DOE/PC/92114--79

GASOLINE FROM NATURAL GAS BY SULFUR PROCESSING

Quarterly Report No. 9 for the Period July-September 1995

By
Erek J. Erekson
R. Gopalakrishnan

October 1995

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

For
U.S. Department of Energy
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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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Accepted 11/3/95

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EXECUTIVE SUMMARY

This report presents the work performed at the Institute of Gas Technology (IGT) during the ninth program quarter from July 1 to September 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 no deactivation over a 6 hour period;
- Tests showed that even with CO_2 in the feed, H_2S conversions of 50% can be achieved.

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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 is 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.

In the previous quarter we found that the addition of carbon dioxide to the feed gases does affect the yield of CS₂ in the methane-hydrogen sulfide reaction. When carbon dioxide and hydrogen sulfide are in equal concentrations in the feed, the yield of CS₂ drops to below 10%. Although the decrease in CS₂ yield was anticipated, these yields are unacceptable for commercial applications. However, we have found that some acid gas removal units are designed to produce an H₂S rich stream. The molar ratio of H₂S/CO₂ from an acid gas removal unit can be as high as 8 to 1. We decided to try the HSM catalysts on a feed with a H₂S/CH₄/CO₂ ratio of 8/2/1. We ran a test on catalyst IGT-MS-103 with 33.1 grams (20 ml) loaded into the 1 inch quartz reactor. The H₂S/CH₄/CO₂ feed ratio was 8/2/1. Nitrogen was used as a diluent, similar to previous runs. The conversions and yields were measured over a three hour period of time. The results are shown in Figure 1.

Figure 1. CS₂ YIELD AND CH₄ AND H₂S CONVERSIONS FOR EXTENDED RUN AT 1100°C WITH H₂S/CH₄/CO₂ FEED RATIO OF 8/2/1

For these runs the CS₂ yield is much higher than the previous runs with equal concentrations of CO₂ and H₂S. The methane conversion remained 100% throughout the period, and the H₂S conversion remained relatively constant, while CS₂ yield began to increase slightly near the end of the period. CO was produced, but no COS was detected in the product gas. This is in contrast to the previous runs where both CO and COS were produced. Our initial assessment from these runs is that the HSM catalysts can be applied to acid gas streams that contain CO₂. Equal molar concentrations of CO₂ and H₂S result in low CS₂ yields and the production of COS and CO. However, at an H₂S/CO₂ ratio of 8, CS₂ yields are above 50%.

In the last few months, efforts in this task have focused on the effects of carbon dioxide on the yields of CS₂. Equimolar amounts of CO₂ and H₂S in the feed cause the yield of carbon disulfide to drop to unacceptable levels. When the ratio of H₂S/CO₂ is 8, the yield of CS₂, based on methane feed, is above 60%. Because of these recent results we have been investigating acid gas removal processes that produce an H₂S stream that is free from CO₂. We contacted Dr. Guido Sartori of Exxon who invented the selective absorbents for Flexsorb process. He sent us

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 . There are at least 27 plants in the U.S. that are using Flexsorb solvents in acid gas removal. We will investigate this process further.

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_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 clean-up is needed	Requires tail gas clean-up unit

We will be following up with our contacts regarding their interest in the HSM technology for refinery applications.

Task 5. Experimental Studies of CS_2 to Liquid Hydrocarbons

During this period efforts have focused on preparing an H-ZSM-5 catalyst partially exchanged with cobalt. The purpose of partial exchange is to provide dual functionality in the catalyst. Cobalt sites promote hydrogenation of CS_2 , and H sites promote chain growth. The catalyst was prepared by ion-exchange method. It was found to have 56% of the available sites exchanged by cobalt as measured by inductively coupled plasma (ICP). The unit has been modified and calibrated to pump CS_2 and to meter hydrogen as feedstocks to the reactor

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. Dr. Erek Erekson attended the DOE-PETC Gas Conversion and Coal Liquefaction Contractors Conference in Pittsburgh on August 29-31. He presented a review of the results and progress of this project.

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.
- Experimental tests showed that even with carbon dioxide present, H₂S conversions of 50% can be achieved.