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GASOLINE FROM NATURAL GAS BY SULFUR PROCESSING

Quarterly Progress Report for the Period January -March 1994
Final Version

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EXECUTIVE SUMMARY

This report presents the work performed at the Institute of Gas Technology (IGT) during the third program quarter from January 1, 1994 to March 31, 1994, under Department of Energy(DOE) Contract No. DE-AC22-93PC92114. This program has co-ordinated funding for Task 1 from IGT's Sustaining Membership Program(SMP), while DOE is funding Tasks 2 through 8. Progress in all tasks is reported here.

The overall objective of this research project is to develop a catalytic process to convert natural gas to liquid transportation fuels. The process consists of two steps that each utilize 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 will be generated to demonstrate the potential of catalysts and the overall process.

During this quarter, progress in the following areas has been made. Five catalysts for step 1 have been prepared. A total of thirty runs with catalysts, IGT-MS-103 and IGT-MS-105, were performed. At 5 seconds residence time and above 1000 °C, the hydrogen sulfide decomposition approached equilibrium. H_2S conversion was 80% at 1131 °C.

A total of fourteen runs were performed for carbon deposition/regeneration studies. Six catalysts as well as quartz wool were used in these studies. During the methane decomposition runs, carbon formation was found on the catalysts surface. During the subsequent hydrogen sulfide regeneration runs, a significant amount of carbon disulfide was detected in the product stream.

Equilibrium calculations for the reaction of carbon with sulfur and with hydrogen sulfide were also performed in this quarter. At 1227 °C, 1 atm , as high as 80% carbon conversion can be obtained at equilibrium.

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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. The expanded use of natural gas as fuel is often hampered because of difficulties in storage 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 gas to gasoline process would decrease dependence on imported oil for transportation fuels. These factors make it very desirable to convert natural gas to more valuable liquids.

There are commercial processes for converting natural gas to gasoline range liquids. These processes such as Fischer-Tropsch synthesis and Mobil's MTG(Methanol To Gasoline) start with the steam reforming of methane. Steam reforming of methane requires the removal of sulfur compounds present in natural gas down to less than 0.1 ppm. This additional gas clean up step which means extra cost is necessary because the catalysts are quickly poisoned by sulfur compounds.

In this program IGT is investigating a two step process that utilizes 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 plus hydrogen. In the second step CS_2 is hydrogenated to gasoline range hydrocarbon liquids. For the proposed process a sulfur removal step down to 0.1 ppm with associated guard beds is not necessary. Sulfur which has been considered as a poison is used as a reactant. This method of methane conversion utilizes H_2S to convert methane to CS_2 . Then CS_2 plus hydrogen can be catalytically converted to gasoline range hydrocarbons. All the H_2S generated during the CS_2 to gasoline reaction is recycled. An additional advantage of the proposed process is that the hydrogen required for the process is produced in step one without using a steam reformer.

The proposed process has 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 and decrease the US dependence on foreign sources of oil.

RESULTS AND DISCUSSION

Task 1. Catalyst Preparation(SMP funded)

Preparation of catalysts for H₂S decomposition reaction continued. Several new high surface area and high temperature stable catalysts were prepared. We have sent all new and used catalysts to IGT analytical department for BET surface area analysis. Moreover, we have also sent IGT-MS-103 (Cr₂S₃ catalyst) and IGT-MS-105 (CeS catalyst) to analytical department for XRD crystal phase analysis.

Table 1 shows the surface area of fresh and used catalysts. No significant surface area changes before and after reactor testing were found for IGT-MS-102, IGT-MS-104 and IGT-MS-105. For IGT-MS-103, after two days testing, the catalyst surface area decreased from 4.2 m²/g to 1.4 m²/g. Catalyst IGT-MS-101 behaved differently. This catalyst's surface area was significantly higher initially. After reactor testing the BET surface area decreased by 90%. However, IGT-MS-101 which is made by IGT's proprietary technique, retained a higher BET surface area than the other catalysts.

Table 1 SURFACE AREA OF FRESH AND USED CATALYSTS

Catalysts	Surface Area (m ² /g)	
	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

The X-ray diffraction results for catalyst IGT-MS-103 and IGT-MS-105 are given in Table 2. No significant phase changes were found for IGT-MS-103. For IGT-MS-105, after two days testing, the major catalyst phase changed from CeS to Ce_2S_3 .

Table 2 MAJOR 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

The IGT-MS-105 catalyst's X-ray diffraction results confirmed our hypothesis that CeS is involved in a bulk phase reaction. This will be discussed later.

Task 2. Experimental Studies of H_2S Decomposition Reaction

Experimental Studies. Experimental work on H_2S decomposition continued during this quarter. A total of 30 data points for two catalysts were collected. IGT-MS-103 (Cr_2S_3 catalyst) and IGT-MS-105 (CeS catalyst) were used in these tests. Preliminary experimental results indicated that as high as 80% H_2S conversion was reached for Cr_2S_3 catalyst at 1131 °C. Comparing catalytic activity for both catalysts, Cr_2S_3 has a higher activity for H_2S decomposition than CeS.

For the first catalyst, IGT-MS-103 (Cr_2S_3), 14.9 g (20 ml) was put into the reactor. The experimental conditions are given in Table 3. Nitrogen was used as a diluent. The feed gas composition was 99% N_2 and 1% H_2S .

**Table 3 TEST MATRIX FOR H₂S CATALYTIC DECOMPOSITION REACTION
OVER Cr₂S₃ CATALYST**

Temperature °C	Pressure (atm)	Flow rate (l/min)	Residence Time (sec)
600,700,800,900,950,1000	1	0.28	5
600,800,900,1000,1050, 1117	1	0.44	3

Table 4 shows H₂S conversion results for 5 seconds residence time(0.28 l/min). As indicated from this table, as high as 80% H₂S conversion was obtained at 1131 °C.

Table 4 H₂S CONVERSION RESULTS AT 5 SECONDS RESIDENCE TIME

Temperature (°C)	600	800	900	1000	1050	1131
H ₂ S conversion	0	39	61	74	79	80

Table 5 shows H₂S conversion results for 3 seconds residence time(0.44 l/min).

Table 5 H₂S CONVERSION RESULTS AT 3 SECONDS RESIDENCE TIME

Temperature (°C)	600	700	800	900	950	1000
H ₂ S conversion	0	19	25	37	50	54

The results in Table 4 and 5 show that a significant amount of H₂S was converted into hydrogen and sulfur at high temperature. H₂S conversion results are plotted in Figure 1. The results at 0.28 l/min are above the equilibrium conversion line. This excess conversion may be explained in two ways. First, H₂S may be decomposing to form a surface sulfur adsorbed specie or compound. The equilibrium conversion line assumes only S₂ (gas) is formed. Second, H₂S may be forming other sulfur compounds including S₈, H₂S₂, H₂S₄, etc., as found by Yang and Kung (1994). These may explain some of the discrepancy of experimental results with equilibrium calculations.

In each of the above tests, a small amount of yellow colored solid was found in product condenser which is cooled by an ice bath. This yellow solid (presumably sulfur) caused some temporary plugging. After these tests we redesigned the product trap lines to avoid sulfur plugging.

The next set of runs were performed with a (IGT-MS-105) CeS catalyst. A total of 40 g (20 ml) of catalyst was put into the reactor. The experimental conditions are given in Table 6. Nitrogen was also used as a diluent.

Table 6 TEST MATRIX FOR H₂S CATALYTIC DECOMPOSITION REACTION
FOR CeS CATALYST

Temperature °C	Pressure (atm)	Flow rate (l/min)	Residence Time (sec)
650,740,830,900,1000,1070	1	0.26	4.6
620,740,830, 900,1010,1070	1	0.49	2.4
620, 740, 830, 900, 1010, 1088	1	0.96	1.2

Initially, catalyst IGT-MS-105 exhibited an entirely different H₂S decomposition activity. During H₂S feed, even at 620 °C significant amounts of hydrogen were detected for the initial 5 hours. Hydrogen balance over the reactor confirmed 100 % H₂S conversion. This is in excess of equilibrium conversion for gaseous H₂S. After 5 hours a different set of results occurred (see the open squared points in Figure 2) This phenomenon is much different than the Cr₂S₃ catalyst. We attribute the 100% H₂S decomposition to a reaction with the bulk CeS phase as follows:

X-ray diffraction results shown above in Table 2 confirmed that the major sulfide phase of this catalyst changed from CeS before testing to Ce₂S₃ after testing. We surmise that hydrogen sulfide and CeS participate in a redox reaction. The metal cation is oxidized and accepts more sulfur, while hydrogen is reduced to H₂, as illustrated above.

After IGT-MS-105 had been operated for 5 hours, the catalyst became stable and the following results were obtained. Table 7 to Table 9 show H₂S conversion results for residence times from 1.2 to 4.6 seconds.

Table 7 H₂S CONVERSION RESULTS AT 4.6 SECONDS RESIDENCE TIME

Temperature (°C)	650	740	830	900	1000	1070
H ₂ S conversion	18	28	37	51	60	65

Table 8 H₂S CONVERSION RESULTS AT 2.4 SECONDS RESIDENCE TIME

Temperature (°C)	620	740	830	900	1010	1070
H ₂ S conversion	9	25	34	43	54	59

Table 9 H₂S CONVERSION RESULTS AT 1.2 SECONDS RESIDENCE TIME

Temperature (°C)	620	740	830	900	1010	1088
H ₂ S conversion	2	11	27	38	52	62

As indicated from these tables, the CeS catalyst has the lower catalytic activity than Cr₂S₃. The maximum H₂S conversion was 65%. Figure 3 shows the H₂S conversions for this catalyst. As indicated from Figure 3 at low temperature, with increasing flow rate, the H₂S conversion decreases. At higher temperature, such as 1070 °C, the flow rate does not have as strong an effect on H₂S conversion, and H₂S conversion approaches equilibrium.

Literature Studies. The search and review of literature related with this project are continuing.

Task 3. Carbon Deposition Studies

Experimental Studies. The initial set of experimental work for this task was completed in this quarter. A total of fourteen tests were performed during this quarter. The experimental conditions are given in Table 10.

Table 10 EXPERIMENTAL CONDITIONS FOR CARBON DEPOSITION STUDIES

Test Number	Test Medium	Gas	Flow-rate, l/min	Temperature °C
1	Quartz wool	CH ₄	0.10	1009
2	Quartz wool	H ₂ S, N ₂	1.077	1011
3	IGT-MS-106	CH ₄	0.10	1017
4	IGT-MS-106	H ₂ S, N ₂	1.077	1013
5	IGT-MS-101	CH ₄	0.10	1009
6	IGT-MS-101	H ₂ S, N ₂	1.077	1011
7	IGT-MS-102	CH ₄	0.10	1001
8	IGT-MS-102	H ₂ S, N ₂	1.077	1012
9	IGT-MS-103	CH ₄	0.10	1000
10	IGT-MS-103	H ₂ S, N ₂	1.077	1013
11	IGT-MS-104	CH ₄	0.10	1000
12	IGT-MS-104	H ₂ S, N ₂	1.077	1014
13	IGT-MS-105	CH ₄	0.10	1019
14	IGT-MS-105	H ₂ S, N ₂	1.077	1020

As we develop catalysts for the conversion of CH₄ + H₂S, we want a catalyst that does not become deactivated by carbon deposition. In the temperature range that we will be testing, carbon formation is thermodynamically possible. We designed a group tests to see whether the catalyst can be regenerated, if some carbon deposition occurred. For tests 1, 3, 5, 7, 9, 11 and 13, the catalyst was heated up to 1000°C in the nitrogen flow environment. At the catalyst bed temperature reached 1000°C, CH₄ was then passed through. CH₄ decomposed at high temperature to form carbon on the catalyst surface. The total time of passing CH₄ over the catalyst surface was one hour. After one hour, CH₄ flow was switched off, and the reactor was cooled down in flowing nitrogen. A part of catalyst was collected and sent for carbon analysis. For the subsequent even numbered tests (2, 4, 6, 8, 10, 12 and 14), the carbon-deposited catalyst was heated in flowing nitrogen. H₂S was introduced at 1000 °C and allowed to react with the carbon for one hour to form carbon disulfide. After one hour, H₂S flow was switched off. The reactor was also cooled down to room temperature in flowing nitrogen. A sample of the catalyst was again collected and sent for carbon analysis. The product gas streams for all tests were analyzed by 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/carbon reaction.

During these tests, we found a small amount of liquid condensed on the wall of product condenser as well as on the quartz reactor wall where it was cooled by a water cooling coil. Since the gas sample point was after product condenser, the condensation of the liquid may affect the samples. In order to make better sampling, a new reactor was designed and ordered. We have modified the sample system for subsequent tests. We have sent all used catalysts to our analytical department for carbon formation testing.

Thermodynamic Studies. Thermodynamic calculations of carbon with sulfur reactions were also performed during this quarter. There are four possible independent reactions involved in this system.

Reaction 5 is a combination of reaction 3 and 4. Table 11 shows the Gibbs free energy data of the chemical substances which take part in these reactions. The data were taken from JANAF Thermochemical Tables, Second Edition (1971).

Table 11 GIBBS FREE ENERGY DATA OF CHEMICAL SUBSTANCES (kcal/mole)

Temperature, K		<u>1000</u>	<u>1100</u>	<u>1200</u>	<u>1300</u>	<u>1400</u>	<u>1500</u>
Substance	H ₂ S	-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

Figures 4 and 5 show the equilibrium carbon conversion at 1027°C (1300 K) and at 1227°C (1500 K) and pressure from 0.1 atm to 2 atm for reaction:

As indicated from Figure 4, in excess of 80% carbon conversion can be obtained at 1027 °C. Also, increasing the system pressure increases the carbon conversion. S_2/C ratio has a significant effect on carbon conversion at S_2/C ratio below 2 range. Throughout the ranges, increasing S_2/C ratio increases carbon conversion. However for S_2/C ratio more than 2, carbon conversion increases are small.

Figure 6 shows the equilibrium carbon conversion at 1 atm and 1000 °C and 1200 °C for reaction:

From Figure 6 the equilibrium carbon conversion at 1200 °C and 1 atm is more than 30%. Increasing temperature increases carbon conversion.

Figures 7 and 8 show the equilibrium carbon conversions at 1 and 0.1 atm, respectively, for the reaction:

In Figure 7 at 1223 °C and 1 atm, more than 40% carbon conversion can be obtained at equilibrium. Also, increasing temperature increases carbon conversion.

As indicated in Figure 8, lowering the total system pressure significantly reduces the carbon conversion. At the 0.1 atm, the maximum carbon conversion is only 10%.

Task 4. Experimental Studies of the Methane Hydrogen Sulfide Reaction

Experimental Studies. The catalyst test unit has been modified to accommodate the flows, temperatures and reactants for this project.

Literature Studies. The search and review of literature related with this project are continuing during this period.

Task 5. Experimental Studies of CS₂ to Liquid Hydrocarbons

This task was inactive this period.

Task 6. Proof of Concept Testing

This task was inactive this period.

Task 7. Environmental Reporting

This task was inactive this period.

Task 8. Project Management and Technology Transfer

Reports are being prepared on a timely basis. A abstract has been submitted to "Symposium on Alternative routes for the production of fuels" on 1994 ACS national Meeting for this project.

REFERENCES

1. Yang, B. L. and Kung, H. H., Industrial and Engineering Chemistry Research, 33, 1090(1994).

Figure 1. H₂S CONVERSION FOR IGT-MS-103 CATALYSTS

Figure 2. H₂S CONVERSION FOR IGT-MS-104 CATALYST.

Figure 3. H₂S CONVERSION FOR IGT-MS-105 CATALYST.

Figure 4. Equilibrium calculations for C conversion for reaction $C + S_2 = CS_2$ at 1027 C

Figure 5. Equilibrium calculations for C and S₂ conversion to CS₂ at 1227 C

Figure 6. Equilibrium calculations for C and H₂S conversion to CS₂ at 1 atm

Figure 7. Equilibrium calculations for C arbon conversion for reaction $C + 4H_2S = CS_2 + S_2 + 4H_2$ at 1 atm

Figure 8. Equilibrium calculations for C carbon conversion for reaction $C+4H_2S=CS_2+S_2+4H_2$ at 0.1 atm

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