1995 COAL LIQUEFACTION AND GAS CONVERSION CONTRACTORS REVIEW CONFERENCE

TITLE: GASOLINE FROM NATURAL GAS BY SULFUR PROCESSING

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OBJECTIVE:

The overall objective of this research project is to develop a catalytic process to convert natural gas to liquid transportation fuels. The process, called the HSM (Hydrogen Sulfide-Methane) Process, consists of two steps that each utilize a catalyst 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 facilitate evaluation of the overall commercial viability of the process.

ACCOMPLISHMENTS & CONCLUSIONS

Catalysts have been found that convert methane to carbon disulfide in yields up to 98%. This exceeds our target of 40% yields for the first step. The best rate for CS_2 formation was 132 g CS_2/kg-cat-h. The best rate for hydrogen production is 220 L H_2 /kg-cat-h. A preliminary economic study shows that in a refinery application hydrogen made by the HSM technology would cost $0.25-$1.00/1000 SCF.

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. It is desirable to convert natural gas to more valuable liquids. The successful implementation of this process would decrease dependence on imported oil for transportation fuels.

There are two commercialized methods for converting natural gas to gasoline range liquids.

1) Fischer-Tropsch synthesis
2) Mobil's MTG process.

Each has two basic steps:

1. Removal of sulfur compounds (H_2S, COS and mercaptans with sulfur adsorbing guard beds to prevent breakthrough of sulfur to the catalysts).
2. Steam reforming to make synthesis gas which requires 2 moles of superheated steam for every mole of methane.

In Fischer-Tropsch synthesis, the third step is the conversion of synthesis gas to hydrocarbons. In Mobil's MTG process, the third step is methanol synthesis and an additional step of methanol conversion to gasoline liquids is required. The commercial steps listed above; i.e., steam reforming, methanol synthesis, or Fischer Tropsch synthesis, require the removal of sulfur compounds present in natural gas down to less than 0.1 ppm. This additional gas clean-up step means extra cost, but it is necessary because the catalysts are quickly poisoned by sulfur compounds.

IGT is developing the HSM Process, a two-step process that uses H_2S as a reactant to convert natural gas to gasoline-range liquids. Sulfur, which has been considered as a poison, is used as a reactant in the HSM process. This process 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 of the H_2S generated during the CS_2 to gasoline reaction is recycled. This

process does not require steam reforming nor the manufacture of hydrogen. This process is actually a net producer of hydrogen.

There are two main reactions involved in this process:

$$1) \quad CH_4 + 2\,H_2S \rightarrow CS_2 + 4\,H_2 \qquad (1)$$

$$2) \quad CS_2 + 3\,H_2 \rightarrow [\text{-}CH_2\text{-}] + 2\,H_2S \qquad (2)$$

The process is a net H_2 producer, and H_2S is recycled. So the overall process would be:

$$3) \quad CH_4 \rightarrow [\text{-}CH_2\text{-}] + H_2 \qquad (3)$$

As we began this project, we found no other references to catalysts for the methane-hydrogen sulfide. The second reaction has been demonstrated by researchers at Mobil Corporation[1] and will be studied during this project. A schematic diagram of the process is shown in Figure 1.

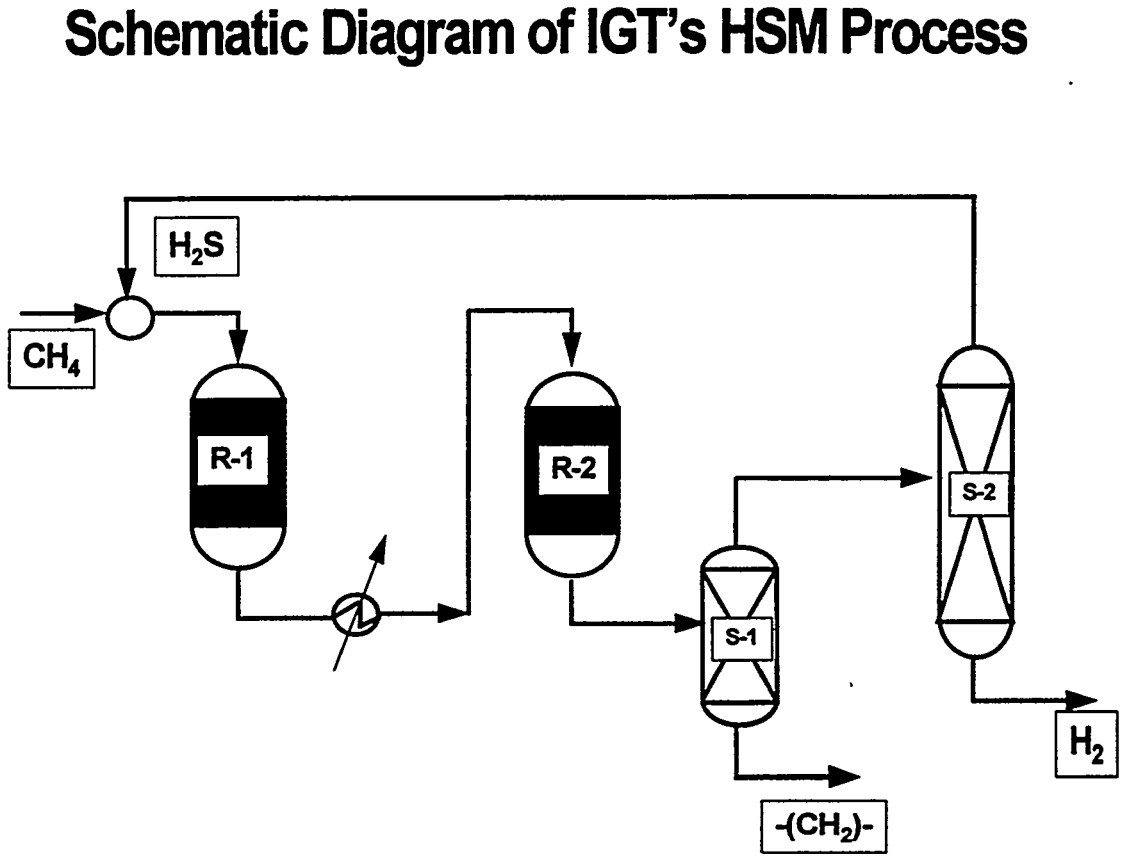

Figure 1. SCHEMATIC DIAGRAM OF HSM(HYDROGEN SULFIDE-METHANE)PROCESS

EXPERIMENTAL

Figure 2 shows the schematic diagram of catalysis reactor system. The feed gas hydrogen sulfide, nitrogen and methane flow rates are controlled by mass flow controllers(Brooks Instruments 5850). The gas flow rates are calibrated by a dry test meter(SINGER, American Meter Company). The gas from mass flow controllers are mixed before flowing into a custom made quartz adapter. There are two openings in the adapter. One is for mixed feed gas; the other is for a ceramic thermowell. The feed gas flows through the adapter into 42 inch long, 22 mm I.D. by 25 mm O.D. quartz reactor. The joint which connects with adapter and quartz reactor were sealed by TFE sleeve. There are three indents around quartz reactor at 26 inch from the top. The catalyst is held above the indents. The temperature of catalyst reactor were measured by a type R high temperature thermocouple which protected by 1/4 inch O.D. ceramic thermowell. The heat was provided by a 2 inch I.D. 32 inch long split tube high temperature furnace with maximum temperature 1540 °C. (Series 3420, APPLIED TEST SYSTEMS, Inc.). The product gas from the catalyst reactor flows into a condenser. The condenser is placed into an ice bath. There is a sample point just after the reactor before the condenser. Gases are analyzed by GC. Before going to the vent gases are scrubbed by a solution of 6M Sodium hydroxide and 30% Hydrogen peroxide. The total product gas flow rate was measured by a wet test meter(Precision Scientific Co.) before being release into the vent system.

Gas samples were analyzed by Gas Chromatograph (HP5890) with a thermal conductivity detector (TCD) and a flame photometric sulfur detector (FPD). A 1/8-inch diameter 10-ft long HayeSep C 80/100 column(SUPELCO Inc.) was used for gas separation. In order to measure hydrogen in the TCD detector, Argon was used as the carrier gas.

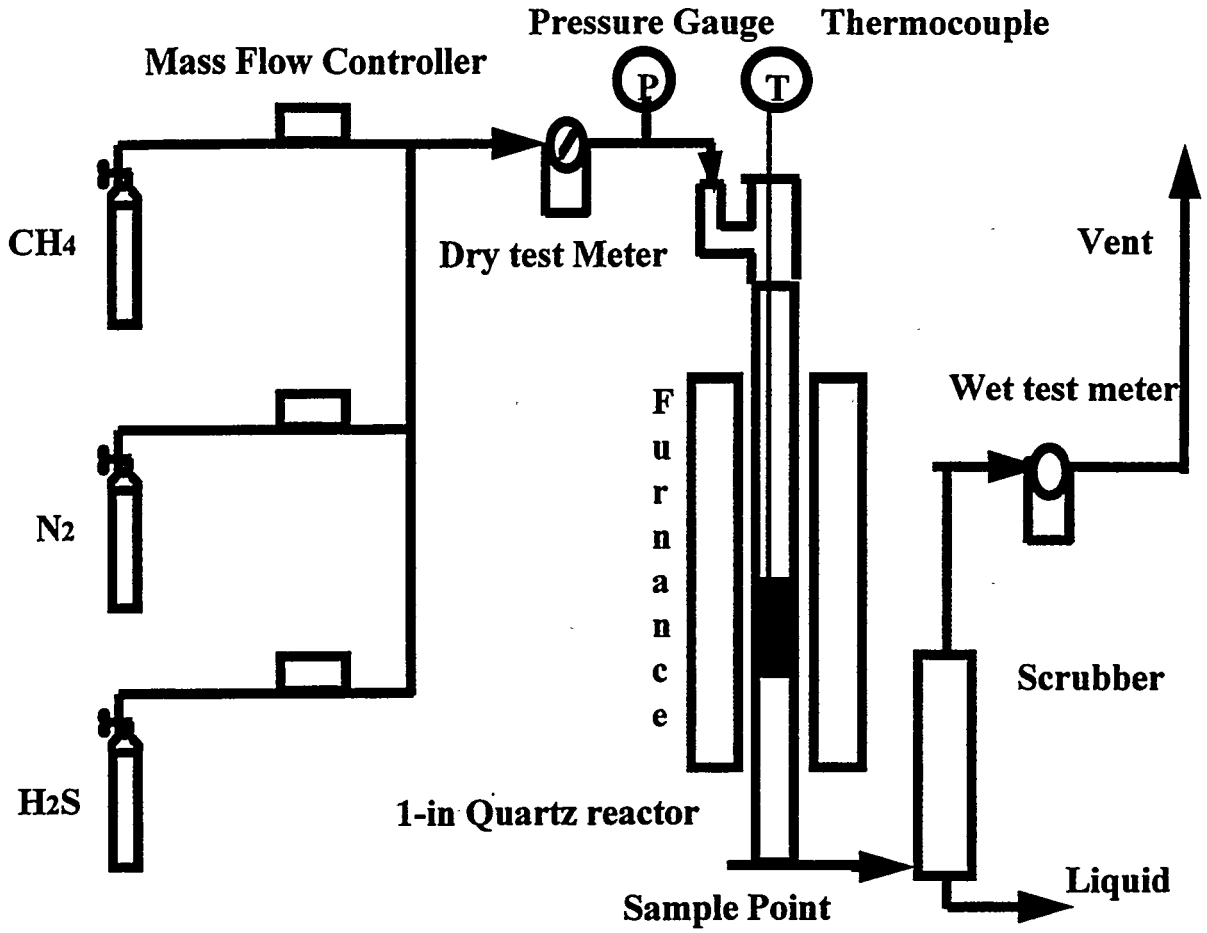

Figure 2. SCHEMATIC DIAGRAM OF EXPERIMENTAL TEST UNIT

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. Ten batches of sulfur processing catalysts have been prepared.

Task 2. Experimental Studies of the H_2S Decomposition Reaction

This Task was completed before the last review meeting. The purpose of this task is to evaluate catalysts for the following reaction:

$$2\,H_2S \rightarrow S_2 + 2H_2 \qquad (4)$$

Catalysts that have activity for this reaction will likely have good activity for reaction 1. We used this reaction as an indicator for screening catalysts for Task 4.

Task 3. Carbon Deposition Studies

This task was completed before the last review meeting. As we develop a catalyst for the conversion of $CH_4 + H_2S$, 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. The catalysts that performed well in being regenerated after carbon deposition also performed well in Task 4, the production of CS_2 and hydrogen.

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 and hydrogen. The task is divided into two parts. During the first part, ten catalysts were 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.

A group of ten catalysts have been evaluated in over 155 runs. The best catalysts for producing CS_2 are shown in Figures 3 and 4. The best conditions for CS_2 yields are an H_2S/CH_4 ratio of 4, temperature 1100°C, and a residence time of 1.2 seconds. These runs used a nitrogen diluent.

We evaluated catalyst IGT-MS-103 for sustained activity. The results of an 8 hour sustained run are shown in Figure 5. There is no indication of deactivation during this run.

Catalyst IGT-MS-105 also showed high yields of CS_2. This catalyst will also be tested for sustained catalyst activity.

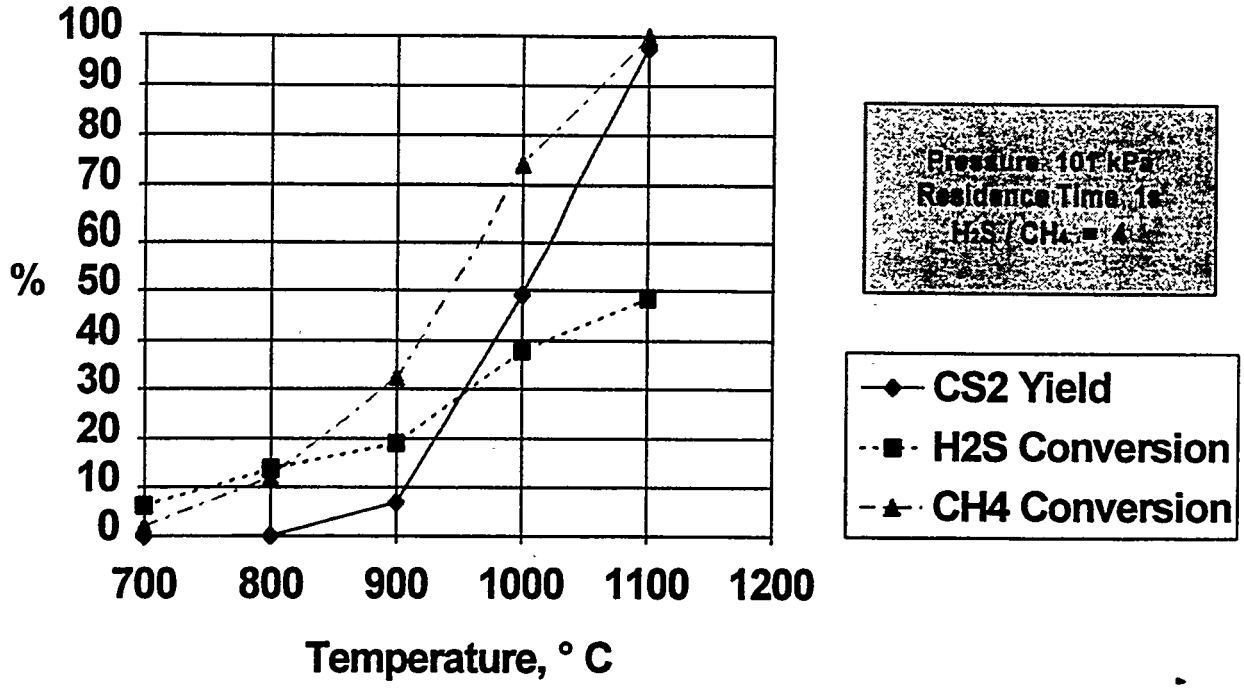

Figure 3. CS_2 YIELDS AND REACTANT CONVERSION FOR IGT-MS-103

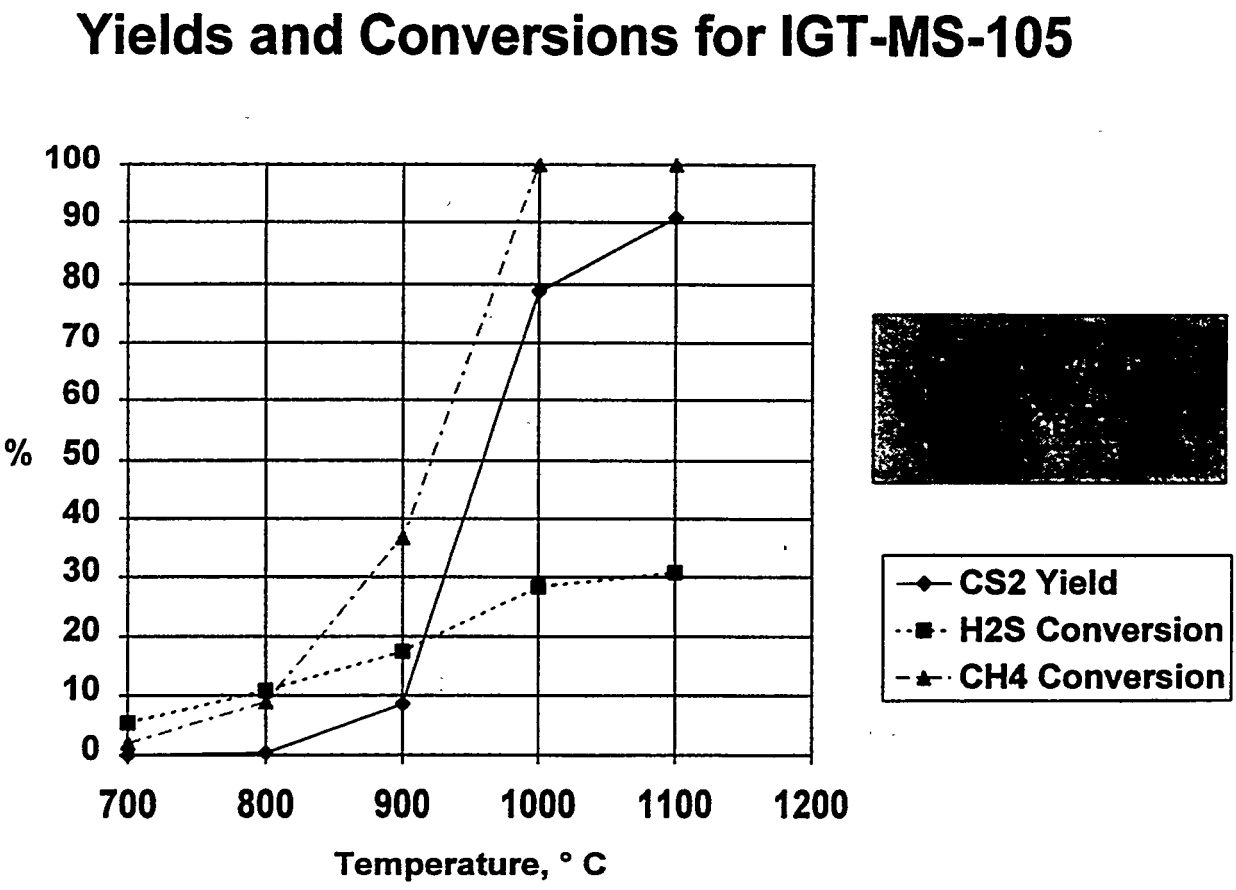

Figure 4. CS_2 YIELDS AND REACTANT CONVERSION FOR IGT-MS-105

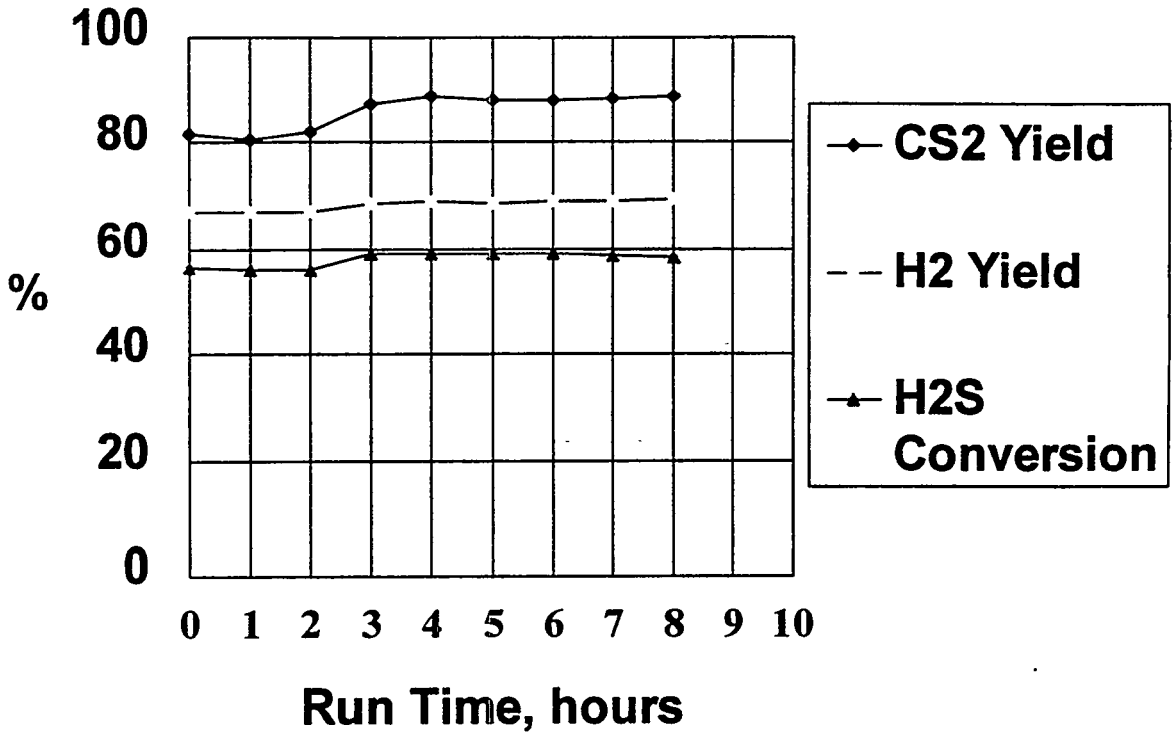

Figure 5. CS_2 AND H_2 YIELDS AND H_2S CONVERSION FOR EXTENDED RUN

In addition to using the HSM process for making gasoline range liquids, we have been investigating the use of reaction 1 alone for use in a refinery situation where H_2 is valuable and H_2S is converted to sulfur in a Claus unit. Reaction 1 would use methane, but it would convert H_2S into hydrogen and a sulfur compound that can be used as a feedstock for sulfuric acid. We have performed a preliminary economic evaluation that shows that hydrogen produced by the HSM technology would cost \$0.25 to \$1.00/ 1000 SCF depending on the price of CS_2. These results are encouraging, and we will be investigating this potential application further.

Task 5. Experimental Studies of CS_2 to Liquid Hydrocarbons

Under this task, a group of catalysts will be developed for the reaction:

$$CS_2 + 3H_2 \rightarrow -[CH_2]- + 2\,H_2S$$

The optimum operating conditions will be determined. The best catalyst will be tested in relatively long duration time to determine catalyst's long-term activity, stability as well as selectivity for above reaction. Work in this task is planned.

Task 6. Proof-of-Concept Testing

For this task, the best catalysts from Task 4 and the best catalysts from Task 5 will be tested in combination to demonstrate that these two steps can be used in combination to make gasoline range liquids from methane. Work in this task will begin after completing Task 4.

FUTURE PLANS

Catalysts will be tested in Task 4 for activity with a refinery type H_2S stream. Such a stream would be coming from an acid gas removal unit and would contain significant amounts of CO_2. The goal here is to see if these catalysts can achieve high conversion of $H_2S + CH_4$ to hydrogen. We will be evaluating this process for application in a refinery situation. We also plan to search for more active and selective CS_2 hydrogenation catalysts. A demonstration of both steps is planned as part of this project.

ACKNOWLEDGMENT

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REFERENCES

1. C.D.Chang, US patent #4,543,434, Sep.24, 1985