

3. SINGLE-STEP SULFUR RECOVERY PROCESS (SSRP)

3.1. Introduction

As an alternative to AHGP (described in the previous section), the Single-Step Sulfur Recovery Process (SSRP) is being developed as a simple, economically attractive process to remove and recover sulfur from raw syngas that can be integrated with coal-based integrated gasification combined cycle (IGCC) power generation. The SSRP involves the direct catalytic oxidation of hydrogen sulfide (H₂S) to elemental sulfur using sulfur dioxide (SO₂) in the presence of >60vol% of highly reducing fuel gas components such as hydrogen (H₂) and carbon monoxide (CO).

RTI has conducted research on SSRP and developed it to the point that a patent application was recently filed (*Gangwal et al., 2002^b*). Based on the promising results of SSRP testing in a lab-scale fixed-bed micro-reactor, a bench-scale 2-liter continuous stirred tank reactor (CSTR) with the catalyst suspended in molten sulfur was used to scale up the process. Results demonstrated the feasibility of sulfur recovery from syngas in a molten sulfur / catalyst slurry. Optimization of reaction conditions (temperature, pressure, feed composition, contact time) and catalyst (type, activation procedure) are critical for enhanced sulfur removal and suppressing the undesirable formation of carbonyl sulfide (COS).

3.2. Process Description

The SSRP is a direct Claus process that consists of injecting SO₂ directly into the quenched coal gas from a coal gasifier, and reacting the H₂S-SO₂ mixture over a selective catalyst to both remove and recover sulfur in a single step:



The key differences between SSRP and the traditional Claus process are: a) in SSRP the catalytic oxidation of H₂S by SO₂ (Claus reaction) occurs selectively in a highly reducing atmosphere containing the highly reactive H₂ and CO fuel gas components, and b) the reaction is carried out at the pressure of the fuel gas (300-1200 psig). The catalyst used needs to be highly selective for the Claus reaction (1) in order to minimize undesirable side reactions such as:



The temperature range of the SSRP is 125°C (257°F) to 160°C (320°F). The lower limit is to prevent solidification (at about 121°C) and the upper limit is because of a rapid increase in liquid sulfur viscosity above 160°C. The operating pressure for SSRP can be the same as the coal gas pressure. In fact, as shown below, higher pressure favors higher sulfur conversion in SSRP. Texaco gasifiers typically operate from 300 up to 1200 psig.

The proposed commercial embodiment of the SSRP involves a liquid phase of molten sulfur with dispersed catalyst in a slurry bubble-column reactor (SBCR, Figure 3.1) and is currently under development (*Gangwal et al, 2002^b*).

The advantages of this embodiment are: a) ease of scale-up and excellent temperature control; and b) the potential to eliminate the Claus plant, amine regenerator, and COS hydrolyzer, by removing COS in addition to H₂S in a single step.

The molten sulfur can act to:

- Moderate the reaction, minimize side reactions, and control the temperature; and
- Dissolve sulfur formed on the catalyst surface, thereby achieving recovery of product as well as a potential shift in thermodynamic limitations on sulfur formation.

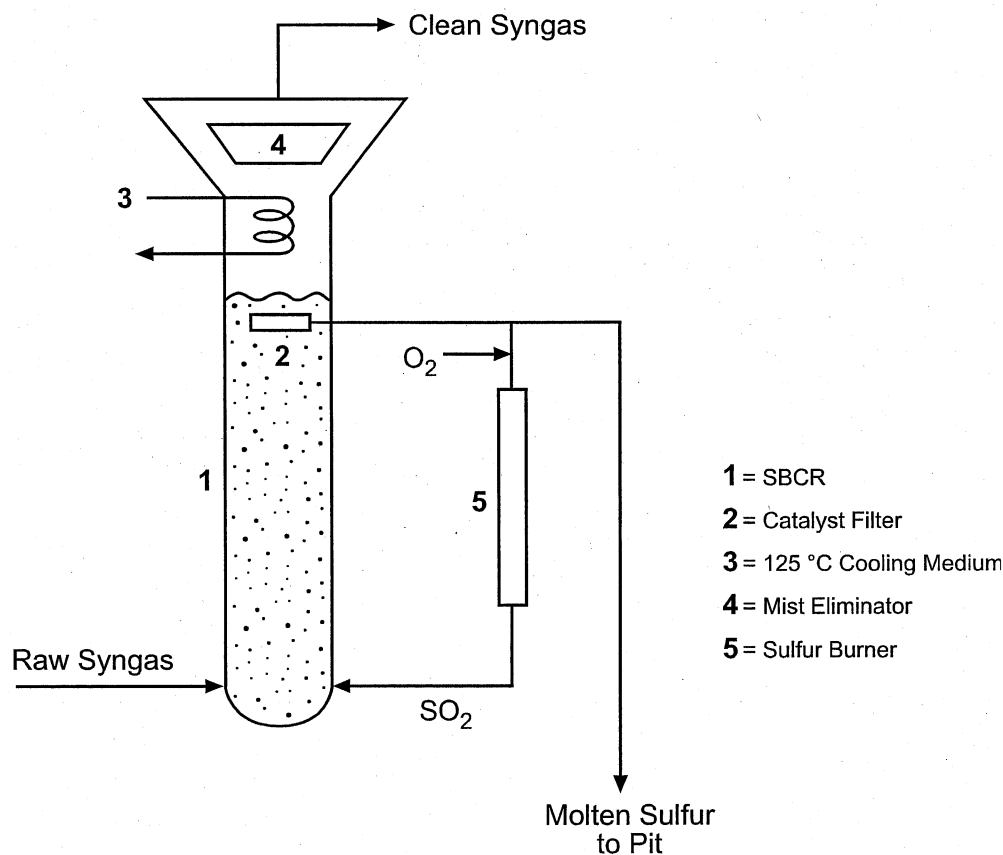


Figure 3.1. Proposed commercial embodiment of the Single-step Sulfur Recovery Process

3.3. SSRP Development

The development of SSRP was conducted under 4 tasks:

Task 1. Literature Review

This task involved a literature review on candidate processes and materials for the direct catalytic oxidation of H₂S in coal-derived synthesis gas. It is presented in Appendix G. The review of the literature did not identify any studies in which the Claus reaction was carried out in the presence of large concentrations of CO and H₂. *Pearson (1976)* studied the Claus reaction at temperatures between 135°C and 175°C using a Claus tail gas containing ca. 3vol% CO+H₂. Conversion of H₂S+SO₂ was 96-98% until his active alumina catalyst reached 60% sulfur loading in the pores. The conversion then declined rapidly to 31%.

Even though the SSRP was counter-intuitive (Claus reaction in the presence of high levels of H₂ and CO), it was decided to go ahead with the initial lab-scale work, since no studies appeared in the literature, especially at high pressure. The very high level of the desirable Claus reaction that was observed in the first experiment undertaken encouraged the accelerated development of SSRP.

Task 2. Lab-Scale Testing

This task included an extensive catalyst screening study on the Claus reaction in the presence of syngas in the feed, using a fixed-bed micro-reactor, and the evaluation of the concept of performing SSRP in a molten sulfur medium, using a micro-bubbler reactor. The lab-scale testing was conducted in a small fixed-bed reactor and a micro-bubbler. These reactor systems and their results are described in detail in Sections 3.3.1 and 3.3.2.

Task 3. Bench-Scale Testing

This task involved a scale-up of the SSRP in molten sulfur using the best catalyst from the screening studies of the previous Task, using a 2-liter continuous stirred tank reactor (CSTR). This apparatus and its results are described in Section 3.3.3.

Task 4. Preliminary Economic Evaluation

This task included a preliminary economic evaluation of SSRP in comparison to amine scrubbing for removing H₂S and recovering sulfur from a coal-derived synthesis gas produced by a Texaco gasifier. The preliminary economic evaluation of the SSRP is described in Section 4.

3.3.1. Catalyst screening: SSRP in a fixed-bed micro-reactor

The SSRP reaction was studied in a 0.5-inch fixed-bed micro-reactor at 125-160°C (257-320°F) and 200-350 psig, over various commercial catalysts such as alumina, a precipitated iron oxide, and a silica gel. The stainless steel reactor was coated with silica to minimize reactions on its walls. The reactant feed consisted of a simulated Texaco coal gas stream (containing 50.8% CO, 35.7% H₂, 12.5% CO₂, and 1.0% H₂S), and a 2.5% SO₂/N₂ stream. A syringe pump provided a constant flow of steam (through water evaporation) into the coal gas line.

A typical reaction composition included ca. 8400 ppm H₂S, ca. 4200 ppm SO₂, 10% steam, and a balance of simulated Texaco gasifier gas (N₂, CO₂, H₂, and CO). A back-pressure-control valve, located downstream of the condenser, controlled the reactor and condenser pressure.

The outlet gases were analyzed in a gas chromatograph with a thermal conductivity detector (TCD) and a flame photometric detector (FPD), for high (above 500 ppm) and low (down to single-digit ppm) sulfur-gas concentrations, respectively. A schematic of the SSRP reaction system is shown in Figure 3.2.

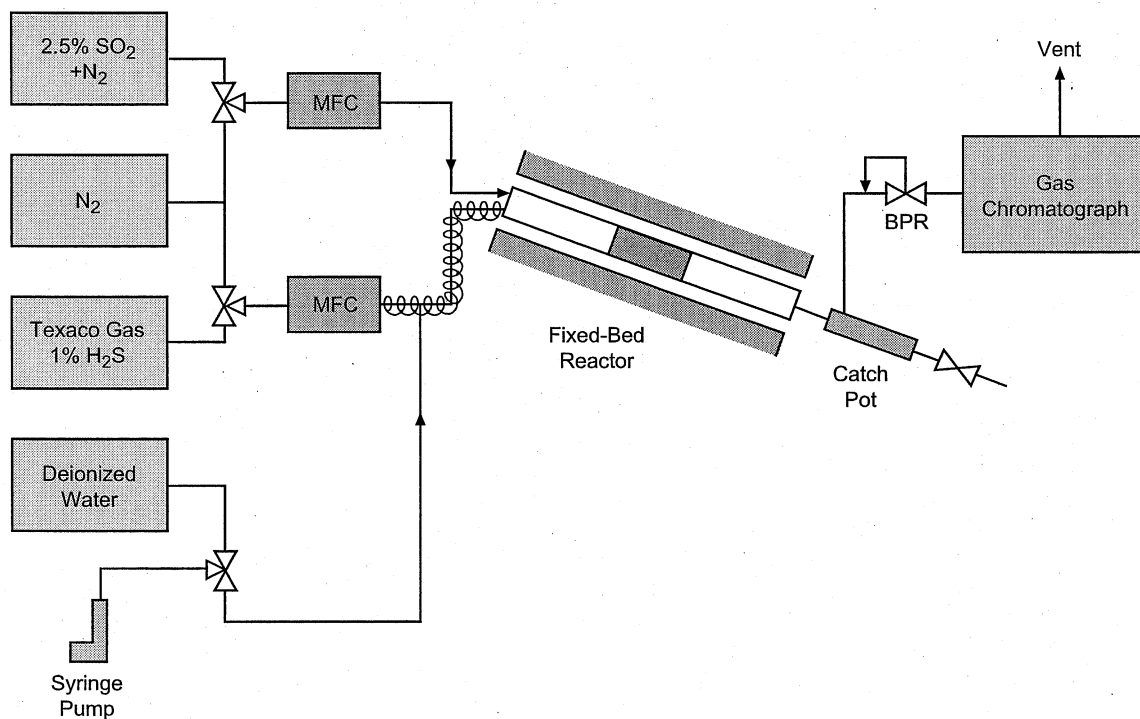


Figure 3.2. Schematic of the SSRP micro-reactor system for catalyst screening

Preliminary reaction experiments involved evaluating the intrinsic activity of the silica-coated (silanized) micro-reactor of Fig. 3.2 in the absence of a catalyst; only inert quartz-wool was loaded instead. The blank reactor activity was measured as a function of temperature under a dry feed (no steam addition), 3950 ppm SO₂ and 8750 ppm H₂S (H₂S/SO₂ = 2.2), and feed flow of 270 sccm at 200 psig. After establishing pseudo steady state at 60°C, the reaction temperature was increased to 120°C in 20°C steps, then to 140°C and finally to 160°C in 10°C steps.

The effect of temperature on the blank reactor activity is given in Figure 3.3. The measured H₂S and SO₂ conversions were less than 6% at any temperature within the 60-160°C range, indicating a minimal reactivity of the blank reactor. All conversions decreased with increasing reaction temperature, suggesting an adsorption-controlled reaction on the reactor walls (homogeneous, and kinetically-controlled or desorption-controlled heterogeneous reaction would be favored with increasing temperature). The formation of COS was also minimal (less than 30 ppm).

The effect of reaction pressure on the blank reactor activity was then examined at 160°C with a feed H₂S/SO₂ ratio of 2.0. The reaction pressure was increased from 200 psig to 300 and then to 400 psig. The results are given in Table 3.1. The sulfur removal activity (expressed as H₂S+SO₂ conversion) increased from ca. 4% to ca. 7%, and the COS formation from 30 ppm to 60 ppm. Thus, under the examined reaction conditions and within the pressure range of interest, the blank silanized reactor exhibits only minimal activity for both the Claus and COS formation reaction.

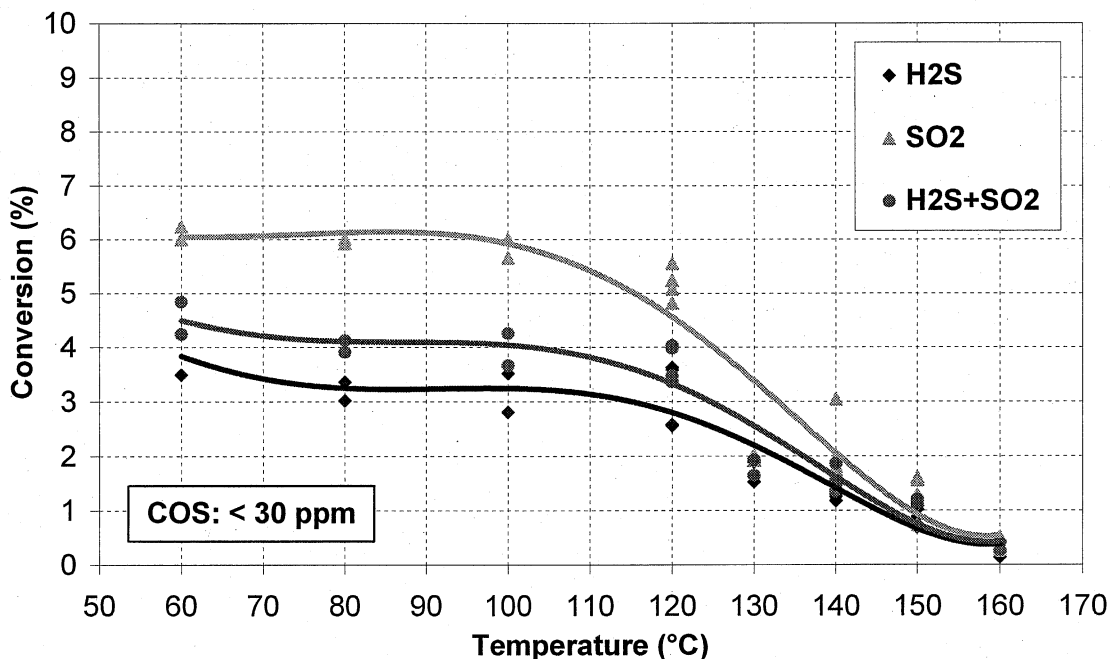


Figure 3.3. Effect of reaction temperature on H₂S, SO₂, and H₂S+SO₂ conversion, and COS formation for SSRP in blank reactor; P: 200 psig; F: 270 sccm; H₂S: 8750±150 ppm; SO₂: 3950±150 ppm; steam: 0%

Table 3.1. Effect of pressure on H₂S, SO₂, and H₂S+SO₂ conversion, and COS formation, for SSRP in blank reactor; T: 160°C; H₂S: 8500 ppm; SO₂: 4300 ppm; steam: 0%

Pressure (psig)	Conversion (%)			COS formation (ppmv)
	H ₂ S	SO ₂	H ₂ S+SO ₂	
200	3.8	3.5	3.7	30
300	4.9	5.3	5.0	40
400	6.9	6.1	6.7	60

The effect of addition of 10% steam on the blank reactor activity at 160°C was also examined. After establishing a pseudo steady state under a feed flow of 270 sccm with a feed H₂S/SO₂ ratio of 2.0 (dry feed) 30 sccm of steam were fed into the reactor, thus increasing the total feed flow to 300 sccm, while maintaining the reaction temperature and pressure. The comparative results are given in Table 3.2. The addition of 10% steam in the feed enhanced the sulfur removal activity of the blank reactor extensively (from ca. 4% to ca. 52%). The formation of COS increased only to a much lesser extent (from 30 ppm to 60 ppm).

The strong promotional effect of steam onto the H₂S+SO₂ reaction could be related to an enhancement in the adsorption of the reactant species onto the reactor walls, possibly through decoking of the reactor surface, or through formation of a reaction complex. Under conditions of industrial interest the H₂S-containing synthesis gas would typically be saturated with steam. Thus, the reactor intrinsic sulfur removal activity can be significant and should not be overseen.

Since the impact of steam addition on the activity of the blank reactor was found to be significant, the effect of reaction pressure on the blank reactor activity was also examined in the presence of steam in the feed. After reaching a pseudo-steady state at 156°C and 200 psig, under a total feed flow of 200 sccm with 10% steam and a feed H₂S/SO₂ of 2.2, the reaction pressure was increased to 300 psig and then to 380 psig. The results are shown in Table 3.3. Higher reaction pressures enhance the adsorption of the reactant species onto the reactor walls, thus promoting the heterogeneous H₂S+SO₂ reaction. The formation of COS was again maintained at low levels (30 ppm or lower).

Table 3.2. Effect of 10% steam addition on H₂S, SO₂, and H₂S+SO₂ conversion, and COS formation, for SSRP in blank reactor; T: 160°C; H₂S: 8500 ppm; SO₂: 4300 ppm

Steam (%)	Conversion (%)			COS formation (ppmv)
	H ₂ S	SO ₂	H ₂ S+SO ₂	
0 (dry feed)	3.8	3.5	3.7	30
10 (steam addition)	50.7	54.3	51.9	60

Table 3.3. Effect of pressure on H₂S, SO₂, and H₂S+SO₂ conversion, and COS formation, for SSRP in blank reactor; T: 156°C; H₂S: 8500 ppm; SO₂: 4300 ppm; steam: 10%

Pressure (psig)	Conversion (%)			COS formation (ppmv)
	H ₂ S	SO ₂	H ₂ S+SO ₂	
200	59.2	62.3	60.2	< 30
300	69.7	78.3	72.3	< 30
380	73.8	89.1	78.5	30

Prior to the experiments with the blank silanized reactor, another series of preliminary experiments was conducted using a similar stainless steel reactor that was not silanized. The sulfur removal activity (measured as H₂S+SO₂ conversion) of the blank stainless steel non-silanized reactor was compared to that of the blank silanized reactor at 156°C and 300 psig. The total feed flow was 86 sccm and 200 sccm, respectively. The SO₂ feed concentration was 4500ppm and 3800ppm, and the H₂S concentration was 9300ppm and 8500ppm, respectively, all other concentrations being the same. The comparative results are given in Table 3.4. The sulfur removal activity of the two reactor types was apparently the same, within the uncertainty of the different total flow. The formation of COS, however, was lower by more than one order of magnitude in the case of the silanized reactor.

The SSRP reaction experiments were then conducted by loading the silica-coated reactor with 5 cm³ of an alumina catalyst (**E-alumina**). For this reactor system, the efficiency for sulfur removal was evaluated in relation to the procedure under which the reactive gases were fed into the reactor, at other conditions (temperature, pressure) constant.

Initially 4300ppm of SO₂ in inert gas (N₂) was fed into the reactor at a feed flow of 540 sccm and the system was allowed to reach pseudo-steady state. Then, a part of the inert gas flow was substituted by an equal syngas flow so as to get a ratio of H₂S/SO₂ of ca. 2 in the absence of steam (Procedure A). The activity for sulfur removal declined from ca. 71% to ca. 42% in a time period of 132 min, as shown in Figure 3.4. The measured COS outlet concentration at 132 min on stream was 575ppm.

Table 3.4. Sulfur removal activity in blank non-silanized reactor vs. blank silanized reactor at 156°C and 300 psig; steam: 10%

Reactor	Temperature	Flow	H ₂ S/SO ₂	Conversion (%)	COS formation
	(°C)	(sccm)	Ratio (-)	H ₂ S+SO ₂	(ppmv)
Non-Silanized	156	86	2.1	83.0	550
Silanized	156	200	2.2	72.3	< 30

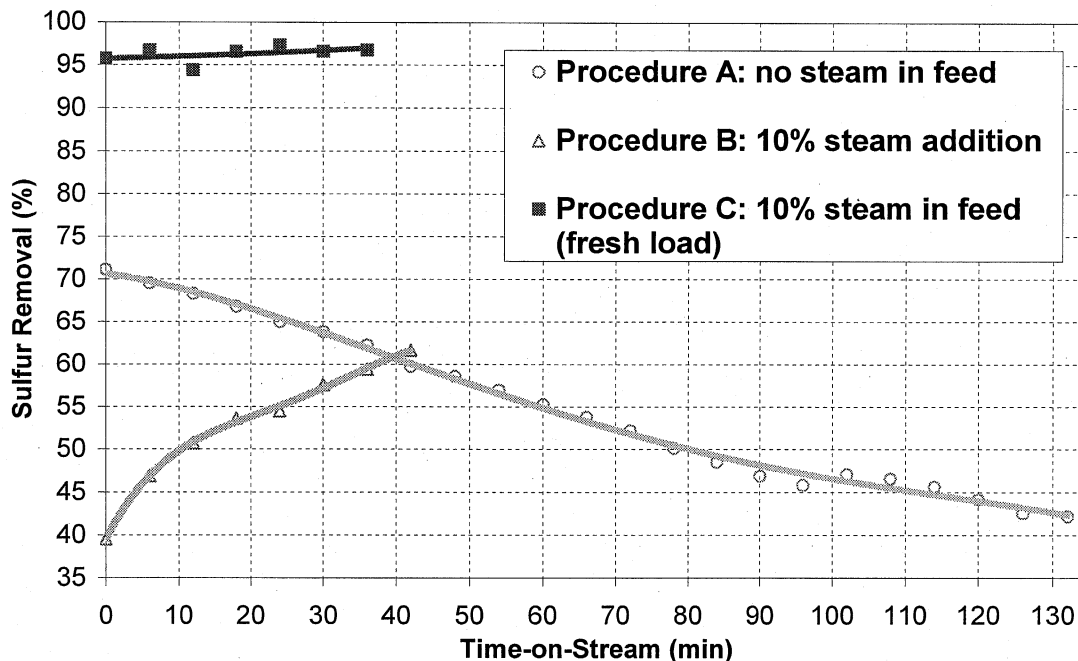


Figure 3.4. Effect of feed procedure on sulfur removal activity for SSRP on E-alumina; T: 154°C; P: 200 psig; F: 600/500 sccm; H₂S: 8550±100 ppm; SO₂: 4300±100 ppm

Then, steam was fed into the reactor at a feed rate of 60 sccm (Procedure B), thus increasing the total flow to 600 sccm, while maintaining the reaction temperature and pressure. The sulfur removal activity (H₂S+SO₂ conversion) increased from ca. 40% to ca. 62% within 42 min, at which point the experiment was terminated without allowing for the reaction to reach a pseudo steady state (Fig. 3.4). The formation of COS declined rapidly down to 15 ppm after the addition of steam and was maintained below 10 ppm for the duration of this run.

A fresh batch of 5cm³ E-alumina was loaded into the reactor which was then heated and pressurized under inert gas (N₂), until attaining the reaction conditions (temperature, pressure) as described above. Initially 4300 ppm of SO₂ in inert gas (N₂) was fed into the reactor at a feed flow of 500 sccm and the system was allowed to reach pseudo steady state. Then, 50 sccm of the inert gas flow were substituted by an equal flow of steam (10% steam addition). After a time period of 30 min, another part of the inert gas flow was substituted by an equal syngas flow so as to get a ratio of H₂S/SO₂ of ca. 2 in the presence of steam, while maintaining the reaction temperature and pressure (Procedure C). The reaction reached pseudo steady state within 20 min. The sulfur removal activity was 96% and remained constant for a period of 36 min (Fig. 3.4). The COS formation was constant at 22 ppm.

These results illustrate the importance of the order in which reactants should be fed into the reactor, as well as the importance of the presence of steam in the feed. The addition of steam prior to exposure of the catalyst to the H₂S-containing syngas results in a stable, very high sulfur removal activity (more than 96%), with minimal formation of COS (less than 25 ppm).

The impact of the feed procedure on the performance of the E-alumina catalyst for the oxidation of H₂S by SO₂ was further examined. One such run involved feeding H₂S-containing syngas only (no SO₂, no steam) at 125°C and 200 psig. The formation of 500 ppm COS was observed (corresponding to a decrease in H₂S from 8500 ppm to 8000 ppm), as shown in the time-on-stream plot of Figure 3.5. Addition of ca. 4300 ppm SO₂ (Procedure A') while maintaining the reaction temperature, pressure, and total feed flow, resulted in a significant decrease in the outlet H₂S concentration (due to the H₂S+SO₂ reaction) and a complete suppression in the formation of COS (Fig. 3.5).

Later in the same run, the syngas flow was substituted by inert (N₂) leaving the SO₂ to reach a steady state outlet value of 4300 ppm. Then, the H₂S-containing syngas flow was again introduced, still in the absence of steam (Procedure A). The outlet SO₂ concentration declined to essentially zero, and then the outlet H₂S gradually increased to ca. 6500 ppm, as shown in Figure 3.6. The data of the H₂S curve in Fig. 3.6 correspond to those of the "Procedure A" curve of Fig. 3.4. Under this procedure, the sulfur removal activity was very low.

Continuing on the same run (Procedure A), the effect of SO₂ removal from the feed on the sulfur removal activity of E-alumina is shown in Figure 3.7. The outlet H₂S concentration increased to ca. 13500 ppm temporarily and at was restored to its inlet value of ca. 8500 ppm at steady state. Interestingly, the outlet COS increased gradually from ca. 500 ppm to more than 7500 ppm before starting to decline with time on stream. This COS appears to be formed by the reaction of CO with the sulfur that was formed by the H₂S+SO₂ reaction prior to removing the SO₂ from the reactant feed.

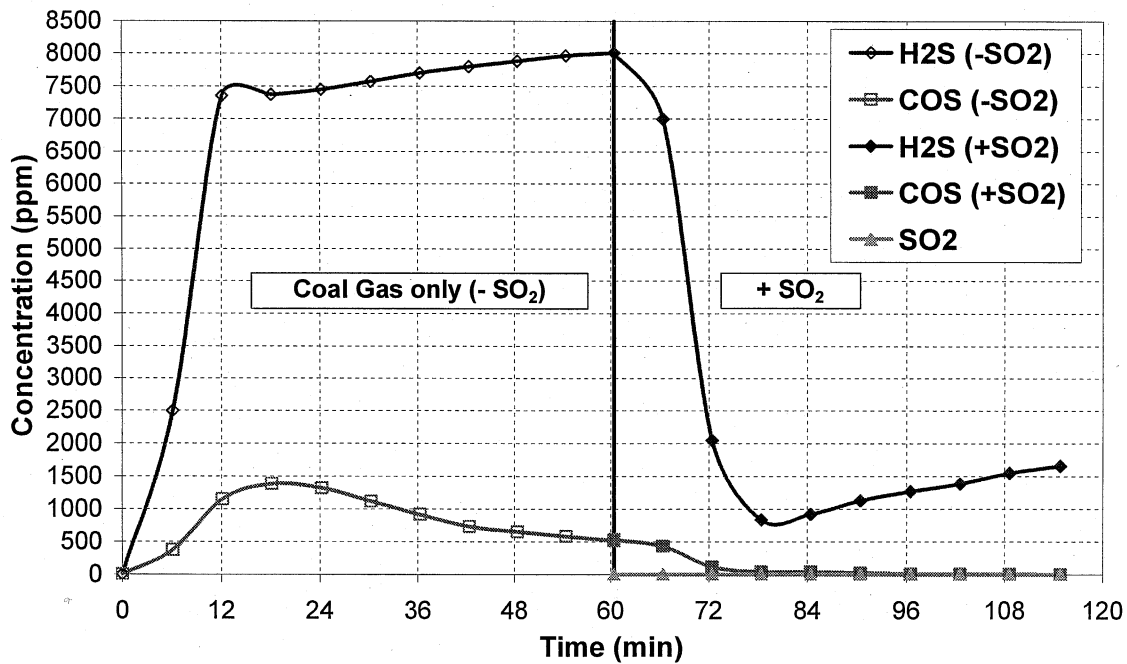


Figure 3.5. Effect of SO₂ addition on sulfur removal activity and COS formation for SSRP on E-alumina (Procedure A'); T: 125°C; P: 200 psig; F: 270 sccm; H₂S: 8500±50 ppm; SO₂: 4300±50 ppm; steam: 0%

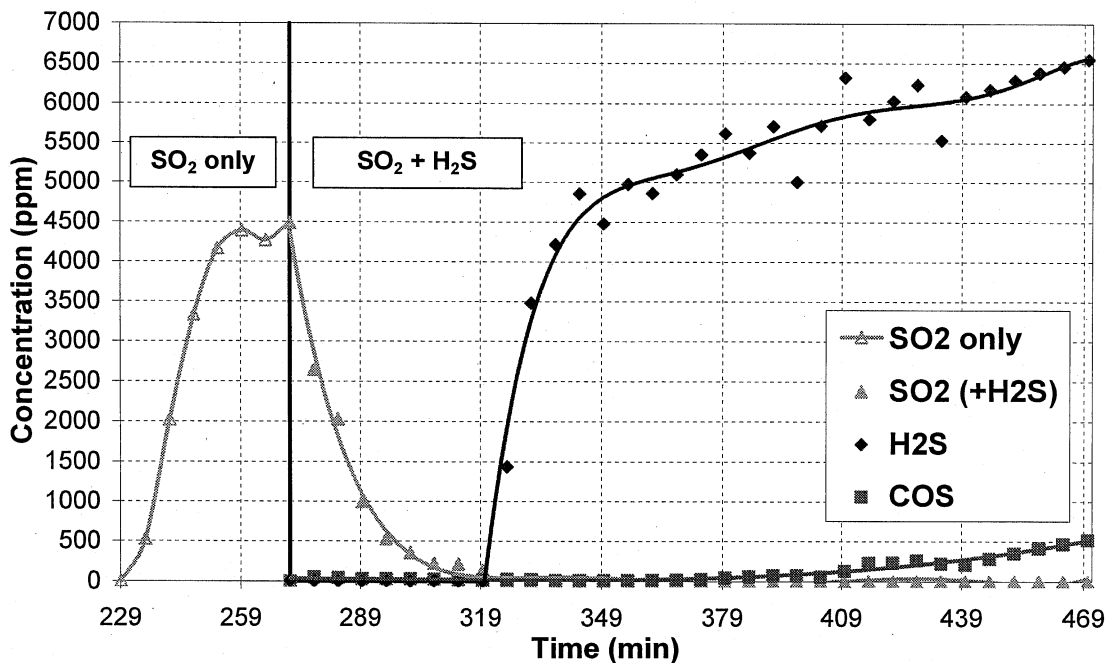


Figure 3.6. Effect of H₂S addition on sulfur removal activity and COS formation for SSRP on E-alumina (Procedure A); T: 125°C; P: 200 psig; F: 270 sccm; H₂S: 8500±50 ppm; SO₂: 4300±50 ppm; steam: 0%

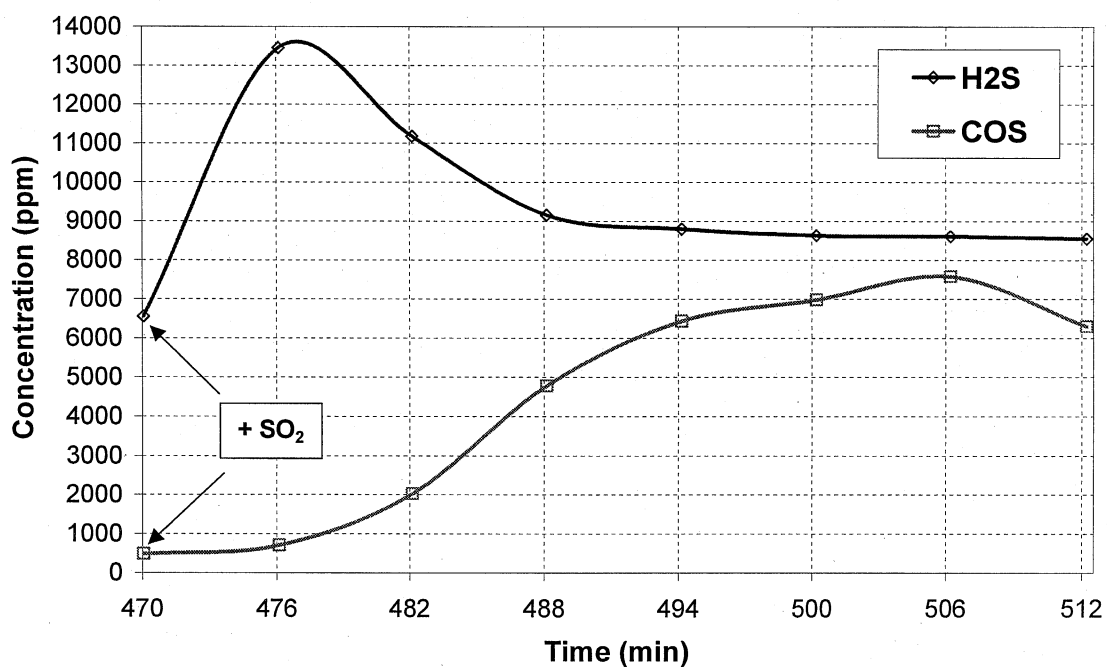


Figure 3.7. Effect of SO₂ removal on sulfur removal activity and COS formation for SSRP on E-alumina (Procedure A); T: 125°C; P: 200 psig; F: 270 sccm; H₂S: 8500±50 ppm; SO₂: 4300±50 ppm; steam: 0%

The effect of SO₂ removal on the sulfur removal performance of E-alumina was also examined under feed Procedure **B**. Referring to Fig. 3.4, after the final data point shown in the “Procedure **B**” curve the SO₂ feed was substituted by inert gas (N₂) feed, while keeping the total flow as well as the reaction temperature and pressure constant. The time-on-stream data for the effect of SO₂ removal under Procedure **B** are shown in Figure 3.8. In clear contrast to the data of Procedure **A** (shown in Fig. 3.7), the outlet H₂S concentration increased to ca. 17000 ppm, which was double its inlet concentration of ca. 8500 ppm. The outlet COS was minimal (less than 10 ppm). Thus, under Procedure **B** the sulfur that was formed by the H₂S+SO₂ reaction prior to removing the SO₂ from the reactant feed appears to form the excess H₂S in the outlet. The presence of steam (the difference between Procedures **A** and **B**) appears to shift the major product in the absence of SO₂ from COS to H₂S.

The effect of SO₂ removal on the sulfur removal performance of E-alumina was finally examined under feed Procedure **C**. Referring to Fig. 3.4, after the final data point shown in the “Procedure **C**” curve the SO₂ feed was again substituted by inert gas (N₂) feed, while keeping the total flow as well as the reaction temperature and pressure constant. The time-on-stream data for the effect of SO₂ removal under Procedure **C** are shown in Figure 3.9. In contrast to the results of Procedure **A** as well as Procedure **B**, the outlet H₂S concentration at steady state was essentially equal to that in the reactor inlet, i.e., ca. 8800 ppm, whereas the outlet COS was limited to ca. 80 ppm or less. Therefore, based on the results presented in Figures 3.4-3.9, the comparison of the various examined feed procedures (**A**, **A'**, **B**, and **C**) indicates that Procedure **C** gave the highest sulfur removal activity along with minimal COS formation for the SSRP on E-alumina.

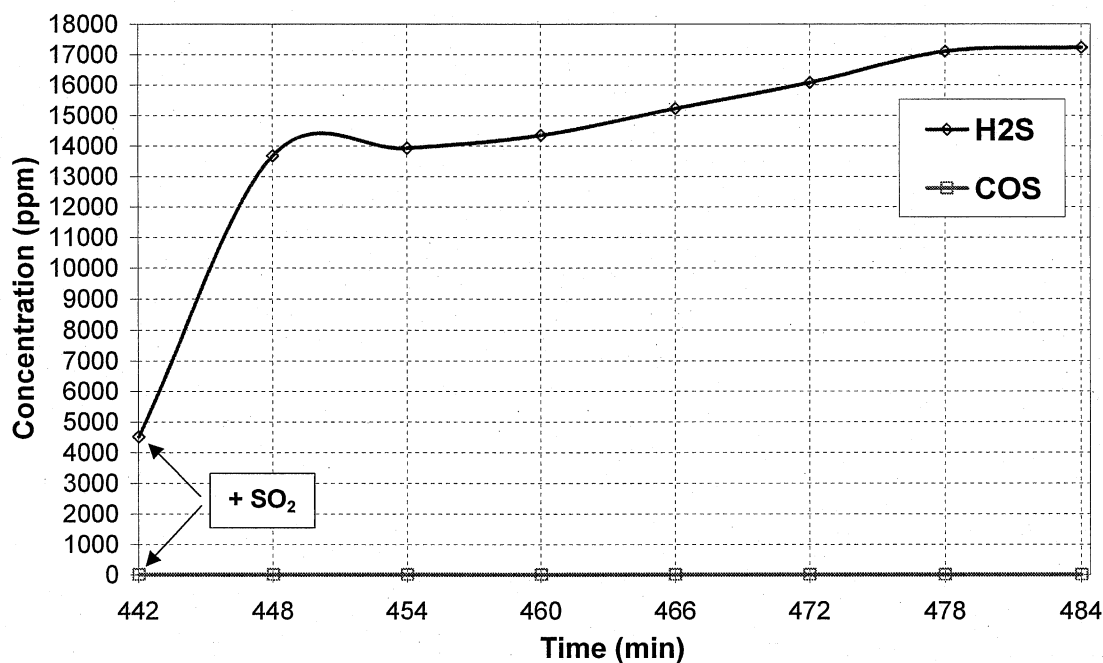


Figure 3.8. Effect of SO₂ removal on sulfur removal activity and COS formation for SSRP on E-alumina (Procedure **B**); T: 154°C; P: 200 psig; F: 590 sccm; H₂S: 8500±50 ppm; SO₂: 4300±50 ppm; steam: 10%

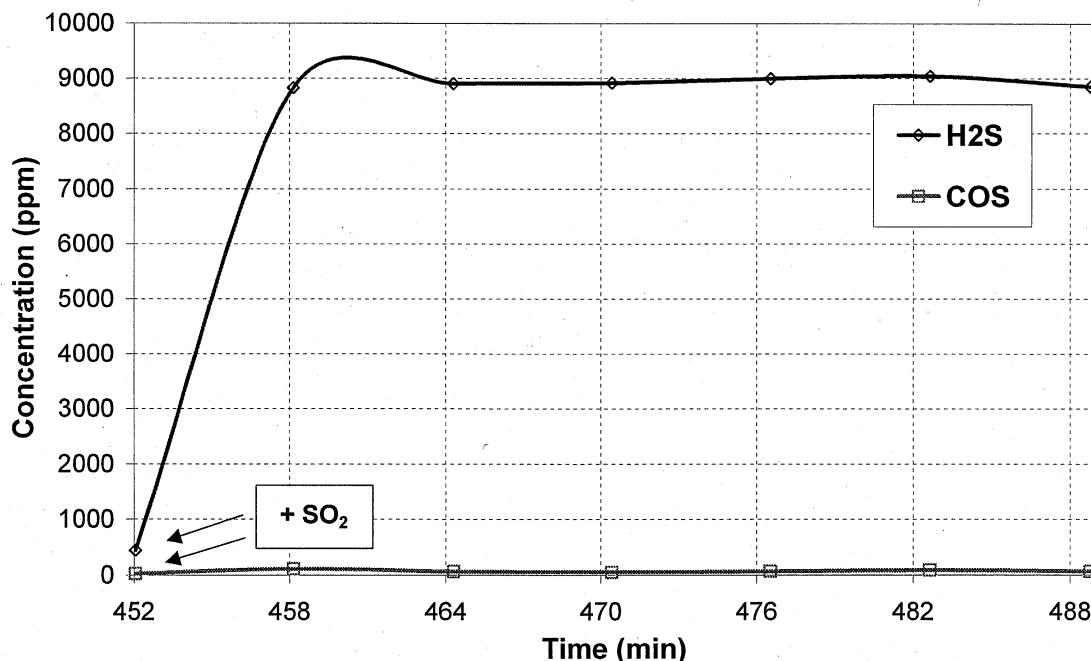


Figure 3.9. Effect of SO₂ removal on sulfur removal activity and COS formation for SSRP on E-alumina (Procedure C); T: 154°C; P: 200 psig; F: 500 sccm; H₂S: 8800±100 ppm; SO₂: 4300±50 ppm; steam: 10%

The efficiency of E-alumina for sulfur removal under Procedure C (SO₂ feed, steam feed, H₂S feed) was compared to that of two other procedures: one where 10% steam was first fed into the reactor, followed by SO₂ feed, and finally by H₂S-containing syngas feed (Procedure D), and another, where the steam feed was followed by H₂S-containing syngas feed and then by SO₂ feed (Procedure D'). The total feed flow was maintained at 100 sccm and 300 sccm, respectively, and all other reaction conditions were the same, to facilitate the comparison. The results are given in Table 3.5. Procedures C and D gave essentially identical results. Procedures C and D' also gave essentially identical results with respect to the sulfur removal activity. The COS formation was slightly higher under Procedure D' compared to Procedure C. Unless otherwise indicated, all the following experiments were performed under one of these three feed procedures.

Table 3.5. Sulfur removal activity and COS formation as function of feed procedure on E-alumina; T: 154°C; P: 200 psig; F: 100 sccm / 300 sccm; steam: 10%

Procedure	Conversion (%)	COS formation
	H ₂ S+SO ₂	(ppmv)
C (SO ₂ feed, steam feed, coal gas feed) @ 100 sccm	98.5	20
D (steam feed, SO ₂ feed, coal gas feed) @ 100 sccm	98.6	20
C (SO ₂ feed, steam feed, coal gas feed) @ 300 sccm	98.4	34
D' (steam feed, coal gas feed, SO ₂ feed) @ 300 sccm	98.9	85

A new series of SSRP reaction experiments was conducted by loading the silica-coated reactor with 5 cm³ of E-alumina, then heating to 154°C (309°F) and pressurizing to 200 psig (14.4 bar) under an inert gas flow of 100sccm. 15sccm SO₂/N₂ (corresponding to ca. 3800 ppm SO₂) were fed into the reactor, followed by feeding 10 sccm steam, substituting an equal flow of N₂. Upon reaching a pseudo steady state, simulated coal gas with H₂S was fed into the reactor (giving ca. 8400 ppm H₂S), at a constant total feed flow of 100 sccm. The total sulfur (H₂S+SO₂) conversion was 86.5%, with less than 20 ppm COS formation.

The effect varying the SO₂ inlet concentration was examined by increasing the SO₂/N₂ flow from 15 to 18 to 20 sccm while keeping the coal gas and steam flows constant, thus increasing the total flow from 100 to 103 to 105 sccm, respectively. The results are shown in Figure 3.10. Upon increasing the SO₂ inlet concentration the conversion of H₂S increased up to 99.5%, while the conversion of SO₂ decreased from essentially 100% down to ca. 87%. Thus the H₂S+SO₂ conversion showed a maximum at an intermediate SO₂ concentration. This implies reaction of SO₂ with H₂S only, and not with H₂ or CO which are in great excess, at least to any appreciable rate. The COS formation was only about 20 ppm.

The effect of space velocity was studied by varying the total wet feed flow from 100 sccm to 500 sccm (space velocity of 1200 h⁻¹ to 6000 h⁻¹) while keeping the other reaction parameters (temperature, pressure, feed composition) constant. This fivefold increase in space velocity resulted in only a minor decrease (from 98.5% to 96%) in H₂S+SO₂ conversion. The formation of COS was again only about 20 ppm. Thus the SSRP reaction is very active and selective even at significantly short contact times.

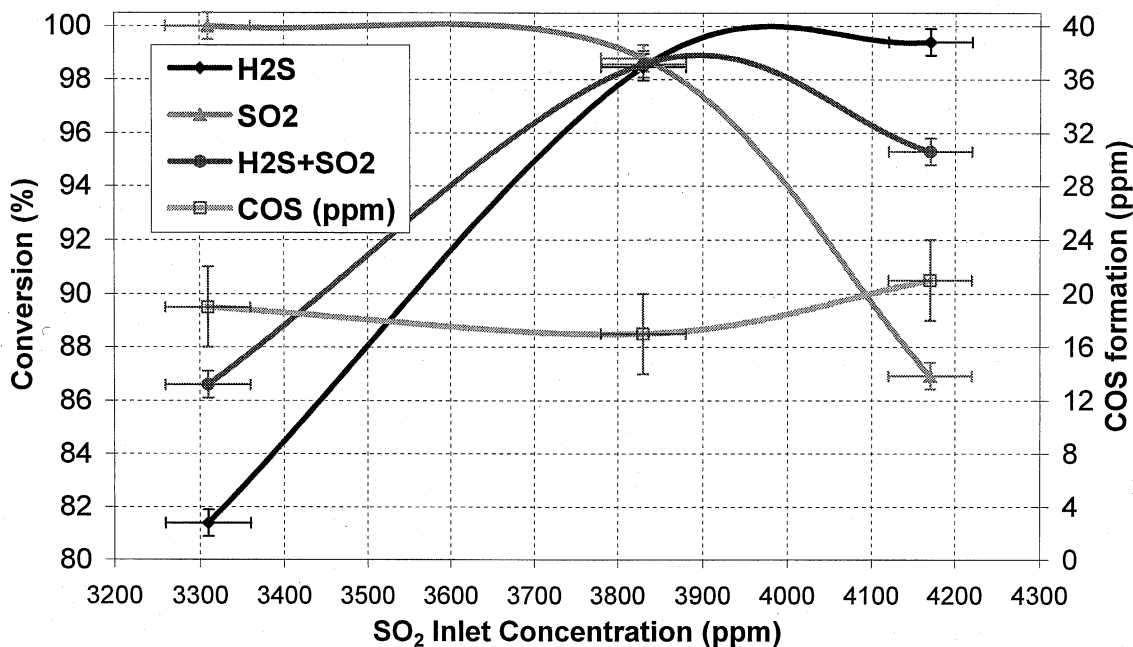


Figure 3.10. Effect of SO₂ inlet concentration on H₂S, SO₂, and H₂S+SO₂ conversion, and COS formation for SSRP on E-alumina; T: 154°C; P: 200 psig; SV: 1200-1260 h⁻¹; H₂S: 8400-8000 ppm; steam: 10%

The effect of pressure was examined by increasing the reaction pressure from 200 psig to 350 psig at 300 sccm total feed flow while keeping the other reaction parameters (temperature, feed composition) constant. The results are given in Table 3.6. The combined H₂S+SO₂ conversion was found to increase up to 99.0%. Higher pressures favor the reaction in terms of thermodynamic equilibrium, so they would be expected to further increase the measured H₂S + SO₂ conversion. The amount of formed COS was below 40 ppm.

Table 3.6. Effect of pressure on H₂S, SO₂, and H₂S+SO₂ conversion, and COS formation, for SSRP on E-alumina; T: 154°C; H₂S: 8400 ppm; SO₂: 4200 ppm; steam: 10%

Pressure (psig)	Conversion (%)			COS formation (ppmv)
	H ₂ S	SO ₂	H ₂ S+SO ₂	
200	98.9	97.3	98.4	34
240	98.9	98.4	98.7	34
300	99.0	99.0	99.0	36
350	98.8	99.3	99.0	38

The effect of temperature was examined by varying the reaction temperature from 154°C (309°F) down to 125°C (257°F). The H₂S+SO₂ conversion was only minimally affected (from 98.6% down to 98.0%), indicating that the reaction has reached thermodynamic equilibrium at these conditions.

The effect of catalytically oxidizing H₂S in the presence of excess H₂ and CO by an oxidant other than SO₂ (such as O₂) was also examined on alumina at 154°C, 200 psig, and a total flow of 100 sccm. After addition of 10% steam for 30 min, 2%O₂/N₂ was fed into the reactor, producing ca. 4300 ppm O₂ in the feed, at a total flow of 105 sccm. Then, coal gas was fed to get a ratio of H₂S/O₂ of ca. 2 and the reaction reached a pseudo steady state. Finally, the O₂ flow was substituted by a flow of SO₂ producing ca. 4300 ppm of SO₂ in the feed (H₂S/SO₂ ratio of ca. 2) and the reaction reached a new pseudo steady state.

The results for the effect of O₂ vs. SO₂ in the feed are given in Figure 3.11. Oxygen is much less selective for the oxidation of H₂S compared to SO₂ and also allows for enhanced undesirable formation of COS. There appears to be a clear unselective consumption of O₂ by H₂ and/or CO of the syngas, thus limiting its availability for the desirable selective reaction with H₂S.

Besides the E-alumina catalyst, three other commercially available catalysts were also examined for SSRP using the previously described fixed-bed micro-reactor: a) another alumina, named P-alumina, with different physical properties (surface area, pore volume) compared to E-alumina, b) a silica gel, and c) a precipitated iron oxide which was treated *in-situ* overnight with the H₂S-containing simulated Texaco coal gas and was thus transformed to iron sulfide. Table 3.7 summarizes the physical properties of these catalysts. Table 3.8 gives a comparison of these 4 catalysts in terms of sulfur removal activity (H₂S+SO₂ conversion) and selectivity (minimized undesirable formation of COS).

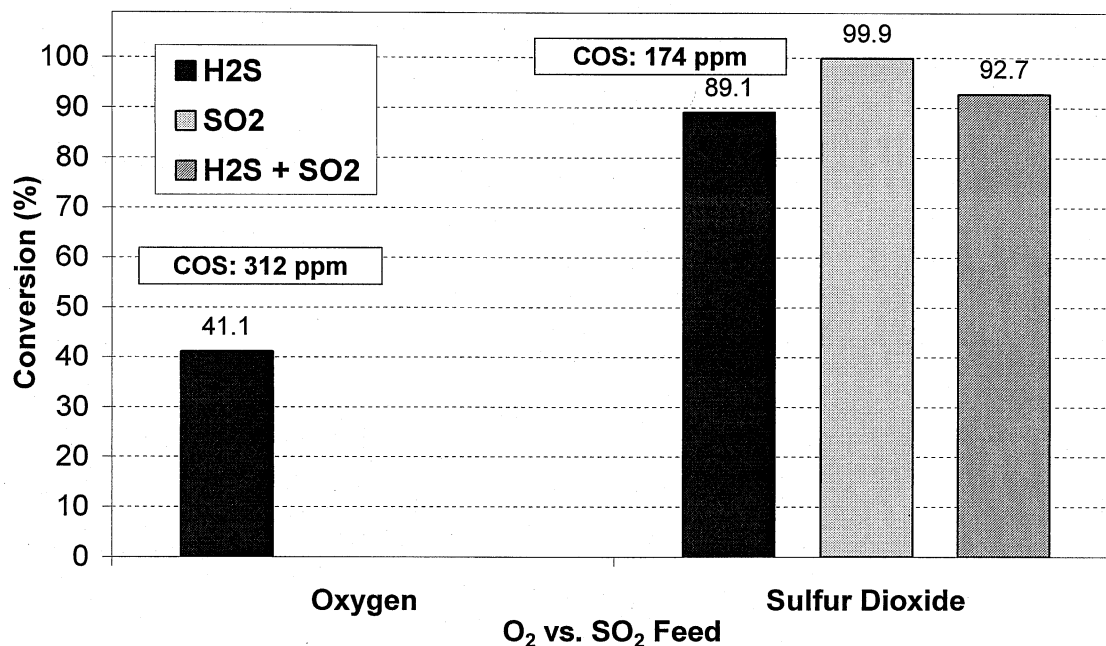


Figure 3.11. Effect of O₂ vs. SO₂ feed on H₂S, SO₂, and H₂S+SO₂ conversion, and COS formation for SSRP on E-alumina; T: 154°C; P: 200 psig; H₂S: 8400 ppm; O₂ (SO₂): 4300 ppm; steam: 10%

Table 3.7. Physical properties of catalysts examined for SSRP

Designation	Type	BET Surface Area (m ² /g)	Pore Volume (cm ³ /g)
E	Alumina	227	0.62
P	Alumina	288	0.14
F	Precipitated Iron Oxide*	153	0.17
S	Silica gel	233	1.05

* *in-situ* sulfided by H₂S-containing simulated Texaco goal gas into iron sulfide

Table 3.8. Comparative ranking of catalysts for SSRP in terms of H₂S+SO₂ conversion, and COS formation; T: 154°C; P: 200 psig; F: 300 sccm; steam: 10%

Catalyst	S Removal Activity (H ₂ S+SO ₂ conv. %)	Catalyst	S Removal Selectivity (COS formation, ppm)
E-alumina	98.4-98.9	E-alumina	35-85
Iron sulfide	96.9-98.4	P-alumina	45
P-alumina	95.6	Silica gel	115-170
Silica gel	87.4-90.7	Iron sulfide	8900-14000

The comparative results of Table 3.8 indicate that E-alumina was the best catalyst for SSRP under the examined conditions, followed closely by P-alumina. Silica gel showed lower activity and higher selectivity for COS formation. Iron sulfide was very active but transformed all the H₂S into COS. Therefore, E-alumina was chosen for all subsequent studies of SSRP.

The effect of oxidizing H₂S by oxygen vs. SO₂ was also examined on the silica gel. At 154°C, 200 psig and 300 sccm, 10% steam was added, followed by SO₂/N₂ to achieve 4450 ppm SO₂ in the feed, and then by H₂S-containing syngas to achieve 8200 ppm H₂S (Procedure D). After reaching pseudo steady state, the SO₂/N₂ flow was substituted by a flow of 2%O₂/N₂ to produce ca. 4450 ppm O₂ in the feed (the total feed flow increased to 314 sccm). Finally, the O₂/N₂ flow was back-substituted with SO₂/N₂ flow (the total flow returned to 300sccm).

The results of the SO₂ to O₂ to SO₂ switch are given in Table 3.9. In agreement to results with E-alumina (Fig. 3.11), oxygen was significantly less selective for the oxidation of H₂S (implied by the lower conversion of H₂S) and also showed enhanced formation of COS. Again, there appears to be an unselective consumption of O₂ by the H₂ and/or CO of the syngas, thus limiting its availability for the selective reaction with H₂S.

Table 3.9. Sulfur removal activity as function of O₂ vs. SO₂ in the feed on silica gel; T: 154°C; P: 200 psig; F: 300 sccm; steam: 10% (Procedure D)

Oxidant (ppmv)	Conversion (%)			COS formation (ppmv)
	H ₂ S	SO ₂	H ₂ S+SO ₂	
SO ₂ (4450)	93.8	85.0	90.7	140
O ₂ (4450)	31.8	-	-	510
SO ₂ (4450)	92.7	83.3	89.4	180

The sulfur that was generated on the catalyst during the SSRP was retained within the catalyst pores (the collected water condensate was clear). Normally in low temperature fixed-bed Claus-type processes, the catalyst is reversibly poisoned by the sulfur plugging its pores (Pearson (1976)). The catalyst would have to be heated to high temperatures to remove the sulfur. The commercial embodiment suggested in Figure 3.1 appears attractive in this context, as the sulfur formed should dissolve into the molten sulfur, thereby facilitating its removal and recovery. The reactor system is analogous to a slurry-bubble column Fischer-Tropsch reaction in which wax is formed in the catalyst pores and is removed by the liquid wax medium.

Some of the most important results of the SSRP experiments on E-alumina described above have been presented in the 19th Annual International Pittsburgh Coal Conference (see Appendix H, Nikolopoulos and Gangwal, 2002). The processed data of the micro-reactor SSRP catalyst screening study, from which the figures and tables presented above were generated, are included in Appendix I. The main conclusions from the overall catalyst screening in the fixed-bed micro-reactor are presented in Section 5.

3.3.2. Concept evaluation: SSRP in a micro-bubbler reactor

The SSRP reaction was also studied in a 0.5-inch micro-bubbler with a 10ml glass liner containing 1 cm³ of E-alumina and 5 cm³ of sublimed sulfur. A 1/8-inch stainless steel tube was closed at its bottom and was drilled with 1/21000th inch bits within 1 inch from its bottom to create a gas distributor. It was then adjusted to the bubbler top with a reducer and a tee and was inserted to the bubbler so that its bottom was positioned at about half the height of the sulfur powder and catalyst mixture. This 1/8-inch tube was used as the feed line to the bubbler, whereas the gas outlet was connected to the outlet gas line in the same manner as the fixed-bed reactor shown in Fig. 3.2.

The reactor was fed with 125 sccm of N₂ and was heated to 140°C and pressurized to 150 psig. The heat added to the reactor caused the sulfur powder to melt and thus form a molten sulfur bath where the catalyst particles would be suspended (due to similar density of the molten sulfur and the catalyst) and the bubbles of the N₂ feed gas would produce sufficient agitation so as to assume the molten sulfur bath as essentially homogenized. A schematic of this micro-bubbler reactor is given in Figure 3.12.

The effect varying the SO₂ inlet concentration was examined at a reaction pressure of 150 psig by increasing the SO₂/N₂ flow while keeping the coal gas and steam flows constant. The results are shown in Figure 3.13. In agreement with the fixed-bed reactor results, the sulfur removal activity (H₂S+SO₂ conversion) showed a maximum of 80.9% at an intermediate SO₂ concentration. The amount of COS formed (400-450 ppm) was essentially unaffected by the variation in SO₂ concentration, but was one order of magnitude greater than in the corresponding fixed-bed run (Fig. 3.10), implying possible reaction of CO with the molten sulfur vapor.

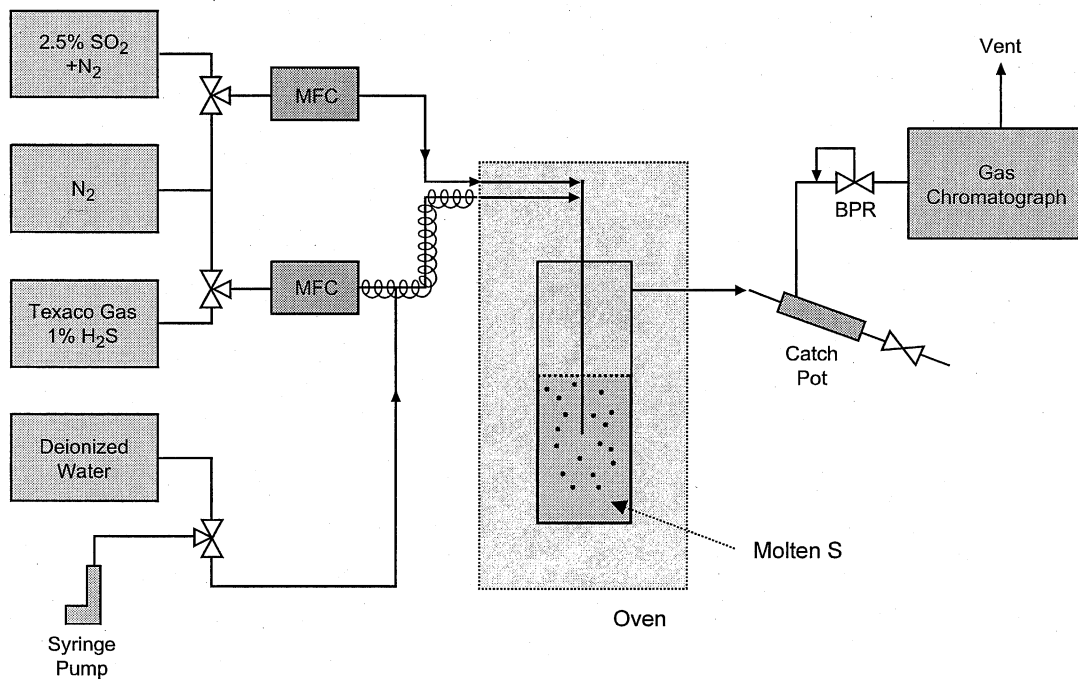


Figure 3.12. Schematic of the SSRP micro-bubbler reactor system for concept evaluation

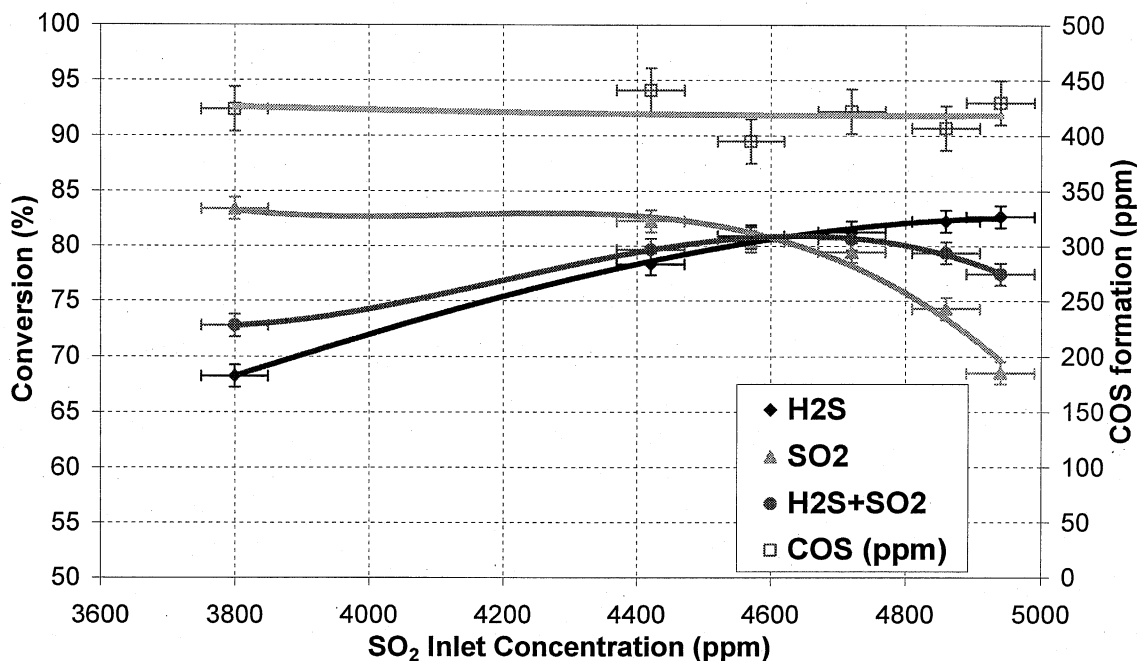


Figure 3.13. Effect of SO₂ inlet concentration on H₂S, SO₂, and H₂S+SO₂ conversion, and COS formation for SSRP on E-alumina in Molten Sulfur; T: 140°C; P: 150 psig; SV: 7500-8100 h⁻¹; H₂S: 8900-8400 ppm; steam: 10%

The effect of pressure was examined by increasing the reaction pressure from 150 psig to 300 psig at 135 sccm total feed flow while keeping the other reaction parameters (temperature, feed composition) constant. The results are shown in Figure 3.14. The H₂S+SO₂ conversion was found to increase from 80.9% to 92.8% with increasing pressure, in agreement with the results of the fixed-bed reactor (Table 3.6). The amount of formed COS increased only moderately with doubling the reaction pressure (from 400 ppm to 475 ppm).

The significantly higher amounts of COS that were measured at the outlet of the micro-bubbler compared to the fixed-bed micro-reactor clearly identify the significance of minimizing the formation of COS during SSRP. A preliminary attempt to investigate the pathways for COS formation involved substituting the H₂S-containing coal gas feed with a pure CO feed, thus simplifying the matrix of possible reactions substantially.

By feeding pure CO only (no SO₂) into the bubbler containing the molten sulfur and E-alumina mixture at 154°C and 300 psig for a brief period of time, a very large amount of COS (ca. 11000 ppm) was measured at the outlet. Addition of SO₂ resulted in strong suppression of COS formation (< 1250 ppm). The inlet and outlet SO₂ concentrations were essentially equal after reaching steady state. After purging the system with N₂, SO₂ was fed (no CO feed) and no reaction was observed (no SO₂ consumption, and no COS formation). Addition of CO in huge excess (80% compared to < 6000 ppm SO₂) gave rise to only 230 ppm COS. Again, the inlet and outlet SO₂ concentrations were essentially equal after reaching steady state.

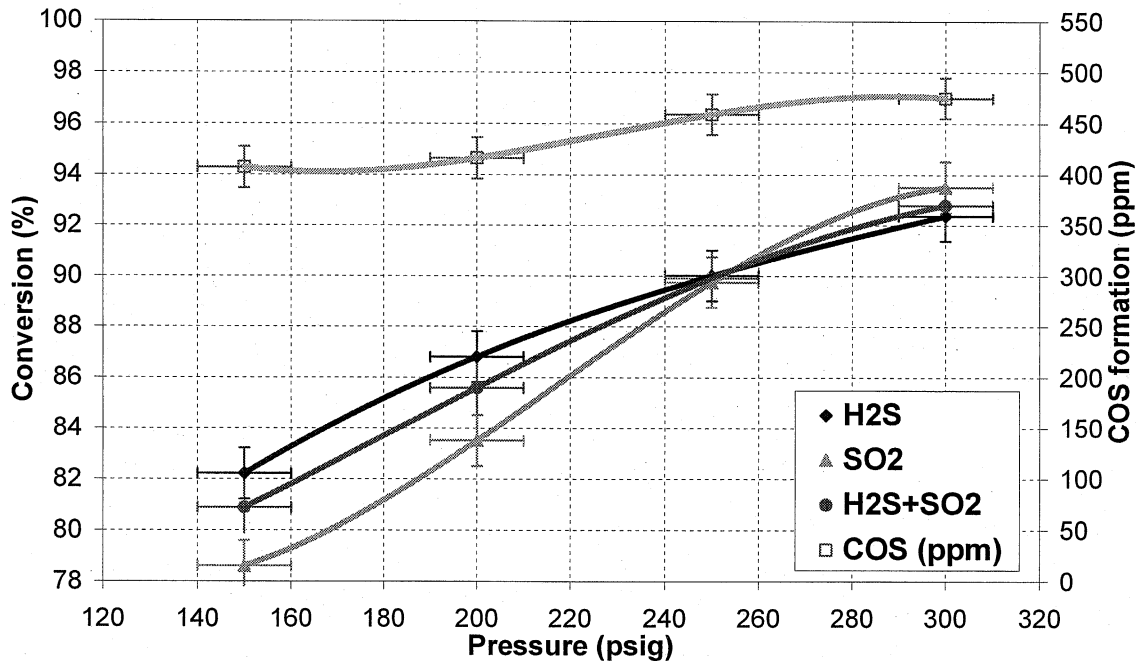


Figure 3.14. Effect of pressure on H₂S, SO₂, and H₂S+SO₂ conversion, and COS formation for SSRP on E-alumina in Molten Sulfur; T: 140°C; SV: 8100 h⁻¹; H₂S: 8400 ppm; SO₂: 4900 ppm; steam: 10%

Furthermore, a decrease in SO₂ inlet concentration (by 22%) resulted in a significant increase in COS formation (from 230 ppm to 420 ppm, an 82% increase). This correlation was found to be reversible, i.e., returning the SO₂ inlet concentration to its original value also caused the COS amount to return to a value close to its original one (200 ppm). Also, these transients were independent of the presence or absence of steam (0% or 10% steam in the feed).

The results of the experiments with the pure CO feed instead of the H₂S-containing syngas feed suggest that the formation of COS was not resulting from any direct reaction involving SO₂ and was negatively correlated with SO₂ concentration. This strong negative correlation implies that COS did not form via direct reaction of CO with molten sulfur, although some CO reaction with adsorbed molten S vapor cannot be excluded based solely on the present evidence. It appears that COS was formed by reaction of CO with an active form of sulfur located at the catalyst sites responsible for sulfur formation during SSRP.

The processed data of the micro-bubbler SSRP experiments, from which the figures and tables presented above were generated, are included in Appendix J. The main conclusions from the SSRP concept evaluation study in the micro-bubbler reactor are presented in Section 5.

3.3.3. Process evaluation: SSRP in a bench-scale continuous stirred tank reactor

The SSRP reaction was studied in a 2-liter continuous stirred tank reactor (CSTR) equipped with a glass liner containing 716 g sublimed sulfur (400 cm^3 of molten sulfur at 155°C) and typically 22.5g (25 cm^3) E-alumina. The stainless steel reactor and the feed tubing inside it were teflonized to minimize reactions on their walls. The reactant feed was the same as that for the reaction systems previously described: a simulated Texaco coal gas stream containing 50.8% CO, 35.7% H_2 , 12.5% CO_2 , and 1.0% H_2S , a 2.5% SO_2/N_2 stream, and a steam stream generated by evaporation of water supplied from a constant-flow syringe pump. A back-pressure-control valve, located downstream of the condenser, controlled the reactor and condenser pressure. The reactor was pressurized to 300 psig under inert gas flow and heated to 155°C . The sulfur melted at about 125°C and the catalyst was suspended in the molten sulfur phase by stirring the liquid, typically at 1000 RPM. The outlet gases were analyzed as previously described (Section 3.2.1). A schematic of the bench-scale SSRP reaction system is shown in Figure 3.15.

Preliminary SSRP reaction experiments involved evaluating the intrinsic activity of the teflonized CSTR of Fig. 3.15 in the absence of both catalyst and molten sulfur (empty glass liner only). After heating to 155°C and pressurizing to 200 psig under inert gas flow of ca. 1.5 SLPM (standard liters per minute), the H_2S -containing syngas was fed into the reactor (no SO_2 , no steam feed). The blank reactor showed minimal activity under these conditions, with only ca. 15 ppm COS formation (see Table 3.10). Addition of SO_2 only (no steam feed, Procedure A') led to an increase in COS formation to 75 ppm, with very low sulfur removal activity (less than 4%). Reaction of CO with active sulfur formed by the SSRP reaction (as discussed in Section 3.3.2) is the most likely path for this limited increase in COS formation. These observations are in agreement with results from the blank silanized micro-reactor (see Appendix I).

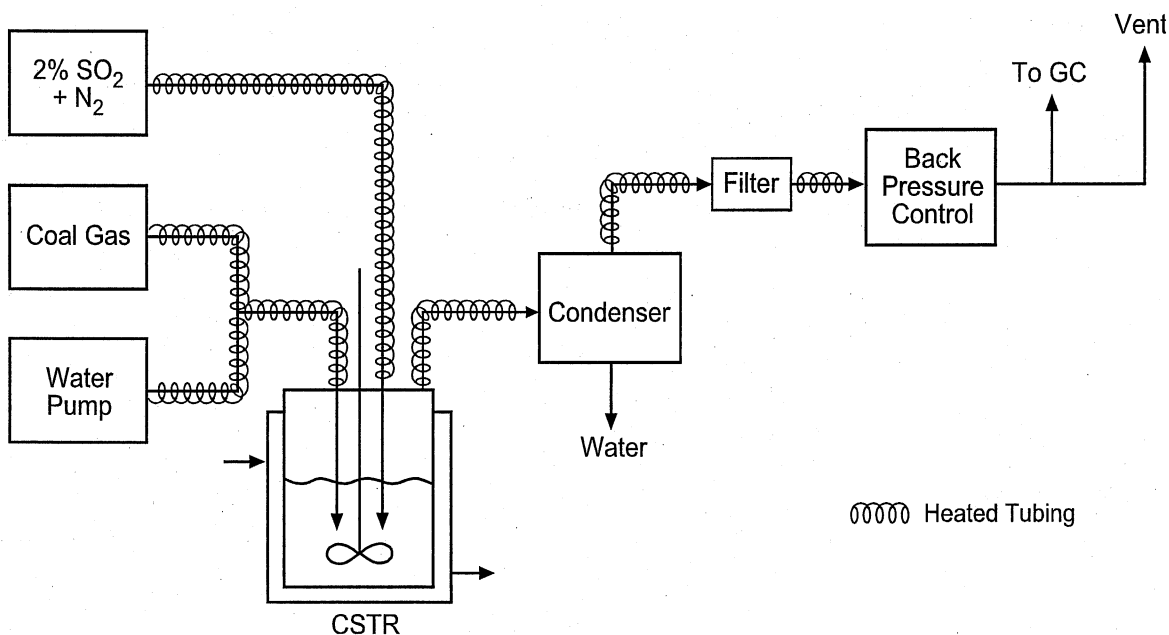


Figure 3.15. Schematic of the SSRP continuous stirred tank reactor (CSTR) system

Table 3.10. Effect of SO₂ addition on sulfur removal activity and COS formation, for SSRP in blank reactor; T: 155°C; P: 200 psig; H₂S: 8350 ppm; steam: 0% (Procedure A')

SO ₂ inlet (ppm)	Conversion (%)			COS formation
	H ₂ S	SO ₂	H ₂ S+SO ₂	(ppmv)
0 (H ₂ S feed only)	0.4	-	-	15
4800 (H ₂ S+SO ₂ feed)	3.7	3.4	3.6	75

Continuing in the same run, the effect of adding 10% steam in the feed was examined (Procedure B'). Steam was fed into the reactor at 150 sccm, thus increasing the total inlet flow to 1.65 SLPM, while maintaining all other reaction parameters. As shown in Table 3.11, the addition of 10% steam enhanced the sulfur removal activity of the blank reactor significantly (from ca. 4% to ca. 51%). This result is in excellent agreement with the corresponding one for the blank micro-reactor (see Table 3.2). The formation of COS was only minimally affected by the steam addition (a decrease from 75 ppm to 55 ppm, whereas in the blank micro-reactor it had increased from 30 ppm to 60 ppm, in either case being insignificant compared to ca. 6500 ppm of sulfur that was removed).

Table 3.11. Effect of 10% steam addition on sulfur removal activity and COS formation, for SSRP in blank reactor; T: 155°C; P: 200 psig; H₂S: 8350 ppm; SO₂: 4800 ppm

Steam (%)	Conversion (%)			COS formation
	H ₂ S	SO ₂	H ₂ S+SO ₂	(ppmv)
0 (dry feed)	3.7	3.4	3.6	75
10 (steam addition)	51.2	50.6	51.0	55

Another set of preliminary experiments involved loading the CSTR with sulfur only (no catalyst), in order to evaluate this configuration in terms of its sulfur removal activity. The glass liner was loaded with 716 g of sublimed sulfur powder and was placed inside the reactor. Upon heating up beyond the melting point of sulfur (ca. 121°C) the reactor contained ca. 400 cc of molten sulfur (MS). The reactor was then heated to 155°C and pressurized to 300 psig under inert gas flow of 0.9 SLPM. A steam flow of 0.1 SLPM was added (i.e., 10% steam) followed by substituting part of the inert gas flow with an equal flow of H₂S-containing syngas (no SO₂ feed). After attaining steady state, the total feed flow was increased from 1 SLPM up to 4 SLPM in 1 SLPM steps by proportionally increasing both the syngas and steam flows. The effect of feed flow variation on H₂S conversion and COS formation is shown in Figure 3.16. A four-fold increase in flow caused a decrease in H₂S conversion (from ca. 7% to ca. 5%) and a significant decrease in COS formation (from 520 ppm to 115 ppm). By interpolation of the COS curve, the COS values for flows of 1.1 SLPM and 1.3 SLPM were 480 ppm and 420 ppm, respectively.

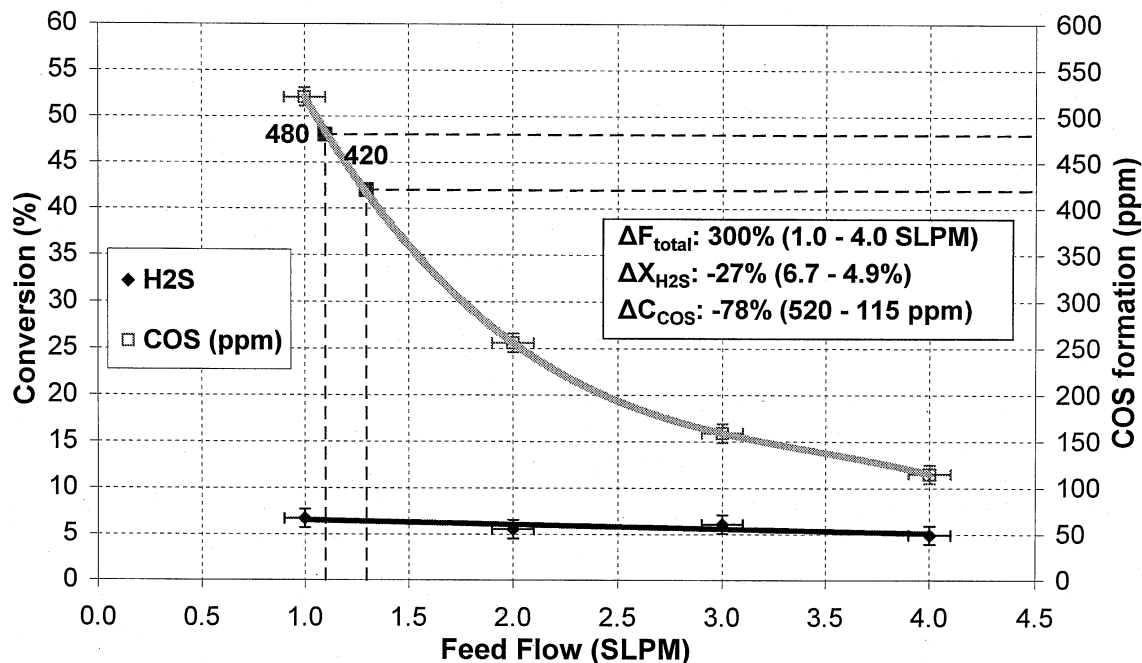


Figure 3.16. Effect of feed flow on H₂S conversion and COS formation for SSRP in Molten Sulfur; T: 155°C; P: 300 psig; H₂S: 9000 ppm; steam: 10%

Continuing in the same run, the syngas and inert flow were then restored to 0.9 SLPM while the steam flow was kept at 0.4 SLPM, thus decreasing the total feed flow from 4 SLPM to 1.3 SLPM and increasing the steam concentration from 10% to 30.8%, all other parameters being the same. The effect of steam concentration variation was then examined by decreasing the steam flow from 0.4 SLPM to 0.2 SLPM and finally to its original value of 0.1 SLPM. This decrease in steam concentration from 30.8% back to 10% led to an increase in H₂S conversion from ca. 4% to ca. 6.5%, and in COS formation from 420 ppm to 520 ppm (see Figure 3.17).

The results of Fig. 3.17 seem to indicate that increasing the steam feed concentration resulted in a decrease in the undesirable formation of COS. Yet, besides the variation in steam concentration, the total feed flow was also varied. As demonstrated in Fig. 3.16, an increase in total feed flow also decreased the COS formation. The data of Fig. 3.17 were plotted vs. the total feed flow in Figure 3.18, in order to identify which of these two variables (feed flow vs. steam concentration) was actually responsible for the observed decrease in COS formation. The COS formation curve from Fig. 3.16 (dashed line) was also plotted for a direct comparison.

The two COS formation curves of Fig. 3.18 almost coincide, with two data point pairs being exactly equal to each other, and the third (middle) data point pair with minimal deviation (460 ppm vs. the interpolated value of 480 ppm). The data on the continuous curve correspond to a variation in both feed flow and steam concentration, whereas the ones on the dashed curve to a variation in feed flow only. Therefore, the presence of steam in the feed apparently did not impede the formation of COS (possibly via COS hydrolysis); the COS formation was simply inversely correlated with the total feed flow.

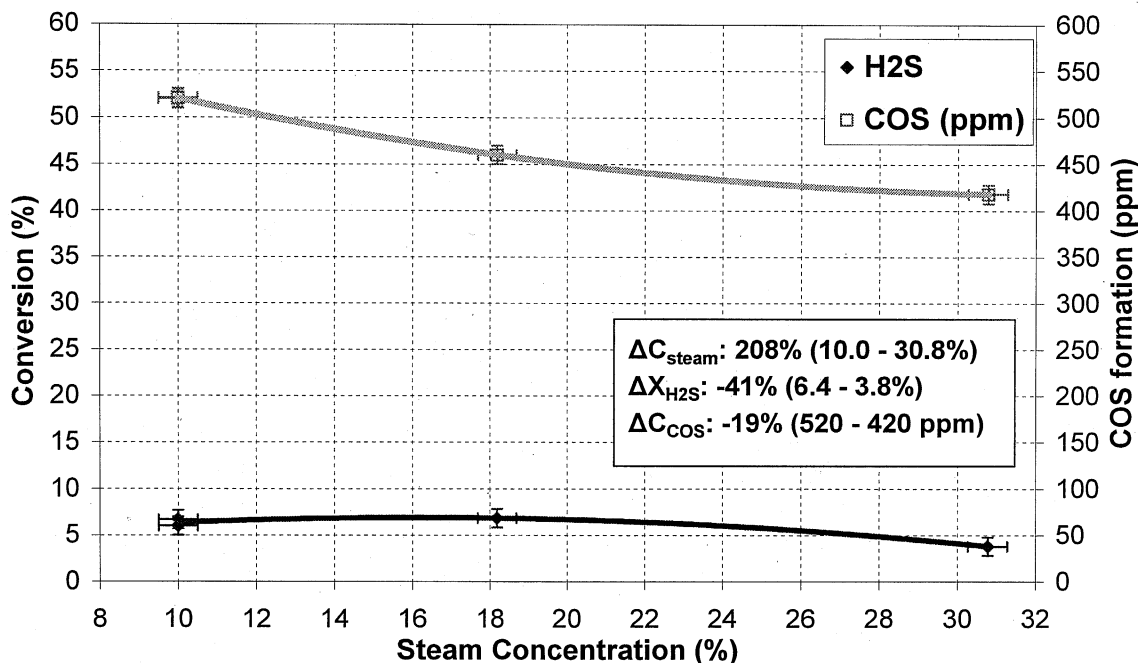


Figure 3.17. Effect of steam feed concentration on H₂S conversion and COS formation for SSRP in Molten Sulfur; T: 155°C; P: 300 psig; H₂S: 9000 ppm; F: 1.0-1.3 SLPM

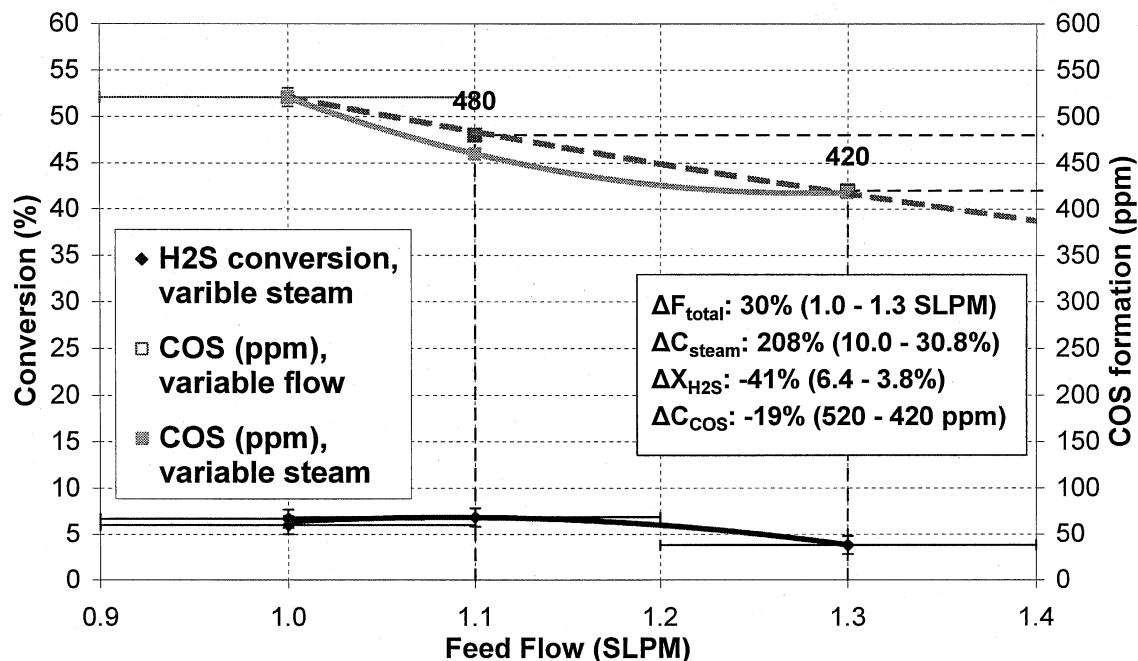


Figure 3.18. Effect of feed flow & steam feed concentration on H₂S conversion and COS formation for SSRP in Molten Sulfur; T: 155°C; P: 300 psig; H₂S: 9000 ppm; steam: 10%-30.8%

The effects of total feed flow and steam feed concentration variation were also examined in the Molten Sulfur configuration under the full SSRP feed (i.e., in the presence of SO_2). As before, after feeding 10% steam (0.1 SLPM in a 1 SLPM total feed), the H_2S -containing syngas was fed into the reactor at 155°C , 300 psig, and 1 SLPM. After reaching steady state, the H_2S conversion was ca. 7% and the outlet COS was ca. 665 ppm. Then, SO_2 was added (ca. 4400 ppm, Procedure **D'**) and the reaction system reached a new steady state. The conversion of H_2S increased to ca. 91% due to the $\text{H}_2\text{S}+\text{SO}_2$ reaction, and the formation of COS increased to ca. 830 ppm. This increase in the outlet COS by SO_2 addition is apparently related to the creation of an alternative pathway for COS formation, i.e., the reaction between CO and active sulfur (not molten sulfur) formed by the $\text{H}_2\text{S}+\text{SO}_2$ reaction, as also discussed previously.

The effect of feed flow on the Molten Sulfur activity under Procedure **D'** was examined by increasing the total (steam and syngas and SO_2) feed flow from 1 SLPM to 2 and finally 3 SLPM, all other reaction parameters remaining constant. As shown in Figure 3.19, this three-fold increase in feed flow resulted in a decrease in both sulfur removal activity (from ca. 93% to ca. 84%) and in the formation of COS (from ca. 830 ppm to ca. 255 ppm). Thus, high feed flows offer the advantage of suppressing the undesirable formation of COS, but also decrease the sulfur removal activity. The total outlet sulfur-gas concentration (sum of unreacted H_2S and SO_2 and formed COS) was found to increase with increasing feed flow. Also, it is interesting to note that the outlet $\text{H}_2\text{S}/\text{SO}_2$ ratio was found to increase with increasing feed flow, possibly implying a significantly different diffusivity of these compounds in the molten sulfur medium.

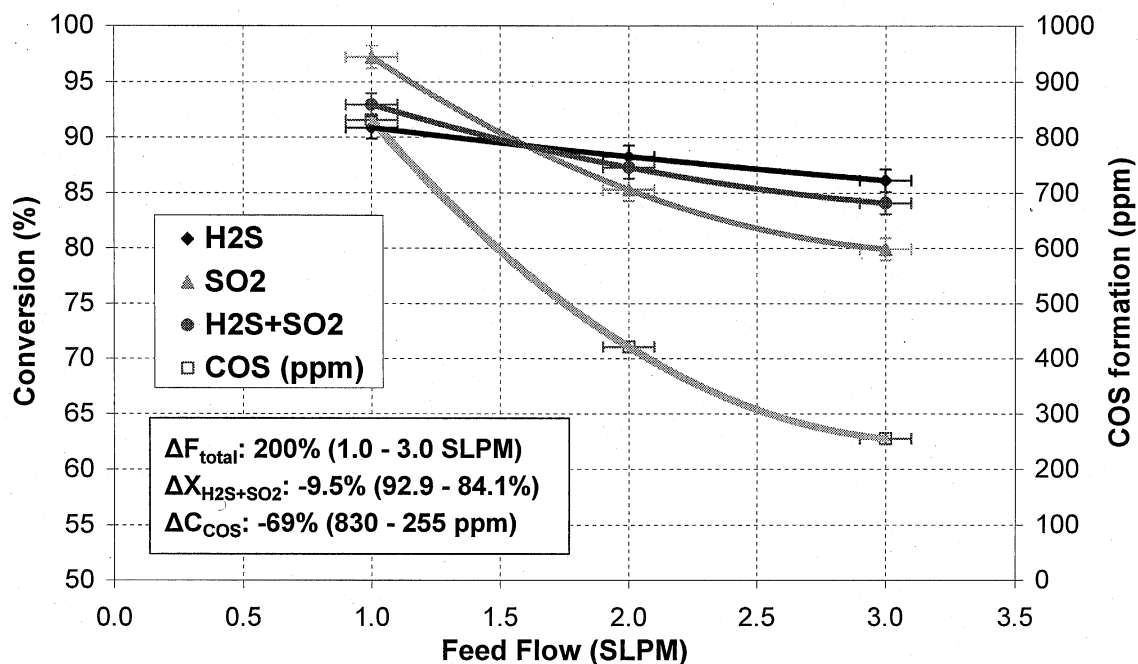


Figure 3.19. Effect of feed flow on sulfur removal activity and COS formation for SSRP in Molten Sulfur; T: 155°C ; P: 300 psig; H_2S : 9000 ppm; SO_2 : 4400 ppm; steam: 10%

Continuing in the same run, the syngas + SO₂ flow was restored to 0.9 SLPM while the steam flow was kept at 0.3 SLPM, thus decreasing the total feed flow from 3 SLPM to 1.2 SLPM and increasing the steam concentration from 10% to 25%, all other reaction parameters being the same. The sulfur removal activity (H₂S+SO₂ conversion) remained essentially constant (from ca. 3% to ca. 92.5%), whereas the COS formation decreased from 830 ppm to 620 ppm by this increase in steam concentration.

Again, in order to decouple the effect of variable steam feed concentration and total feed flow on the sulfur removal activity and COS formation, the results of the previous paragraph were plotted vs. the corresponding feed flow in Figure 3.20, along with parts of the H₂S+SO₂ and COS curves of Fig. 3.19. The two H₂S+SO₂ curves essentially coincide. The COS data point at 1.2 SLPM (620 ppm) deviated measurably from the predicted value of the continuous COS curve (ca. 730 ppm). Despite this deviation, it appears that also in the presence of SO₂, the presence of steam in the feed apparently did not extensively impede the formation of COS; the COS formation was again inversely correlated with the total feed flow, as seen above.

The effect of the H₂S inlet concentration on the formation of COS in the absence of SO₂ was examined in the Molten Sulfur configuration at 155°C, 300 psig, 10% steam in the feed, and a total feed flow of 2 SLPM. The H₂S concentration was varied from 8500 ppm down to 4250 ppm while keeping the total flow, the steam flow, and all other reaction parameters constant. The results are shown in Figure 3.21.

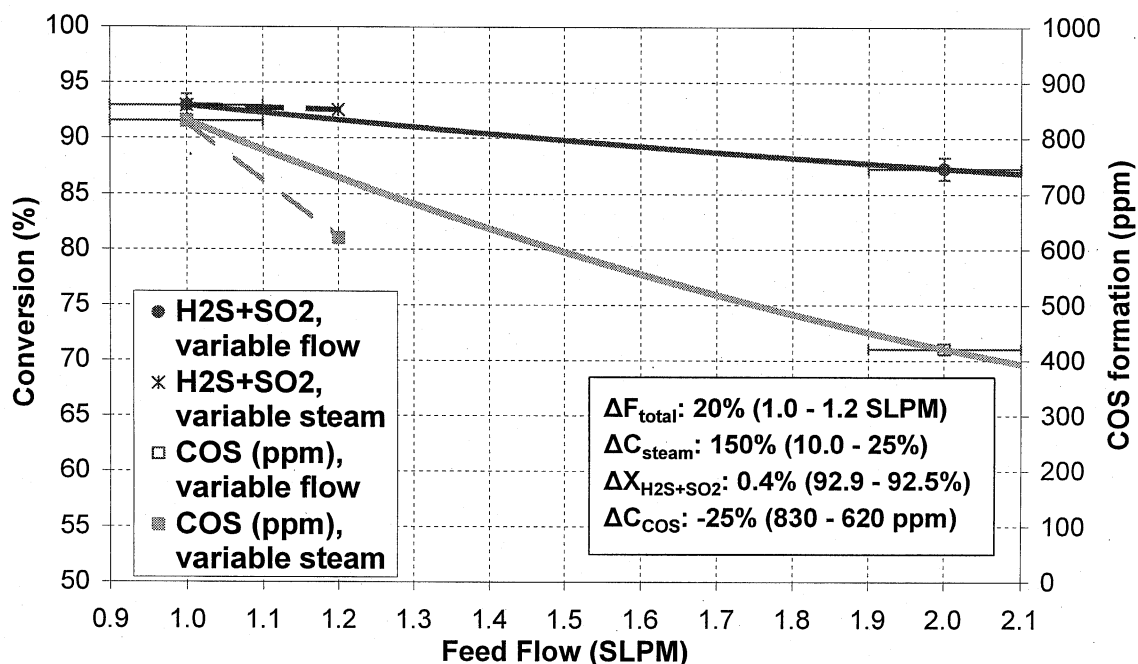


Figure 3.20. Effect of feed flow and steam feed concentration on sulfur removal activity and COS formation for SSRP in Molten Sulfur; T: 155°C; P: 300 psig; H₂S: 9000 ppm; SO₂: 4400 ppm; steam: 10%

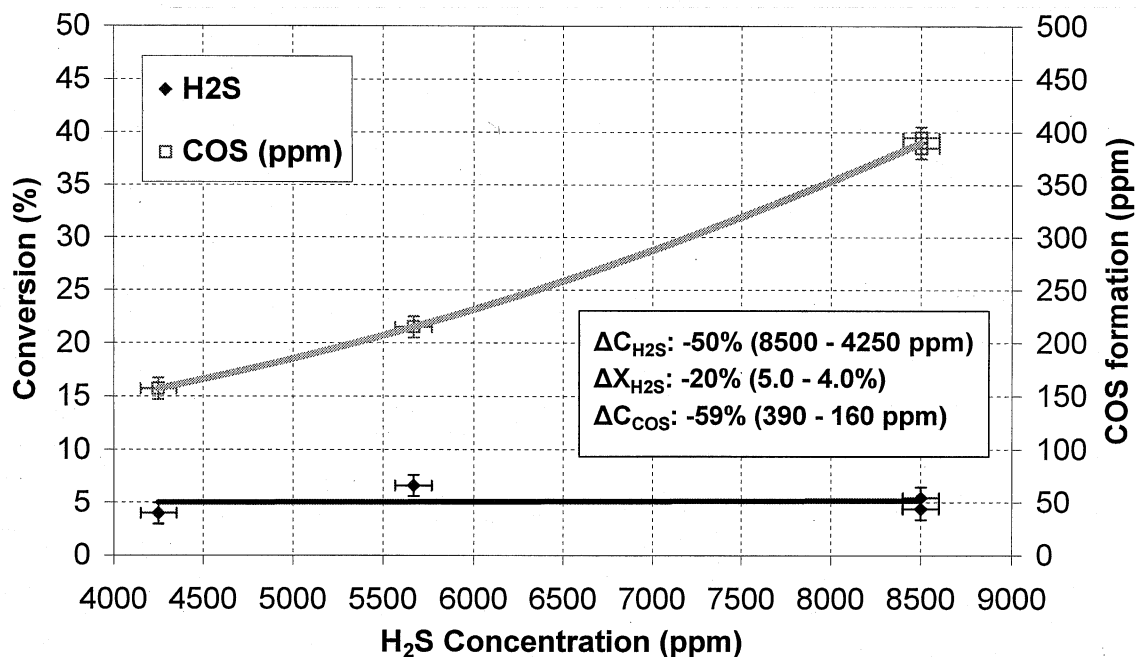


Figure 3.21. Effect of H₂S inlet concentration on H₂S conversion and COS formation for SSRP in Molten Sulfur; T: 155°C; P: 300 psig; F: 2 SLPM; steam: 10%

The conversion of H₂S was essentially constant (between 5% and 4%) upon decreasing the H₂S inlet concentration by half (from 8500 ppm to 4250 ppm), while the COS formation decreased by ca. 60% (from 390 ppm to 160 ppm). These results are indicative of an apparent first-order reaction of H₂S into COS with respect to the inlet concentration of H₂S (the expected apparent reaction order with respect to CO would be zero, due to the great excess of CO in the feed, ca. 50% vs. less than 1% H₂S). These results, however, could not indicate unequivocally whether the formation of COS was controlled by intrinsic kinetics or by diffusion of the reactant H₂S through the molten sulfur medium.

After restoring the H₂S inlet concentration to 8500 ppm, SO₂ was added at an inlet concentration of. 4330 ppm (Procedure **D'**), and a new steady state was attained at 155°C, 300 psig, and a total feed flow of 2 SLPM. The H₂S+SO₂ conversion was ca. 90.5% and the outlet COS was ca. 475 ppm. These results fit quite well with those of Fig. 3.19 at 2 SLPM, indicating that the steady-state reactivity of the system is the same, regardless of whether the addition of SO₂ took place prior to or after a reaction parameter variation (total feed flow in the former case and H₂S inlet concentration in the latter).

The effect of the steam inlet concentration was examined once again at 155°C and 300 psig, under a different feed procedure: steam feed followed by SO₂ feed and finally by the H₂S-containing syngas feed (Procedure **D**). Due to an error in the syngas flow, the H₂S/SO₂ inlet ratio was only ca. 1.36 as opposed to the target value of 2. The results of varying the steam feed concentration from 11.8% to 21.1% (with a corresponding increase in the total feed flow from 1.7 to 1.9 SLPM, with all other reaction parameters constant) are shown in Figure 3.22.

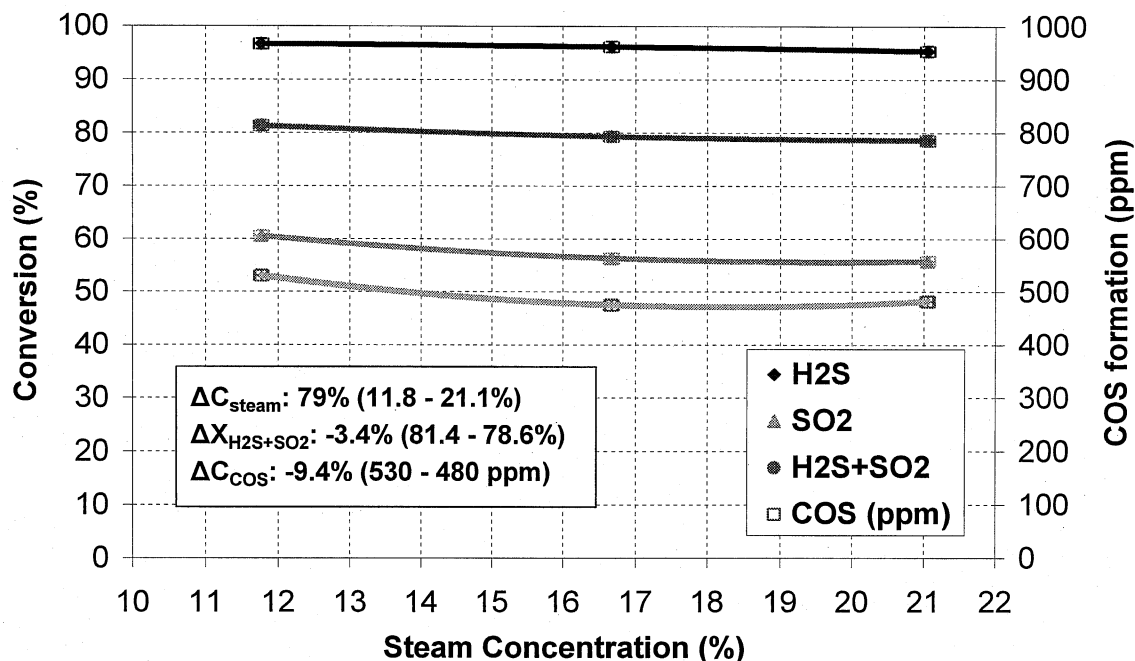


Figure 3.22. Effect of steam feed concentration on sulfur removal activity and COS formation for SSRP in Molten Sulfur; T: 155°C; P: 300 psig; inlet H₂S/SO₂: 1.36; F: 1.7-1.9 SLPM

The significant difference between the H₂S and SO₂ conversion at every examined steam concentration was due to the low H₂S/SO₂ inlet ratio, which is a good indication that the Claus (H₂S+SO₂) reaction is the major reaction under these conditions. Despite this difference in the conversion of the two reactants as shown in Fig. 3.22, the effect of variable steam concentration was minimal for both the sulfur removal activity (ca. 81.5% to 78.5%) and COS formation (ca. 530 ppm to 480 ppm).

Continuing in the same run, the stirring speed was varied from the standard value of 1000 RPM to 1500, 750, and finally 500 RPM, in order to examine its effect on the sulfur removal activity. The results of the variable stirring speed study are shown in Figure 3.23. A three-fold variation in stirring speed (from 500 to 1500 RPM) had minimal effect on sulfur removal activity and COS formation, suggesting the absence of significant mass transfer limitations under the examined reaction conditions.

The effect of varying the reaction temperature was examined at 300 psig, 10% steam in the feed, and a total feed flow of 2 SLPM. After feeding 200 sccm of steam (10% in 2 SLPM), SO₂ was fed followed by H₂S-containing syngas (Procedure **D**) and the system reached steady state. The reaction temperature was decreased from 155°C to 145°C, 136°C, and finally 128°C, with all other reaction parameters constant. As shown in Figure 3.24, the sulfur removal activity decreased from ca. 83.5% to ca. 79.5%, and the outlet COS from ca. 495 ppm to ca. 165 ppm. The total outlet sulfur-gas concentration (sum of unreacted H₂S and SO₂ and formed COS) was found to increase with decreasing temperature, indicating that the efficiency of SSRP is favored at the higher temperatures within the examined range (i.e., 145-155°C).

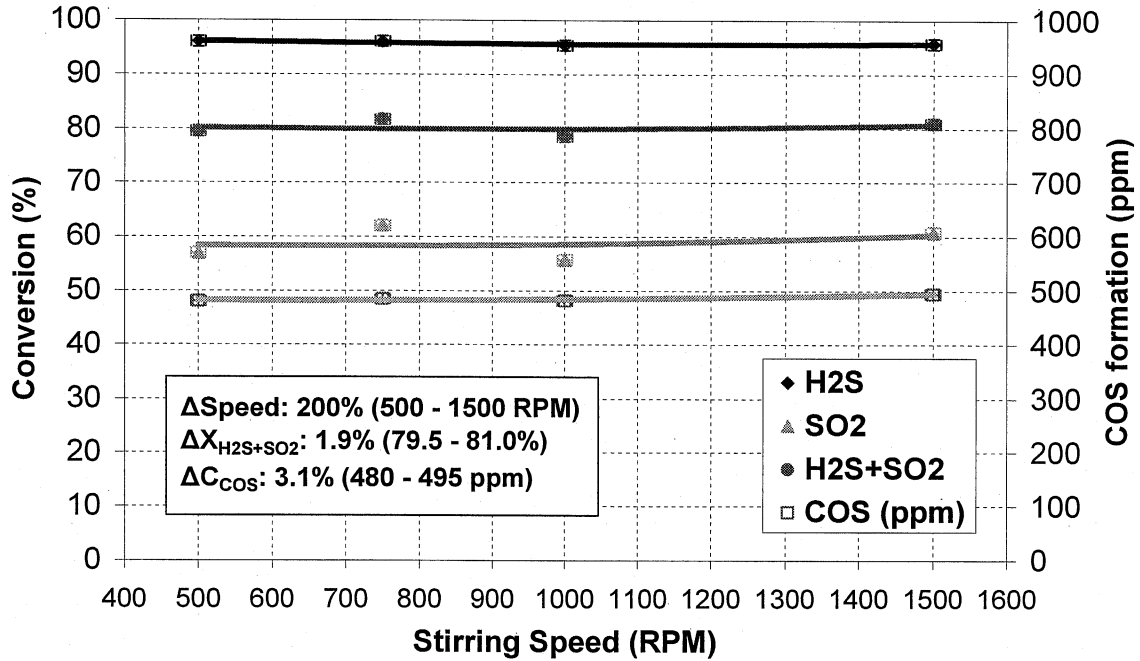


Figure 3.23. Effect of stirring speed on sulfur removal activity and COS formation for SSRP in Molten Sulfur; T: 155°C; P: 300 psig; inlet H₂S/SO₂: 1.36; F: 1.9 SLPM; steam: 21.1%

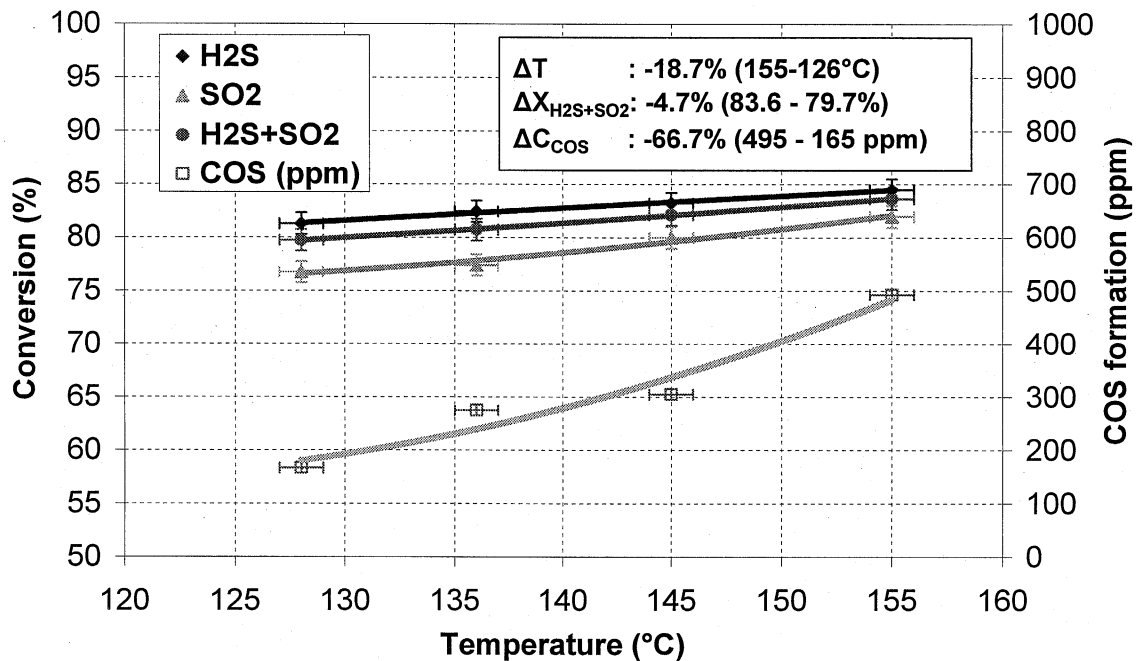


Figure 3.24. Effect of reaction temperature on sulfur removal activity and COS formation for SSRP in Molten Sulfur; P: 300 psig; H₂S: 8500 ppm; SO₂: 4380 ppm; F: 2 SLPM; steam: 10%

A new set of SSRP reaction experiments involved loading the glass liner with ca. 22.5 g (ca. 25 cc) E-alumina and ca. 716 g sublimed sulfur powder and placing it inside the reactor. Upon heating up beyond the melting point of sulfur (ca. 121°C) the reactor contained ca. 400 cc of molten sulfur (MS) into which the catalyst was suspended under stirring. The reactor was then heated to 155°C and pressurized to 300 psig under inert gas flow of 0.9 SLPM. A steam flow of 0.1 SLPM was added (i.e., 10% steam) followed by substituting part of the inert gas flow with an equal combined flow of SO₂ and H₂S-containing syngas, that were fed at the same time (reactant co-feed).

After reaching steady state at a feed flow of 1 SLPM, the flow of each one of the three feed components (steam, SO₂, and H₂S-containing syngas) was decreased by 50%, thus making the total feed flow 0.5 SLPM. The results of this variation in total feed flow are given in Table 3.12. A decrease in feed flow by half (i.e., doubling the residence time) resulted in an increase in both sulfur removal activity (from ca. 91% to ca. 94%) and in the formation of COS (from ca. 745 ppm to ca. 950 ppm). The total outlet sulfur-gas concentration (sum of unreacted H₂S & SO₂ and formed COS) was found to decrease with decreasing feed flow. Therefore, higher residence times appear to enhance the efficiency of SSRP, despite the observed increase in the unfavorable formation of COS.

Table 3.12. Effect of feed flow on sulfur removal activity and COS formation, for SSRP in E-alumina + Molten Sulfur; T: 155°C; P: 300 psig; H₂S/SO₂: 1.85; steam: 10%

Feed Flow (SLPM)	Conversion (%)			COS formation
	H ₂ S	SO ₂	H ₂ S+SO ₂	(ppmv)
1.0	98.4	77.2	90.9	745
0.5	99.1	84.8	94.0	950

In a new run at 155°C following the same feed procedure as above (reactant co-feed) and at a total feed flow of 1 SLPM, steady state was attained at a pressure of 300 psig. Then, the effect of varying the reaction pressure to 400 psig, then to 350 psig, and finally to 250 psig, on the sulfur removal activity of the E-alumina + MS (molten sulfur) configuration was examined. The results of this pressure variation study are shown in Figure 3.25. An increase in reaction pressure from 250 psig to 400 psig resulted in an increase in sulfur removal activity (from ca. 94.5% to ca. 97.5%), as well as in COS formation (from ca. 600 ppm to ca. 730 ppm). The total outlet sulfur-gas concentration (sum of unreacted H₂S & SO₂ and formed COS) was found to increase with increasing pressure, indicating that the efficiency of SSRP is enhanced at higher pressures, which are favored in a commercial application involving gasifier-syngas.

It is also interesting to note that the difference in conversion between H₂S and SO₂ was found to decrease with increasing pressure (the conversion curves appeared to merge above 350 psig). This observation is apparently related to the different effect of pressure on the diffusivity and solubility of these two compounds in molten sulfur.

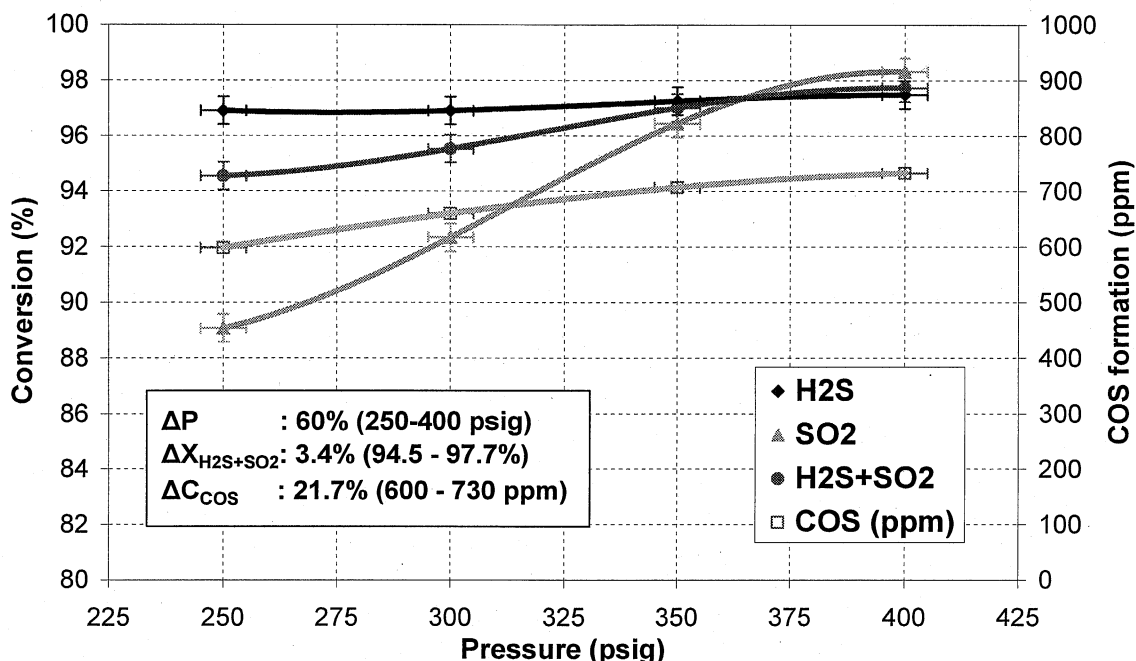


Figure 3.25. Effect of reaction pressure on sulfur removal activity and COS formation for SSRP on E-alumina + Molten Sulfur; T: 155°C; H₂S: 8800 ppm; SO₂: 4600 ppm; F: 1 SLPM; steam: 10%

After completing the pressure study and with the reaction being at steady state at 155°C and 250 psig, the SO₂ was removed from the feed while maintaining the total feed flow and all other reaction parameters constant. As shown in Table 3.13, the removal of SO₂ from the feed resulted in a significant increase in COS formation (from ca. 600 ppm to ca. 930 ppm). This is in clear contrast to the observed trends for the blank CSTR and the Molten Sulfur only (no catalyst) configurations, where addition of SO₂ increased and removal of SO₂ decreased the outlet COS. Furthermore, the H₂S conversion in the present case was minimal (ca. 0.4%), implying that less than ca. 1/10th of the measured COS was formed from H₂S. Therefore, in the presence of the E-alumina catalyst, addition of SO₂ apparently shifts the pathway for COS formation from the (inevitable for H₂S-containing syngas feed) CO+H₂S reaction to that of CO with active sulfur generated by the H₂S+SO₂ reaction, at least to a major extent.

Table 3.13. Effect of SO₂ removal on sulfur removal activity and COS formation, for SSRP on E-alumina + Molten Sulfur; T: 155°C; P: 300 psig; H₂S: 8500 ppm; steam: 10%; F: 1 SLPM

SO ₂ (ppm)	Conversion (%)			COS formation (ppmv)
	H ₂ S	SO ₂	H ₂ S+SO ₂	
4600 (SO ₂ present)	96.9	89.1	94.5	600
0 (SO ₂ removed)	0.4	-	-	930

A comparison between the Molten Sulfur only (no catalyst) and the E-alumina + Molten Sulfur configuration with respect to their sulfur removal activity and COS formation, is given in Table 3.14. The reaction parameters were 155°C, 300 psig, 1 SLPM, and 10% steam in the feed. The presence of the E-alumina catalyst appears to enhance the sulfur removal activity (from ca. 93% to ca. 95.5%), while decreasing the undesirable formation of COS (from ca. 830 ppm to 660 ppm). The total outlet sulfur-gas concentration (sum of unreacted H₂S & SO₂ and formed COS) decreased significantly (by more than 500 ppm) with the E-alumina catalyst. More efficient catalysts (especially in terms of further suppressing the formation of COS, possibly via COS hydrolysis) would further improve the performance of SSRP in terms of sulfur removal.

Table 3.14. Effect of the presence of E-alumina on the sulfur removal activity and COS formation, for SSRP in Molten Sulfur; T: 155°C; P: 300 psig; H₂S/SO₂: 1.9-2.0; steam: 10%; F: 1 SLPM

Configuration	Conversion (%)			COS formation (ppmv)
	H ₂ S	SO ₂	H ₂ S+SO ₂	
Molten Sulfur only	90.9	97.2	92.9	830
MS +E-alumina	96.9	92.3	95.5	660

A new set of SSRP reaction experiments involved loading the glass liner with a fresh batch of ca. 22.5 g (ca. 25 cc) E-alumina and ca. 716 g sublimed sulfur powder and placing it inside the reactor. Upon heating up beyond the melting point of sulfur (ca. 121°C) the reactor contained ca. 400 cc of molten sulfur (MS) into which the catalyst was suspended under stirring. The reactor was then heated to 155°C and pressurized to 300 psig under inert gas flow of 0.9 SLPM. A steam flow of 0.1 SLPM was added (i.e., 10% steam) followed by substituting part of the inert gas flow with SO₂/N₂ to achieve 4400 ppm SO₂ in the feed. Then, the remaining N₂ flow was substituted by an equal coal gas flow, thus achieving 8800 ppm H₂S in the feed and a total feed flow of 1 SLPM. The measured H₂S+SO₂ conversion was ca. 90.5% and the outlet COS was ca. 645 ppm (Figure 3.26).

As expected, the conversion was lower in the CSTR than the fixed-bed micro-reactor that more closely simulates a plug-flow reactor (PFR) and whose results were discussed in Section 3.3.1. This is because in a CSTR the conversion (rate) is determined by the outlet concentration. The commercial embodiment (Fig. 3.1) is conceived to be a slurry bubble column reactor in which the conversion should be closer to that of the fixed-bed reactor.

The effect of feed flow variation on sulfur removal activity and COS formation was examined by increasing the total (steam + SO₂ + H₂S-containing syngas) flow from 1 SLPM to 2 and finally 3 SLPM, all other reaction parameters remaining constant. As shown in Figure 3.26, a three-fold increase in feed flow caused a decrease in H₂S+SO₂ conversion (down to ca. 86.5%) and an almost 60% decrease in COS formation (down to ca. 265ppm). These results are in good agreement with those of Table 3.12 (for 0.5-1 SLPM) and Fig. 3.19 (for Molten Sulfur only).

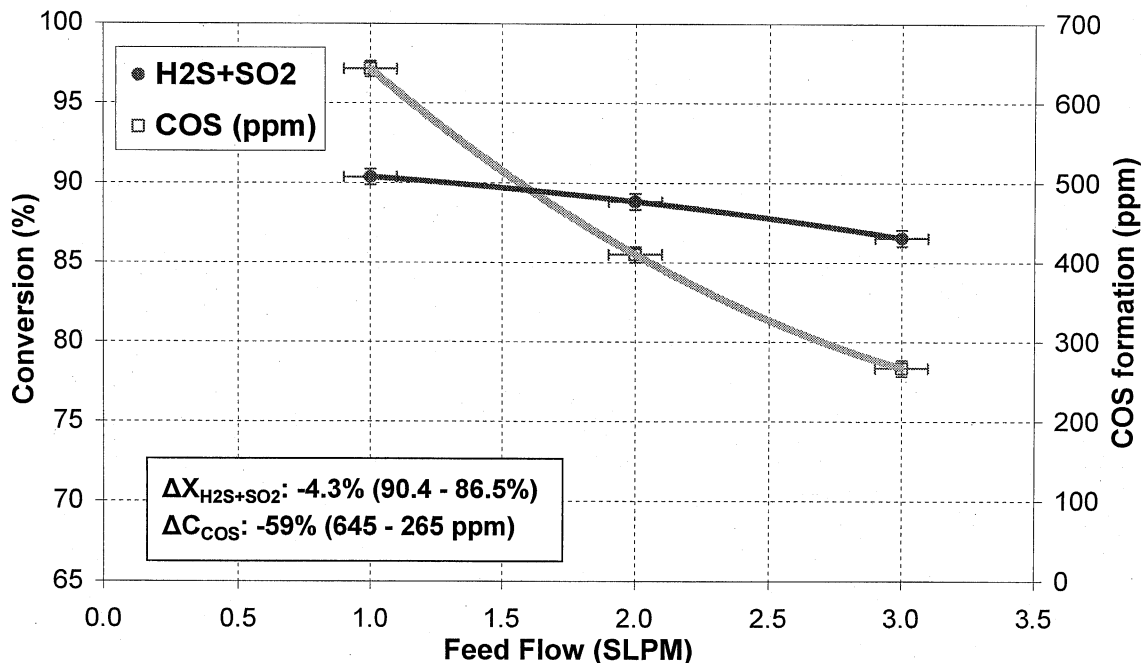


Figure 3.26. Effect of feed flow on sulfur removal activity and COS formation for SSRP on E-alumina + Molten Sulfur; T: 155°C; P: 300 psig; H₂S: 8800 ppm; SO₂: 4400 ppm; steam: 10%

The effect of pressure on sulfur removal activity and COS formation was examined at 155°C and a feed flow of 2.8 SLPM, by varying the reaction pressure from 350 psig to 400 psig and then down to 300, 275, and finally 250 psig. A decrease in pressure from 400 psig to 250 psig resulted in a decrease in sulfur removal activity (the H₂S+SO₂ conversion decreased from ca. 91% to ca. 87%) and only a small decrease in COS formation (from ca. 345 ppm to ca. 290 ppm), as shown in Figure 3.27. These results are in good qualitative agreement with those of Fig. 3.25. The lower H₂S+SO₂ conversion and COS formation values in the present case compared to the corresponding ones of Fig. 3.25 are due to the higher total feed flow (2.8 SLPM vs. 1 SLPM). Therefore, higher reaction pressures enhance the sulfur removal efficiency of SSRP while only moderately increasing the undesirable formation of COS.

After completing the pressure variation study, the reaction was maintained at steady state at 155°C, 250 psig, and a total feed flow of 2.8 SLPM. Then, the SO₂/N₂ flow was substituted by an equal flow of N₂, thus maintaining the reaction pressure and total feed flow into the reactor. In the absence of SO₂ the conversion of H₂S decreased drastically (down to 5% or less), and the formation of COS increased from ca. 290 ppm to ca. 410 ppm. These results are in very good qualitative agreement with those of Table 3.13. The lower COS formation values in both the presence and absence of SO₂ in the present case compared to the corresponding ones of Table 3.13 are due to the higher feed flow (2.8 SLPM vs. 1 SLPM). Thus, removal of SO₂ appears to shift the pathway for COS formation back to the CO+H₂S reaction.

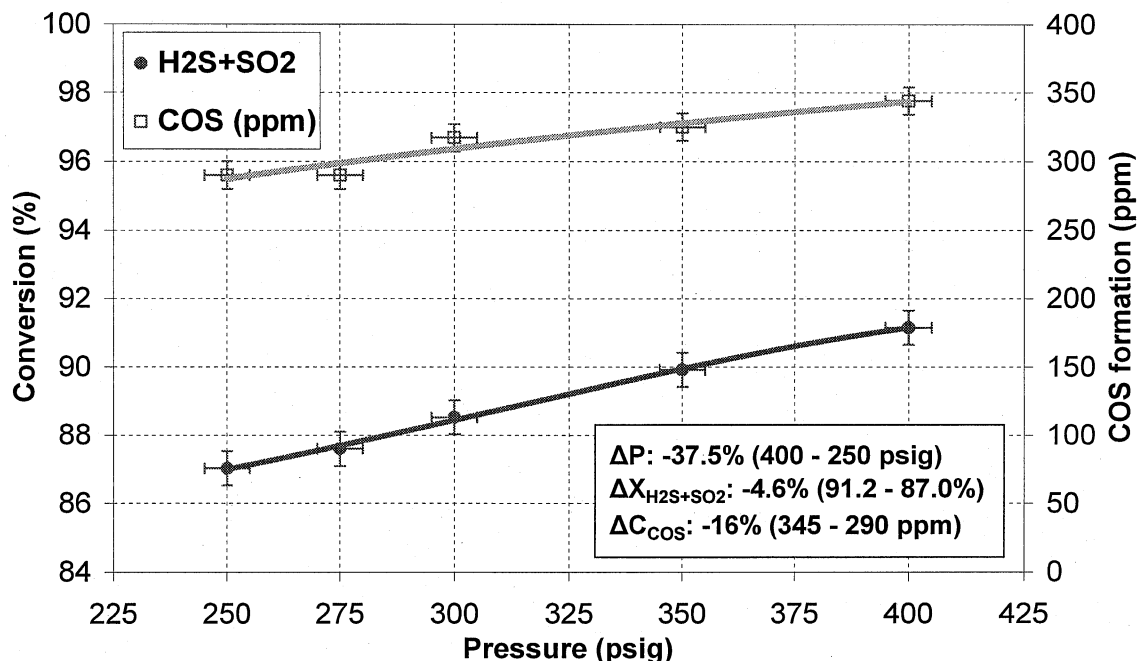


Figure 3.27. Effect of pressure on sulfur removal activity and COS formation for SSRP on E-alumina + Molten Sulfur; T: 155°C; H₂S: 8800 ppm; SO₂: 4400 ppm; steam: 10.7%; F: 2.8 SLPM

In a similar manner, the SSRP reaction was examined at a reaction temperature of 125°C, a reaction pressure of 350 psig, and a feed flow of 2.8 SLPM. After achieving a pseudo steady state under these conditions, the SO₂/N₂ flow was again substituted by an equal flow of N₂, thus maintaining the reaction pressure and total feed flow into the reactor. In the absence of SO₂ the conversion of H₂S decreased from ca. 93.5% down to ca. 1% (corresponding to ca. 90 ppm of converted H₂S), whereas the formation of COS remained essentially constant (from ca. 95 ppm to ca. 85 ppm). Thus, the same observation is valid for these two experiments, despite the differences in reaction temperature (155°C and 125°C) and pressure (250 psig and 350 psig): the good agreement between the amount of converted H₂S and formed COS appears to suggest that in the absence of SO₂ the formation of COS is the result of the reaction between CO (and/or CO₂) and H₂S (reactions 3.7 and 3.9).

The effect of steam concentration was examined at 125°C, 300 psig, and an initial feed flow of 2 SLPM, by varying the steam feed flow from 0.2 SLPM to 0.3 and then to 0.4 SLPM, while keeping all other reaction parameters constant. The corresponding feed concentration of steam was 10%, 14.3%, and 18.2%, respectively. As shown in Figure 3.28, the sulfur removal activity was not affected by this variation in feed steam concentration (H₂S+SO₂ conversion of ca. 90.5%). On the other hand, the formation of COS decreased from ca. 115 ppm to ca. 75 ppm, the lowest achievable outlet COS concentration. This 35% decrease in COS could be partially due to a 10% increase in total feed flow (from 2.2 SLPM to 2.4 SLPM). Reaction temperature, inlet steam concentration, and total feed flow, appear to be important parameters in limiting the formation of COS, without significantly affecting the sulfur removal efficiency of SSRP.

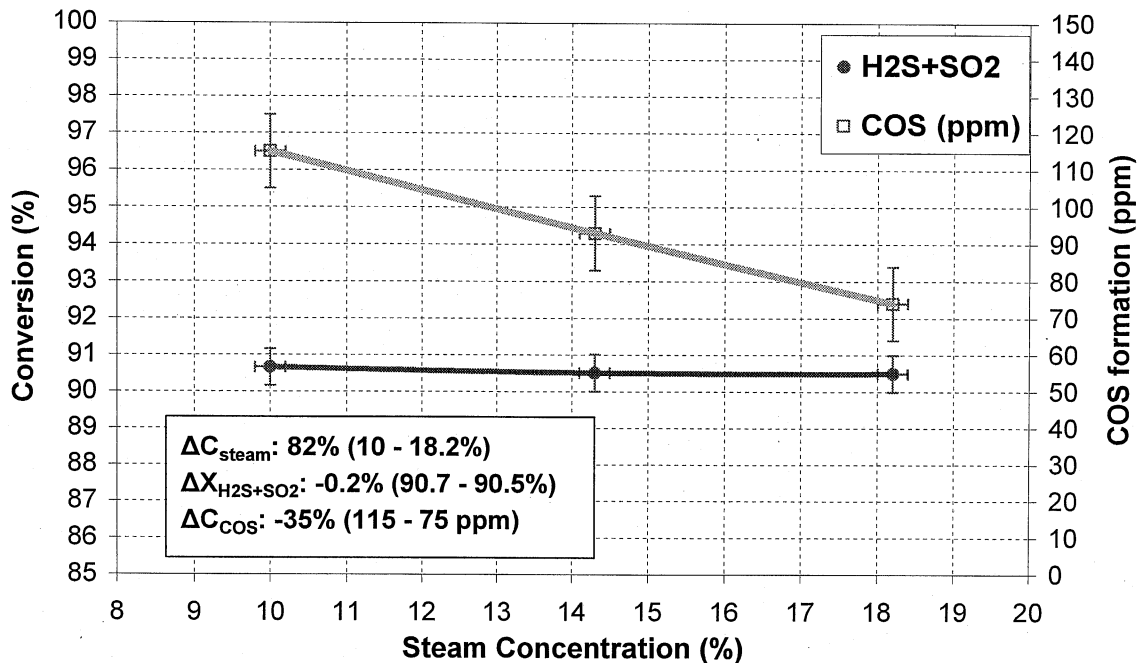


Figure 3.28. Effect of steam inlet concentration on sulfur removal activity and COS formation for SSRP on E-alumina + Molten Sulfur; T: 125°C; P: 300 psig; H₂S: 8480 ppm; SO₂: 3800 ppm; F: 2.0-2.4 SLPM

The final set of SSRP reaction experiments involved loading the glass liner with ca. 45 g (ca. 50 cc) E-alumina and ca. 716 g sublimed sulfur powder and placing it inside the reactor. The scope of these experiments with double the amount of catalyst but same amount of sulfur as above was to evaluate the effect of a higher catalyst load onto the sulfur removal activity of the catalyst + Molten Sulfur configuration in the CSTR. Upon heating up beyond the melting point of sulfur (ca. 121°C) the reactor contained ca. 400 cc of molten sulfur (MS) into which the catalyst was suspended under stirring. The reactor was then heated to 155°C and pressurized to 300 psig under inert gas flow of 1.8 SLPM. A steam flow of 0.2 SLPM was added (i.e., 10% steam) followed by substituting part of the inert gas flow with an equal flow of SO₂ and then with H₂S-containing syngas (Procedure **D**).

After attaining steady state under these conditions, the SO₂ and H₂S-containing syngas flow were decreased by half (from 1.8 SLPM to 0.9 SLPM) while the steam flow was maintained at 0.2 SLPM, thus giving a new total feed flow of 1.1 SLPM with a steam feed concentration of 18.2%. The effect of steam feed concentration was examined by increasing the steam feed flow to 0.3 SLPM (total feed flow of 1.2 SLPM, steam concentration of 25%); then by decreasing it to 0.1 SLPM (total feed flow of 1.0 SLPM, steam concentration of 10%). The results of the steam concentration variation study are shown in Figure 3.29. An increase in steam inlet concentration from 10% to 25% had essentially no effect on sulfur removal activity (H₂S+SO₂ conversion of ca. 95.5%), whereas the formation of COS decreased from ca. 630 ppm to ca. 535 ppm. These results are in very good agreement with those of Fig. 3.28. The decrease in COS formation (less prominent percentage-wise than that in Fig. 3.28), is again apparently related to both the increase in steam concentration and increase in total feed flow.

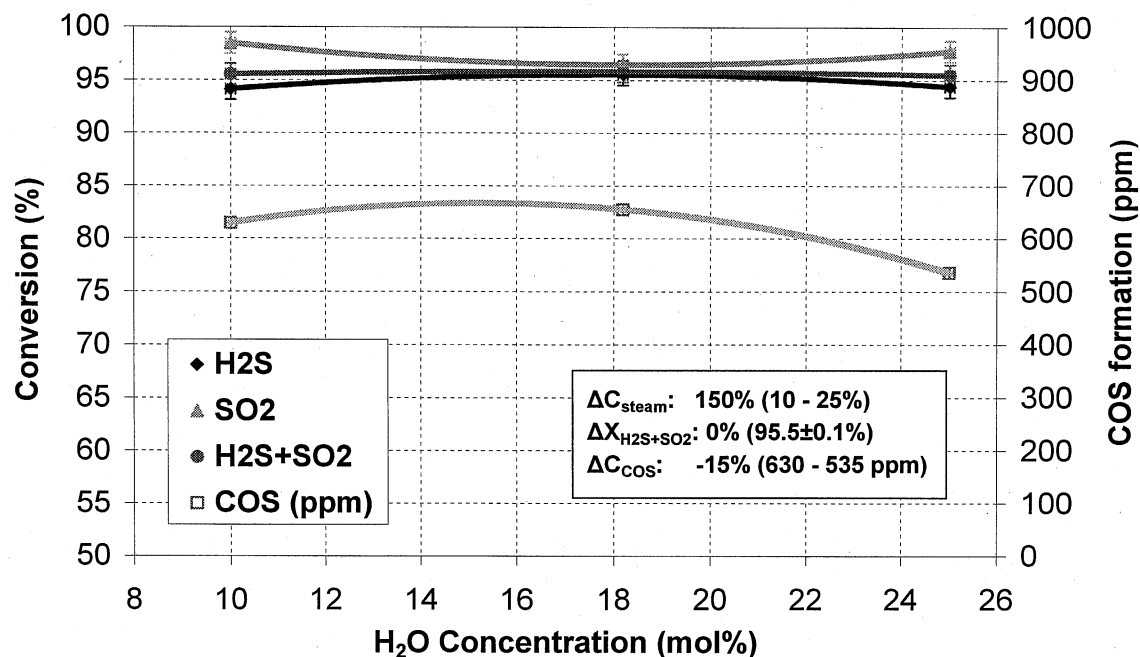


Figure 3.29. Effect of steam inlet concentration on sulfur removal activity and COS formation for SSRP on E-alumina + Molten Sulfur; T: 155°C; P: 300 psig; H₂S: 8500 ppm; SO₂: 4040 ppm; F: 1.0-1.2 SLPM

The effect of feed flow variation under constant steam inlet concentration was examined by comparing the results of the first and last stages of the above run; with a total feed flow of 2.0 SLPM and 1.0 SLPM, respectively, and a steam inlet concentration of 10% in both cases. The results of this comparison are given in Table 3.15. A decrease in the total feed flow by half resulted in a measurable increase in H₂S+SO₂ conversion (from ca. 92% to ca. 95.5%) and in COS formation (from ca. 575 ppm to ca. 630 ppm). These results are in very good agreement with those in Table 3.12 (for 1.0-0.5 SLPM), in Fig. 3.26 (for 1.0–3.0 SLPM), and in Fig. 3.19 (for 1.0-3.0 SLPM, Molten Sulfur only). As seen before, the total outlet sulfur-gas concentration (sum of unreacted H₂S & SO₂ and formed COS) was found to decrease with decreasing feed flow. Therefore, higher residence times again appear to enhance the efficiency of SSRP, despite the observed increase in the unfavorable formation of COS.

Table 3.15. Effect of feed flow on sulfur removal activity and COS formation, for SSRP in E-alumina + Molten Sulfur; T: 155°C; P: 300 psig; H₂S/SO₂: 2.1; steam: 10%

Feed Flow (SLPM)	Conversion (%)			COS formation (ppmv)
	H ₂ S	SO ₂	H ₂ S+SO ₂	
2.0	95.2	85.2	92.0	575
1.0	94.1	98.5	95.5	630

The effect of varying the SO₂ inlet concentration at 155°C and 300 psig was examined by varying the SO₂/N₂ flow while keeping the syngas and steam flows constant. The concentration of SO₂ was varied from 4550 ppm down to 3200 ppm, then up to 3900 ppm, and finally to 5150 ppm. As shown in Figure 3.30, the H₂S+SO₂ conversion exhibited a maximum of ca. 94% at an intermediate SO₂ inlet concentration. The formation of COS was only minimally affected by this variation (outlet COS from 570 ppm to 480 ppm). These results are in very good agreement with those in Fig. 3.10 (fixed-bed micro-reactor) and in Fig. 3.13 (micro-bubbler).

In a new run at 155°C and 300 psig, 0.2 SLPM steam were fed into the reactor under a total feed flow of 2 SLPM, followed by introducing the H₂S-containing syngas feed (no SO₂ feed). Upon attaining steady state, SO₂ was added in the feed (Procedure D') while keeping the total feed flow at 2 SLPM and all other reaction parameters constant. The results of the addition of SO₂ are given in Table 3.16. The outlet COS concentration decreased from 560 ppm to 465 ppm, in very good agreement with the results of Table 3.13 (for SO₂ removal).

Continuing in the same run, the syngas and SO₂ flows were decreased by half whereas the steam feed flow was maintained at 0.2 SLPM, thus making the total feed flow 1.1 SLPM. The results of this variation in feed flow were qualitatively very similar to those of Table 3.15. At these new conditions, the effect of reaction temperature on sulfur removal activity and COS formation was examined by decreasing the temperature from 155°C to 145°C and then to 135°C, while keeping all other reaction parameters constant. The results of this temperature variation study are shown in Figure 3.31.

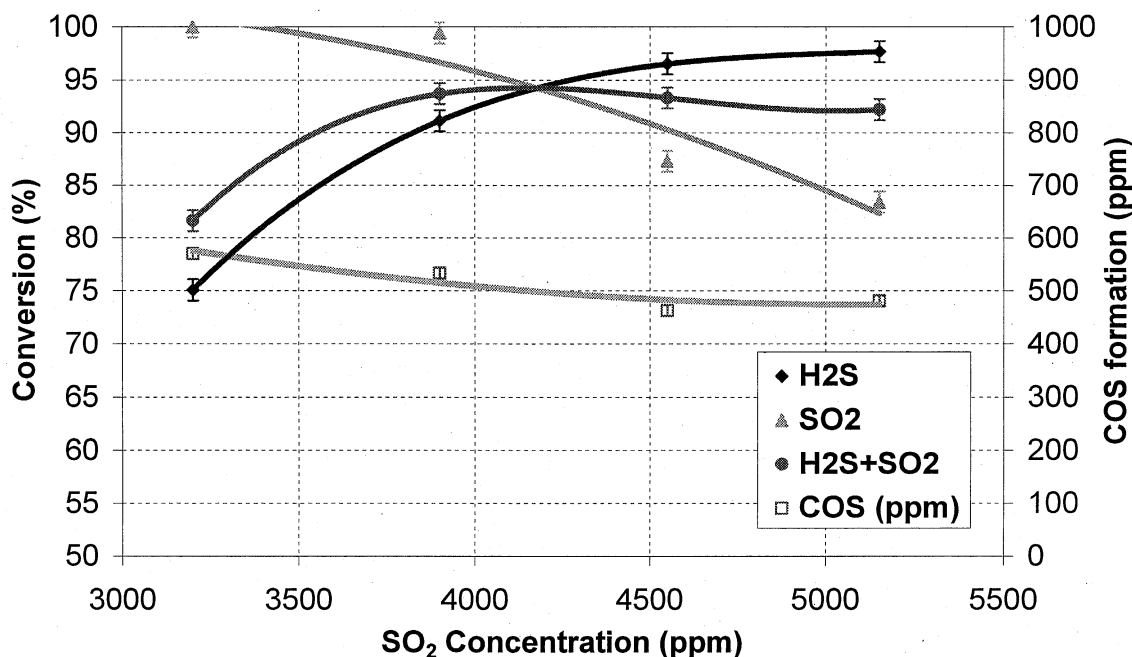


Figure 3.30. Effect of SO₂ inlet concentration on sulfur removal activity and COS formation for SSRP on E-alumina + Molten Sulfur; T: 155°C; P: 300 psig; H₂S: 9000-8270 ppm; steam: 9.75-10.25%; F: 1.90-2.05 SLPM

Table 3.16. Effect of SO₂ removal on sulfur removal activity and COS formation, for SSRP on E-alumina + Molten Sulfur; T: 155°C; P: 300 psig; H₂S: 8760 ppm; steam: 10%; F: 2 SLPM

SO ₂ (ppm)	Conversion (%)			COS formation (ppmv)
	H ₂ S	SO ₂	H ₂ S+SO ₂	
4600 (SO ₂ present)	96.9	89.1	94.5	600
0 (SO ₂ removed)	0.4	-	-	930

A decrease in reaction temperature from 155°C to 135°C was found to have essentially no effect on the sulfur removal activity of the E-alumina + Molten Sulfur configuration (H₂S + SO₂ conversion of ca. 96.5-97%). The outlet COS concentration decreased from ca. 720 ppm to 510 ppm. The total outlet sulfur-gas concentration (sum of unreacted H₂S & SO₂ and formed COS) was found to decrease with decreasing temperature; thus, the overall efficiency of SSRP is favored at lower reaction temperatures. This result is in contrast to that for the Molten Sulfur without a catalyst, where the H₂S+SO₂ conversion decreased with reaction temperature along with COS formation (see Fig. 3.24), making the overall efficiency of SSRP to be favored at higher reaction temperatures. It is obvious that the presence of the E-alumina catalyst changes the relative progress of the H₂S+SO₂ reaction and the COS formation, thus making lower temperatures more favorable for SSRP.

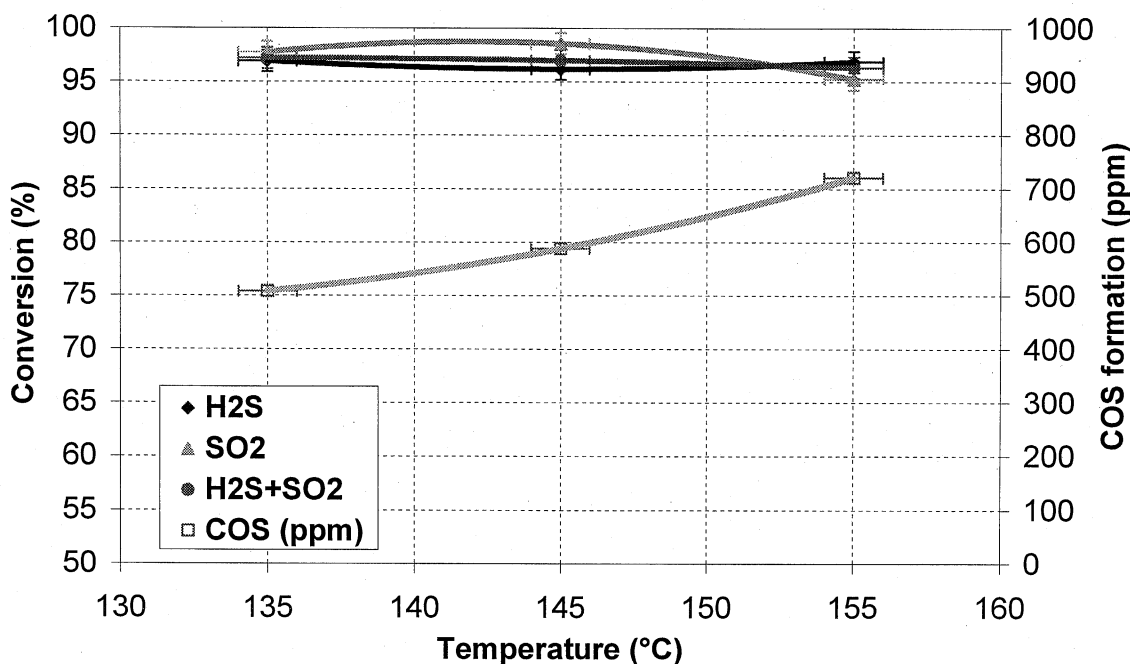


Figure 3.31. Effect of reaction temperature on sulfur removal activity and COS formation for SSRP on E-alumina + Molten Sulfur; P: 300 psig; H₂S: 8760 ppm; SO₂: 4400 ppm; steam: 18.2%; F: 1.1 SLPM

The effect of steam addition was examined at 135°C and 300 psig by adding 0.2 SLPM steam to a flow of SO₂+H₂S-containing syngas of 0.9 SLPM, thus making the total feed flow 1.1 SLPM and the steam inlet concentration from 0% to 18.2%. The results of the steam addition on sulfur removal activity and COS formation are given in Table 3.17. The addition of steam resulted in a measurable increase in sulfur removal activity (H₂S+SO₂ conversion from ca. 94% to ca. 95.5%), and a decrease in COS formation from ca. 450 ppm to ca. 405 ppm. The observed decrease in COS formation was most likely the result of the corresponding increase in total feed flow along with the addition of steam.

Table 3.17. Effect of steam addition on sulfur removal activity and COS formation, for SSRP on E-alumina + Molten Sulfur; T: 135°C; P: 300 psig; H₂S: 8760 ppm; SO₂: 4700 ppm; F: 0.9-1.1 SLPM

Steam (%)	Conversion (%)			COS formation (ppmv)
	H ₂ S	SO ₂	H ₂ S+SO ₂	
0 (steam absent)	98.8	85.5	94.2	450
18.2 (steam added)	98.3	90.2	95.5	405

Continuing in the same run, after the addition of steam the feed flow of the SO₂ and H₂S-containing syngas streams was doubled (from 0.9 SLPM to 1.8 SLPM), thus making the total feed flow increase from 1.1 SLPM to 2.0 SLPM. The corresponding steam inlet concentration was decreased from 18.2% down to 10% by this increase in feed flow. The effect of this flow increase on sulfur removal activity and COS formation are given in Table 3.18 (the first row of which is the same as the last one of Table 3.17). As expected, an increase in the total feed flow led to a decrease in sulfur removal activity (H₂S+SO₂ conversion from ca. 95.5% to ca. 93%) and in COS formation by almost half (from ca. 405 ppm down to ca. 215 ppm). Inspection of the results of Tables 3.17 and 3.18 indicated that the formation of COS (decreasing) was affected by the total feed flow (increasing) rather than by the steam inlet concentration (increasing and then decreasing). On the other hand, the sulfur removal activity was apparently influenced by both these two reaction parameters, in good agreement with previous observations on the importance of steam in the feed for SSRP (see Fig. 3.4).

Table 3.18. Effect of feed flow on sulfur removal activity and COS formation, for SSRP on E-alumina + Molten Sulfur; T: 135°C; P: 300 psig; H₂S: 8760 ppm; SO₂: 4700 ppm; steam: 18.2%-10.0%

Feed Flow (SLPM)	Conversion (%)			COS formation (ppmv)
	H ₂ S	SO ₂	H ₂ S+SO ₂	
1.1 (steam: 18.2%)	98.3	90.2	95.5	405
2.0 (steam: 10.0%)	97.0	85.0	92.8	215

In a new run at 135°C, 300 psig, and a total feed flow of 2 SLPM, 0.2 SLPM (i.e. 10%) of steam were fed into the reactor, followed by SO₂ feed and finally by H₂S-containing syngas feed (Procedure D). After reaching steady state, the reaction pressure was increased to 450 psig in 50 psig steps, and then decreased to 375 psig and finally to 325 psig. The effect of reaction pressure variation on sulfur removal activity and COS formation is shown in Figure 3.31. The H₂S+SO₂ conversion increased from ca. 93% to ca. 95% as a result of the increase in reaction pressure from 300 psig to 450 psig. On the other hand, the formation of COS was essentially unaffected (ca. 230-220 ppm). The total outlet sulfur-gas concentration (sum of unreacted H₂S & SO₂ and formed COS) was found to decrease with increasing pressure; thus, the overall efficiency of SSRP is favored at higher reaction pressures, as was also observed before (see Figs. 3.25 and 3.27).

The effect of reaction pressure was also examined at 135°C under the same procedure (Procedure D), but at a total feed flow of 1 SLPM (instead of 2 SLPM) and a steam inlet concentration of 18.2% (instead of 10%). The reaction pressure was increased from 300 psig to 350 and finally to 400 psig, and the results are shown in Figure 3.33. The observed trends in sulfur removal activity and COS formation are the same as those of Fig. 3.32. The absolute values for both H₂S+SO₂ conversion and outlet COS were higher than those of Fig. 3.32, due to the lower total feed flow (1 SLPM vs. 2 SLPM), the effect of which (i.e., the feed flow) has been clearly demonstrated above. It is interesting to note that the beneficial effect of pressure on the sulfur removal activity of E-alumina + Molten Sulfur appears to be more prominent at lower reaction temperatures.

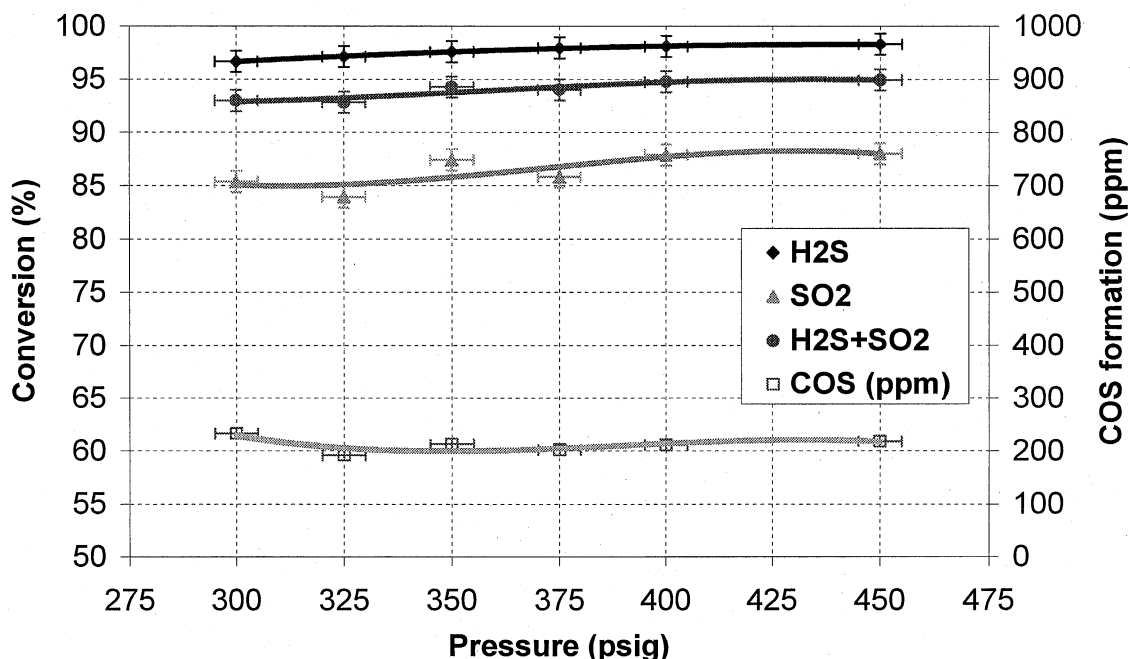


Figure 3.32. Effect of reaction pressure on sulfur removal activity and COS formation for SSRP on E-alumina + Molten Sulfur; T: 135°C; H₂S: 8700 ppm; SO₂: 4200 ppm; steam: 10%; F: 2 SLPM

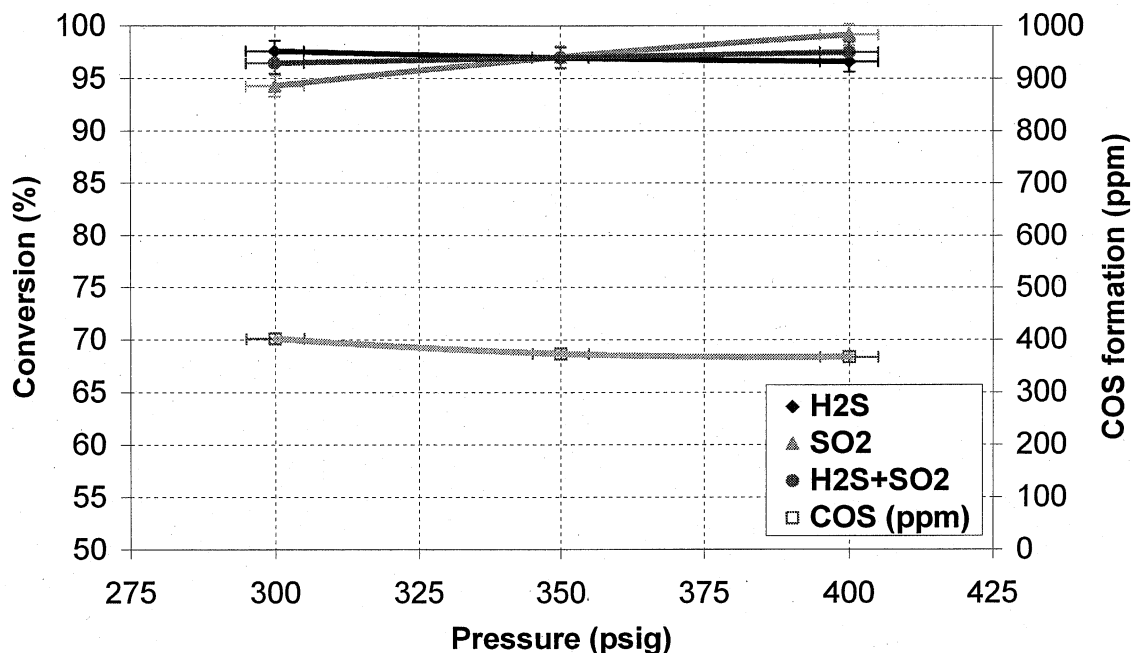


Figure 3.33. Effect of reaction pressure on sulfur removal activity and COS formation for SSRP on E-alumina + Molten Sulfur; T: 135°C; H₂S: 8400 ppm; SO₂: 4400 ppm; steam: 18.2%; F: 1 SLPM

A total of 17 runs were performed using the 45 g (50 cc) of E-alumina in Molten Sulfur. This catalyst was exposed to at least one of the two reactants (H₂S and SO₂) for ca. 145 hours, and to both reactants for ca. 100 hours. Assuming an average total feed flow of 1 SLPM (which is an underestimate) and a total inlet sulfur concentration of 12500 ppm (typically ca. 8400 ppm H₂S and 4200 ppm SO₂), then, on a time basis of 100 hours on stream:

$$1 \text{ SLPM} * 1000 \text{ scc/L} * 60 \text{ min/h} * 100 \text{ h} * 12500 \text{ ppm S} = 75000 \text{ scc S}$$

$$75000 \text{ scc S} / 22400 \text{ (scc/mol)} = 3.35 \text{ mol S, and } 3.35 \text{ mol S} * 32 \text{ (g/mol)} = 107 \text{ g S}$$

Assuming that the produced sulfur has the density of liquid sulfur at 155°C (which is ca. 1.79 g/cc), the total volume of produced sulfur during 100 hours on stream is ca. 60 cc. The pore volume of 45 g E-alumina is ca. 28 cc (see Table 3.7), i.e., less than half of the sulfur produced during this experiment. If even one fifth of the produced sulfur were to remain in the pores of E-alumina, it would have blocked almost 50% of them, causing a very rapid deactivation, which was definitely not observed in the described experiment. These calculations clearly indicate that the majority of the produced sulfur is indeed dissolved into the molten sulfur medium; thus, the SSRP can be performed in molten sulfur with high efficiency and no apparent deactivation.

The processed data of the bench-scale CSTR experiments on SSRP, from which the figures and tables presented above were generated, are included in Appendix K. The main conclusions from the process evaluation study for SSRP in the bench-scale CSTR are presented in Section 5.