

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

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## ABSTRACT

This first quarter report of 2003 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  $\text{H}_2\text{S}$  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 off-shore applications.

CrystaSulf<sup>®</sup> (service mark of CrystaTech, Inc.) is a new nonaqueous sulfur recovery process that removes hydrogen sulfide ( $\text{H}_2\text{S}$ ) 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  $\text{H}_2\text{S}$  in the natural gas is first oxidized to  $\text{SO}_2$  at low temperatures over a heterogeneous catalyst. Low temperature oxidation is done so that the  $\text{H}_2\text{S}$  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. Previous reports described development of a catalyst with the required selectivity and efficiency for producing sulfur dioxide from  $\text{H}_2\text{S}$ . 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. Bench-scale catalyst testing at the CrystaSulf pilot plant using the actual pilot plant gas was successful, and a skid-mounted catalyst pilot unit has been designed for fabrication and testing at the CrystaSulf pilot site.

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## **1.0 INTRODUCTION**

This quarterly report is the ninth 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 process is a new nonaqueous sulfur recovery process that removes hydrogen sulfide ( $\text{H}_2\text{S}$ ) from gas streams and converts it into elemental sulfur. The hybrid CrystaSulf process uses a catalyst to first oxidize about 1/3 of the  $\text{H}_2\text{S}$  to  $\text{SO}_2$ .

## 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  $\text{H}_2\text{S}$  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 off-shore applications.

CrystaSulf is a new nonaqueous sulfur recovery process that removes hydrogen sulfide ( $\text{H}_2\text{S}$ ) 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  $\text{H}_2\text{S}$  in the natural gas is first oxidized to  $\text{SO}_2$  at low temperatures over a heterogeneous catalyst. Low temperature oxidation is done so that the  $\text{H}_2\text{S}$  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  $\text{H}_2\text{S}$  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  $\text{H}_2\text{S}$  conversion (99+%) with essentially no slip of oxygen. Changing the formulation, temperature, and  $\text{O}_2/\text{H}_2\text{S}$  ratio can be used to control  $\text{SO}_2$  selectivity over these catalysts.

The project involved the development of a catalyst using laboratory/ bench-scale catalyst testing, and then demonstration of the catalyst at CrystaTech's pilot plant site in west Texas. Several catalysts were prepared and found to have the required selectivity and efficiency for producing sulfur dioxide from  $\text{H}_2\text{S}$ . 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  $\text{H}_2\text{S}$  is present. Hexane represents the most reactive of the C1 to C6 series of alkanes, and since it exhibits low reactivity under  $\text{H}_2\text{S}$  oxidation conditions, and more importantly, does not change the  $\text{SO}_2$  selectivity, it appears that none of the C1 – C6 hydrocarbons should significantly interfere with the oxidation of  $\text{H}_2\text{S}$  to  $\text{SO}_2$ . 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 performance.

During May 2002, the bench-scale catalyst unit was successfully operated at the pilot plant using the actual pilot plant gas for over 300 hours. This occurred with no loss of catalyst selectivity and no deactivation. The selectivity for  $\text{SO}_2$  was better than 95% for the entire time with an  $\text{H}_2\text{S}$  conversion of 100%. Efforts have continued to be focused on finalizing the design of the catalyst pilot unit and engaging in an agreement with a fabricator to construct the unit.

### **3.0      EXPERIMENTAL**

No experimental work was performed during this quarter of activity. Work done during the quarter in preparation for pilot unit testing is described in Section 4.

## **4.0 RESULTS AND DISCUSSION**

### **4.1 Pilot Unit Testing**

Catalyst pilot unit fabrication did not begin in February 2003 as planned. As discussed with the DOE Project Officer, the goal of this project has been to gather bench scale and then pilot scale test data regarding use of an “SO<sub>2</sub> catalyst” upstream of CrystaSulf. This type of catalyst converts 1/3 of the inlet H<sub>2</sub>S to SO<sub>2</sub>, thus supplying the SO<sub>2</sub> needed for the CrystaSulf process. CrystaSulf utilizes liquid Claus reactions and requires a feed gas with an H<sub>2</sub>S to SO<sub>2</sub> ratio of 2:1. Combining CrystaSulf with this upstream SO<sub>2</sub> catalyst eliminates the costs associated with other options for introducing SO<sub>2</sub> into the system – i.e., operating cost of importing liquid SO<sub>2</sub> or the capital and operating cost of installing and operating a sulfur burner. The result is lower operating costs and possibly lower capital costs, depending on the size of the system.

CrystaTech has been working closely with TDA Research, Inc., regarding the potential use of a catalyst upstream of CrystaSulf that will convert 80-95% of the inlet H<sub>2</sub>S directly to sulfur, and a portion of the remaining H<sub>2</sub>S to SO<sub>2</sub>, so as to meet the H<sub>2</sub>S to SO<sub>2</sub> stoichiometry requirement. TDA has conducted successful pilot tests of this “direct oxidation” catalyst on an associated gas stream in West Texas at low pressure (1500+ hours of operation). CrystaTech has evaluated the benefit of this direct oxidation catalyst for CrystaSulf applications and economics. The conclusion is that the combination of direct oxidation catalyst and CrystaSulf is a substantially lower cost hybrid process than that obtained with SO<sub>2</sub> catalyst. While the combination of CrystaSulf and SO<sub>2</sub> 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 H<sub>2</sub>S and, as a consequence, the back end of the process is only about 10% as large.

The process configuration to use direct oxidation catalyst as the hybrid catalyst is somewhat more complex, since one now has to cool the gas stream exiting the catalyst bed and remove elemental sulfur, at pressure, in a sulfur condenser. As a result, the pilot plant is more complex and more expensive. On the plus side, a plant built to test direct oxidation catalyst can also be used to test SO<sub>2</sub> catalyst. Rather than build an SO<sub>2</sub>-catalyst-only pilot plant and then a second more complex plant for direct oxidation catalyst, CrystaTech plans to raise additional funding to build a pilot plant that can test both catalysts. We have already received a commitment from The Hanover Company to provide the pilot plant, and we have submitted two proposals for funding the additional testing. A portion of this additional funding will be credited to this DOE project as additional cost share.

### **4.2 Other Planned Activities**

Once we have the additional funding arranged, we will submit a revised schedule to DOE. We will likely be requesting a project extension beyond the current June 30, 2003 end date.

## **5.0 CONCLUSIONS**

The oxidation catalyst has been effective in converting  $\text{H}_2\text{S}$  to  $\text{SO}_2$  under synthesized laboratory conditions and actual plant gas with the bench-scale unit. Efforts are on-going to construct a catalyst pilot unit to do further testing on process gas from Oxy-Permian's enhanced oil recovery facility. The objective of these tests will be study the catalyst over a longer period of time and determine if there are scale-up issues that must be considered for large applications.