Hybrid Sulfur Recovery Process for Natural Gas Upgrading Quarterly Technical Report

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ABSTRACT

This second quarter report of 2002 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_2S in quantities equivalent to 0.2-25 metric tons (LT) of sulfur per day. This process is projected to have lower capital and operating costs than the competing technologies, amine/aqueous iron liquid redox and amine/Claus/tail gas treating, and have a smaller plant footprint, making it well suited to both on-shore and offshore applications.

CrystaSulf SM (service mark of CrystaTech, Inc.) is a new nonaqueous sulfur recovery process that removes hydrogen sulfide (H₂S) from gas streams and converts it into elemental sulfur. CrystaSulf features high sulfur recovery similar to aqueous-iron liquid redox sulfur recovery processes, but differs from the aqueous processes in that CrystaSulf controls the location where elemental sulfur particles are formed. In the hybrid process, approximately 1/3 of the total H₂S in the natural gas is first oxidized to SO₂ at low temperatures over a heterogeneous catalyst. Low temperature oxidation is done so that the H₂S can be oxidized in the presence of methane 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. Previous reports described development of a catalyst with the required selectivity and efficiency for producing sulfur dioxide from H_2S . In the laboratory, the catalyst was shown to be robust and stable in the presence of several intentionally added contaminants, including condensate from the pilot plant site. This report describes testing using the laboratory apparatus but operated at the pilot plant using the actual pilot plant gas, which contains far more contaminants than can be simulated in the laboratory. The results are very encouraging, with stable and efficient operation being obtained for a prolonged period of time.

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1.0 INTRODUCTION

This quarterly report is the sixth 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 SM (service mark of CrystaTech, Inc.) process is a new nonaqueous sulfur recovery process that removes hydrogen sulfide (H₂S) from gas streams and converts it into elemental sulfur. The hybrid CrystaSulf process uses a catalyst to first oxidize about 1/3 of the H₂S to SO₂.

Much of the work described in this report was conducted by CrystaTech's subcontractor, TDA Research, Inc., who developed the catalysts.

This report is divided into the following sections:

- Section 1: Introduction
- Section 2: Executive Summary
- Section 3: Experimental
- Section 4: Conclusions
- Section 5: Current Activities

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 H₂S 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 SM (service mark of CrystaTech, Inc.) is a new nonaqueous sulfur recovery process that removes hydrogen sulfide (H_2S) from gas streams and converts it into elemental sulfur. CrystaSulf features high sulfur recovery similar to aqueous-iron liquid redox sulfur recovery processes, but differs from the aqueous processes in that CrystaSulf controls the location where elemental sulfur particles are formed. In the hybrid process, approximately 1/3 of the total H_2S in the natural gas is first oxidized to SO_2 at low temperatures over a heterogeneous catalyst. Low temperature oxidation is done so that the H_2S can be oxidized in the presence of methane while avoiding methane oxidation and fouling due to coking from other hydrocarbon contaminants.

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 H₂S 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 H₂S conversion (99+%) with essentially no slip of oxygen. Changing the formulation, temperature, and O₂/H₂S ratio can be used to control SO₂ selectivity over these catalysts.

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. Several catalysts were prepared and found to have the required selectivity and efficiency for producing sulfur dioxide from H_2S . In the laboratory, the catalyst was shown to be robust and stable in the presence of several intentionally added contaminants. Earlier experiments showed that hexane oxidation is suppressed when H_2S is present. Hexane represents the most reactive of the C1 to C6 series of alkanes, and since it exhibits low reactivity under H_2S oxidation conditions, and more importantly, does not change the SO₂ selectivity, it appears that none of the C1 – C6 hydrocarbons should significantly interfere with the oxidation of H_2S to SO₂. Additional testing evaluated the effect of toluene as a contaminant and concluded that it, too, was not reactive in the system. Contaminants from pilot plant site condensate also had no effect on catalyst

This report describes testing using the laboratory apparatus but operated at the pilot plant using the actual pilot plant gas, which contains far more contaminants than can be simulated in the laboratory. The results are very encouraging, with stable and efficient operation being obtained for a prolonged period of time. Work is underway on designing and building the catalytic reactor for the pilot plant scale plant.

3.0 EXPERIMENTAL

3.1 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.

3.1.1 Background

The hybrid CrystaSulfSM process incorporates T catalytic oxidation of approximately 1/3 of the F total H_2S in the natural gas to generate the SO₂ C required for the CrystaSulfSM process. This eliminates the need for sulfur burning or H shipping liquefied SO₂ to the plant.

The $H_{b}S$ in the gas stream is oxidized to SO_{2} at low temperatures over a heterogeneous catalyst. At low temperatures, the H_bS can be oxidized directly while avoiding oxidation of any of the hydrocarbons in the gas stream. This makes the process especially attractive for directly treating natural gas and other streams where the catalyst should only be reactive toward H_2S . The production of SO₂ in this manner is referred to as catalytic SO₂ production (CSP). CSP is operated at line pressure (about 300 psig) with the catalyst at 200°C to 250°C. The composition of the gas treated in the field test described in this report is shown in Table 1. The bulk of the gas is CO_2 because the gas is recovered from a CO_2 flood for enhanced oil recovery (EOR). Desulfurizing the gas with the Hybrid CrystaSulfSM Process would provide a lower cost way of reusing the CO₂ for additional EOR. The process gas contains about 1900 ppm of H_2S .

The combination of an upstream catalytic reactor that oxidizes H_2S to SO_2 followed by a

Table 1.	Composi	tion of C	0xy-Permia	n
Process	Gas	and	Propertie	s
Calculate	d Using S	Supertrap	p Program	
Common	a		Manan	

<u> </u>	0
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.	437°F
Pressure for Property Calcs.	300 psig
Molecular Weight (g/mole)	40.7418
Compressibility Factor	0.99
Density (lb/ft ³)	1.28474
Enthalpy (Btu/lb)	-3522.01
Entropy (Btu/lb*F)	1.25607
Specific Heat (Btu/lb*F)	0.280693
Cp/Cv	1.23934
Speed of Sound (ft/sec)	1151.58
Joule-Thompson Coefficient	3.39E-02
Viscosity (lb/ft*sec)	1.57E-05
Thermal Conductivity	2.10E-02
(Btu/lb*hr*F)	

downstream CrystaSulfSM unit is referred to as the "Hybrid CrystaSulfSM Process." A schematic of the process is shown in Figure 1. Between 95 and 100% of the H₂S that passes over the catalyst is converted into SO₂ and H₂O. The remaining (< 5%) H₂S is converted into elemental sulfur and water. The elemental sulfur is condensed and collected, and the product gas from the reactor (which now contains SO₂) is blended back into the main flow stream to react with the H₂S in the CrystaSulfSM process.



Figure 1. Flow diagram for hybrid CrystaSulfSM process.

By controlling the ratio of the flow through the catalytic reactor and the flow that goes directly to the CrystaSulfSM unit, the 2:1 H_2S -to-SO₂ stoichiometry required by the CrystaSulfSM unit can be maintained.

The main reactions that can take place over the catalyst in the fixed bed oxidation reactor are the direct oxidation of H_2S into SO_2 (Equation 1, the dominant reaction), the partial oxidation of H_2S into elemental sulfur (Equation 2, which accounts for about 5% of the selectivity), and the Claus reaction between H_2S and SO_2 to produce sulfur (Equation 3, again less than a 5% contribution). The CrystaSulfSM process unit conducts a liquid phase Claus reaction in a proprietary solvent that keeps the sulfur that is formed in solution. Because the sulfur is dissolved in the CrystaSulfSM solvent, sulfur plugging of high-pressure equipment cannot occur. This is in contrast to existing aqueous phase H_2S oxidation processes where the sulfur is never soluble, and can plug the process equipment.

$$H_2S + \frac{3}{2}O_2 \otimes H_2O + SO_2$$

Equation 1. Total H_2S oxidation.

 $H_2S + \frac{1}{2}O_2 \otimes H_2O + S$

Equation 2. Partial oxidation of H_2S .

 $2H_2S + SO_2 = 2H_2O + 3S$

Equation 3. Claus reaction equilibrium.

3.1.2 Requirements of catalyst used to oxidize H₂S to SO₂.

In the Hybrid CrystaSulfSM Process, H_2S is oxidized to SO_2 in a fixed bed catalytic reactor. For the catalytic SO_2 production (CSP) step to function properly the catalyst must: 1) exhibit very low-to-no activity for hydrocarbon oxidation, 2) give high H_2S conversions, 3) exhibit high selectivity for SO_2 and 4) be operable at temperatures above the dew point of any elemental sulfur formed.

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

As part of Task 3, we have conducted a test using real process gas using TDA's small bench scale catalyst test apparatus. We successfully operated our H₂S oxidation catalyst continuously for more than 300 hours and observed no deactivation and no change in selectivity for SO₂. The selectivity for SO₂ was better than 95% for the entire run and the H₂S conversion was 100%. These results are extremely encouraging and therefore we are currently in the process of designing and fabricating a pilot-scale fixed-bed reactor that will hold about 44 lbs of catalyst. This reactor will be placed upstream of the CrystaSulfSM pilot plant and will be used to generate the SO₂ required by the CrystaSulfSM plant in a test of 0.2 MMSCFD of gas (same gas as Table 1). The catalytic reactor itself will be capable of processing about 1/3 of the total flow which is 0.66 MSCFD. At 300 psig (ca. 21 bar) and 250°C, this corresponds to an actual gas flow through the reactor vessel of 4.2 ft³/min (120 liter/min).

3.2.1 Results – Completion of a bench scale field test of catalytic SO₂ production using a slip-stream of process gas from Oxy-Permian CO₂ Recovery Plant.

Figure 2 is a process and instrumentation diagram of TDA's bench scale catalyst test apparatus. The reactor vessel for these tests was made from a ½ inch VCR bulkhead union (Figure 3) that was filled with 17 grams of TDA's oxidation catalyst. Upstream of the reactor both air and process gas are metered into the system using electronic mass flow controllers (MFC-1 and MFC-2). Each gas feed line has a pneumatic shut off valve (PV-1 and PV-2) and a check valve (CV-1 and CV-2). The gases are mixed together and pass into a one-meter long heat-traced section of tubing that serves as a gas preheater. The gas preheater was initially operated at 175°C and was later operated at 200°C. The air flow rate was typically about 95 sccm and the process gas flow rate was approximately 6.5 liters/min.

The system pressure during the test was 300 psig and the average catalyst temperature was maintained at about 240°C. Gases exiting the reactor first pass into a heated

stainless steel cylinder that condenses any elemental sulfur that is formed. Gas exiting the condenser passes through a filter, a pressure control valve (PCV-1), two traps and then goes to an O_2 analyzer, a bleach solution and finally to vent. The filter protects the PCV from plugging (the flow orifice is extremely small). A tee in the line downstream of the traps is 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 O_2 content of the gas is measured by an on-line paramagnetic analyzer (range 0-25 vol% O_2). Before being vented (in this case tied into the flare line at the Oxy plant) the gas is scrubbed through a dilute solution of Clorox. This oxidizes any unreacted H₂S to form water soluble sulfur salts.



Figure 2. Process and instrumentation diagram for bench apparatus used in field test at Denver City.

The air and process gas flow rates as a function of time are shown in Figure 4. 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 1 and the process gas contains about 1900 ppm of H₂S. The bulk of the gas is CO₂ because the gas is recovered from a CO₂ flood for enhanced oil recovery. By desulfurizing the gas, the CO₂ could be reused.

The flow rates are 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 upon telephone discussions with TDA staff back in Colorado and the experiments were quickly resumed.



Figure 3. Detail of fixed bed reactor used in apparatus shown in Figure 2.

Air and Process Gas Flow Rates Denver City Field Test - Catalytic SO2 Production



Figure 4. Process gas and air flow rates during test.

Figure 5 shows the average catalyst bed temperature during the test. Because of the large total gas flow rate of approximately 7 liter/min, some of the gas preheating occurred in the reactor's three-zone furnace. In addition, the H_2S reaction is exothermic. As a result, the top of the catalyst bed was about 50°C cooler than the bottom of the bed. As in Figure 4, the interruptions in the experiment can be seen (in the interruption that starts at about 120 hours, the catalyst was not being heated – the catalyst was heated back to reaction temperature at 159 hr).



Average Catalyst Bed Temperature

Figure 5. Average catalyst bed temperature.

During the test, the H_2S conversion was 100% and the selectivity to SO_2 was > 95% (within experimental error). Figure 6 shows that the O_2 concentration in the product gas was at or below about 0.2 vol% (the spikes in the test occur during the interruptions and at the end of the run when the apparatus was being shut down). The O_2 analyzer's range is 0-25 vol% (it is designed for monitoring O_2 concentrations found in oxygen



Oxygen Concentration in Reaction Product Gas Denver City Field Test - Catalytic SO2 Production

Figure 6. Oxygen concentration in the catalytic reactor product gas.

depleted air) and thus 0.2% is only 0.8% of the range of the instrument. Thus within the accuracy of the O_2 analyzer, a reading of 0.2% corresponds to almost no O_2 .

Figure 7 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 300 ± 2 psig.



Reactor Pressure Denver City Field Test - Catalytic SO2 Production

Figure 7. Reactor pressure during Denver City field test.

Figure 8 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 and during this time the temperature difference between the top and bottom of the catalyst bed was more than 50°C. Therefore, at 225 hr, the preheaters were maintained at 200°C. 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.



Auxiilary Heater Temperatures Denver City Field Test - Catalytic SO2 Production



Figure 9 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 is presumably made by the reaction between H₂S and CO₂. COS has not been calibrated and we estimate that its concentration was no more



Denver City Field Test GC Data

Figure 9. Yield of SO_2 , elemental sulfur and COS during first 150 hours of test as determined by gas chromatographic analysis.

than a few percent of the total sulfur. The elemental sulfur yield was calculated by difference (i.e. H_2S forms only SO_2 or S - from the O_2 balance in laboratory work, we have found that SO_3 is not formed over this catalyst under similar conditions).

The reason for the large fluctuations in the SO₂ and COS yields apparent in Figure 9 is minor pressure fluctuations in the GC sample loop. As the process gas pressure from the plant (nominally 325 ± 25 psig) fluctuated, the pressure in the reactor system (controlled at 300 psig) also fluctuated. At a set-point pressure of 300 psi, there is not much pressure difference between the Oxy plant gas source and the reactor system. This makes pressure control with the PCV somewhat more difficult and permits fluctuations in the Oxy source pressure to propagate through the catalyst test apparatus while the PCV tries to compensate for the fluctuating inlet pressure. This causes the pressure in the GC sample loop to fluctuate and causes 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.

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 H_2S or SO_2 and changes color. A bag sample of the gas is obtained. Then a fixed volume manual pump is used to take a sample from the bag. Results are adjusted for altitude. The absolute accuracy of the tubes is about \pm 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 which has a cycle time of about 20 min).

Denver City Field Test Stain Tube Data



Figure 10. H_2S and SO_2 concentrations in product gas exiting catalytic reactor determined using stain (Sensidyne) tubes.

Figure 10 shows the H_2S concentration at the inlet to the reactor, and the SO_2 concentration at the outlet of the reactor over the course of the test at Denver City. The average inlet H_2S concentration was 1928 ppm and one measurement of the outlet concentration of H_2S gave a reading of 2.5 ppm. Therefore the H_2S conversion is 100% within experimental uncertainty. The average SO_2 concentration in the product gas was 1812 ppm, which corresponds to an average selectivity of 98.9% for SO_2 and 1.1% for elemental sulfur (by difference). The selectivity for SO_2 is plotted in Figure 11, which for practical purposes indicates that only SO_2 is produced by TDA's oxidation catalyst under the conditions of the test.

Denver City Field Test Stain Tube Results



Figure 11. Selectivity to SO_2 determined from Sensidyne tube gas analysis.

4.0 CONCLUSIONS

We have completed a bench scale test using a process gas from Oxy-Permian's enhanced oil recovery facility, and have demonstrated over 300 hours of continuous H_2S oxidation activity with no loss of catalyst selectivity and no deactivation. The selectivity for SO₂ was better than 95% for the entire time with an H_2S conversion of 100%. The yield of elemental sulfur was at most about 1% and a fraction of a percent of COS was formed, apparently by the reaction between H_2S and CO₂.

5.0 CURRENT ACTIVITIES

5.1 Pilot Unit Testing

We are currently designing and fabricating a pilot-scale fixed-bed reactor that will hold about 15 lb of catalyst. This reactor will be placed upstream of the CrystaSulfSM pilot plant and will be used to generate the SO₂ required by the CrystaSulfSM plant in a test of 0.2 MMSCFD of gas (same gas as Table 1). The catalytic reactor itself will process about 1/3 of the total flow which is 0.66 MSCFD.

5.2 Other Planned Activities

The used catalyst from the lab scale test at the pilot plant will be examined to determine if any significant changes in surface area or surface properties occurred during the 300 hour test.