

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

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## ABSTRACT

This first 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  $\text{H}_2\text{S}$  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 offshore applications.

CrystaSulf<sup>SM</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. In a previous reporting period tests were done to determine the effect of hydrocarbons such as n-hexane on catalyst performance with and without  $\text{H}_2\text{S}$  present. The 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. Since hexane exhibits low reactivity under  $\text{H}_2\text{S}$  oxidation conditions, and more importantly, does not change the  $\text{SO}_2$  selectivity, we can conclude that the C1 – C6 hydrocarbons should not significantly interfere with the oxidation of  $\text{H}_2\text{S}$  into  $\text{SO}_2$ . During this quarter the effect of aromatic compounds were also found to have no effect on catalyst performance. This report gives the results of testing using contaminants from the pilot plant site.

## TABLE OF CONTENTS

1.0	Introduction .....	1
2.0	Executive Summary .....	2
3.0	Experimental .....	3
3.1	Background .....	3
3.2	Recent Progress .....	6
	Test #1 .....	7
	Test #2 .....	11
	Test #3 .....	12
4.0	Conclusions .....	14
5.0	Current Activities .....	15
5.1	Bench Unit Testing at the Pilot Site .....	15
5.2	Other Planned Activities .....	15

## LIST OF TABLES

1	Methane-rich CrystaSulf <sup>SM</sup> feed gas .....	4
2	Methane-poor CrystaSulf <sup>SM</sup> feed gas.....	4
3	Typical Composition of a methane poor natural gas.....	7
4	Experimental conditions during test with KO condensate vapors.....	8
5	Composition used to estimate vapor pressure of KO drum condensate.....	8
6	SuperTrapp output for KO condensate at $T_{dp} = 70^{\circ}\text{F}$ .....	9
7	Concentration estimate.....	9

## LIST OF FIGURES

1	Flow diagram for hybrid CrystaSulf <sup>SM</sup> process.....	3
2	P&ID of catalyst test apparatus for tests with knockout drum condensate .....	6
3	KO drum condensate head space vapor introduction device.....	7
4	H <sub>2</sub> S conversion and SO <sub>2</sub> and S selectivities when catalyst is exposed to vapors from knock-out drum condensate (first 50 hours) .....	10
5	Pressure and temperature during KO drum condensate run .....	10
6	Seven hour rerun with 2 <sup>nd</sup> (fresh) charge KO drum condensate .....	11
7	20 hour rerun with 3 <sup>rd</sup> (fresh) charge of KO drum condensate.....	12

## 1.0 INTRODUCTION

This quarterly report is the fifth 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<sup>SM</sup> (service mark of CrystaTech, Inc.) 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>.

The work described in this report was primarily conducted by CrystaTech's subcontractor, TDA Research, Inc., who developed the patented 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  $\text{H}_2\text{S}$  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 offshore applications.

CrystaSulf<sup>SM</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 while avoiding methane oxidation.

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. Tests were previously done to determine the effect of hydrocarbons such as n-hexane on catalyst performance with and without  $\text{H}_2\text{S}$  present. The 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. Since hexane 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 which evaluated the effect of toluene as a contaminant concluded earlier that toluene, too, was not reactive in the system. Testing this quarter evaluated the potential impact on the system of a hydrocarbon condensate from the pilot plant host company and is described here. Next quarter the bench unit will be taken to the field site for tests on the actual gas stream, which will be the final step prior to building and testing the pilot scale equipment at the site.

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. Further investigation for this promising process is planned.

## 3.0 EXPERIMENTAL

### 3.1 Background

CrystaSulf<sup>SM</sup> is a new *nonaqueous* sulfur recovery process that removes 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 CrystaSulf 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 (CH<sub>4</sub>) while avoiding CH<sub>4</sub> oxidation. In contrast, thermal oxidation would consume valuable natural gas.

In this process H<sub>2</sub>S does not have to be separated from the gas stream for sulfur recovery. A little more than 1/3 of the total flow of natural gas to be processed flows over the partial oxidation catalyst in a fixed bed catalytic reactor. The reactor is operated at about 300 psig and 250°C.

Between 95 and 100% of the H<sub>2</sub>S passing over the partial oxidation catalyst is converted into SO<sub>2</sub> + H<sub>2</sub>O (depending on the catalyst and the O<sub>2</sub>/H<sub>2</sub>S ratio). The remaining H<sub>2</sub>S is converted into elemental sulfur and water. The elemental sulfur is condensed and collected, and the product gas from the reactor (which now contains SO<sub>2</sub>) is blended back into the main flow stream. By controlling the splitting ratio to the catalytic reactor, the blended stream will

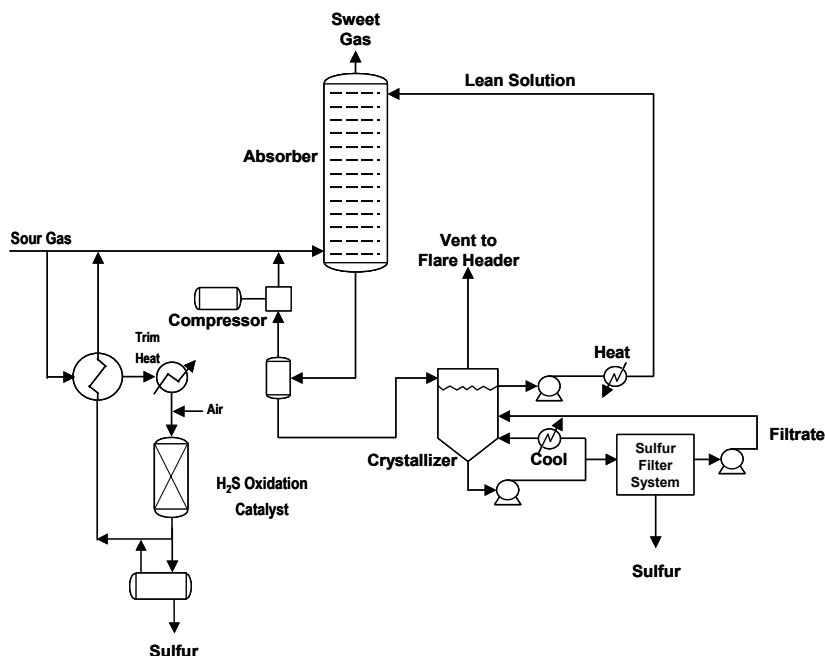


Figure 1. Flow diagram for hybrid CrystaSulf<sup>SM</sup> process.

contain the correct proportions of H<sub>2</sub>S and SO<sub>2</sub> for removal of the remaining sulfur using the CrystaSulf<sup>SM</sup> process. A flow diagram of the hybrid CrystaSulf<sup>SM</sup> process is shown in Figure 1. The composition of a methane-poor/CO<sub>2</sub>-rich natural gas is shown in Table 2, and that of a methane-rich gas is shown in Table 1.

Table 1. Methane-rich CrystaSulf<sup>SM</sup> feed gas.

Property	Value
Temperature	85 - 100°F
Pressure	950 – 1000 psig
Hydrogen sulfide (H <sub>2</sub> S)	0.0019 mol%
Nitrogen (N <sub>2</sub> )	0.3 mol%
Carbon Dioxide (CO <sub>2</sub> )	0.54 mol%
Methane (CH <sub>4</sub> )	95.3 mol%
Ethane (C <sub>2</sub> H <sub>6</sub> )	1.84 mol%
Propane (C <sub>3</sub> H <sub>8</sub> )	0.72 mol%
Butanes (C <sub>4</sub> H <sub>10</sub> )	0.61 mol%
Pentanes (C <sub>5</sub> H <sub>12</sub> )	0.315 mol%
Hexanes (C <sub>6</sub> H <sub>14</sub> )	0.23 mol%
Benzene (C <sub>6</sub> H <sub>6</sub> )	0.07 mol%
Toluene (C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub> )	0.026 mol%
Xylenes (C <sub>6</sub> H <sub>4</sub> (CH <sub>3</sub> ) <sub>2</sub> )	0.01 mol%
Total BTX	1060 ppmv

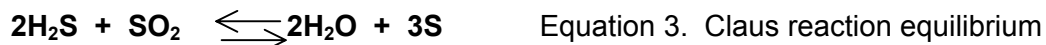
The main reactions that take place over the catalyst are the direct oxidation of H<sub>2</sub>S into SO<sub>2</sub> (Equation 1), the partial oxidation of H<sub>2</sub>S into elemental sulfur (Equation 2), and the Claus reaction between H<sub>2</sub>S and SO<sub>2</sub> to produce sulfur (Equation 3). The CrystaSulf<sup>SM</sup>

Table 2. Methane-poor CrystaSulf<sup>SM</sup> feed gas.

Parameter	Value
H <sub>2</sub> S	2000 ppm
CO <sub>2</sub>	84.46 vol%
N <sub>2</sub>	Negligible
CH <sub>4</sub>	9.95 vol%
C <sub>2</sub> H <sub>6</sub>	2.99 vol%
C <sub>3</sub> H <sub>8</sub>	1.99 vol%
Other	0.32 vol%
Temperature	60 – 110°F
Pressure	250 – 340 psig
Humidity	Sat. at 100°F

process runs the Claus reaction in the liquid phase. The objective of the TDA catalytic process is to oxidize approximately 1/3 of the H<sub>2</sub>S in the natural gas stream into SO<sub>2</sub> via Equation 1 so that the proper H<sub>2</sub>S to SO<sub>2</sub> ratio is present in the natural gas when it enters the CrystaSulf<sup>SM</sup> process. The exact amount of gas sent to the catalytic reactor depends on how much elemental sulfur is recovered directly in the partial oxidation. The more sulfur is recovered from the catalytic step, the greater the proportion of gas flow must be sent to the reactor. However, the more sulfur is recovered from the catalytic

reactor, the lower the sulfur load on the CrystaSulf<sup>SM</sup> process. Thus, there is a trade off between the capital and operating costs between the fixed bed reactor and the absorber. The optimum operating conditions depend on the activity of the solid catalyst and its selectivities to SO<sub>2</sub> and elemental sulfur.



#### *Requirements of Catalyst Used to Oxidize H<sub>2</sub>S to SO<sub>2</sub>.*

The general requirements for a successful catalyst for the hybrid CrystaSulf<sup>SM</sup> process are as follows:

1. The catalyst must exhibit very low activity for hydrocarbon oxidation.
2. The catalyst must give high conversions for H<sub>2</sub>S oxidation (lowers the catalyst bed volume).
3. The catalyst must exhibit high selectivity for SO<sub>2</sub>.
4. Selectivity to sulfur is a bonus.
5. All elemental sulfur formed needs to remain in the vapor phase in the reactor (i.e. the operating temperature of the catalyst must be above the sulfur dew point).

#### *Tasks*

##### **Task 1 - Develop a Bench-Scale, Prototype Process to Remove H<sub>2</sub>S from LowQuality Natural Gas**

This task had been essentially completed at the time the proposal was submitted on 9 August 1999, and the process was described in the proposal. The following material describes the process and the plan developed to scale-up the application.

##### **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**

##### **Task 3 - Complete Laboratory/Bench-Scale Testing of Task 2 and Demonstrate Scale-up Economic Advantages for On-shore and Offshore Applications**

### 3.2 Recent Progress – Testing the Effect of Contamination by Knockout Drum Headspace Vapors on the Performance of TDA #2 Catalyst.

In our previous report we discussed the results of catalyst tests where the feed gas was contaminated with several thousand parts-per-million of toluene and o-xylene. Neither of these aromatic hydrocarbons led to catalyst deactivation suggesting that the catalyst will be resistant to fouling or poisoning by BTX during the actual application of oxidizing  $\text{H}_2\text{S}$  into  $\text{SO}_2$  in natural gas.

While model compounds such as toluene and hexane are useful in determining the sensitivity of the catalyst to hydrocarbon contaminants, a more realistic test is to use condensate from the knockout drum at the actual gas plant where the field test will take place.

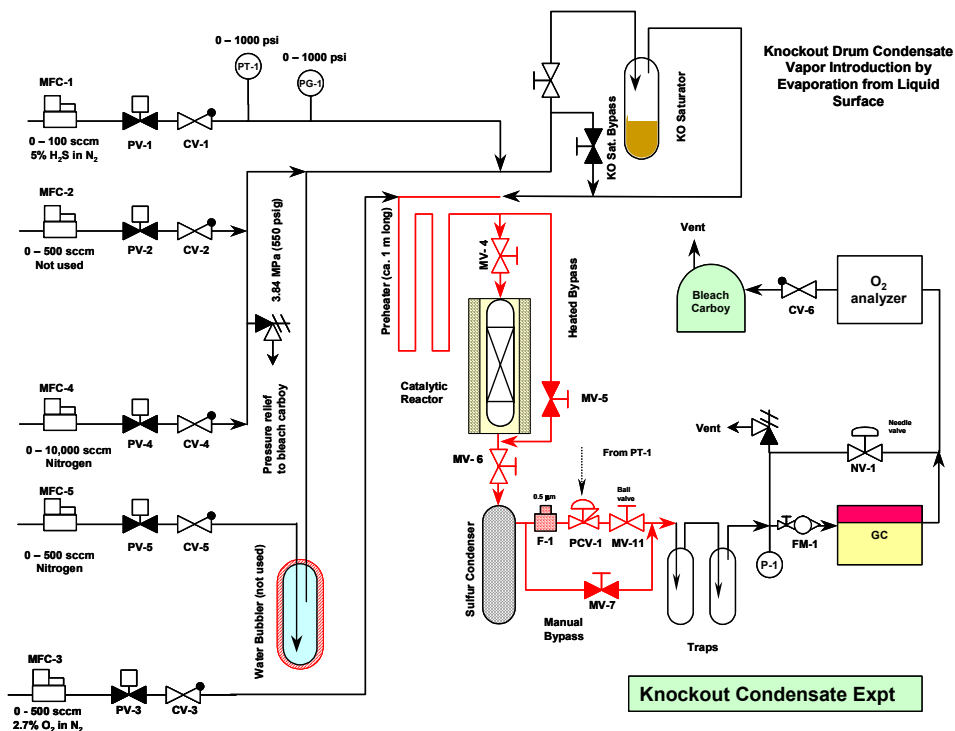


Figure 2. P&ID of catalyst test apparatus for tests with knockout drum condensate.

Figure 2 shows the apparatus modifications for introducing the vapors from the headspace of a sample of the knockout drum condensate from the actual gas plant. The condensate is essentially West Texas Crude oil and down-hole chemicals from an enhanced oil recovery using  $\text{CO}_2$  flood. The gas from the gas plant has a composition roughly the same as that given in Table 3 and the  $\text{CO}_2$  concentration is large because this is the associated gas from the  $\text{CO}_2$  flood.

For these experiments we added a condensate vaporizer (operated at room temperature). The  $N_2$ ,  $H_2S$  and  $O_2$  feed is passed through the headspace of the vaporizer to pick up the VOCs given off by the condensate. A diagram is shown in Figure 3. The device is essentially a regular bubbler except that the gases do not bubble through the liquid but rather pass over the surface of the liquid to pick up volatile components in the liquid. Not bubbling the gas through the liquid both better simulates the actual situation with the KO drum in the field, and also prevents the entrainment of aerosol particles of liquid. Aerosol particles could contain very non-volatile components that might foul the catalyst, be unrepresentative of the actual field conditions, and give false results for catalyst performance with the KO condensate (in the field we will have a coalescing filter located upstream of the catalytic reactor).

### Test #1

Table 4 shows the experimental conditions used in the test with KO condensate vapors. All of the experimental conditions were the same as in the xylene and toluene experiments, except that the space velocity had to be lowered to  $2000 \text{ cm}^3_{\text{gas}}/\text{cm}^3_{\text{catalyst}}/\text{hr}$  in the KO run because of a mass flow controller limitation that occurred because we were using 3%  $H_2S$  in  $N_2$ .

As before, the  $H_2S$  concentration was approximately 2000 ppm and the  $O_2/H_2S$  ratio was 1.5. The pressure was 285 psig and the catalyst temperature was  $225^\circ\text{C}$ . The concentrations of volatiles in the KO condensate sample were estimated based on the properties of West Texas Crude Oil and was not measured directly. We obtained two compositions for West Texas Crude: an intermediate and a sour crude. The compositions are shown in Table 5. For estimating the vapor pressure and thus the concentration of volatiles in our gas stream, we averaged the composition of the crude oils and then calculated the dew point pressure of the mixture at  $70^\circ\text{C}$  using the computer program SuperTrapp which is a vapor liquid equilibrium program developed at the National Institute of Standards and Technology (NIST formerly National Bureau of Standards – NBS). In the case of classifications such as “saturates” we used heptane ( $C_7H_{16}$ ) when we ran SuperTrapp.

Table 3. Typical composition of a methane poor natural gas.

Parameter	Value
$H_2S$	2000 ppm
$CO_2$	84.46 vol%
$N_2$	Negligible
$CH_4$	9.95 vol%
$C_2H_6$	2.99 vol%
$C_3H_8$	1.99 vol%
Other	0.32 vol%
Temperature	60 – $110^\circ\text{F}$
Pressure	250 – 340 psig
Humidity	Sat. at $100^\circ\text{F}$

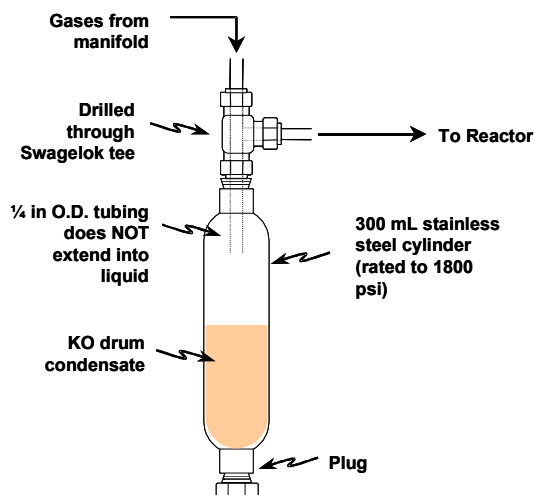


Figure 3. KO drum condensate head space vapor introduction device.

Table 4. Experimental conditions during test with KO condensate vapors.

Parameter	Value
H <sub>2</sub> S concentration	2000 ppmv
O <sub>2</sub> concentration	3000 ppmv
H <sub>2</sub> O concentration	dry
N <sub>2</sub> concentration	99.5%
KO vapor concentration	Estimated = 3400 ppm
Pressure	275 psig
Temperature	225 °C (437°F)
Amount of catalyst tested	4 gm
GHSV (at P&T)	2000 cm <sup>3</sup> <sub>gas</sub> /cm <sup>3</sup> <sub>catalyst</sub> /hr
Flow rate of 4%O <sub>2</sub> / N <sub>2</sub>	107 sccm
Flow rate of 5% H <sub>2</sub> S / N <sub>2</sub>	95 sccm
Flow rate of pure N <sub>2</sub>	1226 sccm
Predicted bed ΔP	0.2 psi (8.3 in H <sub>2</sub> O)
Run time	50+ hours

Table 5. Composition used to estimate vapor pressure of KO drum condensate.

West Texas Crude	Intermediate	Sour	Averaged	Compound used in SuperTrapp Calc.
API Gravity	40.8	30.2	35.5	
Sulphur (wt%)	0.48	1.5	0.99	Ignored
Saturates (wt%)	66	51	58.5	Heptane
Aromatics (wt%)	26	36	31	Benzene
Resins (wt%)	6	9		Ignored
Asphaltenes (wt%)	1	5		Ignored
Waxes (wt%)	4	5		Ignored
Benzene (ppm)	1380	3510	0.002	Benzene
Toluene (ppm)	2860	6980	0.005	Toluene
Ethylbenzene (ppm)	1120	5610	0.003	Ethylbenzene
Xylenes (ppm)	4290	4440	0.004	Ortho-xylene
C3-benzenes (ppm)	5920	7410	0.007	Cumene

The properties of the mixture at a dew point temperature of 70°F calculated with SuperTrapp are shown in Table 6. The program calculated the dew point pressure at 70°F to be P = 0.974 psia.

Table 6. SuperTrapp output for K.O. condensate at T<sub>dp</sub> = 70°F

----Component-----	---Feed---	--Liquid--	--Vapor---
n-Heptane	0.653478	0.843619	6.53E-01
Benzene	0.34631	0.155133	3.46E-01
Toluene	5.59E-05	8.69E-05	5.59E-05
Ethylbenzene	3.35E-05	1.53E-04	3.35E-05
o-Xylene	4.47E-05	2.66E-04	4.47E-05
Isopropylbenzene (cumene)	7.82E-05	7.42E-04	7.82E-05
Molecular Weight	92.5555	96.7948	92.5555
Compressibility Factor	0.993808	3.78E-04	0.993808
Density (lb/ft <sup>3</sup> )	1.60E-02	43.8864	1.60E-02
Enthalpy (BTU/lb)	-439.619	-811.685	-439.619
Entropy (BTU/lb*°F)	1.03011	7.53E-01	1.03011
Heat Capacity (BTU/lb*°F)	0.354985	4.96E-01	0.354985
Cp/Cv		1.29259	1.07E+00
Sound Speed (ft/sec)		3770.19	547.541
Joule-Thompson (°F/psia)		-5.37E-03	0.800956
Viscosity (lb/ft*sec)		2.88E-04	4.23E-06
Thermal conductivity (BTU/ft*hr*F)		0.07385	6.16E-03

Assuming that  $P = 0.974$  psia is the partial pressure of the condensate at room temperature, the total volatiles load in the feed gas would be about 3400 ppm (Table 7).

Table 7. Concentration estimate.

Property	Value
Dew point temperature (°F)	70
Dew point pressure (psia)	0.974
Total Pressure (psia)	287.2
Concentration (ppm)	3392

Figure 4 shows the results for the first 50 hours of testing with the catalyst exposed to KO drum condensate vapors, and the experimental conditions are shown in Table 4. Initially,  $H_2S$  oxidation was done with no KO vapors in the feed, corresponding to the time between 3 and 7 hrs in Figure 4. During this initial time, the  $H_2S$  conversion was 100%, and the selectivities to  $SO_2$  and sulfur were  $S_{SO_2} = 91\%$  and  $S_S = 9\%$ . At about 7.6 hours into the run, the total flow was diverted so that it passed over the KO condensate in the vaporizer shown in Figure 3. When the KO vapors were introduced, the  $SO_2$  selectivity dropped to about 70% but then slowly recovered to 100% over the next 35 hours. This might have been due to slow depletion of the volatiles from the condensate sample as we are trying to simulate a continuous process using a batch method of introducing the KO vapors.

Examining the data at 50 hours, there is a sharp decrease in  $SO_2$  selectivity to 90%. This is the time where the data were downloaded from the process control computer prior to the end of the run. During this time, control of the experiment is temporarily suspended. When control is suspended, the flow rates, temperatures and other parameter values stay latched in the electronics but there is no control. As a result the catalyst temperature briefly dropped to 217°C which may have caused the change in  $SO_2$  selectivity. By 55 hours the temperature was back to 225°C, but the catalyst had not recovered completely. It may be that there was a surge of volatiles from the KO condensate that accompanied the brief shutdown because during this time the pressure

increased to 300 psi, and then when control was restored, abruptly dropped back to 275 psi. The pressure and temperature traces are shown in Figure 5.

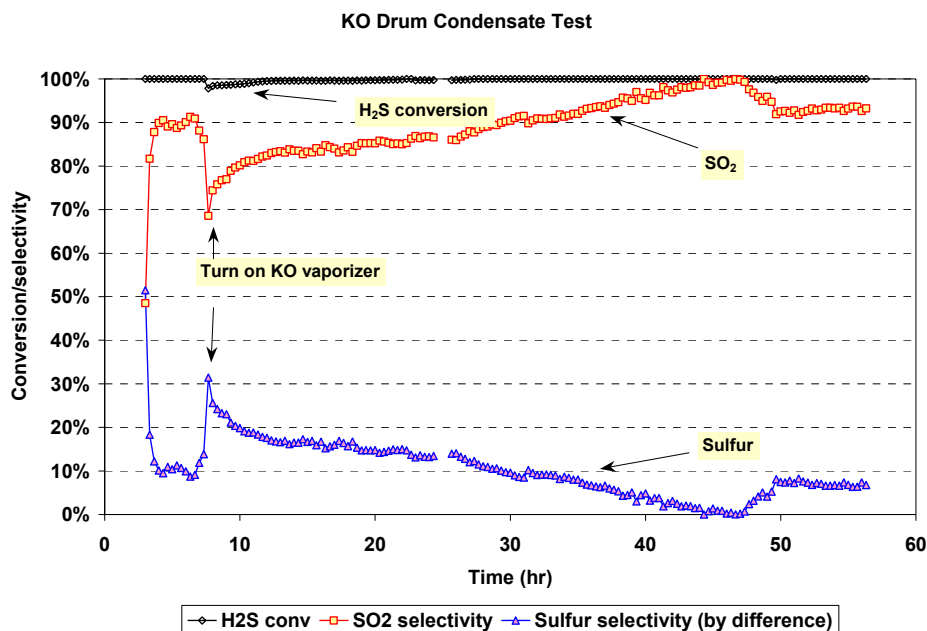


Figure 4. H<sub>2</sub>S conversion and SO<sub>2</sub> and S selectivities when catalyst is exposed to vapors from knock-out drum condensate (first 50 hours).

The gradual increase in SO<sub>2</sub> selectivity with time suggests that the change in selectivity may be due to the volatile components of the KO drum condensate slowly evaporating from the sample and therefore gradually decreasing in concentration. This is expected because we are attempting to simulate a steady state process (continuous processing of gas from the KO drum in the field application) with a semi-batch process where we charge a vaporizer (Figure 3) with condensate.

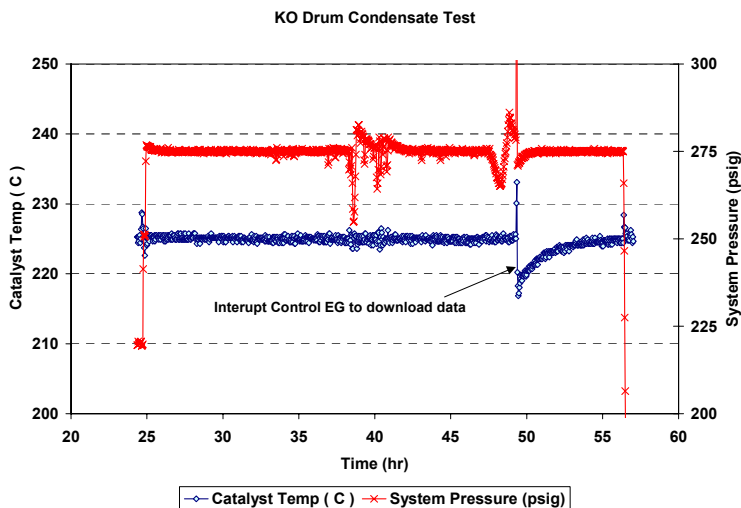


Figure 5. Pressure and temperature during KO drum condensate run.

In the real application the catalyst will be continuously exposed to a nearly constant concentration of volatiles from the KO drum because the gas being processed continuously brings in fresh condensate. To better simulate the continuous gas processing situation, we repeated the test two more times using a fresh charge of KO condensate for each test.

## Test #2

Figure 6 shows the H<sub>2</sub>S conversion, and selectivities to SO<sub>2</sub> and S during a 7 hour test with a fresh charge of KO drum condensate without replacing the catalyst (the catalyst remained in the reactor). This run was only 7 hours long because we wanted to determine if the initial drop in selectivity to SO<sub>2</sub> followed by a gradual increase in selectivity that we saw in the first test (Figure 4) was a real effect.

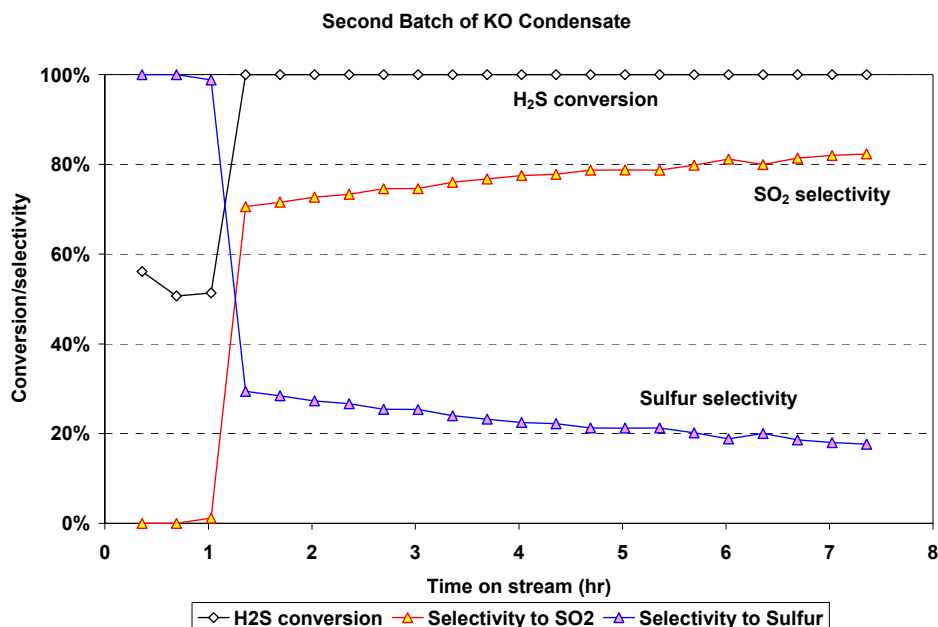


Figure 6. Seven hour rerun with 2<sup>nd</sup> (fresh) charge of KO drum condensate.

The effect of initially low SO<sub>2</sub> selectivity followed by a gradual increase appears to be real. During the first hour in Figure 4, the system was coming to steady state. At 1 hour, the H<sub>2</sub>S conversion was complete (this corresponds to an H<sub>2</sub>S concentration of less than about 5 ppm in the product gas) and the SO<sub>2</sub> selectivity was 71%. This gradually increased to approximately 83% by the end of hour 7.5. During this time the H<sub>2</sub>S conversion remained at 100% indicating that while the SO<sub>2</sub> selectivity depended on the presence of volatile organics in the feed, there was no catalyst deactivation due to these contaminants.

The trend of increasing SO<sub>2</sub> selectivity was observed during the first run and the fact that it occurs here as well suggests that the selectivity of the catalyst is shifted by

the presence of the most volatile components in the condensate because these will be the first to evaporate. Also, the concentration of these volatiles will be highest at the beginning of the run. According to the analysis of West Texas Crude Oil (Table 5) it is likely that the most abundant contaminants in the early part of the test are the BTEX aromatics. These results are similar to those observed during the experiments with toluene and o-xylene; there was no deactivation of the catalyst in those cases either. All of the  $O_2$  was consumed during the 2<sup>nd</sup> run with the KO condensate, and the gas flow rates, temperature and pressure were very stable.

The overall conclusion from the tests with toluene, xylene and vapors from the KO drum condensate is that none of these materials cause catalyst deactivation. The presence of these vapors does appear to affect  $SO_2$  selectivity, however, apparently by shifting the selectivity toward elemental sulfur. Little or no oxidation of the hydrocarbons is apparent because all of the  $O_2$  fed into the system can be accounted for by the combination of  $SO_2$  and S (oxygen mass balance). Also, if  $O_2$  were being consumed by hydrocarbon oxidation, then unconverted  $H_2S$  would break through.

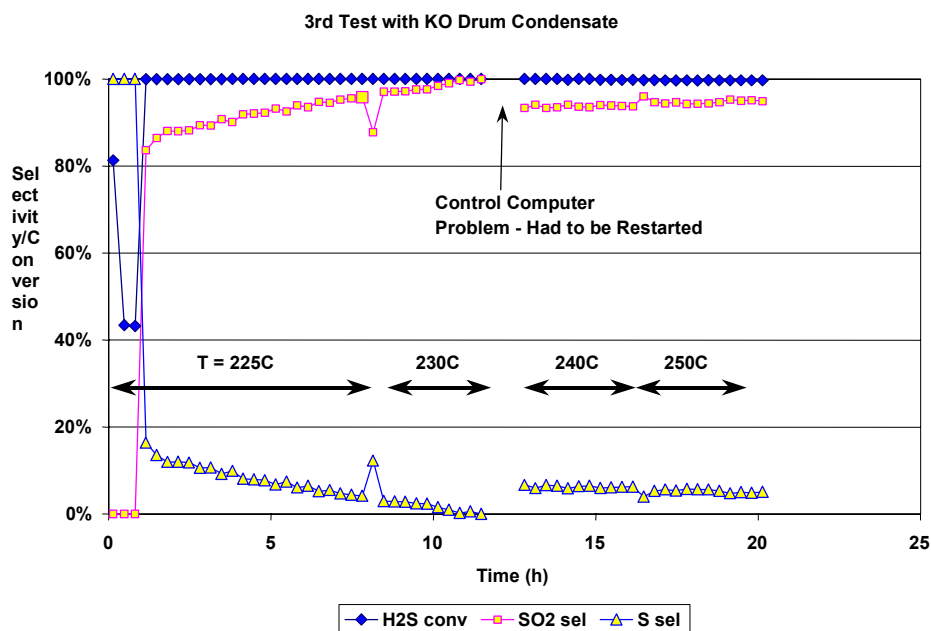


Figure 7. 20 hour rerun with 3<sup>rd</sup> (fresh) charge of KO drum condensate

### Test #3

Figure 7 shows the results for a 15 hour run with a 3<sup>rd</sup>, fresh charge of KO drum condensate. As before, the catalyst was not changed out for this test. Figure 7 shows that there was a gradual increase in selectivity from approximately 84% up to essentially 100% during the first 10 hours of the run. Because this is the same behavior observed in the two previous runs, we suspect that this is due to evaporation and gradual loss of the more volatile components of the KO drum condensate. At 11.5 hr, the process control computer malfunctioned and Control EG had to be restarted. During the time

interval, the gases were still flowing but the catalyst temperature dropped. This is the reason that the SO<sub>2</sub> selectivity abruptly drops to 93% at 12.8 hours.

During the first 8 hours of the 3<sup>rd</sup> batch run, the catalyst temperature was 225°C. The temperature was then increased to 230°C over 4 hours followed by 4 hours at 240°C and 250°C. Examining Figure 7 suggests that above about 230°C, the temperature had little effect on the conversion at this space velocity (2000 cm<sup>3</sup><sub>gas</sub>/cm<sup>3</sup><sub>catalyst</sub>/hr). While the computer problem just before the 240°C portion of the experiment confuses the results somewhat, it appears that operation in the 225-230°C temperature range gives high selectivity to SO<sub>2</sub> with complete H<sub>2</sub>S conversion.

## **4.0 CONCLUSIONS**

The most important observation is that the H<sub>2</sub>S conversion was 100% during the entire experiment indicating that there was no catalyst deactivation due to the presence of the KO drum vapors. Since this was the third batch of KO drum condensate and the catalyst had now been exposed to its vapors for a cumulative time of over 80 hours (including the first two tests), we are confident that the catalyst will not be deactivated by exposure to KO vapors carried over from the KO drum into the catalyst bed by the natural gas stream.

## **5.0 CURRENT ACTIVITIES**

### **5.1 Bench Unit Testing at the Pilot Site**

We met with the host site company, Oxy Permian Ltd., on April 23, 2002, to review plans to test the bench unit at the pilot site near Denver City, Texas, followed by fabrication of the pilot scale catalyst reactor and subsequent testing of that equipment at the site. The host site company agrees with the test objectives and approach and expressed interest in receiving the pilot test results to allow them to evaluate potential commercial applications.

### **5.2 Other Planned Activities**

#### ***5.3.1 Catalyst pellet production***

Once we have determined the best catalyst composition, a qualified supplier of the material is needed. The supplier will need to provide reproducible batches for qualification, and ultimately supply the required quantities for pilot plant testing. When commercial quantities of catalysts and sorbents designed by TDA are needed, TDA generally supplies them through Saint Gobain NorPro (Cleveland, OH). Details concerning NorPro's business and expertise were discussed in a previous report and are not repeated here.

#### ***5.3.2 Durability Testing***

Using our pellet reactor, we will perform a catalyst lifetime/durability test on the pelletized form of the catalyst (a sample manufactured by NorPro). Our pellet reactor is designed specifically to be able to test catalysts in the final physical form (e.g., 1/8 – 1/4 in. pellets) that will be used in the pilot plant. This testing ensures that no unforeseen variations in catalyst performance are introduced when the catalyst is manufactured in its final physical form.