# GASOLINE VIA THE FISCHER-TROPSCH REACTION USING THE HOT-GAS RECYCLE SYSTEM

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## Introduction

One of the principal problems to be overcome in the development of a coal-to-oil process via the Fischer-Tropsch (F.T.) reaction is the removal of the highly exothermic heat of reaction of the synthesis gas ($H_2$+CO). The hot-gas recycle process has been developed over the past several years by the Bureau of Mines to overcome this problem.[1] In this process the heat of reaction is removed by circulating large quantities of recycle gas through a catalyst bed of high porosity. The catalyst in this experiment is a bed of parallel plates sprayed with the catalyst.

The synthesis gas sent to the F.T. reactor should contain a minimum of methane as this is considered an undesirable by-product for a coal-to-oil plant, and the sulfur content should be as low as possible (less than 0.1 ppm). The first requirement would dictate an entrained gasifier operated at very high temperature; and the second requirement can be achieved by a good purification train such as the Bureau of Mines-developed hot-carbonate process followed by a final sulfur-removal unit containing activated charcoal.

The experiment discussed in this paper used Alan Wood magnetite ore as the catalyst. The objective was to improve the product distribution over that found in an earlier test[2] and to test the use of a cheap ore as the catalyst.

## Experimental Procedures and Results

Fig. 1 shows a schematic diagram of the hot-gas recycle system as developed for the synthesis of oils. The feed gas is fed to the reactor with the recycle gas. The recycle gas is a mixture of hot and cold recycle gas streams. The recycle gas temperature and volume are controlled to hold the temperature rise to about 50°C (90°F) over the reactor or the catalyst bed. The cold recycle gas stream is employed to remove product water from the recycle stream and thus control the water content of the entering gas mixture at a low enough level to prevent oxidation of the iron catalyst.

The catalyst for the present test (HGR 34) was prepared by flame-spraying powdered Alan Wood magnetite ore onto pieces of steel sheet to a thickness of about 20 mils. The sprayed steel sheets were then assembled into grids to fit into the 3-inch extra heavy steel pipe reactor. Fig. 2 shows the plates and grids. Fig. 3 shows the method of flame-spraying. The magnetite coated grid sections were dipped into a 6% aqueous solution of potassium carbonate for 5 minutes and after drying were charged to the reactor. (Concentration of $K_2O$ on the impregnated catalyst was 0.13%.) Following reduction with hydrogen at 380-400°C, the unit was put on-stream with synthesis gas, 1.4 parts hydrogen to 1 part carbon monoxide.

The system pressure was held at 400 psig during synthesis. $CO_2$ was scrubbed from the cold recycle gas stream. The cold recycle gas amounted to 1.5 to 2 volumes per volumes of fresh gas. The remaining (about 18 volumes) recycle gas was used hot and unscrubbed.

Reactor Performance

Product yields of experiment HGR 34 for 1000 and 2000 space velocity operation are presented in table 1. Also presented for comparison of product distribution are yields obtained initially in experiment HGR 33 at 600 hourly space velocity operation using a flame-sprayed D3001 iron catalyst, not impregnated with alkali metal. (See analysis.) The presence of alkali metal on the sprayed Alan Wood magnetite catalyst in experiment HGR 34 is believed to be largely responsible for producing a greater proportion of gasoline range hydrocarbon than that shown initially in experiment HGR 33. While the D3001 catalyst contains $K_2O$, it is not as accessible as the $K_2O$ impregnated on the surface of the Alan Wood magnetite. Also, it is believed most of the $K_2O$ in the D3001 catalyst may have been lost in the flame-spraying.

The experimental results also indicate that the catalyst in HGR 34 was quite active. The 98.8% conversion of carbon monoxide at 1000 hourly space velocity and only slightly lower conversion at 2000 hourly space velocity attest to the high activity level of this catalyst.

TABLE 1.- Hot-gas recycle synthesis results

| | Exp. No. HGR 33 | | Exp. No. HGR 34 | |
|---|---|---|---|---|
| Fresh gas space velocity, vol/vol hr | 600 | 1000 | 1000 | 2000 |
| Total recycle in fresh feed, vol/vol | 52 | 15.9 | 20.4 | 14.4 |
| Reactor pressure, psig | 400 | 400 | 400 | 400 |
| Catalyst temperature, °C | | | | |
| Average | 269 | 325 | 320 | 325 |
| Differential | 20 | 50 | 40 | 50 |
| $H_2$ conversion, % | 73.4 | 90.9 | 90.1 | 83 |
| CO conversion, % | 80.6 | 98.8 | 98.2 | 94.4 |
| $H_2$+CO conversion, % | 76.4 | 94.4 | 93.4 | 87.5 |
| Overall weight balance, % | 93.6 | 90.8 | 87.8 | 96.6 |
| Hydrocarbons recovered, lb/1000 SCF fresh gas | 7.4 | 9.5 | 10.3 | 11.6 |
| Hydrocarbons recovered, wt-% | | | | |
| $C_1+C_2$ | 59.7 | 36.5 | 33.9 | 29.5 |
| $C_3$ | 6.6 | 14.1 | 13.3 | 12.8 |
| Gasoline ($C_3^=$ <204°C | 31.8 | 43.7 | 48.5 | 53.0 |
| Diesel oil (204°-316°C) | 1.9 | 5.0 | 4.0 | 3.8 |
| Fuel oil (316°-450°C) | 0 | 0.4 | 0.2 | 0.5 |
| Wax (>450°C) | 0 | 0.3 | 0.1 | 0.4 |

Catalyst Analysis

Analyses of the Alan Wood magnetite catalyst are shown below, as is also the D3001 catalyst used in Exp. 33[2] experiment.

$Fe_{20}C_9$ is known as Hägg carbide and is considered to be a desirable form of catalyst for the F.T. reaction.[3]

| | D3001 | Alan Wood Magnetite | Discharged Alan Wood Magnetite (Section 4) |
|---|---|---|---|
| Iron (Fe) ---------- | 66.8% | 66.1 | 85.2 ($Fe_2O_3$) |
| Chromium oxide ($Cr_2O_2$) ------ | 0.8 | 0.08 | 0.0 |
| Magnesium oxide (MgO) ------- | 4.6 | 0.09 | 0.04 |
| Manganese oxide ($Mn_3O_4$) ----- | 0.05 | 0.04 | 0.02 |
| Potassium oxide ($K_2O$) ------- | 0.61 | 0.13 | 0.10 |
| Silicon dioxide ($SiO_2$) ------ | 0.62 | 5.4 | 0.50 |
| Titanium oxide ($TiO_2$) ------- | | | 0.5 |

The x-ray analysis of the HGR 34 catalyst taken from the 12 sections after discharge are shown below:

| Section | Phase 1 | Phase 2 | Phase 3 |
|---|---|---|---|
| 1 (bottom - gas inlet) | $Fe_3O_4$ | $Fe_{20}C_9$ | |
| 2 | $Fe_3O_4$ | $Fe_{20}C_9$ | |
| 3 | $Fe_3O_4$ | $\alpha Fe$ | |
| 4 | $Fe_3O_4$ | $\alpha Fe$ | |
| 5 | $Fe_3O_4$ | $Fe_{20}C_9$ | |
| 6 | $Fe_3O_4$ | $Fe_{20}C_9$ | |
| 7 | $Fe_3O_4$ | $Fe_{20}C_9$ | |
| 8 | $Fe_3O_4$ | $Fe_{20}C_9$ | |
| 9 | $Fe_3O_4$ | $\alpha Fe$ | $\gamma Fe_2O_3$ |
| 10 | $Fe_3O_4$ | $\alpha Fe$ | $\gamma Fe_2O_3$ |
| 11 | $Fe_3O_4$ | $\alpha Fe$ | |
| 12 (top - gas outlet) | $Fe_3O_4$ | $\alpha Fe$ | $\gamma Fe_2O_3$ |

The experiment was ended voluntarily after 540 hours of synthesis, and the plates were removed and kept under inert gas. The fourth plate from the bottom showed blistering or separation of the coating from the steel sheet although the coating was intact until the samples were taken. The lower eight assemblies were clean but the top four contained loose carbon and loose coating. The top two grids were of stainless steel and lost all their coating; the other 10 were of carbon steel. The use of stainless steel plates is apparently not desirable owing to the difficulty of retaining the Alan Wood magnetite coating. The flow of gas is upward, and the hottest temperature (about 350°C) is at the top where the carbon is formed. It is possible that 350°C is too high a temperature to operate an iron catalyst though this conclusion depends on the CO partial pressure that the catalyst actually "sees".

## Oil and Water Analyses

The oil analyses of the light and heavy oils showed Bromine numbers between 30 and 40 for the light oil and between 8 and 10 for the heavy oil indicating that the olefinic content of the oil is a maximum of about 22%. Most of the product oil is light oil as shown in Table 1. The oil was slightly acidic indicating production of organic acids, principally acetic acid.

The water analysis averaged about 94% water, the balance being alcohols; the major alcohol was ethanol with lesser amounts of methanol, propanols, and butanols.

Gas Analysis

A typical tail gas analysis is:

| | | | | | |
|---|---|---|---|---|---|
| $H_2$ | 44.3% | $C_2H_4$ | 0.3% | $C_4H_{10}$ | 1.3% |
| CO | 9.7 | $C_2H_6$ | 6.5 | $C_5H_{10}$ | 0.6 |
| $N_2$ | 0.9 | $C_3H_6$ | 0.9 | $C_5H_{10}$ | 0.5 |
| $CO_2$ | 7.9 | $C_3H_8$ | 4.5 | $C_6H_{12}$ | 0.2 |
| $CH_4$ | 21.4 | $C_4H_8$ | 1.1 | $C_6H_{14}$ | 0.1 |

Note the lower concentration of the olefins; this is assumed to be due to the formation of alcohols and acids.

The $C_3H_6$ (but not $C_3H_8$) and heavier hydrocarbons are considered in the gasoline fraction. Attempts were made in earlier experiments[2/] to pass the tail gas through a second reactor containing nickel methanation catalyst to form a high-Btu gas and thus have 2 saleable products, the oils and the high-Btu gas. However, the nickel catalyst became plugged with carbon owing to the low $H_2/CO$ ratio of 1.9 and decomposition of the higher hydrocarbons.

It is believed that a satisfactory high-Btu gas could be made from the gas analyzed if the higher hydrocarbons were removed as the $H_2/CO$ ratio is above 3/1. This would be the desirable method of operation since the upgrading of the tail gas increases its value.

Conclusions

The test to make a gasoline product by the Fischer-Tropsch reaction using sprayed plates of magnetite ore was successful. The make of gasoline was about 60% of the hydrocarbon production. The catalyst held up well under 540 hours of synthesis, and the test was ended voluntarily. The hourly space velocity for the latter part of the experiment was 2000. This showed the catalyst had very good activity.

References

1/ Field, J.H., D. Bienstock, A.J. Forney, and R.J. Demski. "Further Studies of the Fischer-Tropsch Synthesis Using Gas Recycle Cooling (Hot-Gas-Recycle Process)," BuMines Rept. Inv. 5871, 1961, 32 pp.

2/ Forney, A.J., R.J. Demski, D. Bienstock, and J.H. Field. "Recent Catalyst Developments in the Hot-Gas-Recycle Process," BuMines Rept. Inv. 6609, 1965, 32 pp.

3/ Schultz, J.F., W.K. Hall, B. Selegman, and R.B. Anderson. "Studies of the Fischer-Tropsch Synthesis. XIV. Hägg Iron Carbide as Catalysts," J. Am. Chem. Soc. 77, 213 (1955).

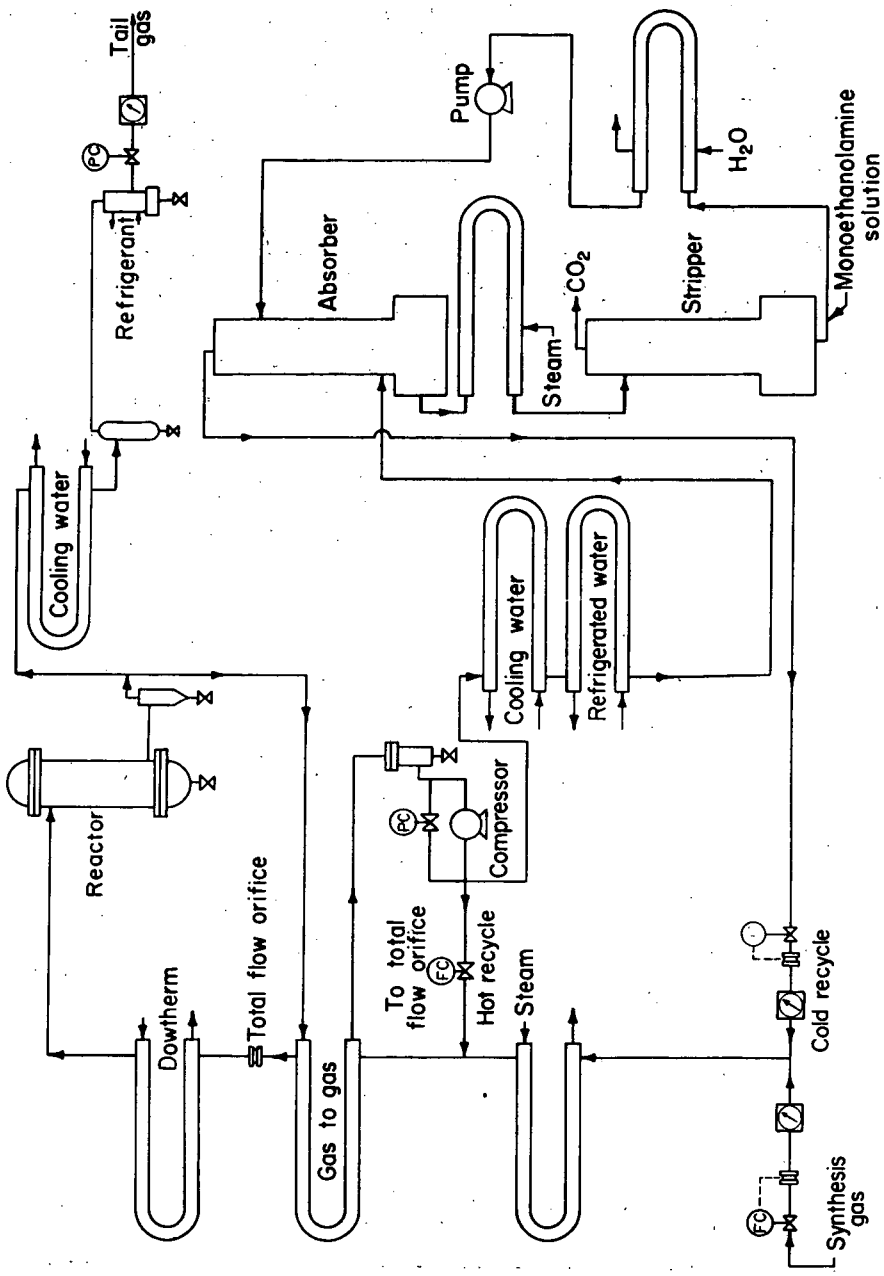


Figure 1. Hot-Gas-Recycle Flowsheet for Production of Gasoline.

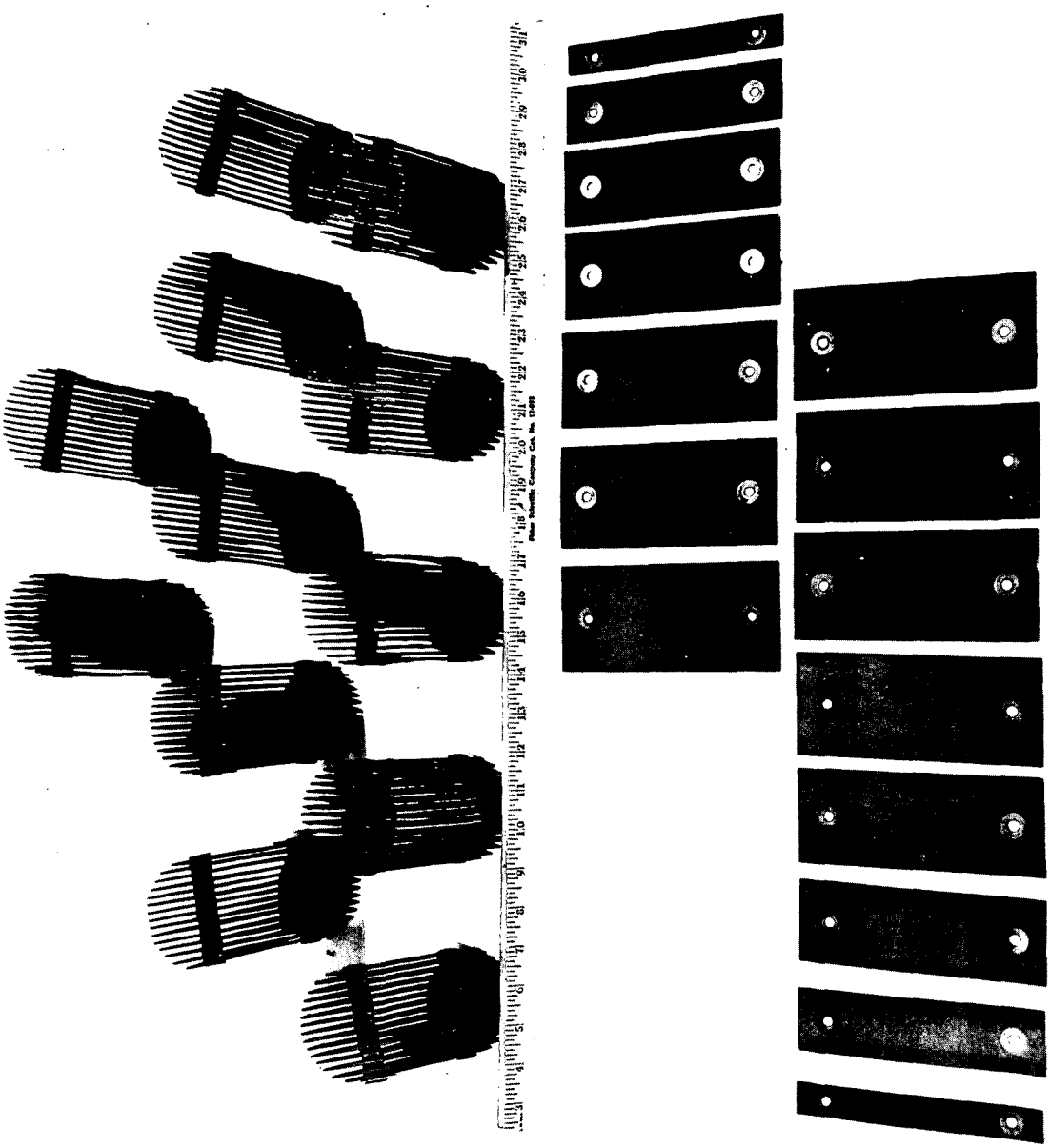

Figure 2. Plates and Grid Assemblies Used in the Production of Gasoline.

Figure 3. Apparatus Used in Thermal Spraying.