

# Catalytic H<sub>2</sub>S Conversion and SO<sub>2</sub> Production over Iron Oxide in Liquid Sulfur

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## Introduction

Many different approaches have been developed for H<sub>2</sub>S conversion from low H<sub>2</sub>S-content gas streams. These include sub-dew point processes, H<sub>2</sub>S recycle processes, catalytic oxidation methods and various scavenging technologies [1]. Designed primarily for Claus tail gas clean-up, these processes also have the potential to be incorporated as a stand alone system for low tonnage sulfur recovery (< 10 ton/day). Low H<sub>2</sub>S content gas streams exist where economically producing a clean effluent gas requires a small scale process with low infrastructure and maintenance costs. For this reason, investigations into new and improved low tonnage sulfur recovery processes are receiving considerable attention.

Using a slurry bed of catalyst containing liquid sulfur for low tonnage sulfur recovery has been shown to have potential. Notable advantages of using liquid sulfur include a thermal mass capable of absorbing the heat of reaction and sub-dew point system operation at < 150 °C, a temperature at which equilibrium Claus conversion exceeds 99 %. Kerr and Jagodzinski first studied the catalytic conversion of H<sub>2</sub>S/SO<sub>2</sub> in liquid sulfur under atmospheric conditions and elevated pressures [2]. Using a slurry reactor assembly (160 °C), a lean acid gas mixture (2.5 % H<sub>2</sub>S: 1.2 % SO<sub>2</sub>) was fed through an alumina containing bed of liquid sulfur. H<sub>2</sub>S conversion being moderate at atmospheric pressure was virtually complete at higher pressures. The design was patented as the Richards Sulfur Recovery Process, but no follow-up to the work either through further scientific studies or commercial application is known.

Our study investigates unsupported iron oxide for its ability to catalyze H<sub>2</sub>S conversion in liquid sulfur. H<sub>2</sub>S conversions were determined comparing initial iron oxide scavenging ability and steady-state catalytic activity. Analysis of H<sub>2</sub>S/O<sub>2</sub> consumption and SO<sub>2</sub> production from the reactor provided insight to the steady-state catalysis. In addition to direct oxidation, Claus activity and liquid sulfur oxidation were investigated using the steady-state iron oxide. In the end, a dual catalyst concept ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub>/steady-state iron oxide) provided high H<sub>2</sub>S conversion to elemental sulfur.

## Materials and Methods

Experiments were performed using a Buchi stirred autoclave system equipped with a magnetic stirrer and hollow shaft gassing turbine. The reaction medium consisted of elemental liquid sulfur with either a 5 wt% iron oxide content or a 5 wt% iron oxide/1 wt%  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> content. Iron oxide catalyst was prepared in our laboratory via a wet precipitation method while the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was crushed, commercial grade product. Both were shaken through a 45  $\mu$ m sieve to ensure particle uniformity. Reactant gases were delivered into the autoclave using calibrated mass flow controllers from Advanced Specialty Gases. Gases were mixed and

fed into the liquid sulfur. For all experimental data sets, reactor conditions were held constant. Steady-state analysis parameters include a stirring rate of 1000 rpm, a reactor temperature of 135 °C and an operating pressure of 30 psig. A stoichiometric (1.60 % H<sub>2</sub>S: 0.80 % O<sub>2</sub>: balance N<sub>2</sub>) gas flow ratio was the primary feed gas, although other inlet gas mixtures were also used. Inlet and outlet gas stream analysis was achieved using a dual column Varian 3800 gas chromatograph equipped with dual TCD detection.

## Results and Discussion

Catalytic activity of unsupported iron oxide for H<sub>2</sub>S conversion was first investigated. Fresh iron oxide acted predominantly as a scavenger for bulk H<sub>2</sub>S removal from the sour gas stream, with the subsequent steady-state iron oxide material maintaining only a low catalytic activity towards H<sub>2</sub>S conversion (30 %). Interestingly however, the modified catalyst surface showed an increased propensity to generate significant amounts of SO<sub>2</sub> from a H<sub>2</sub>S/O<sub>2</sub> gas stream. Removing the H<sub>2</sub>S from the feed gas and passing a 0.80 % O<sub>2</sub>/balance N<sub>2</sub> gas stream over steady-state iron oxide, significant SO<sub>2</sub> was generated. With O<sub>2</sub> consumption equaling SO<sub>2</sub> production (~ 0.30 % respectively) from the reactor and no sulfur species in the feed gas, the steady-state iron oxide promoted the oxidation of the liquid sulfur to SO<sub>2</sub>. Using an inlet feed gas ranging in O<sub>2</sub> concentration from 0.60 % to 17.3 % (balance N<sub>2</sub>), the rate of SO<sub>2</sub> production was shown to be directly proportional to the inlet O<sub>2</sub> concentration. As with all first order kinetic relationships, doubling the inlet O<sub>2</sub> concentration resulted in a doubling of SO<sub>2</sub> concentration in the outlet gas stream. This correlation was observed over the aforementioned O<sub>2</sub> concentration range with a linearity correlation coefficient (R<sup>2</sup>) of 0.9992. SO<sub>2</sub> production could therefore be controlled by controlling the amount of O<sub>2</sub> in the feed gas.

Improvements to the H<sub>2</sub>S conversion were investigated through a dual catalyst concept where the SO<sub>2</sub> generated in the reactor was productively used to promote further H<sub>2</sub>S conversion through the Claus reaction. To accomplish this, a Claus active surface (1 wt%  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) was added to the reactor containing 5 wt% steady-state iron oxide. Our hypothesis was that the steady-state iron oxide would in-situ generate SO<sub>2</sub> (from a H<sub>2</sub>S/O<sub>2</sub> containing feed gas) which would then subsequently react with the H<sub>2</sub>S through the Claus mechanism on the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> surface. Using the same controlled set of experimental parameters, > 97 % H<sub>2</sub>S conversion was attained with no SO<sub>2</sub> detected in the tail gas of the process.

## Significance

A dual catalyst method that uses in-situ generated SO<sub>2</sub> to promote H<sub>2</sub>S conversion through the Claus mechanism is a novel concept in the field of low tonnage sulfur recovery from low H<sub>2</sub>S-content gas streams. Our study highlights liquid sulfur reactivity over steady-state iron oxide to produce SO<sub>2</sub>. Thought as being an undesirable reaction product, a multiple mechanism scheme allows the in-situ generated SO<sub>2</sub> to be consumed through a reaction with H<sub>2</sub>S, thus promoting high H<sub>2</sub>S conversion to elemental sulfur.

## References

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