

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

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## ABSTRACT

This third 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 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 off-shore applications.

CrystaSulf<sup>®</sup> (service mark of CrystaTech, Inc.) 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 site in west Texas.

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## **1.0 INTRODUCTION**

This quarterly report is the eleventh 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 (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>.

## 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 off-shore applications.

CrystaSulf 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 and fouling due to coking from other hydrocarbon contaminants.

CrystaTech, Inc. owns the IP (U.S. Patent No. 6,416,729) associated with using an upstream catalyst in conjunction with CrystaSulf to produce a hybrid process. In CrystaTech's patent, the catalyst can produce SO<sub>2</sub> alone or SO<sub>2</sub> plus sulfur. Previous results from this study showed that the hybrid CrystaSulf process based on SO<sub>2</sub> producing catalyst 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., pressures up to 6.89 MPa (1000 psi) -- could be processed by the hybrid CrystaSulf process. In addition, previous testing with TDA's modified catalysts showed that they exhibit high H<sub>2</sub>S conversion (99+%) with essentially no slip of oxygen. Further, 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. However, the value of a specific catalyst in this hybrid process is not just a function of its performance in lab/pilot studies; it is directly a function of the cost of that catalyst (which may include license fees, transportation, and the cost of the catalyst itself). Unfortunately, good faith attempts (which began in February of 2002) to obtain an economically reasonable license to TDA's catalyst have been unsuccessful.

There have been three main impacts of the failure to reach a reasonable agreement with TDA. First, we have experienced project delays related to not having a catalyst we could pilot test in the field (there is little logic in consuming resources to test a catalyst when the future cost of that catalyst is unknown and subject to monopoly pricing). Second, in August of 2003 (after 18 months of unsuccessful negotiations with TDA) we contacted other catalyst suppliers. Third, we are planning some additional lab testing (to be conducted by Gas Technology Institute (GTI)) of one or more alternate catalysts. These last two items are moving ahead rapidly, as discussed in this report. We will be able to provide the DOE project officer with an update on these activities in the near future and a plan to move forward.

### **3.0 EXPERIMENTAL**

No experimental work was performed during this quarter. The two major activities have been to identify alternate sources of catalyst and to work with GTI to refurbish their catalyst testing equipment to be used in lab and field testing.

#### **3.1 Catalyst Sources**

We have identified several alternate sources of catalyst. The two leading candidates for the catalyst are IFP-Axens North America and Energy 2000, LLC. Axens appears to be the most promising. Axens is a major world-wide supplier of sulfur conversion catalyst. They report that their TiO<sub>2</sub>-based catalyst (CRS-31) can be used for COS hydrolysis and H<sub>2</sub>S-to-sulfur/SO<sub>2</sub> conversion depending on reactor conditions (mainly temperature and oxygen stoichiometry). This catalyst was the original “direct oxidation” catalyst (patents have expired). They provide this catalyst to Claus plants worldwide. It has also been used in many well-known industrial processes which oxidize H<sub>2</sub>S (e.g., Sulfint). Further, they have indicated that hydrocarbon fouling/cracking should not be a problem as long as reactor temperatures are below 250° C (which is 482° F, around the maximum temperature we have contemplated) and they are about to announce an enhancement which will allow much hotter operation. Further, they have extensive catalyst testing and development facilities. In addition, their catalyst is available for less than \$5/lb. GTI and CrystaTech have signed agreements with Axens to test their catalyst.

Energy 2000 LLC’s TiO<sub>2</sub> based catalyst (KTK-3) is of interest as they claim to have a special version which is tailored to high hydrocarbon environments. We have not reached the level of interest and interaction with them that we have with Axens as their catalyst supply chain is not as well established and we do not know if we need an alternative to Axens.

#### **3.2 Laboratory Testing**

CrystaTech has been working with GTI to plan refurbishing some existing GTI catalyst test equipment (located at GTI’s Des Plaines, Illinois, facility). This refurbishing activity is underway. CrystaTech and GTI will review the status of that work and outline the test matrix at a meeting on October 29, 2003. We do not anticipate that extensive testing will be required to define system performance around the three major system variables of temperature, space velocity, and oxygen stoichiometry. We will also conduct limited testing to evaluate interference from hydrocarbons.

#### **3.3 Pilot Unit Testing**

CrystaTech met with the Oxy Permian plant manager and staff at their Denver City, Texas, site on September 24, 2003. CrystaTech’s pilot unit testing facility is located at that site. We reviewed the status of our activities to locate the right catalyst for the hybrid process and our activities with GTI.

## 4.0 RESULTS AND DISCUSSION

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.

We were unsuccessful in our attempt to secure additional funding from RPSEA (Research Partnership to Secure Energy for America). They limited the awards to a narrow segment of offshore gas exploration and production. Future solicitations, assuming the full program is put in place by Congress, will be broader and have significant funding. This solicitation was only \$2 million total and attracted 50+ proposals, of which 6-7 were to be funded. None-the-less, CrystaTech and GTI intend to finish the project scope with other funding. GTI (a part owner of CrystaTech) is currently using FERC funding for the catalyst unit refurbishing. CrystaTech is using money from its recent successful investment round for its ongoing project activities. Use of these non-DOE funds will be shown as cost sharing.

In the near future, we will submit a revised schedule to DOE. We anticipate completion of the project before June 30, 2004, the date of our most recent project extension.

## 5.0 CONCLUSIONS

The oxidation catalyst has been effective in converting H<sub>2</sub>S to SO<sub>2</sub> 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 to study the catalyst over a longer period of time and determine if there are scale-up issues that must be considered for large applications.