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FISCHER-TROPSCH STUDIES WITH CATALYST-SPRAYED TUBE WALL REACTORS

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ABSTRACT

A summary of Fischer-Tropsch studies in bench-scale tube wall reactors using flame-sprayed catalysts is presented. Preliminary studies were conducted with various flame-sprayed catalysts, after which taconite was chosen as the prime candidate for more extensive evaluation. Results from several life tests with promoted and unpromoted taconite are reported, along with a data base that discusses the effects of various process variables on catalyst activity and product selectivity.

INTRODUCTION

Coal can be gasified to form gaseous mixtures containing hydrogen and carbon monoxide (synthesis gas). Synthesis gas, in turn, may react via the Fischer-Tropsch (F-T) synthesis in the presence of a catalyst to form a wide range of hydrocarbon fuels, including substitute natural gas (SNG), liquefied petroleum gas (LPG), gasoline, diesel fuel, and fuel oil. The Fischer-Tropsch synthesis was originally developed in Germany in the early 1920's and was successfully employed during World War II to supply part of Germany's transportation fuels. Today, the only commercial indirect liquefaction plant in operation is the SASOL plant in South Africa. This plant, producing about 9000 barrels per day, has been operated since 1955. A new plant, SASOL-II, with approximately four times the capacity of SASOL I has been completed, and SASOL III, nearly identical to SASOL II, is scheduled to be commissioned in 1984 (14).

Because of the decreasing U.S. reserves of petroleum and natural gas, interest was renewed in the Fischer-Tropsch process as an attractive method for making clean coproducts from coal, namely transportation fuels, petrochemicals, and substitute natural gas. Since the start of this project, emphasis has shifted more toward the production of transportation fuels. This renewed interest in Fischer-Tropsch by the U.S. Department of Energy resulted in a contract with the Ralph M. Parsons Co. (1,2) to consider F-T economics and conceptual plant designs. In 1977, the R.M. Parsons Co. completed a conceptual design and economic analysis of a commercial scale coproducts plant producing about 260 million standard cubic foot (scf) per day of SNG and 50,000 barrels per day of liquefied products. Their analysis showed that the use of extended-surface, tube wall reactors in the shift, F-T synthesis, and methanation unit processes resulted in the production of sufficient high-pressure steam to satisfy the steam requirements for the rest of the plant complex. This eliminates the requirement for a fuel-fired

utility plant under normal operation and increases the predicted overall thermal efficiency to almost 70%. The potential advantages of the tube wall reactor (TWR) system are clear.

Development of the TWR concept began at the Pittsburgh Energy Technology Center to efficiently remove the heat that is generated in converting synthesis gas produced by coal gasification into substitute natural gas (3). The primary incentive for adapting the TWR technology to indirect liquefaction is the requirement to remove large amounts of heat released during Fischer-Tropsch hydrocarbon synthesis reactions. Other advantages are (a) the combined functions of reactor and heat recovery in one vessel, (b) minimal recycle flow of product gas for control of the exothermic heat of reaction, (c) negligible pressure drop across the reactor, and (d) isothermal reaction-conditions.

The TWR concept exploits the advantage of having an intimate contact between the synthesis catalyst and a heat transfer surface. Using a flame or high-temperature plasma, iron oxide catalyst is sprayed onto the outside surface of conventional heat exchanger tube surfaces. The Fischer-Tropsch reaction occurs on the catalyst surface, releasing heat, which is removed by water boiling on the inside of the heat exchanger tubes. The high-pressure steam that is generated in this way can be utilized elsewhere in the plant, thus increasing the overall thermal efficiency of the plant. The TWR concept also permits greater catalyst productivity without excessive local catalyst overheating. Excessive overheating can cause degradation of product quality as well as premature catalyst deactivation. By distributing the catalyst in a thin layer over the heat transfer surface, the poor utilization of the catalyst often encountered in highly exothermic reactions is eliminated. Studies have also shown that the TWR permits easy temperature control and greater stability under minor plant upsets. In order to demonstrate the potential advantages of the TWR system with respect to Fischer-

Tropsch synthesis, a research and development program was implemented, and the results of this study are presented in the following report.

In the early stages of this program, it was not known what type of Fischer-Tropsch catalyst would be most suitable for application in the tube wall reactor system. The objective of the first phase of testing was to address this question. Various iron catalysts were screened in bench-scale TWR reactors. Alan Wood magnetite was considered a possible candidate because of a prior PDU experiment that used the catalyst sprayed onto plate assemblies (4). Raney iron, consisting of 45% iron and 44% aluminum, was also tried, since the spraying characteristics of Raney nickel were very favorable in previous methanation work (5). Taconite was also included as a candidate for the screening program because it was the cheapest catalyst and the most easily activated.

Two units, formerly used in methanation catalysis work, were operated during the initial experimental phase after several modifications were made. These experiments were conducted at gas hourly space velocities comparable to those used in previous tests in process development units. For example, Hot-Gas-Recycle reactors employing Alan Wood magnetite flame-sprayed onto parallel plates were normally operated at space velocities in the range 600 to 2000 hr^{-1}, with attendant CO conversions from 80% to 98% (4). In this series of bench-scale tests, the space velocities were 1000 to 1300 hr^{-1}. Figure 1 is a schematic of the bench-scale TWR units. Synthesis gas, dried and desulfurized, flows downward through the tube wall reactor, and the F-T reaction occurs on the outer surface of the catalyst support tube. The exothermic heat of reaction is removed by boiling Dowtherm contained within the tube. The heavy liquid products are gathered in a steam trap, and the remaining liquid products are condensed in a water-cooled trap. The gaseous products and unreacted synthesis gas are then

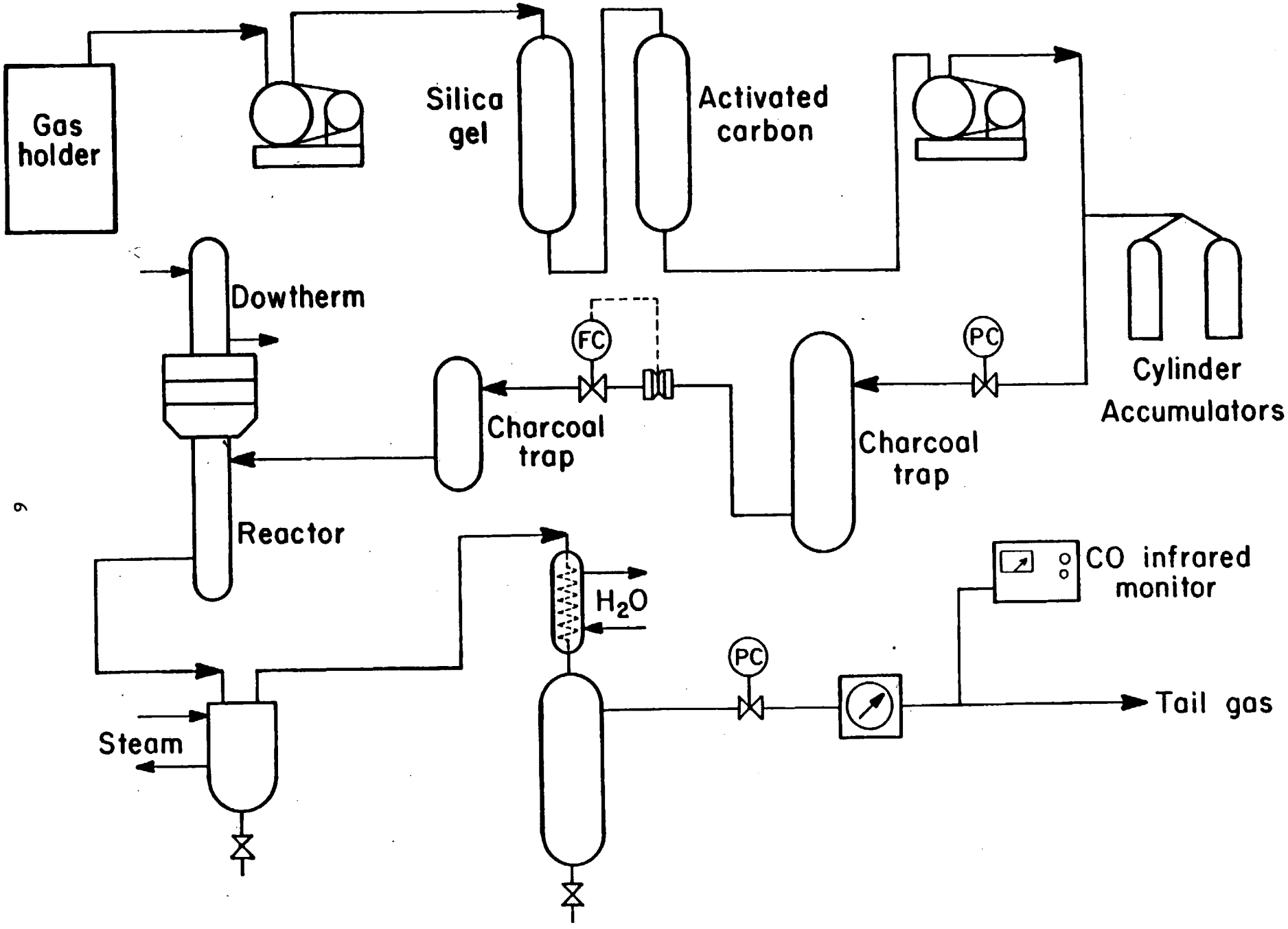


Figure 1. FISCHER-TROPSCH bench-scale unit.

metered, and the carbon monoxide content is continually monitored with an infrared analyzer.

Figure 2 is a drawing of the bench-scale TWR. The reactor consists of two carbon steel pipes; the outer one is 1 1/2-inch nominal pipe size by 30 inches in length, and the inner one is 3/4-inch nominal pipe size by 24 inches in length. The inner pipe (referred to as the catalyst support tube) is welded to a support flange and can readily be positioned in the center of the reactor shell. The overall length of reactor is 53 inches. Boiling Dowtherm in the support tube is condensed in the top section (upper 23 inches) of the reactor and transferred back to the bottom of the tube via a dip tube. The Dowtherm temperature and hence the reactor temperature are maintained by controlling the Dowtherm vapor pressure. The entire reactor is insulated and heated by electrical resistance heaters to counteract radiation and convective heat losses. When the support tube is positioned in the reactor, the top of the catalyst is 3 inches below the gas inlet. The width of the annulus section for gas flow is 0.20 inches. Thermocouple wells, parallel to and in contact with the support tube, permitted temperature profiles to be measured over the length of the reaction zone.

Catalyst and Catalyst Preparation.

The catalysts employed during these experiments were the following: a magnetite ore (Alan Wood Magnetite), taconite, supplied by the U.S. Steel Corporation, and an iron-aluminum alloy (Raney iron). The composition of each of these catalysts is shown in Table 1.

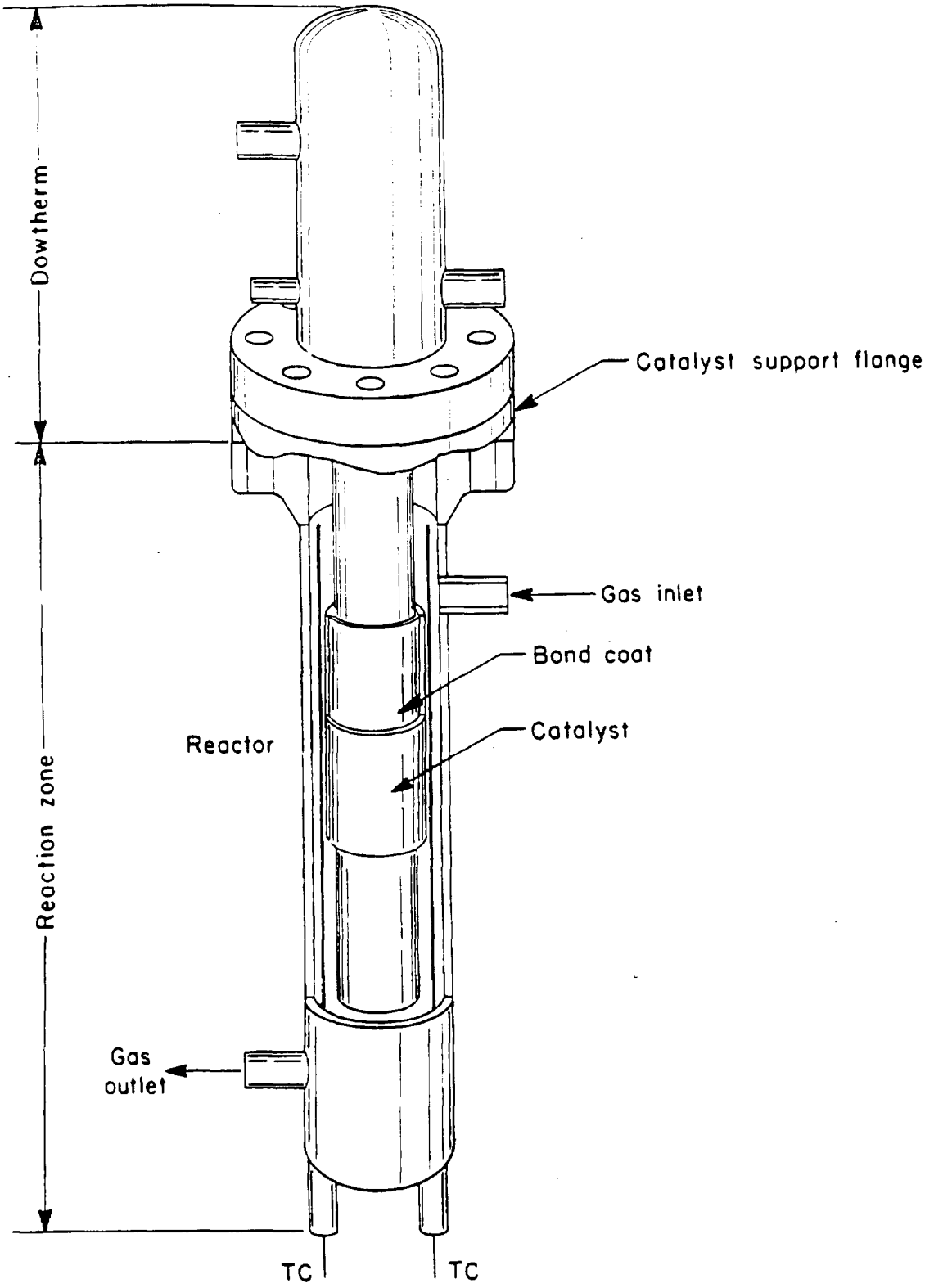


Figure 2. Tube wall reactor.

Table 1. Catalyst Composition in Weight Percent

Element	Magnetite	Taconite	Raney Iron
Fe	66.1	66.7	44.7
Al	0.3	0.1	43.6
K	1.0	0.1	0.1
Si	2.8	1.6	1.1
Mg	0.1	0.1	< 0.1
Cr	< 0.1	< 0.1	< 0.1
Mn	< 0.1	0.1	0.2
Ti	0.4	0.1	0.1
Ca	0.2	0.3	0.1
V	< 0.1	< 0.1	< 0.1
S	< 0.1	0.1	0.1
Ni	0.4	0.2	2.1

The catalyst was applied to the support tube by either a flame-spraying or a plasma-spraying operation (5). The flame-spraying technique utilizes an oxygen-hydrogen flame to melt the powdered iron oxide feed. The plasma-spraying technique does not require a combustible gas mixture but instead excites a plasma gas (a mixture of H_2 and N_2) to a "flame" temperature of approximately 30,000°F. This temperature is about five times that obtained by the O_2-H_2 flame. Prior to catalyst application, the support tube was grit-blasted with aluminum oxide powder to clean the surface. When the iron catalyst was applied via the flame-spraying technique, the grit-blasted surface was first coated with a nickel aluminide bond coat. The catalytically inactive bond coat, which consists of 95% Ni and 5% Al, was flame-sprayed to a thickness of 0.003 inches. When the catalyst was applied by the plasma-spraying, a bond coat was not needed. In both spraying procedures, the catalyst was applied to a thickness of 0.0225 $\pm$ 0.0016 inches over a well-defined 6-inch section of the support tube. The catalyst and support tube are illustrated in Figure 3 and the accompanying photograph.

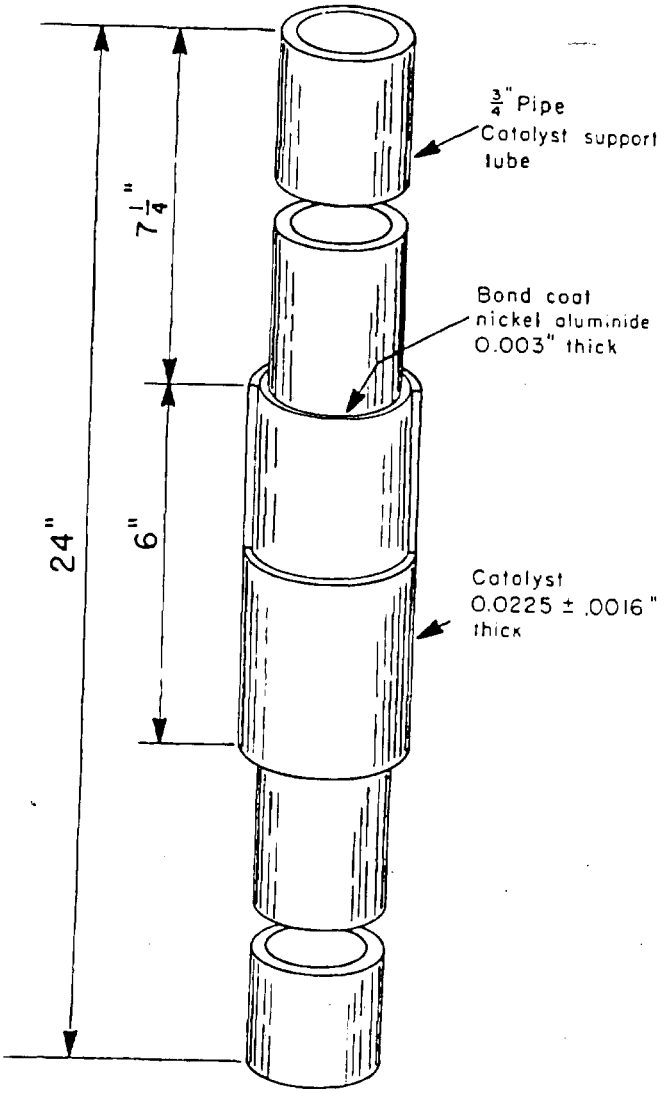
Catalyst Activation.

Magnetite and Taconite. Magnetite and taconite were thermally sprayed in the oxide form, and the active catalyst surface was prepared by reducing the catalyst with hydrogen at an elevated temperature and at atmospheric pressure.

The reactions proceeding during reduction are the following:

$$Fe_3O_4 + 4H_2 \rightleftharpoons 3Fe + 4H_2O$$

$$Fe_2O_3 + 3H_2 \rightleftharpoons 2Fe + 3H_2O$$



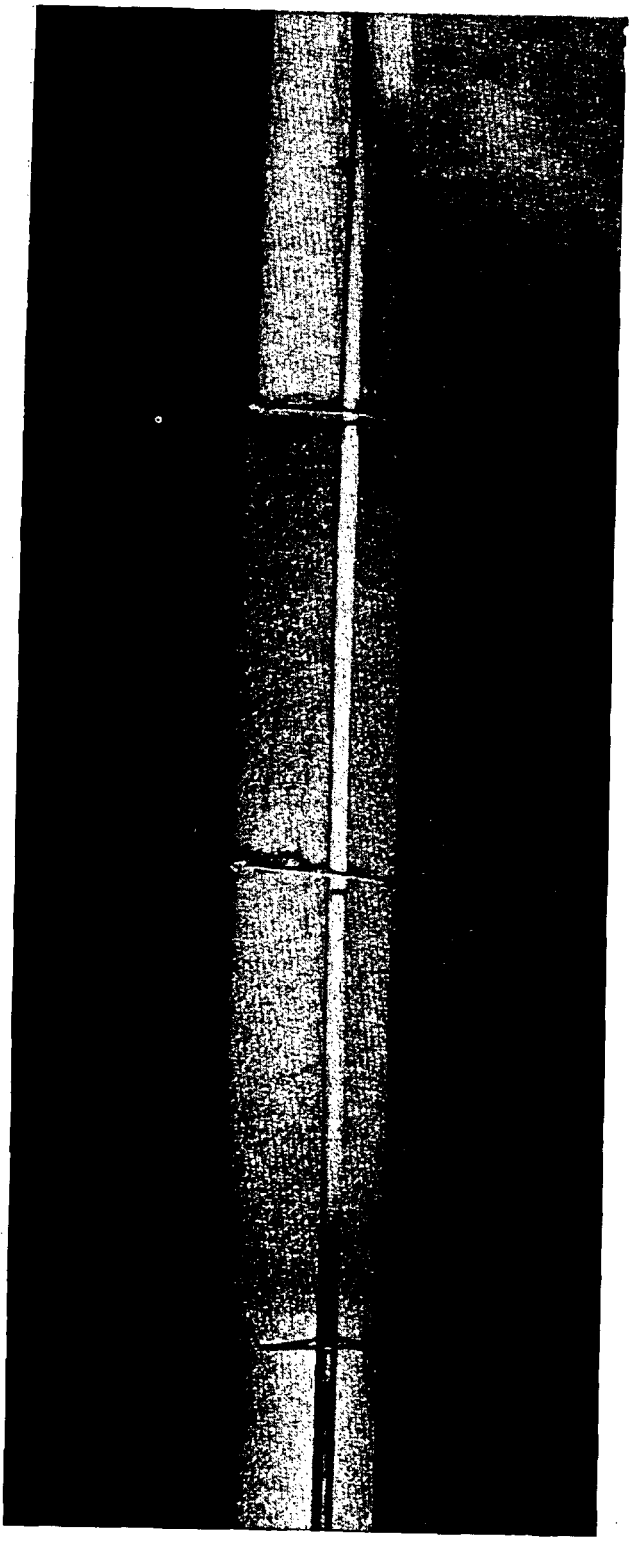


Figure 3. Catalyst on support tube

The degree of reduction was determined by monitoring the water content in the exit stream. The reduction period for these experiments was continued for 24 hours after the formation of water (collected in cold trap) ceased.

Raney Iron. The Raney iron catalyst was activated by extraction of the aluminum followed by a reduction in hydrogen. A solution of 5% sodium hydroxide was used to digest 70% of the aluminum from the alloy. The reactions occurring during the leaching of the aluminum are the following:

$$2Al + 2NaOH + 2H_2O \rightarrow 2NaAlO_2 + 3H_2$$

$$2Al + NaOH + 4H_2O \rightarrow NaAlO_2 + Al(OH)_3 + 3H_2$$

$$2Al + 3H_2O \rightarrow Al_2O_3 + 3H_2$$

The extent of leaching was determined by monitoring the volume of hydrogen evolved using a wet test meter. The remaining catalyst material, consisting of unreacted alloy and elemental iron, was washed with water until a pH approximately that of the rinse water was obtained. However, during the rinsing of the leached alloy, the elemental iron is slightly oxidized, necessitating a reduction with hydrogen. The reduction procedure followed was identical to that described for the oxide catalysts. The leaching, rinsing, and subsequent reduction of all catalysts were performed in situ.

Catalyst Induction

Induction or carbonization is achieved by exposing the catalyst to carbon monoxide to produce a carbided catalyst surface prior to bringing the catalyst to synthesis conditions. Two experiments were conducted with a precarbided catalyst. During precarbiding, the carbon monoxide reacts with the iron to produce an iron carbide plus carbon dioxide. The type of carbide formed is temperature dependent, producing

exclusively Hagg Fe_2C at 300°C and 324°C, only hexagonal Fe_2C at 200°C, and a mixture of the two carbides at 250°C (6).

Synthesis Gas

Synthesis gas was produced by the reaction of natural gas with steam and carbon dioxide by the conventional catalytic hydrocarbon-reforming process. Hydrogen to carbon monoxide ratios used were 3.2/1 and 2.1/1. Typical compositions of the synthesis gas are given in Table 2.

Table 2. Synthesis Gas Composition; volume %

Component	2.1	3.2
H_2	66.2	75.3
CO	31.0	23.5
CO_2	0.5	0.1
N_2	0.5	0.4
CH_4	1.9	0.7

As shown in the table, hydrogen and carbon monoxide constitute a minimum of 97% of the feed gas. Silica gel was used to dry the synthesis gas prior to its introduction into the bench-scale system, and activated carbon traps were used to remove metal carbonyls and sulfur compounds. The total sulfur content of the incoming feed was maintained at less than 6.5×10^{-3} grams/1000 ft^3.

During each run, the CO content in the exit gas was continually monitored by an infrared analyzer. On a daily basis, product gas samples were collected for mass spectroscopy and gas chromatography analyses, and temperature profiles along the length of the catalyst bed were taken. At the termination of a period, the condensed products were collected and separated into oil and aqueous fractions. The analytical laboratories performed simulated distillation, bromine numbers, and mass spectroscopic analyses of the oil fraction.

The experimental results from the six Fischer-Tropsch catalyst screening experiments conducted in a bench-scale TWR unit using commercially available iron catalysts were reported in detail by Haynes et al. (7). Several conclusions can be made. First, an induction period is necessary to produce an active, stable catalyst, as shown by the two catalysts that were precarburized. Second, low temperatures favor selectivity towards liquid hydrocarbon products. Increasing synthesis temperature will increase the CO conversion and shift the yield towards light hydrocarbons and a more olefinic product. Third, with high pressures, the CO conversion, the gasoline weight fraction, and the oxygenate yields increase. Finally, taconite catalysts demonstrated very good stability and an acceptable activity. Catalyst deactivation was not appreciable, as indicated by the immobility of the catalyst "hot spot," which remained at the inlet of the catalyst bed throughout the run. As a result of these findings, coupled with the abundance and low cost of taconite, it was decided to pursue this type of catalyst in more detail.