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GASOLINE FROM NATURAL GAS BY SULFUR PROCESSING

Quarterly Report No. 10 for the Period October-December 1995

By
Erek J. Erekson
R. Gopalakrishnan

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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

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Approved 1/29/96

EXECUTIVE SUMMARY

This report presents the work performed at the Institute of Gas Technology (IGT) during the tenth program quarter from October 1 to December 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:

- Short duration activity test on catalyst IGT-MS-103 showed no deactivation over a 6 hour period;
- Preliminary data of CS_2 reaction with H_2 at 400 - 410 °C and at atmospheric pressure indicates that IGT-HS-103 is an active catalyst for hydrocarbon synthesis from CS_2 and H_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.

A batch of IGT-HS-103, metal ion exchanged zeolite based hydrogenation catalysts, was prepared by ion exchange method and characterized for metal loading (56 %) and BET surface area (347 m²/g).

Task 2. Experimental Studies of the H₂S 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 CS₂, 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 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 of tests to see if some carbon deposition occurred, whether the catalyst can be regenerated, and whether CS₂ 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.

Catalyst testing was inactive this quarter.

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 quarter efforts have focused on converting CS_2 to hydrocarbons using H_2 on IGT-HS-103 catalyst. 20 cc of the catalyst was loaded in a quartz reactor. The reaction was carried out by feeding CS_2 and H_2 at atmospheric pressure and at different temperatures and flow rates. The results are given in Table 1. During this study the runs were often interrupted due to

unsteady CS₂ liquid flows. The liquid has a boiling point of 46 °C, and it vaporizes easily in the piston area of the pump creating a gas bubble. The flow stops when gas bubbles move into the check valve. Therefore, the results of Table 1 are preliminary and need to be repeated.

Table 1. Hydrogenation of CS₂ on IGT-HS-103

Catalyst volume = 20 cc; Pressure = 1 atm.

Temperature (°C)	CS ₂ flow (LHSV)	H ₂ flow (GHSV)	CS ₂ /H ₂ (mole ratio)	CS ₂ conversion (%)
407	0.664	399	0.69	16
400	0.521	399	0.54	12
417	0.403	399	0.42	50

Under the experimental conditions (CS₂/H₂ = 0.42 to 0.69), no condensation of CS₂ in the products was found. The vapor pressure of CS₂, for example, at 25 °C is about 0.45 atm. The gas products were analyzed in GC and the CS₂ conversions were calculated from the feed and exit concentrations. Hydrocarbons were observed by GC (the GC could detect only up to C4) but they were not quantified. Further experiments will focus on quantifying individual hydrocarbons and also changing the reaction parameters, feed concentration, temperature, etc.

The results can be compared with previous Mobil work (US Patent 1985, US 4,543,434). The results of Mobil study are given in Table 2.

Table 2. Hydrogenation of CS₂ over a mixture of 50% HZSM-5/Al₂O₃ and 50% Co/SiO₂

Catalyst volume = unknown; Pressure = 250 psig.

Temperature (°C)	CS ₂ flow (LHSV)	H ₂ flow (GHSV)	CS ₂ /H ₂ (mole ratio)	CS ₂ conversion (%)
482	1	400	0.93	40.3

In order to obtain a constant flow of CS₂ liquid, we used a syringe pump, but the o-rings in the piston expanded when it came into contact with CS₂. Eventually the syringe stopped

operation. To solve the CS₂ delivery problem and to obtain constant flow, we changed the delivery configuration to a pressurized container with a micrometer valve to control the flow. Nitrogen is used to pressurize the container to 7 psig. CS₂ liquid flows out of the bottom of the container. Test runs were carried out to repeat the conditions of earlier Mobil work where CS₂/H₂ = 1. However, at this higher CS₂/H₂ ratio CS₂ was condensing in the quartz bulb after the reactor. Since the products were sampled by a gas syringe, it was difficult to quantify CS₂ concentration. To alleviate this, we have installed a heating mantle to prevent the liquid condensation in the quartz bulb after the reactor. Also, we have installed a GC-sampling point close to the quartz bulb with additional heating along the gas line up to the sampling point to keep the products in vapor phase. Test runs will be conducted soon and will be reported in the next monthly report.

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

This task was inactive this period.

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.
- Preliminary data of CS₂ reaction with H₂ at 400 - 410 °C and at atmospheric pressure indicates that IGT-HS-103 is an active catalyst for hydrocarbon synthesis from CS₂ and H₂.