

Conversion of Hydrogen Sulfide in Coal Gases to Liquid Elemental Sulfur with Monolithic Catalysts

Kyung C. Kwon, Claudell Burnell, and Laneddye Carter

Chemical Engineering Department
Tuskegee University

Robie Lewis

U.S. Department of Energy National Energy Technology Laboratory,
Morgantown, WV 26507 -0880

Outline

- Introduction
- Motivation
- Objectives
- Experimental Setup
- Results and Discussion
- Summary

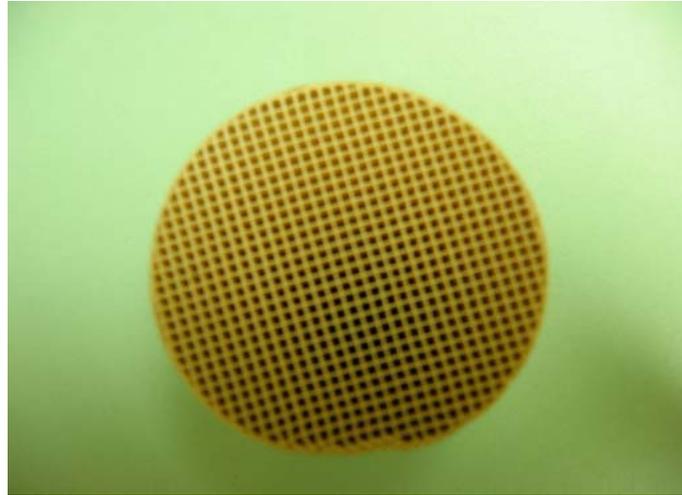
Motivation

- Conversion of coal into clean raw syngas by coal gasification is the primary step in advanced coal utilization processes
- Increased removal of hydrogen sulfide (H_2S) and reduced formation of carbonyl sulfide (COS) from raw syngas and elemental sulfur recovery are necessary.
- Conventional amine-based processes for sulfur removal and recovery are equipment intensive and expensive, requiring upstream COS hydrolysis reactor, amine scrubber, amine regenerator, Claus plant and tail-gas treatment plant.
- Tuskegee University (TU) is developing the Single-Step Sulfur Recovery Process (SSRP) using Claus catalysts in monolithic form instead of conventional Claus catalysts in fine pellet form.

Objectives

- To study kinetics of direct oxidation of H_2S to elemental sulfur and formation of COS over selective catalysts in the presence of SO_2 , moisture, CO, CO_2 , and hydrogen, using a monolithic catalyst-loaded reactor.
- To investigate effects of concentrations of H_2S , SO_2 , and moisture, as well as pressure, space time, catalyst age, and temperature on conversion of H_2S into elemental sulfur and formation of COS.
- To formulate catalysts for the Single-Step Sulfur Recovery Process (SSRP) and regenerate elemental sulfur poisoned catalyst.
- To develop kinetic rate equations and model the direct oxidation process with experimental data.

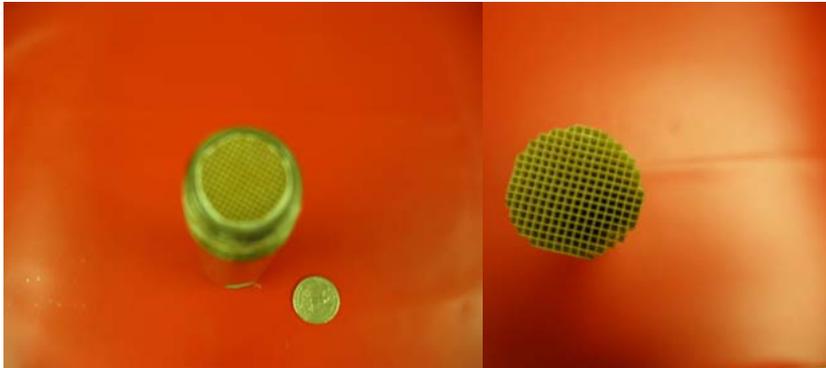
Monolithic Catalyst Support



Cell Shape	square
Cells/inch ² (CPSI)	400
Wall Thickness, cm	0.02
Flat Area/Cell/Length, cm ² /cell/cm-length	0.345
Chemical Composition, (2MgO-2AL ₂ O ₃ -SIO ₂)	Cordierite

Monolithic Catalyst

Top View



Side View



Diameter, cm

2

Length, cm

15

Number of Square Cells

200

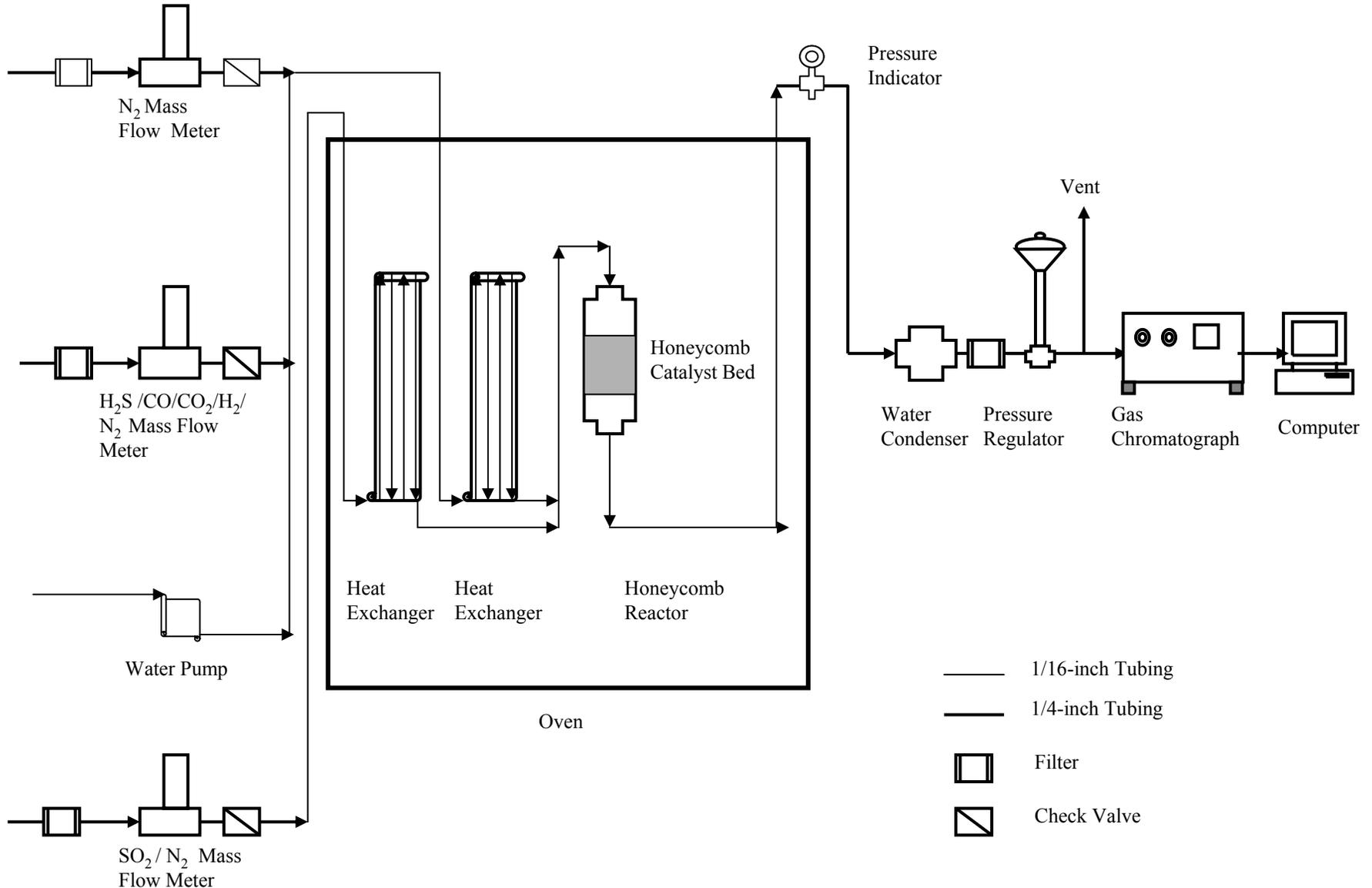
Flat Surface Area, cm²

1,040

Wash Coat

$\gamma\text{-Al}_2\text{O}_3$

Schematic Diagram of the Monolithic Catalyst Reactor Assembly.



Monolithic Catalyst Reactor Assembly

- The monolithic catalyst loaded reactor assembly consists of one high pressure liquid pump for water, three mass flow meters for gases, three filters and check valves for gases, two preheaters, one monolithic catalyst reactor, one oven, one water condenser, and one pressure regulator protected by a filter.
- The monolithic catalyst reactor is fabricated with a γ -alumina-wash-coated 400-CPSI monolithic catalyst and a 2.2-cm-ID x 15-cm-long stainless steel HPLC column.
- A heat exchanger is made of 20-ft-long 1/16-inch Teflon tubing.
- Most surfaces in contact with process gas mixtures are Teflon.

Experimental Setup



Mass Flow Meters



Water Pump



Rotameter, Gas Bag, and Pressure Indicator

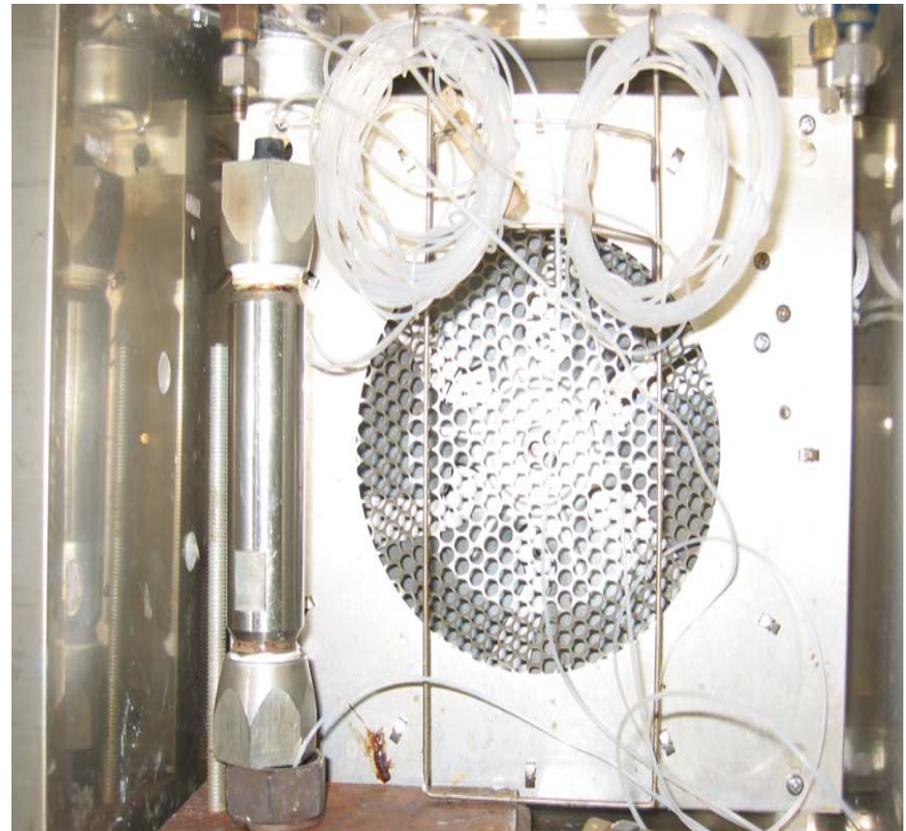


Reactor, Condenser, and Heaters

Reactor and Condenser



Reactor and Heat Exchangers in the oven



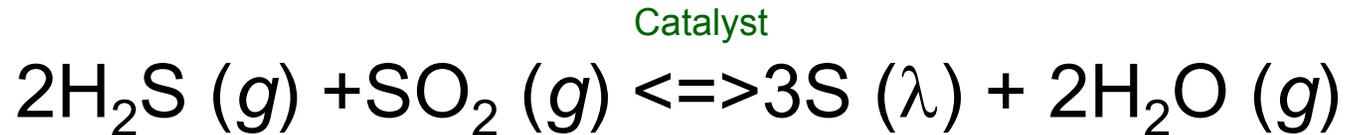
Experimental Procedures

- The reactor, loaded with a γ -alumina wash-coated monolithic catalyst, is placed inside the oven to be heated to a desired temperature.
- Nitrogen is introduced into the catalyst-loaded reactor during testing leakage of the fittings for the reactor and preheating the reactor.
- When the temperature of the reactor is raised to the desired temperature, a gaseous reaction mixture was introduced into the reactor, by switching nitrogen with the reaction mixture.
- Conversion of H_2S into elemental sulfur and formation of COS are analyzed with a gas chromatograph and a computer.

Typical Experimental Conditions

Volume of the monolithic catalyst bed, cm ³ :	47
Temperature, °C:	120 -150
Reaction Pressure, psia:	118 -205
Space Time under the reaction conditions, s:	90 - 560
Gas Feed Rate, cc/min at room temperature and 1 atm (SCCM):	30 -180
Concentration of H ₂ S, ppmv:	3,600 - 4,000
Concentration of SO ₂ , ppmv:	1,800 - 2,000
Carbon monoxide, vol %:	36 - 41
Hydrogen, vol %:	23 - 27
Carbon dioxide, vol %:	10 - 12
Moisture, vol %:	0 - 10
Nitrogen, vol %:	Remainder

Stoichiometric Reaction Formula



Le Chatelier's Principal

- Conversion of H_2S increases with increased total pressure, and increased concentrations of both H_2S and SO_2 .
- Conversion of H_2S decreases with increased moisture and increased temperature, since the reaction is exothermic
- Conversion of H_2S is not affected by amounts of liquid elemental sulfur, since volume of liquid elemental sulfur is negligible in comparison with volume of water vapor produced.

Properties of Liquid Elemental Sulfur

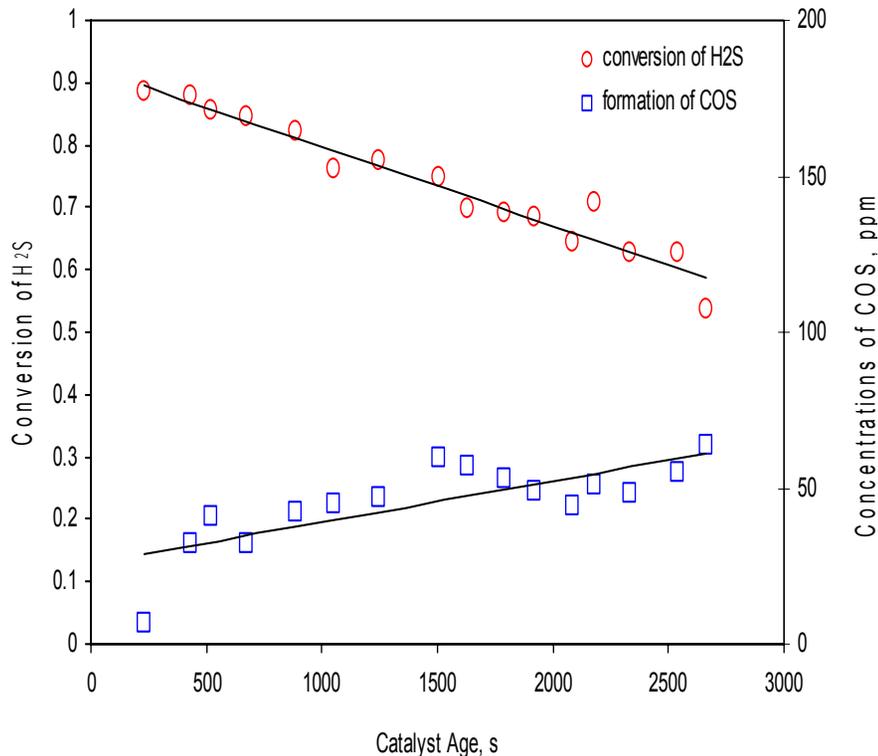
Melting point of solid elemental sulfur, °C	110 - 119
Boiling point of solid elemental sulfur, °C	445
Density of elemental solid sulfur at 20 °C, g/cm ³	1.92 - 2.07
Density of elemental liquid sulfur at 125 °C, g/cm ³	1.7988
Surface tension at 120 °C, dyne/cm	60.83
Apparent viscosity of liquid elemental sulfur at 120 °C, poise	0.011 - 0.035

- Liquid elemental sulfur is non-Newtonian fluid.
- Viscosity of liquid elemental sulfur decreases with temperature up to 157°C,
- and then rapidly increases with temperature.

Experimental Difficulties

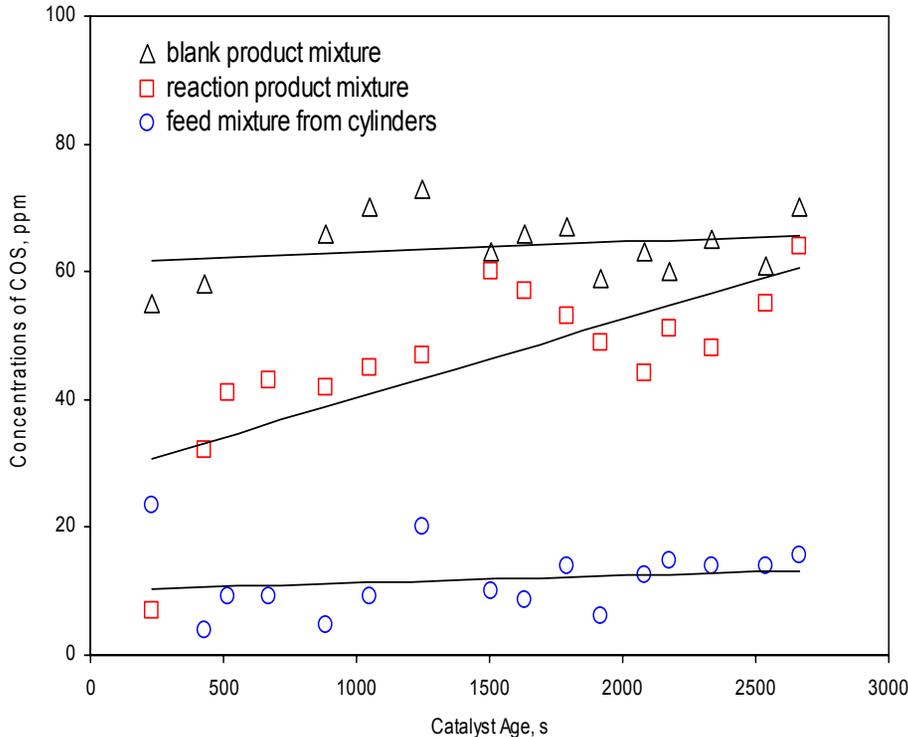
- Poor reproducibility of experimental data, since both SO_2 and H_2S are very reactive in addition of peculiar behavior of liquid elemental sulfur.
- Plugging problems, since viscous non-Newtonian liquid sulfur as well as solid sulfur are produced out of gaseous H_2S and SO_2 .
- Leakage of reaction gas mixtures through Teflon fittings due to irreversible thermal deformations of Teflon fittings and tubing under the reaction conditions.
- Frequent upset of the gas chromatograph

Figure 7. **Effects of catalyst age on conversion of H₂S** to elemental sulfur and formation of COS with a 120 SCCM feed stream containing 3,600-ppm H₂S, 1,800-ppm SO₂ as an oxidant, and 10-v% moisture at 140°C, 119 -124 psia, and 139 – 143 s space time.



- Removal of H₂S decreases and formation of COS increases with increased catalyst age
- Poor diffusion of the reaction products such as liquid sulfur and H₂O vapor from the monolithic catalyst internal surface to the external monolithic catalyst surface through the monolithic catalyst pores.
- Deposition of some liquid element sulfur on the internal and external monolithic catalyst surface

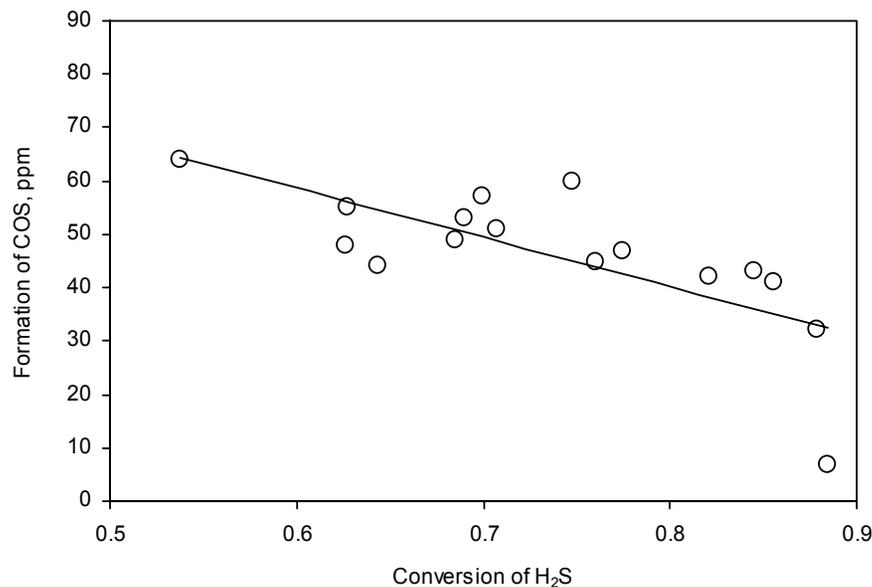
Figure 8. **Effects of catalyst age on formation of COS** with a 120 SCCM feed stream containing 3600-ppm H₂S, 1800-ppm SO₂ as an oxidant, and 10-v% moisture at 140°C, 119 - 124 psia, and 139 – 143 s space time



- Formation of COS increases with catalyst age
- Formation of COS is higher in the absence of catalyst than in the presence of catalyst
- COS is formed by both thermal reaction and catalytic reaction.



Figure 9. Effects of conversion of H₂S to elemental sulfur on formation of COS with a 120 SCCM feed stream containing 3,600-ppm H₂S, 1,800-ppm SO₂ as an oxidant, and 10-v% moisture at 140°C, 119 -124 psia, 139 – 143 s space time, and 230 – 2670 s catalyst age.



- Formation of COS decreases with increased conversion of H₂S.
- COS is formed by combining H₂S with CO in addition to S with CO

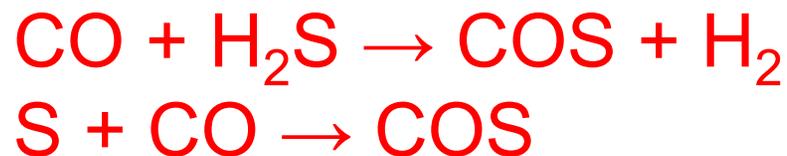
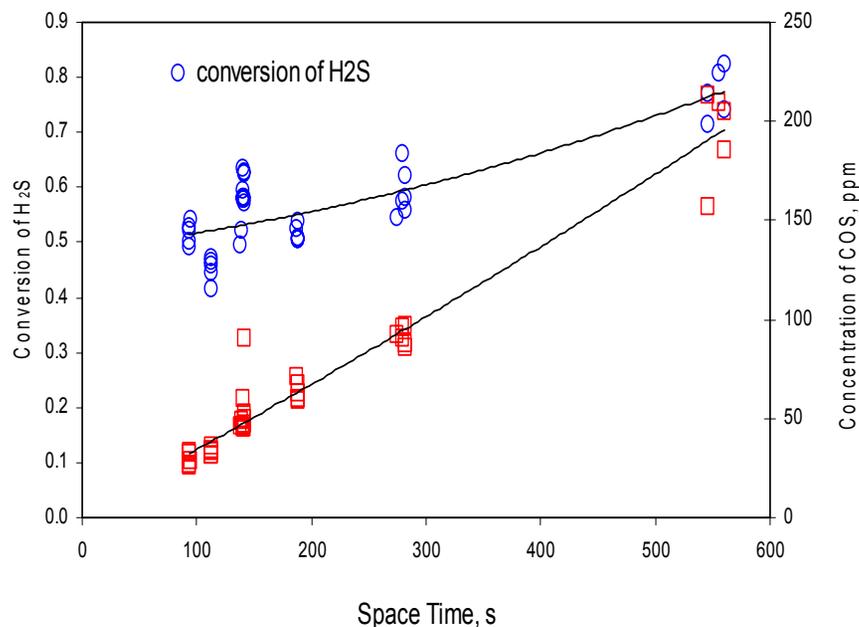
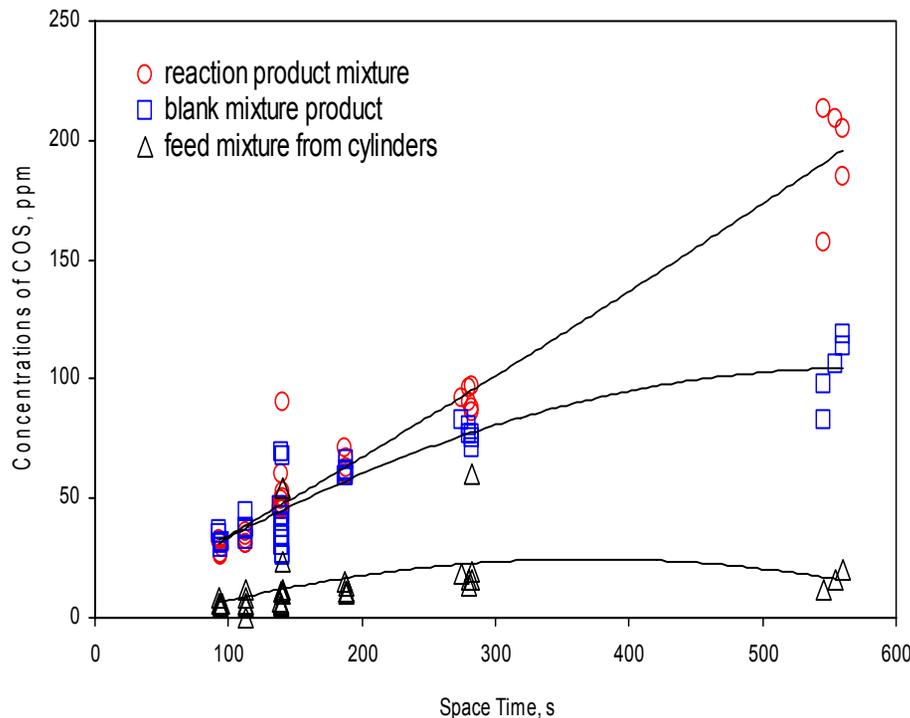


Figure 2. Effects of space time on conversion of H_2S to elemental sulfur and formation of COS with a 30 - 180 SCCM feed stream containing 3600-ppm H_2S , 1800-ppm SO_2 as an oxidant, and 10-v% moisture at $140^\circ C$, 118 - 123 psia, and 90 -560 s space time.



Removal of H_2S and formation of COS increase with increased space time.

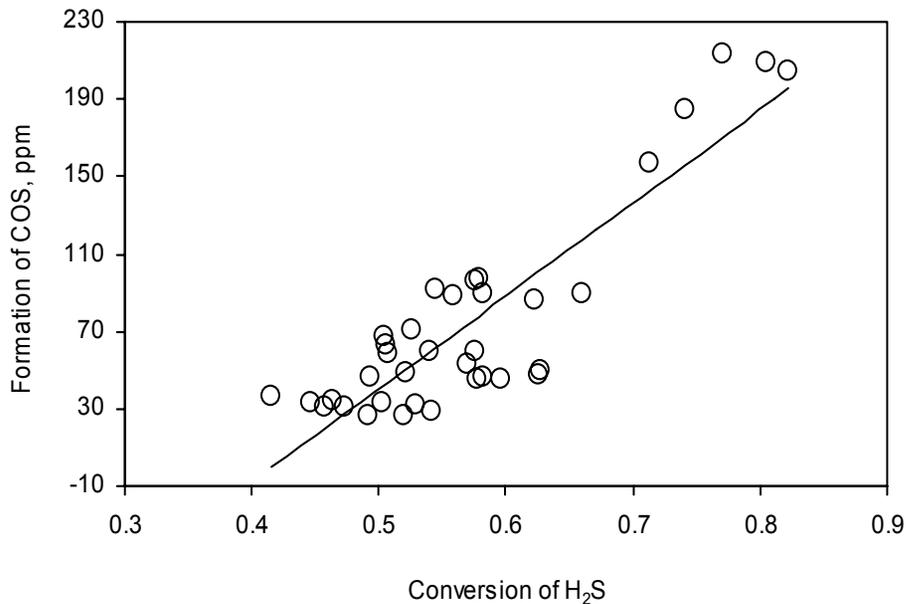
Figure 3. **Effects of space time on formation of COS** with a 30 - 180 SCCM feed stream containing 3,600-ppm H₂S, 1,800-ppm SO₂ as an oxidant, and 10-v% moisture at 140°C, 118 - 123 psia, and **90 -560 s space time.**



■ Formation of COS increases with space time in the presence and in the absence of catalyst.

■ Formation of COS is higher in the presence of catalyst than in the absence of catalyst.

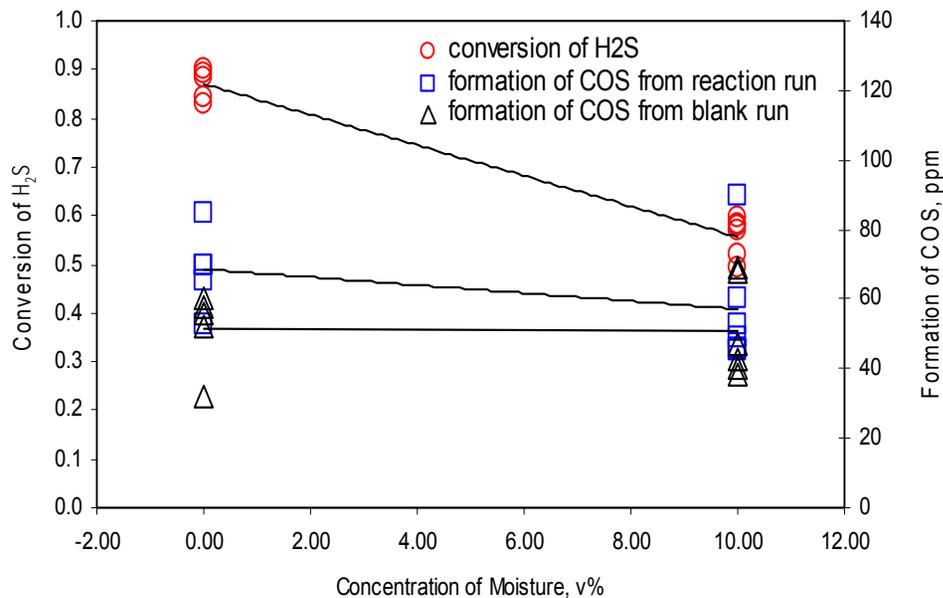
Figure 4. **Effects of conversion of H₂S on formation of COS** with a 30 - 180 SCCM feed stream containing 3,600-ppm H₂S, 1,800-ppm SO₂ as an oxidant, and 10-v% moisture at 140°C, 118 - 123 psia, and **90 – 560 s space time**.



- Formation of COS increases with conversion of H₂S.
- COS is mostly formed by combining elemental sulfur with CO.



Figure 6. **Effects of moisture on conversion of H₂S to elemental sulfur and formation of COS** with a 108 – 120 SCCM feed stream containing 3,600 - 4,000 ppm H₂S, 1800 - 2,000 ppm SO₂, and **0 - 10-v% moisture** at 140oC and 118 - 123 psia.



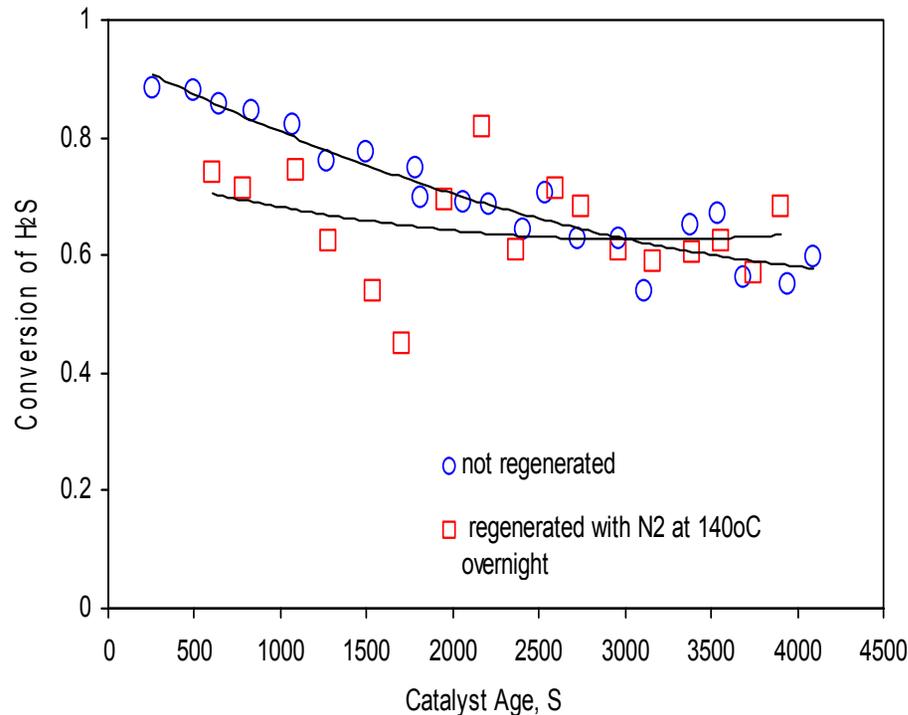
■ Removal of H₂S decreases with increased moisture.



■ Formation of COS decreases with increased moisture.

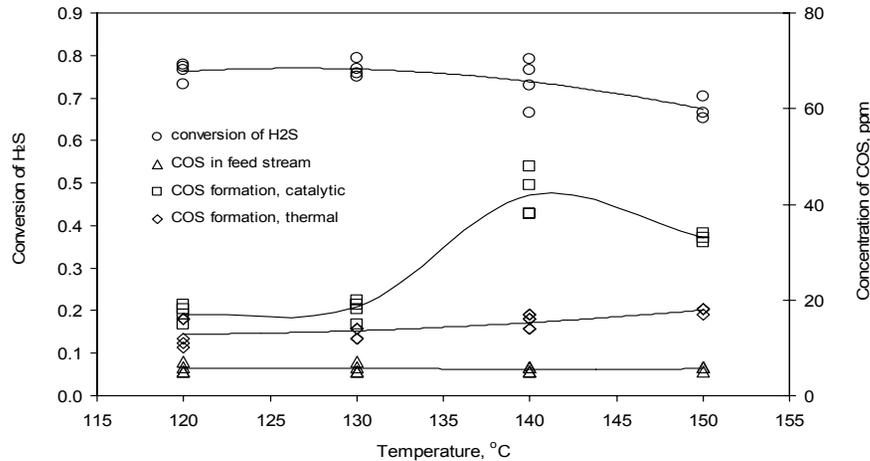


Figure 10. **Effects of catalyst regeneration on conversion of H₂S** for conversion to elemental sulfur with a feed stream containing 3600-ppm H₂S, 1800-ppm SO₂ and 10-v% moisture at 121- 122 psia . Catalyst is regenerated with 140°C N₂ overnight



- Catalyst poisoned with elemental sulfur
- Catalyst can be regenerated by removing liquid elemental sulfur from catalyst with N₂ at 140°C

Figure 5. **Effects of temperature on conversion of H₂S** to elemental sulfur and formation of COS with a feed stream containing 3,600-ppm H₂S, 1,800-ppm SO₂ and 10-v% moisture at 121- 123 psia and 136 - 142 s space time, using **regenerated catalysts**.



- Removal of H₂S decreases with increased reaction temperature.

- Formation of COS increases with reaction temperature.

- COS is mainly formed by reacting CO with vapor sulfur.

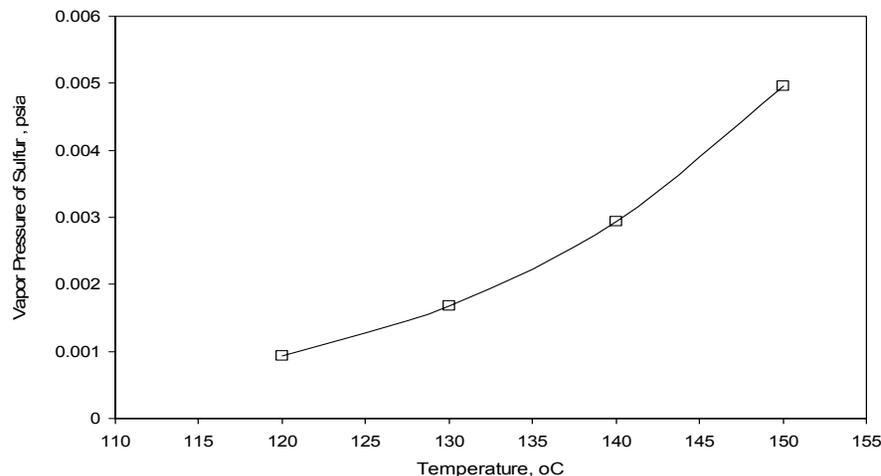
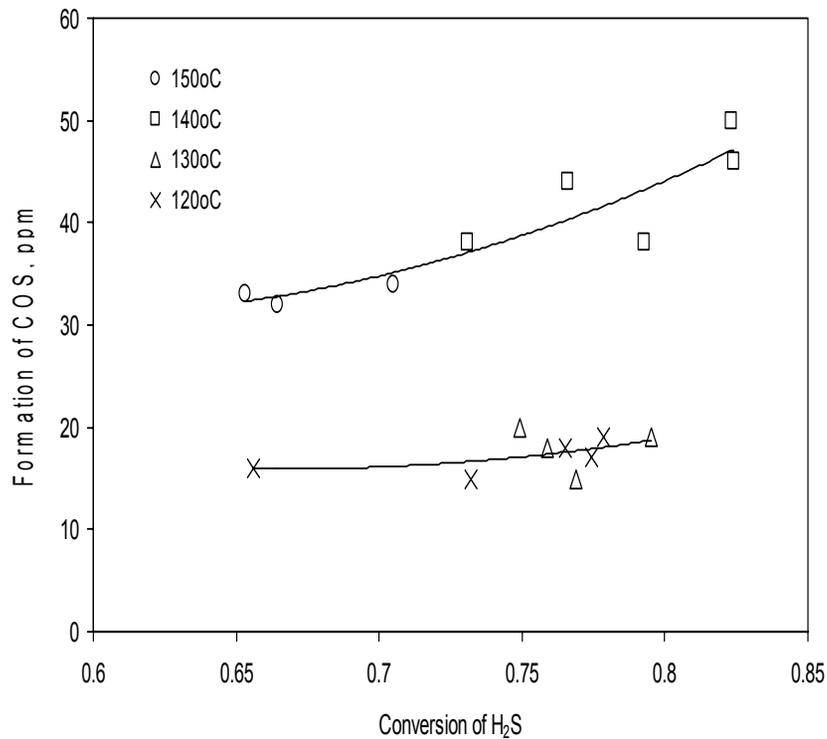
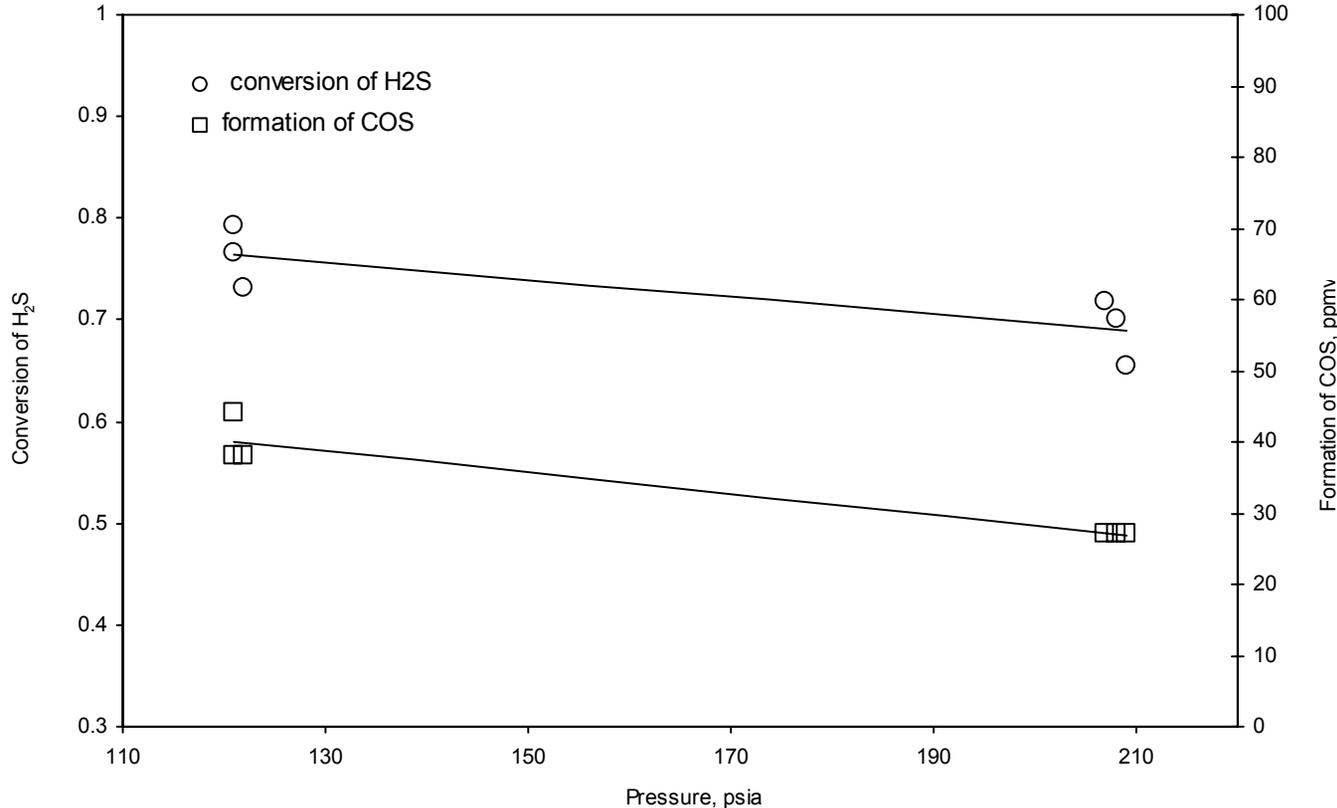


Figure 10. **Effects of conversion of H₂S on formation of COS** with a 120-SCCM feed stream containing 3,600-ppm H₂S, 1,800-ppm SO₂ and 10-v% moisture at 121- 123 psia and 120 - 150°C, using **regenerated catalysts.**



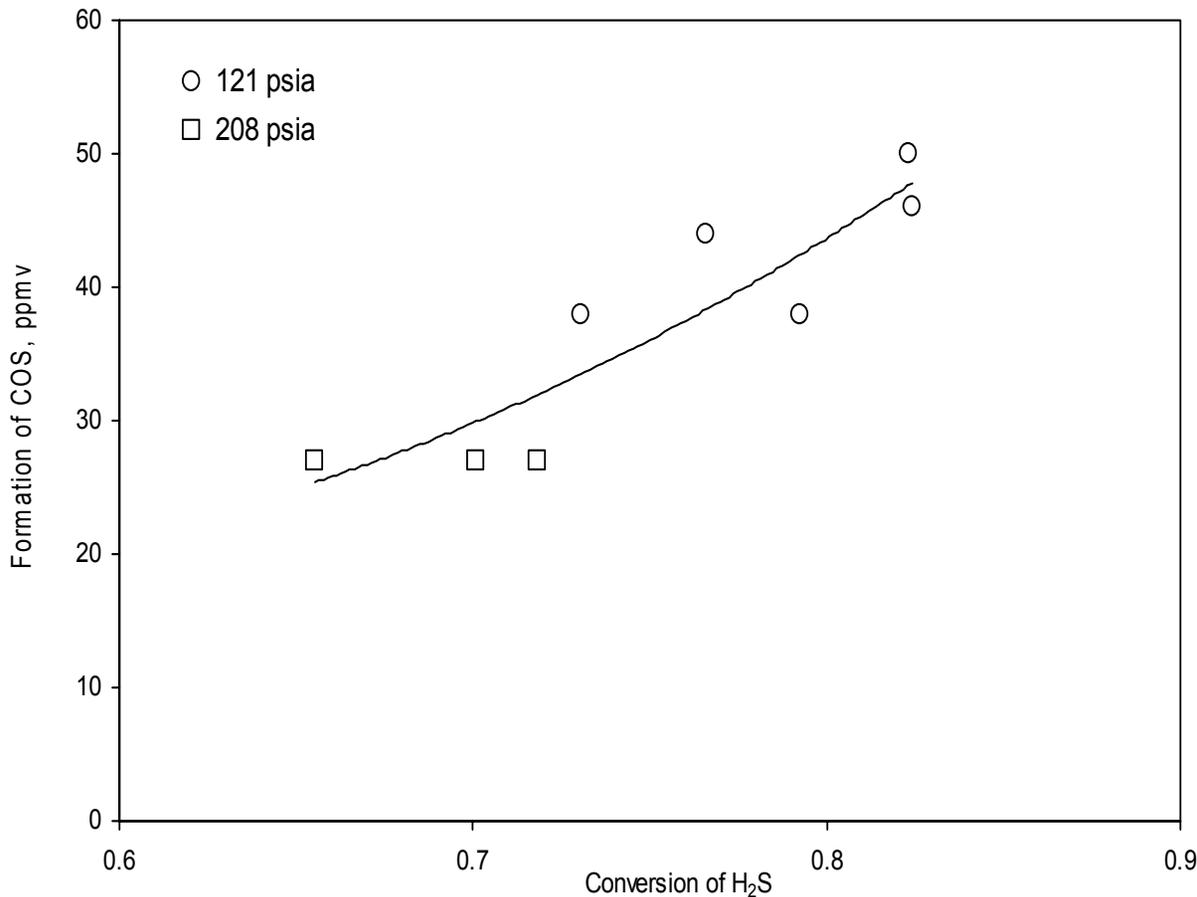
- Formation of COS increases steeply with conversion of H₂S over the temperature range of 140 – 150°C.
- Formation of COS increases slightly with conversion of H₂S over the temperature range of 120 – 130°C

Figure 12. Effects of pressure on conversion of H₂S and formation of COS with a 120-SCCM feed stream containing 3,600-ppm H₂S, 1,800-ppm SO₂ and 10-v% moisture at 121- 208 psia and 140°C, using a regenerated catalyst.



Conversion of H₂S and formation of COS decrease slightly with pressure

Figure 12. **Effects of conversion of H₂S on formation of COS** with a 120-SCCM feed stream containing 3,600-ppm H₂S, 1,800-ppm SO₂ and 10-v% moisture at **121- 208 psia** and 140°C, using a regenerated catalyst.



Formation of COS increases with conversion of H₂S

Summary

- Removal of H_2S increase with increased space time. Formation of COS increases with space time in the presence and in the absence of catalyst. Formation of COS increases with conversion of H_2S . Formation of COS is higher in the presence of catalyst than in the absence of catalyst. COS in the presence of catalyst may be mostly formed by combining elemental sulfur with CO. COS in the absence of catalyst may be mostly formed by combining hydrogen sulfide with CO.
- Removal of H_2S and formation of COS decreases with increased moisture. decreases with increased moisture.
- Removal of H_2S decreases and formation of COS increases with increased catalyst age. Poor diffusion of the reaction products such as liquid sulfur and H_2O vapor through the monolithic catalyst pores and deposition of liquid element sulfur on the internal monolithic catalyst surface may reduce catalytic activities. Formation of COS is lower in the presence of catalyst than in the absence of catalyst. COS is formed by both thermal reaction and catalytic reaction. Formation of COS decreases with increased conversion of H_2S . COS is formed by combining H_2S with CO in addition to S with CO.
- Catalyst can be regenerated by removing liquid elemental sulfur from catalyst with N_2 .
- Removal of H_2S decreases and formation of COS increases with increased reaction temperature. COS is mainly formed by reacting CO with vapor sulfur.
- Removal of H_2S and formation of COS is affected slightly by pressure

Acknowledgements

U. S. Department of Energy National Energy Technology Laboratory supports this research project through the contract number DE-FG26-04NT42129.