Claus Process Reactor Simulation

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ABSTRACT

A model was developed to simulate the reaction, concentration field, flow field, and temperature distribution inside a Claus reactor for converting hydrogen sulfide to sulfur. The model considered two ideal reactors, a continuous stirred tank reactor and a plug flow reactor. As expected to two ideal reactors showed much different behaviors in terms of reactant conversion and operating temperature. Operation in the plug flow reactor was much less severe.

A full 1-D model was developed for this system as well. This is a dispersed plug flow model able to mimic the performance of the two idea reactors discussed above. The model included the thermodynamics of the reactions, the actual transport properties of the gaseous species, the fluid flow and heat transfer that would occur in a more realistic version of the Claus system. The problem was an especially challenging one due to the flow rates of material involved, the overall size of the reactor, and the highly exothermic nature of the reactions. Temperatures approaching 1800 K were predicted within the flame zone.

A 2-D simulation was also conducted. We modeled a checkerwall and simplified VectorWall™, static mixer systems. Experimental evidence suggests the static mixers significantly increase the throughput of the reactors. We are planning to look at similar systems for incinerators where we have evidence we can increase throughput and decrease pollutant output levels.

Keywords: Claus process, sulfur production, reactor simulation

1. INTRODUCTION

The Claus process is the largest volume gas desulfurizing process and is used to recover elemental sulfur from hydrogen sulfide [1]. The process was first patented in 1883 by Carl Friedrich Claus and is used to recover sulfur from petroleum refining, natural gas processing, tar sands processing, coal gasification, smelters, coke ovens and other industries. In addition to hydrogen sulfide extracted from by-product gases by an absorption process, petroleum refineries also derive hydrogen sulfide from the steam distillation of wastewaters containing dissolved hydrogen sulfide. Those wastewaters are referred to as sour water and the steam distillation of those wastewaters is referred to as sour water stripping [2].

Gases that contain over 25% H2S content are suitable for processing in straight-through Claus plants while alternate configurations such as a split-flow set up or feed and air preheating can be used to process gases with much lower H2S contents [3]. Worldwide, approximately 64 million metric tons of sulfur are produced via this process. While desulfurization produces an important product, it also extracts sulfur that would eventually end up in the atmosphere as SO2 and so represents an important pollution prevention process. The Claus process generally proceeds in two stages as shown in the figure below

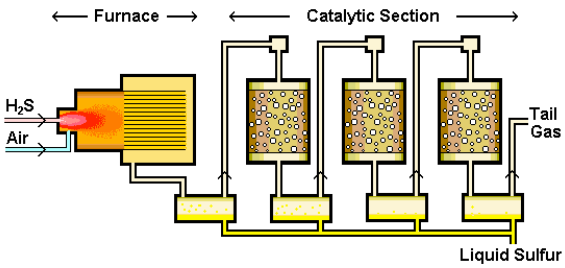


Figure 1 Schematic diagram of the Claus process.

The first stage of the Claus process is the thermal step, where hydrogen sulfide-laden gas reacts with sub-stoichiometric amounts of air in a furnace at temperatures above 850 °C [4]. The combustion reaction is highly exothermic producing sulfur dioxide that reacts with the excess hydrogen sulfide to produce elemental sulfur. The simplified reaction sequence is:

$$2H_2S + 3O_2 \rightarrow 2SO_2 + 2H_2O$$

$$2H_2S + SO_2 \rightarrow 3S + 2H_2O$$

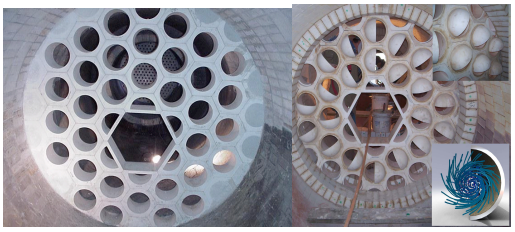
so that the overall reaction can be written as:

$$8H_2S + 5O_2 \rightarrow SO_2 + 7S + 8H_2O$$

Though these are the main reactions, carbon sources and especially ammonia are common

contaminants that also get burned along with the hydrogen sulfide [5]. These additional reactions must also be added to the kinetic scheme.

The Claus reactor generally includes a flow control element called a checkerwall that protects the catalytic section from the furnace. This study looks at replacing the checkerwall with a ceramic static mixing element as shown in Figure 2. In very limited tests, these elements were shown to significantly improve reactor throughput and yield. We model the furnace portion of the reactor with the flow control element in place.



(a) (b)

Figure 2 a) Conventional checkerwall used in a Claus furnace. b) Blasch VectorWall™ system for Claus furnaces.

2.0 MODEL DEVELOPMENT

The basic model was chosen to consist of 7 reactions with eleven separate species. The set of reactions along with the reaction kinetics were chose from a paper by Jones et al [4] who performed a kind of optimization of the Claus process using ASPEN. The model was designed to solve the fluid mechanics, heat transfer, reaction kinetics, and mass transfer components governing the behavior of the reactor. The data describing the physical properties of the individual gases we incorporated into the program in terms of NASA polynomials. These are polynomial representations that describe the enthalpy, entropy, and heat capacity of the individual components. The thermal conductivity, viscosity, and diffusivity of the individual species were calculated using the kinetic theory of gases approach. The NASA polynomial equations and kinetic theory of gases representations are incorporated as part of the Chemical Engineering module in COMSOL.

The model coupled the Chemical Engineering, CFD, and Heat Transfer modules together and assumed compressible flow. Model parameters included those listed in Table 2.

Table 1 Reaction Features

Reaction and Rate Law
$H_2S+\frac{3}{2}O_2 \xrightarrow{k_1} SO_2+H_2O$ $r_1 = k_1 P_{H_2S} P_{O_2}^{1.5}$ $k_1 = 1.4\times10^7 \exp\left[-\frac{46024}{RT}\right]$
$NH_3+\frac{3}{4}O_2 \xrightarrow{k_2} \frac{3}{2}H_2O+\frac{1}{2}N_2$ $r_2 = k_2 P_{NH_3} P_{O_2}^{0.75}$ $k_2 = 4.43\times10^9 \exp\left[-\frac{167360}{RT}\right]$
$H_2+\frac{1}{2}O_2 \xrightarrow{k_3} H_2O$ $r_3 = k_3 C_{H_2} C_{O_2}$ $k_3 = 1.08\times10^{12} \exp\left[-\frac{125520}{RT}\right]$
$CO+\frac{1}{2}O_2 \xrightarrow{k_4} CO_2$ $r_4 = k_4 C_{O_2}^{0.25} C_{CO} C_{H_2O}^{0.5}$ $k_4 = 3.98\times10^{20} \exp\left[-\frac{167360}{RT}\right]$
$NH_3+\frac{3}{4}SO_2 \xrightarrow{k_5} \frac{3}{8}S_2+\frac{3}{2}H_2O+\frac{1}{2}N_2$ $r_5 = k_5 C_{NH_3}^{0.25} C_{SO_2}^{0.5}$ $k_5 = 2.29\times10^7 \exp\left[-\frac{115060}{RT}\right]$
$CH_4+2O_2 \xrightarrow{k_6} CO_2+2H_2O$ $r_6 = k_6 C_{CH_4}^{0.2} C_{O_2}^{1.3}$ $k_6 = 6.8\times10^{18} \exp\left[-\frac{202505.6}{RT}\right]$
$H_2+\frac{1}{2}S_2 \underset{k_{7r}}{\overset{k_{7f}}{\rightleftharpoons}} H_2S$ $r_{7f} = k_{7f} P_{H_2} P_{S_2}$ $r_{7r} = k_{7r} P_{H_2S} P_{S_2}^{0.5}$ $k_{7f} = 5.26\times10^9 \exp\left[-\frac{188280}{RT}\right]$ $k_{7r} = 1.4\times10^7 \exp\left[-\frac{97905.6}{RT}\right]$

Table 2
Input Parameters

Name	Expression	Description
Temp	400	Temperature (K)
Patm	101325	Atmospheric Pressure (Pa)
Press	2.38*Patm	Reactor Pressure (Pa)
Mair	800000/3600	Air molar flow rate through reactor (mole/s)
Mflow	388000/3600	Gas molar flow rate through reactor (mole/s)
Mtot	Mair + Mflow	Total molar flow rate through reactor (mole/s)
xh2s	0.276	H2S inlet fraction
xco2	0.193	CO2 inlet fraction
xnh3	0.361	NH3 inlet fraction
xn2	0.015	N2 inlet fraction
xco	0.024	CO inlet fraction
xar	0.015	Ar inlet fraction
xh2o	eps	H2O inlet fraction
xh2	0.116	H2 inlet fraction
xso2	eps	SO2 inlet fraction
xo2	0.2	O2 inlet fraction
xch4	eps	CH4 inlet fraction
xs2	eps	S2 inlet fraction

3.0 RESULTS

A two-dimensional version of a flow reactor including a checkerwall and a static mixer element were simulated. Though the actual reactor operates in the turbulent flow regime, coupling a turbulence model to the rest of the formulation was beyond the capability of a desktop computer and will be studied once the model is ported over to Rensselaer's supercomputing cluster.

Several issues made for a very difficult simulation. The reaction rates and heat generation rates are very high and so the equations were extremely stiff. COMSOL had trouble with reaction rates containing fraction orders. Raising a negative number or number close to zero was not possible unless the exponent was of integer order. One way to work around this was to express the rate laws in logarithmic form and reconvert. However, due to the stiffness of the equations, it was still possible for COMSOL to overshoot and lead to negative or near zero concentrations that the log function would also not evaluate. Therefore, penalty functions and conditional statements were also included to insure that all concentrations remained in bounds. Adaptive meshing was also required and a solution could not be obtained unless the heat generation was ramped up slowly to its ultimate value. Figure 3 shows an example of the mesh required.

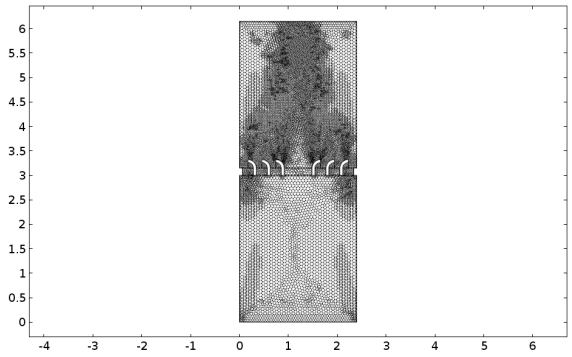


Figure 3 Mesh geometry for the reactor simulation.

Figures 4 - 6 show the velocity field within the reactor. This reactor is 2.4 m in diameter and 6.2 m long, as a test. In Figure 4 it is easy to see the jets of fluid passing through the checkerwall and there are recirculation zones near the walls of the reactor and between holes in the checkerwall that affect the reaction. In Figures 5 and 6, we have inserted a simple VectorWall™, static mixer element. The velocity patterns have changed substantially. Here it appears that a central hole within the wall is likely to give a better profile than a central obstruction, one of the features we will be looking to optimize in future simulations. Peak velocities are higher with the VectorWall™ element in place.

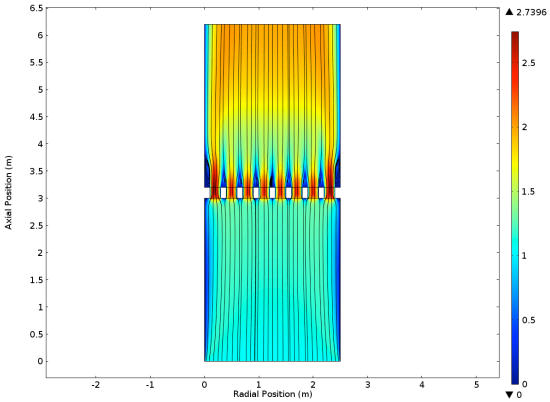


Figure 4 Flow field through a conventional checkerwall element.

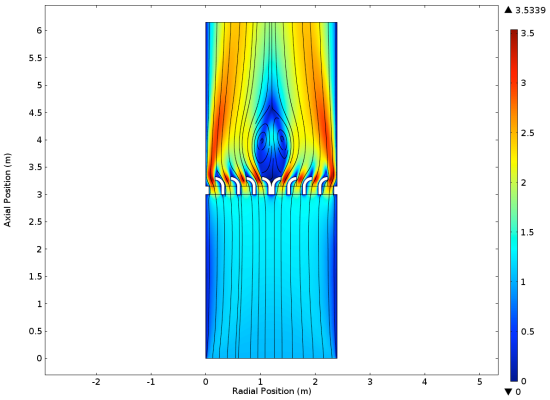


Figure 5 Flow field through a static mixer configuration with a central obstruction.

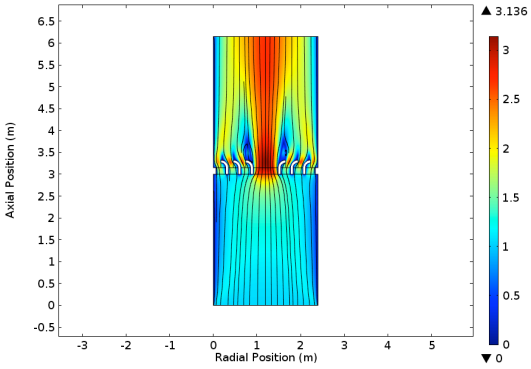


Figure 6 Flow field through a static mixer configuration without a central obstruction.

Figures 7 - 9 show the temperature profile within the reactor. The temperature is still a bit low since heat inputs were only 10% of theoretical maximum load. Still, the combination of reaction and flow shows where the hot spots in the system are likely located. Figures 8 and 9 show the profile with the VectorWall™, mixing element. Temperatures are higher here however the conversion of H_2S is also greater. The hot spot here is at the center of the reactor, far removed from the walls.

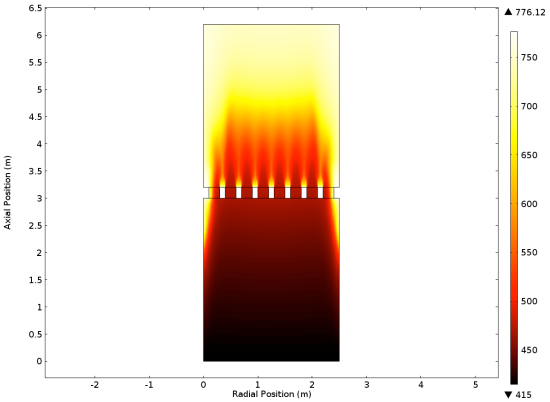


Figure 7 Temperature distribution in a checkerwall reactor configuration.

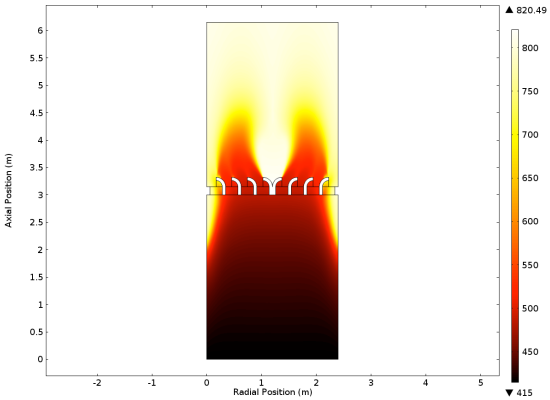


Figure 8 Temperature distribution in a static mixer configuration with a central obstruction.

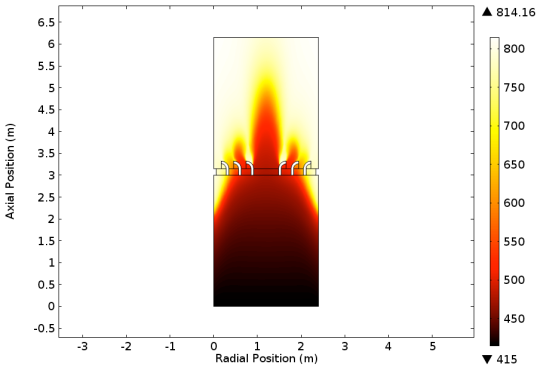


Figure 9 Temperature distribution in an a static mixer configuration without a central configuration.

Figures 10 - 12 show the heat generation rate within the reactor configurations. This view shows a bit more clearly where the hot spots are, where the flame is striking within the reactor and where the mixing system may prove beneficial. The stagnant zones between wall openings provide for very high heat generation rates and high temperatures. Using the VectorWall™ mixing element significantly alters the distribution of where the energy is being generated and peak generation rates are higher following the increased consumption of H_2S.

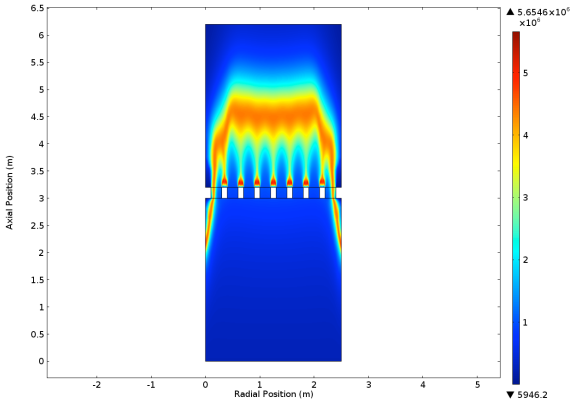


Figure 10 Flame front in a conventional checkerwall reactor configuration.

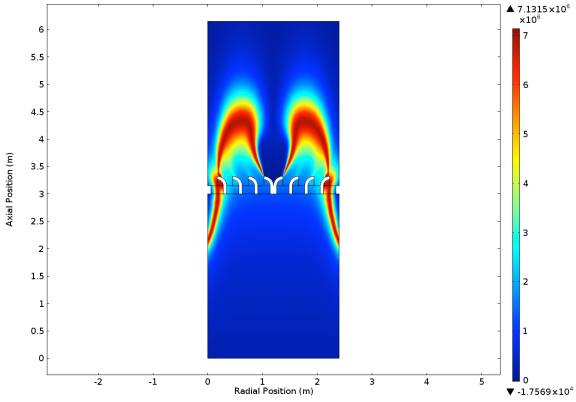


Figure 11 Flame front in a static mixer configuration with a central obstruction.

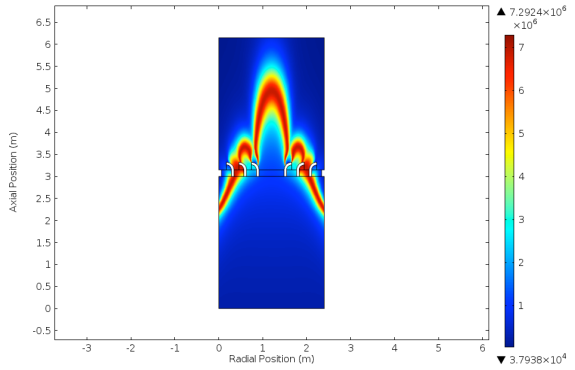


Figure 12 Flame front in a static mixer configuration without a central obstruction.

4.0 CONCLUSIONS

We successfully simulated the Claus process in ideal chemical reactors, in a dispersed, plug flow reactor, and a two-dimensional flow reactor with a checkerwall and VectorWall™, static mixing configuration. We considered seven total reactions containing eleven separate components and included the variation in physical properties with temperature as well as the heat of reaction. The hydrodynamics, heat transfer, mass transfer and chemical reaction were all included within the model. The reaction set is highly exothermic and so a large amount of heat is generated. The 2-D simulations showed where problem spots may lie and where the enhanced mixing of the static mixing element may be put to best use. The next steps will be to apply this kind of modeling effort to incinerators, coal combustors, or fertilizer operations.

5.0 REFERENCES

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