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GASOLINE FROM NATURAL GAS BY SULFUR PROCESSING

Quarterly Progress Report for the Period June-September 1993 Final Version

By
Erek J. Erekson
Frank Q. Miao

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
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3424 S. State Street
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IGT Project #61104

October 1993

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EXECUTIVE SUMMARY

This report presents the work performed at the Institute of Gas Technology(IGT) during the first program quarter from June 24, 1993 to September 30, 1993, under Department of Energy(DOE) Contract No. DE-AC22-93PC92114. This program has co-ordinated funding for Task 1 from IGT's Sustaining Membership Program(SMP), while DOE is funding Tasks 2 through 8. Progress in all tasks will be 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 utilize catalysts and sulfur containing intermediates: 1)to convert natural gas to CS_2 , and 2) to convert CS_2 to gasoline range liquids. Experimental data will be generated to demonstrate the potential of catalysts and the overall process.

During this first quarter, progress in the following areas has been made. One high surface area molybdenum catalyst has been prepared. An existing unit at IGT is being modified to accommodate the sulfur feedstocks and the higher temperatures(>1300 °K) required for studying the reactions of hydrogen sulfide and methane as proposed in Tasks 2 through 5. An HP 5890 gas chromatograph with a TCD(thermal conductivity detector) for detecting fixed gases including hydrogen and an FPD(flame photometric detector) for detecting sulfur compounds was purchased using SMP funds and has been received.

Both Dr. Erik Erikson and Dr. Frank Miao attended the ACS National Meeting in Chicago and made contacts with many researchers in the gas to liquids area. They received important advice and insight from Dr. Clarence Chang and Dr. Scott Han of Mobil who both have worked on the conversion of C_1 sulfur compounds such as CS_2 to gasoline liquids. Drs. Erikson and Miao also attended the PETC liquefaction contractors which provided an excellent overview of the gas to liquids research area.

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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 storage 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 gas to gasoline process would decrease dependence on imported oil for transportation fuels. These factors make it very desirable to convert natural gas to more valuable liquids.

There are commercial processes for converting natural gas to gasoline range liquids. These processes such as 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 clean up step which means extra cost is necessary because the catalysts are quickly poisoned by sulfur compounds.

In this program IGT is investigating a two step process that utilizes 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 plus 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 which has been considered as a poison is used as a reactant. This method of methane conversion utilizes H_2S to convert methane to CS_2 . Then CS_2 plus 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 one 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 and decrease the US dependence on foreign sources of oil.

ACHIEVEMENTS

Task 1. Catalyst Preparation(SMP funded)

Preparation of catalysts for H₂S decomposition reaction and methane plus hydrogen sulfide reaction was initiated. These catalysts are based on IGT's proprietary technique for making high surface area and high temperature stable sulfide catalysts. Chemicals for making high surface area sulfides of molybdenum, tungsten, vanadium, and cerium have been ordered.

A new HP 5890 gas chromatograph with an FPD(Flame Photometric Detector) for sulfur compounds and a TCD(thermal conductivity detector) has arrived. The GC is being calibrated for the anticipated reactants and products of Tasks 2 through 5. In addition we have been modifying a catalyst reactor test unit to operate at 1300 °C. A new high temperature furnace is being shipped to our location. After this item arrives, experimental work Tasks 2 through 5 will be initiated.

Task 2. Experimental Studies of H₂S Decomposition Reaction

The catalyst test unit is being modified to accommodate the flows, temperatures and reactants for this project.

A review of significant literature follows. This review will be updated with each progress report as significant articles become available.

The H₂S decomposition reaction is a significant part of the first step in the overall gas to gasoline process. The first step is:



This reaction can be separated into two reactions.



Reaction 2) is a known methane conversion reaction. CS₂ is the product. However, hydrogen is not produced. H₂S is the by-product and must be dealt with. Hydrogen is an essential reactant for the conversion of CS₂ to gasoline range hydrocarbons. Our reasoning for studying the H₂S decomposition reaction is to produce a catalyst with activity for reaction 3) as well as reaction 2). Thus, the summation of these two reactions will provide both CS₂ and hydrogen, making the operation more efficient, so that no outside source of hydrogen is required.

There are many cases in the research and development of catalysts that a bi-functional catalyst has become the catalyst of choice. Some examples are:

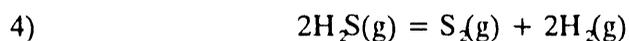
A. Platinum on alumina or zeolites for hydrocarbon reforming¹. Platinum provides dehydrogenation activity while the alumina/zeolite provides acidity for skeletal carbon rearrangement. the two functions in one catalyst provide for higher activity and selectivity in reforming straight chain hydrocarbons into high octane gasoline.

B. Bi-metallic cluster catalysts for reforming². John Sinfelt at Exxon found that by putting two metals into one catalyst a much more active and selective catalyst could be formed. One metal was active for a desired reaction(carbon bond scission) and an undesired reaction(dehydrogenation). The second metal had very low activity for the desired reaction but it poisoned the undesired reaction. By putting the two metals together in one catalyst as bi-metallic clusters the overall effect was to produce a catalyst that had high activity for the desired reaction and almost no activity for the undesired reaction. This made a highly selective and active catalyst.

C. Higher alcohol synthesis catalysts³. A methanol synthesis catalyst was modified with a chain growing Fischer-Tropsch catalyst. The result was a catalyst that made C₁ to C₅ alcohols. The methanol synthesis catalyst by itself would not produce higher alcohols, and the Fischer-Tropsch catalyst alone would not produce alcohols. Together in one catalyst the result is a catalyst active for making C₁ to C₅ alcohols.

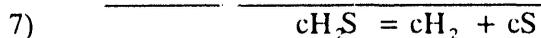
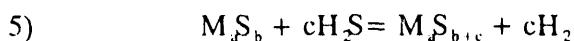
As for the decomposition of hydrogen sulfide there are several groups that have studied the problem. Thermochemical^{4-8,13-16}, electrolytic⁹ and photochemical¹⁰⁻¹² processes have been investigated as possible methods have been used for recovering both hydrogen and sulfur from hydrogen sulfur. Thermochemical methods for the decomposition of hydrogen sulfide will be briefly reviewed here.

The first method is direct thermal decomposition of hydrogen sulfide to hydrogen and sulfur under catalytic conditions.

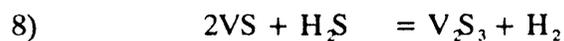


MoS₂, WS₂, Li₂S and Cr₂S₃ were reported⁴ to be the most effective catalysts for direct hydrogen sulfide decomposition. X-ray diffraction measurements of the solid phase demonstrate that the composition of these sulfides after the reaction is identical to that of the original material. The higher surface area will increase the reaction rate.

The second method of thermochemical decomposition involves two steps in which the reaction of hydrogen sulfide with a "lower" metal sulfide to give hydrogen and a "higher" metal sulfide is followed by thermal decomposition of "higher" sulfide to produce sulfur and regenerate a "lower" metal sulfide.



In order to be a suitable candidate for this process a metal sulfide M_aS_b must be readily sulfided by hydrogen sulfide to give M_aS_{b+c} and hydrogen. Then the thermal decomposition of this "higher" sulfide to regenerate M_aS_b. The vanadium sulfide appear to meet these criteria⁷. At 1023 °K(750 °C), VS was first sulfided by hydrogen sulfide to V₂S₃, up to 90% yield hydrogen was also produced. V₂S₃ begins to decompose to VS and S at 373 °K(100 °C) and complete conversion to VS occurs on heating at 773 °K(500 °C). The total two step process are as follow:



By this two step process, the hydrogen sulfide can be decomposed to hydrogen and sulfide with higher conversion than those of one step equilibrium limitation.

In addition to vanadium sulfide, nickel sulfide and iron sulfide also have this property¹³. For nickel sulfide, the Ni₃S₂ was sulfurized in the temperature range of 773-873 °K(500-600 °C) with releasing hydrogen gas. The thermal decomposition of NiS was carried at 1073 °K(800 °C) with gas phase sulfide being produced.

A thermodynamic program which describe the hydrogen sulfide thermal decomposition reaction has been developed. We will use this program to calculate results and compare with experimental test results in the near future.

Task 3. Carbon Deposition Studies

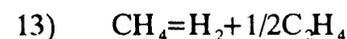
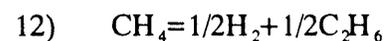
This task was inactive this quarter.

Task 4. Experimental Studies of the Methane Hydrogen Sulfide Reaction

The catalyst test unit is being modified to accommodate the flows, temperatures and reactants for this project.

The search and review of literature related with this project is continuing. Recently one research group from National Technical University of Athens, Greece(17) reports the thermodynamic reaction equilibrium calculation of CH₄/H₂S/H₂/CS₂/S₂/C₂H₆/C₂H₄ gas mixture system at 973 to 1098 K temperature and 101 kPa(1 atm) pressure. Experiments were also performed in a thermal non-catalytic and in a MoS₂ catalytic tubular reactor.

For thermodynamic equilibrium study, four independent reactions were taken into account:



From their calculations, it was found that:

A) When the initial gas mixture contains CH₄ and H₂S only, an increase in the CH₄ initial concentration and/or in the temperature of gas mixture will increase the total H₂S conversion.

B) The H₂ percentage in the gas mixture at equilibrium increase when the temperature of

the mixture is increased. The H_2 percentage reaches its highest value when the $CH_4:H_2S$ ratio in the initial mixture is equal to the stoichiometric ratio of the reaction 10.

C) CS_2 has a similar behavior to that of H_2 . The $H_2:CS_2$ ratio in the gas mixture at the equilibrium is 4:1.

D) The S_2 percentage in the gas mixture at equilibrium is maximum when pure H_2S is decomposed and decreases drastically when the CH_4 percentage in the initial mixture exceeds 10%.

E) C_2H_6 and C_2H_4 concentration below 0.1% when the initial H_2S percentage in the gas mixture exceeds 10%.

Although much valuable information is contained in this paper, this paper did not address the thermal crackling of methane to carbon soot and H_2 reaction:



The above reaction will account the soot formation in high temperature reaction of methane with hydrogen sulfide. As they indicated in their experimental results section, during the experiments S_2 generation and carbon black deposition on the reactor's wall were observed.

In our efforts we have included all of five reactions into our thermodynamic calculation model. We will report our calculations in near future.

Besides thermodynamic calculations, the researchers at the University of Athens experimental work on both non-catalytic and heterogeneous catalytic $CH_4:H_2S$ reactions.

In non-catalytic experiments, S_2 generation and carbon black deposition on the reactor's wall were observed. The percentage of H_2 produced is below 10% of the respective value at previously equilibrium calculation. Only a few conditions were tested for non-catalytic reaction. Most conditions are at high methane and low hydrogen sulfide ratio range.

In heterogeneous catalytic reaction, only MoS_2 was used as catalyst during their tests. No C_2H_6 and C_2H_4 were detected at outlet of the reactor. Furthermore, no carbon black has been traced on the surface of the catalyst after the end of the experiments. S_2 generation was observed. The amount of hydrogen obtained at the outlet of the reactor are in general agreement with the values anticipated from the thermodynamic equilibrium study. They did not show CS_2 as a product, but they did show a preliminary design for a $CH_4:H_2S$ hydrogen plant with CS_2 as a product stream.

Task 5. Experimental Studies of CS_2 to Liquid Hydrocarbons

This task was inactive this month.

Task 6. Proof of Concept Testing

This task was inactive this month.

Task 7. Environmental Reporting

A Hazardous Substance Plan Report as required in the subject DOE contract has been prepared and sent to DOE-PETC.

Task 8. Project Management and Technology Transfer

A Milestone Plan as well as a Project Management Plan have been prepared and sent to DOE-PETC.

Both Dr. Erikson and Dr. Miao attended 1993 DOE Coal Liquefaction and Gas Conversion Contractors Review Conference in Pittsburgh. During this meeting, we enjoyed presentations on gas conversion, indirect coal liquefaction as well as DOE's overall policy for fuels research. We found that PETC has organized a broad approach to investigating gas conversion to liquids. We met several experts in this area and were able to exchange ideas on gas conversion and the direction of future research.

Dr. Erikson give a presentation to IGT SMP Proposal Review Committee on the goals and progress of this project.

Both Dr. Erikson and Miao attended ACS 1993 National Meeting at Chicago. During this meeting, we met several experts in catalyst area and listen most presentations on zeolite catalyst as well as hydrodesulfurization catalyst sections. We also have discussed our project with Drs. Clarence D. Chang and Scott Han from Mobil Research & Development Corporation. Both Dr. Chang and Dr. Han are the key inventors for sulfur compounds to gasoline patents(similar to our task 5 work). Dr. Han has intensive experience on CS₂ conversion process. He is very interested our approach and is willing provide suggestions and advice. He also agreed to provide assistant during our task 5 experimental work. We also received all papers that Dr. Han wrote about ZSM-5 catalyst on methane conversion application after meeting.

During this ACS meeting, Dr. Miao also met Dr. Larry H Hsing from Research & Development Division of Texaco Inc. at Port Arthur, Texas, Mr. Stephen J. Miller from Chevron Research and Technology Company at Richmond, Dr. Jason Wu from W.R.Grace as well as Mr. E. K. Saforo from ZEOCHEM, a joint venture company of Chemie Uetikon and United Catalysts, Inc. Like Dr. Chang and Dr. Han, all these peoples also have experience on ZSM-5 catalyst. These people will be very useful for our future ZSM-5 catalyst for carbon disulfide to gasoline conversion study. Mr. Saforo and Dr. Wu are also willing provide some ZSM-5 catalyst sample for us. In addition, we got some ZSM-5 sample from INTERCAT, the company produce ZSM-5 catalyst as additive for FCC process.

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