**Hybrid Sulfur Recovery Process for Natural Gas Upgrading
Last Technical Report before Novation from URS Corp. to CrystaTech, Inc.**

Reporting Period Start Date: 10/1/99
Reporting Period End Date: 12/19/00

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February 2001

DOE No. DE-FC26-99FT40725

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ABSTRACT

This project was funded by the U.S. Department of Energy (DOE) to test a hybrid sulfur recovery process for natural gas upgrading. The process concept represents a low cost option for direct treatment of natural gas streams to remove H_2S in quantities equivalent to 0.2-25 metric tons (LT) of sulfur per day. This process is projected to have lower capital and operating costs than the competing technologies, amine/aqueous iron liquid redox and amine/Claus/tail gas treating, and have a smaller plant footprint, making it well suited to both on-shore and offshore applications.

CrystaSulfSM (service mark of Gas Research Institute) is a new nonaqueous sulfur recovery process that removes hydrogen sulfide (H_2S) from gas streams and converts it into elemental sulfur. CrystaSulf features high sulfur recovery similar to aqueous-iron liquid redox sulfur recovery processes, but differs from the aqueous processes in that CrystaSulf controls the location where elemental sulfur particles are formed. In the hybrid process, approximately 1/3 of the total H_2S in the natural gas is first oxidized to SO_2 at low temperatures over a heterogeneous catalyst. Low temperature oxidation is done so that the H_2S can be oxidized in the presence of methane while avoiding methane oxidation.

The project involved the development of a detailed plan for laboratory and bench scale-up application, laboratory/bench-scale catalyst testing, and demonstration of scale-up economic advantages. The bench-scale tests examined two different catalysts that are promoted modifications of TDA's patented partial oxidation catalyst used to make elemental sulfur. The experiments showed that catalyst TDA#2 is superior for use with the hybrid CrystaSulf process in that much higher yields of SO_2 can be obtained. Continued testing is planned.

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1.0 INTRODUCTION

This report serves as the last technical report before novation from URS Corporation to CrystaTech, Inc. for DOE Contract No. DE-FC26-99FT40725 entitled “Hybrid Sulfur Recovery Process for Natural Gas Upgrading.” The CrystaSulfSM (service mark of Gas Research Institute) is a new nonaqueous sulfur recovery process that removes hydrogen sulfide (H₂S) from gas streams and converts it into elemental sulfur. The hybrid CrystaSulf process uses a catalyst to first oxidize the H₂S to SO₂ at low temperatures.

The work described in this report was primarily conducted by URS Corporation’s subcontractor TDA Research, Inc., which developed the patented catalysts.

This report is divided into the following sections:

- Section 1 – Introduction
- Section 2 – Executive Summary
- Section 3 – Experimental
- Section 4 – Results and Discussion
- Section 5 – Conclusion

2.0 EXECUTIVE SUMMARY

This project was funded by the U.S. Department of Energy (DOE) to test a hybrid sulfur recovery process for natural gas upgrading. The process concept represents a low cost option for direct treatment of natural gas streams to remove H_2S , in quantities equivalent to 0.2-25 metric tons (LT) of sulfur per day. This process is projected to have lower capital and operating costs than the competing technologies, amine/aqueous iron liquid redox and amine/Claus/tail gas treating, and have a smaller plant footprint, making it well suited to both on-shore and offshore applications.

CrystaSulfSM (service mark of Gas Research Institute) is a new nonaqueous sulfur recovery process that removes hydrogen sulfide (H_2S) from gas streams and converts it into elemental sulfur. CrystaSulf features high sulfur recovery similar to aqueous-iron liquid redox sulfur recovery processes, but differs from the aqueous processes in that CrystaSulf controls the location where elemental sulfur particles are formed. In the hybrid process, approximately 1/3 of the total H_2S in the natural gas is first oxidized to SO_2 at low temperatures over a heterogeneous catalyst. Low temperature oxidation is done so that the H_2S can be oxidized in the presence of methane while avoiding methane oxidation.

The project involved the development of a detailed plan for laboratory and bench scale-up application, laboratory/bench-scale catalyst testing, and demonstration of scale-up economic advantages. The bench-scale tests examined two different catalysts that are promoted modifications of TDA's patented partial oxidation catalyst used to make elemental sulfur. The experiments showed that catalyst TDA#2 is superior for use with the hybrid CrystaSulf process in that much higher yields of SO_2 can be obtained. Continued testing is planned.

The results from this study show that the hybrid CrystaSulf process is a viable process for treating natural gas. The calculations provided in this report indicate that natural gas streams containing a fairly wide range of H_2S concentrations and pressures of interest (i.e., pressure up to 6.89 MPa (1000 psi)) could be processed by the hybrid CrystaSulf process. TDA's modified catalysts, especially TDA#2, exhibit high H_2S conversion (99+%) with essentially no slip of oxygen. Changing the formulation, temperature, and $\text{O}_2/\text{H}_2\text{S}$ ratio can be used to control SO_2 selectivity over these catalysts. Further investigation for this promising process is planned.

3.0 EXPERIMENTAL

3.1 Task 1 – Develop a Bench-Scale, Prototype Process to Remove H₂S from Low-Quality Natural Gas

This task had been essentially completed at the time the proposal was submitted on 9 August 1999, and the process was described in the proposal. The following section describes the process and the plan developed to scale-up the application.

3.2 Task 2 – Develop a Detailed Plan for Laboratory/Bench Scale-up Application of the Task 1 Process for Both On-shore and Offshore Applications; Provide a Detailed Engineering Laboratory/Bench Scale-up Application Plan

3.2.1 Background

CrystaSulfSM is a new *nonaqueous* sulfur recovery process that removes H₂S from gas streams and converts it into elemental sulfur. CrystaSulf features high sulfur recovery similar to aqueous-iron liquid redox sulfur recovery processes but differs from the aqueous processes in that CrystaSulf controls the location where elemental sulfur particles are formed. In the hybrid CrystaSulf process, approximately 1/3 of the total H₂S in the natural gas is first oxidized to SO₂ at low temperatures over a heterogeneous catalyst. Low temperature oxidation is done so that the H₂S can be oxidized in the presence of methane (CH₄) while avoiding CH₄ oxidation. In contrast, thermal oxidation would consume valuable natural gas.

The main reactions that take place over the catalyst are the direct oxidation of H₂S into SO₂ (Equation 1), the partial oxidation of H₂S into elemental sulfur (Equation 2), and the Claus equilibrium reaction between H₂S and SO₂ to produce sulfur (Equation 3). The CrystaSulf process runs the Claus reaction in the liquid phase at low temperature where the equilibrium conversion is more favorable. The objective of the TDA catalytic process is to oxidize 1/3 of the H₂S in the natural gas stream into SO₂ via Equation 1 so that the proper H₂S to SO₂ ratio is present in the natural gas when it enters the CrystaSulf process.

Equation 1. Total H₂S oxidation

Equation 2. Partial oxidation of H₂S

Equation 3. Claus equilibrium

3.2.2 Requirements of Catalytic H₂S Oxidation

The general requirements for a successful catalytic H₂S oxidation step for the hybrid CrystaSulf process are that:

1. The catalyst exhibits no activity toward methane oxidation.
2. The catalyst gives high conversions for H₂S oxidation (lowers the catalyst bed volume).
3. The catalyst exhibits high selectivity for SO₂.
4. Formation of elemental sulfur over the catalyst is acceptable as it can be removed by the CrystaSulf sorbent.
5. Any elemental sulfur that is formed directly needs to remain in the vapor phase in the H₂S oxidation reactor so that it can be captured downstream in the CrystaSulf unit.

Figure 3-1 is a process and instrumentation diagram for the apparatus used by TDA Research to test catalysts for the hybrid CrystaSulf process. The major components of the apparatus are a gas feed system, a water saturator, a preheater, a fixed bed reactor, a sulfur condenser, and analysis instruments. The sulfur vaporizer is not used in the catalyst testing discussed in this report.

Figure 3-1. Process and Instrumentation Diagram for Catalyst Test System

Nitrogen, dilute O₂ (2.77% O₂ in N₂), dilute H₂S (5% H₂S in N₂), and CH₄ are metered into the apparatus using computer controlled, electronic mass flow controllers. Water is introduced by passing one of the N₂ streams through a bubbler maintained at a temperature that gives the proper partial pressure of water to achieve the desired humidity level. The humid N₂ and the dry O₂ and H₂S streams are mixed in a heat-traced line, and preheated to reaction temperature. The preheated feed stream then passes downward over the catalyst that is held in a fixed bed reactor (Figure 3-2). The reactor is enclosed in a three-zone tube furnace. The process control computer regulates the furnace temperature.

Figure 3-2. Fixed Bed Catalytic Reactor Based on 12.7 mm (1/2-in) VCR Bulkhead Union

The H₂S is oxidized by the O₂ into SO₂ and elemental sulfur. The sulfur is collected in a sulfur condenser. The unreacted H₂S and dilution N₂ then pass through filter F1, and through the pressure control valve (PCV-1). The pressure control valve is pneumatically actuated and controlled by the process computer. The pressure upstream of the PCV is maintained at the desired system pressure, e.g., 2.15 MPa (300 psig). Downstream of the PCV, water is dropped out in two traps. The dry gas is first analyzed by gas chromatography (for H₂S and SO₂) and then passed through a paramagnetic O₂ analyzer before passing into a large carboy filled with bleach that destroys any residual H₂S and the SO₂. The scrubbed gas is sent to the laboratory fume hood system.

In previous work, TDA developed a catalyst (Cu/Nb/TiO₂) that exhibited excellent activity for the oxidation of H₂S into SO₂ without making much elemental sulfur. However, in those experiments, the H₂S concentration was 3% and the O₂ concentration was 5.5%. In the hybrid CrystaSulf process, the concentration of H₂S in the natural gas is about 2000 ppm, and to avoid O₂ slip, the O₂ concentration has to be as low as possible. Furthermore, only 1/3 of the H₂S should be oxidized. An O₂ concentration that is too high will result in either too much H₂S

oxidation or else contamination of the gas by residual O₂, neither of which is desirable. An O₂ concentration of 1000-2000 ppm was desirable for these experiments.

The bench-scale tests consisted of examining two different catalysts (referred to as TDA#1 and TDA#2) that are promoted modifications of TDA patented partial oxidation catalyst used to make elemental sulfur. The promoters significantly increase the selectivity for making SO₂. The experiments were done at temperatures between 473°K (392°F) and 523°K (482°F) with H₂S/O₂ ratios between 1 and 1.5. Experimental pressures were between 1.8 MPa (250 psig) and 2.15 MPa (300 psig), and the gas flow rates used were between 1900 and 3400 m³_{gas}/m³_{catalyst}/hr (STP values). The concentrations of H₂S and SO₂ exiting the catalyst bed were measured by gas chromatography using a flame photometric detector that is highly sensitive to sulfur compounds. The O₂ concentration in the gas exiting the reactor was measured with the on-line paramagnetic O₂ analyzer.

3.3 Task 3 – Complete Laboratory/Bench-Scale Testing of Task 2 and Demonstrate Scale-up Economic Advantages for On-shore and Offshore Applications

3.3.1 Avoiding Methane Oxidation

The first consideration before starting the catalyst tests was to determine if the CH₄ in the feed would undergo catalytic oxidation (undesirable). To determine if this might occur, TDA first performed a flammability analysis (mostly for safety considerations) and, then when assured that there was no hazard, experimentally verified that methane oxidization was not occurring over the catalyst.

H₂S is present in relatively low concentrations (Table 3-1) in the natural gas stream for which the CrystaSulf process is being initially developed. Very small amounts of O₂ are added (e.g., 1000 ppm of O₂ for a 2000 ppm H₂S feed) to oxidize 1/3 of the H₂S into SO₂ that is subsequently used as the feed to the CrystaSulf process. The low O₂ concentrations are very much below the upper flammability limits of methane or the other hydrocarbons in the natural gas, and the temperatures are low enough (473 ± 50°K) that catalytic oxidization of the hydrocarbons does not occur over the transition metal oxide catalysts used for H₂S oxidation. Thus, it is possible to convert the proper amount of H₂S into SO₂ for the CrystaSulf process by processing the entire natural gas stream continuously.

Table 3-1. Gas Composition for CrystaSulf Tests

H ₂ S	2000 ppm
CO ₂	84.46 vol%
N ₂	Negligible
CH ₄	9.95 vol%
C ₂ H ₆	2.99 vol%
C ₃ H ₈	1.99 vol%
Other	0.32 vol%
Temperature	289°K (60°F) – 316°K (110°F)
Pressure	1.8 MPa (250 psig) – 2.4 MPa (340 psig)
Humidity	Sat. at 311°K (100°F)

In the experiments to demonstrate H₂S oxidation in the presence of natural gas, TDA formulated catalysts that are selective for SO₂ production at low temperatures but do not have activity for hydrocarbon oxidation. The feed gas mixture used in the experiment contained N₂, CH₄, H₂O and H₂S in a composition similar to that of the real gas stream (Table 3-1). The required amount of O₂ (ca. 1000 ppm) was added separately. Calculations and experimental results that demonstrate that explosive mixtures cannot be formed at these low O₂ concentrations are presented in Section 4 - Results and Discussion.

4.0 RESULTS AND DISCUSSION

This section presents the results of the experiments described in Section 3.

4.1 Calculations Demonstrating the Avoidance of Methane Oxidation

These calculations demonstrate that explosive mixtures cannot be formed at the low O_2 concentrations used in the hybrid process testing. Figure 4-1 is a plot of the adiabatic temperature rise with an initial methane concentration of 10% as a function of O_2 added (balance CO_2). Mashuga and Crowl (1999) have shown that for combustion to take place in O_2/CH_4 mixtures, the adiabatic flame temperature must be 1250 K (1791°F) or higher. The O_2 concentration that gives this temperature is about 15 vol% (Figure 4-1). This is well above the O_2 concentration used to oxidize the H_2S in TDA's experiments; therefore, no thermal oxidation of CH_4 is expected to occur.

Figure 4-1. Adiabatic Reaction Temperature as a Function of Composition for Simulated Natural Gas

Figure 4-2 shows similar calculations done for a natural gas containing 85% CH_4 . As in the case of the 10% CH_4 gas, the mixture is not flammable until the O_2 concentration is substantially higher (ca 9%) than the 1000 ppm used for H_2S oxidation. Thus, thermal oxidation of methane is not expected in the hybrid CrystaSulf process for methane-rich gas streams either.

Both cases are for thermal oxidation. In TDA's case, a catalyst is present that could lower the activation energy sufficiently that methane oxidation would occur. The only way to determine if this occurs is experimentally.

Figure 4-2. Adiabatic Temperature Calculated Using HSC Chemistry for Windows

To verify that methane oxidation would not occur over the catalyst, TDA conducted a test where the temperature of the catalyst were varied while monitoring the reaction for O₂ consumption. Figure 4-3 shows the result for a methane light-off test done using TDA's patented partial oxidation catalyst. In that experiment, the methane concentration was 10 vol% and the O₂ concentration was 1.2%. The temperature was initially 573°K (572°F), and then ramped and held the temperature for 2 hrs at 623°K (662°F), 673°K (752°F) and 698°K (797°F). The experiment was done at ambient pressure. No O₂ consumption was observed at any temperature (Figure 4-3) indicating that no oxidation of methane was occurring.

Figure 4-3. Catalytic Methane Light-off Test

4.2 Catalytic Oxidation of H₂S to SO₂

Two promoted versions of TDA's partial oxidation catalyst, which is based on Mo, Nb, and TiO₂, were tested. In the first catalyst (designated TDA#1), a transition metal was added that is known to improve the selectivity of the catalyst for SO₂ at the expense of forming elemental sulfur. In the second catalyst (TDA#2), a different transition metal was added that is even more active for total H₂S oxidation, and as expected, more SO₂ was formed over this second catalyst.

Table 4-1 shows the range of experimental conditions. All of the experiments were done at temperatures between 473°K (392°F) and 523°K (482°F), pressures between 1.8 MPa (250 psig) and 2.15 MPa (300 psig), at space velocities (gas flow rates) between 1000 and 3400 m³_{gas}/m³_{catalyst}/hr (STP). Water vapor was added that was equivalent to the dew point pressure at a temperature of 311°K (100°F) which corresponds to P_{water} = 6.5 kPa (0.95 psi). The mole fraction of water at this partial pressure is y_{water} = 0.36% at a total pressure of 1.8 MPa (250 psig) and y_{water} = 0.3% at P_{total} = 2.15 MPa (300 psig). The inlet H₂S concentration in all cases was 2000 ppm, and the feed gas contained 10% methane. The balance of the gas was N₂.

Table 4-1. Experimental Conditions

H ₂ S	2000 ppm
O ₂	1000 - 3000 ppm
N ₂	89.5 - 89.7 vol %
CH ₄	10 vol %
Temperature	473°K - 523°K (392°F - 482°F)C
Pressure	1.8 MPa (250 psig) – 2.15 MPa (300 psig)
Humidity	Sat. at 311°K (100°F)

4.2.1 Testing of TDA#1 Catalyst

Effect of Temperature and O₂ Concentration

Figure 4-4 is a plot of the H₂S conversion, selectivity to SO₂ and selectivity to elemental sulfur for a 2² full factorial experimental design performed with the TDA#1 catalyst (a promoted version of TDA's partial oxidation catalyst). The experimental variables and responses are shown in Table 4-2. The table shows the sequence of runs in so-called standard order for clarity; in the experiments, the runs were done in random order to ensure statistical validity. The values for Table 4-2 are median values from Figure 4-4. The best selectivity to SO₂ is obtained for higher O₂ concentration and higher temperature. Importantly, the results shown in Table 4-2 indicate that the O₂ concentration has a larger effect on increasing the yield of SO₂ than temperature.

Figure 4-4. Test at 473°K (392°F) and 523°K (482°F) with Different H₂S/O₂ Ratios for TDA#1

Table 4-2. 2² Factorial Experiment with TDA#1 Catalyst

Temperature °K (°F)	O ₂ /H ₂ S Molar Ratio	H ₂ S Conversion (mol %)	Selectivity to SO ₂ (mol %)	Selectivity to Elemental S (mol %)
473°K (392°F)	0.7	91	5	97
523°K (482°F)	0.7	34	12	89
473°K (392°F)	1	83	13	87
523°K (482°F)	1	78	42	59

Catalyst Stability Test

Based on the quick screening of process conditions for the TDA#1 catalyst, TDA performed a longer steady state test (22 hrs) with the temperature at 523°K (482°F) and the O₂/H₂S ratio = 1. The pressure was 1.8 MPa (250 psig). The results are shown in Figure 4-5. The average H₂S conversion was approximately 65% slowly increasing to about 70%. The source of the oscillations in the H₂S conversion is not known at this time. The selectivity to elemental sulfur started out at about 70% and decreased slightly to about 60% after 22 hours. Meanwhile, the selectivity to SO₂ increased slightly from 30% to almost 40% over this time period.

TDA#1 catalyst: 22hr test at 523K (482F), 1.8 MPa (250 psig), $O_2/H_2S = 1$, GHSV = 1910 h^{-1} (at T&P)

Figure 4-5. Stability Test with TDA#1 Catalyst

Importantly, no O_2 slip was observed during the reaction. Figure 4-6 shows the O_2 concentration measured by the paramagnetic O_2 analyzer during the 22 hr test with TDA#1 catalyst. Between 2 hr and 5 hr the feed gas flow went through a heated line that bypasses the catalytic reactor to measure the initial concentration of H_2S with the gas chromatograph. During this time the O_2 analyzer read approximately 1600 ppm. The reading is lower than 2000 ppm because this is near the low end of the range of the analyzer (0 - 5%) where there is less

Oxygen content in gas exiting system.

Figure 4-6. O_2 Concentration Exiting Reactor during 22 hr Test with TDA#1 Catalyst

accuracy. When the feed gases were directed over the catalyst bed at $t = 5$ hr, the O_2 concentration abruptly fell to zero and remained there during the duration of the experiment indicating that no O_2 slip was occurring. A mass balance on O_2 indicated that all of the oxygen could be accounted for by SO_2 ; thus we also conclude that no SO_3 was produced.

The absence of SO_3 in the products is consistent with thermodynamic equilibrium calculations done using HSC Chemistry for Windows. Figure 4-7 shows the equilibrium diagram for H_2S oxidation between 423°K (302°F) and 573°K (572°F) starting with 1 mole of H_2S and 1 mole of O_2 allowing the formation of SO_2 , SO_3 , S, and H_2O . It shows that SO_3 formation is not thermodynamically favored under our experimental conditions. While catalysts affect chemical kinetics (but not thermodynamics) the fact that SO_3 formation is energetically unfavorable, suggests that SO_3 should not be observed. Taken together, these results show that modification of TDA's partial oxidation catalyst (to produce TDA#1) improves the selectivity for SO_2 as required by the hybrid CrystaSulf process.

Figure 4-7. Equilibrium Calculation for H_2S Oxidation with 1 Mole of H_2S and O_2/H_2S Ratio = 1

4.2.2 Testing of TDA#2 Catalyst

The TDA#1 catalyst is a promoted version of TDA's patented partial oxidation catalyst that is based on Mo, Nb, and TiO_2 . In the case of TDA#1, the promoter is a transition metal oxide (TMO). While the TMO added to produce the TDA#1 catalyst improved SO_2 selectivity, a higher SO_2 yield was desired. Therefore, the testing included a second TMO promoted version of the partial oxidation catalyst (TDA#2) using a TMO that was expected to have greater total oxidation activity than did the TMO used to formulate the TDA#1 catalyst.

Figure 4-8 shows a 20-hour stability test done with a catalyst that used the second transition metal oxide promoter (TDA#2 catalyst). This test involved increasing the space velocity to $GHSV = 3350 \text{ m}^3_{\text{gas}}/\text{m}^3_{\text{catalyst}}/\text{hr}$ to determine if acceptable activity and selectivity

could be obtained at an increased flow rate. Increasing the flow rate is equivalent to decreasing the amount of catalyst (smaller reactor) or increasing the throughput for a fixed reactor size.

The first conditions were $P = 2.15 \text{ MPa}$ (300 psig), $T = 523^\circ\text{K}$ (482°F), $\text{GHSV} = 3350 \text{ m}^3_{\text{gas}}/\text{m}^3_{\text{catalyst}}/\text{hr}$, $[\text{H}_2\text{S}]_{\text{inlet}} = 2000 \text{ ppm}$, and $\text{O}_2/\text{H}_2\text{S} = 1.5$. At this O_2 concentration (3000 ppm), the H_2S conversion was complete (100%) and the selectivity to SO_2 was 92%. The selectivity to elemental sulfur was 8%. Again no O_2 slip was observed, and the oxygen mass balance indicated that no SO_3 formed. When the O_2 concentration was reduced to 2000 ppm ($\text{O}_2/\text{H}_2\text{S} = 1$), the selectivity to SO_2 decreased to about 70% while the selectivity to elemental sulfur increased to 30%. Meanwhile, the H_2S conversion dropped slightly to about 97%. Thus, it was concluded that the best performance obtained for the TDA#2 catalyst was at $T = 523^\circ\text{K}$ (482°F) and $\text{O}_2/\text{H}_2\text{S} = 1.5$. As before (TDA#1) the O_2 concentration had a larger effect on SO_2 selectivity than temperature.

Figure 4-8. 20-Hour Stability Test with TDA#2 Catalyst

Comparing the results for TDA#1 and TDA#2 catalysts suggests that TDA#2 is superior for use with the hybrid CrystaSulf process because higher yields of SO_2 can be obtained (as much as 70 mol%). Testing of additional catalysts is currently underway where the promoters used in TDA#1 and TDA#2 are separately supported on an inert support material (silica) to determine if there is an important interaction between the transition metal oxide promoters and the partial oxidation catalyst to which they were added, or whether the promoters are acting alone to improve the selectivity for SO_2 .

4.2.3 Effect of Operation Conditions on Catalyst Performance

These tests show that by changing the catalyst formulation with different transition metal oxide promoters and by changing the temperature and O_2 concentration, both high H_2S conversion and high selectivity for SO_2 can be achieved. Thus, these parameters can be adjusted

to achieve the SO₂ and sulfur selectivities necessary to fit the process requirements for a given application.

4.3 Sulfur Dew Point

In order for the hybrid CrystaSulf process to use a fixed bed reactor upstream, it is necessary to operate the catalytic reactor in a pressure and temperature regime where any elemental sulfur formed in the reaction will not condense in the catalyst bed (thereby fouling the catalyst). By keeping elemental sulfur in the vapor phase, it can be captured downstream in the CrystaSulf unit. The experiments show that for the best catalyst to date, the best operating temperature is 523°K (482°F). Thus, the dew point pressure for sulfur determines the maximum allowable sulfur selectivity at 523°K (482°F), which in turn, places an upper limit on the process pressure.

Figure 4-9 shows sulfur vapor-liquid-equilibrium calculations done at 523°K (482°F) for 2000 ppm of S vapor. For this concentration of sulfur vapor, condensation would start at a pressure of 7.1 MPa (70 bar, 1030 psia). For the TDA#2 catalyst the best conditions were O₂/H₂S = 1.5 and T = 250°C. Under these conditions the selectivity for sulfur was 30% and the selectivity for SO₂ was 70%. Assuming that the pressure only affects the sulfur dew point (which would need to be verified experimentally), then the maximum allowable concentration of H₂S in a natural gas stream would be 6666 ppm. These pressures and concentrations are somewhat approximate because the calculations do not include corrections for non-ideal gas behavior; however, the calculations show that natural gas streams containing a fairly wide range of H₂S concentrations (0 – 6666 ppm) and pressures (up to 7.1 MPa (70 bar, 1030 psi)) could be processed with the hybrid CrystaSulf process.

Figure 4-9. Sulfur VLE at T = 523°K (482°F) as a Function of Pressure

5.0 CONCLUSION

5.1 Summary

The results from this study show that the hybrid CrystaSulf process is a viable process for treating natural gas. The calculations provided in this report indicate that natural gas streams containing a fairly wide range of H₂S concentrations and pressures of interest (i.e., pressure up to 6.9 MPa (1000 psi)) could be processed by the hybrid CrystaSulf process. TDA's modified catalysts, especially TDA#2, exhibit high H₂S conversion (99+%) and high selectivity for SO₂ with no oxygen slip. Furthermore, by changing the temperature and O₂/H₂S ratio, the selectivity for SO₂ can be controlled.

5.2 Planned Activities

Further investigation is planned, including the following activities:

- **Further Parametric Studies** – Statistical experimental design methods will be used to develop an empirical model of catalyst performance (Montgomery 1978). In particular, the combinations of full and fractional factorial designs can be used to develop quantitative equations that predict H₂S conversion, SO₂ selectivity and sulfur selectivity, as a functions of temperature, O₂/H₂S ratio, space velocity, system pressure, humidity level, promoter concentration, and other variables of interest. This approach will be used to optimize the catalyst formulation and process conditions.
- **Pellet Formation** – Once the best pellet composition has been determined, a pelletized form will be fabricated by Norton Chemical Products.
- **Durability Tests** – Using TDA's "pellet reactor," the pelletized catalyst will be tested for lifetime/durability. TDA's reactor is specifically designed to test catalysts in the final form (e.g., 3.18 mm (1/8 in) to 6.35 mm (1/4 inch) pellets) used in the actual chemical process. This testing will ensure that no unforeseen variations in catalyst performance are introduced when the catalyst is manufactured in its final physical form.

6.0 REFERENCES

- Mashuga, C.V. and Crowl, D.A. (1999). "Flammability Zone Prediction Using Calculated Adiabatic Flame Temperatures," *Process Safety Progress*, 18(3), 127.
- Montgomery, D.C (1976). *Design and Analysis of Experiments*, Wiley Publishing Company.