

**Hybrid Sulfur Recovery Process for Natural Gas Upgrading  
Quarterly Technical Report**

Reporting Period Start Date: 4/1/01  
Reporting Period End Date: 6/30/01

Principal Authors:

Girish Srinivas, TDA Research, Inc.  
Steven C. Gebhard, TDA Research, Inc.  
David W. DeBerry, CrystaTech, Inc.

August 2001

DOE No. DE-FC26-99FT40725

CrystaTech, Inc.  
4616 West Howard Lane, Suite 2500  
Austin, Texas 78728

TDA Research, Inc.  
12345 West 52<sup>nd</sup> Avenue  
Wheat Ridge, Colorado 80033

## **Disclaimer**

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

## ABSTRACT

This first quarter report of 2001 describes progress on a project funded by the U.S. Department of Energy (DOE) to test a hybrid sulfur recovery process for natural gas upgrading. The process concept represents a low cost option for direct treatment of natural gas streams to remove H<sub>2</sub>S in quantities equivalent to 0.2-25 metric tons (LT) of sulfur per day. This process is projected to have lower capital and operating costs than the competing technologies, amine/aqueous iron liquid redox and amine/Claus/tail gas treating, and have a smaller plant footprint, making it well suited to both on-shore and offshore applications.

CrystaSulf<sup>SM</sup> (service mark of Gas Research Institute) is a new nonaqueous sulfur recovery process that removes hydrogen sulfide (H<sub>2</sub>S) from gas streams and converts it into elemental sulfur. CrystaSulf features high sulfur recovery similar to aqueous-iron liquid redox sulfur recovery processes, but differs from the aqueous processes in that CrystaSulf controls the location where elemental sulfur particles are formed. In the hybrid process, approximately 1/3 of the total H<sub>2</sub>S in the natural gas is first oxidized to SO<sub>2</sub> at low temperatures over a heterogeneous catalyst. Low temperature oxidation is done so that the H<sub>2</sub>S can be oxidized in the presence of methane and other hydrocarbons without oxidation of the hydrocarbons.

The project involves the development of a catalyst using laboratory/bench-scale catalyst testing, and then demonstration of the catalyst at CrystaTech's pilot plant in west Texas. During this reporting period tests were done to determine the effect of hydrocarbons such as n-hexane on catalyst performance with and without H<sub>2</sub>S present. The experiments showed that hexane oxidation is suppressed when H<sub>2</sub>S is present. Hexane represents the most reactive of the C1 to C6 series of alkanes. Since hexane exhibits low reactivity under H<sub>2</sub>S oxidation conditions, and more importantly, does not change the SO<sub>2</sub> selectivity, we can conclude that the C1 – C6 hydrocarbons should not significantly interfere with the oxidation of H<sub>2</sub>S into SO<sub>2</sub>. Plans to determine the effect of aromatic compounds on catalyst performance for extended periods, and for catalyst pelletization and continued testing are described.

## TABLE OF CONTENTS

1.0	Introduction.....	1
2.0	Executive Summary.....	2
3.0	Experimental.....	3
3.1	Task 1 - Develop a Bench-Scale, Prototype Process to Remove H <sub>2</sub> S from Low-Quality Natural Gas .....	5
3.2	Task 2 - Develop a Detailed Plan for Laboratory/Bench Scale-up Application of the Task 1 Process for Both On-shore and Offshore Applications; Provide a Detailed Engineering Laboratory/Bench Scale-up Application Plan .....	5
3.3	Task 3 – Complete Laboratory/Bench-Scale Testing of Task 2 and Demonstrate Scale-up Economic Advantages for On-Shore and Offshore Applications.....	5
4.0	Results and Discussion	10
5.0	Conclusions .....	11
5.1	Summary.....	11
5.2	Planned Activities.....	11
6.0	References.....	13

## LIST OF TABLES

1	Methane-poor CrystaSulf <sup>TM</sup> feed gas .....	3
2	Methane-rich CrystaSulf <sup>TM</sup> feed gas.....	3
3	Summary of TDA catalysts and #3 catalyst with hexane in feed.....	9

## LIST OF FIGURES

1	Flow diagram for hybrid CrystaSulf <sup>SM</sup> process.....	4
2	Hexane oxidation test over TDA Catalyst #3 with no H <sub>2</sub> S in the feed (catalyst in oxide form)...	6
3	Hexane oxidation test over TDA Catalyst #3 with 2000 ppm H <sub>2</sub> S in the feed .....	7
4	Oxygen in product gas during hexane oxidation test over TDA Catalyst #3 with 2000 ppm H <sub>2</sub> S in the feed.....	8

## 1.0 INTRODUCTION

This quarterly report is the second technical report for DOE Contract No. DE-FC26-99FT40725 entitled “Hybrid Sulfur Recovery Process for Natural Gas Upgrading” following novation of the project from URS Corporation to CrystaTech, Inc. The CrystaSulf<sup>SM</sup> (service mark of Gas Research Institute) is a new nonaqueous sulfur recovery process that removes hydrogen sulfide (H<sub>2</sub>S) from gas streams and converts it into elemental sulfur. The hybrid CrystaSulf process uses a catalyst to first oxidize about 1/3 of the H<sub>2</sub>S to SO<sub>2</sub>.

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

This report is divided into the following sections:

- Section 1 – Introduction
- Section 2 – Executive Summary
- Section 3 – Experimental
- Section 4 – Results and Discussion
- Section 5 – Conclusions
- Section 6 – References

## 2.0 EXECUTIVE SUMMARY

This project was funded by the U.S. Department of Energy (DOE) to test a hybrid sulfur recovery process for natural gas upgrading. The process concept represents a low cost option for direct treatment of natural gas streams to remove H<sub>2</sub>S, in quantities equivalent to 0.2-25 metric tons (LT) of sulfur per day. This process is projected to have lower capital and operating costs than the competing technologies, amine/aqueous iron liquid redox and amine/Claus/tail gas treating, and have a smaller plant footprint, making it well suited to both on-shore and offshore applications.

CrystaSulf<sup>SM</sup> (service mark of Gas Research Institute) is a new nonaqueous sulfur recovery process that removes hydrogen sulfide (H<sub>2</sub>S) from gas streams and converts it into elemental sulfur. CrystaSulf features high sulfur recovery similar to aqueous-iron liquid redox sulfur recovery processes, but differs from the aqueous processes in that CrystaSulf controls the location where elemental sulfur particles are formed. In the hybrid process, approximately 1/3 of the total H<sub>2</sub>S in the natural gas is first oxidized to SO<sub>2</sub> at low temperatures over a heterogeneous catalyst. Low temperature oxidation is done so that the H<sub>2</sub>S can be oxidized in the presence of methane while avoiding methane oxidation.

The project involves the development of a catalyst using laboratory/bench-scale catalyst testing, and then demonstration of the catalyst at CrystaTech's pilot plant in west Texas. . During this reporting period tests were done to determine the effect of hydrocarbons such as n-hexane on catalyst performance with and without H<sub>2</sub>S present. The experiments showed that hexane oxidation is suppressed when H<sub>2</sub>S is present. Hexane represents the most reactive of the C1 to C6 series of alkanes. Since hexane exhibits low reactivity under H<sub>2</sub>S oxidation conditions, and more importantly, does not change the SO<sub>2</sub> selectivity, it appears that none of the C1 – C6 hydrocarbons should significantly interfere with the oxidation of H<sub>2</sub>S to SO<sub>2</sub>. Plans for further contaminant testing and catalyst pelletization are described.

Previous results from this study 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 H<sub>2</sub>S concentrations and pressures of interest (i.e., pressure up to 6.89 MPa (1000 psi)) could be processed by the hybrid CrystaSulf process. TDA's modified catalysts exhibit high H<sub>2</sub>S conversion (99+%) with essentially no slip of oxygen. Changing the formulation, temperature, and O<sub>2</sub>/H<sub>2</sub>S ratio can be used to control SO<sub>2</sub> selectivity over these catalysts. Further investigation for this promising process is planned.



### 3.0 EXPERIMENTAL

#### *Background*

CrystaSulf<sup>SM</sup> is a new *nonaqueous* sulfur recovery process that removes H<sub>2</sub>S from gas streams and converts it into elemental sulfur. CrystaSulf features high sulfur recovery similar to aqueous-iron liquid redox sulfur recovery processes but differs from the aqueous processes in that CrystaSulf controls the location where elemental sulfur particles are formed. In the hybrid CrystaSulf process, approximately 1/3 of the total H<sub>2</sub>S in the natural gas is first oxidized to SO<sub>2</sub> at low temperatures over a heterogeneous catalyst. Low temperature oxidation is done so that the H<sub>2</sub>S can be oxidized in the presence of methane (CH<sub>4</sub>) while avoiding CH<sub>4</sub> oxidation. In contrast, thermal oxidation would consume valuable natural gas.

In this process H<sub>2</sub>S does not have to be separated from the gas stream for sulfur recovery. A little more than 1/3 of the total flow of natural gas to be processed flows over the partial oxidation catalyst in a fixed bed catalytic reactor. The reactor is operated at about 300 psig and 250°C.

Between 95 and 100% of the H<sub>2</sub>S passing over the partial oxidation catalyst is converted into SO<sub>2</sub> + H<sub>2</sub>O (depending on the catalyst and the O<sub>2</sub>/H<sub>2</sub>S ratio). The remaining H<sub>2</sub>S is converted into elemental sulfur and water. The elemental sulfur is condensed and collected, and the product gas from the reactor (which now contains SO<sub>2</sub>) 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 H<sub>2</sub>S and SO<sub>2</sub> for removal of the remaining sulfur using the CrystaSulf<sup>TM</sup> process. A flow diagram of the hybrid CrystaSulf<sup>TM</sup> process is shown in Figure 1. The composition of a methane-poor/CO<sub>2</sub>-rich natural gas is shown in Table 1, and that of a methane rich gas is shown in Table 2.

Table 1. Methane poor CrystaSulf<sup>TM</sup> feed gas.

Parameter	Value
H <sub>2</sub> S	2000 ppm
CO <sub>2</sub>	84.46 vol%
N <sub>2</sub>	Negligible
CH <sub>4</sub>	9.95 vol%
C <sub>2</sub> H <sub>6</sub>	2.99 vol%
C <sub>3</sub> H <sub>8</sub>	1.99 vol%
Other	0.32 vol%
Temperature	60 – 110? F
Pressure	250 – 340 psig
Humidity	Sat. at 100? F

Table 2. Methane rich CrystaSulf<sup>TM</sup> feed gas.

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

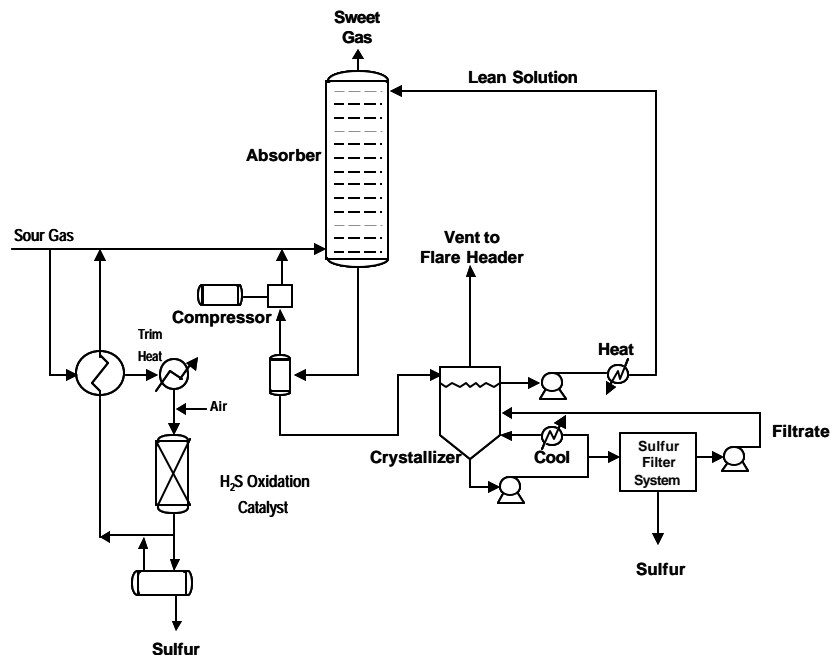
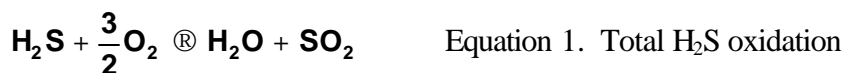


Figure 1. Flow diagram for hybrid CrystaSulf<sup>TM</sup> process.

The main reactions that take place over the catalyst are the direct oxidation of H<sub>2</sub>S into SO<sub>2</sub> (Equation 1), the partial oxidation of H<sub>2</sub>S into elemental sulfur (Equation 2), and the Claus reaction between H<sub>2</sub>S and SO<sub>2</sub> to produce sulfur (Equation 3). The CrystaSulf<sup>TM</sup> process runs the Claus reaction in the liquid phase. The objective of the TDA catalytic process is to oxidize approximately 1/3 of the H<sub>2</sub>S in the natural gas stream into SO<sub>2</sub> via Equation 1 so that the proper H<sub>2</sub>S to SO<sub>2</sub> ratio is present in the natural gas when it enters the CrystaSulf<sup>TM</sup> process. The exact amount of gas sent to the catalytic reactor depends on how much elemental sulfur is recovered directly in the partial



oxidation. The more sulfur is recovered from the catalytic step, the greater the proportion of gas flow must be sent to the reactor. However, the more sulfur is recovered from the catalytic reactor, the lower the sulfur load on the CrystaSulf<sup>TM</sup> process. Thus, there is a trade off between the capital and operating costs between the fixed bed reactor and the absorber. The

optimum operating conditions depend on the activity of the solid catalyst and its selectivities to SO<sub>2</sub> and elemental sulfur.

***Requirements of Catalyst Used to Oxidize H<sub>2</sub>S to SO<sub>2</sub>.***

The general requirements for a successful catalyst for the hybrid CrystaSulf™ process are as follows:

1. The catalyst must exhibit very low activity for hydrocarbon oxidation.
2. The catalyst must give high conversions for H<sub>2</sub>S oxidation (lowers the catalyst bed volume).
3. The catalyst must exhibit high selectivity for SO<sub>2</sub>.
4. Selectivity to sulfur is a bonus.
5. All elemental sulfur formed needs to remain in the vapor phase in the reactor (i.e. the operating temperature of the catalyst must be above the sulfur dew point).

**3.1 Task 1 - Develop a Bench-Scale, Prototype Process to Remove H<sub>2</sub>S from Low-Quality Natural Gas**

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

**3.2 Task 2 - Develop a detailed plan for laboratory/bench-scale-up application of the Task 1 process for both on-shore and offshore applications; provide a detailed engineering laboratory/bench scale-up application plan.**

**3.3 Task 3 - Complete laboratory/bench-scale testing of Task 2 and demonstrate scale-up economic advantages for on-shore and offshore applications.**

***Recent Progress – Test of the Effect of Contamination by n-Hexane***

In all of our previous catalyst tests we added 10% methane to the feed and found that no methane oxidation occurred over our catalysts at T = 250°C and P = 300 psig. Methane, however, is the most difficult of the hydrocarbons to oxidize (highest activation energy) and in the real gas application (that we will encounter in the pilot plant), C<sub>2</sub> and higher hydrocarbons will be present. While the concentrations of these hydrocarbons are a few percent or less each (Table 1 and Table 2), their combustion is undesirable because this consumes oxygen and

reduces the BTU value of the gas. In addition, aromatic hydrocarbons have the potential to foul the catalyst with coke if they decompose on the catalyst without oxidizing.

The catalysts we use for partial oxidation of  $\text{H}_2\text{S}$  to produce both  $\text{SO}_2$  and S are promoted versions of our  $\text{MoO}_3/\text{Nb}_2\text{O}_5/\text{TiO}_2$  catalyst that we use to produce elemental sulfur in high yields by direct  $\text{H}_2\text{S}$  partial oxidation.

Figure 2 shows the results for the test with 500 ppm n-hexane ( $\text{C}_6\text{H}_{14}$ ) added to the

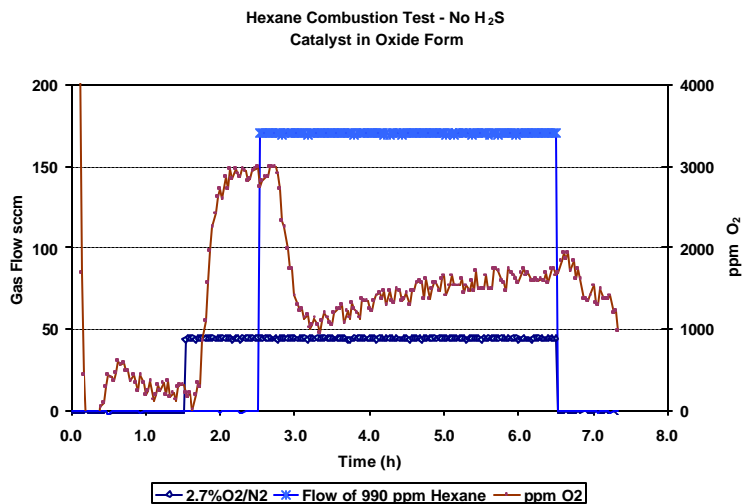


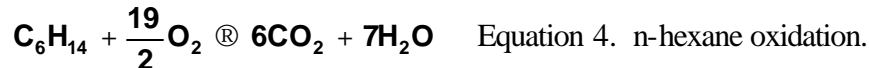
Figure 2. Hexane oxidation test over TDA Catalyst #3 with no  $\text{H}_2\text{S}$  in the feed (catalyst in oxide form).

feed when no  $\text{H}_2\text{S}$  was present. The catalyst temperature was  $250^\circ\text{C}$  and the pressure in the reactor was 200 psig. Fresh (never exposed to  $\text{H}_2\text{S}$ ) catalyst was used in this experiment, and therefore, the compounds in the catalyst were present as oxides.

Figure 2 shows three curves. The first is the flow of 2.7%  $\text{O}_2$  in  $\text{N}_2$  that was used as the  $\text{O}_2$  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 ppm. The appropriate amount of pure  $\text{N}_2$  was added to dilute the 2.7%  $\text{O}_2$  down to 3,000 ppm. At about 2.5 hours, the flow of n-hexane was started. The cylinder concentration was 990 ppm of  $\text{C}_6\text{H}_{14}$  in  $\text{N}_2$  which was added at a flow rate that gave 500 ppm of  $\text{C}_6\text{H}_{14}$  in the feed gas flowing over the catalyst (pure  $\text{N}_2$  was added as to adjust the  $\text{C}_6\text{H}_{14}$  concentration to 500 ppm). Immediately the  $\text{O}_2$  concentration was reduced to about 1,000 ppm suggesting that some hexane oxidation was occurring. The  $\text{O}_2$  concentration gradually increased over the next 5 hours and then leveled out at 2,000 ppm which corresponds to a consumption of 1000 ppm of  $\text{O}_2$ .

Equation 4 gives the balanced equation for complete oxidation of  $\text{C}_6\text{H}_{14}$  into  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . Thus, 1,000 ppm of  $\text{O}_2$  will oxidize 105.26 ppm of n-hexane. Since the total n-hexane concentration was 500 ppm, the fraction of  $\text{C}_6\text{H}_{14}$  oxidized was 21.05%. Because

the catalyst had not been exposed to H<sub>2</sub>S 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 ppm of C<sub>6</sub>H<sub>14</sub> was oxidized indicates that the catalyst has modest to low hydrocarbon oxidation activity.



This experiment had to be done in order to compare the results with a similar experiment done using H<sub>2</sub>S. If the H<sub>2</sub>S conversion were not complete, but the O<sub>2</sub> consumption was, we would not be able to determine what proportion of O<sub>2</sub> consumption was due to sulfur formation and what portion was due to C<sub>6</sub>H<sub>14</sub> oxidation (this is because the apparatus is not currently configured to analyze for CO, CO<sub>2</sub> and C<sub>6</sub>H<sub>14</sub> at these low concentrations). However, if all of the O<sub>2</sub> is consumed, and the sulfur mass balance (unconverted H<sub>2</sub>S + SO<sub>2</sub> + S) accounts for all of the O<sub>2</sub> we can be reasonably certain that C<sub>6</sub>H<sub>14</sub> oxidation is negligible. Figure 3 shows the results of that experiment.

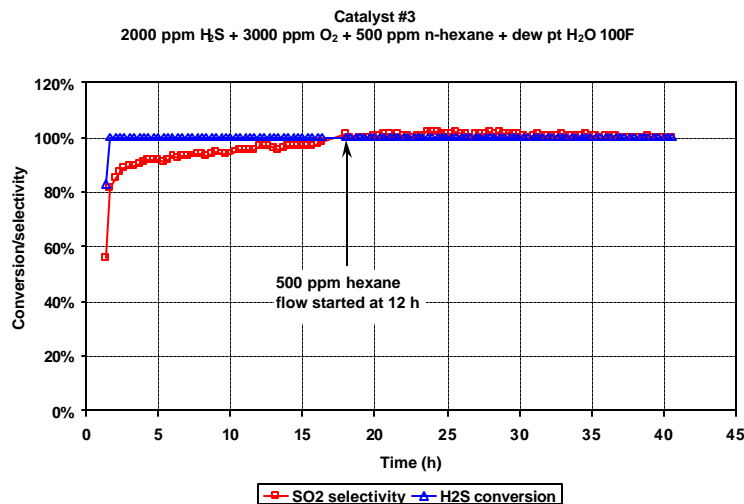


Figure 3. Hexane oxidation test over TDA Catalyst #3 with 2000 ppm H<sub>2</sub>S in the feed.

The test with H<sub>2</sub>S present was done with a feed containing 500 ppm of C<sub>6</sub>H<sub>14</sub>, 2,000 ppm of H<sub>2</sub>S and 3000 ppm of O<sub>2</sub> was about 41 hours long. As in the experiment without H<sub>2</sub>S we first established the flow of 2.7% O<sub>2</sub> in N<sub>2</sub> to give an O<sub>2</sub> concentration of 3000 ppm and let the system stabilize. The flow of H<sub>2</sub>S was then started and again the concentrations were allowed to stabilize. The pressure was 200 psig, the catalyst temperature was 250°C, the gas was humidified to a concentration that corresponded to the dew point of water at 100°F, and the space velocity was 3350 cm<sup>3</sup><sub>gas</sub>/cm<sup>3</sup><sub>catalyst</sub>/hr. We ran the experiment for about 18 hours under these conditions where there was no hexane in the feed.

During the H<sub>2</sub>S only oxidation phase of the experiment (out to 18 hours in Figure 3), the H<sub>2</sub>S conversion was 100% (within our ability to measure it). Also during this time the selectivity of the catalyst (we used the TDA#3 catalyst) slowly shifted away from forming about 10% elemental sulfur and 90% SO<sub>2</sub> to virtually 100% selectivity for SO<sub>2</sub>.

At 18 h, the 500 ppm hexane flow was started (by this time the SO<sub>2</sub> selectivity and H<sub>2</sub>S conversion were both essentially 100% and appeared to have stabilized). The mixed flow of gases (containing C<sub>6</sub>H<sub>14</sub>) was then continued out to over 40 hours when the experiment was stopped.

Figure 4 shows the flow of 5% H<sub>2</sub>S in N<sub>2</sub>, the flow of 900 ppm C<sub>6</sub>H<sub>14</sub>, and the O<sub>2</sub> concentration in the product gas exiting the reactor. The 5% H<sub>2</sub>S and 900 ppm C<sub>6</sub>H<sub>14</sub> in the legend refer to the concentrations of the bottled gas; the H<sub>2</sub>S concentration was 1,900 ppm and the C<sub>6</sub>H<sub>14</sub> concentration was 500 ppm over the catalyst. Figure 4 shows that at about 2 hrs the H<sub>2</sub>S flow was started and that at 18 hrs the flow of C<sub>6</sub>H<sub>14</sub> gas was started. The period between 2 and 18 hrs is the H<sub>2</sub>S oxidation only phase of the experiment, and between 18 hr and about 46 hr was the time period where H<sub>2</sub>S oxidation occurred in the presence of C<sub>6</sub>H<sub>14</sub>. Figure 4 also shows the output of the paramagnetic O<sub>2</sub> sensor that is in line with the product gas exit.

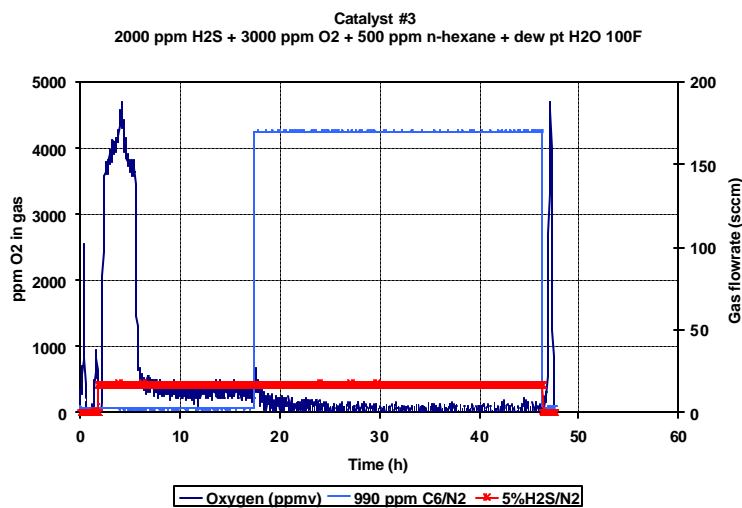


Figure 4. Oxygen in product gas during hexane oxidation test over TDA Catalyst #3 with 2,000 ppm H<sub>2</sub>S in the feed.

The spike in the O<sub>2</sub> concentration between about 2.8 and 5.5 hrs is due to the flow changes when switching on the gases and adjusting the flowrate of the gases already on line. Between 5 and 18 hrs, some O<sub>2</sub> slip appeared to be occurring (500 ppm), and when the hexane flow was started, all of the O<sub>2</sub> was consumed. Importantly, there was no change whatsoever in the H<sub>2</sub>S conversion or SO<sub>2</sub> selectivity during the run (see Figure 3) which suggests that only a small amount of extra O<sub>2</sub> needs to be added to the feed gas if hydrocarbons are present. If only 500 ppm of O<sub>2</sub> was consumed by the hexane then, in the presence of H<sub>2</sub>S only 50 ppm of hexane is oxidized which is only 10% of the original hexane in the feed. Thus

we can conclude that hexane is much less reactive than H<sub>2</sub>S over the catalyst under these conditions.

Future experiments using toluene at a concentration of 1000 ppmv (described below) will be more demanding of the catalyst and will give us more information about how well the catalyst tolerates hydrocarbon contamination in the feed gas. was added.

Table 3 summarizes the catalyst test results previously reported along with the results for the tests where n-C<sub>6</sub>H<sub>14</sub> was added.

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

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

## 4.0 Results and Discussion

Our results with the 500 ppm n-hexane in the feed clearly indicate that hexane oxidation is suppressed during H<sub>2</sub>S oxidation. At most we observed that 50 ppm out of 500 ppm 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 H<sub>2</sub>S oxidation conditions, and more importantly, does not change the SO<sub>2</sub> selectivity, we can conclude that the C1 – C6 hydrocarbons should not significantly interfere with the oxidation of H<sub>2</sub>S to SO<sub>2</sub>.

In the methane poor gas (Table 1) the hydrocarbons present in addition to methane are mostly ethane and propane with minor amounts of higher hydrocarbons. In methane rich gas not only are the C2 through C6 alkanes present, but there are significant quantities of aromatic hydrocarbons, specifically benzene, toluene and xylenes (Table 2). Because of the increased tendency of aromatic hydrocarbons to decompose and foul a catalyst with deposited carbon (Hughes 1984) it is 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 plan to repeat 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.

In these experiments, the feed gas will contain 1000 ppm of toluene (C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>), 1,900 ppm of H<sub>2</sub>S, 3800 ppm of O<sub>2</sub>, humidified to 100°F, with the balance being N<sub>2</sub> gas. The experiments will be conducted at a temperature of 250°C (482°F) at a pressures 200 – 300 psig (15 – 22 bar). We will use TDA #3 catalyst because it has performed the best to date and was used in the hexane experiments. We will examine O<sub>2</sub> consumption and any changes in the H<sub>2</sub>S conversion or selectivity to SO<sub>2</sub>. The test will be run continuously for about 100 hours.



## 5.0 CONCLUSIONS

### 5.1 Summary

We have tested our H<sub>2</sub>S to SO<sub>2</sub> oxidation catalyst (TDA #3) with 500 ppm of n-hexane in the feed gas to determine if hydrocarbon contamination in the feed gas stream for the CrystaSulf<sup>TM</sup> process would have a deleterious effect on the performance of the catalyst. A small amount (105 ppm out of 500 ppm) of the hexane was oxidized when the experiment was conducted with fresh catalyst that had not been exposed to H<sub>2</sub>S. When we repeated the experiment, but this time establishing steady state H<sub>2</sub>S oxidation before adding the hexane, we found that only 50 ppm out of 500 ppm of hexane was oxidized, and more importantly, the selectivity of the catalyst for SO<sub>2</sub> was not affected and remained close to 100%. While the reactivity of hexane for oxidation is not especially large to begin with, when competing with 1,900 ppm of H<sub>2</sub>S (3.8 times the concentration of hexane), the oxidation of hexane is suppressed even more. This is consistent with the ease with which H<sub>2</sub>S is oxidized.

The results also indicate that either the remaining C<sub>6</sub>H<sub>14</sub> (450 ppm unreacted) simply passed out of the reactor unchanged, or that any deactivation of the catalyst was so slow that we could not measure it in 40 hours. We are in the process of running similar experiment where 1,000 ppm of toluene is added to the feed to simulate the effects of BTX contamination in the process gas. BTX is a more serious contaminant and is much more demanding on the catalysts because of its increased (relative to hexane) coke-forming tendency.

### 5.2 Planned Activities

#### *Catalyst pellet production*

Once we have determined the best catalyst composition, a qualified supplier of the material is needed. The supplier will need to provide reproducible batches for qualification, and ultimately supply the required quantities for pilot plant testing. When commercial quantities of catalysts and sorbents designed by TDA are needed, TDA generally supplies them through Saint Gobain NorPro (Cleveland, OH). Details concerning NorPro's business and expertise were discussed in the previous report and will not be repeated here.

#### *Durability Testing*

Using our pellet reactor, we will perform a catalyst lifetime/durability test on the pelletized form of the catalyst (a sample manufactured by NorPro). Our pellet reactor is designed specifically to be able to test catalysts in the final physical form (e.g. 1/8 – 1/4 in pellets) that will be used in the pilot plant. This testing ensures that no unforeseen variations in catalyst performance are introduced when the catalyst is manufactured in its final physical form.

## 6.0 REFERENCES

Olah, G.A. and Molnar, A. (1995) Hydrocarbon Chemistry, Wiley

Hughes, R. (1984) Deactivation of Catalysts, Academic Press, p.111