

GASOLINE FROM NATURAL GAS BY SULFUR PROCESSING

**EREK J. EREKSON
INSTITUTE OF GAS TECHNOLOGY
1700 S. MOUNT PROSPECT ROAD
DES PLAINES, IL 60018**

OBJECTIVE:

The overall objective of this research project is 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 utilize a catalyst and sulfur-containing intermediates: 1) converting natural gas to CS_2 and 2) converting CS_2 to gasoline-range liquids. Experimental data will be generated to facilitate evaluation of the overall commercial viability of the process.

ACCOMPLISHMENTS & CONCLUSIONS

Catalysts have been found that convert methane to carbon disulfide in yields up to 98%. This exceeds our target of 40% yields for the first step. The best rate for hydrogen production is 9.7 mole H_2 /kg-cat-h. An improved catalysts for the hydrogenation of CS_2 to gasoline range liquids has been found. The conversion of methane to gasoline range liquids has been demonstrated in a single experimental unit. A preliminary economic study shows that HSM technology may be applied to making hydrogen in a refinery depending on the price of CS_2 .

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. It is desirable to convert natural gas to more valuable liquids. The successful implementation of this process would decrease dependence on imported oil for transportation fuels.

There are two commercialized methods for converting natural gas to gasoline range liquids.

- 1) Fischer-Tropsch synthesis
- 2) Mobil's MTG process.

Each has two basic steps:

1. Removal of sulfur compounds (H_2S , COS and mercaptans with sulfur adsorbing guard beds to prevent breakthrough of sulfur to the catalysts).
2. Steam reforming to make synthesis gas which requires 2 moles of superheated steam for every mole of methane.

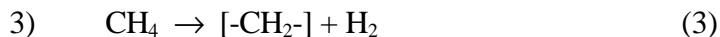
In Fischer-Tropsch synthesis, the third step is the conversion of synthesis gas to hydrocarbons. In Mobil's MTG process, the third step is methanol synthesis and an additional step of methanol conversion to gasoline liquids is required. The commercial steps listed above; i.e., steam reforming, methanol synthesis, or Fischer Tropsch synthesis, require the removal of sulfur compounds present in natural gas down to less than 0.1 ppm. This additional gas clean-up step means extra cost, but it is necessary because the catalysts are quickly poisoned by sulfur compounds.

IGT is developing the HSM Process, a two-step process that uses H_2S as a reactant to convert natural gas to gasoline-range liquids. Sulfur, which has been considered as a poison, is used as a reactant in the HSM process. This process 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 of the H_2S generated during the CS_2 to gasoline reaction is recycled. This process does not require steam reforming nor the manufacture of hydrogen. This process is actually a net producer of hydrogen.

There are two main reactions involved in this process:



The process is a net H_2 producer, and H_2S is recycled. So the overall process would be:



As we began this project, we found no other references to converting methane-hydrogen sulfide to carbon disulfide. The second reaction has been demonstrated by researchers at Mobil Corporation¹. A schematic diagram of the process is shown in Figure 1.

Schematic Diagram of IGT's HSM Process

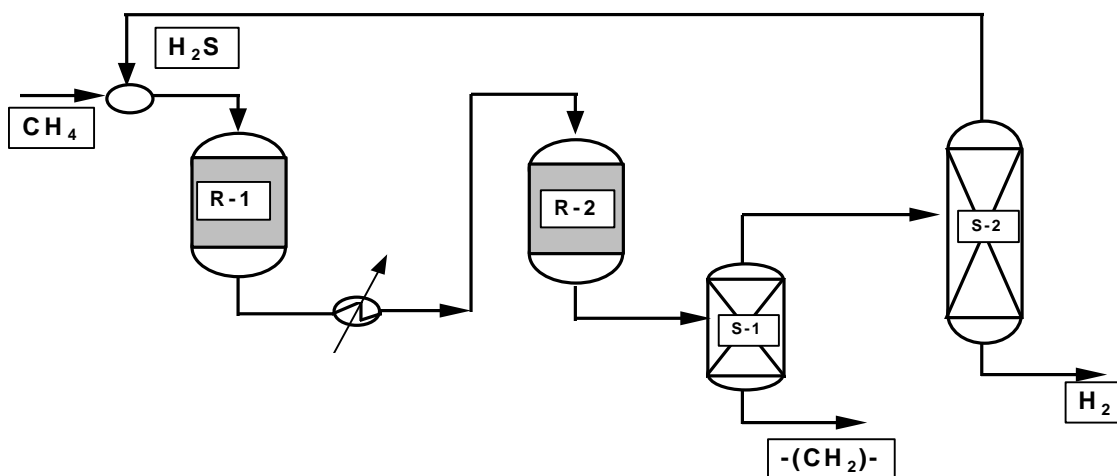


Figure 1. SCHEMATIC DIAGRAM OF HSM PROCESS

EXPERIMENTAL

Descriptions and a diagram of the experimental equipment and methods have been described before². Briefly the methane-hydrogen sulfide reactions were performed by setting flows of mixed gases over a 20 ml volume of catalyst in a quartz reactor. CS₂ hydrogenation runs were performed by bubbling hydrogen through CS₂ liquid at a controlled temperature. The catalyst for this reaction was placed in a 3/4 inch schedule 80 stainless steel pipe reactor.

RESULTS AND DISCUSSION

Methane H₂S Reaction Tests

Ten catalysts and the empty reactor were tested in 278 runs for the reaction of methane with hydrogen sulfide. During these tests 5 temperatures, two flow rates and three H₂S/CH₄ ratios were investigated. The primary products were carbon disulfide and hydrogen. A summary of the carbon disulfide yield results for H₂S/CH₄ ratio of 4 is shown in Figure 2. At H₂S/CH₄ = 4 there is twice the stoichiometric amount of H₂S in the feed. The highest yields of CS₂ were achieved at this ratio.

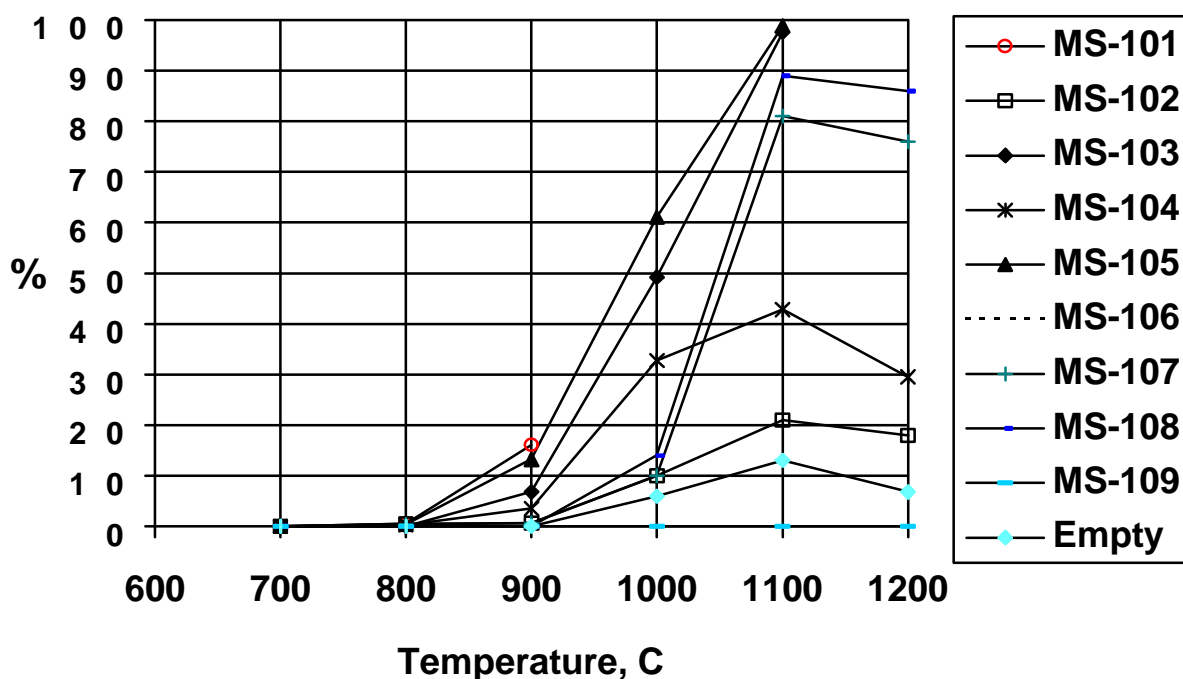


Figure 2. SUMMARY OF CARBON DISULFIDE YIELDS FOR NINE CATALYSTS AND THE EMPTY REACTOR WITH H₂S/CH₄ RATIO = 4 AND RESIDENCE TIME = 1 SECOND.

Generally the yield of CS₂ increases with temperature up to 1100 °C. Above that the yields decreases. 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 H₂S/CH₄ ratios of 2 and 8.

To show the trends of a typical run a summary of the CS₂ and H₂ yields along with H₂S and CH₄ conversions for IGT-MS-103 are shown in Figure 3.

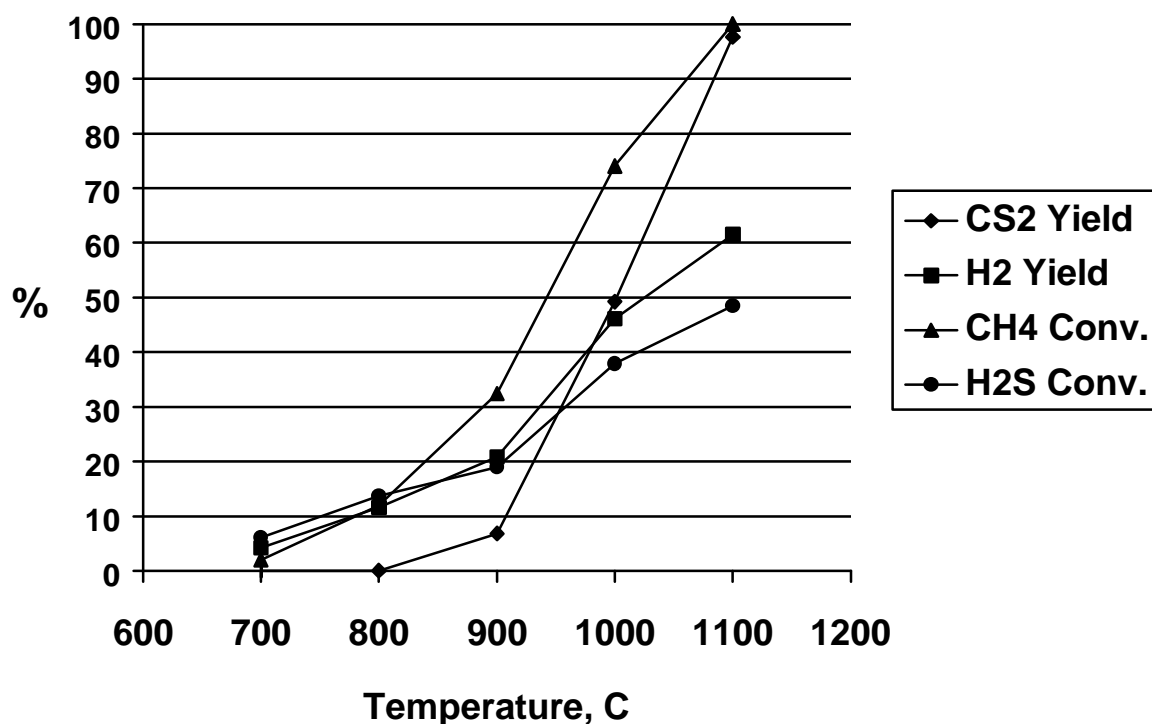


Figure 3. YIELDS AND CONVERSION FOR IGT-MS-103 WITH H₂S/CH₄ = 4 AND RESIDENCE TIME = 1 SECOND.

For this catalyst the trend is for CS₂ yield increasing sharply above 900 °C to a maximum of near 100 % at 1100 °C. CS₂ yield is based on the moles of CS₂ produced divided by the moles of methane fed. Methane conversion reaches 100% at 1100 °C. 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 H₂S. The yield of hydrogen is also shown. This yield is based on the gram atoms of H in the product H₂ divided by the gram atoms of H in the feed gases. The theoretical maximum yield of hydrogen is 67%. The highest yields actually achieved was 62%. The rate of hydrogen production at 1100°C for IGT-MS-103 was 9.7 moles H₂/kg catalyst-h.

Hydrogenation of CS₂ to Hydrocarbons

In addition to hydrogen sulfide-methane reaction efforts also focused on converting CS₂ to hydrocarbons using a mixture of MoS₂ hydrogenation catalyst and H-ZSM-5 catalyst. The feed was delivered by bubbling hydrogen through liquid CS₂ maintained at 0 °C. These experiments were at space velocity of 343 h⁻¹ and three temperatures. Results of these runs are shown in Table 1. CS₂ and H₂ conversions are shown in Table 1 along with the liquid hydrocarbon selectivity. Liquid hydrocarbon selectivity was calculated by finding the ratio of gram-atoms of carbon of C₄⁺ products to the total gram-atoms of carbon in the product.

Table 1. CS₂ Hydrogenation over a mixture of 15 ml MoS₂ and 15 ml H-ZSM-5 at ambient pressure. Effect of Temperature on the Conversion of CS₂ and H₂. H₂/CS₂ = 5.1

Space Velocity (h ⁻¹)	Temperature (°C)	% Conversion H ₂	% Conversion CS ₂	% Selectivity C ₄ ⁺
343	434	38	100	11
	350	36	98	45
	325	27	95	51

The results in Table 1 show that CS₂ hydrogenation is occurring. The use of the MoS₂ hydrogenation catalyst in conjunction with the HZSM-5 zeolite catalyst result near complete conversion of CS₂. The MoS₂ catalyst is active for the conversion of CS₂ to methyl mercaptan. Indeed, we found up to 1 % methyl mercaptan in the raw product gas. Also in reference to work performed at Mobil (See patents US #4,543,434 and #4,480,143) H-ZSM-5 also converts methyl mercaptan to liquid hydrocarbons. These results appear to confirm this. This set of runs shows the highest conversion of CS₂ accompanied by a 51% selectivity to C₄⁺ hydrocarbons.

COMMERCIALIZATION PLANS

With respect to the commercialization of the technology developed in this project, we have sent out brief summaries to managers at petroleum companies and designers of hydrogen plants. The summaries 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. A brief comparison of HSM and Claus follows.

HSM	Claus
Converts H ₂ S to useful products (H ₂ , CS ₂)	Converts H ₂ S to useful product (S)
Produces hydrogen for use in refinery	Hydrogen in H ₂ S becomes water vapor
Sulfur product (CS ₂) can be burned for H ₂ SO ₄	Sulfur is burned for H ₂ SO ₄
No waste is vented to the atmosphere	Water vapor and other gases are vented

No tail gas clean-up is needed

Requires tail gas clean-up unit

ACKNOWLEDGMENT

This work was supported by the U.S. Department of Energy, Pittsburgh Energy Technology Center, Pittsburgh, Pennsylvania under Contact No. DE-AC22-93PC92114, and IGT's Sustaining Members Program(SMP), Project #80023.

REFERENCES

1. C.D.Chang, US patent #4,543,434, Sep.24, 1985
2. E. J. Erekson and F. Q. Miao, "Gasoline from Natural Gas by Sulfur Processing," 1995 Coal Liquefaction and Gas Conversion contractors Review Conference Proceedings, Pittsburgh Energy Technology Center, 553(1995)