F O S S I L E N E R G Y

GASOLINE FROM NATURAL GAS BY SULFUR PROCESSING

Quarterly Report No. 8 for the Period April-June 1995

**By
Erek J. Erekson**

July 1995

Work Performed Under Contract No.: DE-AC22-93PC92114

**For
U.S. Department of Energy
Pittsburgh Energy Technology Center
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Printed in the United States of America

Available from

National Technical Information Service

U.S. Department of Commerce

5285 Port Royal Road

Springfield, VA 22161

NTIS price codes

Printed copy: A01

Microfiche copy: A01

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Approved 8/3/95

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EXECUTIVE SUMMARY

This report presents the work performed at the Institute of Gas Technology (IGT) during the eighth program quarter from April 1 to June 30, 1995, under Department of Energy (DOE) Contract No. DE-AC22-93PC92114. This program has coordinated 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 use catalysts 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 demonstrate the potential of catalysts and the overall process.

During this quarter, progress in the following areas has been made:

- Short duration activity test on catalyst IGT-MS-103 showed that no deactivation over a 10 hour period.
- A preliminary economic estimate for the application of the HSM process technology in a refinery showed potential for profitable commercialization. Engineers at oil companies have requested further information.
- Tests with equimolar amounts of H_2S and CO_2 in the feed showed that CS_2 yield decrease with the addition of CO_2 .

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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 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 processes for converting natural gas to gasoline-range liquids. These processes, such as the 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 cleanup step, with its additional cost, is necessary because the catalysts are quickly poisoned by sulfur compounds.

In this program, IGT is investigating 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:

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, 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 is 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 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, thus, decreasing the U.S. dependence on foreign sources of oil.

RESULTS AND DISCUSSION

Task 1. Catalyst Preparation (SMP Funded)

The purpose of this task is to prepare the catalysts according to both conventional and IGT proprietary methods for evaluation in the reactions studied in Tasks 2 through 5.

The preparation of catalysts for the reaction of H_2S with CH_4 are continuing.

Task 2. Experimental Studies of the H_2S Decomposition Reaction

The purpose of this task is to evaluate catalysts for the following reaction:

In this task, we designed a group of tests for evaluating IGT catalysts. The reason for studying this reaction is to produce a group of catalysts that make gaseous sulfur. Gaseous sulfur is known to react with methane to form CS_2 , the desired product of Step 1.

This task was inactive this quarter.

Task 3. Carbon Deposition Studies

As we develop a catalyst for the conversion of $\text{CH}_4 + \text{H}_2\text{S}$, 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 of tests to see if some carbon deposition occurred, whether the catalyst can be regenerated, and whether CS_2 would be formed from the carbon on the catalyst surface.

This task was inactive this quarter.

Task 4. Experimental Studies of the Methane/Hydrogen Sulfide Reaction

The objective of this task is to develop a group of catalysts for the direct conversion of methane and hydrogen sulfide to carbon disulfide. This task is divided into two parts. During the first part, 10 catalysts will be prepared and evaluated. A group of the best catalysts will be identified. The optimum operating conditions will also be determined. In the second part of this task, the most promising catalysts will be tested under the best operating conditions for sustained periods of time.

Activity and short duration tests were performed on catalyst IGT-MS-103 for the methane with hydrogen sulfide reaction. Near the end of the quarter activity tests with carbon dioxide in the feed were performed. All these tests are discussed in this section. A total of 33.1g(20 ml) of catalyst was loaded into the 1 inch quartz reactor. Nitrogen was used as a diluent, similar to previous runs. These runs were performed after the repair of the quartz reactor, mentioned in previous reports. The test matrix for the first two runs is shown in Table 1.

Table 1. TEST MATRIX FOR METHANE WITH HYDROGEN SULFIDE REACTIONS USING CATALYST IGT-MS-103

<u>H₂S/CH₄ Ratio</u>	<u>Residence time, s</u>	<u>Temperature °C</u>
4	1.2	1192
4	1.2	1102

For the first run it was noticed that the R-type thermocouple in the reactor thermowell was not giving stable readings. This thermocouple was replaced by a K-type thermocouple. The reactor was held at 1192°C for about 2 hours. The yield of CS₂ was 80.9%. This is lower than the highest yield previously obtained on this catalyst, but it is consistent with earlier results that CS₂ yield decreases above 1100°C. 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 1100°C. The CS₂ yield was 88%, the H₂S conversion was 59%, and the methane conversion was 100%. These results remained for the duration of the run which lasted 5.5 hours.

A short duration activity test was performed on catalyst IGT-MS-103 for the methane with hydrogen sulfide reaction. A total of 33.1g(20 ml) of catalyst was loaded into the 1 inch quartz reactor. The $\text{H}_2\text{S}/\text{CH}_4$ ratio was 4. Nitrogen was used as a diluent, similar to previous runs. This run was performed to see if the catalyst maintains activity over a period of eight hours. The results are shown in Figure 1. There is no indication of deactivation during this run. The CS_2 yield, hydrogen yield, and H_2S conversion were maintained near or above initial rates for the eight hour run.

Figure 1. CS_2 AND H_2 YIELDS AND H_2S CONVERSION FOR EXTENDED RUN

As a means of investigating how the catalysts developed in this project might be applied in commercial situations, we 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. Carbon dioxide is an acid gas and is often found in mixtures with hydrogen sulfide. 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 1 inch quartz reactor. The $\text{H}_2\text{S}/\text{CH}_4/\text{CO}_2$ 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 2.

Figure 2. 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 another reaction pathway. CO and COS were produced. The yield of CS_2 is below 10% for this temperature range. For the previously reported runs CS_2 yields were based on the conversion of methane. In this case 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. The salient result from this run is that carbon dioxide in the feed negatively affects hydrogen sulfide conversions and CS_2 yields.

An extended run was also performed using the $\text{CO}_2/\text{H}_2\text{S}/\text{CH}_4$ feed gas. The results of the extended run are shown in Figure 3. For this run the conversions and yields remained steady for this short duration test.

Figure 3. CS_2 AND H_2 YIELDS AND H_2S CONVERSIONS FOR EXTENDED RUN WITH CO_2 IN THE FEED

During this quarter we performed an economic estimate on the use of the HSM process technology for making hydrogen in a refinery setting. The HSM process would use methane, but it would convert H_2S into hydrogen. CS_2 would be produced as a by-product, but one 200,000 barrel per day refinery using HSM would double the US production of CS_2 . For this reason we have looked for other uses of CS_2 . CS_2 can be used as a feedstock for sulfuric acid. A preliminary economic evaluation shows that hydrogen produced by the HSM technology would cost from \$3.20 to less than \$0.00/ 1000 SCF depending on the price of CS_2 . The range of the price of CS_2 was from \$0.04 to \$0.23 / lb. This range was selected from the current market price for CS_2 at \$0.23 /lb and the current market price for sulfur at from \$0.04 to \$0.15 / lb. These results are encouraging, and we will be investigating the potential of this application further.

Task 5. Experimental Studies of CS₂ to Liquid Hydrocarbons

We have obtained samples of ZSM-5 and have begun preparing these in a silica matrix. We have also made Co on silica hydrogenation catalysts. We will test a physical mixture of both ZSM-5 and hydrogenation catalysts for the reaction of CS₂ to hydrocarbons.

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

We have contacted people from Ashland Oil and Mobil Corp., as well as AKZO Nobel concerning commercial applications of all or part of IGT's HSM process. In addition to using the HSM technology for making liquid hydrocarbons, several petroleum companies are interested in using HSM for making hydrogen for refinery applications while removing hydrogen sulfide.

CONCLUSIONS

- There is interest within the oil companies we contacted for a process that converts natural gas to liquid hydrocarbons. In addition there is also interest in a process that produces hydrogen for a refinery, while at the same time it removes hydrogen sulfide.