Hybrid Sulfur Recovery Process for Natural Gas Upgrading
Quarterly Technical Report

Reporting Period Start Date: 10/1/02
Reporting Period End Date: 12/31/02

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January 2003

DOE No. DE-FC26-99FT40725

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ABSTRACT

This fourth 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 ® (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 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. 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 eighth 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_2S) 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_2S to SO_2.

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

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_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 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 H_2S 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_2S conversion (99+%) with essentially no slip of oxygen. Changing the formulation, temperature, and O_2/H_2S ratio can be used to control SO_2 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 site 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 SO_2 selectivity, it appears that none of the C1 – C6 hydrocarbons should significantly interfere with the oxidation of H_2S to 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 SO_2 was better than 95% for the entire time with an H_2S 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. Construction of the unit will begin February 2003.

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 design of the catalyst pilot unit is complete and fabrication will begin February 2003. The fixed-bed reactor will hold about 8 lb of catalyst. This reactor will be placed upstream of the CrystaSulf pilot plant and will be used to generate the SO_2 required by the CrystaSulf plant. The catalytic reactor itself will process 0.1 MMSCFD of gas, which is about 1/3 of the total flow of 0.3 MMSCFD.

4.2 Other Planned Activities

Equipment procurement and catalyst module fabrication is planned for the next quarter. During this time, site preparation and piping tie-ins will be performed to get ready for pilot tests beginning in the second quarter of 2003.

5.0 CONCLUSIONS

The oxidation catalyst has been effective converting H_2S to SO_2 under synthesized lab 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. 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.