

**Hybrid Sulfur Recovery Process for Natural Gas Upgrading
Final Report**

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ABSTRACT

This final report describes the objectives, technical approach, results and conclusions for a project funded by the U.S. Department of Energy to test a hybrid sulfur recovery process for natural gas upgrading. The process concept is a configuration of CrystaTech, Inc.'s CrystaSulf[®] process which utilizes a direct oxidation catalyst upstream of the absorber tower to oxidize a portion of the inlet hydrogen sulfide (H₂S) to sulfur dioxide (SO₂) and elemental sulfur. This hybrid configuration of CrystaSulf has been named CrystaSulf-DO and represents a low-cost option for direct treatment of natural gas streams to remove H₂S in quantities equivalent to 0.2-25 metric tons (LT) of sulfur per day and more. This hybrid 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 onshore and offshore applications.

CrystaSulf is a nonaqueous sulfur recovery process that removes H₂S from gas streams and converts it to elemental sulfur. In CrystaSulf, H₂S in the inlet gas is reacted with SO₂ to make elemental sulfur according to the liquid phase Claus reaction: $2\text{H}_2\text{S} + \text{SO}_2 \rightarrow 2\text{H}_2\text{O} + 3\text{S}$. The SO₂ for the reaction can be supplied from external sources by purchasing liquid SO₂ and injecting it into the CrystaSulf solution, or produced internally by converting a portion of the inlet gas H₂S to SO₂ or by burning a portion of the sulfur produced to make SO₂. 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, the needed SO₂ is produced by placing a bed of direct oxidation catalyst in the inlet gas stream to oxidize a portion of the inlet H₂S. Oxidation catalysts may also produce some elemental sulfur under these conditions, which can be removed and recovered prior to the CrystaSulf absorber.

The CrystaSulf-DO process can utilize direct oxidation catalyst from many sources. Numerous direct oxidation catalysts are available from many suppliers worldwide. They have been used for H₂S oxidation to sulfur and/or SO₂ for decades. It was believed at the outset of the project that TDA Research, Inc., a subcontractor, could develop a direct oxidation catalyst that would offer advantages over other commercially available catalysts for this CrystaSulf-DO process application. This project involved the development of several of TDA's candidate proprietary direct oxidation catalysts through laboratory bench-scale testing. These catalysts were shown to be effective for conversion of H₂S to SO₂ and to elemental sulfur under certain operating conditions. One of these catalysts was subsequently tested on a commercial gas stream in a bench-scale reactor at CrystaTech's pilot plant site in west Texas with good results.

However, commercial developments have precluded the use of TDA catalysts in the CrystaSulf-DO process. Nonetheless, this project has advanced direct oxidation catalyst technology for H₂S control in energy industries and led to several viable paths to commercialization. TDA is commercializing the use of its direct oxidation catalyst technology in conjunction with the SulfaTreat[®] solid scavenger for natural gas applications and in conjunction with ConocoPhillips and DOE for gasification applications using ConocoPhillips

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gasification technology. CrystaTech is commercializing its CrystaSulf-DO process in conjunction with Gas Technology Institute for natural gas applications (using direct oxidation catalysts from other commercial sources) and in conjunction with ChevronTexaco and DOE for gasification applications using ChevronTexaco's gasification technology.

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1.0 INTRODUCTION

This final report describes the objectives, technical approach, results and conclusions for a project funded by the U.S. Department of Energy to test a hybrid sulfur recovery process for natural gas upgrading. This report is the final report for DOE Contract No. DE-FC26-99FT40725 entitled “Hybrid Sulfur Recovery Process for Natural Gas Upgrading” for the period following novation of the project from URS Corporation to CrystaTech, Inc., *i.e.*, January 1, 2001 to June 30, 2004. The work described in this report was conducted by CrystaTech and by its subcontractor, TDA Research, Inc., which developed proprietary catalysts under this project. Results of efforts prior to the novation are documented in “Hybrid Sulfur Recovery Process for Natural Gas Upgrading, Last Technical Report before Novation from URS Corp. to CrystaTech, Inc.” report dated February 2001, Report No. 5C26-99FT40725-01 and quarterly reports through December 2000.

2.0 EXECUTIVE SUMMARY

The hybrid sulfur recovery process concept is a configuration of CrystaTech, Inc.'s CrystaSulf[®] process which utilizes a direct oxidation catalyst in the CrystaSulf process upstream of the absorber tower to oxidize a portion of the inlet hydrogen sulfide (H₂S) to sulfur dioxide (SO₂) and elemental sulfur to improve overall process economics. This hybrid configuration of CrystaSulf has been named CrystaSulf-DO and represents a low-cost option for direct treatment of natural gas streams to remove H₂S in quantities equivalent to 0.2-25 metric tons (LT) of sulfur per day (TPD) and more. 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 onshore and offshore applications.

The objective of the project was to demonstrate this hybrid process concept for upgrading low-quality, sour natural gas to pipeline quality. This effort targeted the removal of H₂S from onshore and offshore low quality natural gas and associated gas reservoirs, including coal beds and landfills. A cost-shared, teaming approach was employed, using existing equipment wherever possible; to develop innovative catalysts for the hybrid process and to demonstrate the process at a pilot scale with one or more of those catalysts. Radian International (later URS Corporation), the Gas Research Institute (later Gas Technology Institute (GTI)), CrystaTech, Inc.; and TDA Research, Inc. (subcontractor) supplied the personnel, facilities, equipment, and materials for the project. Shell Oil Company (later Altura Ltd. and then Occidental Permian Ltd.), owner and operator of the DUCRP facility in Denver City, Texas, allowed the use of its facility for testing of oxidation catalysts on its high-pressure commercial gas stream. The gas stream is recovered gas from a CO₂ flood for enhanced oil recovery (EOR).

CrystaSulf is a nonaqueous sulfur recovery process that removes H₂S from gas streams and converts it to elemental sulfur. In CrystaSulf, H₂S in the inlet gas is reacted with SO₂ to make elemental sulfur according to the liquid phase Claus reaction: $2\text{H}_2\text{S} + \text{SO}_2 \rightarrow 2\text{H}_2\text{O} + 3\text{S}$. The SO₂ for the reaction can be supplied from external sources by purchasing liquid SO₂ and injecting it into the CrystaSulf solution, or produced internally by converting a portion of the inlet gas H₂S to SO₂ or by burning a portion of the sulfur produced to make SO₂. 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, the needed SO₂ is produced by placing a bed of direct oxidation catalyst in the inlet gas stream to oxidize a portion of the inlet H₂S. Oxidation catalysts may also produce some elemental sulfur under these conditions, which can be removed and recovered prior to the gas stream entering the CrystaSulf absorber.

The CrystaSulf-DO process can utilize direct oxidation catalyst from many sources. Numerous direct oxidation catalysts are available from many suppliers worldwide. They have been used for H₂S oxidation to sulfur and/or SO₂ for decades. It was believed at the outset of the project that TDA Research, Inc., a subcontractor, could develop a direct oxidation catalyst that would offer advantages over other commercially available catalysts for this CrystaSulf-DO

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process application. This project involved the development of several of TDA's candidate proprietary direct oxidation catalysts through laboratory bench-scale testing. These catalysts were shown to be effective for conversion of H₂S to SO₂ and to elemental sulfur under the conditions needed for the CrystaSulf-DO process. TDA's modified catalysts exhibit high H₂S conversion (99+%) with essentially no slip of oxygen. Changing the formulation, temperature, and oxygen (O₂)/H₂S ratio can be used to control selectivity to produce SO₂ over these catalysts. One of these catalysts was subsequently tested on a commercial gas stream in a bench-scale reactor at CrystaTech's pilot plant site in west Texas with good results.

The economic assessments presented in this report show that the hybrid CrystaSulf process does offer significant cost savings for desulfurizing sour natural gas. The analysis shows that for desulfurizing gas high pressure natural gas wells that while CrystaSulf without direct oxidation catalyst offers savings for plants in the 1-20 TPD sulfur range, CrystaSulf-DO offers much greater savings in that range and extends the range to plant sizes over 100 TPD. Cost analyses for ChevronTexaco and for DOE related to gasification applications show that CrystaSulf-DO offers significant cost savings and other benefits for coal gasification/IGCC applications.

The original intent of this project was for TDA to develop proprietary catalysts specifically targeted to the CrystaSulf-DO process and then to test them under this project in conjunction with the CrystaSulf pilot unit in Denver City, Texas. However, incorporating a particular catalyst within CrystaSulf-DO involves both technical/performance considerations and economic considerations. Unfortunately, after more than two years of negotiations and despite the efforts of the DOE Project Officer to resolve the issues, CrystaTech and TDA could not reach agreement on license terms. Simply stated, the price that TDA required for use of their catalyst was so high that CrystaTech deemed it an unreasonable burden on the CrystaSulf-DO technology and its chances for successful commercialization. As a result, CrystaTech and TDA began proceeding down separate commercial paths, precluding the possibility of demonstrating CrystaSulf-DO with TDA catalysts under this project as originally planned.

Nonetheless, this project did demonstrate that oxidation catalysts can be successfully applied in the process conditions required for use within CrystaSulf-DO. Further, this project resulted in the development of several specific oxidation catalysts by TDA. During the course of the project, TDA submitted an invention disclosure to DOE in the form of an interim Patent Certification form and corresponding Patent Application. CrystaTech intellectual property regarding the use of oxidation catalysts in the CrystaSulf process is covered in U.S. patent 6,416,729 and was not an invention of this project.

Several technology commercialization initiatives are currently underway which have benefited from DOE's support of this research into direct oxidation catalysts for H₂S oxidation. TDA is commercializing the use of its direct oxidation catalyst technology in conjunction with the SulfaTreat solid scavenger for natural gas applications. TDA has signed an exclusive agreement with M-I Swaco (parent company of SulfaTreat) for use of TDA catalysts in natural gas applications. Further, TDA entered into agreements with Global Energy (since acquired by ConocoPhillips) and DOE regarding testing of TDA's direct oxidation catalysts for gasification applications using ConocoPhillips gasification technology.

On a separate path, CrystaTech is commercializing its CrystaSulf-DO process for both natural gas and coal gasification applications. CrystaTech is working with GTI, a shareholder of CrystaTech, for use of CrystaSulf-DO for natural gas applications. GTI will conduct bench-scale tests of the industry standard direct oxidation catalyst, Axens CRS 31, to determine if it is suitable for use with CrystaSulf-DO for natural gas applications. CRS 31 is supplied worldwide for sulfur conversion. It was the original direct oxidation catalyst. Patents have expired and it is available at for only a few dollars per pound. Separately, CrystaTech has signed agreements with ChevronTexaco and DOE to evaluate catalysts for use in CrystaSulf-DO for gasification applications. ChevronTexaco's gasification technology has been purchased by GE Power Systems, who will thus be the commercialization partner in the future. For this application of CrystaSulf-DO, DOE will supply the direct oxidation catalyst and will conduct bench-scale testing at its NETL laboratories in Morgantown, West Virginia.

3.0 EXPERIMENTAL

In the original scope of work Phase I, Concept Assessment / Development / Economics of Prototype, Bench-Scale Process, was structured in three tasks. Phase II, Demonstration / Field Tests / Commercialization Plan, was conducted partially in parallel with Phase I and consisted of two additional tasks. The methods and findings presented in this report cover the work accomplished since the project novation to CrystaTech on January 1, 2001. However, since the background for this project was developed prior to that time, some of the earlier findings appear here to provide the reader with a comprehensive view of the development and status of the hybrid CrystaSulf sulfur recovery process. Below are a description of the hybrid process and a description of each task and a list of the activities (subtasks) within each. The specific results are given in Section 4.

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

The CrystaSulf hybrid process concept and its state of development were documented previously in a feasibility concept report, including an initial economic assessment. No new work under this task was included in the novated project. This task had been essentially completed at the time the proposal for this 40725 project was submitted in August 1999. The process was described in the proposal. Provided below is an overview of the hybrid process, its process chemistry, and catalyst requirements, which form the basis for this project's experimental approach.

3.1.1 Overview of the Hybrid CrystaSulf Process

CrystaSulf is a nonaqueous sulfur recovery process that removes H₂S from gas streams and converts it to elemental sulfur. CrystaSulf features high sulfur recovery similar to aqueous-iron liquid redox sulfur recovery processes, but differs from aqueous processes in that CrystaSulf controls the location where elemental sulfur particles are formed. CrystaSulf utilizes liquid Claus reactions and requires a feed gas with an H₂S to SO₂ ratio of 2:1. When using CrystaSulf, H₂S does not have to first be separated from the gas stream for sulfur recovery.

The hybrid CrystaSulf process incorporates catalytic oxidation of a portion of the total H₂S in the natural gas feed stream to generate the SO₂ required for the CrystaSulf process. This eliminates the need for sulfur burning or shipping liquid SO₂ to the plant. Depending on the catalyst and the conditions in the catalyst bed (primarily oxygen stoichiometry) a portion of the inlet H₂S will typically be converted to sulfur. To achieve the desired conversions to SO₂ and sulfur, a portion or all of the total flow of natural gas to be processed is passed through a catalyst in a fixed-bed catalytic reactor where the H₂S is oxidized to sulfur and SO₂ at low temperatures over the oxidation catalyst. Low temperatures are key so that the H₂S can be oxidized directly in the natural gas stream while avoiding hydrocarbon oxidation and fouling due to coking from other hydrocarbon contaminants. However, the temperature must be high enough so that any elemental sulfur formed does not condense on the catalyst and plug the reactor. In contrast, thermal oxidation of hydrocarbons at high temperatures would consume valuable natural gas. This makes the hybrid process especially attractive for directly treating natural gas and other

streams where the catalyst should only be reactive toward H₂S. Catalytic sulfur and SO₂ production is operated at line pressure (up to about 8 MPa, or 1200 psig) with the catalyst typically at 180 to 280°C (356 to 536°F). The sulfur produced by the catalytic converter is condensed and collected, and the product gas from the reactor (which now contains SO₂) is blended back into the main flow stream. By controlling the splitting ratio to the catalytic reactor, the blended stream will contain the correct proportions of H₂S and SO₂ for removal of the remaining sulfur using the CrystaSulf process (i.e., 2 to 1). A flow diagram of the hybrid CrystaSulf process is shown in Figure 3-1.

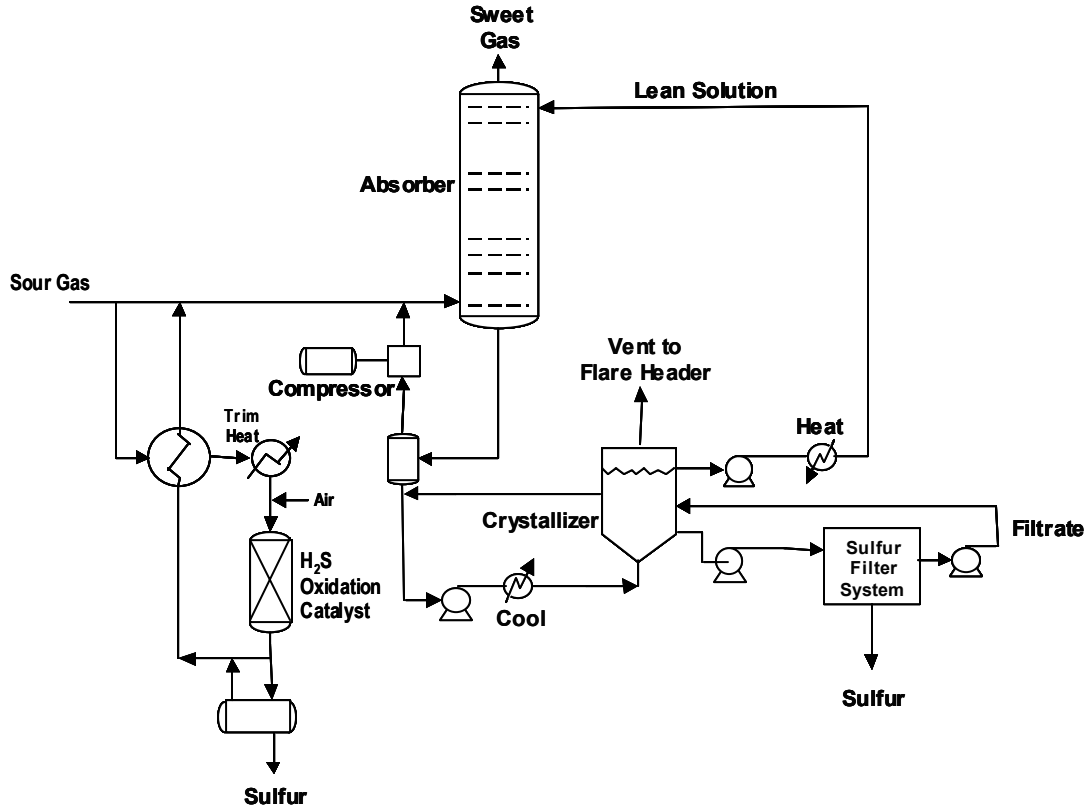


Figure 3-1. Flow Diagram for Hybrid CrystaSulf Process

The hybrid CrystaSulf process is very flexible and can be operated in a range of modes catering to the sulfur removal needs of the energy producing facility. The two operating modes shown below illustrate the extend of the range:

1. Divert 1/3 of the total gas stream to the catalyst bed where 95% of the H₂S in the diverted stream is converted to SO₂ and H₂O, and the remaining 5% of the H₂S is converted to elemental sulfur and H₂O.
2. Pass the entire gas stream through the catalyst bed where the majority of the H₂S is converted to elemental sulfur (e.g., 80-95% of all H₂S in the stream converted to sulfur), and 1/3 of the remaining H₂S is converted to SO₂ to fulfill the SO₂ requirement of the liquid Claus reaction in the CrystaSulf process.

For applications with smaller sulfur loadings (e.g., those with 1-5 TPD sulfur in the inlet gas), mode 1 is the most economic approach. For large sulfur removal needs, 5-200 TPD, mode 2 is the most economic.

The field test program for this project was performed at Oxy Permian's DUCRP facility in Denver City, Texas, where the bulk of the gas treated is recovered from a CO₂ flood for enhanced oil recovery (EOR). Desulfurizing this gas with the hybrid CrystaSulf process would provide a lower cost method of reusing the CO₂ for additional EOR. The composition of this methane-poor / CO₂-rich natural gas stream is shown in Table 3-1. For comparison, the composition of a typical methane-rich / CO₂-poor natural gas is shown in Table 3-2.

Table 3-1. Methane-Poor Feed Gas

Parameter	Value
H ₂ S	2000 ppmv
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	16-43°C (60–110°F)
Pressure	1.7-2.3 MPa (250–340 psig)
Humidity	Sat'd. at 38° (100°F)

Table 3-2. Methane-Rich Feed Gas

Parameter	Value
Temperature	32-38°C (85-100°F)
Pressure	6.6-6.9 MPa (950–1000 psig)
Hydrogen sulfide (H ₂ S)	0.0019 mol%
Nitrogen (N ₂)	0.3 mol%
Carbon Dioxide (CO ₂)	0.54 mol%
Methane (CH ₄)	95.3 mol%
Ethane (C ₂ H ₆)	1.84 mol%
Propane (C ₃ H ₈)	0.72 mol%
Butanes (C ₄ H ₁₀)	0.61 mol%
Pentanes (C ₅ H ₁₂)	0.315 mol%
Hexanes (C ₆ H ₁₄)	0.23 mol%
Benzene (C ₆ H ₆)	0.07 mol%
Toluene (C ₆ H ₅ CH ₃)	0.026 mol%
Xylenes (C ₆ H ₄ (CH ₃) ₂)	0.01 mol%
Total BTX	1060 ppmv

3.1.2 Chemistry of the Hybrid CrystaSulf Process

A primary objective of the catalytic process is to oxidize a portion of the H₂S in the natural gas stream to SO₂ via Equation 3-1 so that the proper H₂S to SO₂ ratio is present in the natural gas for the liquid-phase Claus reaction which occurs in the CrystaSulf process solution. Another objective is the direct oxidation of H₂S to elemental sulfur by the catalyst itself. The

main reactions that can take place over the catalyst in the fixed-bed oxidation reactor are: Equation 3-1, the oxidation of H₂S into SO₂; Equation 3-2, the direct oxidation of H₂S into elemental sulfur; and Equation 3-3, the Claus reaction between H₂S and SO₂ to produce elemental sulfur. Because the sulfur formed by the liquid-phase Claus reaction is dissolved in the CrystaSulf solvent, sulfur plugging of high-pressure equipment cannot occur. This is in contrast to existing aqueous-phase H₂S oxidation processes where the sulfur is never soluble and can plug the process equipment.



The exact amount of gas sent to the catalytic reactor depends on how much elemental sulfur is formed by direct oxidation of H₂S. As the amount of elemental sulfur recovered in the catalytic step increases, the proportion of gas flow sent to the reactor must be increased in order to generate enough SO₂ for the liquid-phase Claus reaction. However, as more sulfur is recovered by the catalytic reactor, the sulfur load on the CrystaSulf process is reduced. Thus, there is a trade-off between the capital and operating costs of the fixed-bed reactor and the absorber. The optimum operating conditions depend on the activity of the solid catalyst and its selectivities for conversion of H₂S to SO₂ and/or elemental sulfur.

3.1.3 Requirements of Catalyst Used to Oxidize H₂S to SO₂

For proper catalytic SO₂ production, the catalyst should meet the following criteria:

1. Exhibit no activity for hydrocarbon oxidation;
2. Give high conversions for H₂S oxidation (this lowers the catalyst bed volume);
3. Exhibit high selectivity for producing SO₂;
4. Exhibit selectivity for producing sulfur;
5. Be stable at temperatures above the sulfur dew point to assure that all elemental sulfur formed remains in the vapor phase in the reactor.

3.2 Task 2. Develop a Detailed Plan for Lab Testing of the Task 1 Process for Both Onshore and Offshore Applications

A detailed plan for laboratory / bench scale-up application of the hybrid process for onshore and offshore applications was developed and documented in a detailed engineering plan. This part of the testing included only the upstream catalytic oxidation portion of the hybrid process since the CrystaSulf process has already been demonstrated successfully at the pilot scale. No new work under this task was included in the novated project.

3.3 Task 3. Complete Lab Testing of Task 2 and Demonstrate Scale-up Economic Advantages for Onshore and Offshore Applications

Laboratory bench-scale testing of the upstream catalytic portion of the hybrid process was completed using an existing bench-scale catalyst test unit at the research facilities of TDA Research, Inc. and at the CrystaSulf pilot plant site. The bulk of the work completed during this project took place within the framework of this task. The methods and rationale employed for the activities listed below are described in this section. Note that presentation and discussion of all results are in Section 4 of this report.

- Testing of TDA catalyst #3
- Comparison of TDA catalysts #1, #2, and #3
- Oxidation of C₂₊ hydrocarbons
- Effect of BTX in the feed on catalyst performance
- Effect of knockout drum condensate
- Bench unit testing of catalytic oxidation at the pilot plant
- Economic assessment of scale-up to onshore and offshore locations

3.3.1 Catalyst Testing Equipment and General Methodology

Previous results from this overall project showed that the hybrid CrystaSulf process is a viable process for treating natural gas. Calculations indicated 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. Several patented catalyst formulations developed by TDA Research, Inc. were tested in TDA's research facilities in Wheatridge, Colorado. Three promoted versions of TDA's partial oxidation catalyst which is based on molybdenum, niobium, and titanium dioxide were included in the study. In the first catalyst (designated TDA #1) a transition metal was added that is known to improve the selectivity of the catalyst for producing 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. Changing the formulation, temperature, and O₂/H₂S ratio can be used to control SO₂ production selectivity over these catalysts. The results for catalysts TDA #1 and TDA #2 were reported earlier in a

quarterly prior to the novation (Srinivas, Gebhard and DeBerry, 2001), but are summarized in this document for completeness. In the current study the third catalyst (TDA #3) was investigated as described below.

Figure 3-2 is a process and instrumentation diagram for the apparatus used by TDA to test catalysts for the hybrid CrystaSulf process (Srinivas, Gebhard and DeBerry, 2001). The major components of the apparatus are a gas feed system, a water saturator, a preheater, a fixed-bed catalyst, a sulfur condenser, and analytical instruments. The sulfur vaporizer shown in the figure was not used in the catalyst testing discussed in this report.

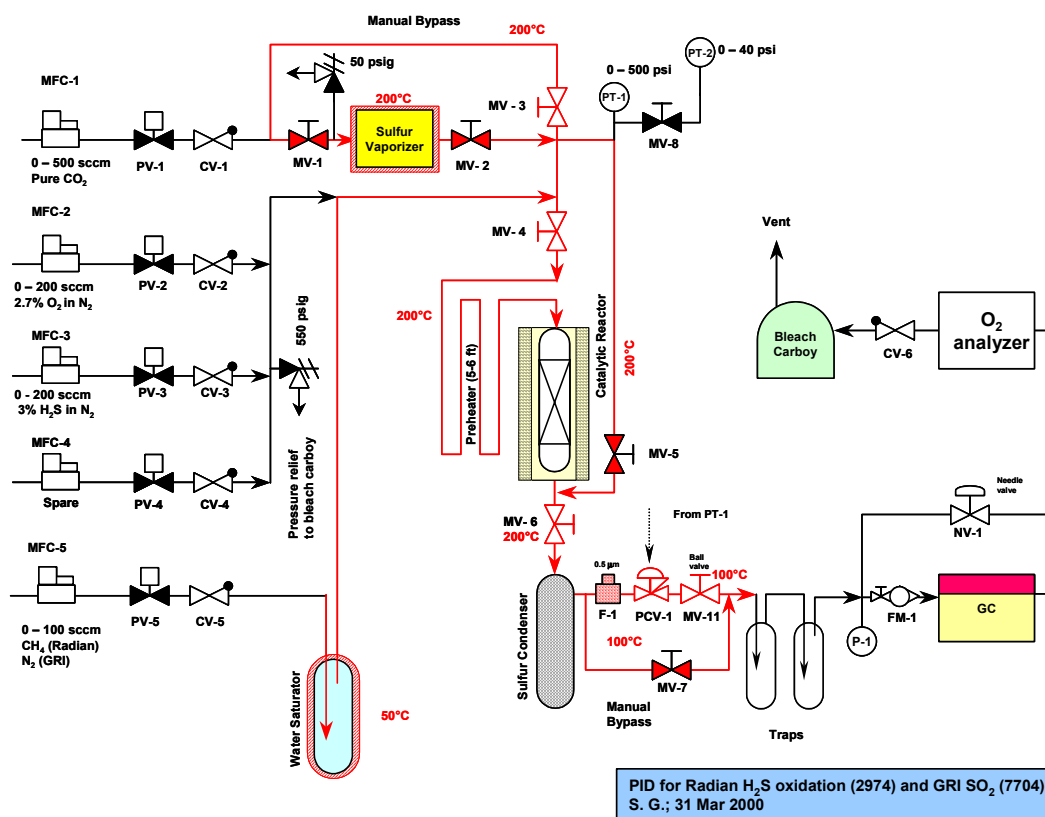


Figure 3-2. Process and Instrumentation Diagram for Catalyst Test System

Nitrogen, dilute O₂ (2.77% O₂ in N₂), dilute H₂S (5% H₂S in N₂), and CH₄ were metered into the apparatus using computer controlled, electronic mass flow controllers. Water was introduced by passing one of the nitrogen 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 were mixed in a heat-traced line, and preheated to reaction temperature. The preheated feed stream was then passed downward over the catalyst that was

held in a fixed-bed reactor (Figure 3-3). The reactor was enclosed in a three-zone tube furnace. The process control computer regulated the furnace temperature.

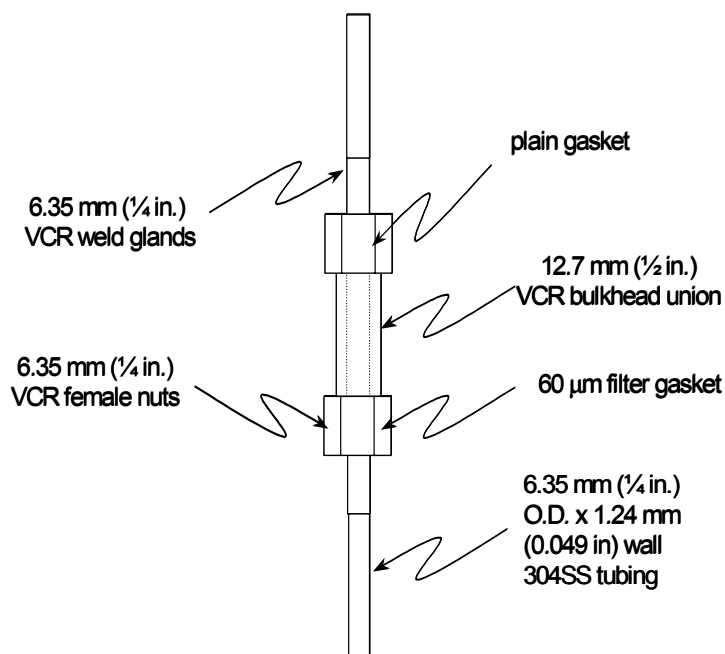


Figure 3-3. Fixed Bed Catalytic Reactor Based on 12.7 mm (1/2-in) VCR Bulkhead Union

The H_2S was oxidized by the O_2 to SO_2 and elemental sulfur, and the sulfur was collected in a sulfur condenser. The unreacted H_2S and dilution N_2 then passed through filter F1, and through the pressure control valve (PCV-1). The pressure control valve was pneumatically actuated and controlled by the process computer. The pressure upstream of the PCV was maintained at the desired system pressure, e.g., 2.07 MPa (300 psig). Downstream of the PCV, water was knocked out in two traps. The dry gas was first analyzed by gas chromatography (for H_2S and SO_2) and then passed through a paramagnetic O_2 analyzer before passing into a large carboy filled with bleach that destroyed any residual H_2S and the SO_2 .

In previous work, TDA developed a catalyst (Cu/Nb/TiO_2) that exhibited excellent activity for the oxidation of H_2S to SO_2 without making much elemental sulfur. However, in those experiments, the H_2S concentration was 3% and the O_2 concentration was 5.5%. In the hybrid CrystaSulf process, the concentration of H_2S in the natural gas is about 2000 ppmv, and to avoid O_2 slip, the O_2 concentration has to be as low as possible. Furthermore, only 1/3 of the H_2S that isn't converted to elemental sulfur should be oxidized to SO_2 . An O_2 concentration that is too high will result in either too much H_2S oxidation or else contamination of the gas by residual O_2 , neither of which is desirable. An O_2 concentration of 1000-2000 ppmv was desirable for these experiments.

Oxygen Mass Balance – Because of the experimental design, there was no way to directly measure the amount of sulfur produced during the reaction; therefore an oxygen mass

balance was relied on to check the assumptions that only two reactions are occurring (the first two equations in Figure 3-4). The results from the O₂ analyzer indicated that in all runs with TDA #3, all of the O₂ was consumed (outlet concentration of zero).

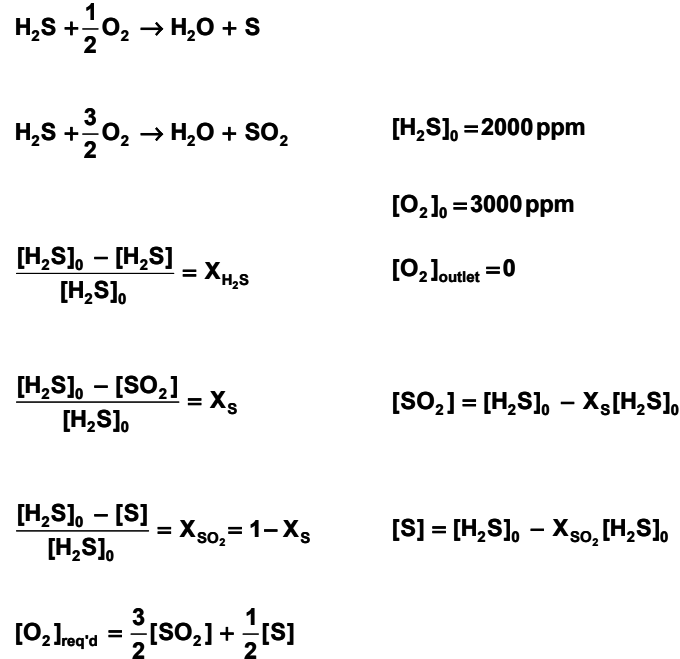


Figure 3-4. Equations for Oxygen Mass Balance Check

The concentration of sulfur dioxide was measured during the experiment using gas chromatography. From this value and the known inlet concentration of H₂S and the known H₂S conversion, the conversions to SO₂ (X_{SO₂}) and sulfur (X_S) were calculated. The unknown sulfur vapor concentration [S] was then calculated using the mass balance equations shown in Figure 3-4. Finally the amount of O₂ required was calculated. If this is close to the actual inlet concentration of oxygen, then the assumptions in the mass balance are valid and one can conclude that only SO₂ and S are formed.

As indicated in Figure 3-4, the inlet concentration of H₂S was [H₂S]₀ = 2000 ppmv, and the inlet concentration of oxygen was [O₂]₀ = 3000 ppmv. [O₂]_{req'd} in Figure 3-4 is the inlet O₂ concentration that would be required to produce all of the SO₂ and sulfur produced during the experiment. The closer this value is to the inlet O₂ concentration used (i.e., [O₂]₀ = 3000 ppmv), the better the mass balance for oxygen. The inlet concentrations of SO₂ and sulfur were zero.

3.3.2 Testing of TDA #3 Catalyst

Table 3-3 shows the experimental conditions employed for testing the TDA #3 catalyst. All of the experiments were carried out with the catalyst at a temperature of 250°C (482°F) and

the pressure equal to 2.07 MPa (300 psig). The space velocity was $3350 \text{ cm}^3_{\text{gas}}/\text{cm}^3_{\text{catalyst}}/\text{hr}$. Water vapor was added that was equivalent to the dew point pressure of water at 38°C (100°F), which is 6.6 kPa (0.96 psia). This corresponds to a mole fraction of 0.3% at 2.07 MPa (300 psig). The barometric pressure at the TDA laboratory facility located near Denver, Colorado is approximately 84 kPa (12 psia). The inlet H_2S concentration in all cases was 2000 ppmv, and the feed gas contained 10% methane. The experiments were conducted at two concentrations of oxygen, 2000 ppmv ($\text{O}_2/\text{H}_2\text{S} = 1$) and 3000 ppmv ($\text{O}_2/\text{H}_2\text{S} = 1.5$), and the balance gas was N_2 .

Table 3-3. Experimental Conditions for TDA #3 Catalyst

Parameter	Value
H_2S	2000 ppmv
O_2	2000 & 3000 ppmv
N_2	Balance
CH_4	10 vol %
Temperature	250°C (482°F)
Pressure	2.07 MPa (300 psig)
Humidity	Sat'd. at 38°C (100°F)

3.3.3 Comparison of TDA Catalysts 1, 2 and 3

The bench-scale tests consisted of examining two different catalysts (referred to as TDA #1 and TDA #2) that are promoted modifications of a TDA patented oxidation catalyst used to make elemental sulfur. The promoters significantly increase the selectivity for making SO_2 . The experiments were done at temperatures between 200°C (392°F) and 250°C (482°F) with $\text{H}_2\text{S}/\text{O}_2$ ratios between 1 and 1.5. Experimental pressures were between 1.72 MPa (250 psi) and 2.07 MPa (300 psi), and the gas flow rates used were between 1900 and 3400 $\text{m}^3_{\text{gas}}/\text{m}^3_{\text{catalyst}}/\text{hr}$ (STP values). The concentrations of H_2S and SO_2 exiting the catalyst bed were measured by gas chromatography using a flame photometric detector that is highly sensitive to sulfur compounds. The O_2 concentration in the gas exiting the reactor was measured with the on-line paramagnetic O_2 analyzer.

The results of this comparison are presented in Section 4, Results and Discussion.

3.3.4 Oxidation of C_{2+} Hydrocarbons

In all of the catalyst tests 10% methane was added to the feed. Methane is the most difficult of the hydrocarbons to oxidize since it has the highest activation energy. In real gas applications, C_2 , C_3 and possibly C_4 hydrocarbons will be present. While the concentrations of

these hydrocarbons are only a few percent each, their combustion is undesirable because this consumes oxygen and reduces the BTU value of the gas. In the earlier portion of this overall project (prior to the novation), it was verified that no methane oxidation was occurring over the catalysts at $T = 250^{\circ}\text{C}$ (482°F) and $P = 2.07\text{ MPa}$ (300 psig) (Srinivas, Gebhard and DeBerry, 2001).

The potential catalytic oxidation of any ethane and propane that might be in a feed stream was investigated through a literature search and experimentally. Based on the literature in this area, we expected that these hydrocarbons would not be oxidized to a significant extent, especially given the relatively low operating temperature of 250°C (482°F).

Since in real gas applications, higher more reactive alkanes are also likely to be present, additional tests were conducted. Hexane represents the most reactive of the C1 to C6 series of alkanes. If hexane can be shown to exhibit low reactivity under H_2S oxidation conditions and, more importantly, not change the elemental sulfur and SO_2 production selectivities, we can conclude that the C1 to C6 contaminants would not present a problem to the hybrid CrystaSulf process.

Literature Study of C_{2+} Hydrocarbon Oxidation – Several studies have examined the catalytic oxidation of C_{2+} hydrocarbons (Guliants 1999; Hernandez and Ozkan 1990; Ozkan et al. 1990; Udea et al. 1999) and while the main interest of these researchers was to develop partial oxidation catalysts for converting low cost hydrocarbons into value added chemicals (e.g., butanes into maleic anhydride), their observations provided insights as to what to expect for hydrocarbon oxidation (partial or complete) over the TDA catalysts.

The review of supported vanadia catalysts by Guliants discusses how the nature of the support is important in controlling the selectivity of vanadia catalysts for partial versus total oxidation. For example, when microcrystallites of V_2O_5 are present on the catalyst during the oxidation of butene, the selectivity shifts toward deep oxidation to yield CO_2 . In contrast, when the vanadia is highly dispersed, the selectivity to maleic anhydride is improved. The specific phase of the support and how it is prepared are less important in determining catalyst selectivity and activity than are the molecular structures of the vanadia overlayers (Guliants 1999).

This effect of monolayer dispersion is likely relevant for other oxide on oxide catalysts such as TDA's catalysts that contain MoO_3 and Nb_2O_5 supported in TiO_2 (with a promoter added for catalysts TDA #1, 2 and 3). At low loadings, MoO_3 and Nb_2O_5 tend to wet the TiO_2 surface forming thin layers. Thin layers of oxides are crystallographically quite different from the bulk oxides and thus can be expected to exhibit different catalytic activities (Kiselev and Krylov 1989). If the behavior of MoO_3 follows the same pattern as vanadia, then thin MoO_3 layers should be less active for total oxidation than bulk MoO_3 .

The TDA catalysts under investigation here for oxidation of H_2S to produce both SO_2 and sulfur are promoted versions of TDA's $\text{MoO}_3/\text{Nb}_2\text{O}_5/\text{TiO}_2$ catalyst that has been used to produce elemental sulfur in high yields by H_2S oxidation. This catalyst contains MoO_3 which is generally a good oxidation catalyst, and while relatively low hydrocarbon oxidation activity is to be expected because it is highly dispersed, the literature that discusses MoO_3 as a catalyst for the

partial/total oxidation of alkanes and alkenes is useful to examine when attempting to anticipate how the C₂+ components of natural gas will behave in the hybrid CrystaSulf process when H₂S is oxidized to sulfur and SO₂ over the TDA catalyst.

In the study by Hernandez and Ozkan (1990), the authors prepared two versions of MoO₃ by using different thermal treatments. In one case, the crystallites exhibited an abundance of exposed flat basal (100) planes of MoO₃ and in the other case; there was a higher percentage of the (010) planes exposed. The (010) planes have more coordinatively unsaturated atoms than the (100) planes. The authors then examined the oxidation of 1-butene, 1,3-butadiene, furan and maleic anhydride over these catalysts. The reaction temperatures were between 410°C (770°F) and 600°C (1112°F). They found that with the MoO₃ catalysts that had mostly (100) planes exposed, better selectivity for partial oxidation was observed. In contrast, when the catalysts had a higher fraction of MoO₃ (010) planes exposed, deeper oxidation to CO and CO₂ was found. The authors suggested that this was due to sites that break C-C bonds being present on the (010) face, and that the (100) face has a limited capability to donate oxygen to the adsorbed hydrocarbon. This would be consistent with the accepted thought in catalysis that coordinatively unsaturated sites (on any catalyst) are usually more reactive than sites that have nearer neighbors. Not infrequently, the more active sites produce undesirable side reactions.

The temperatures used in the Hernandez and Ozkan study were considerably higher than the temperature used in this study (250°C, or 482°F). Furthermore, the basal planes of (100) MoO₃ only produced partial oxidation. Thus, even if there were defect sites in the MoO₃ phase in the TDA catalysts [which would have reactivity similar to (010) surface of MoO₃], much higher temperatures appear to be required to obtain significant amounts of hydrocarbon oxidation even on these more energetic surfaces.

In support of our hypothesis that our temperatures are too low to obtain significant C₂+ oxidation over our catalysts, the work of Ozkan et al. (1990) shows that the activity of MoO₃ for the oxidation of 1-butene is modest even at a temperature of 480°C (896°F). In that work, the authors compared the activities of CdMoO₄, CdMoO₄/MoO₃, and pure MoO₃ in 1-butene oxidation and found that the overall conversion was highest with CdMoO₄ (80%) intermediate with CdMoO₄/MoO₃ (40%), and lowest with MoO₃ (10%). The catalytic activity for the deep oxidation of 1,3-butadiene to CO₂ at 480°C (896°F) was somewhat larger because the diene is more reactive, but was still only 35% with MoO₃. Again, the high temperatures and the fact that olefins are much more reactive than alkanes suggests that we will see little if any ethane or propane oxidation with our catalysts at 250°C (482°F).

Finally, the work of Ueda et al. (1999) examined the oxidative dehydrogenation of ethane to form ethylene that subsequently oxidized to acetic acid. Their catalyst was a Mo-V-M based oxide (M = Al, Fe, Cr), and as in the other work, the temperature had to be fairly high (340°C, 644°F) to achieve acceptable rates. This catalyst could also oxidize methane, but the temperature had to be 400°C (752°F), again much higher than the temperature of interest in this study 250°C (482°F). Also, containing Cr and V in significant amounts, their catalyst will be more active total oxidation compared to TDA's promoted Mo-Nb-TiO₂ catalyst.

Experimental Study of Effect of *n*-hexane on Catalyst Performance – Hexane represents the most reactive of the C1 to C6 series of alkanes. Based on literature findings for lower alkanes described above and the higher reactivity of *n*-hexane in general, tests were designed and carried out to determine if hexane exhibits low reactivity under H₂S oxidation conditions, and more importantly, does not change the elemental sulfur and SO₂ production selectivities. That would allow the conclusion to be drawn that the C1 to C6 hydrocarbons should not significantly interfere with the oxidation of H₂S to elemental sulfur and SO₂.

A series of tests were conducted with 500 ppmv *n*-hexane (C₆H₁₄) added to the feed with and without H₂S present. The catalyst temperature was 250°C (482°F) and the pressure in the reactor was 1.38 MPa (200 psig). Fresh (never exposed to H₂S) catalyst was used in this experiment, and therefore, the compounds in the catalyst were present as oxides. Results are presented in Section 4, Results and Discussion.

3.3.5 Effect of BTX Contamination on Catalyst Performance

In methane-poor gas the hydrocarbons present in addition to methane are mostly ethane and propane with minor amounts of higher hydrocarbons. As shown previously in Table 3-2, in methane-rich gas, not only are the C2 through C6 alkanes present, but there can be several percent of natural gas liquid (NGL) in addition to aromatic hydrocarbons, specifically benzene, toluene and xylenes (BTX) on the order of 1000+ ppmv. Because of the increased tendency of aromatic hydrocarbons to decompose and foul a catalyst with deposited carbon (Hughes 1984), it was important to evaluate how these hydrocarbons affect catalyst performance. Of the three, benzene is the least reactive, with toluene being significantly more reactive (Olah and Molnar 1995). For this reason we repeated the experiments that we performed with hexane using toluene to determine if BTX will be detrimental to catalyst performance and if so, to what extent.

Literature background – The catalysts used for oxidation of H₂S to produce both SO₂ and elemental sulfur are promoted versions of TDA's MoO₃/Nb₂O₅/TiO₂ catalyst that produce elemental sulfur in high yields by direct H₂S oxidation. Furthermore, Nb₂O₅ supported on TiO₂ exhibits acidic behavior that could increase the tendency for coking from BTX. Acid sites can catalyze the carbonium ion chemistry that is thought to be responsible for the polymerization that leads to coke formation (Butt and Petersen 1988).

Coke consists of polyaromatic condensed ring structures that tend to be similar to graphite in structure (Butt and Petersen 1988). Coking also appears to be more of a polymerization process than a degradation process and thus relatively low molecular weight compounds (e.g., BTX and C₄ olefins such as butadiene) can lead to significant catalyst fouling if coking occurs on the surface.

Discussion of method selected – In order to determine the effect of BTX in the feed on catalysts performance, experiments similar to those done using hexane were conducted with toluene using the TDA #2 catalyst. The aromatic ring in toluene is significantly more reactive than the benzene ring, and thus toluene testing will more realistically predict the effects of BTX in the feed. Toluene is also an excellent surrogate for BTX because it can undergo disproportionation reactions that generate benzene and xylene according to the following reaction (Hughes 1984).



Equation 3-4. Toluene Disproportionation

The TDA #2 catalyst was chosen because the promoter that gives the high selectivity for producing SO₂ and elemental sulfur is less expensive than the promoter for TDA #3 while giving identical performance.

Figure 3-5 shows the process and instrumentation diagram for the catalyst test apparatus configured for injecting toluene into the feed stream. Gases (5% H₂S in N₂, and 4% O₂ in N₂ and pure N₂) were metered into a common preheated manifold using mass flow controllers. There was a tee in this section just upstream of the reactor that was used for introducing toluene (Figure 3-6). Toluene was metered into the tee using a high-pressure liquid chromatography (HPLC) pump at 0.05 mL/min through 1.6-mm (1/16-inch) stainless steel tubing. The tubing extended into the tee via a drilled-through fitting so that the end of the 1.6-mm (1/16-inch) tube just touched the wall of the tee. The gases swept through the tee and this, in addition to the contact between the 1.6-mm (1/16-inch) tubing, ensured complete toluene vaporization.

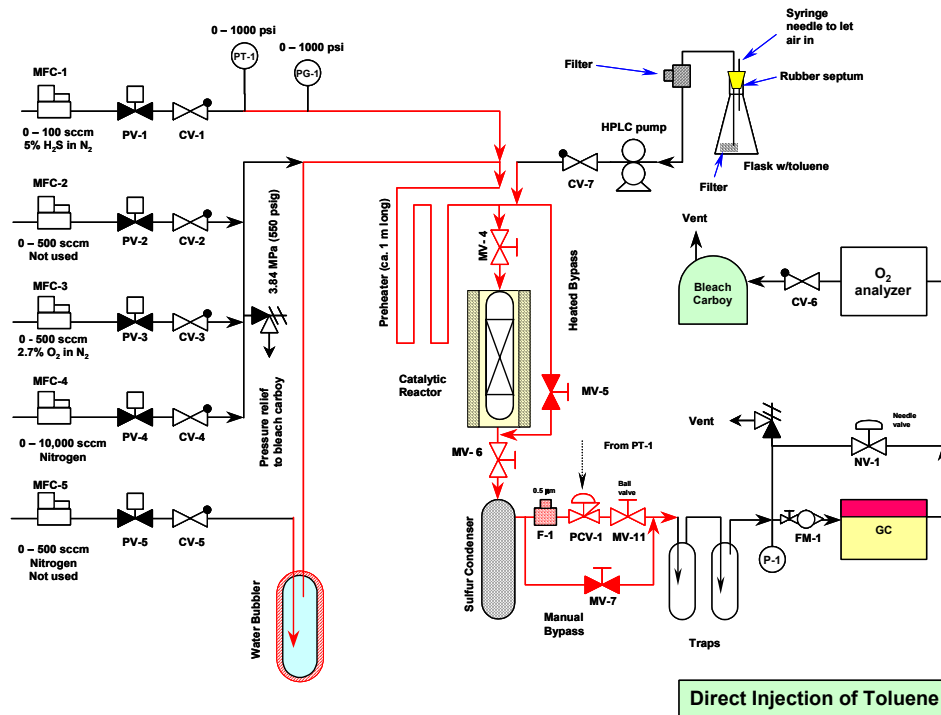


Figure 3-5. Process and Instrumentation Diagram (P&ID) for Apparatus Configured for Injecting Toluene into the Feed Stream

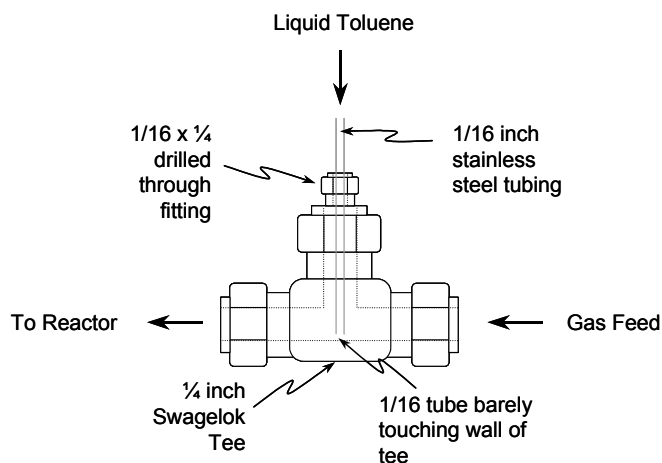


Figure 3-6. Toluene Injection Tee

After the vaporized toluene and gases were mixed, the concentrations were those shown in Table 3-4. The reactant mixture then flowed through either a reactor bypass (used to measure initial H₂S and O₂ concentrations) or through the reactor and over the catalyst bed. The reactor was charged with 4 grams of catalyst and heated to 225°C (437°F). Downstream of the reactor, a condenser (stainless pressure vessel) maintained at 70°C (158°F) was used to knock out any elemental sulfur vapor formed. Downstream of the sulfur condenser was the pressure control valve (PCV) and manual bypass. During the experiments, the manual bypass was closed and the PCV was controlled by the computer to maintain backpressure on the system. The PCV, a Research Control Valve manufactured by Badger Meter Company, was essentially a pneumatically controlled needle valve with a very small flow coefficient. Downstream of the PCV were two traps to remove water vapor. Finally the sample gas (at this point with an ambient pressure water dew point) was analyzed by GC and the paramagnetic O₂ analyzer. The main flow passed through the O₂ analyzer and a slipstream was taken for GC analysis to measure the H₂S and SO₂ concentrations.

The GC analysis of H₂S and SO₂ was done using a flame photometric detector (FPD), which gave excellent sensitivity, enabling reliable measurements of H₂S down to 5 ppmv. Water (as well as higher concentrations of H₂S and SO₂) was detected using a standard thermal conductivity detector (TCD). The GC column was operated isothermally at 20°C (68°F) to avoid any Claus reaction between the SO₂ and H₂S. Each analysis required about 19.5 min; therefore, the exit gas was sampled every 20 minutes. The GC was calibrated using certified standard gases (H₂S and SO₂ in N₂ at concentrations between 500 and 2500 ppmv).

Table 3-4 lists the flow rates and concentrations of the feed gas that were used in the catalysts test that used toluene as a surrogate for BTX contamination in natural gas. As in previous tests the O₂/H₂S ratio was 1.5 because this was found to give the best SO₂ production selectivity over elemental sulfur. The pressure of 1.90 MPa (275 psig) and temperature of 225°C (437°F) were previously found to give excellent catalyst performance with TDA catalyst #3.

Table 3-4. Experimental Parameters for Testing Catalyst with Toluene in the Feed

Parameter	Value
H ₂ S concentration	2000 ppmv
O ₂ concentration	3000 ppmv
H ₂ O concentration	0.95 psi
N ₂ concentration	98.7%
Toluene concentration	4400 ppm
Pressure	1.9 MPa (275 psig)
Temperature	225°C (437°F)
Amount of catalyst tested	4 gm
GHSV (at STP)	3350 cm ³ _{gas} /cm ³ _{catalyst} /hr
Toluene flow rate	0.05 mL/min
Flow rate of 4%O ₂ / N ₂	179 sccm
Flow rate of 5% H ₂ S / N ₂	95.7 sccm
Flow rate of pure N ₂	2100 sccm
Predicted bed Δ P	0.3 psi (8.3 in. H ₂ O)
Run time	31 hours

3.3.6 Effect of Knockout Drum Condensate

Real world gas streams contain a wide variety of potential contaminants. Results of previous task activities with *n*-hexane indicated that light hydrocarbon contamination was not a problem with TDA catalyst. In addition, catalyst tests where the feed gas was contaminated with several thousand parts-per-million toluene showed that catalyst deactivation will be resistant to fouling or poisoning by BTX during the oxidation of H₂S to elemental sulfur and SO₂ in natural gas applications. While model compounds such as toluene and *n*-hexane are useful in determining the sensitivity of the catalyst to hydrocarbon contaminants, a more realistic test was conducted using actual condensate from the knockout drum at the gas plant where the field test would take place. The objective of the tests with the knockout (KO) drum condensate was to obtain information primarily related to the extent of BTX and possibly organic sulfur compound contamination.

Therefore, about 1 liter of knockout drum condensate was obtained from the CrystaSulf pilot plant located at Oxy Permian's plant in Denver City, Texas and shipped to the TDA research facility in Colorado. The KO drum is located upstream of the CrystaSulf unit; the KO condensate is essentially a combination of West Texas crude oil along with down-hole chemicals used in enhanced oil recovery. Table 3-5 shows the compositions of an intermediate and a sour West Texas crude oil, which indicates that aromatic hydrocarbons (BTX + ethylbenzene + C₃-benzenes) along with some light hydrocarbons are likely to be present in the natural gas exiting the KO drum. A CO₂ flood was used for oil recovery and consequently the associated gas at Oxy Permian is approximately 85% CO₂. The gas from the plant has a composition roughly the same as that given earlier in Table 3-1. The high CO₂ concentration is typical of associated gas from a CO₂ flood.

Table 3-5. Example Composition for West Texas Crude Oils (Environmental Technology Centre, Canada)

Component	Intermediate	Sour
Sulphur (wt%)	0.48	1.5
Saturates (wt%)	66	51
Aromatics (wt%)	26	36
Resins (wt%)	6	9
Asphaltenes (wt%)	1	5
Waxes (wt%)	4	5
Benzene (ppm)	1380	3510
Toluene (ppm)	2860	6980
Ethylbenzene (ppm)	1120	5610
Xylenes (ppm)	4290	4440
C3-benzenes (ppm)	5920	7410

For this series of tests a condensate vaporizer as shown in Figure 3-7 was built for adding the KO drum condensate vapors to the feed gas for catalyst testing. This saturator was a vertical 300 mL stainless steel sampling cylinder rated to 12 MPa (1800 psi) (more than adequate) with two NPT end fittings. The bottom one was plugged and the top one was fitted with an adapter to a 6.4 mm (¼-inch) Swagelok tee. The tee was drilled through so that a 6.4 mm (¼-inch) O.D. stainless steel tube could reach into the vessel but the end of the tube would not go below the liquid surface.

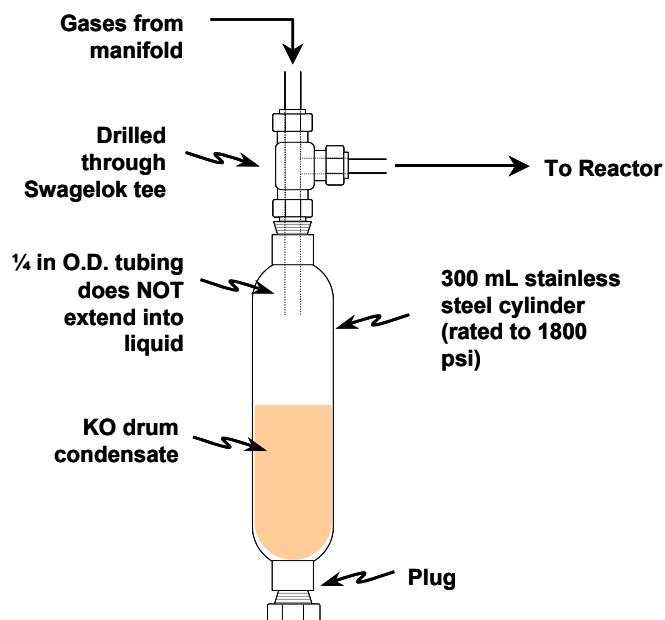


Figure 3-7. Schematic of Vessel to Introduce KO Drum Condensate Vapors into the Feed Gas for Catalyst Testing

Figure 3-8 shows the apparatus modifications for introducing the vapors from the headspace of a sample of the knockout drum condensate from the actual gas plant. The vaporizer was placed downstream of the manifold where the H_2S , O_2 and N_2 were mixed, just before the entrance to the reactor (the same location where we introduced toluene). The saturator was equipped with a bypass so steady state H_2S oxidation could be established prior to introducing the KO vapors. The pressure in the KO drum was approximately constant at 2.07 MPa (300 psig); the drum processes $5.36 \times 10^6 \text{ Nm}^3/\text{day}$ ($200 \times 10^6 \text{ SCFD}$) of gas. The drum was approximately 1.8 m (6 feet) in diameter, about 4.8 (15 feet) tall, and had a volume of approximately 12 m^3 (420 cubic feet). For operation at 20°C (68°F), the residence time of the gas in the drum was about 1.9 - 3.7 seconds depending on how much of the drum volume was filled with liquid. The superficial velocity in the drum is about 1.2 m/sec (4 ft/sec). The vaporizer was sized so that the residence time of the gas, the temperature and pressure to give approximately the same concentrations of contaminants in the feed gas as in previous catalyst tests.

The N_2 , H_2S and O_2 feed was passed through the headspace of the vaporizer to pick up the VOC's given off by the condensate. The device was essentially a regular bubbler except that the gases did not bubble through the liquid but rather passed over the surface of the liquid to pick up volatile components in the liquid. Passing the gases over the liquid surface had two advantages: (1) resulted in better simulation of the actual situation with the KO drum in the field, and (2) prevented the entrainment of aerosol particles of liquid. Aerosol particles: could have contained very non-volatile components that may have fouled the catalyst, may have been unrepresentative of the actual field conditions, and may have given false results for catalyst

performance with the KO condensate. In the field a coalescing filter located upstream of the catalytic reactor would have produced the same effect.

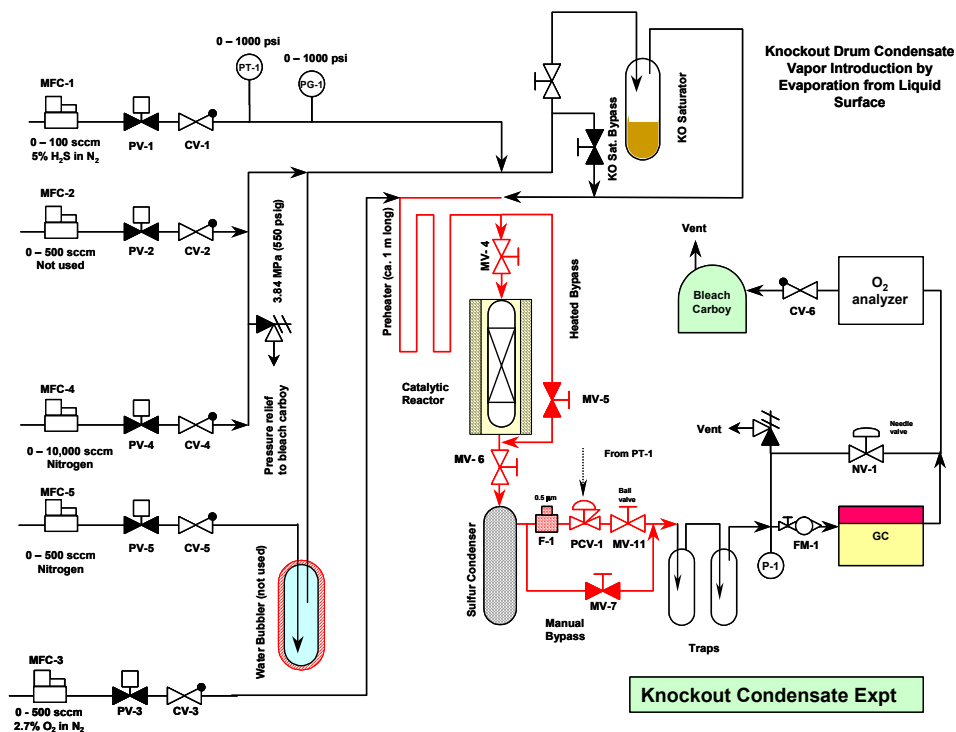


Figure 3-8. P&ID of Catalyst Test Apparatus for Tests with Knockout Drum Condensate

3.3.7 Bench Unit Testing at the Pilot Plant Site

Figure 3-9 is a process and instrumentation diagram of TDA's bench scale catalyst test apparatus. The reactor vessel for these tests was made from a 12.7 mm (½ inch) VCR bulkhead union (Figure 3-10) that was filled with 17 grams of TDA's oxidation catalyst. Upstream of the reactor both air and process gas were metered into the system using electronic mass flow controllers (MFC-1 and MFC-2). Each gas feed line had a pneumatic shut off valve (PV-1 and PV-2) and a check valve (CV-1 and CV-2). The gases were mixed together and passed into a one-meter (3.3-foot) long heat-traced section of tubing that served as a gas preheater. The gas preheater was initially operated at 175°C (347°F) and was later operated at 200°C (392°F). The air flow rate was typically about 95 sccm and the process gas flow rate was approximately 6500 sccm.

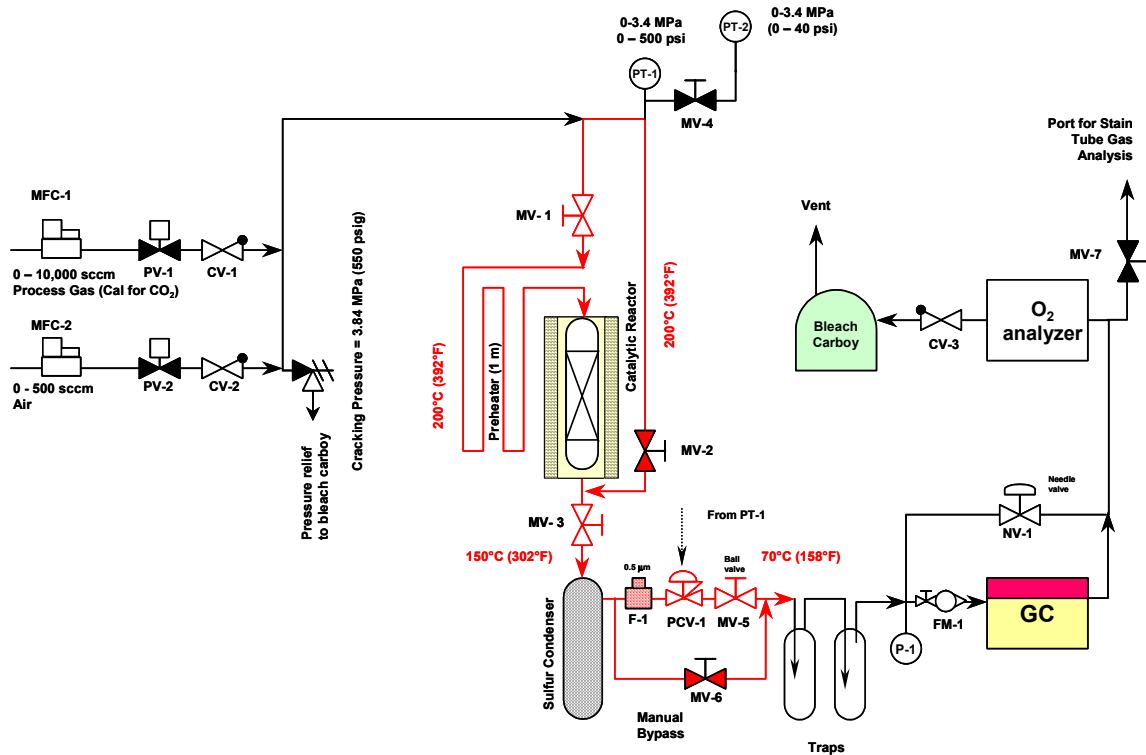


Figure 3-9. Process and Instrumentation Diagram for Bench Apparatus Used in Field Test at Denver City

The system pressure during the test was 2.07 MPa (300 psig) and the average catalyst temperature was maintained at about 240°C (464°F). Gases exiting the reactor first passed into a heated stainless steel cylinder that condensed any elemental sulfur that was formed. Gas exiting the condenser passed through a filter, a pressure control valve (PCV-1), two traps and then to an O₂ analyzer, a bleach solution and finally to vent. The filter protected the PCV from plugging (the flow orifice is extremely small). A tee in the line downstream of the traps was used to divert a small flow of gas through the gas chromatograph (GC) for analysis. The needle valve, NV-1, supplies a small amount of back-pressure to force some flow through the GC. The O₂ content of the gas was measured by an on-line paramagnetic analyzer (range 0-25 vol% O₂). Before being vented (in this case tied into the flare line at the Oxy plant), the gas was scrubbed through a dilute solution of bleach. This oxidized any unreacted H₂S to form water-soluble sulfur salts.

The air and process gas flow rates as a function of time are shown in Figure 3-11. The air flow rate was approximately 95 sccm and the process gas flow rate was about 6500 sccm. The composition of the process gas is given in Table 3-6 and the process gas contained about 1900 ppmv of H₂S. The bulk of the gas was CO₂ because the gas was recovered from a CO₂ flood for enhanced oil recovery. By desulfurizing the gas, the CO₂ could be reused.

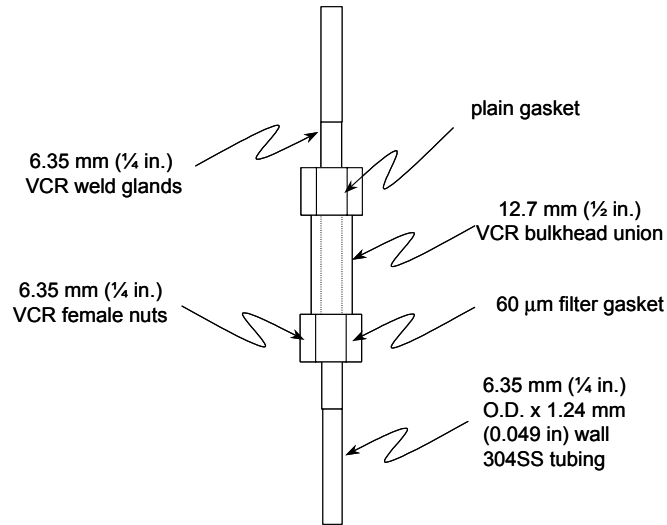


Figure 3-10. Detail of Fixed Bed Reactor Used in Apparatus Shown in Figure 3-9

The flow rates were very steady except for two interruptions in operations between about 125 h and 160 h and again between 210 and 230 hours. During these times there were difficulties (e.g., reset windup in the control valve, heaters needing to be retuned) with the apparatus that required shutting down the experiment temporarily. These difficulties were resolved quickly and the experiments were resumed.

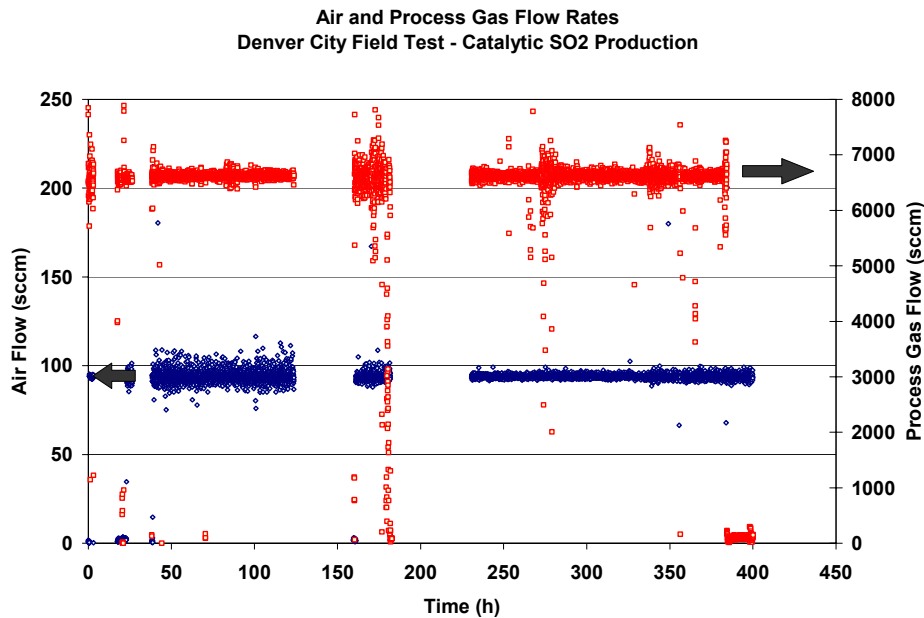


Figure 3-11. Process Gas and Air Flow Rates During Test

Table 3-6. Composition of Oxy-Permian Process Gas and Properties Calculated Using Supertrapp Program

Component	Vapor
H ₂ S	0.197%
H ₂ O	0.298%
CH ₄	10.613%
N ₂	1.408%
O ₂	0.296%
CO ₂	83.803%
ethane	1.814%
propane	0.327%
n-butane	0.601%
n-pentane	0.311%
n-hexane	0.227%
benzene	0.069%
toluene	0.026%
o-xylene	0.010%
Temp. for Property Calcs.	225°C (437°F)
Pressure for Property Calcs.	2.07 MPa (300 psig)
Molecular Weight (g/mole)	40.7418
Compressibility Factor	0.99
Density (kg/m ³) (lb/ft ³)	20.58 (1.28474)
Enthalpy (cal/g) (Btu/lb)	-1956.83 (-3522.01)
Entropy (cal/g*°C) (Btu/lb*F)	1.25607 (1.25607)
Specific Heat (cal/g*°C)(Btu/lb*F)	0.280693 (0.280693)
Cp/Cv	1.23934
Speed of Sound (m/sec) (ft/sec)	29.2501 (1151.58)
Joule-Thompson Coefficient	3.39E-02
Viscosity (lb/ft*sec)	1.57E-05
Thermal Conductivity (Btu/lb*hr*F)	2.10E-02

3.3.8 Economic Assessment of Scale-up to Onshore and Offshore Locations

As previously discussed, CrystaSulf uses liquid-phase Claus reactions to convert H₂S and SO₂ to elemental sulfur, where H₂S and SO₂ react in a 2-to-1 ratio. This SO₂ requirement can be met by incorporating a sulfur burner, by importing liquid SO₂, or by catalytically oxidizing H₂S to SO₂. The major thrust of this project has been to evaluate enhancing CrystaSulf by combining it with an upstream H₂S oxidation catalyst – the hybrid CrystaSulf process. There are two basic modes of operation, one in which SO₂ is preferentially produced and the other in which elemental sulfur is preferentially produced. In addition to modes of operation, different catalyst composition can also be chosen to help selectively produce SO₂ or elemental sulfur. The direct oxidation catalyst converts large amounts of H₂S to elemental sulfur at low cost, but does not achieve high enough sulfur control for stand-alone use in most applications. Furthermore, the gas stream exiting this process contains elemental sulfur vapors and SO₂, both of which must be handled and removed. Using direct oxidation within the CrystaSulf process (as a hybrid version of the CrystaSulf process) overcomes the limitations of using direct oxidation as a stand-alone process the hybrid process achieves near 100% sulfur control with the elemental sulfur and SO₂ generated by the oxidation catalyst being readily and beneficially absorbed into CrystaSulf solution. The major limitation of CrystaSulf (without catalyst enhancement) is that the operating cost is partially a function of the amount of sulfur in the inlet. With direct oxidation catalyst incorporated within CrystaSulf, 80-95% of the sulfur is removed prior to the CrystaSulf absorber with a substantial benefit to operating cost. A second limitation to CrystaSulf is that SO₂ must be added to the solution to support the process reactions. The addition of liquid SO₂ adds operating cost; a sulfur burner adds cost and complexity. Utilizing an oxidation catalyst within the process provides the needed SO₂ by merely adjusting the catalyst bed conditions.

The economics of the hybrid CrystaSulf process were developed using Aspen modeling software with input from fabricators to supply current cost for sub-units of the hybrid process. The most economically favorable version or mode of operation of the hybrid CrystaSulf process is direct oxidation catalyst followed by CrystaSulf, i.e., CrystaSulf-DO. An economic comparison of CrystaSulf-DO with Amine/Claus/TGT, Amine/Aqueous Iron Redox, and CrystaSulf is presented in Section 4, Results and Discussion.

3.4 Task 4 – Develop a Test Plan for Pilot-Scale Demonstration of the Hybrid Process; Conduct Modifications to Existing Pilot Plant

Initially, CrystaTech and TDA Research focused primarily on SO₂ catalysts – i.e., catalysts having the primary objective of partially oxidizing H₂S to sulfur dioxide to feed the Claus reaction in the CrystaSulf process. After successful bench-scale tests of TDA's catalysts in the laboratory, identification of the most effective upstream catalyst, and successful testing of the selected TDA catalyst on a slip stream of the actual pilot plant gas, efforts began to scale up the bench catalytic unit to pilot scale.

The TDA #2 catalyst was chosen because the promoter that gives the high selectivity for producing SO₂ is less expensive than the promoter for TDA #3 while giving identical performance. TDA conducted successful pilot tests of this catalyst on an associated gas stream

at CrystaTech's pilot plant at Oxy Permian's DUCRP site at low pressure with over 1500 hours of operation.

Planning activities ensued for pilot testing of a front-end H₂S oxidation unit plus the existing CrystaSulf unit at the DUCRP site. However, two developments altered the course of the project. The first caused a shift in the direction of the pilot testing portion of the program. The second development ultimately led to the inability to move the hybrid process toward commercialization utilizing TDA-developed catalysts.

Regarding the first development, while the production of some sulfur by the catalyst was expected, the initial economic evaluations indicated that mode of the hybrid process that converting the bulk of the inlet H₂S to sulfur in the catalyst section offered substantially better economic benefits for many/most applications. Thus, to be of most benefit, any pilot testing needed to include equipment for cooling the stream from the catalyst bed and removing the sulfur prior to the CrystaSulf absorber. Such a pilot scale catalyst section would involve substantially more equipment and cost than originally anticipated. Efforts to secure additional funding for the pilot testing were unsuccessful.

The second development involved the ability to utilize TDA-developed oxidation catalysts for the hybrid CrystaSulf process. Incorporating a particular catalyst within CrystaSulf-DO involves both technical/performance considerations and economic considerations. Unfortunately, after more than two years of negotiations, and despite the efforts of the DOE Project Officer to resolve the issues, CrystaTech and TDA could not reach agreement on license terms. As a result, CrystaTech and TDA began proceeding down separate commercial paths, precluding the possibility of demonstrating CrystaSulf-DO with TDA catalysts under this project as originally planned.

As a result of these two developments, the technical approach for this task was modified during the course of the project and ultimately consisted of the following steps (not all of which were completed):

- Design of scaled-up catalytic oxidation reactor
- Catalyst pellet production
- Catalyst durability study
- Selection of catalyst
- Investigation of alternate catalysts for direct oxidation CrystaSulf process
- Direct oxidation catalyst testing (at GTI)
- Prepare test plan for pilot-scale testing of hybrid CrystaSulf process
- Modifications of pilot plant to accommodate hybrid process test

3.4.1 Design of Scaled-up Catalytic Oxidation Reactor

TDA conducted successful bench-scale tests of oxidation catalyst under this program, operating continuously for more than 300 hours with no deactivation observed and no change in

selectivity for production of SO₂. The selectivity for production of SO₂ was better than 95% for the entire run and the H₂S conversion was 100%. The results are presented in Section 4 of this report.

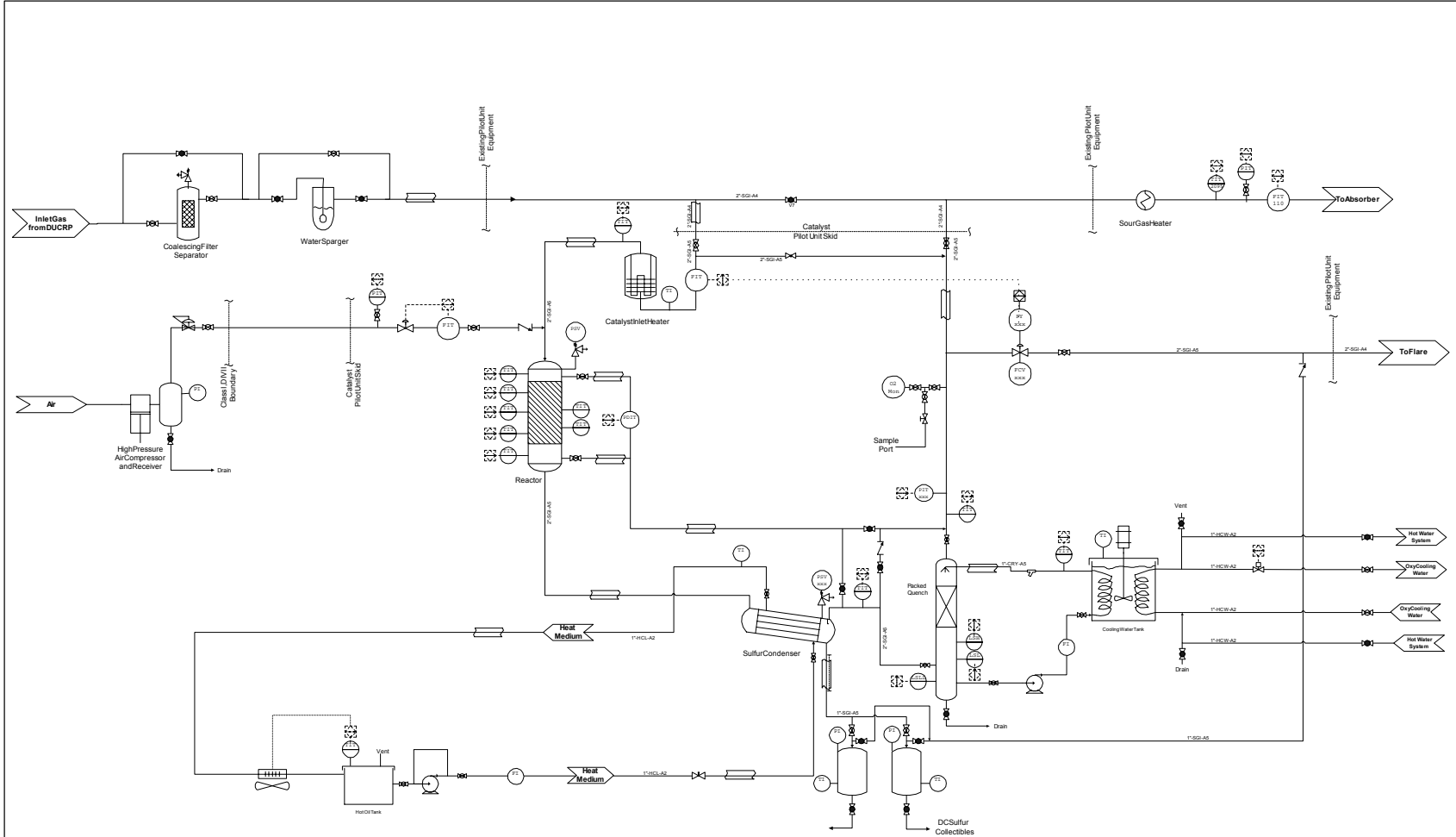
Based on the encouraging results of the bench catalytic unit at the pilot unit facility, a pilot-scale catalyst unit was designed to be placed upstream of the existing CrystaSulf pilot unit. The unit was designed to run in predominately H₂S to SO₂ mode or in H₂S to sulfur plus SO₂ mode. The final design of this fixed-bed reactor was sized to hold 3.6 kg (8 pounds) of catalyst. The catalytic reactor itself was designed to process 0.0027 Nm³/day (0.1 MMscfd) of gas, which is about 1/3 of the total flow of 0.0080 Nm³/day (0.3 MMscfd). At 2.07 MPa (300 psig or ca. 21 bar) and 250°C (482°F), this corresponds to an actual gas flow through the reactor vessel of 120 liters/min (4.2 ft³/min). This reactor was to be placed upstream of the CrystaSulf pilot plant. A process flow diagram of the catalyst unit is shown in Figure 3-12. The equipment required for the catalyst unit was sized and suppliers contacted to determine cost and delivery timeframes. In addition, several fabrication companies were provided bid packages to provide cost estimates for constructing the pilot-scale catalyst module.

CrystaTech soon concluded that there was insufficient funding to complete the pilot-scale testing of CrystaSulf-DO and efforts to secure additional funding were undertaken. These were unsuccessful, and this task area was subsequently put on hold while the project focused on identifying alternate catalysts and pursuing alternate paths to commercialize the hybrid process. This program shift toward alternate catalysts was in response to the inability to reach an agreement with TDA for use of TDA-developed catalyst which CrystaTech believed was conducive to successful commercialization of the hybrid process (as discussed earlier).

3.4.2 Catalyst Pellet Production

(This activity preceded the developments in the program discussed in the previous section which resulted in a shift toward identifying catalysts that could be used instead of TDA-developed catalysts). Once the best catalyst composition was determined, a qualified supplier of the material was needed to provide reproducible batches for qualification and the required quantities for pilot plant testing. The supplier generally used by TDA for commercial quantities of catalysts and sorbents is Saint Gobain NorPro (Cleveland, OH).

NorPro is one of the Nation's largest suppliers of catalysts with annual sales exceeding \$100 million. NorPro is a wholly owned subsidiary of Saint Gobain Corporation Inc., which is a subsidiary of Compagnie de Saint-Gobain. Saint-Gobain is one of the 100 leading industrial companies in the world in producing and transforming basic materials, including glass, cast iron, plastics and ceramics. Saint-Gobain has annual sales of around \$23 billion worldwide. NorPro is a leading supplier of distillation and separation equipment, heat storage technology and catalyst carriers and ceramics for the chemical, petrochemical, and petroleum refining industries.



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REV.	DATE	DESCRIPTION	BY	CHECKED	APPROVED	APPROVED
1	JUL 31, 2002		BJP			



CrystaTech, Inc.
4616 W. Howard Lane
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Austin, Texas 78728

PIPING AND INSTRUMENT DIAGRAM Pilot Catalyst Unit	
CLIENT SITE DOE/HydroP/02ct	JOB NUMBER
DRAWING NUMBER	SCALE NONE

NorPro has three operating groups, specializing in Mass Transfer, Catalytic Products, and Ceramics. The Catalytic Products are used by the chemical and allied processing industries worldwide. The Catalytic Products group produces porous ceramic catalyst carriers in three sites in the U.S., upon which catalytically active materials are absorbed. Control of porosity optimizes the carrier for a particular catalytic reaction. NorPro produces what is considered to be the industry's largest selection of standard and specialty formulated porous ceramic catalyst carriers in a wide variety of surface areas, porosities, and shapes. They have extensive experience with alumina, titania, silica, and other inorganic materials. The expertise that NorPro has acquired is directly related to the emphasis placed on research and development.

NorPro owns and operates a Research and Development Laboratory located in Stow, Ohio. A significant part of this laboratory is devoted to the development of tailored porous ceramic materials. These materials are produced by mixing, extrusion, shaping, drying and calcination. Other forming methods are also utilized, such as various agglomeration techniques. The equipment available includes full size apparatus for these various stages, in order to virtually eliminate scale up problems. Full-scale calcination equipment (tunnel, rotary, and periodic kilns) is available at NorPro's production facilities in Bryan, Texas; Ravenna, Ohio; and Daisy, Tennessee. NorPro maintains a very well equipped analytical laboratory for the chemical and physical measurements that may be required. Relevant equipment available includes the following: Surface Area Analyzers, Micromeritics 2300, Flowsorb Micromeritics 2600, Digisorb Micromeritics 2405 ASAP, Mercury Porosimeters, Quantochrome Autoscan SP-60-3, Quantochrome Autoscan 25, AS-25-1 Amonco-Winslow (0 - 3,000 lb), Flat Plate Crush Strength Gauges, Comten 945 KVC0300 (to 5,000 lb), and Comten 50-02 (to 600 lb). In addition, a wide range of other analytical instrumentations is available, including: X-Ray Diffraction, Scanning Electron Microscopy (with Energy Dispersive Spectroscopy), Thermogravimetry (DTA, TGA, TMA), Particle size analysis Atomic Absorption (with graphite furnace), Sulfur analysis, X-Ray Florescence (XRF) and Inductively Coupled Plasma Atomic Emission Spectrometer (ICP AES).

3.4.3 *Catalyst Durability Study*

Durability testing ensures that no unforeseen variations in catalyst performance are introduced when the catalyst is manufactured in its final physical form. TDA has a pellet reactor designed specifically to be able to test catalysts in the final physical form (e.g., 3-6 mm, or 1/8– 1/4 in. pellets) that would have been used in the pilot plant work had that work proceeded.

3.4.4 *Selection of Catalyst*

While the project evaluated catalysts that primarily produced SO₂, the economic benefits of using catalysts/conditions that also produced sulfur dictated that the hybrid CrystaSulf process development program should include evaluation of that mode. Therefore, the catalysts and operating parameters of the commercial hybrid CrystaSulf process need to include catalysts/conditions which convert 80-95% of the inlet H₂S will be directly to elemental sulfur in

the catalyst section, with a portion of the remaining H₂S oxidized to SO₂, so as to meet the H₂S to SO₂ stoichiometry requirement of the CrystaSulf process.

3.4.5 Investigation of Alternate Catalysts for CrystaSulf-DO

As noted earlier, commercial developments dictated that alternatives to the TDA-developed catalyst be pursued. As has long been recognized in the industry, the key to successful catalyst deployment will likely be to identify catalysts that display high conversion efficiencies for H₂S at relatively low temperatures, for example 200 – 250°C (about 390 – 480°F). The use of low temperatures greatly reduces the chance of oxidation of organic components of the gas stream, which could lead to fouling or coking of the catalyst surface with organic reaction products. For example, in a series of patents, most of which have expired, Hass et al. described efficient conversion of H₂S in actual natural gas streams and gave detailed analytical results showing that the organic constituents of the stream showed very little if any conversion (Hass, *Process for removal of hydrogen sulfide from gas streams*, U.S. Patent 4,243,647, 1981). There are many other examples of catalysts in the open and patent literature which had "mixed" selectivities for producing elemental sulfur and SO₂ from H₂S in gas streams. Many were discarded or abandoned because the users were seeking extremely high selectivities for one or the other product.

Although the absolute production selectivity at any one set of conditions is not vitally important, it is necessary that the catalyst be able to deliver desired amounts of sulfur and SO₂ over some range of O₂/H₂S ratios and temperatures. Another key property of the catalyst is long-term stability. Some selection for these properties can be done by contacts with catalyst manufacturers and by literature consultation. However, testing will be needed to verify the selectivity results and to determine long-term stability.

Direct Oxidation Catalyst Testing at GTI – GTI and CrystaTech developed a plan to utilize existing GTI bench-scale catalyst test equipment to perform the bench-scale testing at GTI's Des Plaines laboratories, and then utilize portions of that equipment in the field effort at the pilot plant at Oxy Permian. This approach would avoid having to build a separate, larger-scale pilot unit, but would still generate the data needed. GTI dedicated one of these existing bench-scale catalyst test units to this program, worked with CrystaTech to develop a design basis, and then modified the unit to meet the program needs. Figure 3-13 is a schematic of the GTI bench-scale catalyst test rig, and Figure 3-14 is a picture of the unit. The work to get the unit ready for testing was nearly completed, but was put on hold due to GTI budget constraints. In the summer of 2004 GTI was able to allocate funding for this effort, which is scheduled to begin in late July/early August of 2004. Initially, GTI will test Axens CRS 31 catalyst, which is the industry standard for catalysts of this type and is commercially-available at a relatively inexpensive price.

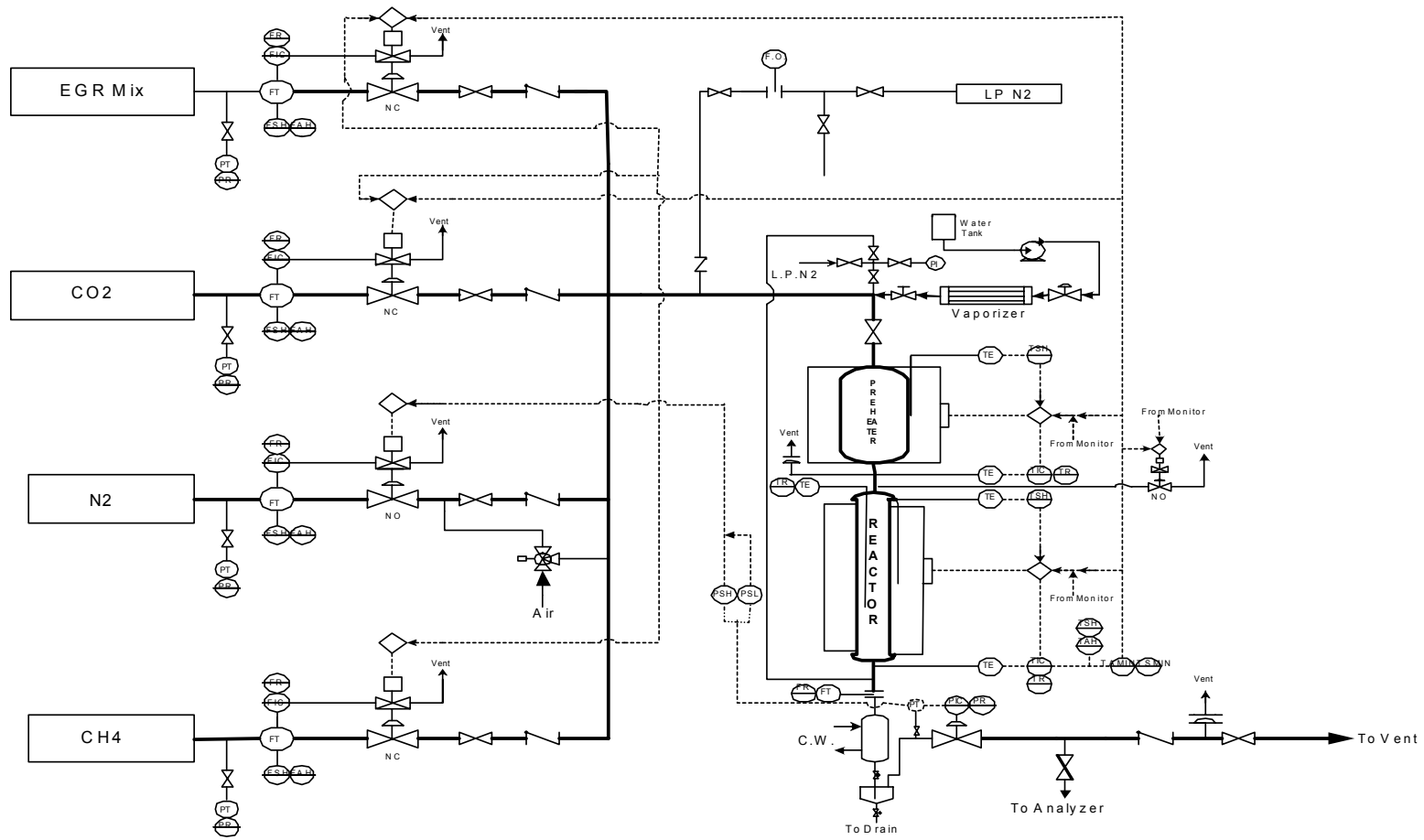


Figure 3-13. Schematic of GTI Bench-Scale Catalyst Test Rig



Figure 3-14. Picture of GTI Bench-Scale Catalyst Test Rig

Direct Oxidation Catalyst Testing at DOE. CrystaTech has had several discussions with the DOE about use of CrystaSulf-DO for sulfur control in coal gasification/IGCC plants. These conversations and presentations to DOE led to the suggestion by project managers that DOE viewed CrystaSulf-DO as a promising technology for these applications and could perform direct oxidation catalyst testing in their NETL labs. The DOE also informed us that they have catalyst technology which may be satisfactory for use as the oxidation catalyst in the hybrid process. This work will be performed under a Cooperative Research and Development Agreement (CRADA) which has been executed between CrystaTech and DOE. Each will fund their respective portion of the testing. This testing will help advance the hybrid CrystaSulf process which is the subject of this program and this final report.

3.4.6 Modification of Existing Pilot Plant

CrystaTech's pilot unit testing facility is located at Oxy Permian's DUCRP plant just outside Denver City, Texas. As discussed earlier, as a result of budget limitations, pilot testing was not conducted under this program. CrystaTech's site agreement with Oxy Permian called for CrystaTech to dismantle and remove the CrystaSulf unit once scheduled testing was completed. As no testing could be scheduled, CrystaTech was required to dismantle the CrystaSulf pilot unit and remove it. That activity occurred in June 2004.

3.5 Task 5 – Conduct and Document Pilot-Scale Demonstration of Hybrid Process; Develop Commercialization Plan

The activities planned pilot testing at the CrystaSulf pilot plant at Oxy Permian in West Texas were cancelled as discussed earlier. However, the commercialization activities for CrystaSulf-DO continue in the following projects:

- Investigation of alternate catalysts for use in CrystaSulf-DO, especially those which produce predominantly sulfur in the catalyst bed;
- Testing of catalysts at GTI; and
- Testing of catalysts at DOE.

4.0 RESULTS AND DISCUSSION

4.1 Testing of TDA #3 Catalyst

Three promoted versions of TDA's partial oxidation catalyst based on Mo, Nb, and TiO₂ have been tested, the first two prior to the novation. In the first catalyst (designated TDA #1) a transition metal was added that is known to improve the selectivity of the catalyst for producing 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. The third promoter (found in TDA #3) is somewhat better than that used in TDA #2. The results for the tests with TDA #1 and TDA #2 were reported earlier (Srinivas, Gebhard and DeBerry, 2001). In this report the third catalyst (TDA #3) that is even more selective for SO₂ production is discussed. Two molar ratios of oxygen to H₂S were tested in these studies.

Experimental Results When H₂S to O₂ ratio = 1.5

Figure 4-1 shows the results for TDA catalyst #3 when the O₂/H₂S ratio = 1.5. The feed contained 2000 ppmv H₂S, 3000 ppmv O₂, approximately 0.3 vol% H₂O (3000 ppmv), and 10% CH₄, with the balance being N₂. The experiment was run for approximately 20 hours at 250°C (482°F) and P = 2.07 MPa (ca. 310 psia). The H₂S conversion was 100% during the entire experiment. At the beginning of the run, the selectivity for producing elemental sulfur was almost 90% with very little SO₂ being formed. Gradually over the next 10 hours, the production selectivities shifted to approximately 10% for sulfur and 90% for SO₂. By 20 hours, the SO₂ production selectivity had slowly increased to 94% (6% sulfur). Because the H₂S conversion was 100%, the yields of sulfur and SO₂ are numerically equal to their production selectivities.

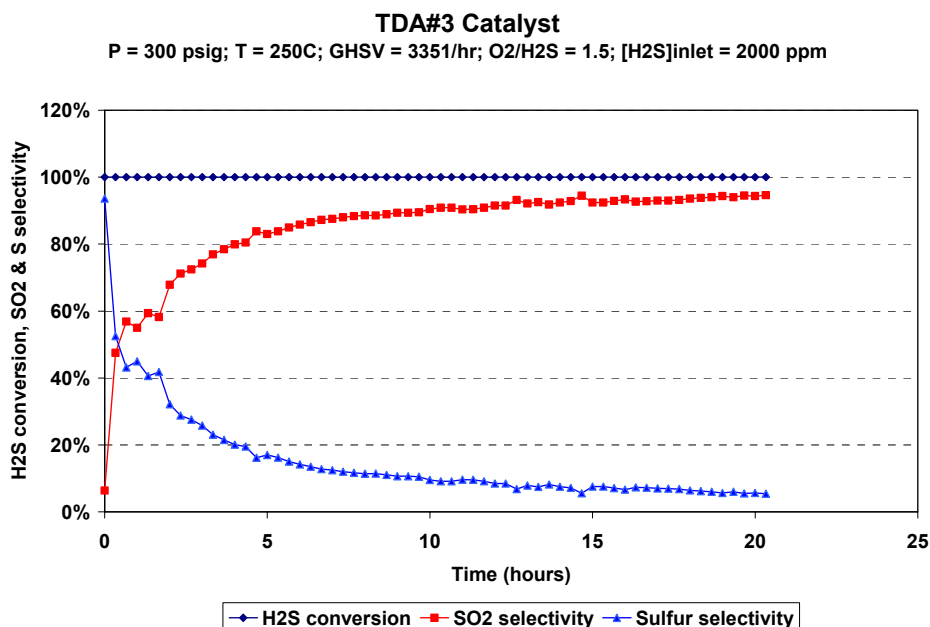


Figure 4-1. Experimental run with TDA#3, O₂ to H₂S ratio = 1.5

Experimental Results When H₂S to O₂ Ratio = 1.0

The same charge of TDA #3 catalyst was then tested at an O₂/H₂S ratio of 1. These results are shown in Figure 4-2. Note that the induction time is much shorter in this test as compared to the results shown in Figure 4-1 where the O₂/H₂S ratio was 1.5. This is due to the fact that fresh catalyst (still in the oxide form) was used for the experiment shown in Figure 4-1, whereas we used the already-tested catalyst for the experiment with O₂/H₂S = 1.0, shown in Figure 4-2. As a result, some of the induction time in Figure 4-1 is undoubtedly due to conversion of the oxide components in the catalyst to steady state concentrations of sulfide (with possibly chemisorbed sulfite/sulfate because of the presence of oxygen in the feed). The short induction time in Figure 4-2 is probably due to the lag time in switching the flow from the bypass (where the inlet H₂S concentration is measured) to flow over the catalyst. At a pressure of 2.07 MPa (ca. 300 psig), the residence time in the catalyst bed (approximately 1 cm³, or 0.06 in³, volume) is about 1 second. The total volume of the reactor and all tubing is about 500 cm³ (30 in³), so there is approximately a 20 minute lag time for several reactor volumes to pass through the system and the concentrations in the gas phase at the GC to become equal to those over the catalyst.

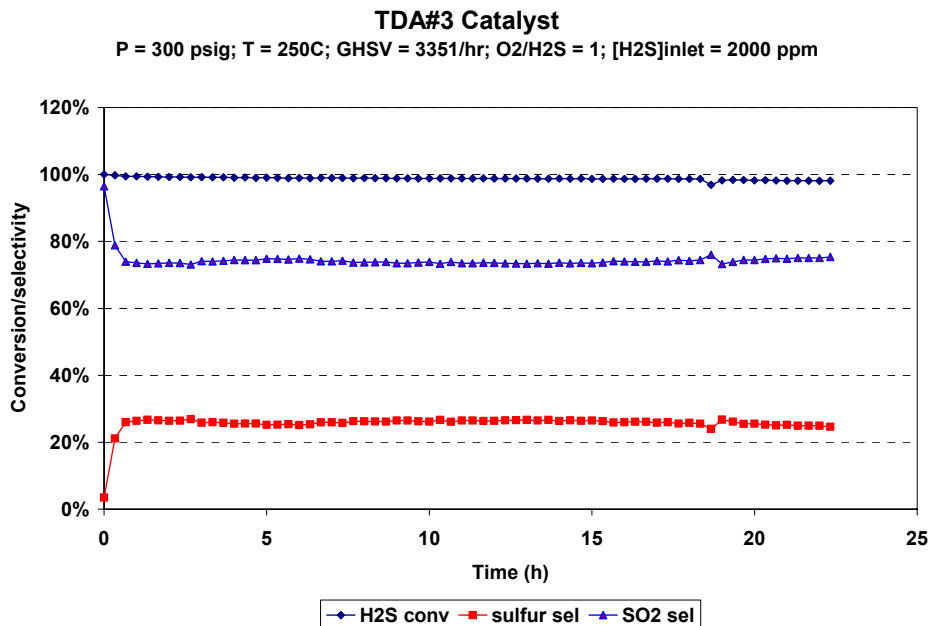


Figure 4-2. Experimental run with TDA#3, O₂ to H₂S ratio = 1

The selectivity for producing SO₂ was reduced from 94% when O₂/H₂S = 1.5, to 74% (26% sulfur) when O₂/H₂S = 1.0. Again because the H₂S conversion was 100%, the production selectivities are numerically equal to the yields for SO₂ and elemental sulfur. Reduced selectivity for producing SO₂ with decreasing O₂/H₂S is consistent with the results obtained earlier with the TDA #2 catalyst.

Figure 4-3 shows the data from the paramagnetic O₂ analyzer during the test of TDA catalyst #3 at an O₂/H₂S ratio = 1.0. The inlet concentration into the reactor was 3000 ppmv (0.3%) and the full range of the analyzer is 0 – 5% (hence the noisy signal). The less noisy line is the feedback flow signal from the mass flow controller used to meter in 2.7% O₂/N₂ and shows that O₂ was flowing into the reactor during the experiment.

Figure 4-3 also shows that there was no O₂ in the outlet gas, so all of the oxygen was being consumed by catalytic reaction. Figure 4-4 shows the results for rerunning TDA #3 catalyst at 2 MPa (300 psi), 250°C (482°F) and O₂/H₂S = 1.5. Because the catalyst was not in the oxide form there was essentially no induction time during the test shown in Figure 4-4. As was the case with the first run of TDA #3 shown in Figure 4-1, the selectivity for producing SO₂ was quite high (96%) with the selectivity for producing sulfur being 4%. This is within experimental error of being identical to the performance of fresh TDA #3 catalyst after 20 hours on-stream.

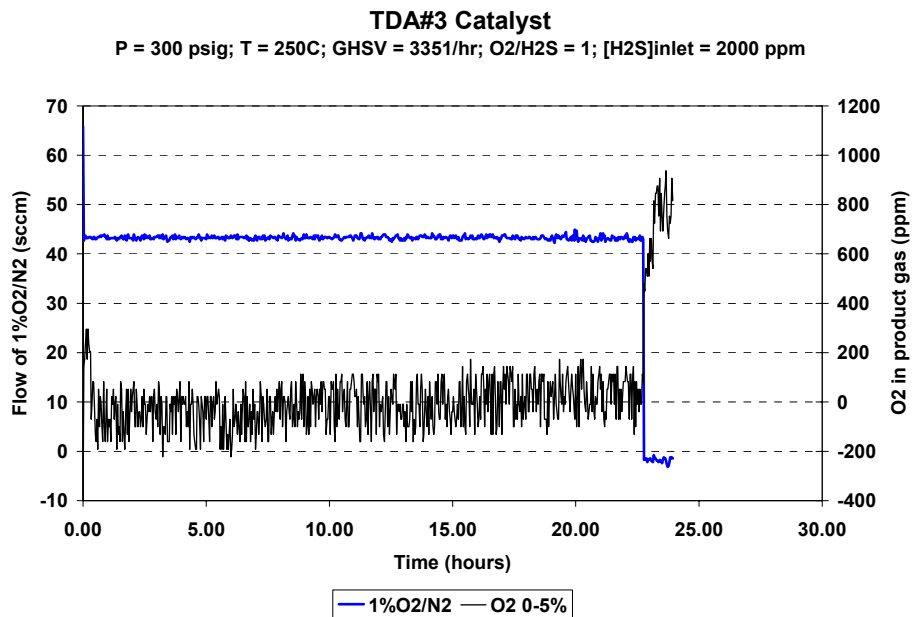


Figure 4-3. Experimental run with TDA#3, O₂ to H₂S ratio = 1

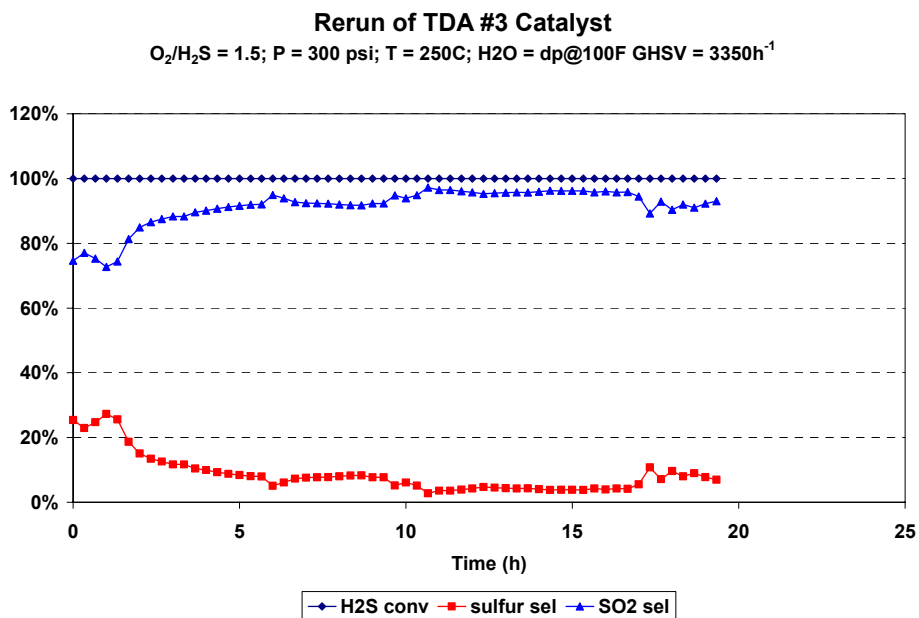


Figure 4-4. Rerun of TDA #3 test at O₂/H₂S = 1.5

Oxygen Mass Balance

Because we had no way to directly measure the amount of sulfur produced during the reaction, we relied on the oxygen mass balance to check our assumptions that only two reactions are occurring, as discussed earlier in Section 3.3.1. The results from the O₂ analyzer indicated that in all of the runs with TDA #3, all of the O₂ was consumed (outlet concentration of zero).

For the test of TDA #3 shown in Figure 4-4, the production selectivity for SO₂ was $X_{SO_2} = 0.95$ (average) and the production selectivity for elemental sulfur was $X_S = 0.05$ (average). For an inlet concentration of $[H_2S]_0 = 2000$ ppmv, $X_{SO_2} = 0.95$ and $X_S = 0.05$, and an SO₂ concentration of 1918.5 ppmv, the calculated sulfur vapor concentration is $[S] = 81.52$ ppmv.

These concentrations of SO₂ and S require $[O_2]_{req'd} = 1.5(1918.5) + 0.5(81.52) = 2919$ ppmv of O₂. The inlet concentration was $[O_2]_0 = 3000$ ppmv so we can account for 97.3% of the oxygen by forming only SO₂ and sulfur. This degree of accuracy is well within the experimental accuracy of the mass flow controllers and GC analysis of the product gases. In conclusion, with TDA #3 catalyst run at O₂/H₂S = 1.5, only SO₂ and sulfur are formed and no SO₃ is formed. These results are consistent with earlier results for the TDA #1 and TDA #2 catalysts where the oxygen mass balance closure was greater than 95%; therefore, only SO₂ and sulfur were formed over these catalysts.

Also, based on the descriptions of the industrial synthesis of SO₃ via SO₂ oxidation found in the literature (Stocchi 1990), minimal SO₃ formation is expected. Sulfur trioxide is used for sulfuric acid manufacture and is made by oxidizing SO₂ with O₂ over V₂O₅ catalysts. The optimum temperature for industrial synthesis, from both a kinetic and thermodynamic standpoint, is between 400 and 500°C (752 and 932°F) (Stocchi 1990). These temperatures are much higher than normal operating temperatures with the catalysts tested here (250°C, or 482°F), and thus very poor activity for SO₃ formation would be expected. Also, V₂O₅ is a more aggressive oxidation catalyst than the catalysts tested here.

4.2 Comparison of TDA Catalysts 1, 2 and 3

Previously the results from similar tests for two other catalysts, TDA #1 and TDA #2, which are also promoted versions of TDA's oxidation catalyst, were reported (Srinivas, Gebhard and DeBerry, 2001). Figures 4-5 and 4-6 show the results for TDA #1 and TDA #2, respectively. Figure 4-5 shows that the average H₂S conversion was about 70% and the selectivity for production of SO₂ was about 30% for the TDA #1 catalyst. This corresponds to only 21% yield of SO₂. The selectivity for production of sulfur was about 70%, so the yield of elemental sulfur was only 49%. Because of the rather poor performance of this version of the catalyst, TDA #1 is no longer under consideration for any version of the hybrid CrystaSulf process.

TDA#1 catalyst: 22hr test at 250 psi and $O_2/H_2S = 1$; GHSV = 1910 h^{-1} (at T&P)

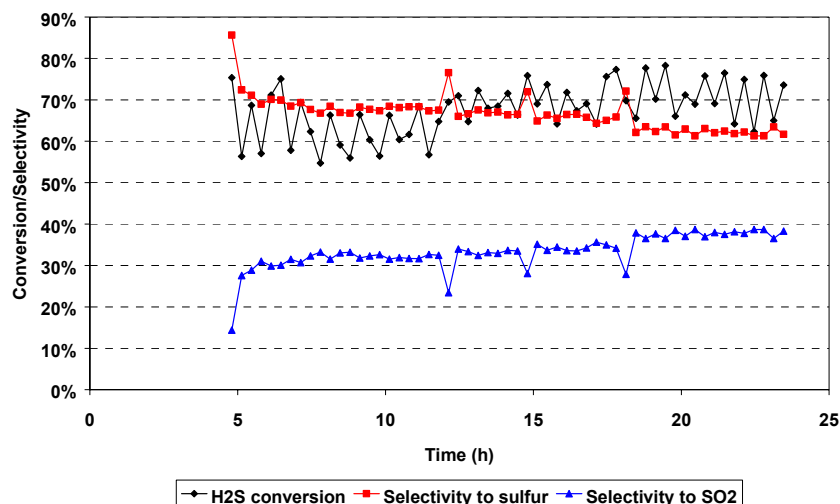


Figure 4-5. Results for TDA #1 catalyst

The performance of the TDA #2 catalyst was considerably better than catalyst TDA #1, especially when the O_2/H_2S ratio was 1.5. At the higher O_2/H_2S ratio, the H_2S conversion was complete (100%), the selectivity for producing sulfur was only 8%, and the selectivity for producing SO_2 was 92%. When the O_2/H_2S ratio was decreased to $O_2/H_2S = 1$, the H_2S conversion was slightly reduced (98%), the selectivity for producing SO_2 was 74% and the sulfur production selectivity was 29%. These correspond to a SO_2 yield of 73% and a sulfur yield of 28%. The amount of oxygen added (appearing as the O_2/H_2S ratio) is the most sensitive variable that we found for controlling the selectivity of the catalyst for SO_2 and sulfur. The effect of the O_2/H_2S is greater than the effects of temperature, pressure or space velocity in determining SO_2 yields and therefore we can use the oxygen concentration to control the selectivity for producing SO_2 to different levels as required by the process.

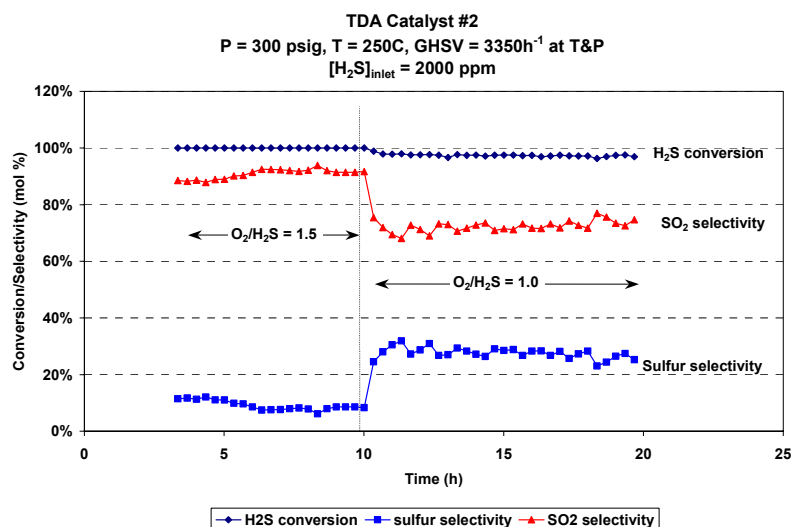


Figure 4-6. Results for TDA #2 catalyst

The performance of the TDA #3 catalyst was virtually the same as the performance of TDA #2 under conditions where O₂/H₂S = 1; however, increasing the O₂/H₂S ratio to 1.5 clearly improved the performance of both catalysts, with TDA # 3 being slightly better. The differences between TDA #2 and TDA #3 are minimal when operated at O₂/H₂S =1.5 (TDA #3 has only a 4% better SO₂/sulfur production selectivity). Because the promoter used in TDA #3 is considerably more expensive than the promoter used in TDA #2, TDA #2 is the best candidate for use in a SO₂-producing mode of the hybrid CrystaSulf process.

The results for all three TDA catalysts tested along with the operating conditions used in each test are given in Table 4-1.

Table 4-1. Summary of Catalyst Test Results for TDA #1, #2 and #3

Catalyst	O ₂ /H ₂ S	Temp °C (°F)	Pressure MPa (psig)	GHSV (h ⁻¹)	H ₂ S conv. (%)	SO ₂ yield (%)	Sulfur yield (%)
TDA#1	1.0	250 (482)	1.72 (250)	1910	70	27	43
TDA #2	1.0	250 (482)	2.07 (300)	3350	96	69	27
TDA #2	1.5	250 (482)	2.07 (300)	3350	100	92	8.6
TDA #3	1.0	250 (482)	2.07 (300)	3350	100	74	26
TDA #3	1.5	250 (482)	2.07 (300)	3350	100	94 ^a	6 ^a
TDA #3	1.5	250 (482)	2.07 (300)	3350	100	96 ^b	4 ^b

^aafter 20 hrs (10 hr induction time with fresh TDA #3)

^brerun of O₂/H₂S = 1.5 with TDA #3 using tested catalyst

4.3 Oxidation of C₂₊ Hydrocarbons

Earlier work demonstrated that methane is inert as it passes over the catalysts evaluated during this project. In most of the catalyst tests, 10% methane was added to the feed. No methane oxidation occurred at T = 250°C (482°F) and P = 2 MPa (300 psig). Methane, however, is the most difficult of the hydrocarbons to oxidize since it has the highest activation energy. Since in real gas conditioning applications, higher more reactive alkanes are likely to be present, additional tests were conducted. Hexane represents the most reactive of the C1 to C6 series of alkanes. Since hexane was shown to exhibit low reactivity under H₂S oxidation conditions, and more importantly, not change the SO₂ production selectivity, we concluded that the C1 – C6 hydrocarbons should not significantly interfere with the oxidation of H₂S to sulfur and SO₂. The detailed results of the hexane test conducted with TDA catalyst #3 are presented in this section.

Figure 4-7 shows the results for the test with 500 ppmv *n*-hexane (C₆H₁₄) added to the feed when no H₂S was present. The catalyst temperature was 250°C (482°F) and the pressure in the reactor was 1.38 MPa (200 psig). Fresh (never exposed to H₂S) catalyst TDA #3 was used in this experiment, and therefore, the compounds in the catalyst were present as oxides.

Figure 4-7 shows three curves. The first is the flow of 2.7% O₂ in N₂ that was used as the O₂ source. The flow was started at about 1.5 hours into the run, and during this time the oxygen concentration exiting the reactor rose to and stabilized at 3,000 ppmv. The appropriate amount of pure N₂ was added to dilute the 2.7% O₂ down to 3,000 ppmv. At about 2.5 hours, the flow of *n*-hexane was started. The cylinder concentration was 990 ppmv of C₆H₁₄ in N₂ that was added

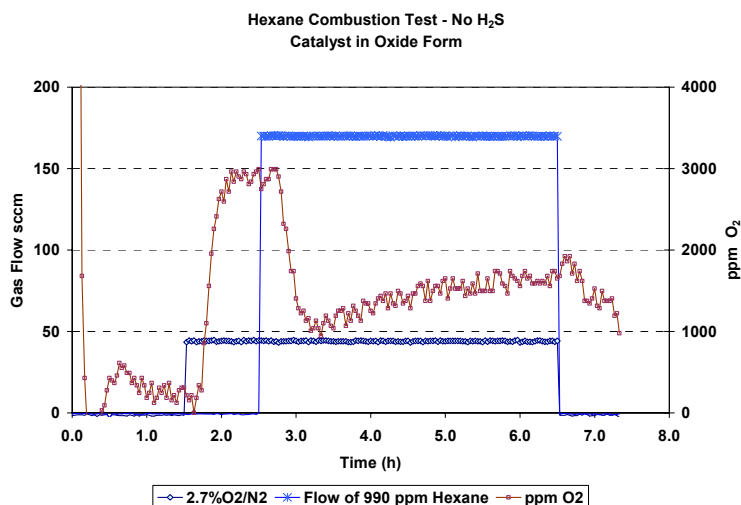
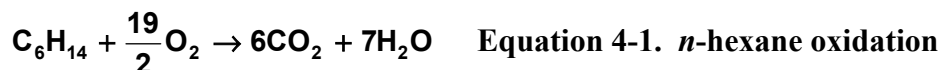


Figure 4-7. Hexane oxidation test over TDA Catalyst #3 with no H₂S in the feed (catalyst in oxide form)

at a flow rate that gave 500 ppmv of C₆H₁₄ in the feed gas flowing over the catalyst; pure N₂ was added to adjust the C₆H₁₄ concentration to 500 ppmv. Immediately the O₂ concentration decreased to about 1,000 ppmv suggesting that some hexane oxidation was occurring. The O₂

concentration gradually increased over the next 5 hours and then leveled out at 2,000 ppmv which corresponds to a consumption of 1000 ppmv of O₂.

Equation 4-1 gives the balanced equation for complete oxidation of C₆H₁₄ into CO₂ and H₂O. Thus, 1,000 ppmv of O₂ will oxidize 105.26 ppmv of *n*-hexane. Since the total *n*-hexane concentration was 500 ppmv, the fraction of C₆H₁₄ oxidized was 21.05%. Because the catalyst had not been exposed to H₂S and was therefore in the oxide form, we expect that the catalyst was in a condition to have its highest activity for hydrocarbon oxidation. The fact that, even as the oxide, only 21% of the 500 ppmv of C₆H₁₄ was oxidized indicated that the catalyst has modest to low hydrocarbon oxidation activity.



The experiment depicted in Figure 4-7 was performed to compare the results to a similar experiment conducted using H₂S. If the H₂S conversion were not complete, but the O₂ consumption was, we would not be able to determine what proportion of O₂ consumption was due to sulfur formation and what portion was due to C₆H₁₄ oxidation. (This is because the apparatus was not configured to analyze for CO, CO₂ and C₆H₁₄ at these low concentrations.) However, if all of the O₂ is consumed and the sulfur mass balance (unconverted H₂S + SO₂ + S) accounts for all of the O₂, we can be reasonably certain that C₆H₁₄ oxidation is negligible. Figure 4-8 shows the results of that experiment.

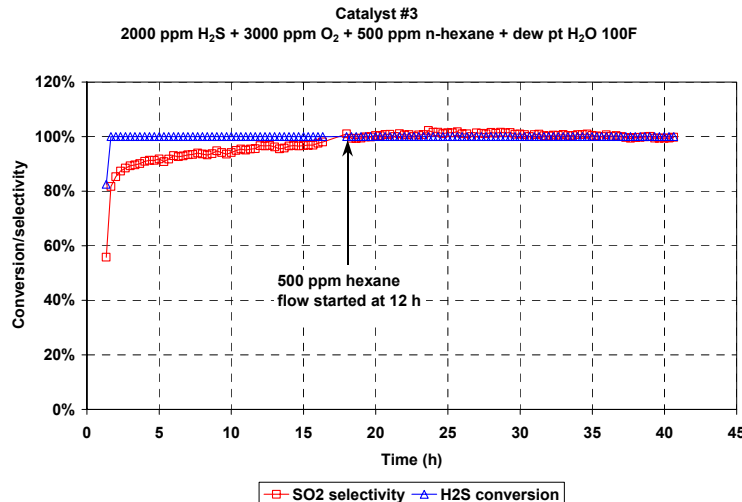


Figure 4-8. Hexane oxidation test over TDA Catalyst #3 with 2000 ppm H₂S in the feed

The test with H₂S present was carried out with a feed containing 500 ppmv of C₆H₁₄, 2,000 ppmv H₂S and 3000 ppmv O₂. Run time was about 41 hours. As in the experiment without H₂S we first established the flow of 2.7%O₂ in N₂ to give an O₂ concentration of 3000 ppmv and let the system stabilize. The flow of H₂S was then started and again the concentrations were allowed to stabilize. The pressure was 1.38 MPa (200 psig), the catalyst temperature was

250°C (482°F), the gas was humidified to a concentration that corresponded to the dew point of water at 38°C (100°F), and the space velocity was 3350 cm³_{gas}/cm³_{catalyst}/hr. This experiment ran for about 18 hours under these conditions where there was no hexane in the feed.

During the H₂S-only oxidation phase of the experiment (out to 18 hours in Figure 4-8), the H₂S conversion was 100% (within our ability to measure it). Also during this time the selectivity of the catalyst (TDA #3) slowly shifted away from forming about 10% elemental sulfur and 90% SO₂ to virtually 100% production selectivity for SO₂.

At 18 hours, the 500 ppmv hexane flow was started; by this time the SO₂ production selectivity and H₂S conversion were both essentially 100% and appeared to have stabilized. The mixed flow of gases (containing C₆H₁₄) was continued out to over 40 hours when the experiment was stopped.

Figure 4-9 shows the flow of 5% H₂S in N₂, the flow of 900 ppmv C₆H₁₄, and the O₂ concentration in the product gas exiting the reactor. The 5% H₂S and 900 ppmv C₆H₁₄ in the legend refer to the concentrations of the bottled gas; the H₂S concentration was 1,900 ppm and the C₆H₁₄ concentration was 500 ppmv over the catalyst.

Figure 4-9 shows that at about 2 hours the H₂S flow was started, and that at 18 hours the flow of C₆H₁₄ gas was started. The period between 2 and 18 hours is the H₂S oxidation only phase of the experiment, and during the time period between 18 and about 46 hours, H₂S oxidation occurred in the presence of C₆H₁₄.

Figure 4-9 also shows the output of the paramagnetic O₂ sensor that is in line with the product gas exit.

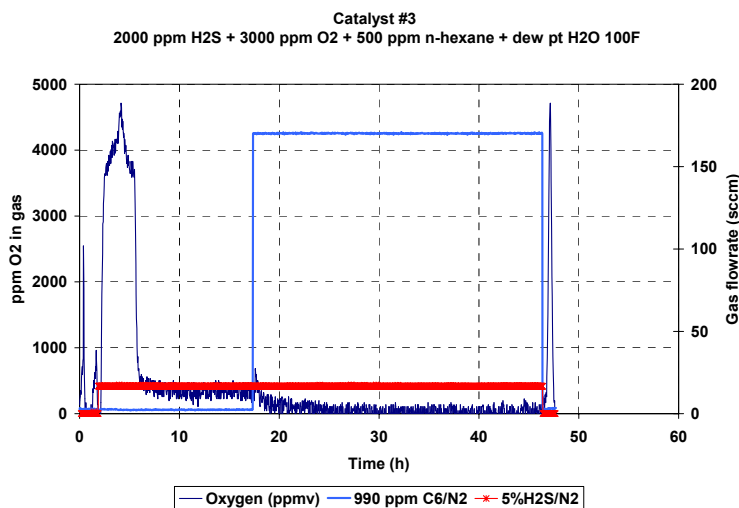


Figure 4-9. Oxygen in product gas during hexane oxidation test over TDA Catalyst #3 with 2,000 ppmv H₂S in the feed

The spike in the O₂ concentration between about 2.8 and 5.5 hours was due to the flow changes when switching on the gases and adjusting the flowrate of the gases already on line. Between 5 and 18 hours, some O₂ slip appeared to be occurring (500 ppmv), and when the hexane flow was started, all of the O₂ was consumed. Importantly, there was no change whatsoever in the H₂S conversion or SO₂ production selectivity during the run (see Figure 4-8) which suggests that only a small amount of extra O₂ needs to be added to the feed gas if hydrocarbons are present. If only 500 ppmv of O₂ was consumed by the hexane, then in the presence of H₂S only 50 ppmv of hexane is oxidized which represents only 10% of the original hexane in the feed. Thus we concluded that hexane is much less reactive than H₂S over the catalyst under these conditions.

Table 4-2 summarizes the catalyst test results previously reported along with the results for the tests in which *n*-C₆H₁₄ was added.

Table 4-2. Summary of catalysts and TDA #3 catalyst with hexane in feed

Catalyst	O ₂ /H ₂ S	T (°C)(°F)	P MPa(psig)	GHSV (h ⁻¹)	HC added to feed	H ₂ S conversion (%)	SO ₂ yield (%)	Sulfur yield (%)
TDA #1	1.0	250 (482)	1.72 (250)	1910	10% CH ₄	70	27	43
TDA #2	1.0	250 (482)	2.07 (300)	3350	10% CH ₄	96	69	27
TDA #2	1.5	250 (482)	2.07 (300)	3350	10% CH ₄	100	92	8.6
TDA #3	1.0	250 (482)	2.07 (300)	3350	10% CH ₄	100	74	26
TDA #3	1.5	250 (482)	2.07 (300)	3350	10% CH ₄	100	94	6
TDA #3	1.5	250 (482)	2.07 (300)	3350	10% CH ₄	100	96+	4
TDA #3	1.5	250 (482)	1.38 (200)	3350	500 ppm <i>n</i> -hexane	100	≈100	0

The results with the 500 ppmv *n*-hexane in the feed clearly indicate that hexane oxidation is suppressed during H₂S oxidation. At most we observed that 50 ppmv out of 500 ppmv of the hexane in the feed appeared to be oxidized. In earlier work we showed that methane is inert as it passes over the catalyst. Hexane represents the most reactive of the C1 to C6 series of alkanes. Since hexane exhibits low reactivity under H₂S oxidation conditions, and more importantly, does not change the SO₂ production selectivity, we concluded that the C1 to C6 hydrocarbons should not significantly interfere with the oxidation of H₂S to SO₂.

4.4 Effects of BTX Contamination on Catalyst Performance

As described previously in this report, both TDA #2 and TDA #3 catalysts gave excellent yields of SO₂ when the O₂/H₂S ratio was 1.5 with no O₂ slip. While TDA #3 gave a slightly higher SO₂ yield, the promoter in TDA #2 is significantly less costly than the promoter used in

TDA #3, and thus TDA #2 is a much more economical catalyst. For this reason, we concentrated development efforts on TDA #2 catalyst for the pilot testing.

Figure 4-10 shows the catalyst temperature, system pressure and the concentration of O₂ in the gas as a function of time for the experiment with 4400 ppmv of toluene added. Initially the H₂S + O₂ + N₂ + H₂O vapor feed was sent through a line that bypasses the reactor to measure the initial concentrations. The figure shows that the initial O₂ concentration was 0.3% (3000 ppmv) as desired. It also shows that the catalyst temperature (225°C, 437°F) and system pressure (1.90 MPa, 275 psig) were stable during this time.

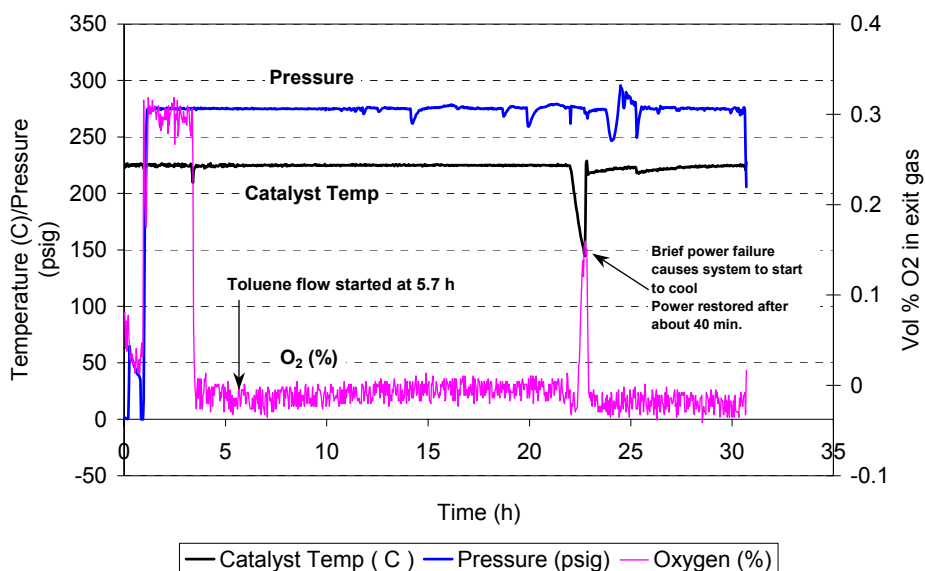


Figure 4-10. Pressure, catalyst temperature and vol % O₂ in exit gas during test with toluene

Four hours into the run, the flow was switched to pass over the catalyst in the reactor. Within a few minutes, the O₂ concentration dropped to zero indicating complete consumption of the 3000 ppmv of O₂ in the feed. At the same time the H₂S concentration dropped to zero as shown in Figure 4-11. Also, the SO₂ concentration increased to about 2000 ppmv indicating that all of the H₂S was being oxidized to SO₂ with essentially no formation of elemental sulfur.

At 5.7 hours, the toluene flow was started at 0.05 mL/min. This amount of liquid gives a final toluene concentration of 4400 ppmv with the flow rates of the other gases in the feed. Soon after the introduction of the toluene, the SO₂ concentration decreased to about 1850 ppmv and the H₂S concentration increased from zero to 24 ppm. This indicates that the overall catalytic activity dropped about 1.2% and the selectivity for producing SO₂ decreased from essentially 100% to 94%. This difference suggests that either some elemental sulfur is formed when toluene is introduced into the feed, or that a small amount of the toluene itself is being oxidized.

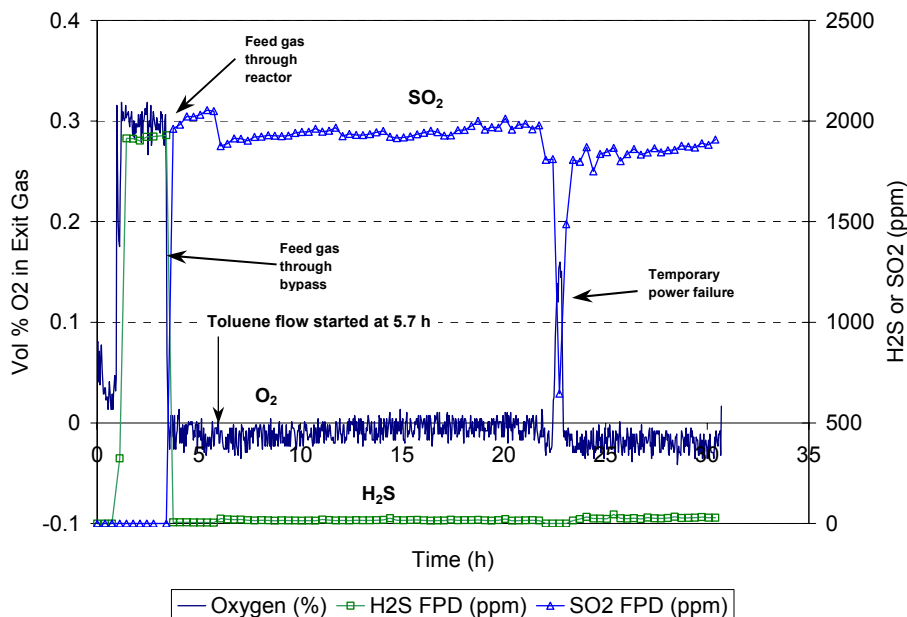


Figure 4-11. H₂S, SO₂ and O₂ concentrations during the toluene experiment

Because toluene (4400 ppmv) is present in over twice the concentration of the H₂S (2000 ppmv), it is likely that the adsorption of toluene on the catalyst competes with sites for H₂S oxidation. This could either deplete the amount of surface oxygen available for H₂S oxidation (because of toluene oxidation) or it may be that the site requirement for the H₂S → SO₂ reaction is different than the H₂S → S reaction and that toluene blocks sites needed for total oxidation. Regardless of the mechanism, it appears that the only effect of toluene is to cause a slight change in catalyst selectivity and activity, and therefore the effect of toluene on catalyst performance is minimal. This is particularly important because the experimental results suggest that BTX contamination in the natural gas will have almost no effect on the oxidation of H₂S to form SO₂ that is needed for the SO₂-production operating mode of the hybrid CrystaSulf process.

The laboratory test was continued out to 22 hours at which time there was a temporary power interruption to the laboratory building. This caused the automated apparatus to trip its safety power relays, resulting in a short time when the tube furnace was off-line. This caused the catalyst to cool down until the apparatus was reset. The cooling of the catalyst caused a drop in SO₂ level to about 800 ppmv (the H₂S increased to about 1200 ppmv). The temperature at this lowest point was about 140°C (284°F). Interestingly, even at this low temperature the catalyst performed moderately well; there was no poisoning or fouling effect of the toluene (which continued to flow), and when the temperature was restored to 225°C (437°F), essentially all of the catalytic activity was restored. Thus, the unplanned power interruption ended up providing data that suggests that the process could withstand a loss of catalyst temperature and survive such a process upset.

Note in Figures 4-12 and 4-13 that the SO₂ did not quite reach the 2000 ppmv level when the system was restarted after the power failure. This occurred because we increased the water

bubbler temperature to 85°C (185°F) in order to obtain a higher water vapor concentration at the elevated pressure. It was previously shown that as the water concentration increases, the selectivity for producing SO₂ is somewhat diminished and the overall H₂S conversion is slightly decreased. Apparently this is due to competitive adsorption of water along with the possibility of the participation of water in the Claus equilibrium. Again, for practical purposes the SO₂ production selectivity is 94% with 98% conversion, which gives a 93% yield of SO₂, and therefore water has a minimal effect at its concentration of 38°C (100°F) dew point.

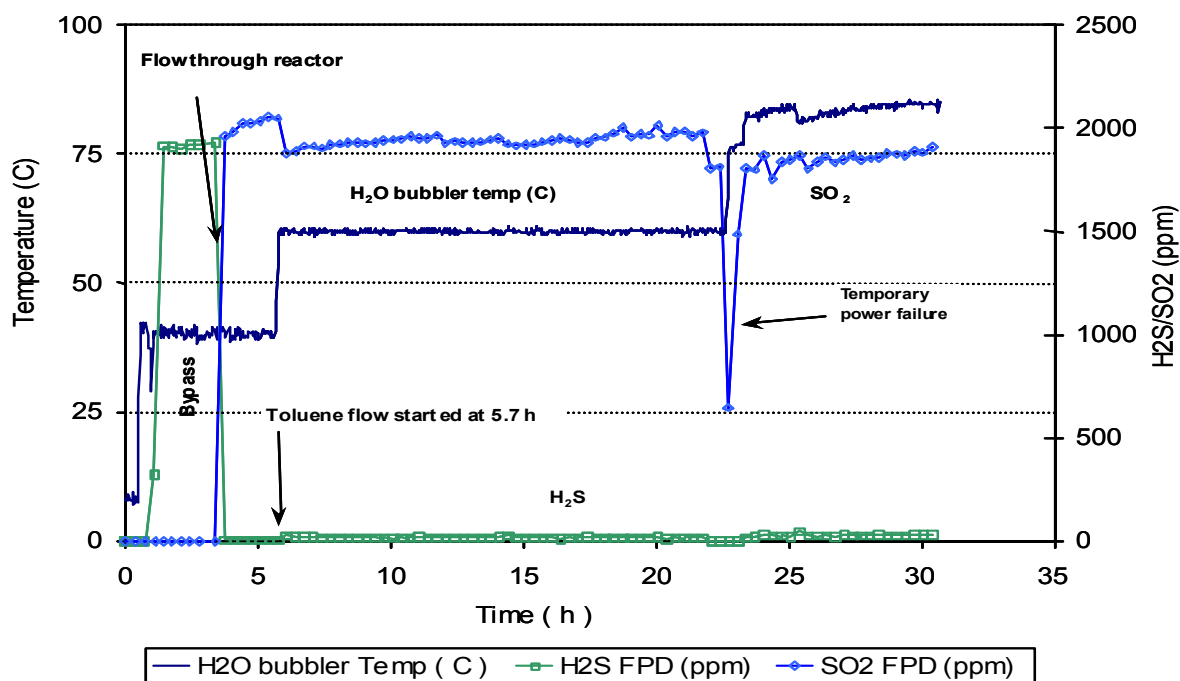


Figure 4-12. Effect of water on catalyst performance during toluene test

The conversion of H₂S, and the selectivities of TDA catalyst #2 for producing SO₂ and elemental sulfur as a function of time are summarized in Figure 4-13. The conversion of H₂S and the selectivity for producing SO₂ are known well because the concentrations of these gases are measured in the feed gas and downstream of the catalytic reactor. The selectivity for producing elemental sulfur is less certain, and for simplicity in Figure 4-13 selectivity for producing sulfur was calculated by difference (i.e., assuming that only SO₂ and sulfur are made). Based on the results of our previous work with this catalyst, we found that the oxygen balance was closed by assuming that only SO₂ and sulfur were formed. While that method was indirect, it strongly suggested that no SO₃ was made during H₂S oxidation (not much SO₃ would be expected at these low temperatures for thermodynamic reasons). Using this logic, we can infer that either a small production selectivity shift (ca 6% elemental sulfur) from SO₂ occurs when toluene is added, or that a small amount of the toluene is oxidized. We know that large amounts of toluene are not oxidized because this would consume most or all of the oxygen, and the H₂S would then pass through in large amounts (proportional to how much O₂ was consumed by the toluene). We always saw very low concentrations of H₂S in the product gas (no larger than about 20 ppmv when the toluene was flowing). Also, when the heaters were off during the

power failure, the temperature dropped to about 140°C, and not surprisingly, the production selectivity of the catalyst shifted toward making elemental sulfur. Note that at this low temperature the H₂S conversion was still greater than 95%.

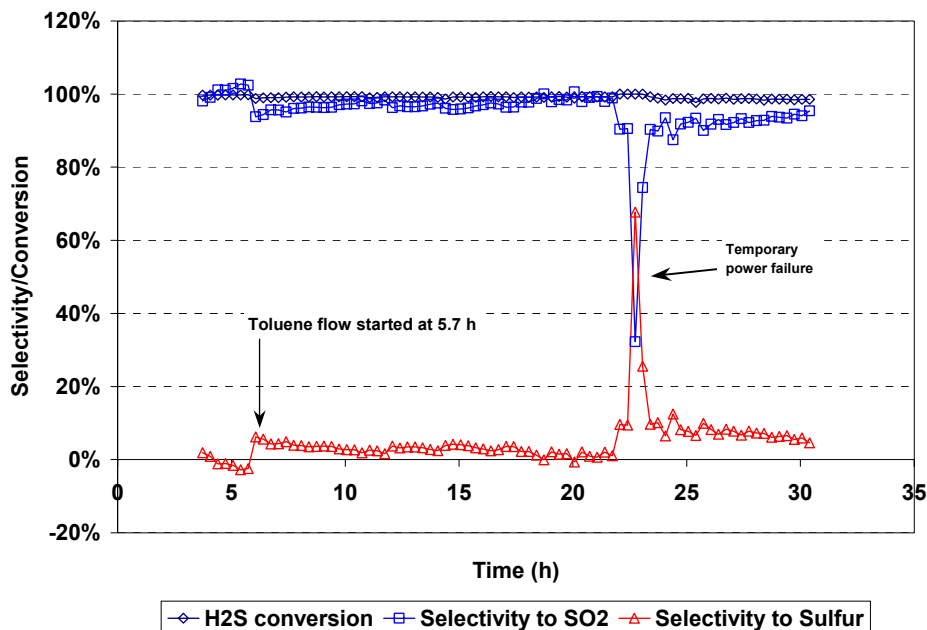


Figure 4-13. Conversion of H₂S and selectivities for producing SO₂ and elemental sulfur (by difference) during toluene test

4.5 Knockout Condensate Test Results

4.5.1 Knockout Condensate Test #1

Table 4-3 shows the experimental conditions used in the test with knockout (KO) condensate vapors. All of the experimental conditions were the same as in the toluene experiments, except that the space velocity had to be lowered to 2000 cm³_{gas}/cm³_{catalyst}/hr in the KO run because of a mass flow controller limitation that occurred because we were using 3% H₂S in N₂.

As before, the H₂S concentration was approximately 2000 ppmv and the O₂/H₂S ratio was 1.5. The pressure was 1.96 MPa (285 psig) and the catalyst temperature was 225°C (437°F). The concentrations of volatiles in the KO condensate sample were estimated based on the properties of West Texas crude oil and were not measured directly. We obtained two compositions for West Texas crude: an intermediate and a sour crude. The compositions are shown in Table 4-4. To estimate the vapor pressure and thus the concentration of volatiles in the gas stream, the composition of the crude oils was averaged, and then the dew point pressure of the mixture at 70°C (158°F) was calculated using the computer program SuperTrapp which is a

vapor liquid equilibrium program developed at the National Institute of Standards and Technology (NIST formerly National Bureau of Standards – NBS). Heptane (C₇H₁₆) was used in the case of classifications such as “saturates” when the SuperTrapp program was run.

Table 4-3. Experimental conditions during test with KO condensate vapors

Parameter	Value
H ₂ S concentration	2000 ppmv
O ₂ concentration	3000 ppmv
H ₂ O concentration	Dry
N ₂ concentration	99.5%
KO vapor concentration	Estimated = 3400 ppmv
Pressure	1.90 MPa (275 psig)
Temperature	225°C (437°F)
Amount of catalyst tested	4 gm
GHSV (at P&T)	2000 cm ³ _{gas} /cm ³ _{catalyst} /hr
Flow rate of 4%O ₂ / N ₂	107 sccm
Flow rate of 5% H ₂ S / N ₂	95 sccm
Flow rate of pure N ₂	1226 sccm
Predicted bed ΔP	0.2 psi (8.3 in H ₂ O)
Run time	50+ hours

Table 4-4. Composition used to estimate vapor pressure of KO drum condensate

West Texas Crude	Intermediate	Sour	Averaged	Compound used in SuperTrapp Calc.
API Gravity	40.8	30.2	35.5	
Sulphur (wt%)	0.48	1.5	0.99	Ignored
Saturates (wt%)	66	51	58.5	Heptane
Aromatics (wt%)	26	36	31	Benzene
Resins (wt%)	6	9		Ignored
Asphaltenes (wt%)	1	5		Ignored
Waxes (wt%)	4	5		Ignored
Benzene (ppm)	1380	3510	0.002	Benzene
Toluene (ppm)	2860	6980	0.005	Toluene
Ethylbenzene (ppm)	1120	5610	0.003	Ethylbenzene
Xylenes (ppm)	4290	4440	0.004	Ortho-xylene
C3-benzenes (ppm)	5920	7410	0.007	Cumene

The properties of the mixture at a dew point temperature of 21°C (70°F) calculated with SuperTrapp are shown in Table 4-5. The program calculated the dew point pressure at 21°C (70°F) to be P = 6.72 kPa (0.974 psia). Assuming that 6.72 kPa (0.974 psia) is the partial pressure of the condensate at room temperature, the total volatiles load in the feed gas would be about 3400 ppmv (Table 4-6).

**Table 4-5. SuperTrapp Output for KO Condensate
at T_{dp} = 21°C (70°F)**

Component	Feed	Liquid	Vapor
n-Heptane	0.653478	0.843619	6.53E-01
Benzene	0.34631	0.155133	3.46E-01
Toluene	5.59E-05	8.69E-05	5.59E-05
Ethylbenzene	3.35E-05	1.53E-04	3.35E-05
o-Xylene	4.47E-05	2.66E-04	4.47E-05
Isopropylbenzene (cumene)	7.82E-05	7.42E-04	7.82E-05
Molecular Weight	92.5555	96.7948	92.5555
Compressibility Factor	0.993808	3.78E-04	0.993808
Density (lb/ft ³)	1.60E-02	43.8864	1.60E-02
Enthalpy (BTU/lb)	-439.619	-811.685	-439.619
Entropy (BTU/lb*°F)	1.03011	7.53E-01	1.03011
Heat Capacity (BTU/lb*°F)	0.354985	4.96E-01	0.354985
Cp/Cv		1.29259	1.07E+00
Sound Speed (ft/sec)		3770.19	547.541
Joule-Thompson (°F/psia)		-5.37E-03	0.800956
Viscosity (lb/ft*sec)		2.88E-04	4.23E-06
Thermal conductivity (BTU/ft*hr*F)		0.07385	6.16E-03

Table 4-6. Concentration Estimate

Property	Value
Dew point temperature (°F)	70
Dew point pressure (psia)	0.974
Total Pressure (psia)	287.2
Concentration (ppm)	3392

Figure 4-14 shows the results for the first 50 hours of testing with the TDA #2 catalyst exposed to KO drum condensate vapors, and the experimental conditions are shown in Table 4-3. Initially, H₂S oxidation was conducted with no KO vapors in the feed, corresponding to the time between 3 and 7 hrs in Figure 4-14. During this initial time, the H₂S conversion was 100%, and the production selectivities for SO₂ and sulfur were S_{SO₂} = 91% and S_S = 9%. At about 7.6 hours into the run, the total flow was diverted so that it passed over the KO condensate in the vaporizer shown in Figure 3-7. When the KO vapors were introduced, the SO₂ production selectivity dropped to about 70% but then slowly recovered to 100% over the next 35 hours. This might have been due to slow depletion of the volatiles from the condensate sample since we were trying to simulate a continuous process using a batch method of introducing the KO vapors.

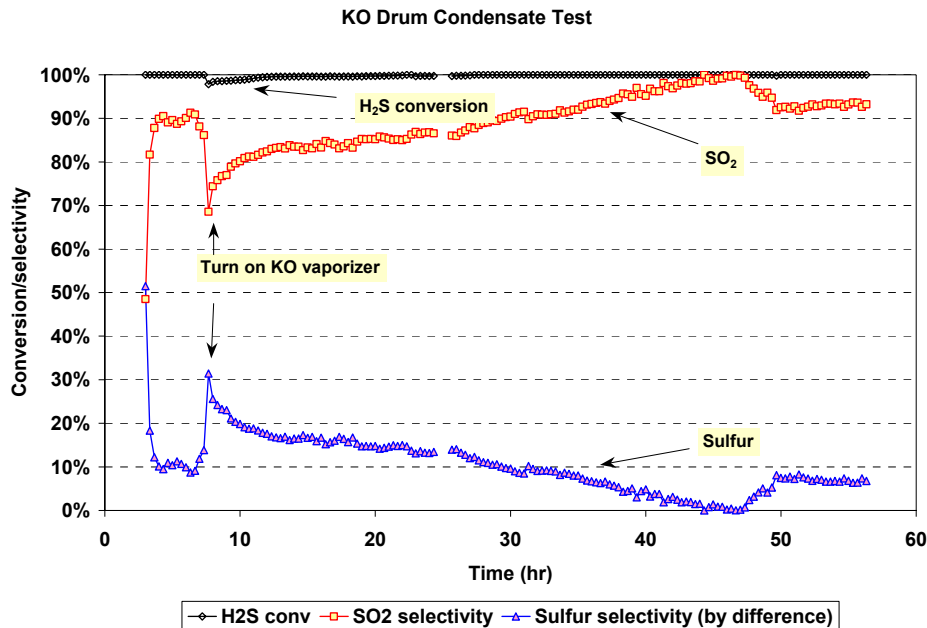


Figure 4-14. H₂S conversion and SO₂ and sulfur production selectivities when catalyst is exposed to vapors from knock-out drum condensate (first 50 hours)

Examining the data at 50 hours, there was a sharp decrease in SO₂ production selectivity to 90%. This occurred when the data were downloaded from the process control computer prior to the end of the run. During this time, control of the experiment is temporarily suspended. When control is suspended, the flow rates, temperatures and other parameter values stay latched in the electronics but there is no control. As a result the catalyst temperature briefly dropped to 217°C (423°F) that may have caused the change in SO₂ production selectivity. By 55 hours the temperature had returned to 225°C (437°F), but the catalyst had not recovered completely. It may be that there was a surge of volatiles from the KO condensate that accompanied the brief shutdown because during this time the pressure increased to 2 MPa (300 psi), and then abruptly

dropped back to 1.8 MPa (275 psi) when control was restored. The pressure and temperature traces are shown in Figure 4-15.

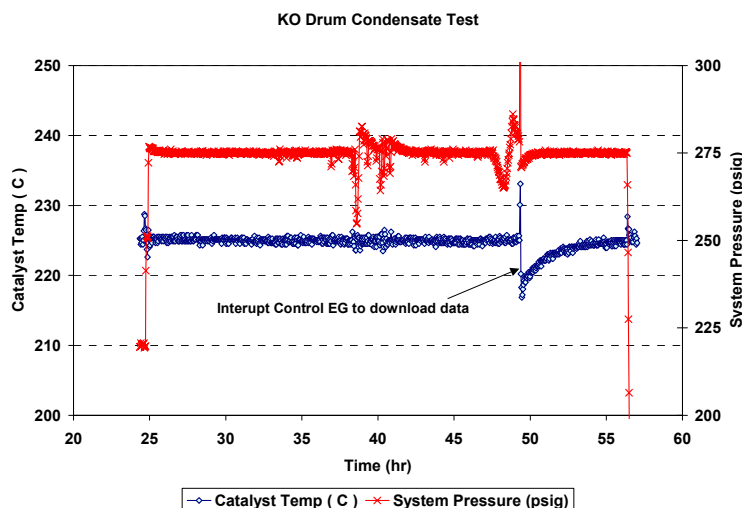


Figure 4-15. Pressure and Temperature During KO Drum Condensate Run

The gradual increase in SO₂ production selectivity with time suggests that the change in selectivity may have been due to the volatile components of the KO drum condensate slowly evaporating from the sample and therefore gradually decreasing in concentration. This was expected because we were attempting to simulate a steady state process (continuous processing of gas from the KO drum in the field application) with a semi-batch process where we charged a vaporizer with condensate.

In the commercial application the catalyst will be continuously exposed to a nearly constant concentration of volatiles from the KO drum because the gas being processed continuously brings in fresh condensate. To better simulate the continuous gas processing situation, we repeated the test two more times using a fresh charge of KO condensate for each test.

4.5.2 Knockout Condensate Test #2

Figure 4-16 shows the H₂S conversion, and production selectivities for SO₂ and sulfur during a 7 hour test with a fresh charge of KO drum condensate without replacing the catalyst (the catalyst remained in the reactor). This run was only 7 hours long so that we could determine if the initial drop in selectivity for producing SO₂ followed by a gradual increase in production selectivity that we saw in the first test (Figure 4-14) was a real effect.

The effect of initially low SO₂ production selectivity followed by a gradual increase appears to be real. During the first hour in Figure 4-14, the system was coming to steady state.

At 1 hour, the H₂S conversion was complete (this corresponds to an H₂S concentration of less than about 5 ppmv in the product gas) and the SO₂ production selectivity was 71%. This gradually increased to approximately 83% by the end of hour 7. During this time the H₂S conversion remained at 100% indicating that while the SO₂ production selectivity depended on the presence of volatile organics in the feed, there was no catalyst deactivation due to these contaminants.

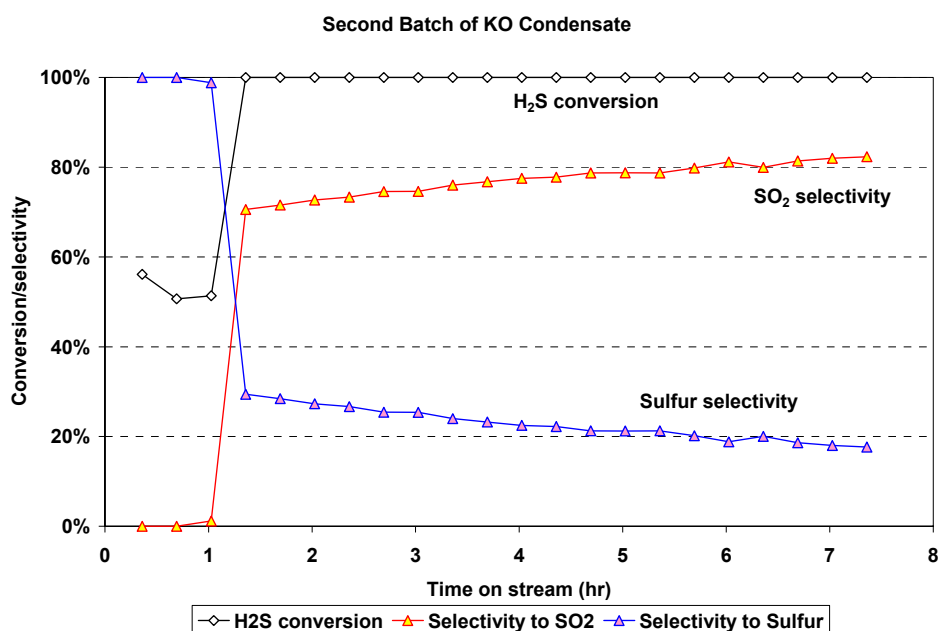


Figure 4-16. Seven hour rerun with 2nd (fresh) charge of KO drum condensate

The trend of increasing SO₂ production selectivity was observed during the first run and the fact that it occurred here as well suggests that the selectivity of the catalyst is shifted by the presence of the most volatile components in the condensate because these will be the first to evaporate. Also, the concentration of these volatiles will be highest at the beginning of the run. According to the analysis of West Texas Crude Oil (Table 4-4), it is likely that the most abundant contaminants in the early part of the test are the BTEX aromatics. These results are similar to those observed during the experiments with toluene; there was no deactivation of the catalyst in those cases either. All of the O₂ was consumed during the 2nd run with the KO condensate, and the gas flow rates, temperature and pressure were very stable.

The overall conclusion from the tests with toluene and vapors from the KO drum condensate is that none of these materials cause catalyst deactivation. The presence of these vapors does appear to affect SO₂ production selectivity, however, apparently by shifting the selectivity toward producing elemental sulfur. Little or no oxidation of the hydrocarbons is apparent because all of the O₂ fed into the system can be accounted for by the combination of SO₂ and sulfur (oxygen mass balance). Also, if O₂ were being consumed by hydrocarbon oxidation, then unconverted H₂S would break through.

4.5.3 Knockout Condensate Test #3

Figure 4-17 shows the results for a 15 hour run with a 3rd, fresh charge of KO drum condensate. As before, the catalyst was not changed out for this test. Figure 4-17 shows that there was a gradual increase in selectivity for producing SO₂ from approximately 84% up to essentially 100% during the first 10 hours of the run. Because this is the same behavior observed in the two previous runs, we concluded that this is due to evaporation and gradual loss of the more volatile components of the KO drum condensate. At 11.5 hours, the process control computer malfunctioned and had to be restarted. During the time interval, the gases were still flowing but the catalyst temperature dropped. As a result, the SO₂ production selectivity abruptly dropped to 93% at 12.8 hours.

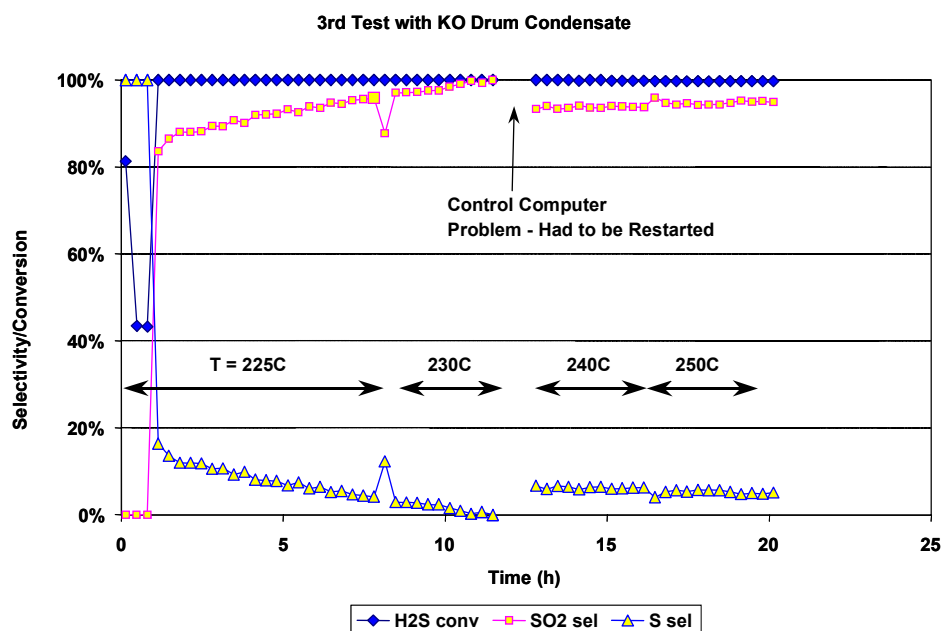


Figure 4-17. 20 hour rerun with 3rd (fresh) charge of KO drum condensate

During the first 8 hours of the 3rd batch run, the catalyst temperature was 225°C (437°F). The temperature was then increased to 230°C (446°F) over 4 hours followed by 4 hours at 240°C (464°F) and 250°C (482°F). Examining Figure 4-17 suggests that above about 230°C (446°F), the temperature had little effect on the conversion at this space velocity (2000 cm³_{gas}/cm³_{catalyst}/hr). While the computer problem just before the 240°C (464°F) portion of the experiment confused the results somewhat, it appears that operation in the 225-230°C (437-446°F) temperature range gives high selectivity for producing SO₂ with complete H₂S conversion.

4.6 Results of Bench Unit Testing with Pilot Plant Gas

A meeting was held with the host site company, Oxy Permian Ltd. in April 2002 to review plans to test the bench unit at the pilot site, to be followed by fabrication of the pilot-scale catalyst reactor and subsequent testing of that equipment at the site. The host site company agreed with the test objectives and approach and supported the test effort at their site, expressing interest in receiving the test results to allow them to evaluate potential commercial applications.

The experimental apparatus and test conditions were presented in Section 3.3.7. Results of the catalyst bench unit test with a slip stream of gas from the pilot plant are presented below.

Figure 4-18 shows the average catalyst bed temperature during the test. Because of the large total gas flow rate of approximately 7 liter/min (0.245 cfm), some of the gas preheating occurred in the reactor's three-zone furnace. In addition, the H₂S reaction is exothermic. As a result, the top of the catalyst bed was about 50°C (90°F) cooler than the bottom of the bed. As explained earlier in Section 3.3.7 and shown in Figure 4-18, the interruption that started at about 120 hours in the experiment can be seen resulting in the catalyst not being heated; the catalyst was heated back to reaction temperature at 159 hours.

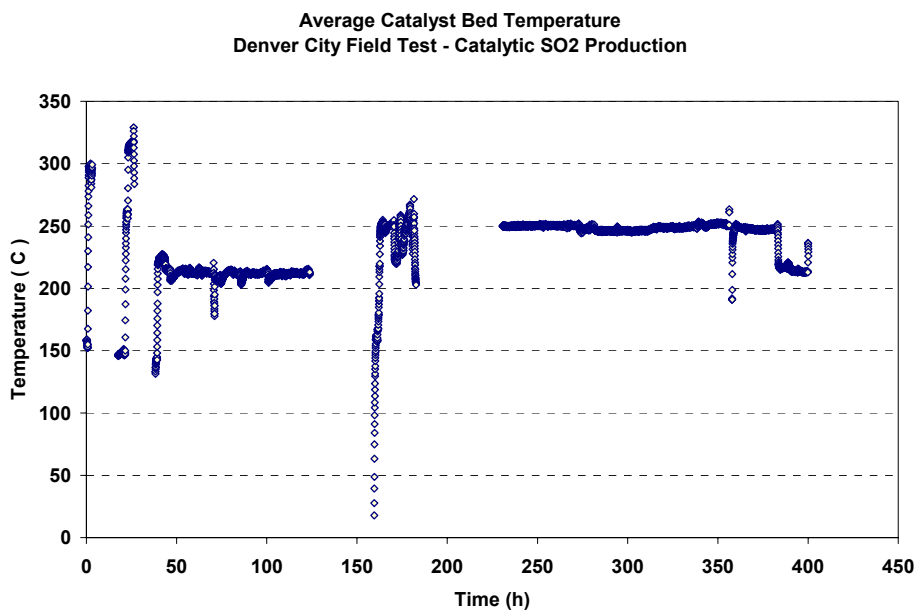


Figure 4-18. Average catalyst bed temperature

During the test, the H₂S conversion was 100% and the selectivity for producing SO₂ was > 95% (within experimental error). Figure 4-19 shows that the O₂ concentration in the product gas was at or below about 0.2 vol% (the spikes in the test occurred during the interruptions and at the end of the run when the apparatus was being shut down). The O₂ analyzer's range is 0-25 vol% (it is designed for monitoring O₂ concentrations found in oxygen depleted air) and thus

0.2% is only 0.8% of the range of the instrument. Thus, within the accuracy of the O₂ analyzer, a reading of 0.2% corresponds to almost no O₂.

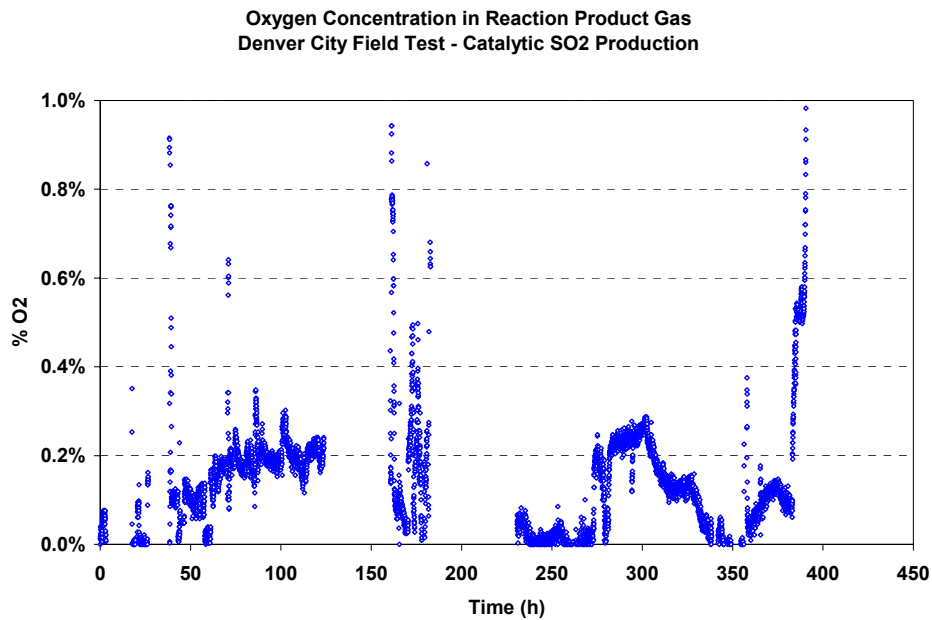


Figure 4-19. Oxygen concentration in the catalytic reactor product gas

Figure 4-20 shows the pressure trace during the experiment. As before, the interruptions in the run where the experiment was temporarily shut down are apparent. The disturbances in the system pressure around 260 hours are due to the operator readjusting the valve and correcting control wind-up problems. For the majority of the time, however, the pressure was constant at ca. 2.07 MPa (300 ± 2 psig).

Figure 4-21 shows the stability of the other heated sections of the apparatus (preheaters, PCV bypass, reactor bypass, etc.) during the run. As before, the interruptions are apparent. During the first 175 hours, the preheater temperatures were maintained at about 175°C (347°F) and during this time the temperature difference between the top and bottom of the catalyst bed was more than 50°C (90°F). Therefore, at 225 hours the preheaters were maintained at 200°C (392°F). This minimized the amount of gas preheating that had to occur in the tube furnace housing the catalytic reactor and decreased the temperature difference between the top and bottom of the catalyst bed.

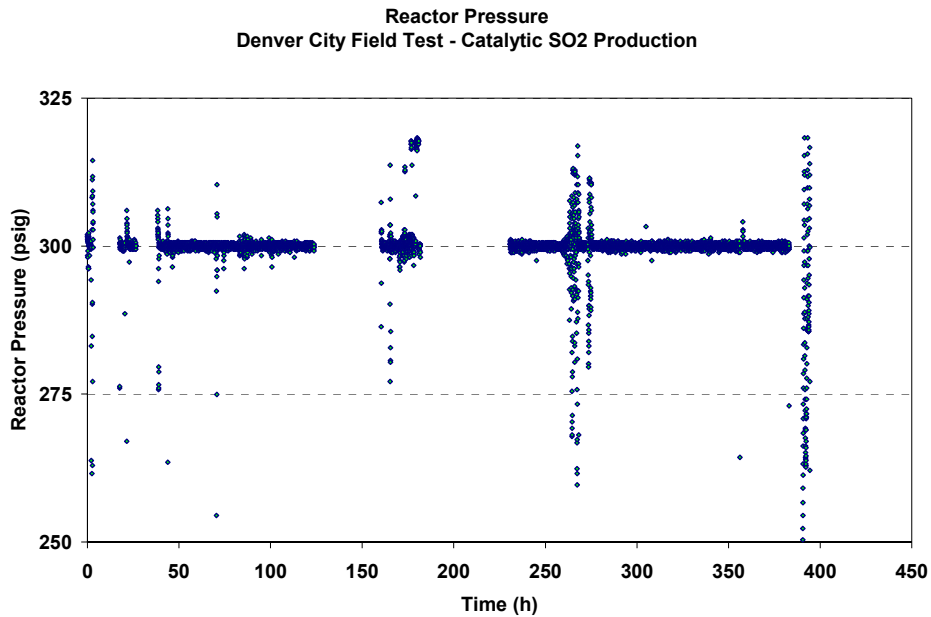


Figure 4-20. Reactor pressure during Denver City field test

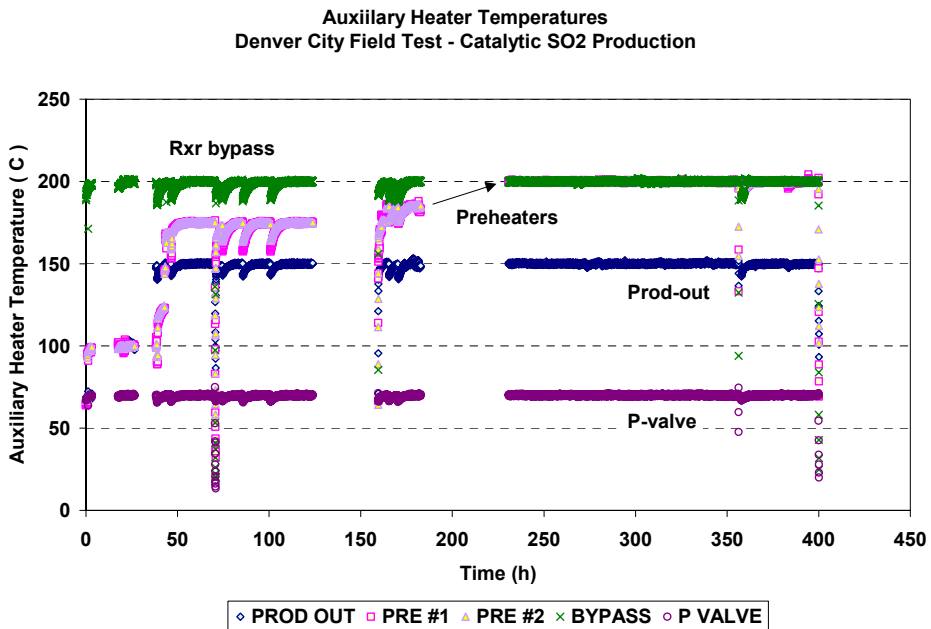


Figure 4-21. Temperatures of preheater, outlet, bypass and other heat traced lines

Figure 4-22 shows the yields of SO₂, elemental sulfur and COS during the first 150 hours of the run. Within experimental error, the SO₂ yield was better than 99%. A small amount of

COS was also detected and was presumably made by the reaction between H₂S and CO₂. COS had not been calibrated and we estimated that its concentration was no more than a few percent of the total sulfur. The elemental sulfur yield was calculated by difference (i.e., H₂S forms only SO₂ or sulfur based on the O₂ balance in laboratory work, which showed that SO₃ is not formed over this catalyst under similar conditions).

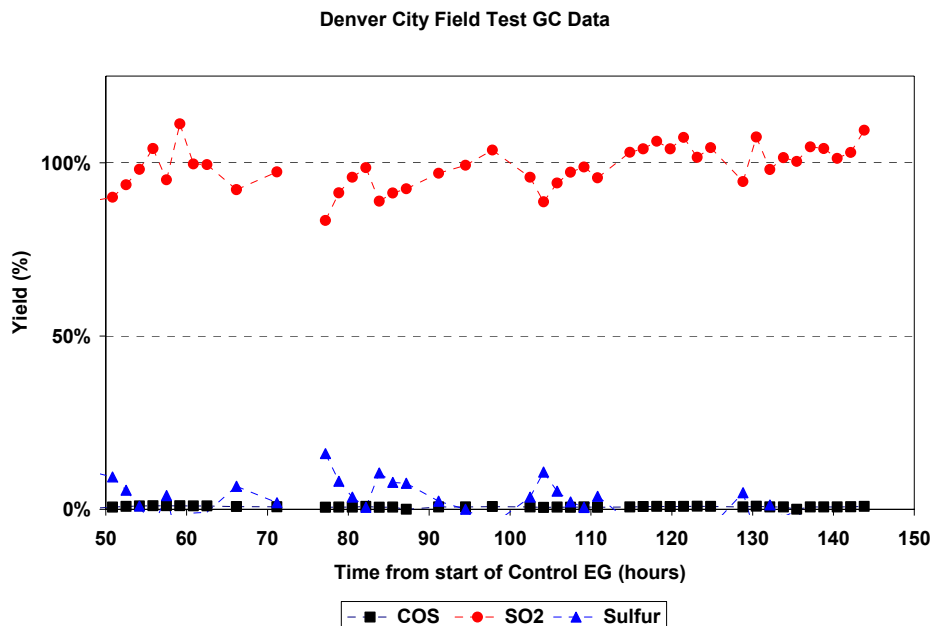


Figure 4-22. Yield of SO₂, elemental sulfur and COS during first 150 hours of test as determined by gas chromatographic analysis

The large fluctuations in the SO₂ and COS yields apparent in Figure 4-22 were due to minor pressure fluctuations in the GC sample loop. As the process gas pressure from the plant (nominally 2.24 MPa, or 325 ± 25 psig) fluctuated, the pressure in the reactor system (controlled at 2.07 MPa, or 300 psig) also fluctuated. At a set-point pressure of 2.07 MPa (300 psig), there was not much pressure difference between the Oxy plant gas source and the reactor system. This made pressure control with the PCV somewhat more difficult and permitted fluctuations in the Oxy source pressure to propagate through the catalyst test apparatus while the PCV tried to compensate for the fluctuating inlet pressure. This caused the pressure in the GC sample loop to fluctuate and the amount of gas injected into the GC to vary slightly depending on the pressure in the loop at the time of the injection (the loop is a fixed volume of 1 cm³). At higher pressures more moles of gas are present in the loop and the concentration appears to be high because the GC is calibrated at a fixed sample loop pressure. If the pressure during the injection is different from the calibration pressure because of a system pressure fluctuation, the reading will be off. For an ideal gas in a 1 cm³ loop, the error is about 3% per psi (1 psi is 6.895 kPa).

To compensate for the inaccuracies introduced into the GC analysis by fluctuations in the source pressure, the gas exiting the reactor was also analyzed using stain tubes such as Sensidyne tubes. Stain tubes use a colorimetric indicator that reacts with the H₂S or SO₂ and changes color.

A bag sample of the gas was obtained. Then a fixed volume manual pump was used to take a sample from the bag. Results were adjusted for altitude. The absolute accuracy of the tubes is about ± 10 percent. One advantage of the stain tube method over GC is that a more average sample is obtained; with GC one gets a “snapshot” for each analysis that has a cycle time of about 20 min.

Figure 4-23 shows the H₂S concentration at the inlet to the reactor, and the SO₂ concentration at the outlet of the reactor over the course of the test at Denver City. The average inlet H₂S concentration was 1928 ppmv and one measurement of the outlet concentration of H₂S gave a reading of 2.5 ppmv. Therefore, the H₂S conversion is 100% within experimental uncertainty. The average SO₂ concentration in the product gas was 1812 ppmv, which corresponds to an average production selectivity of 98.9% for SO₂ and 1.1% for elemental sulfur (by difference). The selectivity for producing SO₂ is plotted in Figure 4-24, which for practical purposes indicates that only SO₂ was produced by TDA’s oxidation catalyst under the conditions of the test.

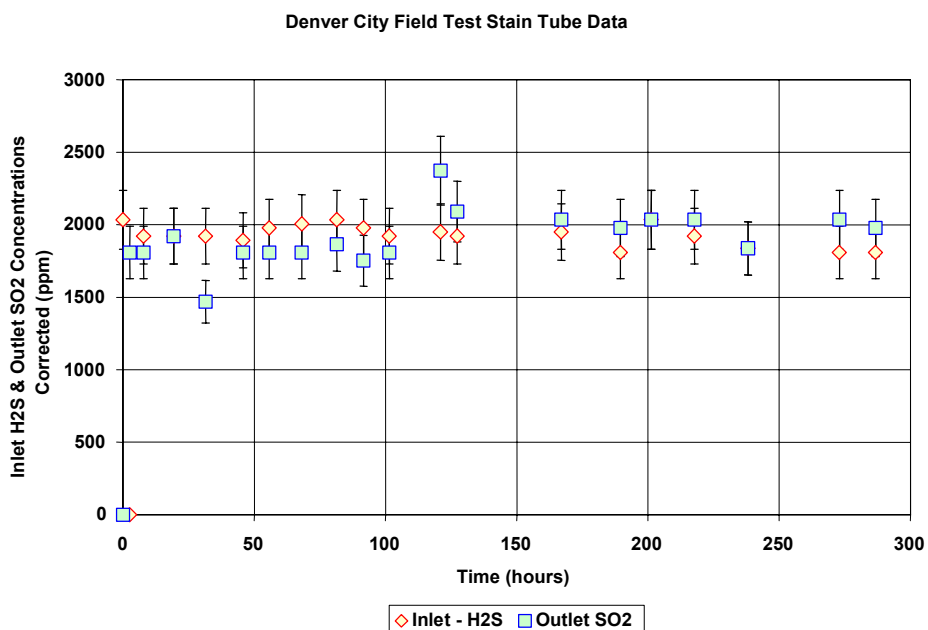


Figure 4-23. H₂S and SO₂ concentrations in product gas exiting catalytic reactor determined using stain (Sensidyne) tubes

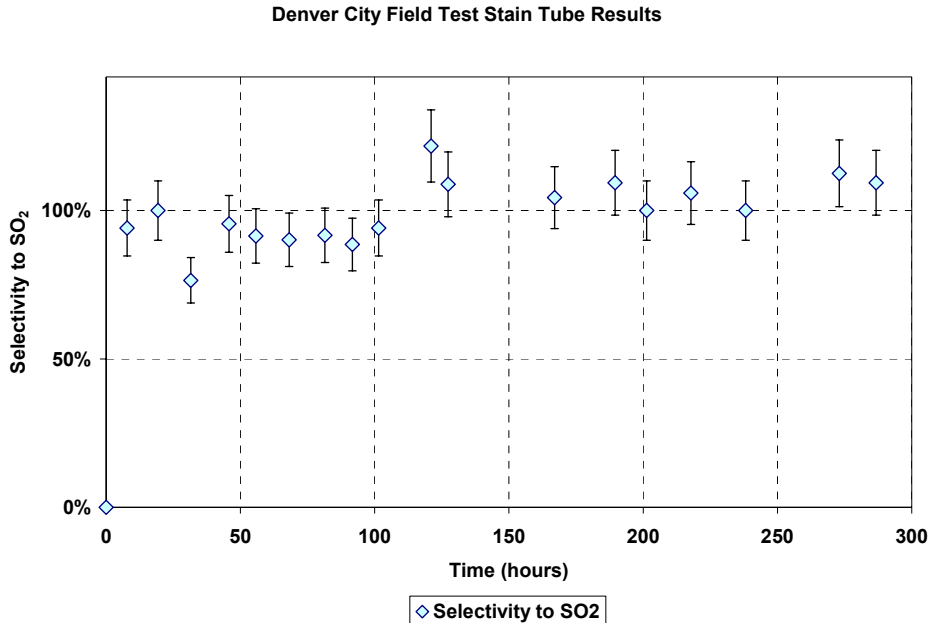


Figure 4-24. Selectivity for producing SO₂ determined from Sensidyne tube gas analysis

4.7 Economic Assessment of Scale-up to Onshore and Offshore Locations

During the project CrystaTech developed and refined the engineering and economic analyses to evaluate the benefits of using CrystaSulf in conjunction with upstream catalytic oxidation. As results from previous catalyst testing tasks became available, the focus moved toward using a direct oxidation catalyst upstream of CrystaSulf -- i.e., the CrystaSulf-DO process.

4.7.1 Economic Assessment of Ultra-Deep Gas Sulfur Recovery

An economic assessment was made to evaluate the use of the hybrid CrystaSulf process for removing H₂S from ultra-deep natural gas resources. Ultra-deep gas generally refers to gas produced from reservoirs at depths greater than 5330 m (17,500 feet). Ultra-deep gas is emerging as an area of unconventional gas that is of particular interest. Deep gas is found offshore in the Gulf of Mexico, in much of the mid-continent, and elsewhere.

Ultra-deep reserves tend to be gas, not oil, as oil is unstable at the temperatures and pressures involved. Due to the high pressures at the depths involved, the density of the gas is very high and as a result, the amount of fuel energy per unit volume is very high. This feature of ultra-deep reserves gives rise to high production rates and large reserves per well/field. Flow rates of 536,000-1,610,000 Nm³ per day (20-60 MMscfd) per well are common.

Data on the composition of natural gas reserves worldwide is spotty at best. As much as 25 percent of the gas produced in the U.S. may contain H₂S, and worldwide the percentage may be as high as 30 percent. In Canada, the Alberta Energy and Utilities Board (EUB) reports that 30% of the gas in Alberta is sour, and Alberta accounts for 80% of the gas production in Canada. Clearly, a significant portion of the world's natural gas resources is sour with H₂S.

A common trend in gas produced from shallow- to medium-depth reservoirs has been that if it is sour with H₂S the deeper the well the more sour the gas. Occasionally gas with 5-30% H₂S has been found. While there have been relatively few ultra-deep wells drilled to date, public and private confidential data on H₂S concentration indicates that much of this ultra-deep gas may be only slightly to moderately sour. H₂S levels from hundreds of ppmv to a maximum of 2-3% appear to be the norm for sour wells deeper than 5330 m (17,500 feet). The high pressures and temperatures of these reservoirs not only tend to make them produce gas versus oil, but also to have lower H₂S levels than one might expect. Figure 4-25 shows the H₂S concentration distribution for ultra-deep sour gas wells in Texas. This data came from the Texas Railroad Commission H-9 forms, which producers must file when they encounter sour gas. Definitive information is not available regarding how much of ultra-deep gas is sweet, but private industry information indicates that much of it is slightly sour. Around 80% of the sour ultra-deep gas found in Texas has H₂S levels between 100 ppmv and around 1% (10,000 ppmv).

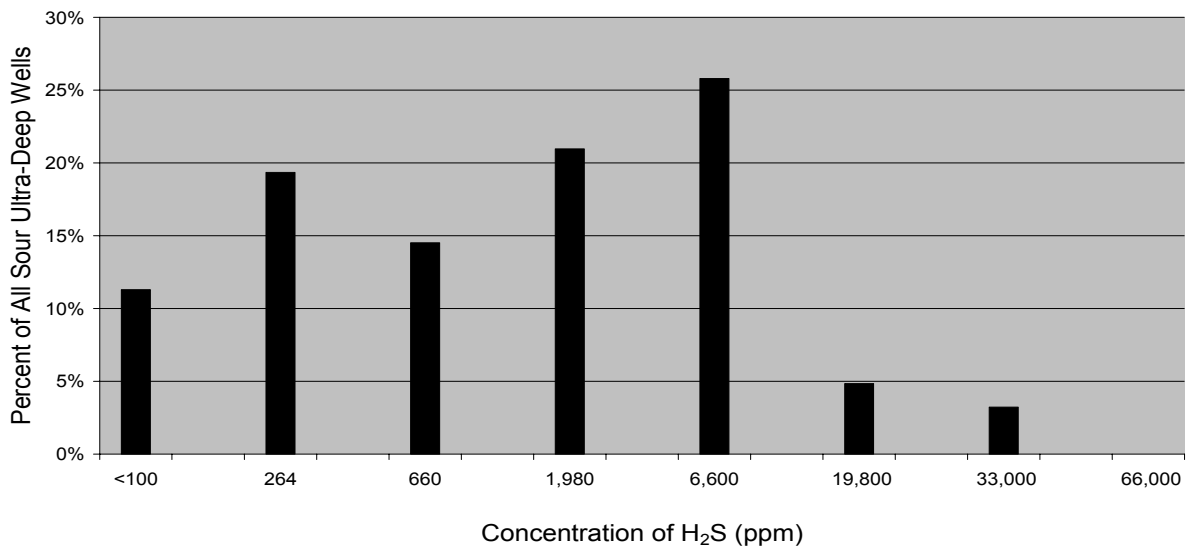


Figure 4-25. H₂S Concentration Distribution for Sour Ultra-Deep Gas Wells in Texas

Pipeline specifications generally require that CO₂ be less than 2-3%. Often there is a specification for total inerts, and in that case CO₂ contributes toward that value. Figure 4-26 shows the CO₂ concentration distribution in U.S. natural gas as measured in a survey conducted by the American Petroleum Institute (API) in the early 1980's. Most U.S. natural gas (85%) has less than 2% CO₂. Comprehensive information of CO₂ levels in ultra-deep natural gas is not available. A reasonable assumption is that it is similar to the levels shown in the API data. Private industry information from limited sources supports that assumption. It appears that CO₂

removal will not be required for much of the gas from ultra-deep reservoirs. If removal is required, likely only a portion of the CO₂ would need to be removed. For example, if the CO₂ level was 2.5% and the specification was 2%, less than one-third of the CO₂ would need to be removed.

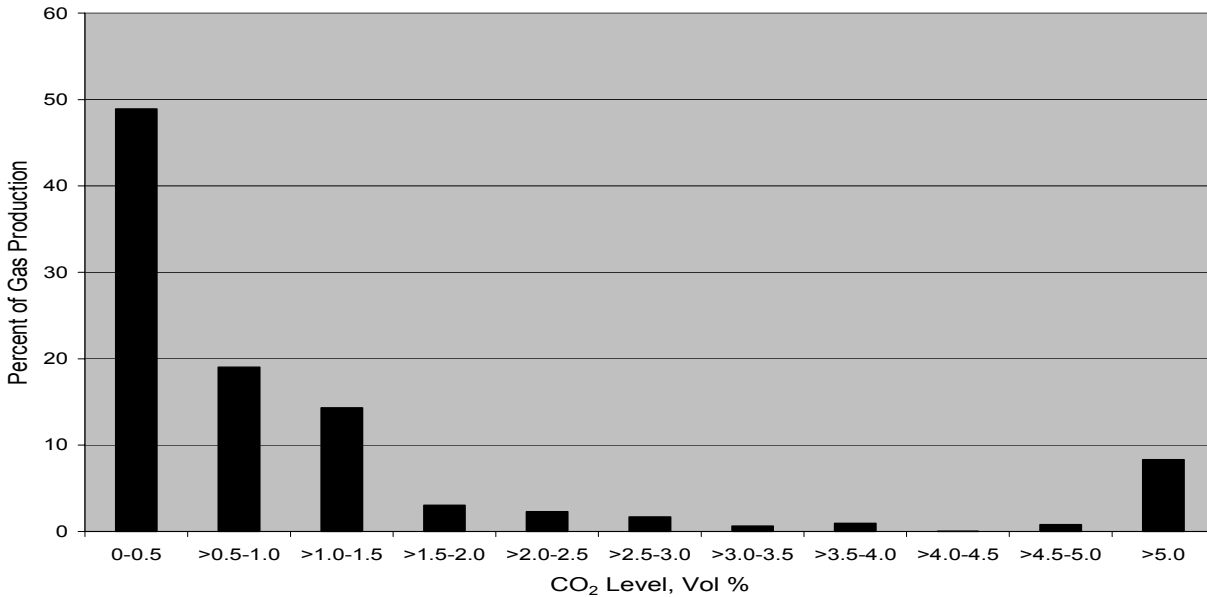


Figure 4-26. CO₂ Content of U.S. Natural Gas, API Survey of U.S. Natural Gas Production

Figure 4-27 compares the total treating cost to remove sulfur from 1.1×10^6 Nm³/day (40 MMscfd) of 6.9 MPa (1000 psi) natural gas for the gas concentrations shown in Figure 4-25 for two traditional approaches (amine/Claus/tailgas and amine/aqueous iron redox) and then for CrystaSulf and for CrystaSulf – DO. In this analysis, the mode of the hybrid CrystaSulf-DO process used is the one where the predominant product of the catalyst is elemental sulfur. The “SO₂” mode was not competitive with the other options for the sulfur loadings of the study. Use of direct oxidation catalyst to form sulfur upstream of CrystaSulf greatly reduces the sulfur load on the CrystaSulf plant and the associated processing cost. The H₂S concentrations used in the figure correspond to 0.3 – 50 TPD sulfur throughputs as shown in the figure. CrystaSulf offers cost benefits over traditional technology in the liquid redox niche of 0.2 to 20-25 TPD, but “runs out of steam” at 30-50 TPD versus amine/Claus/tailgas. The CrystaSulf-DO hybrid process in this configuration reduces the cost of CrystaSulf substantially for applications containing over approximately 2-3 TPD sulfur. The result is a very beneficial effect on CrystaSulf cost in the traditional liquid redox niche, and also the ability to lower processing costs versus the next best traditional approach, amine/Claus/tail gas at 30 TPD, 50 TPD, and beyond

Table 4-7 compares the treating costs at 1 TPD and 5 TPD for amine/aqueous iron redox versus CrystaSulf and CrystaSulf-DO. These costs are the same as were shown in Figure 4-27, but are difficult to compare on the figure due to the scale. CrystaSulf offers an 8% savings versus amine/aqueous iron redox at 1 TPD (the benefit here is primarily operating reliability). At

5 TPD the benefit is over 30%. The benefit for the CrystaSulf-DO configuration versus amine/aqueous iron redox for these two tonnages is 30% and 61%, respectively. Table 4-8 compares treating costs for amine/Claus/tailgas versus CrystaSulf and CrystaSulf-DO for plant sizes from 10 to 100 TPD. CrystaSulf offers a 20% cost benefit at 10 TPD, but at 30 TPD and above is more expensive than the amine/Claus option. CrystaSulf-DO, by contrast, continues offers cost savings of over 60% at 10 TPD to around 50% at 100 TPD. These CrystaSulf-DO cost estimates were prepared using very conservative costing assumptions for handling sulfur dew point.

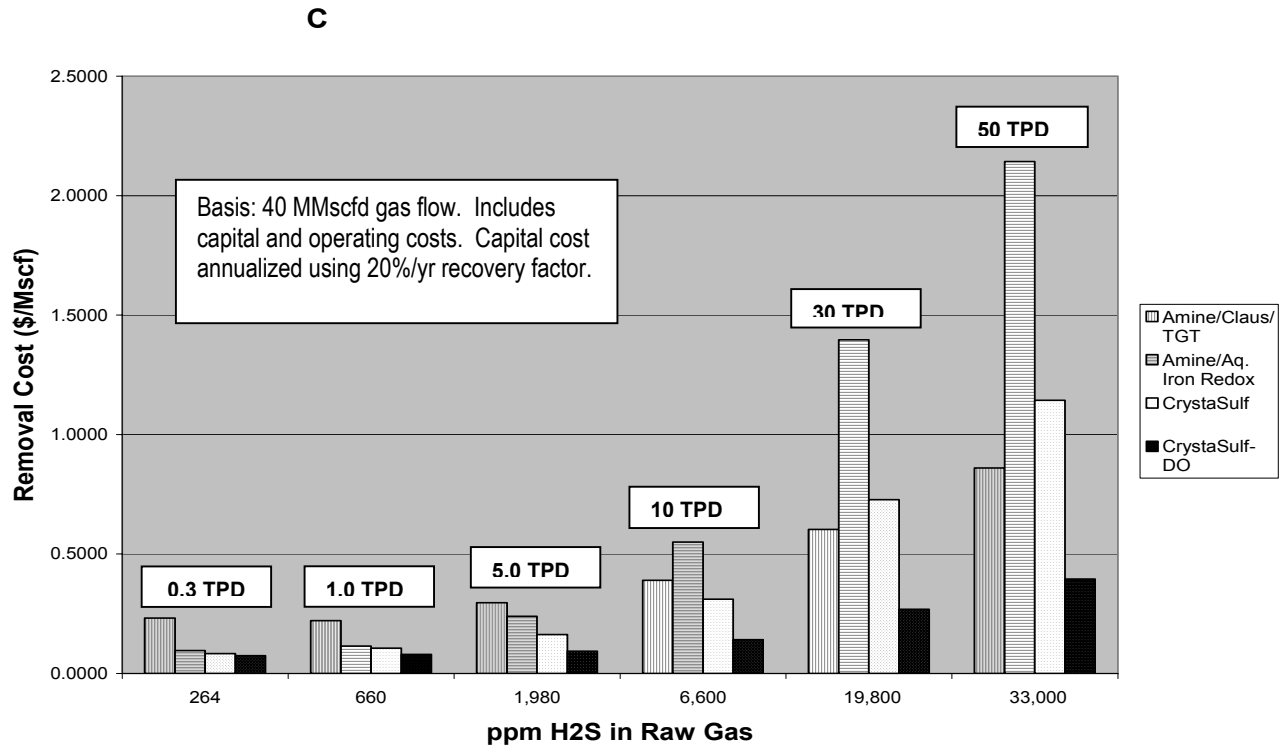


Figure 4-27. Cost to Remove H₂S from 6.9 MPa (1000 psi) Natural Gas

Table 4-7. Treating Costs for Removing 1 and 5 TPD Sulfur from Natural Gas*

Sulfur TPD	Amine/Aqueous-Iron Redox	CrystaSulf	CrystaSulf-DO
Total Treating Cost in \$/ Mcf			
1	0.115	0.106	0.080
5	0.239	0.163	0.093
Total Treating Cost in Percent			
1	100%	92%	70%
5	100%	68%	39%

* Basis: Treating 1.1x10⁶ Nm³/day (40 MMscfd) natural gas at 6.9 MPa (1000 psi)

Table 4-8. Treating Costs for Removing 10, 30, 50, & 100 TPD Sulfur from Natural Gas*

Sulfur TPD	Amine/Claus/ Tailgas	CrystaSulf	CrystaSulf-DO
	Total Treating Cost in \$/Mcf		
10	0.390	0.311	0.141
30	0.602	0.727	0.268
50	0.860	1.143	0.395
100	1.397	2.183	0.744
	Total Treating Cost in Percent		
10	100%	80%	36%
30	100%	121%	45%
50	100%	133%	46%
100	100%	156%	53%
* Basis: Treating 1.1x10 ⁶ Nm ³ /day (40 MMscfd) natural gas at 6.9 MPa (1000 psi)			

The Energy Information Administration (EIA) publication “International Energy Outlook 2002, Natural Gas” (from EIA’s website) gives historical and projected natural gas demand values for North America. EIA provided natural gas consumption values/estimates in TCF per year for 1999, 2005, 2010, and 2015. Interpolating, one can estimate that North American natural gas consumption per year will increase from 29 TCF in 2003 to 36 TCF per year in 2013. This would mean that over the 10-year period 2004 through 2013 an incremental 39 TCF of new natural gas would be produced.

Estimating how much of this 39 TCF will be sour is difficult. If 25% of the 39 TCF of new North American gas production were sour, then approximately 10 TCF of new sour gas would be produced in North America over the 10-year period 2004 through 2013. The estimated savings shown in Tables 4-7 and 4-8 for using CrystaSulf or CrystaSulf-DO depending on the plant size are substantial on an individual plant basis. Furthermore, they represent large savings for industry as a whole when applied to amounts of gas in the TCF range. For example, a savings of \$0.10/Mcf corresponds to \$100,000,000 for 1 TCF of gas.

4.7.2 Comparative Economics for CrystaSulf and CrystaSulf-DO Versus Other Options for Desulfurizing High-Pressure Natural Gas

Additional economic analysis performed during this project has better defined the niche for CrystaSulf and CrystaSulf-DO compared to common treating options for H₂S removal from high-pressure natural gas. Again, the CrystaSulf-DO mode shown is where the catalyst section produces primarily sulfur. Figure 4-28 compares the total treating cost in \$/Mscf for the following approaches:

- Liquid scavenger in direct injection;
- Solid scavenger in tower;
- Amine/aqueous redox;
- Amine/Claus/TGT;
- CrystaSulf; and
- CrystaSulf-DO.

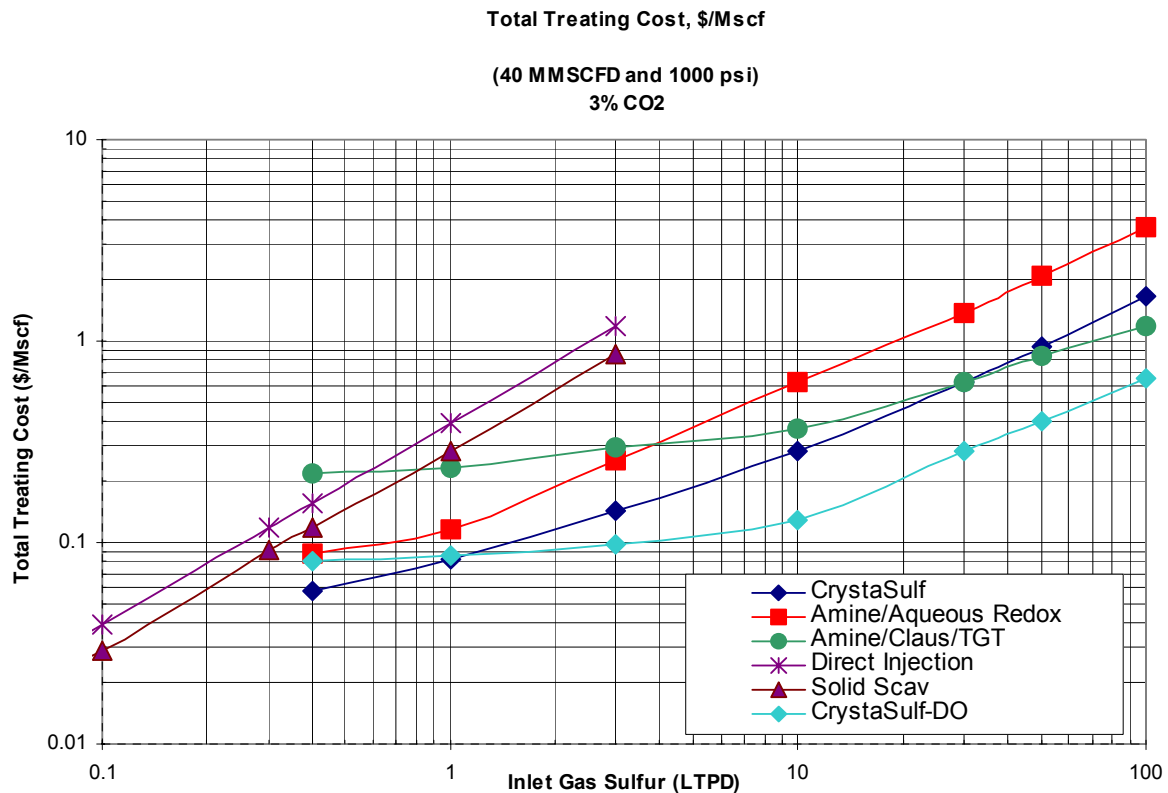


Figure 4-28. Total Treating Cost for H₂S Removal Options, \$/Mscf

For this analysis, it was assumed that the gas stream had a flowrate of 1,130,000 Nm³ per day (40 MMscfd) and was treated at 6.9 MPa (1000 psig). The H₂S level was varied to generate different plant sizes (in LTPD). The CO₂ level was assumed to be 3% and no CO₂ removal would be required. Since CO₂ level has a significant impact on amine/aqueous redox and amine/Claus/TGT costs, special attention was given to normalizing earlier cost data for these approaches to 3% CO₂. Cost values for different plant sizes and CO₂-to-H₂S ratios were plotted and then regressed to give the estimated value at 3% CO₂. These values differ slightly from earlier estimates, but are thought to provide the best comparative information.

Note that the costs on Figure 4-28 are on a log-log scale, so relatively small differences on the figure can be relatively large on an absolute basis. This figure clearly illustrates the CrystaSulf niche of approximately 0.2 to 25 LTPD sulfur throughputs. Below 0.2 LTPD, scavenging is more cost effective; above 25 LTPD amine/Claus/TGT is the lowest cost option. Amine/aqueous redox is never the lowest cost option. Further, this figure illustrates that CrystaSulf-DO can be the lowest cost option for all plant sizes greater than 1 LTPD. At some large plant size amine/Claus/TGT will be less expensive than CrystaSulf-DO, but that size is clearly well above 100 LTPD.

4.8 Pilot-Scale Demonstration and Development of Commercialization Plan for Hybrid Process (CrystaSulf-DO)

Based in part on the results of this program, CrystaTech has decided to proceed with the commercialization of hybrid CrystaSulf process. The process has been named “CrystaSulf-DO” for future development and catalyst selection and catalyst section operating conditions will emphasize modes of operation which produce primarily elemental sulfur (versus SO₂) in the catalyst bed. This section outlines ongoing initiatives to advance the CrystaSulf-DO hybrid process toward commercialization.

4.8.1 Selection of Direct Oxidation Hybrid Process Mode

Based on the results of the economic analysis as well as the laboratory and pilot test results for the TDA catalysts, CrystaTech concluded that the use of sulfur producing catalysts and bed conditions direct oxidation catalyst rather than an SO₂-producing catalyst provides far greater benefits for CrystaSulf applications and economics. These types of catalysts are often referred to as “direct oxidation” catalysts. (They are also called “partial oxidation” catalysts.) In this mode, the catalyst will convert 80-95% of the inlet H₂S directly to sulfur, and a portion of the remaining H₂S to SO₂, thereby meeting the H₂S to SO₂ stoichiometry requirement for CrystaSulf. The combination of direct oxidation catalyst and CrystaSulf is a substantially lower cost hybrid process than that obtained with catalyst that produces primarily SO₂. While the combination of CrystaSulf and SO₂ catalyst lowers the total treating cost approximately 10-15%, more recent economics show that using a direct oxidation catalyst can lower the total treating cost 50-60%. This economic advantage is possible because the catalyst section serves as a bulk removal step at very low operating cost; thus the CrystaSulf absorber only has to remove about 10% as much H₂S and, as a consequence, the back end of the process is only about 10% as large.

Thus, exploration of future testing options was expanded to include the combination of direct oxidation catalyst with CrystaSulf.

Although CrystaTech has been working with TDA Research regarding their SO₂ and direct oxidation catalysts for several years, CrystaTech and TDA have been unable to negotiate an agreement that would provide access to TDA's catalysts on terms that would not have substantial negative impacts on the overall hybrid process economics. TDA has signed an agreement with M-I Swaco (parent company of SulfaTreat[®]) which gives M-I Swaco exclusive license to TDA's direct oxidation catalyst. M-I Swaco now markets a process, SulfaTreat-DO, which uses TDA's catalyst upstream of SulfaTreat scavenger. M-I Swaco, TDA, and this technology are now competing in the marketplace with CrystaSulf-based sulfur technology. This development complicates and possibly eliminates our ability to use TDA's catalyst for future commercial plants.

4.8.2 Alternate Funding Sources for Direct Oxidation Testing

One opportunity to move the hybrid technology forward is working with ChevronTexaco and DOE in the area of syngas treatment. CrystaTech has gained support from ChevronTexaco for evaluating and developing the incorporation of this hybrid process variant into their gasification plant technology. ChevronTexaco would build from the results of this Hybrid Project and take the technology forward with joint funding from ChevronTexaco and DOE targeted at improving coal gasification technology. We will use a proprietary DOE catalyst in that program with a commercial catalyst such as Axens CRS 31 catalyst being a backup. Contracts were signed in June 2004.

Another funding opportunity for continued catalyst testing is through GTI. We developed a plan to utilize existing GTI bench-scale catalyst test equipment to perform the bench-scale testing at GTI's Des Plaines laboratories. GTI dedicated one of these existing bench-scale catalyst test units to this program, worked with CrystaTech to develop a design basis, and then modified the unit to meet the program needs. Schematics and pictures of the GTI test unit are included in Section 3.4.5. The work to get the unit ready for testing has been completed as of June 30, 2004, and testing to evaluate additional catalyst for CrystaSulf-DO is schedule to begin in July-August 2004.

4.8.3 Investigation of Alternate Catalysts for Direct Oxidation CrystaSulf

CrystaTech identified suitable alternate sources of direct oxidation catalyst when the ability to use TDA catalyst became in doubt. One benefit of examining alternate sources of catalyst was that opened up the possibility to utilize existing catalyst products and distribution networks. A risk area regarding the TDA catalysts was that they has not been produced commercially and were not in commerce domestically or internationally.

Several alternate catalyst suppliers were contacted and discussions were held regarding relevant experience, interest in participating in an evaluation program, and the commercial availability of their catalysts. Information regarding catalyst properties, capabilities, costs and

availability were gathered. In general, we found that the suppliers had not tried their catalysts on raw gas at pressure but did not believe there were any fatal flaws to such application of their catalysts.

Focusing on catalysts that are in commerce, a shortlist of possible catalysts was developed:

- Axens CRS 31;
- UOP Selectox;
- Linde CLINSULF DO;
- CRITERION 099;
- Comprimo SUPERCLAUS; and
- Energy 2000 LLC KTK-3.

The most promising commercially available catalyst for the hybrid process is CRS 31, which is supplied by Axens North America. Axens is a major worldwide supplier of sulfur conversion catalyst. Axens' CRS 31 is the original TiO₂ direct oxidation catalyst and has been in commerce worldwide for more than a decade. It is widely available at commodity type prices without a license. This catalyst was the original "direct oxidation" catalyst, and Axens provides it to Claus plants worldwide; these patents have now expired. This catalyst has also been used in many well-known industrial processes which oxidize H₂S (e.g., Linde's Clinsulf process). Axens reports that CRS 31 can be used for COS hydrolysis and H₂S-to-sulfur/SO₂ conversion depending on reactor conditions (mainly temperature and oxygen stoichiometry). Information from Axens regarding the main area of concern, resistance to hydrocarbons, indicates that hydrocarbons are seldom reactive below bed temperatures of 250°C (about 480°F), approximately the maximum temperature considered for the hybrid process. All of TDA's catalyst runs were below that temperature. There is reason to believe that due to the temperatures involved in this application, CRS 31 will be successful.

The main question, therefore, is whether other catalysts will have conversions similar to that of the TDA catalysts, or at least acceptable for use in conjunction with CrystaSulf. If we encounter problems getting adequate conversions at low enough temperatures, Axens has a possible solution. Axens recently announced a new catalyst, CSM 31, which is used in conjunction with CRS 31 and provides high conversions and system resistance to hydrocarbon fouling/cracking at temperatures well in excess of 250° (482°F). Product information on CRS 31 catalyst is given in Table 4-9. While we do not anticipate operating at these temperatures, the flexibility to do so if needed could be an asset in the future. As additional benefits to the Axens catalysts, they have extensive catalyst testing and development facilities, and their catalyst is available for less than \$5/lb. GTI and CrystaTech signed agreements with Axens to test their catalyst.

Table 4-9. CRS 31 Catalyst Information

Parameter	Value
Recommended H ₂ S concentration ranges	All H ₂ S concentrations
Recommended usages	Direct oxidation, lean gas treatment, Claus
Form	Cylindrical extrudates
Physical properties:	
Diameter	3-4 mm
Loss on ignition (550°C)	4 wt%
Tapped bulk density	0.9-1.1 kg/l
Surface area	100 m ² /g
Particle crush strength	1.3 daN/mm
Chemical analysis	85 wt% TiO ₂

While the opportunities associated with using Axens as the source of catalyst for the hybrid process sound very promising, DOE also has catalyst technology that may fit. In discussions held in March 2004 with the NETL staff in Morgantown, we learned that DOE had earlier developed and tested metal oxide direct oxidation catalysts along the development path of DOE's SCOHS (Selective Catalytic Oxidation of Hydrogen Sulfide) process. The DOE metal oxide catalysts performed satisfactorily for bulk H₂S removal, but the target for SCOHS is ppb levels of H₂S in the product gas so they were abandoned in favor of carbon based materials. Use of DOE catalyst technology in the hybrid process is a very real possibility.

Energy 2000 LLC's TiO₂ based catalyst (KTK-3) was also investigated as they claim to have a special version tailored to high hydrocarbon environments. We have not reached the level of interest and interaction with them that we have with Axens because their catalyst supply chain is not as well established.

We determined that the Criterion and Selectox catalysts were both alumina-based and tended to be more prone to react with hydrocarbons. The other catalysts were all predominately TiO₂ based (typically 85% TiO₂ by weight).

4.8.4 Direct Oxidation Catalyst Testing

As outlined in Section 4.8.3, several opportunities for funding of the direct oxidation catalyst tests have been explored. At the close of this DOE project, the likely sources are GTI, DOE, and ChevronTexaco.

Testing at GTI – As discussed previously in Section 3.4.5, GTI and CrystaTech developed a plan to utilize existing GTI bench-scale catalyst test equipment to perform the bench-scale testing at GTI's Des Plaines laboratories. GTI dedicated one of these existing bench-scale catalyst test units to this program, worked with CrystaTech to develop a design basis, and then modified the unit to meet the program needs. Schematics and pictures of the GTI test unit are included in Section 3.4.5. The work to get the unit ready for testing has been completed as of June 30, 2004, and testing to evaluate additional catalyst for CrystaSulf-DO is schedule to begin in July-August 2004.

Testing at DOE – As discussed earlier, CrystaTech has had several discussions with and has made presentations to the DOE about catalyst testing in conjunction with improvements or upgrades to CrystaSulf. As a result, the DOE has offered to perform catalyst testing using DOE labs and has also informed us that they have catalysts that could be used as candidates for CrystaSulf-DO. This work would be performed under a Cooperative Research and Development Agreement (CRADA) under which CrystaTech and DOE would each fund their respective portion of the testing. The CRADA was approved by DOE project managers and executed in June 2004. Testing of catalysts is expected to begin in July 2004. A separate agreement between CrystaTech and ChevronTexaco provides for some funding to help support that work.

5.0 CONCLUSIONS

The catalysts tested during this project are functional in generating the required SO₂ for the CrystaSulf process. Catalysts TDA #2 and #3 performed very well in producing SO₂ preferentially with TDA #2 having the economic advantage of lower cost. Early in this project, even before the novation of this project to CrystaTech, we discovered that the most economical choice for the hybrid CrystaSulf process would be to use a direct oxidation catalyst that provides not only the SO₂ required by CrystaSulf but also, and more importantly, the removal of the bulk amount of H₂S as elemental sulfur. This case would be operating the hybrid process in the direct oxidation mode, where the bulk of the inlet H₂S is converted to elemental sulfur in the catalyst section - i.e., CrystaSulf-DO.

During this project the factors that affect catalyst function for producing SO₂ were identified: temperature, hydrocarbon type and concentration, water content, and O₂/H₂S ratio. One of the most important findings of this project which will impact future work is the confirmation that low temperature operation is sufficient to oxidize the inlet H₂S without causing oxidation of valuable hydrocarbons (maintains BTU value). Less than 10% of the hexane in the test was oxidized by the catalyst. In addition, low temperature and limited hydrocarbon oxidation causes increased catalyst life due to the fact that coking of hydrocarbons and plugging/deactivation does not occur on the catalyst surface. In particular, the catalyst was not deactivated during tests that included condensate vapors in the gas stream and while testing on an operating EOR gas stream at the CrystaSulf pilot unit. These results may be used as the foundation for future studies involving catalyst-based gas conditioning to improve economics for the energy industry.

During this project we also discovered that there are other companies working in the production and supply of catalysts that may be used for service such as in CrystaSulf-DO. Thus no single company holds a monopoly on catalysts for the improvement of gas conditioning which will only improve the economics for such processes as CrystaSulf-DO.

While the funds and co-funds for this project were insufficient to complete pilot scale testing, CrystaTech plans further testing of additional, perhaps less expensive, catalysts for CrystaSulf-DO in two separate follow-on projects, one with DOE – ChevronTexaco and the other with GTI. The object of those tests is to solidify support for a demonstration CrystaSulf-DO unit to be installed at the facilities of a major energy company. The results from this project have been instrumental in persuading energy companies such as ChevronTexaco, and research funding agencies such as GTI and DOE to continue developing CrystaSulf-DO.

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