GASOLINE FROM NATURAL GAS BY SULFUR PROCESSING

Quarterly Report No. 7 for the Period January-March 1995

**By
Erek J. Erekson**

April 1995

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

**For
U.S. Department of Energy
Pittsburgh Energy Technology Center
P.O. Box 10940
Pittsburgh, Pennsylvania 15236-0940**

**By
Institute of Gas Technology
1700 South Mount Prospect Road
Des Plaines, Illinois 60018-1804**

**TECHNICAL INFORMATION CENTER
OFFICE OF SCIENTIFIC AND TECHNICAL INFORMATION
UNITED STATES DEPARTMENT OF ENERGY**

RECEIVED
USDOE/PTC
95 JUN -9 11 30
ACQUISITION & ASSOCIATE DIV.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

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

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

DOE/PC/92114--T7

GASOLINE FROM NATURAL GAS BY SULFUR PROCESSING

Quarterly Report No. 7 for the Period January-March 1995

**By
Erek J. Erikson**

April 1995

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

**For
U.S. Department of Energy
Pittsburgh Energy Technology Center
P.O. Box 10940
Pittsburgh, Pennsylvania 15236-0940**

**By
Institute of Gas Technology
1700 South Mount Prospect Road
Des Plaines, Illinois 60018-1804**

Approved 5/1/95

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED
mu

MASTER

EXECUTIVE SUMMARY

This report presents the work performed at the Institute of Gas Technology (IGT) during the seventh program quarter from January 1 to March 31, 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:

- Two new batches of catalysts were prepared for the reaction of methane with hydrogen sulfide to produce carbon sulfide.
- Potential commercializing partners were contacted. Several companies expressed interest in possible applications of this technology.

TABLE OF CONTENTS

	<u>Page</u>
INTRODUCTION	1
RESULTS AND DISCUSSION	2
Task 1. Catalyst Preparation (SMP Funded)	2
Task 2. Experimental Studies of the H ₂ S Decomposition Reaction	2
Task 3. Carbon Deposition Studies	2
Task 4. Experimental Studies of the Methane/Hydrogen Sulfide Reaction	3
Task 5. Experimental Studies of CS ₂ to Liquid Hydrocarbons	3
Task 6. Proof-of-Concept Testing	3
Task 7. Environmental Reporting	4
Task 8. Project Management and Technology Transfer	4
CONCLUSIONS	4

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. Two new batches of catalysts, IGT-MS-103 and IGT-MS-105, were prepared in the same manner as previous batches of these catalysts.

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.

The activity test unit for the methane-hydrogen sulfide reaction was modified for long term operation. A 94 hour activity test on catalyst IGT-MS-103 for the methane with hydrogen sulfide reaction was performed. A total of 21.62(20ml) of catalyst was loaded into the reactor. The $\text{H}_2\text{S}/\text{CH}_4$ ratio was 4 and the temperature was 1100°C . Nitrogen was used as a diluent, similar to previous runs. During this run the unit was brought to a steady state for 14 to 16 hours per day. Each night the reactor was flushed with nitrogen and held at 1100°C . Feed gas flows were resumed in the morning, and a subsequent 14 to 16 hour steady state run was performed. This procedure was continued for 4 days. The analytical results from this test varied widely. We recalibrated the gas chromatograph at the end of the run and found no change from the calibration at the beginning of the run. After the run we removed the catalyst from the quartz reactor and found a crack in the reactor near where the catalyst bed is held. If this crack was open during the run, it could explain the erratic analytical results. The reactor was sent to the glassblowers for repair. This long-term run will be repeated.

Task 5. Experimental Studies of CS_2 to Liquid Hydrocarbons

We have begun contacting sources for obtaining ZSM-5 catalyst for these runs. ZSM-5 catalyst will be used in a physical mixture with other hydrogenating catalysts for the CS_2 to hydrocarbon reaction.

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.

Dr. Scott Han of Mobil Oil Corporation, who is one of inventors of the Mobil process which converts CS_2 to gasoline range hydrocarbons (See U.S. patents #4,822,938; #4,864,073; and #4,964,074), visited us on February 13 to discuss the implications of this research. He had several helpful suggestions on how to adjust the selectivity of the hydrogenation of CS_2 reaction. He also said that one of the key intermediates in the conversion of CS_2 is methyl mercaptan.

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 at the same time it removes hydrogen sulfide for refinery application.