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GASOLINE FROM NATURAL GAS BY SULFUR PROCESSING

Quarterly Report No. 11 for the Period January-March 1996

By
Erek J. Erekson

May 1996

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

For
U.S. Department of Energy
Pittsburgh Energy Technology Center
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EXECUTIVE SUMMARY

This report presents the work performed at the Institute of Gas Technology (IGT) during the eleventh program quarter from January 1 to March 31, 1996, 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:

- Hydrogenation of CS_2 to liquid hydrocarbons was accomplished on two sets of catalyst a cobalt exchanged ZSM-5 and a mixture containing MoS_2 hydrogenation catalyst and HZSM-5. CS_2 conversions of up to 100% were achieved. The highest selectivity to C_4^+ hydrocarbons was 52%.
- 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.

 

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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 HZSM-5 and GRI-I-800 MoS₂ catalyst was made for testing in Task 5.

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 we set up a reliable CS_2 liquid delivery system for the experimental unit. While the pressurized container with a needle valve achieved reliable flows, condensation in the feed lines was experienced. In addition to condensation in the feed lines, condensation of CS_2 and hydrocarbons was occurring in the product lines as well. Even with the heat tracing that

was installed last month, flow fluctuations were still occurring. It was decided to change the flow system to a gas/liquid bubbler-saturator. The hydrogen feed gas was bubbled through a container of CS₂ which was maintained at 0°C. Thus, the ratio of CS₂/H₂ is set by the equilibrium saturation of hydrogen. Flow fluctuations and unwanted condensations were no longer experienced.

During this quarter we performed CS₂ to liquid hydrocarbon experiments using the Co-H-ZSM-5-56 catalyst. These experiments covered a range of three space velocities and four temperatures. 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. Some of the results shown in Table 1 have been previously presented.

Table 1. CS₂ Hydrogenation over Co-H-ZSM-5-56 at ambient pressure. Effect of Temperature and Space Velocity on the Conversion of CS₂ and H₂. H₂/CS₂ = 5.1

Space Velocity	Temperature	% Conversion	% Conversion	% Selectivity
(h ⁻¹)	(°C)	H ₂	CS ₂	C ₄ ⁺
478	407	13	25	NA
	431	16	33	25
	450	20	40	25
	471	27	52	15
415	405	22	23	52
	430	29	36	34
	450	32	42	25
	470	37	51	17
343	405	39	23	49
	430	39	36	30
	450	45	45	26
	470	47	55	17

The results in Table 1 show that CS₂ hydrogenation is occurring. Our Co-H-ZSM-5-56 cobalt exchanged catalyst achieved a higher conversion and in some cases higher selectivities than the results reported by Mobil in US patent #4,543,434. Our catalyst is an ion exchanged ZSM-5,

while Mobil used a physical mixture of HZSM-5 and Co on silica. 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

Figures 1 and 2 present some of the results from Table 1 in graphical form. Figure 1 shows that both CS₂ conversion and C₄⁺ hydrocarbon selectivity have strong temperature dependencies.

Figure 1. CS₂ CONVERSION AND C₄⁺ HYDROCARBON SELECTIVITY CS₂ WITH H₂/CS₂ FEED RATIO = 5.1, GAS HOURLY SPACE VELOCITY = 415 H⁻¹.

CS₂ conversion increases dramatically as temperature is raised from 405 to 470 °C. On the other hand, C₄⁺ selectivity decreases with increasing temperature. This suggests that an optimum yield of liquid hydrocarbons will occur somewhere in the middle of this temperature range. Figure 2 shows CS₂ conversion and C₄⁺ selectivity plotted against space velocity. While there is some effect on both conversion and selectivity, space velocity does not have as dramatic effect as temperature in this range.

Figure 2. CS₂ CONVERSION AND C₄⁺ HYDROCARBON SELECTIVITIES WITH H₂/CS₂ FEED RATIO = 5.1, TEMPERATURE = 430 °C.

In addition to experiments with Co-H-ZSM-5-56 we performed CS₂ to liquid hydrocarbon experiments on a mixture of MoS₂ hydrogenation catalyst and H-ZSM-5 catalyst. 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 3 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 3. 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	Temperature	% Conversion	% Conversion	% Selectivity
(h ⁻¹)	(°C)	H ₂	CS ₂	C ₄ ⁺
343	434	38	100	11
	350	36	98	45
	325	27	95	51

The results in Table 3 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.

Task 6. Proof-of-Concept Testing

We have made modifications to our experimental unit to accommodate both the natural gas-hydrogen sulfide reaction(Step 1) and the carbon disulfide hydrogenation reaction(Step 2) into one reactor system. The unit can now be fed with methane, H₂S, and nitrogen. Sampling points before the reactors, between the reactors, and after the reactors have been mounted so the intermediate conversion can be measured. Initial calibration of the flows through the reactor have been made.

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. We have discussed exchanging information with researchers at Amoco for them to perform an economic evaluation of the HSM process for the conversion of refinery H₂S to hydrogen and CS₂. We are looking forward to their evaluation of this technology.

CONCLUSIONS

- Hydrogenation of CS_2 to liquid hydrocarbons was accomplished on two sets of catalyst, 1) a cobalt exchanged ZSM-5 and 2) a mixture containing MoS_2 hydrogenation catalyst and HZSM-5. CS_2 conversions of 23 to 100 % were achieved. The highest selectivity to C_4^+ hydrocarbons was 52%.
- 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.