

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

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ABSTRACT

This second 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 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 off-shore applications.

CrystaSulf[®] (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 H₂S. 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 tenth 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 (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.

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 off-shore applications.

CrystaSulf 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 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., pressures 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 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 H₂S. 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 H₂S is present. Hexane represents the most reactive of the C1 to C6 series of alkanes, and since it exhibits low reactivity under H₂S 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 H₂S 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 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 SO₂ was better than 95% for the entire time with an H₂S conversion of 100%.

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

The goal of this project has been to gather bench scale and then pilot scale test data regarding use of an “SO₂ catalyst” upstream of CrystaSulf. This type of catalyst converts 1/3 of the inlet H₂S to SO₂, thus supplying the SO₂ needed for the CrystaSulf process. CrystaSulf utilizes liquid Claus reactions and requires a feed gas with an H₂S to SO₂ ratio of 2:1. Combining CrystaSulf with this upstream SO₂ catalyst eliminates the costs associated with other options for introducing SO₂ into the system – i.e., operating cost of importing liquid SO₂ 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.

As discussed in last quarter’s report and with the DOE project officer, we have discovered that the use of a “direct oxidation” catalyst upstream of CrystaSulf rather than “SO₂ catalyst” provides far greater benefits for most applications. Direct oxidation catalyst will convert 80-95% of the inlet H₂S directly to sulfur, and a portion of the remaining H₂S to SO₂, so as to meet the H₂S to SO₂ stoichiometry requirement. 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 SO₂ catalyst. 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.

For that reason, we have been evaluating options to be able to test both catalyst types. 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 to enable valid data collection. As a result, the pilot plant is more complex. On the plus side, a plant built to test direct oxidation catalyst can also be used to test SO₂ catalyst. Rather than build an SO₂-catalyst-only pilot plant and then a second more complex plant for direct oxidation catalyst, CrystaTech has been attempting to raise additional funding to build a pilot plant that can test both catalysts.

We have already received funding from The Hanover Company and funding and support commitments from the Gas Technology Institute (GTI) to conduct this more comprehensive testing. A portion of this additional funding will be credited to this DOE project as additional cost share. We are currently working with GTI to evaluate refurbishing an existing catalyst test unit for this testing. Further we are in the process of soliciting additional funding for this work from the Research Partnership to Secure Energy for America (RPSEA).

4.2 Other Planned Activities

Once we have the additional funding arranged, we will submit a revised schedule to DOE. We have requested a project extension to June 30, 2004.

5.0 CONCLUSIONS

The oxidation catalyst has been effective in converting H₂S to SO₂ 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.