among unreacted H_2S , Claus reaction sulfur, and SO_2 . Figure 6 gives the distribution of oxygen to water and SO_2 in the products. All these fractions were plotted against the normalization factor, O_2 uptake/sulfur in H_2S feed.

Figure 4

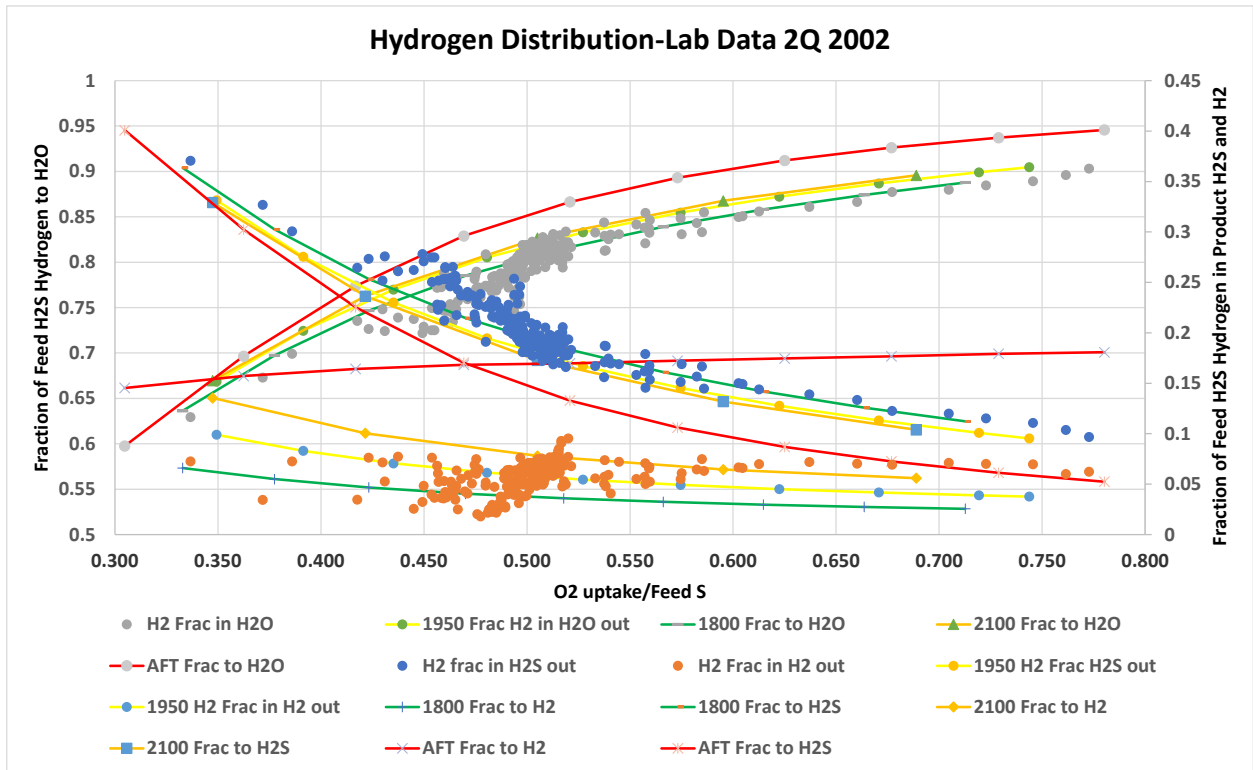


Figure 5

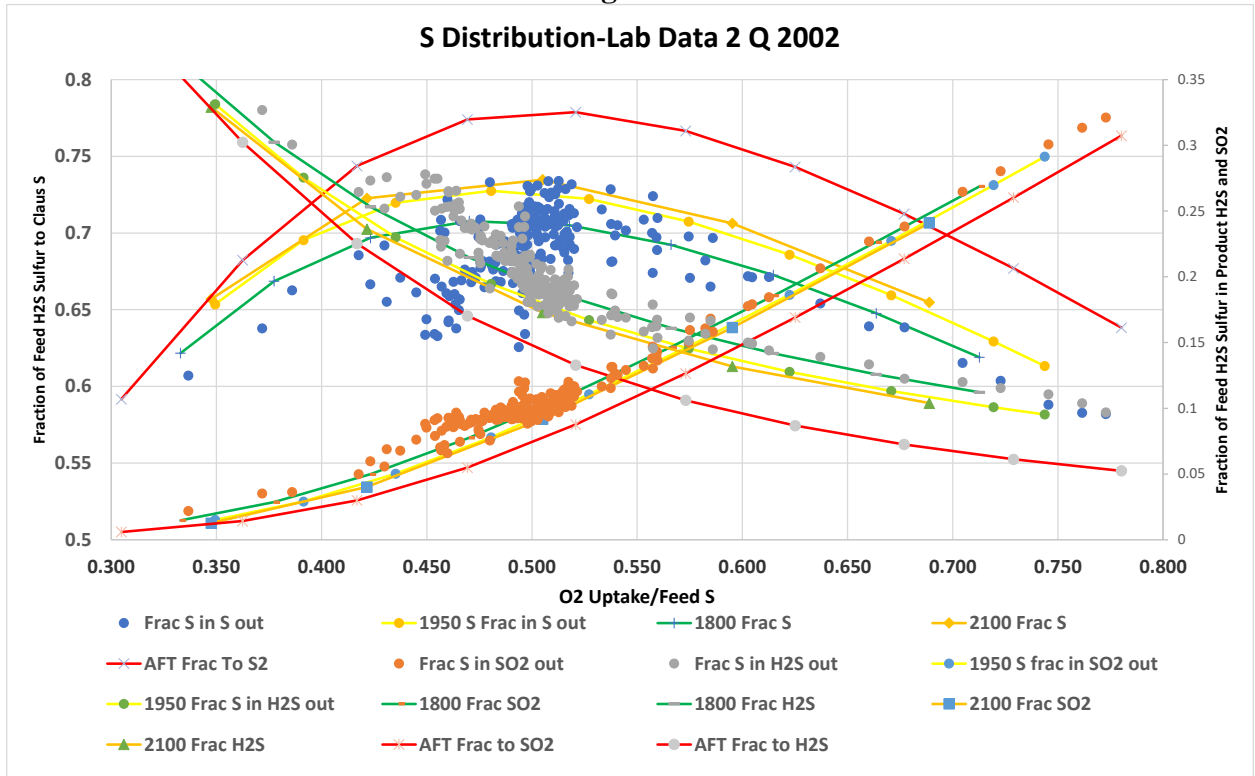
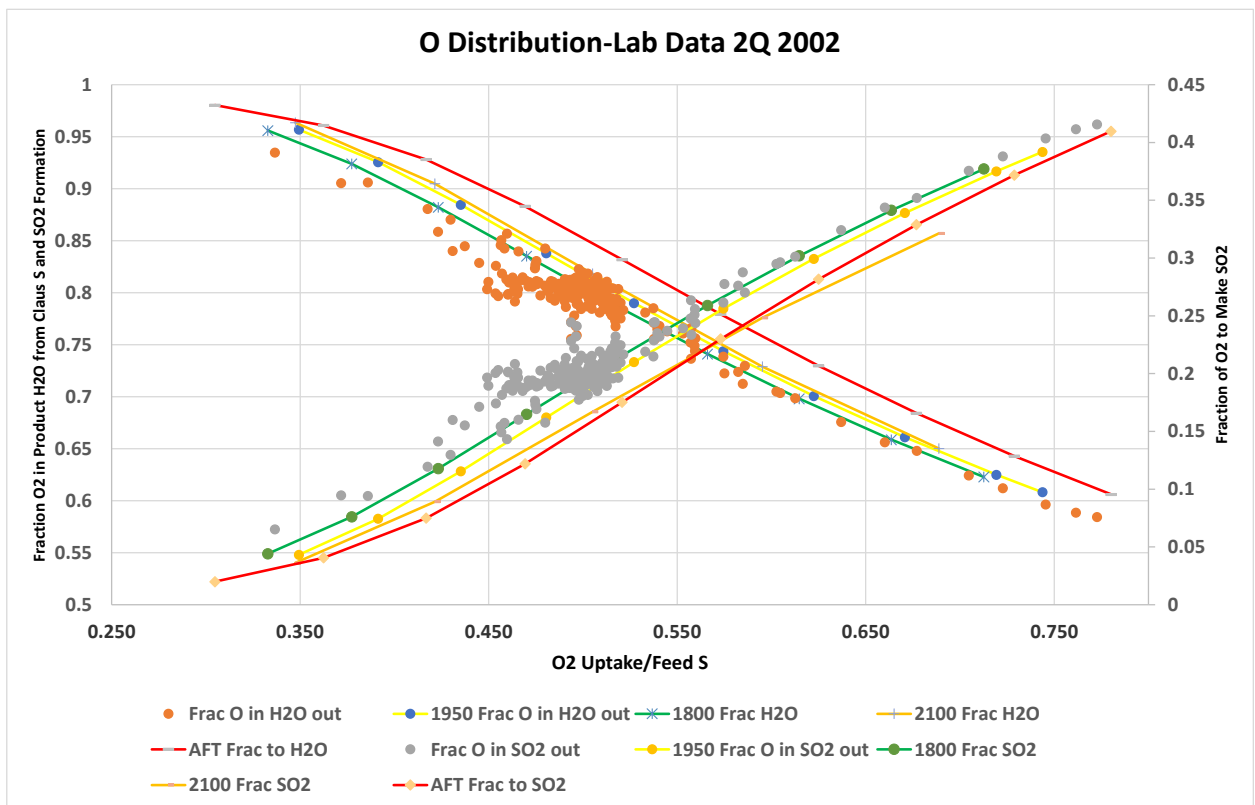


Figure 6



The red lines in each graph are the AFT computed fractions for each component in the product. The green lines represent the FEM computations assuming heat losses cause the final mixture to go to 1800 °F, and the other lines represent FEM computations at 1950 °F and 2100 °F.

It is readily apparent the yields are not close to the AFT computed values. Most of the values appear to be in the range of the lines depicted with some data reflecting values below those computed for 1800 °F.

Hydrogen Distribution (Figure 4)

Since the observed yields are not consistent with AFT computations, and since the lab reactor as shown was not insulated to warrant being considered adiabatic, the loss of heat obviously moved the reaction to different yields by LeChatlier's principal. If the new state for the observed yields was a true equilibrium state, the yields for the same feed conditions should have produced a uniform set of yields. It is obvious however from the wide variation in hydrogen yields over small ranges of O₂ uptake/H₂S feed that the loss of heat played a significant role in the final hydrogen yield.

Sulfur and Oxygen Distribution (Figures 5 and 6)

In Figure 6 at lower O₂ uptake/H₂S feed, O₂ going to form H₂O is lagging while O₂ going to SO₂ is greater than computations show. This is consistent with the reduced Claus sulfur make and greater amount of unreacted H₂S shown in Figure 5. There are two possibilities to consider. One possibility is the catalyst did not facilitate the reaction to equilibrium extent. The other possibility is the heat loss caused a significant shift toward a new equilibrium position.

Plant Data

Figures 7 and 8 show the hydrogen and sulfur distribution in the products respectively versus O₂ uptake/H₂S for both AFT computations based on the measured acid gas feed compositions, rates, and adjusted metered air rates and the actual values computed from the first condenser gas analysis. As with the lab results, the plant data also shows a wide gulf between AFT computed values and actual measured values.

Figure 7

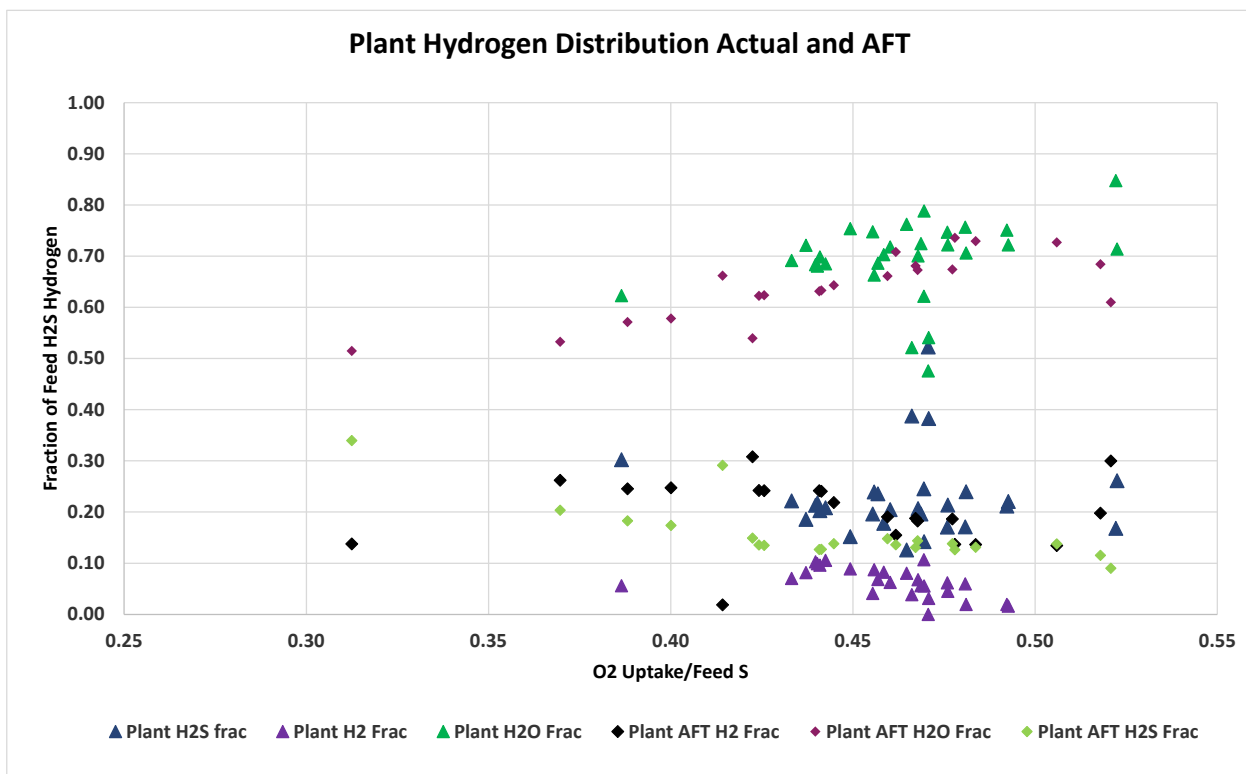
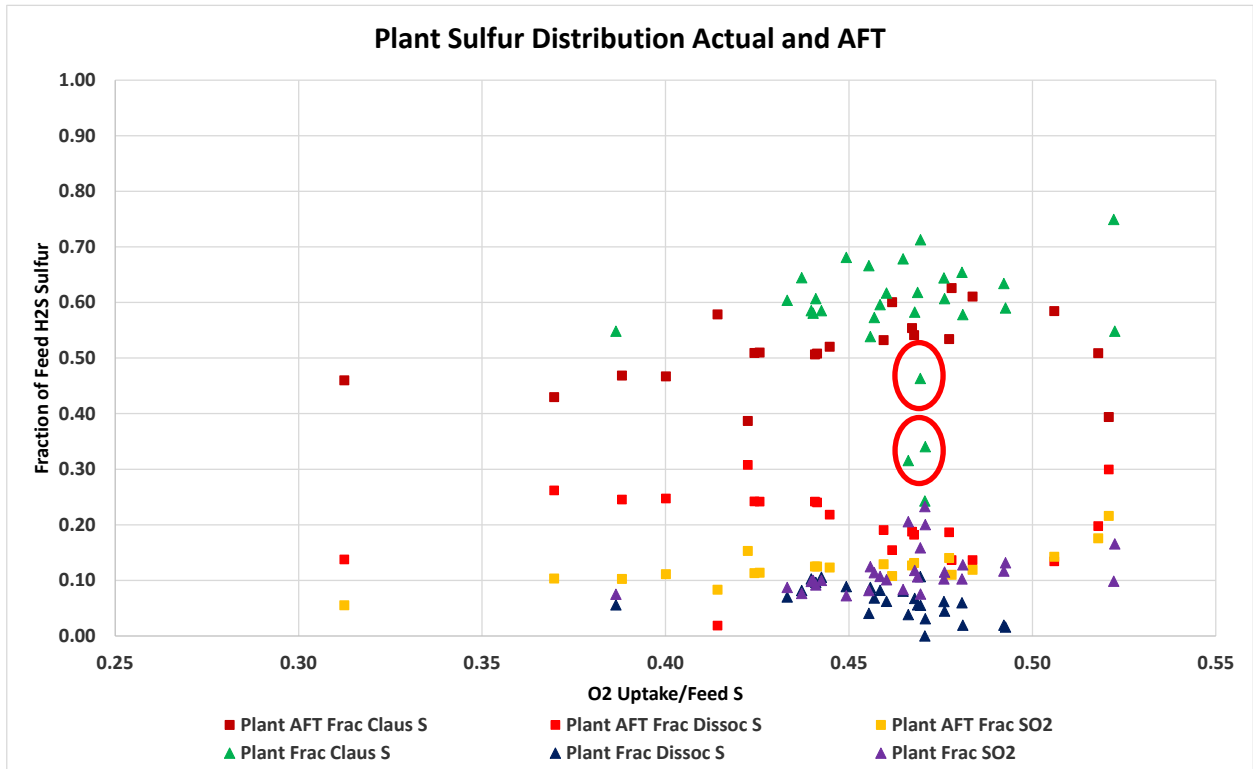


Figure 8



Most notable are:

Plant dissociation hydrogen/sulfur are much lower than AFT computed fractions

Plant fraction of Claus sulfur is higher than AFT computed Claus sulfur

Points in red ovals came from test of same plant, but different rate conditions. This plant's thermal reactor has a very low residence time before entering a firetube style WHE. The two lower numbers in the oval were tests done at maximum unit rates, the other one taken during minimal unit rate.

Lab/Plant Yields Versus Equilibrium

While AFT calculations used for modeling Claus burner-thermal reactor appear to be helpful in establishing the design temperatures necessary to choose the appropriate thermal reactor refractory lining, they appear wholly inadequate to predict the gas yields one would observe taking a gas sample after the first condensing stage.

The first question one may ask is whether the differences in yields make any difference in the downstream design. There are two places where these differences may change design decisions.

Where the two points in the ovals on the Claus sulfur yields in Figure 8 were extremely low compared to the AFT computed yields, the first converter ran at nearly 100 F higher at the outlet than would normally be expected with the yields seen in the oval with one data point. Jumping

from a 580 F outlet temperature to a 680 F outlet temperature could change the decision on metallurgy in the outlet line of the first converter and the inlet channel on the following condenser.

An AFT modeled hydrogen yield may convince a designer that the hydrogenation system of the TGU may not need a supplemental hydrogen source with such an abundance of hydrogen. Without the supplemental hydrogen, the plant would be ill equipped for upsets leading to high SO₂ leaving the Claus section.

Figures 4-8 show AFT calculations for the Claus burner-thermal reactor put the modeler in the position of having to apply adjustment factors to better match what occurs. Most adjustment factors deal with the amount of hydrogen to be expected, usually justified solely by attributing the change to recombination of H₂ and S₂ to H₂S. (Our current scope excludes COS and CS₂ adjustment). However, further examination shows this may be too simple a correction.

The Controlling Factor

Adjustment factors are most useful if they are easily defined and relate to some well-known principle in a straightforward way. Prime mover efficiencies and activity coefficients are prime examples of examples of empirically determined adjustment factors.

For the Claus burner-thermal reactor it appears that modeling must consider reaction limitations in the waste heat exchanger (WHE). What are the primary factors to consider when constructing a model to adjust the AFT results to predictable burner-thermal reactor-WHE results?

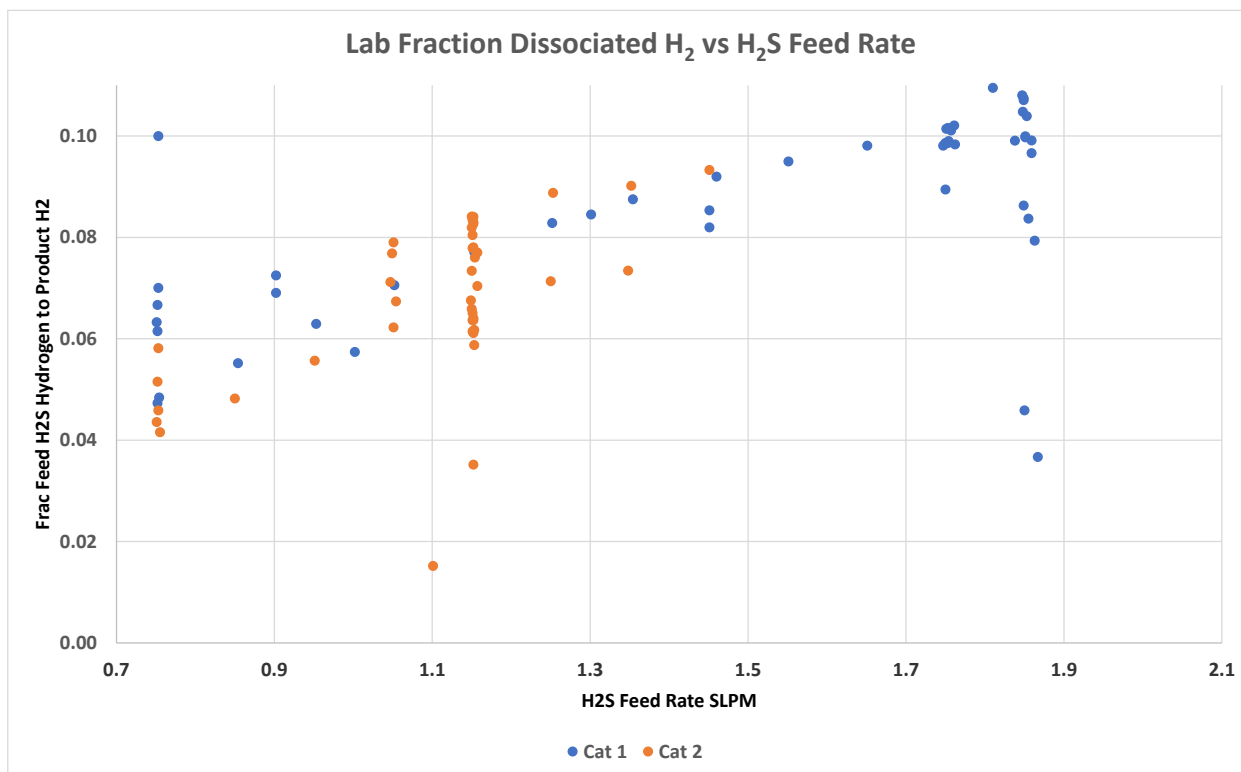
The spread in both the lab and plant yields shown in Figures 4-8 precludes the existence of a single temperature that the reaction mixture traveling through post-reactor heat exchange stops at. If the freeze temperature were a true phenomenon, then all the data points would have fallen exactly on one curve.

Studies have been done and papers presented on H₂/S₂ recombination kinetics⁵. Stringent measures of scientific rigor were not set up to collect cooling section data in the SPOC™ apparatus (temperature measurements, heat transfer controls, multiple sampling points). These stringent measures can't be incorporated economically in operating plants to obtain accurate kinetic models. Other issues with kinetic modeling are having multiple reaction's kinetics to consider, rate of heat transfer, and multiple equilibria to consider.

Kinetic and Heat Transfer Issues

Figure 9 shows the dissociation hydrogen yields for two different SPOC™ catalysts over a specific range of feed H₂S gas and at varying O₂ uptake to H₂S feed ratios.

Figure 9



There is a near linear change in dissociation H₂ yield with respect to feed H₂S rate ignoring obvious outliers, and there is a linear change in yield with respect to O₂ uptake/H₂S feed at constant rate. The yields improve up to 2.5 times at higher flow rates than lower flow rates.

Let's consider the following in interpreting the results:

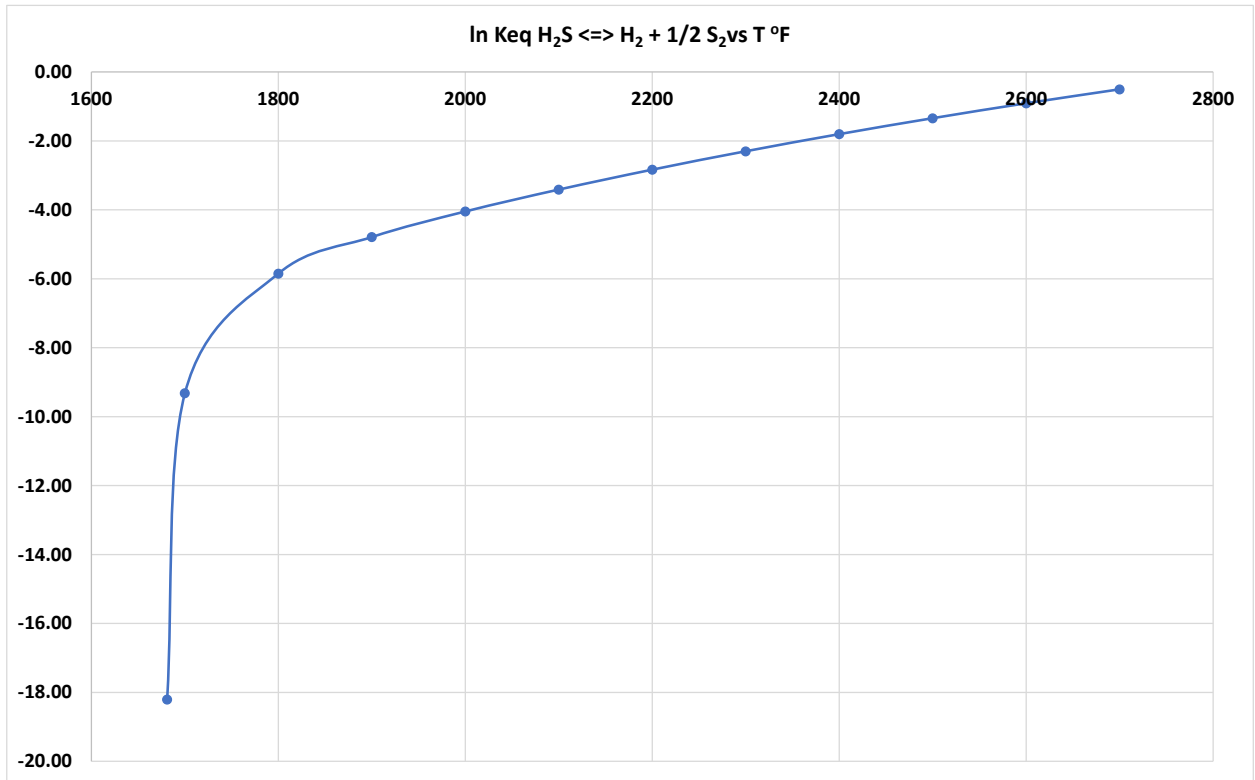
- Higher feed rate ~ higher heat release
- Higher feed rate ~ higher overall flow rate ~ lower residence time
- More heat to remove and lower residence time affects end point of recombination reaction

Kinetic sensibilities suggest having higher residence time leads to more recombination. The data supports this. However, these kinetic sensibilities suggest that having less heat to remove with the same heat transfer surface and similar LMTD implies faster cooling and thus slower recombination kinetics. The data shows the opposite effect. It appears that kinetic control and not necessarily heat transfer rate is more determinative.

Equilibrium-Kinetic Conundrum

If we take the approach that only kinetics matter, then Figure 10, computed from FEM computations of lab feeds, would suggest kinetics would help ensure no hydrogen remained. Below about 2000 F, the amount of dissociated H₂ becomes small, and becomes almost non-existent below 1800 F. The yields in Figures 4, 7, and 9 indicate that recombination kinetics are very temperature dependent and slow to where they stall, thwarting the power of equilibrium.

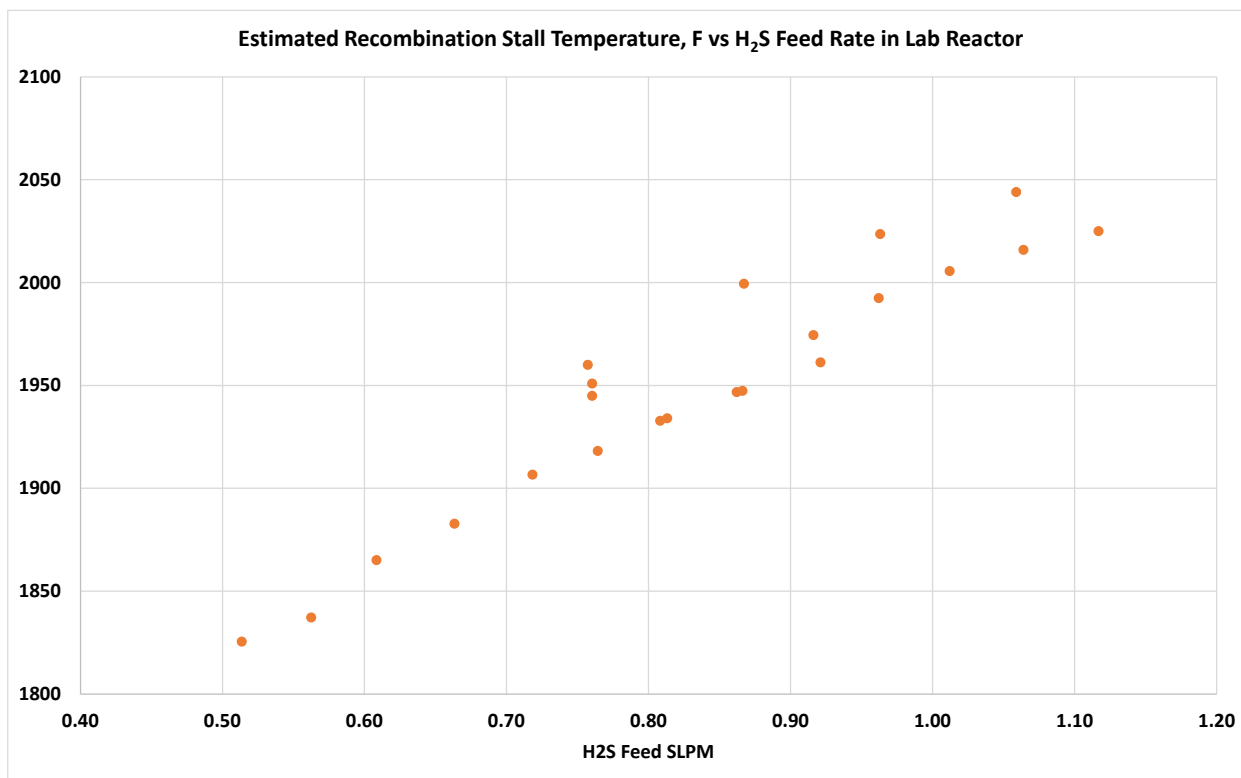
Figure 10 Dissociation of H₂S Equilibrium



Can we figure what temperature this kinetic stall took place? Normally, we would take the temperature and use the equilibrium relationship to find the concentration of each component needed to obtain the equilibrium constant at the selected temperature. In this case, we have the final concentrations of the participating species and can use the $\ln K_{eq}$ vs T graph in Figure 10 (the FEM program is doing all the work in reducing the real equation, $\Delta G = -RT \ln K_{eq}$ to get the relationship in the graph).

Using this method, we can take lab yields and compute the estimated “stall temperature” versus H_2S feed rate for a set of the SPOC™ data. This is shown in Figure 11.

Figure 11



With higher residence time and lower heat release, the reaction mixture is stalling at a temperature closer to the cliff where no hydrogen remains. The approach to the final yield appears to be controlled by heat transfer from the reactor and air-cooled sections. As heat release and residence time decrease, heat loss in these zones as a percentage of the total heat release likely drops and more heat is transferred from the mixture to the cooling oil in the condensing zone where a more rapid temperature descent stalls the recombination kinetics.

Comparison of Claus Reaction and Recombination Reaction

At the beginning of the paper, the two equilibrium reactions were isolated from all the other reactions by the acid-base mole accounting method applied to the products. So far, we have only looked at heat loss and kinetics effects for hydrogen yield. Does the Claus reaction follow the pattern of reaching a stall temperature, and is it the same as the recombination stall temperature? Also, do the both reactions in both the laboratory and plant settings follow the recombination pattern from the lab?

We turn to Figure 12 (lab) and Figure 13 (plant) to check the patterns.

Figure 12

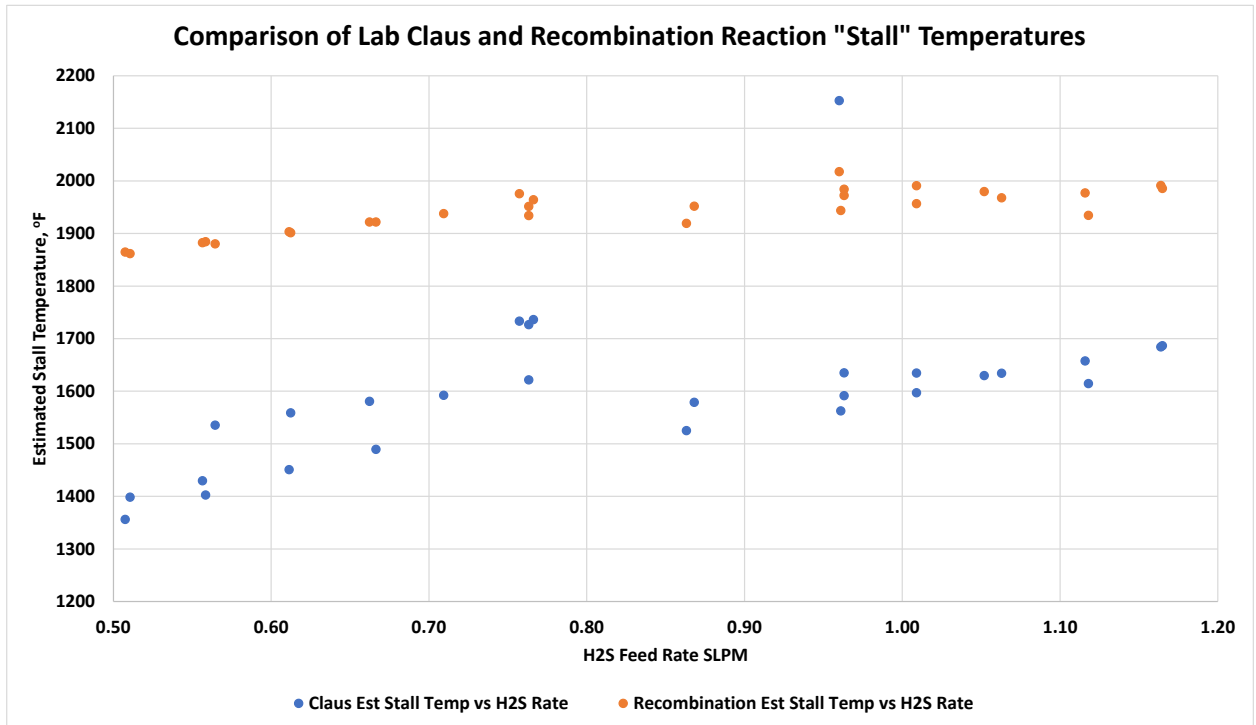


Figure 13

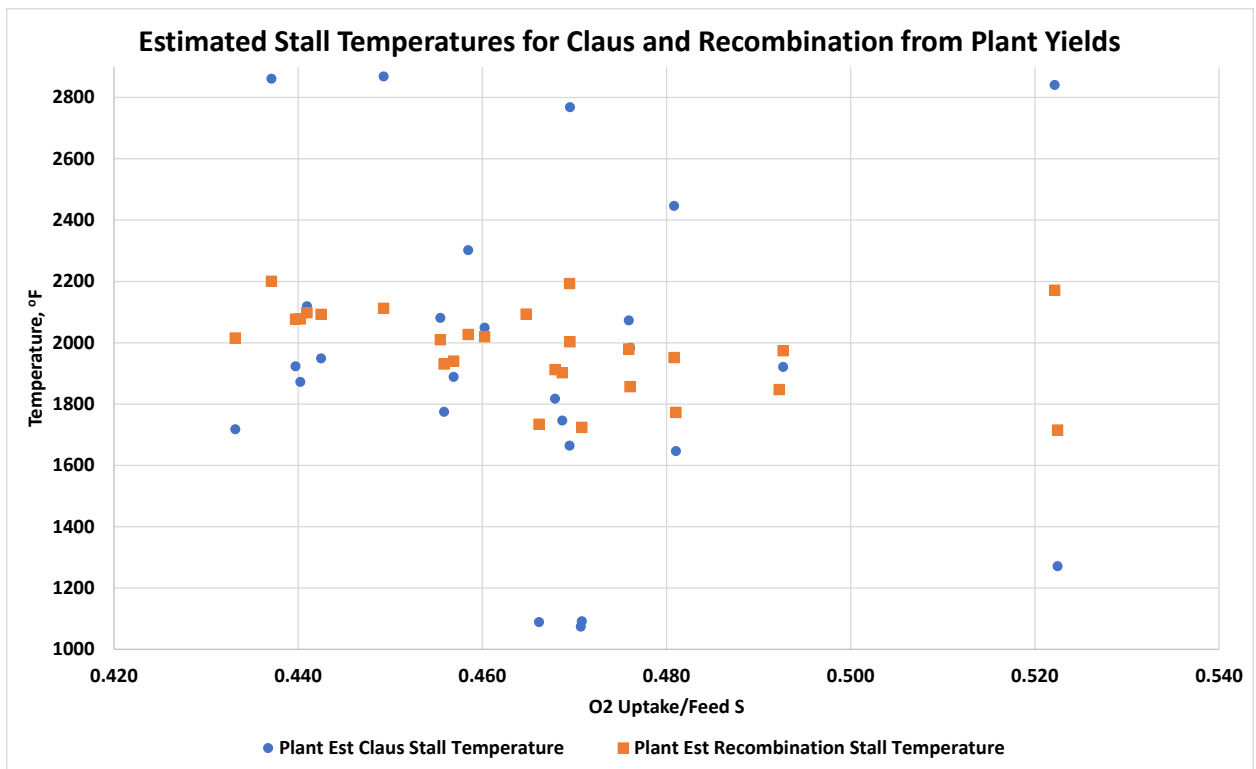


Figure 12 not only shows the Claus reaction shows a similar pattern of change versus flow rate of H_2S feed as the recombination reaction, but also shows that the kinetics of that reaction can continue at a much lower temperature than where the recombination reaction stalls. Most modeling tends to account for the shift in H_2S in the product solely to recombination reaction, and all but ignores the shift in the Claus reaction.

Since plant data was not available for varying rates, the O_2 uptake/ H_2S feed was used for the independent variable axis. Figure 13 doesn't give us the same flow/heat transfer effect perspective, but shows that in general, recombination stall temperatures are higher than the corresponding Claus stall temperatures. There are a few exceptions. These exceptions appear to be a function of a particular WHE design entity that runs somewhat contrary to typical industry designer's preferences.

Burner Design Effect

BUT MY BURNER DESIGN IS MORE EFFECTIVE! YOU DID NOT CONSIDER THAT!

If it is mixing in the burner that makes a bigger difference, the SPOC™ lab system could be considered the “gold standard” as all the ingredients were premixed and preheated before entering the catalytic zone.

However, we can plot the stall temperatures to see if the burner type played a significant role in yields. Estimated stall temperatures for the Claus reaction versus burner type are shown in Figure 14, and for the recombination reaction in Figure 15.

Figure 14

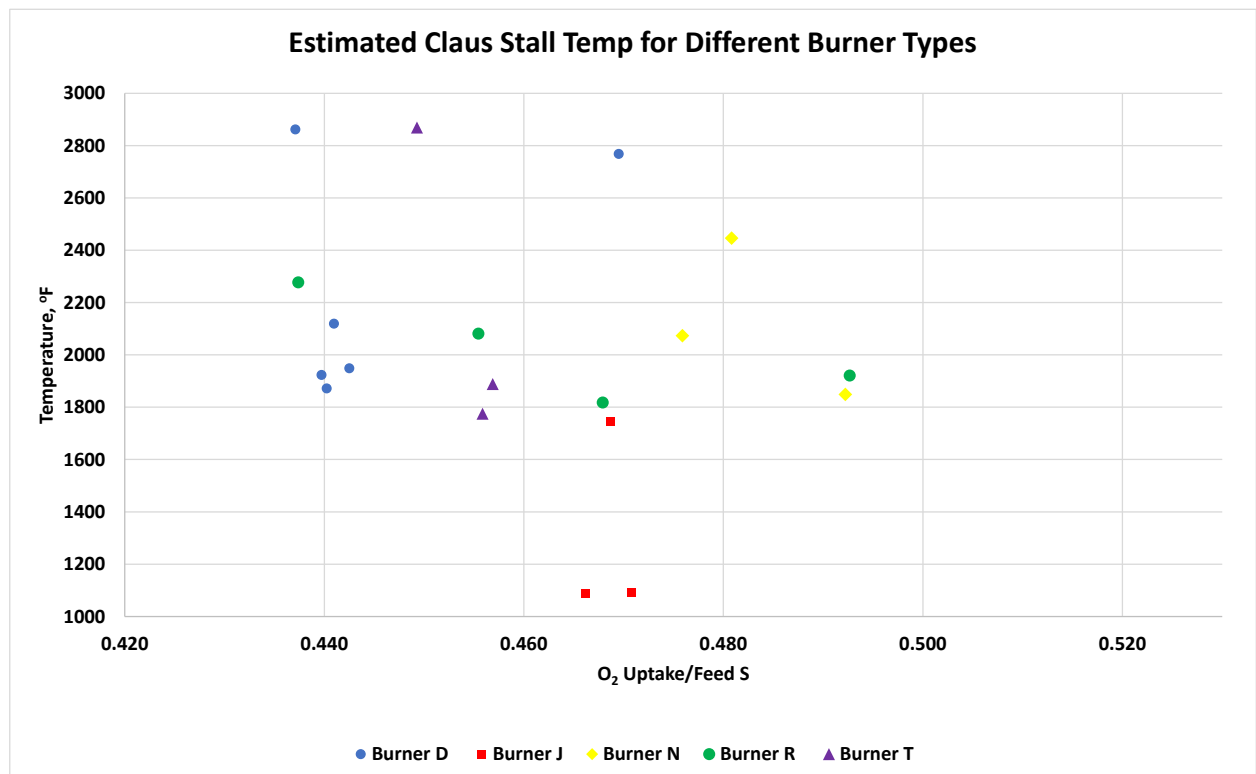
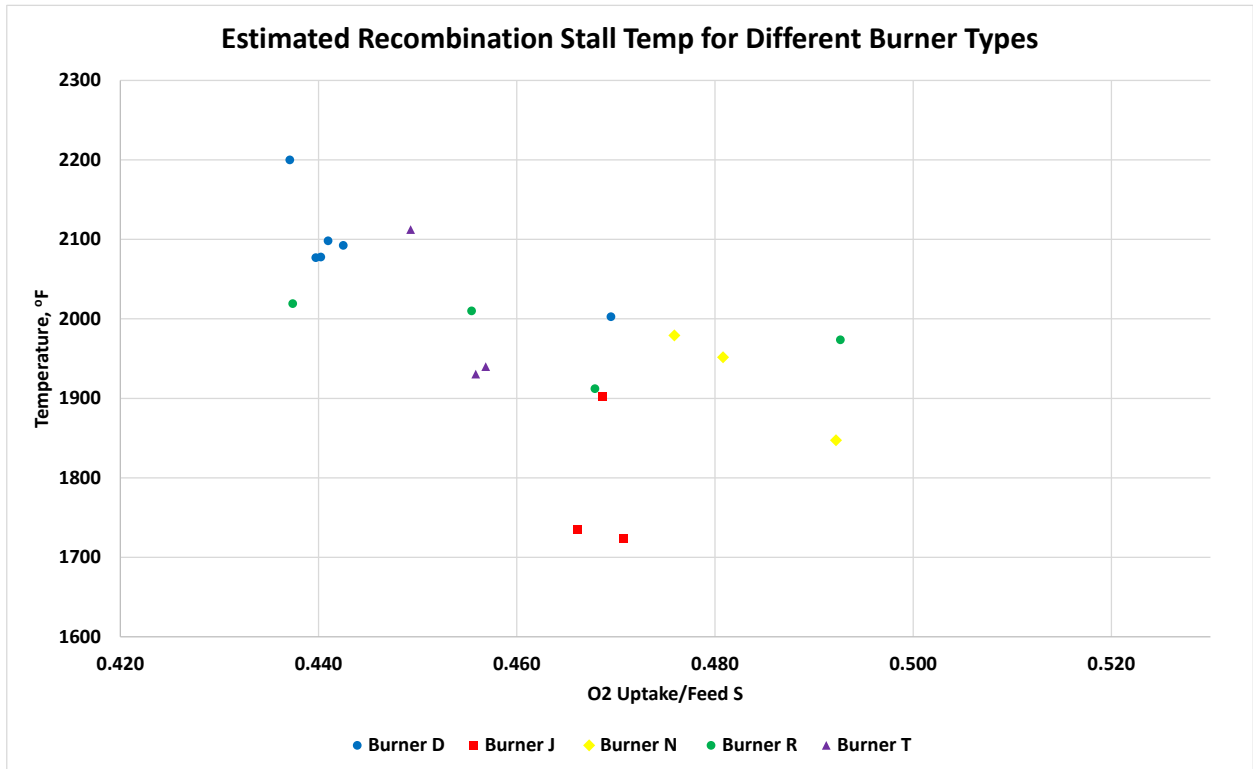


Figure 15



Burner J is a high intensity mixing burner but the thermal reactor is very small in comparison to the other systems. At higher residence time in the thermal reactor, its stall temperatures were like the other burner-thermal reactor-WHE systems. Burners R and T would not be considered high intensity mixing, and both use two chamber thermal reactors for ammonia destruction purposes. However, they follow the general stall temperature profile of the other burner types. Again, it is more likely the design of the WHE contributes more to the final yield structure in each individual plant than does the burner-thermal reactor.

Conclusions

The major conclusions from studying the lab and plant yield data are summarized below:

- Thermal Reactor Modeling is inadequate to account for shifts in both Claus reaction and H_2/S recombination reaction yields accurately
- Data from plant and lab suggest AFT models overpredict both Claus sulfur and dissociation sulfur yields
- Data from plant and lab suggest Claus and recombination reactions are active over different temperature ranges
- Further yield research should concentrate on heat transfer effects in the WHE on both Claus and recombination reactions

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