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GASOLINE FROM NATURAL GAS BY SULFUR PROCESSING

Final Technical Report for the Period June 1993-July 1996

By
Erek J. Erekson

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For
U.S. Department of Energy
Pittsburgh Energy Technology Center
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EXECUTIVE SUMMARY

This report presents the work performed at the Institute of Gas Technology (IGT) for Project No. 61104 from June 23, 1993, to July 15, 1996, under Department of Energy (DOE) Contract No. DE-AC22-93PC92114. This program had coordinated funding from IGT's Sustaining Membership Program (SMP) along with funding from DOE.

During this project, the following accomplishments were made:

- This project was the first to discover and develop two catalysts that react methane and hydrogen sulfide in high conversions to hydrogen and carbon disulfide. In over 327 runs, the best yield of CS_2 was 98% with catalyst IGT-MS-103.
- CS_2 hydrogenation with a mixture of Co exchanged ZSM-5 zeolite and MoS_2 hydrogenation catalyst achieved 95% conversion of CS_2 and 51% selectivity to C_4^+ hydrocarbons.
- The concept of converting methane to gasoline range hydrocarbons was demonstrated in a single unit with two reactors — one for the conversion of methane to carbon disulfide and the second for the conversion of carbon disulfide to liquid hydrocarbons.
- In catalyst screening tests it was demonstrated that activity for H_2S decomposition and activity for carbon regeneration were strong indicators for catalytic activity for the methane-hydrogen sulfide reaction.
- The sulfur tolerant MoS_2 catalyst used in hydrogenating CS_2 showed activity for making methyl mercaptan.
- A preliminary economic study of the application of HSM technology to producing hydrogen for a refinery showed that this is a potential replacement for Claus units and Tail Gas Cleanup units and could be a profitable means of making refinery hydrogen depending on the price of co-produced CS_2.

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OBJECTIVE

The overall objective of this research project was to develop a catalytic process to convert natural gas to liquid transportation fuels. The process, called the HSM (Hydrogen Sulfide-Methane) Process, consists of two steps that each use catalysts and sulfur-containing intermediates: 1) to convert natural gas to CS_2 and 2) to convert CS_2 to gasoline-range liquids. Experimental data generated in this project were for use in evaluating the commercial potential of the process.

INTRODUCTION

Natural gas is an abundant resource in various parts of the world. The major component of natural gas is methane, often comprising over 90% of the hydrocarbon fraction of the gas.[1] The expanded use of natural gas as fuel is often hampered because of difficulties in storing and handling a gaseous fuel. This is especially true for natural gas in remote areas, such as the North Slope of Alaska. The successful implementation of a natural gas-to-gasoline process would decrease dependence on imported oil for transportation fuels. These factors make it very desirable to convert natural gas into valuable liquids.

There are commercial or nearly commercial processes for converting natural gas to gasoline-range liquids. These processes, such as the Fischer-Tropsch synthesis[7,29] and Mobil's MTG[1] (Methanol to Gasoline), start with the steam reforming of methane. Steam reforming accounts for 50% to 60% of the capital cost of a gas-to-liquids plant. In addition, steam reforming of methane requires the removal of sulfur compounds present in natural gas down to less than 0.1 ppm. This additional gas cleanup step, with its additional cost, is necessary because the catalysts are quickly poisoned by sulfur compounds.

In this program, IGT has investigated a two-step process that uses H_2S as a reactant to convert natural gas to gasoline-range liquids. In the first step of the process, methane is converted to CS_2 and hydrogen:

$$2\,H_2S + CH_4 \rightarrow CS_2 + 4H_2 \qquad (1)$$

In the second step, CS_2 is hydrogenated to gasoline-range hydrocarbon liquids:

$$CS_2 + 3H_2 \rightarrow -[CH_2]- + 2\,H_2S \qquad (2)$$

For the HSM process, a sulfur-removal step down to 0.1 ppm with associated guard beds is not necessary. Sulfur, usually considered a poison, is used as a reactant. This method of methane conversion uses H_2S to convert methane to CS_2. Then CS_2 and hydrogen can be catalytically converted to gasoline-range hydrocarbons. All the H_2S generated during the CS_2-to-gasoline reaction can be recycled. An additional advantage of the proposed process is that the hydrogen required for the process is produced in Step 1 without using a steam reformer.

The impetus for studying the HSM process was the potential for improving the overall economics of natural gas conversion, which could result in much more natural gas being used to make liquid fuels, thus decreasing the U.S. dependence on foreign sources of oil.

BACKGROUND

Literature Review

At the commencement of this project no catalysts for Reaction 1 were known, while in Reaction 2 there were catalysts as noted in patents[3,4] by the Mobil researchers. Because the conditions, catalysts, and thermodynamics are quite different for the two steps, they will be discussed separately in this section.

The Hydrogen Sulfide Methane Reaction

A non-catalytic approach to converting methane and H_2S is the subject of a much earlier study.[10] More recently, researchers[20] at the National Technical University of Athens studied the conversion of methane and hydrogen sulfide to hydrogen. In this study they calculated equilibrium conversions and allowed for the formation of many products including $CH_4/H_2S/H_2/CS_2/S_2/C_2H_6/C_2H_4$. They calculated equilibrium concentrations of H_2 as high as 25% and CS_2 as high as 9%. However, they worked within the narrow temperature range of 700° to 825°C. In their thermodynamic calculations they allowed for the formation of ethylene and ethane, but did not allow the formation of elemental carbon. In addition to calculations, experiments were performed in a reactor. They showed homogeneous thermal conversions and heterogeneous catalytic conversions in the 700° to 860°C range. The heterogeneous catalyst was a pelletized MoS_2 powder. Their results for H_2S conversion were from 2% to 10% for the thermal reaction and from 11% to 35% for the catalytic reaction.

Thermodynamics

The thermodynamics of the methane-hydrogen sulfide reaction (see Reaction 1) were calculated over the temperature range 727° to 1227°C (1000 to 1500 K). The values of Gibbs Free Energy are shown below in Table 1.

Table 1. GIBBS FREE ENERGY DATA IN kcal/mol

Temp, °C		727	827	927	1027	1127	1227
Temp, K		1000	1100	1200	1300	1400	1500
Substance	H_2S	-9.841	-8.668	-7.490	-6.309	-5.129	-3.949
	CS_2	-4.163	-4.325	-4.482	-4.639	-4.796	-4.957
	CH_4	4.625	7.247	9.887	12.535	15.195	17.859
	H_2	0.000	0.000	0.000	0.000	0.000	0.000
Reaction*		+10.894	+5.764	+0.611	-4.556	-9.733	-14.918

* $2\,H_2S + CH_4 \rightarrow CS_2 + 4H_2$

From the table above, one can find that the Gibbs Free Energy of reaction changes from positives values (non-spontaneous) to negative values (spontaneous) above 927°C (1200 K). The advantages of operating at temperatures above 900°C are that this reaction becomes spontaneous as written and the prospect for high conversions of the reactants is realized.

The H_2S decomposition reaction is a significant part of the first step in the overall gas to gasoline process. Reaction 1 can be separated into two reactions:

$$CH_4 + 2\,S_2 \rightarrow CS_2 + 2\,H_2S \qquad (3)$$

$$4\,H_2S \rightarrow 4\,H_2 + 2\,S_2 \qquad (4)$$

Reaction 3 is a known methane conversion reaction and is used commercially to produce CS_2. Yet, hydrogen is not produced. H_2S is the by-product and must be dealt with. Hydrogen is an essential reactant for the conversion of CS_2 to gasoline-range hydrocarbons. Our reasoning for studying the H_2S decomposition reaction is to produce a catalyst with activity for Reaction 3, as well as Reaction 4. Thus, the summation of these two reactions will provide both CS_2 and hydrogen, making the operation more efficient, so that no outside source of hydrogen is required.

There are many cases in the research and development of catalysts that indicate that a bi-functional catalyst has become the catalyst of choice. Some examples follow:

a. Platinum on alumina or zeolites for hydrocarbon reforming:[13] Platinum provides dehydrogenation activity while the alumina/zeolite provides acidity for skeletal carbon rearrangement. The two functions in one catalyst provide for higher activity and selectivity in reforming straight chain hydrocarbons into high-octane gasoline.

b. Bi-metallic cluster catalysts for reforming:[26] John Sinfelt at Exxon found that by putting two metals into one catalyst, a much more active and selective catalyst could be formed. One metal was active for a desired reaction (carbon bond scission) and an undesired reaction (dehydrogenation). The second metal had very low activity for the desired reaction, but it poisoned the undesired reaction. By putting the two metals together in one catalyst as bi-metallic clusters the overall effect was to produce a catalyst that had high activity for the desired reaction and almost no activity for the undesired reaction. This made a highly selective and active catalyst.

c. Higher alcohol synthesis catalysts:[27] A methanol synthesis catalyst was modified with a chain growing Fischer-Tropsch catalyst. The result was a catalyst that made C_1 to C_5 alcohols. The methanol synthesis catalyst by itself would not produce higher alcohols, and the Fischer-Tropsch catalyst alone would not produce alcohols. Together in one catalyst the result is a catalyst active for making C_1 to C_5 alcohols.

As for the decomposition of hydrogen sulfide there are several groups that have studied the problem. Thermochemical,[5,6,11,12,16,18,19,24,25] electrolytic,[15] and photochemical[14,21,30] processes have been investigated as possible methods have been used for recovering both hydrogen and sulfur from hydrogen sulfur. Thermochemical methods for the decomposition of hydrogen sulfide will be briefly reviewed here.

The direct thermal decomposition of hydrogen sulfide (Reaction 4) to hydrogen and sulfur under catalytic conditions has been reported by many.[5,15,19,21] MoS_2 , WS_2 , Li_2S, and Cr_2S_3 were reported[6] to be the most effective catalysts for direct hydrogen sulfide decomposition.

X-ray diffraction measurements of the solid phase demonstrate that the composition of these sulfides after the reaction is identical to that of the original material. The higher surface area will increase the reaction rate.

The second method of thermochemical decomposition involves two steps in which the reaction of hydrogen sulfide with a "lower" metal sulfide to give hydrogen and a "higher" metal sulfide is followed by thermal decomposition of "higher" sulfide to produce sulfur and regenerate a "lower" metal sulfide.

$$M_aS_b + cH_2S = M_aS_{b+c} + cH_2 \tag{5}$$

$$M_aS_{b+c} = M_aS_b + cS \tag{6}$$

$$cH_2S = cH_2 + cS \tag{7}$$

To be a suitable candidate for this process, a metal sulfide M_aS_b must be readily sulfided by hydrogen sulfide to give M_aS_{b+c} and hydrogen. Then the thermal decomposition of this "higher" sulfide is used to regenerate M_aS_b. By this two step process, the hydrogen sulfide can be decomposed to hydrogen and sulfide with higher conversion than those of one-step equilibrium limitation. Vanadium sulfide, nickel sulfide, and iron sulfide have this property.[23] For nickel sulfide, the Ni_3S_2 was sulfurized in the temperature range of 500° to 600°C (773 to 873 K) with releasing hydrogen gas. The thermal decomposition of NiS was carried at 800°C (1073 K) with gas phase sulfide being produced.[23]

The CS_2 Hydrogenation Reaction

Researchers[3,4] at Mobil have done some earlier work on the conversion of sulfur compounds to hydrocarbons. The examples in these patents show that carbon disulfide can be hydrogenated to gasoline-range hydrocarbons over ZSM-5 catalyst. The conversions were higher for a mixture of ZSM-5 zeolite and a Co on silica catalyst. The highest conversion of CS_2 was 40.3% with a selectivity to C_4^+ liquids of 45%. The non-selective carbon product was methane and light gases. No CO or CO_2 was produced. Hydrogen sulfide is a by-product to this reaction. The patents also show that other sulfur compounds, including methyl mercaptan, can be the starting point for hydrocarbon synthesis. The conversions and selectivity from these runs may not be high enough to commercialize the process as reported; their work did show that the ZSM-5 zeolite is active for the conversion of sulfur compounds to hydrocarbons and that this zeolite is stable in the presence of high concentrations of H_2S. The Mobil work also assumed that hydrogen would be produced by steam reforming or by decomposing H_2S on metal surfaces. The use of CS_2 or methyl mercaptan for making hydrocarbons is another demonstration of the conversion of functionalized methane to higher hydrocarbons over ZSM-5 zeolite. Other examples of making hydrocarbons from functionalized methane are methanol and dimethyl ether, used commercially at Mobil's plant in New Zealand and methyl chloride used by Noceti and Taylor.[28]

EXPERIMENTAL METHODS

Preparation of Catalysts

Preparation of catalysts for this project were performed in IGT's catalyst preparation lab using proprietary techniques for producing high surface area and high-temperature stable sulfide catalysts. Solid catalyst powders were made by sulfide conversion, drying, reduction, and calcination. The powders were pressed into 2 mm by 15 mm I.D. wafers to a pressure of 10,000 psig. The wafers were crushed and sieved into -8+20 mesh granules before being placed into the catalyst reactors. Two non-sulfide catalysts, IGT-MS-107 and IGT-MS-108, were prepared differently. IGT-MS-107 and IGT-MS-108 were both silicon dioxide catalysts. IGT-MS-107 was a low surface area silicon dioxide that was crushed and sieved to -8+20 mesh. IGT-MS-108 was a high surface area silicon dioxide prepared from silica gel. The powder was mixed with deionized water to incipient wetness and dried at 100°C for overnight. The granules were crushed and sieved to -8+20 mesh. In addition to the MS series of catalysts, a zeolite catalyst, Co-HZSM-5-56, was made by ion exchanging cobalt into an HZSM-5 zeolite. Also, IGT-HS-103 was prepared as a high surface area molybdenum sulfide catalyst. This catalyst has been shown to have a high activity for hydrogenation.

Reactor Tests

A catalyst test unit at IGT was modified to accommodate the flows, temperatures, and reactants for this project. Figure 1 shows the schematic diagram of a catalyst reactor system. The feed gases, hydrogen sulfide, nitrogen, and methane were controlled by mass flow controllers (Brooks Instruments 5850). The gas flow rate was calibrated by a dry test meter (American Meter Company). The gases from mass flow controllers were mixed as they flowed into a custom-made quartz adapter. There were two openings in the adapter. One was for mixed feed gas; another was for a ceramic thermowell. The feed gas flows through the adapter into 1.07-m-long, 22-mm-I.D. and 25-mm-O.D. quartz reactor. The joint, which connects with the adapter and quartz reactor, was sealed by TFE sleeve. There were three indents around the quartz reactor at 0.66 m from the top. The catalyst granules were held above the indents with quartz wool. The pressure of the reactor system was measured by a pressure gauge. The temperature of the catalyst reactor was measured by a Type R, high-temperature thermocouple, which was protected by a 6.4-mm-O.D. ceramic thermowell. The furnace for the high-temperature work was a 51-mm-I.D., 0.81-m-long, split-tube, high-temperature furnace (Series 3420, Applied Test Systems, Inc.) with a maximum temperature of 1540°C (1813 K). Product gases were sampled at a point before the flowmeter. The product gas flow rate was measured by a dry test meter (American Meter Company). At the end of the project the dry test meter was replaced by a digital flowmeter (Fisher Scientific Model 650). Before releasing the product gases to the vent, the gases were sent through a 2-liter scrubber containing a solution of 6M NaOH and 6M H_2O_2. This proved to be an effective means of removing H_2S and other sulfur gases from the exhaust. This reactor unit was used for H_2S decomposition tests, carbon regeneration tests, and methane-hydrogen sulfide tests. For the carbon disulfide hydrogenation tests the quartz reactor was replaced with a 3/4-inch, Schedule 80 stainless-steel pipe reactor (18.8-mm-I.D.).

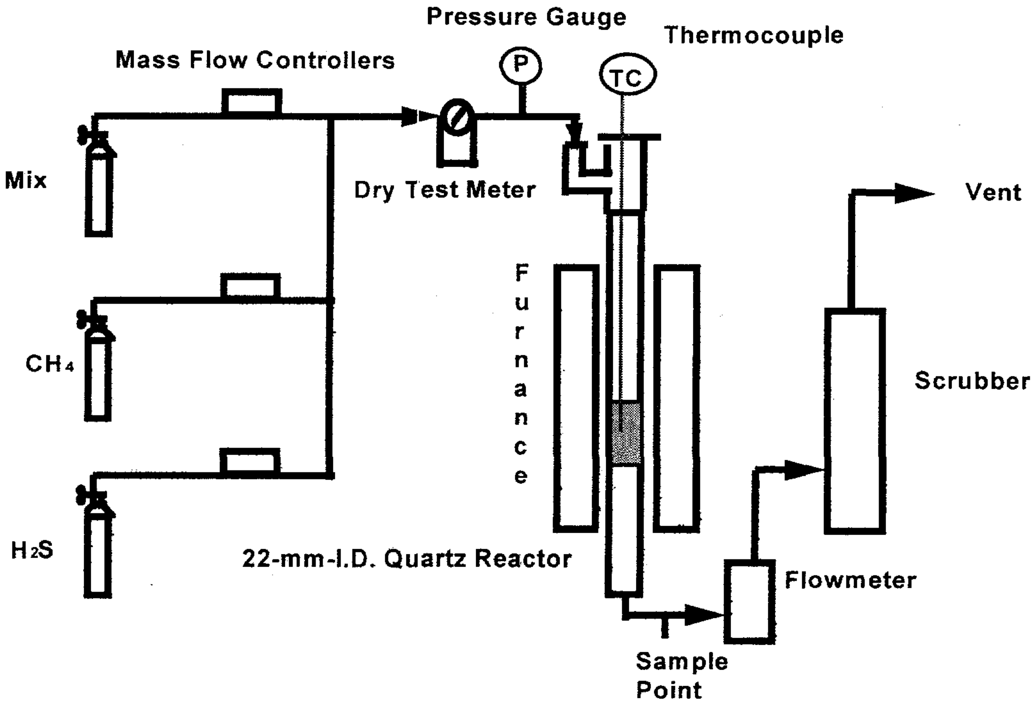

Figure 1. SCHEMATIC DIAGRAM OF QUARTZ REACTOR UNIT

Gas samples were analyzed by gas chromatograph (HP5890) with a thermal conductivity detector (TCD) and a flame photometric sulfur detector (FPD). A 3.2-mm-diameter, 3-m-long HayeSep C 80/100 column (SUPELCO Inc.) was used for gas separation. Argon was used as the carrier gas to measure hydrogen in the TCD detector.

Description of H_2S Decomposition Tests

The decomposition of hydrogen sulfide, which is an integral reaction in the network of reactions that take place in the conversion of methane to hydrogen and carbon disulfide, was studied by placing 20 ml of granulated catalyst into a 22-mm-O.D. quartz reactor. The experimental conditions for a typical set of runs are given in Table 2. Nitrogen was used as a diluent. The feed gas composition was 99% N_2, 1% H_2S.

Table 2. TEST MATRIX FOR H_2S THERMAL DECOMPOSITION REACTION

Test Number	Temp, °C	Pressure, atm	Flow, liter/min
1	600,700,800,900,1000,1100	1	0.28
2	600,700,800,900,1000,1100	1	0.44
3	600,700,800,900,1000,1100	1	1.08

Description of Carbon Regeneration Tests

In developing a catalyst for the conversion of CH_4 + H_2S, it was desirable to find a catalyst that does not become deactivated by carbon deposition. In the temperature range above 700°C, carbon formation is thermodynamically possible. A group of tests with a twofold purpose was designed to determine whether carbon formation occurred, and if so, how could it be removed. For these tests methane was decomposed over each catalyst. Then, the regeneration/removal of carbon was performed by passing H_2S over the catalyst. For these tests 20 ml of catalyst granules were loaded into the quartz reactor. A flow of 0.1 liter/min of methane was started. The catalyst was heated to 1000°C. and held at that temperature for 1 hour. The reactor was purged with nitrogen and cooled to room temperature. A small sample of the catalyst was analyzed for carbon. The reactor was resealed, and the a flow of nitrogen was started as the catalyst was heated to 1000°C. At that temperature the gas was switched to a mixture of 1% H_2S in nitrogen. This flow and temperature were maintained for 1 hour. During this treatment the product gases were analyzed for carbon disulfide and hydrogen. The catalyst was cooled in flowing nitrogen. The reactor was opened, and the catalyst was analyzed for carbon.

Description of Methane-H_2S Reaction Tests

The objective of this task is to develop a group of catalysts for the direct conversion of methane and hydrogen sulfide to carbon disulfide. For these tests the same reactor that was used for the H_2S decomposition tests was used. The feed gases for these runs were H_2S, CH_4, and N_2. N_2 was added as a diluent. For a few runs CO_2 was added to the feed to test the effects of CO_2 on the overall reaction. The tests were prepared by placing 20 ml of granulated catalyst into a

22-mm-I.D. quartz reactor. During a typical run the temperature was varied from 700°C to above 1100°C. In addition the ratio of H_2S/CH_4 was varied from 2 to 8, and the residence time was varied from 1 to 5 seconds. An experimental test matrix is shown in Table 3.

Table 3. EXPERIMENTAL TEST MATRIX FOR METHANE-HYDROGEN SULFIDE REACTION

H_2S/CH_4 Ratio	Residence Time, s	Temp, °C
2	1	700, 800, 900, 1000, 1100
2	5	700, 800, 900, 1000, 1100
4	1	700, 800, 900, 1000, 1100
4	5	700, 800, 900, 1000, 1100
8	1	700, 800, 900, 1000, 1100
8	5	700, 800, 900, 1000, 1100

Description of Carbon Disulfide to Liquid Hydrocarbons Tests

For these tests the purpose was to see if CS_2 could be hydrogenated to gasoline-range hydrocarbons. The conditions and catalyst for this reaction differ from those of the methane-hydrogen sulfide reaction, but the pressure of this reaction can be from atmospheric to 400 psig or greater. Thus, the operating pressure of this reaction can be adjusted to match the exit of the first reactor so that a booster compressor would not be required. This could save considerable processing cost. For these tests a sample of 20 cc of catalyst was loaded into a 3/4-inch, Schedule 80 stainless-steel pipe reactor (18.8 mm I.D.) The flow of the reactants was established by bubbling hydrogen gas through a vessel containing liquid CS_2. The CS_2 vessel was maintained at a specified temperature, usually 0°C. This produced a feed stream with a constant concentration of CS_2.

Description of Proof-of-Concept Tests

For these tests the unit was further modified to accommodate two reactors. The first reactor was the 22-mm-I.D. quartz reactor. After this reactor a sample port was added for sampling the gases before they were sent to the second reactor. In the second reactor a mixture of H-ZSM-5 zeolite and MoS_2 catalyst was placed. After the reactor a sampling port and a flow meter were installed to measure the flow and take samples for gas analysis. In addition a condenser was installed to recover liquids.

DATA AND RESULTS

Catalyst Characterization

Catalysts prepared at IGT were characterized by BET measurements for surface area and by X-ray diffraction for bulk phases. The results of BET measurements for fresh and used catalysts are shown in Table 1. Catalyst IGT-MS-101 began with the highest surface area. After reactor testing the surface area dropped significantly. While the proprietary technique was successful in making a high surface sulfide, the temperatures of reactor testing caused the catalyst powder to sinter. Less rigorous methods were used to make the other catalysts shown in Table 4. These catalysts started out with less surface. Catalyst IGT-MS-103 lost a little more than half of its surface area. No significant surface area changes were found for catalysts IGT-MS-102, IGT-MS-104, and IGT-MS-105.

The X-ray diffraction results for catalyst IGT-MS-103 and IGT-MS-105 are given in Table 5. IGT-MS-103, which is a chromium sulfide catalyst, does not go through bulk phase changes during reactor testing. However, IGT-MS-105, which is a cerium sulfide catalyst, starts out as CeS, but it is converted to Ce_2S_3. The used catalyst contains more sulfur than the fresh sample. More will be mentioned about this in the section on H_2S decomposition. This transformation occurs without significantly changing surface area (see Table 4).

Table 4. SURFACE AREA OF FRESH AND USED CATALYSTS

	Surface Area (m^2/g)	
Catalysts	Fresh Catalyst	Used Catalyst
IGT-MS-101	34.1	2.9
IGT-MS-102	1.7	1.7
IGT-MS-103	4.2	1.4
IGT-MS-104	2.0	1.9
IGT-MS-105	0.6	0.7

Table 5. BULK PHASES OF FRESH AND USED CATALYSTS

Catalysts	Fresh Catalyst	Used Catalyst
IGT-MS-103	Cr_2S_3	Cr_2S_3
IGT-MS-105	CeS	Ce_2S_3

H_2S Decomposition Tests

H_2S decomposition tests were performed using the methods described above. The results are shown in Figure 2.

For these tests at 1000°C the order of activity for H_2S conversion is IGT-MS-103> IGT-MS-105>IGT-MS-101>IGT-MS-102>IGT-MS-104. This test showed that these sulfide catalysts were active for the decomposition of H_2S. Equilibrium conversion was not achieved, but catalysts, IGT-MS-101, -103, -105 achieved conversions within 10 percentage points of equilibrium conversion.

Carbon Regeneration Tests

Carbon regeneration tests were performed according to the method described above. These tests provided insight into the activity the catalyst has for methane decomposition according to the reaction:

$$CH_4 \rightarrow C + 2\ H_2 \qquad (8)$$

In addition, these tests were performed to see how well each of the catalysts could be regenerated if carbon accumulated on the surface. The actual temperatures and flows for each catalyst is shown in Table 6.

The product gas streams for all tests were analyzed by gas chromatography (GC). Carbon disulfide was found in product gas streams for Tests 2, 4, 6, and 10. However for Test 8, carbon disulfide was not detected. This catalyst appeared to inhibit hydrogen sulfide reaction with carbon. Results of this test on five catalysts are shown in Figure 3. Results are also tabulated in Table 7.

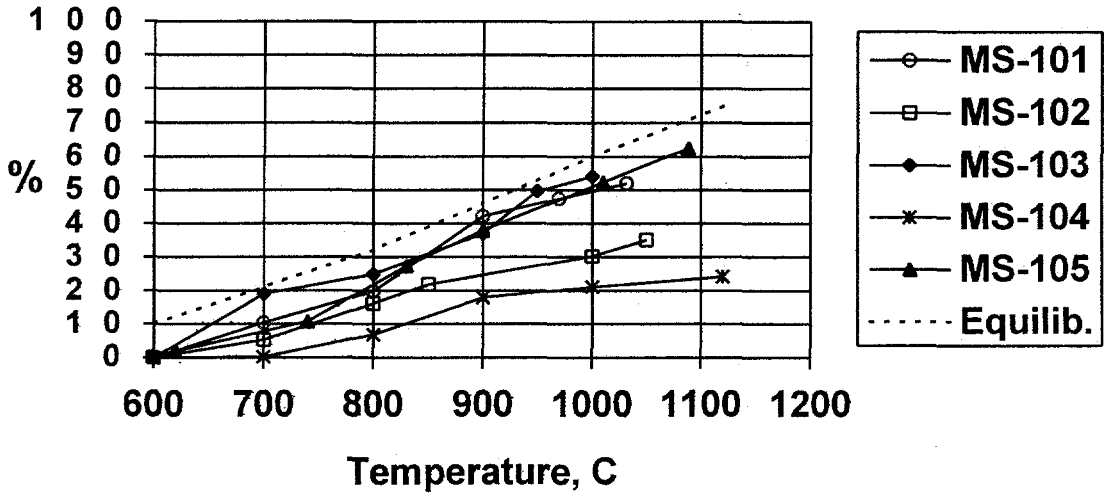

Figure 2. H_2S DECOMPOSITION TESTS FOR FIVE CATALYSTS

Table 6. EXPERIMENTAL CONDITIONS FOR CARBON REGENERATION STUDIES

Test Number	Test Medium	Gas	Flow Rate, liter/min	Temp, °C
1	Quartz wool	CH_4	0.10	1009
2	Quartz wool	H_2S, N_2	1.077	1011
3	IGT-MS-106	CH_4	0.10	1017
4	IGT-MS-106	H_2S, N_2	1.077	1013
5	IGT-MS-101	CH_4	0.10	1009
6	IGT-MS-101	H_2S, N_2	1.077	1011
7	IGT-MS-102	CH_4	0.10	1001
8	IGT-MS-102	H_2S, N_2	1.077	1012
9	IGT-MS-103	CH_4	0.10	1000
10	IGT-MS-103	H_2S, N_2	1.077	1013
11	IGT-MS-104	CH_4	0.10	1000
12	IGT-MS-104	H_2S, N_2	1.077	1014
13	IGT-MS-105	CH_4	0.10	1019
14	IGT-MS-105	H_2S, N_2	1.077	1020

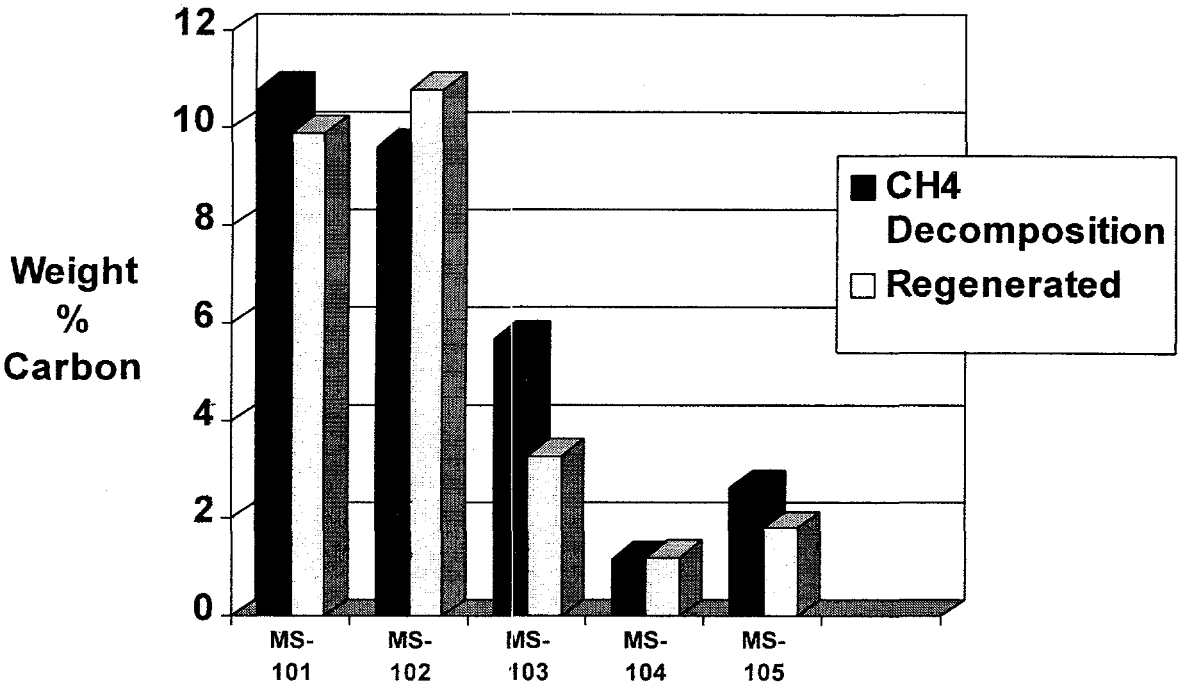

Figure 3. METHANE DECOMPOSITION/CARBON REGENERATION TESTS ON FIVE CATALYSTS

Table 7. CARBON CONCENTRATION AND SURFACE AREA OF CATALYSTS

	After CH_4 Decomposition		After Regeneration With H_2S	
Catalyst	Wt % Carbon	Surface Area, m^2/g	Wt % Carbon	Surface Area, m^2/g
IGT-MS-101	10.80	3.0	9.91	2.7
IGT-MS-102	9.61	2.0	10.80	1.9
IGT-MS-103	5.69	1.1	3.29	1.4
IGT-MS-104	1.16	3.1	1.20	3.0
IGT-MS-105	2.64	0.9	1.80	0.9
IGT-MS-106	ND*	2.1	3.86	0.3

* ND = Not determined.

A comparison of carbon content for five of the catalysts is given in Figure 3. IGT-MS-106, after exposure to methane, was partially reduced to metal. After regeneration, agglomerated particles of metal were still evident. This catalyst was not stable at these conditions. As indicated in Figure 3 and Table 3, for IGT-MS-103 and IGT-MS-105 carbon concentration was reduced by 43% and 32%, respectively. After exposure to hydrogen sulfide, IGT-MS-101 catalyst had an 8% reduction in carbon concentration. Carbon disulfide was detected by GC in the off gas of catalysts IGT-MS-101, -103, and -105. For the IGT-MS-102 and IGT-MS-104 catalysts, no reduction of carbon concentration was observed, and no carbon disulfide was detected in the off-gas.

From these tests two salient points are important to note. First, the amount of carbon deposition on the catalysts varies. IGT-MS-101 and -102 acquired nearly 10% carbon during the methane decomposition portion of the test. IGT-MS-103, -104, and -105 had significantly lower carbon accumulations. Second, IGT-MS-101, -102, and -104 achieved little carbon removal under these conditions. Both catalysts IGT-MS-103 and IGT-MS-105 achieved reductions of the carbon during the short regeneration phase of this experiment. From these test it appears that the best catalysts for the inhibition of carbon formation, as well as for the regeneration after carbon formation, are IGT-MS-103 and IGT-MS-105.

Methane H_2S Reaction Tests

Nine catalysts and the empty reactor were tested in 327 runs for the reaction of methane with hydrogen sulfide. During these tests, five temperatures, two flow rates, and three H_2S/CH_4 ratios were investigated. The primary products were carbon disulfide and hydrogen. A summary of the carbon disulfide yield results for H_2S/CH_4 ratio of 4 is shown in Figure 4. At $H_2S/CH_4 = 4$ there is twice the stoichiometric amount of H_2S in the feed. The highest yields of CS_2 were achieved at this ratio.

Generally the yield of CS_2 increases with temperature up to 1100°C. Above that the yields decrease. The highest yields were achieved by catalysts IGT-MS-103 and IGT-MS-105. At 1100°C the order of conversion was IGT-MS-103, IGT-MS-105>IGT-MS-108, IGT-MS-107>IGT-MS-104> IGT-MS-102> empty reactor > IGT-MS-101, IGT-MS-106, IGT-MS-109.

Runs were also made at H_2S/CH_4 ratios of 2 and 8. The summaries of those runs are shown in Figures 5 and 6.

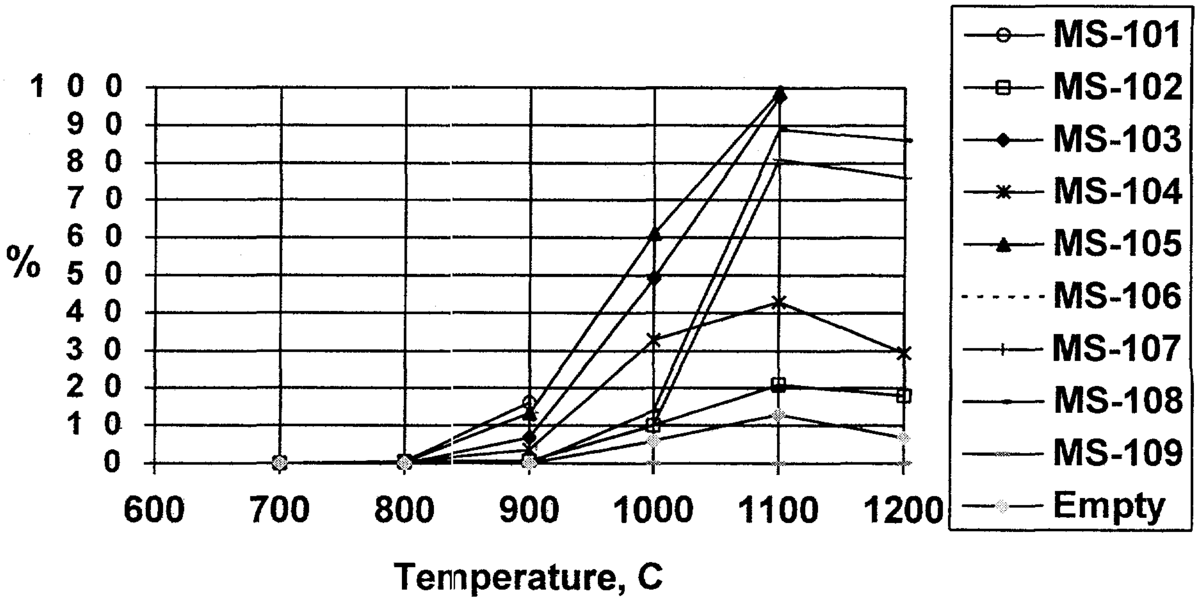

Figure 4. SUMMARY OF CARBON DISULFIDE YIELDS FOR NINE CATALYSTS AND THE EMPTY REACTOR WITH H_2S/CH_4 RATIO = 4 AND RESIDENCE TIME = 1 SECOND

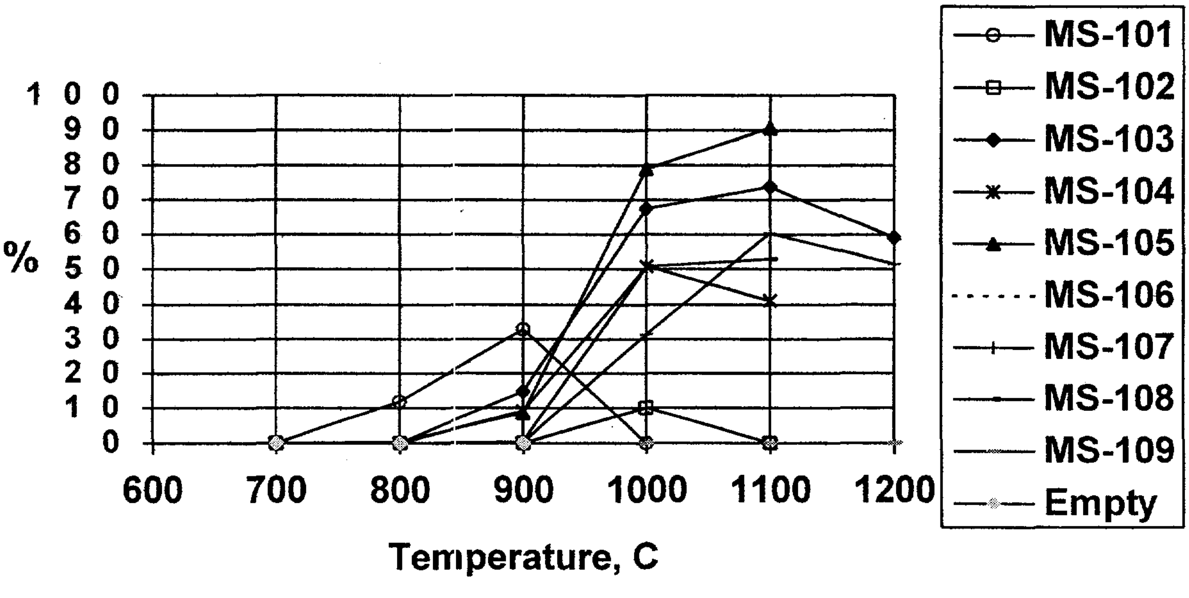

Figure 5. SUMMARY OF CARBON DISULFIDE YIELDS FOR NINE CATALYSTS AND THE EMPTY REACTOR WITH H_2S/CH_4 RATIO = 8 AND RESIDENCE TIME = 1 SECOND

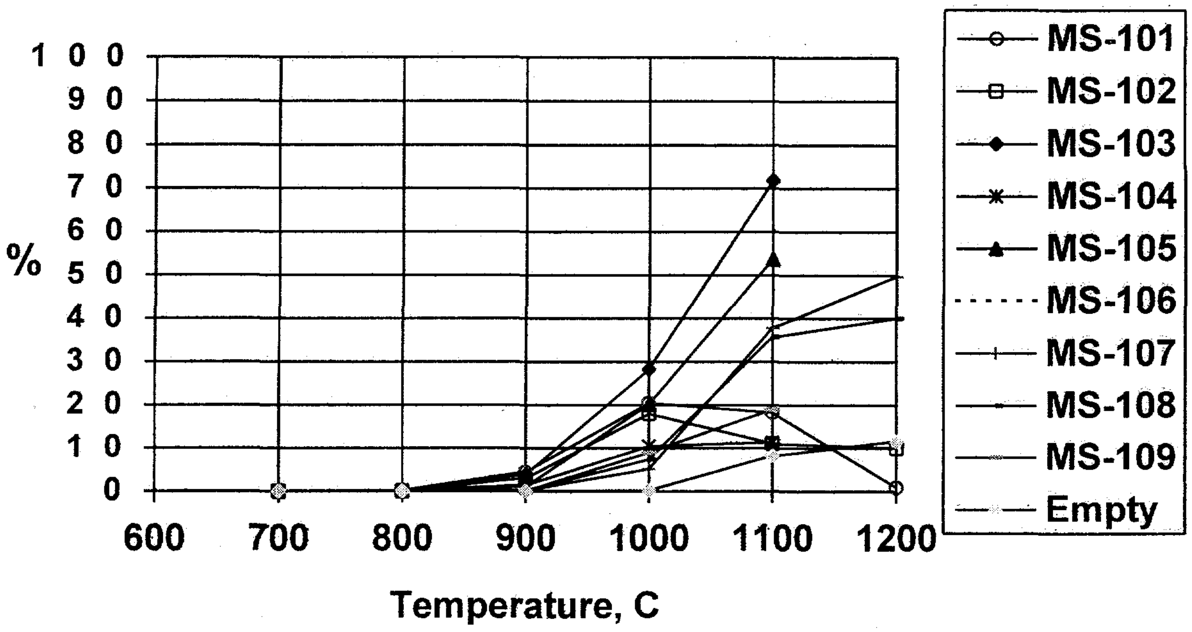

Figure 6. SUMMARY OF CARBON DISULFIDE YIELDS
FOR NINE CATALYSTS AND THE EMPTY REACTOR WITH
H_2S/CH_4 RATIO = 2 AND RESIDENCE TIME = 1 SECOND

In Figure 5 the yield of CS_2 generally increases with temperature. However, for some catalysts the yields go through a maximum. For IGT-MS-101 the maximum yield was achieved at 900°C (1173 K). This may be due in part to a decrease in surface area (see Table 1). At 1100°C (1373 K) the order of yields is as follows: IGT-MS-105>IGT-MS-103>IGT-MS-107>IGT-MS-108>IGT-MS-104>IGT-MS-101, IGT-MS-102, IGT-MS-106, IGT-MS-109, empty reactor.

A summary of the CS_2 yields at the H_2S/CH_4 ratio = 2 is shown in Figure 6. This ratio is the stoichiometric ratio. In Figure 6 the yields of carbon disulfide are not as great as when an excess of hydrogen sulfide is in the feed. Generally the trend is the same, however, with yields increasing with reaction temperature up to 1000°C (1273 K). IGT-MS-101 appears to reach a maximum around 1000°C (1273 K). The highest yield is with IGT-MS-103 at 71% at 1100°C (1373 K).

To show the trends of a typical set of runs, a summary of the CS_2 and H_2 yields along with H_2S and CH_4 conversions for IGT-MS-103 are shown in Figure 7. A similar graph for IGT-MS-105 is shown is Figure 8.

For both these catalysts the trend is the same. CS_2 yield is based on the moles of CS_2 produced divided by the moles of methane fed. CS_2 yield increases sharply above 900°C (1173 K) to a maximum of near 100% at 1100°C (1373 K). Methane conversion reaches 100% at 1100°C (1373 K). Hydrogen sulfide conversion reaches only 49% at the same temperature. This is consistent with the fact that the feed has twice the stoichiometric amount of H_2S. The yield of hydrogen is also shown. This yield is based on the gram atoms of hydrogen in the product H_2 divided by the gram atoms of hydrogen in the feed gases. The theoretical maximum yield of hydrogen is 67%. The highest yields actually achieved were 61% and 62%, respectively. The rate of hydrogen production at 1100°C (1373 K) for IGT-MS-103 was 9.7 moles H_2/kg catalyst-h, and for IGT-MS-105 was 5.9 moles H_2/kg catalyst-h. The bulk density of IGT-MS-105 was 1.8 g/ml, while the bulk density of IGT-MS-103 was 1.1 g/ml. While both catalysts achieved nearly the same yields of hydrogen and CS_2, under similar conditions of residence time, the catalyst with the higher bulk density will have a lower rate per kg catalyst.

Activity and short duration tests were also performed on catalyst IGT-MS-103 for the methane with hydrogen sulfide reaction. Tests with carbon dioxide in the feed were performed. All these tests are discussed in this section. A total of 33.1 g (20 ml) of catalyst was loaded into the 22-mm-I.D. quartz reactor. Nitrogen was used as a diluent, similar to previous runs. These runs were performed using the quartz reactor. The test matrix for the first two runs is shown in Table 8.

The reactor was held at 1192°C (1465 K) for about 2 hours. The yield of CS_2 was 80.9%. This is lower than the highest yield previously obtained on this catalyst, but it is consistent with earlier results that CS_2 yield decreases above 1100°C (1373 K). A second run using the same loading of catalyst IGT-MS-103 was performed to see if the catalyst held activity for a short duration. For this run the temperature was 1102°C (1375 K). The CS_2 yield was 88%, the H_2S conversion was 59%, and the methane conversion was 100%. The results are shown in Figure 9.

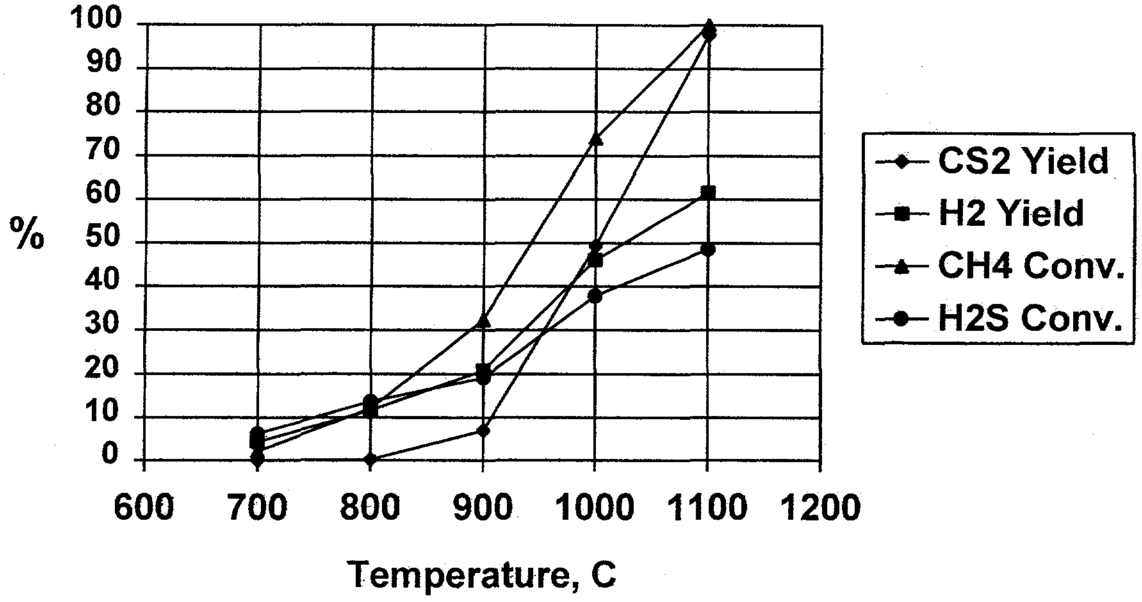

Figure 7. YIELDS AND CONVERSION FOR IGT-MS-103 WITH $H_2S/CH_4 = 4$ AND RESIDENCE TIME = 1 SECOND

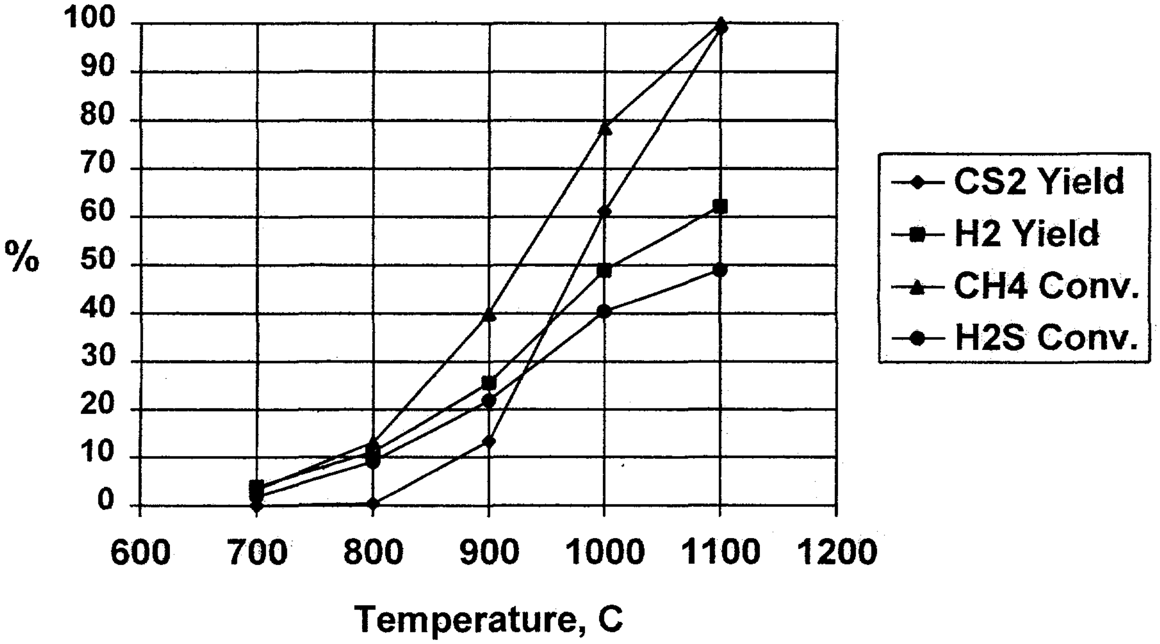

Figure 8. YIELDS AND CONVERSION FOR IGT-MS-105 WITH $H_2S/CH_4 = 4$ AND RESIDENCE TIME = 1 SECOND

Table 8. TEST MATRIX FOR METHANE WITH HYDROGEN SULFIDE REACTIONS USING CATALYST IGT-MS-103

H_2S/CH_4 Ratio	Residence Time, s	Temp, °C
4	1.2	1192
4	1.2	1102

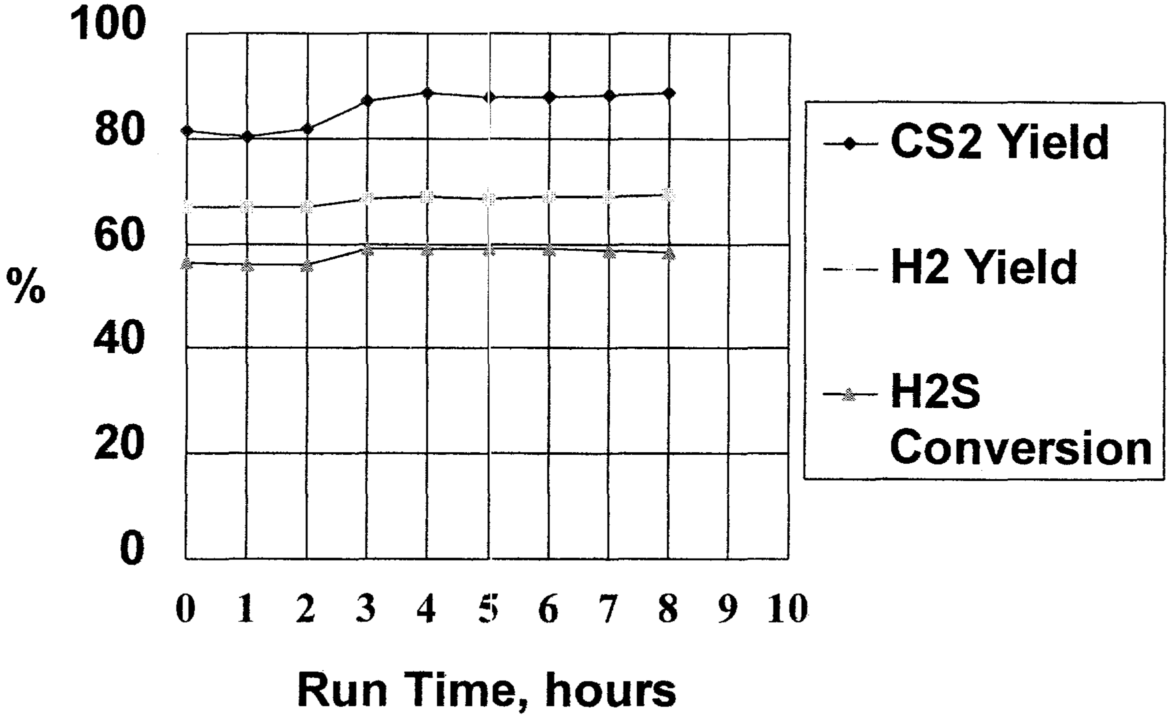

Figure 9. CS_2 AND H_2 YIELDS AND H_2S CONVERSION FOR EXTENDED RUN

There is no indication of catalyst deactivation during this run. The CS_2 yield, hydrogen yield, and H_2S conversion were maintained near or above initial rates for the 8-hour run.

CO_2 Effects on Activity

As a means of investigating how the catalysts developed in this project might be applied in commercial situations, it was decided to include other gas components in the feed. The most likely component to be encountered in a commercial application of the HSM process technology is carbon dioxide. The off-gas from an acid gas removal unit normally contains both hydrogen sulfide and carbon dioxide. We ran a test on catalyst IGT-MS-103 with carbon dioxide, methane, and hydrogen sulfide in the feed gas. A total of 33.1g (20 ml) of catalyst was loaded into the 22-mm-I.D. quartz reactor. The $H_2S/CH_4/CO_2$ ratio was 1:1:1. Nitrogen was used as a diluent, similar to previous runs. The conversions and yields were measured at four temperatures. The results are shown in Figure 10.

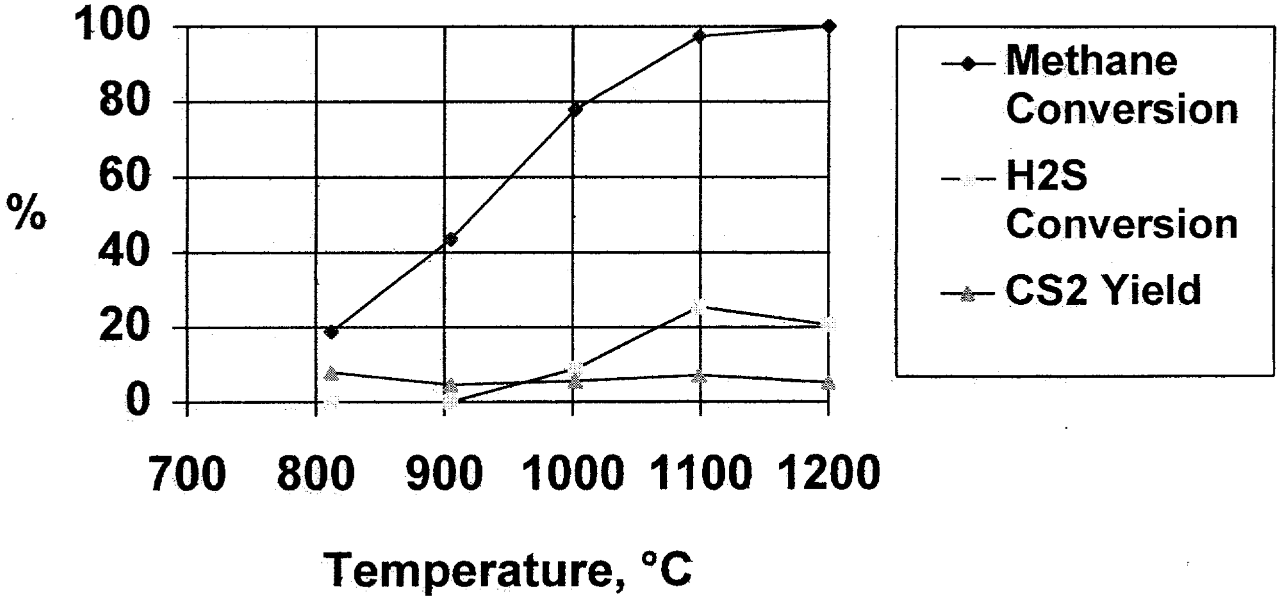

Figure 10. CS_2 YIELD AND CH_4 AND H_2S CONVERSIONS FOR IGT-MS-103 WITH CO_2 IN THE FEED

For these runs the H_2S conversion was much lower than previously reported runs. The addition of carbon dioxide to the feed gives methane more reaction pathways. CO and COS were produced. The yield of CS_2 was below 10% for this temperature range. For the previously reported runs, CS_2 yields were based on the conversion of methane. With the addition of CO_2 and with the additional carbon-containing products that are made, the carbon disulfide yield is based on the sulfur in the feed for this run only. The salient result from this run is that carbon dioxide in the feed negatively affects hydrogen sulfide conversions and CS_2 yields.

Many acid gas removal units in the United States operate with selective solvents which absorb H_2S preferentially over CO_2. The molar ratio of H_2S/CO_2 coming off the acid gas removal unit is 8:1 or greater. It was decided to try the HSM catalysts on a feed with a $H_2S/CH_4/CO_2$ ratio of 8:2:1. We ran a test on catalyst IGT-MS-103 with 33.1 grams (20 ml) loaded into the 22-mm-I.D. quartz reactor. The $H_2S/CH_4/CO_2$ feed ratio was 8:2:1. Nitrogen was used as a diluent, similar to previous runs. The conversions and yields were measured over a 3-hour period of time. The results are shown in Figure 11.

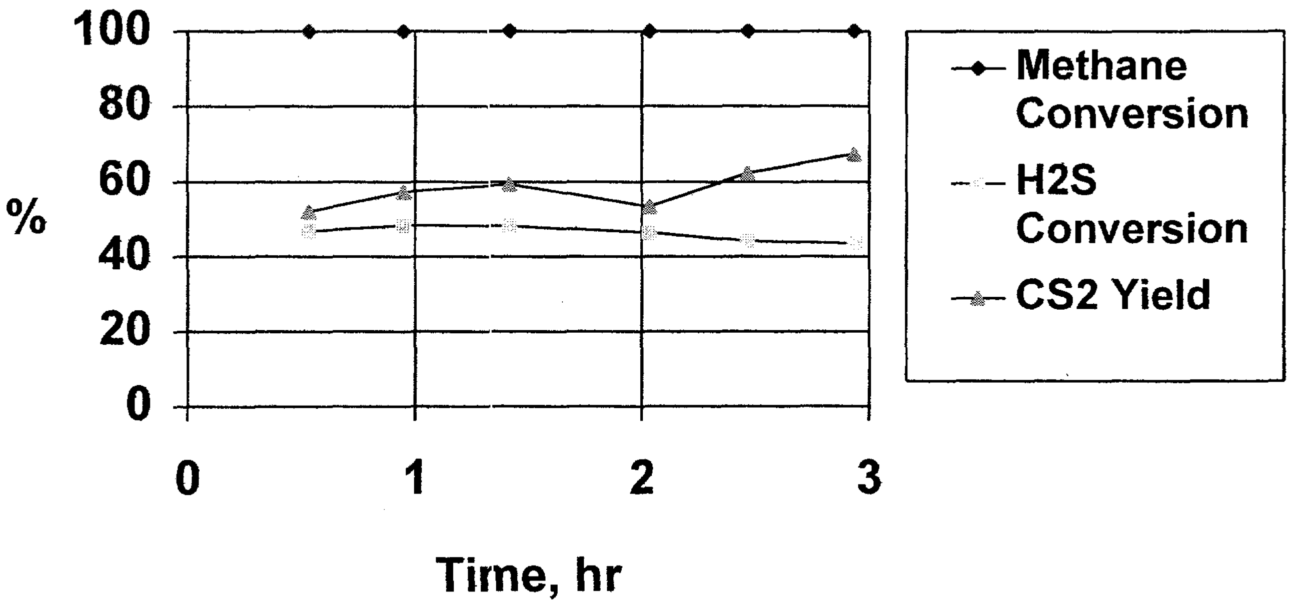

Figure 11. CS_2 YIELD AND CH_4 AND H_2S CONVERSIONS FOR EXTENDED RUN AT 1100°C WITH $H_2S/CH_4/CO_2$ FEED RATIO OF 8:2:1

For these runs the CS_2 yield is much higher than the previous run with equal concentrations of CO_2 and H_2S. The methane conversion remained 100% throughout the period, and the H_2S conversion remained relatively constant, while CS_2 yield began to increase slightly near the end of the period. CO was produced, but no COS was detected in the product gas. Our initial assessment from these runs is that the HSM catalysts can be applied to acid gas streams that contain CO_2. Equal molar concentrations of CO_2 and H_2S result in low CS_2 yields and the production of COS and CO. However, at an H_2S/CO_2 ratio of 8, CS_2 yields are above 50%.

Hydrogenation of CS_2 to Hydrocarbons

The hydrogenation of CS_2 to hydrocarbons was investigated using two sets of catalysts. An exchanged zeolite alone and a mixture of zeolite and molybdenum sulfide catalysts were tested. The zeolite alone results are presented first.

Co-H-ZSM-5-56, a cobalt-exchanged ZSM-5 zeolite catalyst, was pelletized and sized to -8+20 mesh, and 20 ml was loaded into a 3/4-inch, Schedule 80 stainless-steel pipe reactor (18.8 mm I.D.) These experiments covered a range of three space velocities and four temperatures. CS_2 and H_2 conversions are shown in Table 9 along with the liquid hydrocarbon selectivity. Liquid hydrocarbon selectivity was calculated by finding the ratio of gram-atoms of carbon in C_4^+ products to the total gram-atoms of carbon in the hydrocarbon fraction of the product.

Table 9. CS_2 HYDROGENATION OVER Co-H-ZSM-5-56
AT AMBIENT PRESSURE AND H_2/CS_2 RATIO = 5.1

Space Velocity, h^{-1}	Temp, °C	% Conversion H_2	% Conversion CS_2	% Selectivity C_4^+
478	407	13	25	NA
	431	16	33	25
	450	20	40	25
	471	27	52	15
415	405	22	23	52
	430	29	36	34
	450	32	42	25
	470	37	51	17
343	405	39	23	49
	430	39	36	30
	450	45	45	26
	470	47	55	17

The results in Table 9 show that CS_2 hydrogenation is occurring. Our Co-H-ZSM-5-56 cobalt-exchanged catalyst achieved a higher conversion and in some cases higher selectivities than the results reported by Mobil researchers in U.S. Patent No. 4,543,434.[4] Our catalyst is an ion-exchanged ZSM-5, while Mobil used a physical mixture of HZSM-5 and Co on silica. The results from U.S. Patent No. 4,543,434 are given in Table 10.

Table 10. HYDROGENATION OF CS_2 OVER A MIXTURE OF 50% HZSM-5/Al_2O_3 AND 50% Co/SiO_2, PRESSURE = 250 psig[4]

Temp. °C	CS_2 flow (LHSV)	H_2 flow (GHSV)	CS_2/H_2 (mole ratio)	CS_2 Conversion %
482	1	400	0.93	40.3

Figures 12 and 13 present some of the results from Table 9 in graphical form. Figure 12 shows that both CS_2 conversion and C_4^+ hydrocarbon selectivity have strong temperature dependencies. CS_2 conversion increases dramatically as temperature is raised from 405° to 470°C

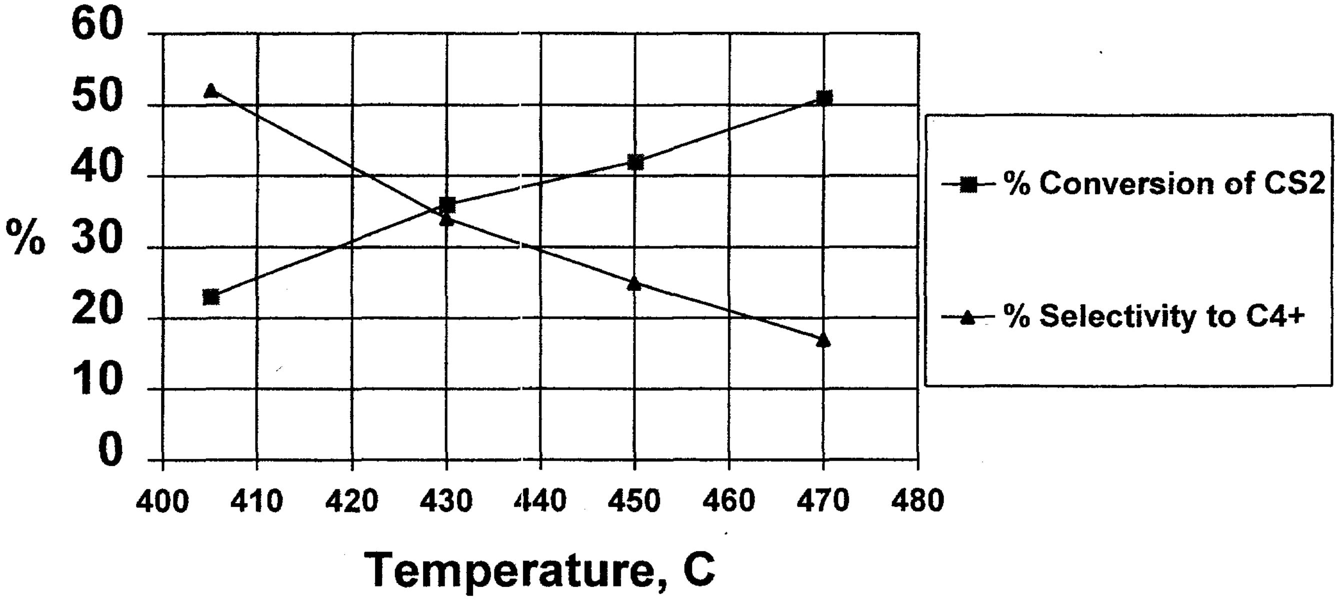

Figure 12. CS_2 CONVERSION AND C_4^+ HYDROCARBON SELECTIVITY WITH H_2/CS_2 FEED RATIO = 5.1 AND GAS HOURLY SPACE VELOCITY = 415 h^{-1}

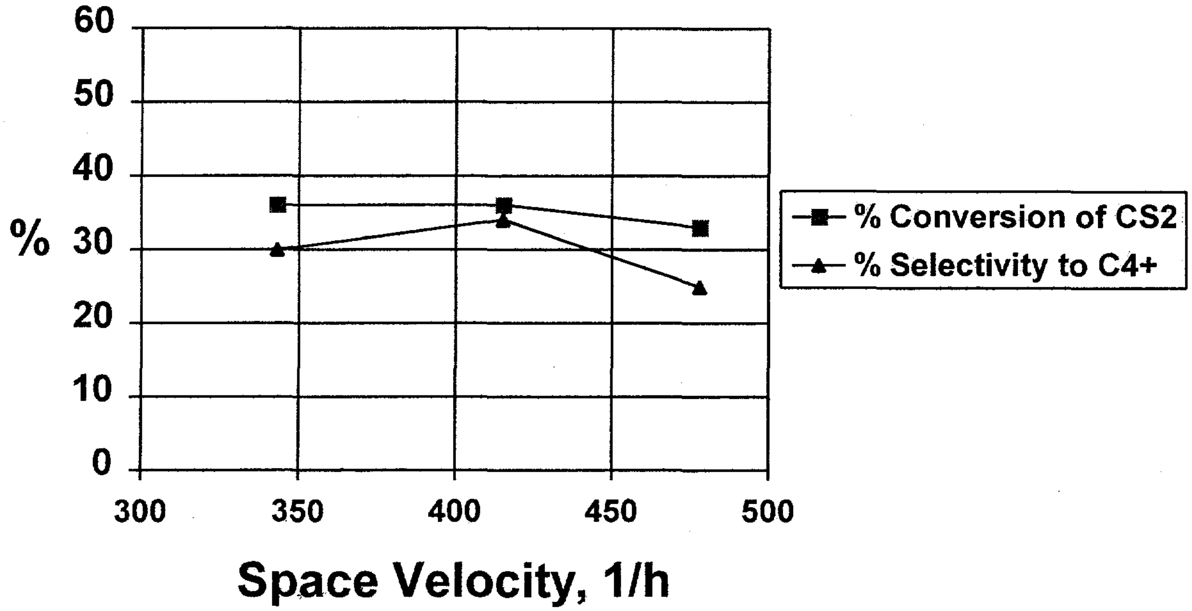

Figure 13. CS_2 CONVERSION AND C_4^+ HYDROCARBON SELECTIVITIES WITH H_2/CS_2 FEED RATIO = 5.1 AND TEMPERATURE = 430°C

(678 to 743 K). On the other hand, C_4^+ selectivity decreases with increasing temperature. This suggests that an optimum yield of liquid hydrocarbons will occur somewhere in the middle of this temperature range. Figure 13 shows CS_2 conversion and C_4^+ selectivity plotted against space velocity. While there is some effect on both conversion and selectivity, space velocity does not have as dramatic an effect as temperature in this range.

In addition to the zeolite alone, CS_2 hydrogenation was carried out using a mixture of 15 ml MoS_2 hydrogenation catalyst and 15 ml Co-HZSM-5-56 catalyst. The feed was delivered by bubbling hydrogen through liquid CS_2 maintained at 0°C. These experiments were performed at a space velocity of 343 h^{-1} and three temperatures. CS_2 and H_2 conversions are shown in Table 11 along with the liquid hydrocarbon selectivity.

The results in Table 11 again show that CS_2 hydrogenation is occurring. However, the surprising result is that the use of the MoS_2 hydrogenation catalyst in conjunction with the HZSM-5 zeolite catalyst cause near complete conversion of CS_2. The MoS_2 catalyst is an active

Table 11. CS_2 HYDROGENATION OVER A MIXTURE OF MoS_2 AND Co-HZSM-5-56 AT AMBIENT PRESSURE AND H_2/CS_2 RATIO = 5.1

Space Velocity, h^{-1}	Temp, °C	% Conversion H_2	% Conversion CS_2	% Selectivity C_4^+
343	434	38	100	11
	350	36	98	45
	325	27	95	51

catalyst for hydrogenation reactions in the presence of sulfur. We found up to 1% methyl mercaptan in the raw product gas. In this case the MoS_2 catalyst may be hydrogenating CS_2 to methyl mercaptan, which is converted to hydrocarbons over ZSM-5 catalysts. In reference to work performed at Mobil,[3,4] HZSM-5 also converts methyl mercaptan to liquid hydrocarbons. These results appear to confirm this. This set of runs shows 95% conversion of CS_2 accompanied by a 51% selectivity to C_4^+ hydrocarbons.

Proof-of-Concept Tests

Two proof-of-concept runs were made. The methane-sulfur unit was modified to accommodate two reactors. The first reactor (22-mm-I.D. quartz reactor) contained 20 ml of IGT-MS-103 catalyst. The second reactor contained a mixture of 15 ml of IGT-HS-103, a high surface area molybdenum sulfide catalyst and 15 ml of Co-HZSM-5-56, a cobalt-exchanged zeolite. Between the two reactors a sampling port was added. The flows of methane, hydrogen sulfide, and nitrogen were metered into the reactor using electronic mass flow controllers. The reactor system was operated in two modes: 1) with a nitrogen diluent and 2) with only methane and H_2S in the feed. Results are presented in Table 12.

Table 12. RESULTS FROM PROOF-OF-CONCEPT TESTING

	Reactor 1				Reactor 2		
Diluent	Space Velocity, h^{-1}	Temp, °C	% CH_4 Conversion	% CS_2 Yield	Temp, °C	% CS_2 Conversion	% C_4^+ Selectivity
N_2	1695	1102	100	85	417	5	67
none	732	1102	94	94	419	75	52

The results in Table 12 show that methane is being converted to CS_2 in Reactor 1, and that CS_2 is converted to hydrocarbons in Reactor 2. The nitrogen diluent affects the CS_2 conversion in the second reactor by decreasing the concentration of CS_2 and hydrogen. Without the diluent the yield of CS_2 in the first reactor is above 90%, and the conversion of CS_2 in the second reactor is 75%. In this case the selectivity to liquid hydrocarbons was 52%. Not counted in the C_4^+ selectivity is the methyl mercaptan that was made (1% of the product gases). Methyl mercaptan can be converted to higher hydrocarbons using the ZSM-5 zeolite catalyst.

DISCUSSION AND APPLICATIONS

This project began with a search for a catalyst to promote the reaction of methane and hydrogen sulfide to carbon disulfide and hydrogen. The hydrogen sulfide decomposition tests showed that many of the catalytic materials selected for this study were active in the decomposition of H_2S, an essential reaction in this reaction pathway. The H_2S decomposition studies showed that most of the sulfide catalysts were stable at temperatures above 1000°C (1273 K). However, the high surface area IGT-MS-101 did not retain its surface area during this short test. This showed that, while this technique is effective for creating a high surface area sulfide catalyst for reaction such as hydrogenation and hydrotreating, the technique becomes less effectual at the temperatures required for methane-hydrogen sulfide conversion. The sintering of the sulfide during short reaction times was evident. For the remainder of sulfide catalysts, less rigorous methods were used to make the powders. These sulfide started with less surface area (2-5 m^2/g), but retained most of this area during reactor testing above 1000°C (1273 K).

Earlier work on the conversion of methane and hydrogen sulfide operated at temperatures ($< 850°C = 1123$ K) to avoid carbon deposition in the reactor. However, to achieve more favorable Gibbs Free Energy of reaction, higher temperatures ($> 900°C = 1173$ K) are needed. At these higher temperatures carbon deposition is more favorable and the effects of carbon deposition and possible methods to remove carbon from the catalyst surface must be considered.

In the carbon regeneration tests, we found that some catalysts were better suited to inhibit carbon formation from the decomposition of methane. These catalysts were IGT-MS-103, In the carbon regeneration tests, we found that some catalysts were better suited to inhibit carbon formation from the decomposition of methane. These catalysts were IGT-MS-103, IGT-MS-104, and IGT-MS-105. In addition to testing the prevention of carbon formation, the regeneration of catalysts, which had carbon deposited, was also performed. Three of the sulfide catalyst showed little or no regeneration, that is, the concentration of carbon on the surface did not change much in spite of passing hydrogen sulfide over the catalyst at 1000°C (1273 K). IGT-MS-104 apparently did not have activity for reacting H_2S and the carbon on its surface. However, two catalysts were effective in promoting the reaction of H_2S and the carbon on their surfaces. These were IGT-MS-103 and IGT-MS-105. As will be discussed later, these were also the catalysts with the highest activity for converting methane and H_2S to carbon disulfide and hydrogen.

The reaction of methane and hydrogen sulfide was studied over nine catalysts and the empty reactor. While none of the catalysts had activity for the CH_4-H_2S reaction at 700°C (973 K), as temperature increased the activity increased also. However, even the most active catalysts went through a maximum conversion at 1100°C (1373 K). The feed ratio of CH_4/H_2S had a strong effect on the yield of carbon disulfide. The stoichiometric ratio of two produced yields of carbon disulfide, but the highest yields, >95%, were achieved at $CH_4/H_2S = 4$. The excess hydrogen sulfide in the gas phase may have been reacting with dehydrogenated carbon species on the surface of the sulfide catalysts. The reaction —

$$2\,H_2S + C \rightarrow CS_2 + 2\,H_2 \tag{9}$$

may account for this higher yield of carbon disulfide. Besides the gas phase hydrogen sulfide, another factor in the higher yield of carbon disulfide is temperature. At temperatures above 1000°C (1273 K), the conversion of methane nearly reached completion. At these temperatures, dehydrogenated methane or carbon precursors on the surface would be in greater abundance, and with the excess hydrogen sulfide in the gas phase, the production of carbon disulfide increased.

The best yields of carbon disulfide and hydrogen were achieved by catalysts IGT-MS-103 and IGT-MS-105. Both these catalysts were transition metal sulfide powders. The high yields of carbon disulfide, >95%, were encouraging for further study of the economic potential of this process both for making gasoline-range liquids, as well as for making carbon disulfide and hydrogen. The high yields achieved in these tests were greater than predicted by theoretical calculations, but they are thermodynamically possible because a diluent was used. For carbon formation, Gibbs Free Energy minimization techniques predict a much higher yield of carbon graphite than was shown in the experiments. Others[9,17,22] have shown conversions to carbon sulfides greater than theoretically predicted at high temperatures (>1000°C = 1273 K). This may be an artifact of insufficient data at high temperatures for CS_2 or an inhibition of the reaction of CS_2 to graphite.

In an effort to apply the results of this project to commercial situations, it was decided to test the effect of CO_2 on the yields of carbon disulfide. The tests showed that equimolar amounts of CO_2 and H_2S in the feed cause the yield of carbon disulfide to drop to unacceptable levels. However, when the ratio of H_2S/CO_2 is 8, the yield of CS_2 is above 50%. Because of the strong negative effects of CO_2 on CS_2 yields, efforts were made to find commercial acid gas removal processes that produce H_2S streams free of CO_2. Dr. Guido Sartori of Exxon who worked on selective absorbents for the Flexsorb process was contacted. Information on the Flexsorb SE and the Flexsorb SE Plus processes, which selectively remove H_2S from feed gases containing high concentrations of CO_2, was sent to IGT. There are at least 27 plants in the United States that are using Flexsorb solvents in acid gas removal. Selective acid gas removal solvents have the advantage of reducing the gas load to a Claus plant. CO_2 goes through the Claus plant as an inert and only adds to the gas duty. For an HSM plant, CO_2 is a detriment to yields, so selective solvents would be very advantageous.

The hydrogenation of CS_2 to hydrocarbon liquids was demonstrated. In the work performed in this project, it was found that a cobalt-exchanged ZSM-5 zeolite catalyst was more active for CS_2 hydrogenation than the earlier work by researchers at Mobil with an HZSM-5 catalyst. The H form of the ZSM-5 zeolite or HZSM-5 has its acid sites titrated with hydrogen. The cobalt-exchanged ZSM-5 zeolite used in this study had 56% of the acid sites titrated with cobalt ions. In addition we tested a mixture of cobalt-exchanged zeolite and an MoS_2 hydrogenation catalyst. This MoS_2 catalyst is a sulfur-tolerant catalyst and has been used for many other reactions where high activity for hydrogenation in the presence of sulfur compounds is needed. This mixture of catalysts achieved much higher conversion and selectivities than the earlier work, where a mixture of HZSM-5 and cobalt on silica was used. The best conversion of carbon disulfide reached 100% with a 51% selectivity to C_4^+ hydrocarbons. This striking yield shows that the addition of a sulfur-tolerant hydrogenation catalyst has a synergistic effect in promoting the conversion of CS_2 to hydrocarbons. Further studies in this area should consider the use of sulfur-tolerant hydrogenating catalysts for the conversion of carbon disulfide.

As proof-of-concept of converting natural gas (methane) to higher hydrocarbons, both steps of the HSM reactions were performed in one reactor system. This system had a methane-hydrogen sulfide reactor and a carbon disulfide hydrogenation reactor. Hydrogen and carbon disulfide were produced in the first reactor. In the second reactor, carbon disulfide was converted to hydrocarbons. The selectivity to C_4^+ hydrocarbons was 52%. At IGT a preliminary economic study was performed to assess the potential of using this two-step HSM process for making hydrocarbon liquids. This study showed that the overall economics of a plant converting natural gas to hydrocarbon liquids would require the liquids to be sold at \$40-60/barrel. The economic study used the conversions and selectivities presented in the Mobil patents. Our later results showed significant improvements over the results presented in the patents. Even so, under current economic circumstances where oil is selling in the range of \$20/barrel, the overall conversion of natural gas to liquid hydrocarbons does not appear economic. However, if the price of oil doubles, then one might want to reopen the study of the economics of the HSM process with the more recent results from this project.

Notwithstanding the less than desirable economics for the overall conversion of methane to hydrocarbon liquids, there was another potential commercial application for the HSM technology that was studied. Step 1 of the HSM process is the reaction of methane with hydrogen sulfide. The product is carbon disulfide and hydrogen. The chemical reaction of the first step of the HSM process is —

$$2\,H_2S + CH_4 \rightarrow CS_2 + 4H_2 \qquad (1)$$

In petroleum refineries hydrogen sulfide is a waste that is produced in processes including hydrodesulfurization. The H_2S waste is converted to elemental sulfur by the Claus reaction. The overall Claus reaction is —

$$H_2S + 1/2\,O_2 \rightarrow S + H_2O \tag{10}$$

In a refinery, a considerable amount of hydrogen is used to convert sulfur compounds in the petroleum fractions to H_2S. The hydrogen in the H_2S is converted in the Claus reaction to water vapor, which is usually exhausted to the atmosphere. If a method could be found to recover the hydrogen in H_2S, the refinery would have an immediate use for that hydrogen. The conversion of H_2S and methane to hydrogen would have some synergy that might be advantageous to the refiner. Summaries in Table 13 show how the catalysts developed for this task might be used in a refinery for the production of hydrogen and the conversion of hydrogen sulfide. The first step of the HSM process technology has advantages over conventional Claus and Tail Gas Cleanup technologies.

Table 13. COMPARISON OF HSM TECHNOLOGY WITH CLAUS PROCESS

HSM	Claus
Converts H_2S to useful products (H_2, CS_2)	Converts H_2S to useful product (S)
Produces hydrogen for use in refinery	Hydrogen in H_2S becomes water vapor
Sulfur product (CS_2) can be burned for H_2SO_4	Sulfur is burned for H_2SO_4
No waste is vented to the atmosphere	Water vapor and other gases are vented
No tail gas cleanup is needed	Requires tail gas cleanup unit

A schematic diagram of the HSM process is shown in Figure 14. No oxygen (air) is required. Also, a Tail Gas Cleanup unit is not needed because no waste is released to the atmosphere.

In the HSM process, a Claus-type H_2S feedstock is mixed with natural gas or a methane-containing fuel gas. These gases are fed to a direct-fired, multi-tubular, fixed-bed reactor at 1100°C (1373 K) and a space velocity of 3000 h^{-1}. After this reactor the product gases are cooled, and CS_2 is recovered as a liquid. Unreacted H_2S is separated and recycled. Hydrogen is used in other parts of the refinery.

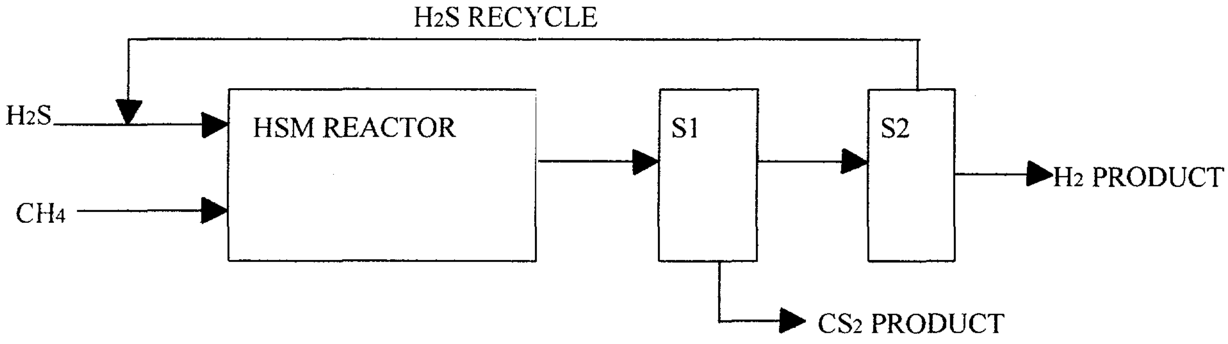

Figure 14. SCHEMATIC DIAGRAM OF HSM PROCESS FOR MAKING REFINERY HYDROGEN

Claus units are used in refineries to convert H_2S to elemental sulfur. Elemental sulfur is sold as a feedstock for sulfuric acid manufacture. In the Claus unit H_2S is partially burned with air to make elemental sulfur and H_2O, according to Reaction 10. The hydrogen in the H_2S is lost as water vapor. In addition, since Claus units do not convert all the H_2S to sulfur, Tail Gas Cleanup units are required to remove traces of sulfur dioxide before the off-gases can be vented to atmosphere.

ECONOMIC ANALYSIS

IGT performed a preliminary economic study of the HSM process for a refinery application. The following process assumptions were made:

1. H_2S is available from an Acid Gas Removal unit.
2. H_2S conversion is 100%.
3. Hydrogen production is 13 million SCF/d.

Capital and operating costs were estimated without taking credit for eliminating the need for operating the Claus process and its associated tail gas cleanup. The cost of hydrogen was calculated using a range of by-product credit for CS_2 from \$0.04 to \$0.23/lb. The lower limit of this price range corresponds to the price of recovered sulfur (see Chemical Marketing Reporter, 1/9/95). Sulfur sells in the range of \$0.04 to \$0.15/lb depending on purity. The upper limit corresponds to the price of CS_2 in conventional markets. Table 14 shows how the cost of hydrogen varies with CS_2 selling price.

Table 14. COMPARISON OF CS_2 SELLING PRICE AND HYDROGEN COST

CS_2 Selling Price, \$/lb	Hydrogen Cost, \$/1000 SCF
0.04	3.19
0.06	2.25
0.10	0.18
0.15	-2.32
0.23	-6.29

As one would expect, the results show that as the market value of CS_2 increases, the cost of hydrogen decreases until at the higher values for CS_2 it results in negative cost for hydrogen. This is an artifact of the calculation program and only shows that the revenue from CS_2 would be more than enough to pay for hydrogen.

If markets could bear it, the best price for CS_2 would come from selling it into established markets. These include rayon, agri-chemicals, rubber, cellophane, and carbon tetrachloride. U.S. production was 114,000 tons in 1990. One 200,000-barrel per day refinery using the HSM process would double U.S. production of CS_2. Established markets are not an outlet for CS_2 from a refinery.

A large outlet for CS_2 is in the production of H_2SO_4. Refineries are already selling the sulfur from Claus for this purpose. Process engineers at Enviro-Chem Systems, the largest designer of sulfuric acid plants, have said that CS_2 can be a feedstock for a sulfuric acid plant.

CS_2 is currently not used because it is more expensive than elemental sulfur. When burned CS_2 will provide more heat than elemental sulfur. The heat can be used to raise more steam. The CO_2 formed does not absorb into sulfuric acid solutions and would not pose particular handling problems to a sulfuric acid plant.

The HSM process can be used to recover valuable hydrogen from a waste stream. HSM converts waste H_2S into a marketable sulfur product. Because HSM does not use air to burn sulfur, no off-gas stream is produced and sulfur emissions from refineries can be reduced.

CONCLUSIONS

- This project is the first to discover and develop two catalysts that react methane and hydrogen sulfide in high conversions to hydrogen and carbon disulfide. In over 327 runs, the best yield of CS_2 was 98% with catalyst IGT-MS-103.
- CS_2 hydrogenation with a mixture of Co-exchanged ZSM-5 zeolite and MoS_2 hydrogenation catalyst achieved 95% conversion of CS_2 and 51% selectivity to C_4^+ hydrocarbons.
- The concept of converting methane to gasoline-range hydrocarbons was demonstrated in a single unit with two reactors: one for the conversion of methane to carbon disulfide and the second for the conversion of carbon disulfide to liquid hydrocarbons.
- In catalyst screening tests it was demonstrated that activity for H_2S decomposition and activity for carbon regeneration were strong indicators for catalytic activity for the methane-hydrogen sulfide reaction.
- The sulfur-tolerant MoS_2 catalyst used in hydrogenating CS_2 showed activity for making methyl mercaptan.
- A preliminary economic study of the application of HSM technology to producing hydrogen for a refinery showed that this is a potential replacement for Claus units and Tail Gas Cleanup units and could be a profitable means of making refinery hydrogen depending on the price of co-produced CS_2.

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REFERENCES CITED

1. Bose, A. C., Stiegel, G. J. and Srivastava, R. D., Americal Chemical Society, Fuel Division PREPRINTS 39, No. 4, 1006-12 (1994).

2. Chan, I. H. *et al.*, "Cooperative Development of Direct Methanation Technology," Gas Research Institute, Chicago, Report No. 91-0008 (1991).

3. Chang, C. and Lang, W. H., U.S. Patent 4,480,143 (October 30, 1984).

4. Chang, C., U.S. Patent 4,5423,434 (September 24, 1985).

5. Chivers, T., Hyne, J. B. and Lau, C., International Journal of Hydrogen Energy 5, 499 (1980).

6. Chivers, T. and Lau, C., International Journal of Hydrogen Energy 12, 235-43 (1987).

7. Choi, G. N. *et al.*, Americal Chemical Society, Fuel Division PREPRINTS 39, No. 4, 1157-61 (1994).

8. Erekson, E. J. and Miao, F. Q., American Chemical Society, Fuel Division PREPRINTS 39, No. 4, 1017-21 (1994).

9. Fischer, H., "Burner/Firebox Design Improves Sulfur Recovery," Hydrocarbon Processing 53, No. 10, 125-30 (October 1974).

10. Folkins, H. O., Miller, E. and Hennig, H., Industrial and Engineering Chemistry 42, 2202 (1950).

11. Fukuda, K., Kotera, Y. and Todo, N., U.S. Patent 3,962,409 (June 8, 1976).

12. Fukuda, K., Kotera, Y. and Todo, N., U.S. Patent 4,039,613 (August 2, 1977).

13. Gates, B. C., Katzer, J. R. and Schuit, G. C. A., Chemistry of Catalytic Processes, 184-318. New York: McGraw-Hill, 1979.

14. Gratzel, M., Chemical and Engineering News 59, 40, July 27, 1981.

15. Jorgensen, P., Czernichowski, A. and Chapelle, J., Fr.Demande FR 2,620,436.

16. Kaloidas, V. and Papayannakos, N., Chemical Engineering Science 44, No.11, 2493-2500 (1989).

17. Kerr, R. K. and Paskall, H. G., "Claus Process: Catalytic Kinetics Part2-COS and CS_2 Hydrolysis," Energy Processing Canada 69, No. 2, 38-44 (November-December 1976).

18. Kiuchi, H. *et al.*, International Journal of Hydrogen Energy 7, No. 6, 477-82 (1983).

19. Kiuchi, H. *et al.*, International Journal of Hydrogen Energy 8, No. 1, 5-13 (1983).

20. Megalofonos, S. K. and Papayannakos, N. G., International Journal of Hydrogen Energy 16, 319-27 (1991).

21. Muradov, N. Z., Rustamv, M. I. and Bazhutin, A. D., Reaction Kinetics and Catalysis Letters 33, No. 2, 279-83 (1987).

22. Pearson, M. J., "Special Catalyst Improves C-S Compounds Conversion," Hydrocarbon Processing 60, No. 4, 131-34 (April 1981).

23. Raymont, M.E.D. and Kerr, R. K., Alberta Sulphur Research Quarterly Bulletin 12, No. 4, 38 (1976).

24. Raymont, M.E.D., Hydrocarbon Processing 54, No. 7, 139 (1974).

25. Raymont, M.E.D., Ph.D. Dissertation, The University of Calgary, Alta., Canada (1974).

26. Sinfelt, J. H., Journal of Catalysis 29, 308-15 (1973).

27. Sun, J. Y. and Erekson, E. J., U.S. Patent 4,766,155 (August 23, 1988).

28. Taylor, C. E. and Noceti, R. P., U.S. Patents 5,139,991 (August 18, 1991) and 4, 769,504 (September 6, 1988).

29. Tijm, P. J. A., American Chemical Society, Fuel Division PREPRINTS 39, No. 4, 146-1150 (1994).

30. Vilesov, N. G., Journal of Applied Chemistry of the USSR 53,1763 (1981).