

GASOLINE FROM NATURAL GAS BY SULFUR PROCESSING

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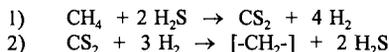
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ABSTRACT

The conversion of natural gas to transportable liquids continues to be an area of research interest. New processes for the direct oxidation of methane either to ethylene or to methanol, are hampered by apparent yield barriers due to CO_x production. In addition new processes for fuel production from non-petroleum sources such coal, shale oil, tar sands are often hampered by the need for hydrogen. The subject process circumvents these difficulties in fuel production. The process consists of two steps that each utilize catalysts and sulfur containing intermediates:

- 1) to convert natural gas to CS₂, and
- 2) to convert CS₂ to liquid hydrocarbons.

The general equations for the two steps are:



H₂S is recycled, and the overall process is a net hydrogen producer.

A catalyst is being developed for the first step. The second step has been studied by others¹. Initial results are reported. Engineering aspects and economic implications of the overall process will be discussed.

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:

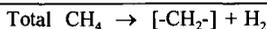
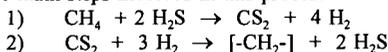
1. Removal of sulfur compounds (H₂S, COS and mercaptans with sulfur adsorbing guard beds to prevent breakthrough of sulfur to the catalysts).
2. Steam reforming to make synthesis gas which requires 2 moles of superheated steam for every mole of methane.

In Fischer-Tropsch synthesis, the third step is the conversion of synthesis

gas to hydrocarbons. A fourth step consisting of mild hydrocracking is necessary in high wax producing Fischer-Tropsch synthesis such as Shell's Middle Distillate Synthesis Process. In Mobil's MTG process, the third step is methanol synthesis, and the fourth step is 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 gas clean-up step adds cost, but it is necessary because the catalysts are quickly poisoned by sulfur compounds.

IGT has begun investigating a two-step process that uses H₂S 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 proposed process. This method of methane conversion utilizes H₂S to catalytically convert methane to CS₂. Then CS₂ plus hydrogen can be catalytically converted to gasoline range hydrocarbons. All of the H₂S generated during the CS₂ to gasoline reaction is recycled. This process does not require steam reforming nor the manufacture of hydrogen.

There are two main steps involved in this process:



H₂S is recycled, and the overall process is a net hydrogen producer.

Catalysts are being developed for the first step. The second step which has been demonstrated by researchers at Mobil¹ will be studied later in this project to try to improve yields of gasoline range hydrocarbons. In this paper, we will discuss the ASPEN simulation as well as experimental results for step 1.

EXPERIMENTAL

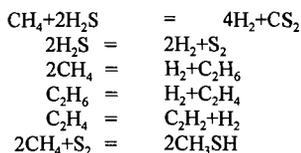
Figure 1. shows the schematic diagram of catalysis reactor system for step 1. Feed gas flows of hydrogen sulfide, nitrogen and methane are controlled by mass flow controllers(Brooks Instruments 5850). Gas flow rates are calibrated by a dry test meter(SINGER, American Meter Company). The feed gas flows through the adapter into 42 inch long, 22 mm I.D. and 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 by a plug of quartz wool. The temperature of catalyst reactor were measured by a type R high temperature thermocouple which is 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). There is a sample point just after the reactor. The product gas is sampled before it flows into condenser. The gases were analyzed by GC. The product gas from the catalyst reactor flows into a liquid condenser which is put into an ice bath. The sulfur was cooled and condensed in condenser. After the condenser product gases flow into a 30% Hydrogen peroxide and 6M Sodium hydroxide solution to scrub hydrogen sulfide. The composition of gas from the scrubber was also analyzed by GC. The gas flow rate was measured by a wet test meter(PRECISION WET TEST METER, Precision Scientific Co) before it is released into the vent system.

Gas samples are 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.

RESULTS AND DISCUSSION

1) Equilibrium calculations

Equilibrium calculations were performed with ASPEN PLUS process simulator. The Gibbs Energy Minimization method was used for the simulation of equilibrium conditions. Six independent reactions have been taken into account for the chemical equilibrium study:



Equilibrium for three feed gas compositions at 700 to 1200°C was calculated using the following feed gas compositions:

	<u>CH₄</u>	<u>H₂S</u>	<u>N₂</u>	<u>H₂S/CH₄ Ratio</u>
Case 1	3.33 %	6.67 %	90 %	2
Case 2	2.00	8.00	90	4
Case 3	1.11	8.89	90	8

Nitrogen was added as a diluent for all cases studied. Carbon graphite formation was not included in these calculations. At the temperatures of these equilibrium calculations, carbon graphite is so much more stable thermodynamically than methane or the other carbon compounds that including it would result in all the carbon going to graphite.

At equilibrium significant amounts of CS₂ and H₂ are predicted. In Figures 2, 3 and 4 equilibrium concentrations of CS₂ and CH₄ as well as experimental results are shown. The concentration of CS₂ at equilibrium increases with temperature. At 1100°C nearly all of CH₄ was converted in all three cases. There was very little of C₂H₆, C₂H₄, C₂H₂ as well as CH₃SH calculated in the products. The amount of C₂H₆, C₂H₄, C₂H₂ as well as CH₃SH was less than 10⁻⁶. In comparing the equilibrium calculations in Figures 2, 3 and 4 it appears that increasing the temperature as well as increasing H₂S/CH₄ ratio will increase CS₂ concentration and decrease the CH₄ concentration at equilibrium.

2) Experimental Results

Reactor tests of IGT-MS-105, a sulfide catalyst, were performed using the same feed compositions as cases 1, 2 and 3 above. The experiments were performed at atmospheric pressure and in the range from 700 to 1200°C. The residence times were 1 to 5 seconds. 40 g. catalyst was put into the reactor. Only H₂, CS₂, S₂ as well as small amount of carbon soot were found in product steam. Figure 2, 3 and 4 show the concentration of the CS₂ in the product steams for these experiments as well as equilibrium concentrations calculated for cases 1 through 3. Hydrogen was

formed, but is not shown in these figures. As indicated from Figure 2. at 700°C CS₂ concentration is low compared to the equilibrium line. Catalyst activity increases until at 1100°C, CS₂ concentration is approaches close to equilibrium. The yield of CS₂ from methane at 1100°C for all three cases was above 90%. Methane concentration drops off as temperatures increases. In Figure 2. at 1100°C the concentration of methane for the 5 second residence time experiments falls below the equilibrium line. This may be attributed to the formation of some carbon solids in the reactor. As mentioned above carbon solids were not included in the equilibrium calculations. Carbon balances for these runs were in the range of 90 to 95%.

The results in this paper indicate that a catalyst for the first step, the conversion of CH₄ and H₂S to CS₂ and hydrogen, has been found. We are continuing to develop catalysts from this beginning.

ACKNOWLEDGMENT

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REFERENCES

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

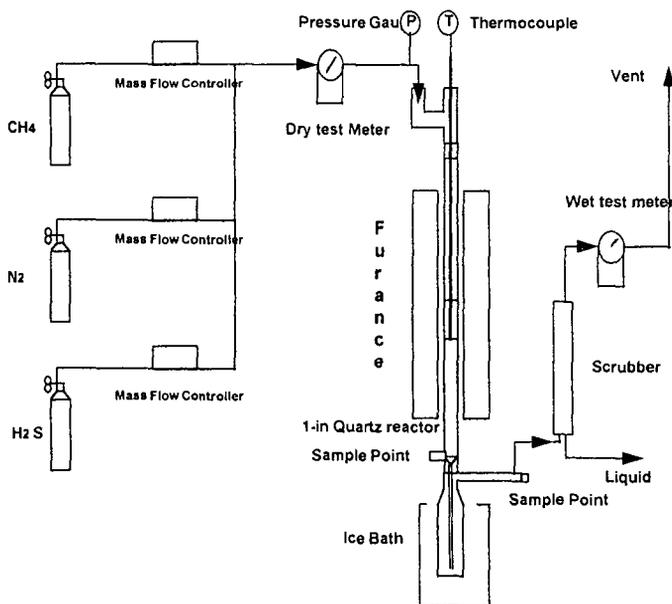


Figure 1. Schematic diagram of flow reactor system

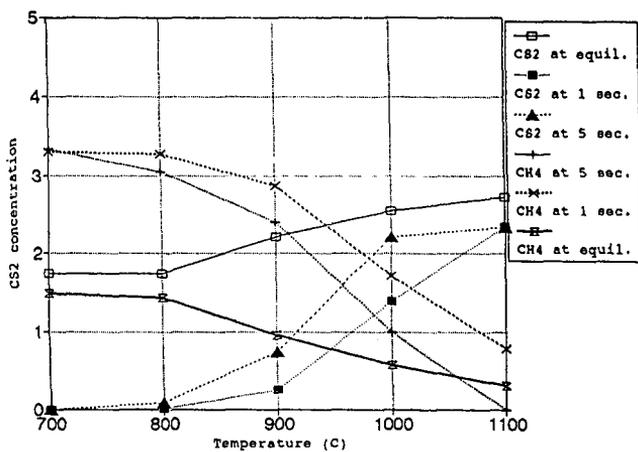


Figure 2. CS₂ production at H₂S/CH₄=2. for catalyst 1.

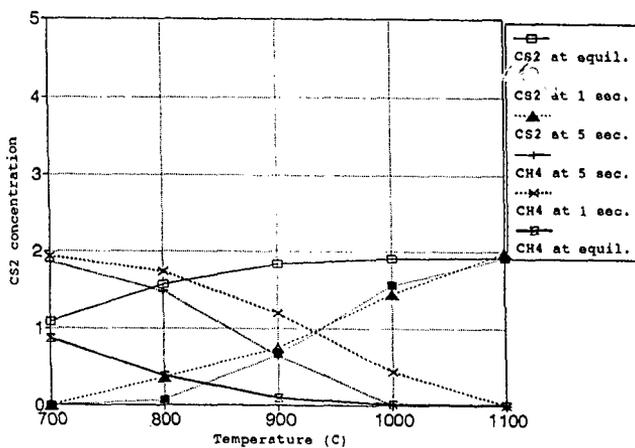


Figure 3. CS₂ production at H₂S/CH₄=4. for IGT-MS-105 catalyst.

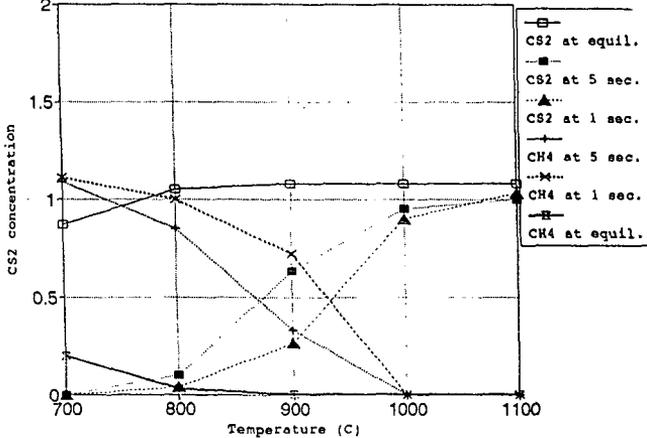


Figure 4. CS₂ production at H₂S/CH₄=8. for IGT-MS-105 catalyst.