CHAPTER 7. - THE FISCHER-TROPSCH SYNTHESIS

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Status of Fischer-Tropsch Process in 1944

The hydrogenation of carbon monoxide on catalysts of iron, cobalt, and nickel has been termed the "gas synthesis process" in some earlier Bureau of

Mines reports; however, the name "Fischer-Tropsch synthesis" is now generally accepted. The names "Hydrocol process" and "Synthine process" have also been used to a limited extent in the United States. All of these terms refer to the same general process.

Catalyst Development

In 1902 Sabatier and Senderens reported the hydrogenation of carbon monoxide and of carbon dioxide to methane, on nickel and cobalt catalysts at atmospheric pressure and at 200° to 300° C. (64). In the ensuing half century, catalysts were developed for the reaction between hydrogen and carbon monoxide to form straight- and branched-chain olefins and paraffins, methanol and higher alcohols with both straight and branched chains, as well as other oxygenated organic molecules. During this period the search for suitable catalysts involved exhaustive empirical testing. In a sense, catalyst development still follows this course, but today the chemist is guided by the immense store of experimental and theoretical knowledge collected in the intervening years.

In 1913 and 1914 the Badische Anilin- und Soda-Fabrik described the hydrogenation of carbon monoxide on alkali-activated cobalt and osmium oxides, supported on asbestos, at 100 to 200 atmospheres and 300° to 400° C.; the liquid products contained alcohols, aldehydes, ketones, fatty acids, and some aliphatic hydrocarbons (7, 55).

Franz Fischer and Hans Tropsch reported in 1923 the production of an oily liquid by the hydrogenation of carbon monoxide on alkalized-iron turnings at 100 to 150 atmospheres (1,500 to 2,200 p.s.i.) and 400° to 450° C. (750° to 842° F.) (24). The process was called "Synthol" and the product "Synthin." The product contained chiefly oxygenated molecules with small amounts of hydrocarbons, similar to the high-pressure product described above. However, at about 7 atmospheres (100 p.s.i.), the synthol catalyst produced chiefly olefinic and paraffinic hydrocarbons and only small quantities of oxygenated organic compounds. At atmospheric pressure and 200° to 250° C. (329° to 482° F.), nickel and cobalt catalysts produced higher hydrocarbons in addition to methane. However, the catalysts lost activity rapidly, and a search was started for improved catalysts.

Early results led to the premise that higher pressures were unsuitable for the synthesis of higher hydrocarbons; accordingly, tests usually were made at atmospheric pressure. This choice of pressure, although satisfactory for cobalt and nickel, was not suitable for iron catalysts, which operate best at 7 to 30 atmospheres. As a result, the development of practical iron catalysts was delayed many years.

The first catalyst operating at atmospheric pressure with high activity and moderately long life was precipitated nickel-thoria-kieselguhr (21). The best of these, after reduction in hydrogen at 450° C., gave a contraction of 70 percent at 178° C., with a flow of $2H_2+1CO$ gas of 1 liter per hour per gram of nickel. The yield of C_5+ reached 90 grams per cubic meter, and the catalyst remained active for at least 5 weeks. In 1934 Ruhrchemie employed a nickel-type

catalyst in a pilot plant of about 1,000-ton-per-year capacity, where the deficiencies of nickel for commercial use - poor selectivity, short life, and excessive loss of nickel and promoters in the synthesis and regeneration - became readily apparent.

Cobalt-thoria-kieselguhr (100 : 18 : 100), prepared in essentially the same manner as the active nickel catalyst, proved to be better [20]. After reduction in hydrogen at 350° C., this catalyst produced yields of C_{5+} hydrocarbons as high as 100 grams per cubic meter of $2H_2+1CO$ at 195° C. and an average yield for 2 months of 82 grams per cubic meter. Further development of cobalt catalyst, undertaken at the Ruhrchemie laboratory by Roelen, led to a $Co-ThO_2-MgO-kieselguhr$ (100 : 5 : 8 : 200) preparation, the standard catalyst for large-scale synthesis in Germany during 1938 to 1944 [30, 31]. Studies at the British Fuels Research Station, Greenwich, gave comparable results [27].

Fischer and Pichler reported improved performance with kieselguhr-supported cobalt catalysts at 5 to 15 atmospheres (74 to 220 p.s.i.), that is, in the medium-pressure synthesis [23]. These results were contrary to early experience with other catalysts. At medium pressure lower yields of gaseous hydrocarbons were obtained, the catalyst life was greater than in atmospheric-pressure synthesis, and periodic reactivation of the catalyst was unnecessary. Future research was directed into this range of pressure and led to development of satisfactory iron catalysts.

Results with iron catalysts were not promising during 1930-36. Precipitated and supported iron catalysts showed only slight improvement over earlier types. Catalyst lives from 4 to 6 weeks and maximum yields of liquid hydrocarbon of 50 to 60 grams per cubic meter were attained. In the winter of 1936-37, Fischer and Pichler increased the gas pressure on the precipitated iron catalyst from 1 to 15 atmospheres [22, 48, 57]. Yields were almost doubled, and the life was increased severalfold. This discovery led to intensive research on iron catalysts by several German laboratories.

As cobalt was in short supply in Germany at this time, the principal objective of this research was development of suitable iron catalysts to replace cobalt in commercial plants. However, the research programs followed divergent paths, and in 1943 the German Government arranged comparative tests, the "Reichsamtversuch," to select the most suitable iron catalyst [31, 53, 57, 75]. The behavior of all catalysts was moderately good, indicating that remarkable progress had been made since discovery of the medium-pressure synthesis. Five of the six catalysts tested were precipitated iron oxide gels, either with or without carriers; the sixth was a typical fused catalyst for the ammonia synthesis. Although various promoters and carriers were used, the only additive essential to activity and selectivity appeared to be alkali. Before synthesis these catalysts were treated with hydrogen or H_2+CO mixtures to effect partial reduction and, in some instances, conversion to carbides.

Sulfur poisoning of metal catalysts had been observed in early studies of the synthesis of ammonia [54]. Similar poisoning phenomena were found with iron, cobalt, nickel, and ruthenium catalysts in the Fischer-Tropsch synthesis.

Although practical upper limits for the concentration of sulfur compounds in the synthesis gas were established for cobalt and nickel (19), few data were available for iron, so that the practical limit for cobalt and nickel was also applied to iron.

Mechanism Studies

In the period 1926-44, new methods for studying catalysis were developed, notably the use of tagged atoms, determination of surface areas from physical adsorption, chemisorption, X-ray and electron diffraction, and spectrometric analysis of reaction products. Studies of the Fischer-Tropsch synthesis and catalysts, with only a few exceptions, did not keep pace with these developments. The slow application of new tools of research may be attributed in part to the complexity of the catalytic system and to the urgency of developing workable processes, especially in Germany. Experiments on the influence of operating variables also reflect this urgency, for most tests were made under conditions for maximum production of useful products. Data of this kind are usually valueless for elucidating the kinetics of the process.

Fischer and Tropsch postulated that metal carbides were intermediates in synthesis (25). Although several variations were proposed in later papers, the principal hypotheses were that metal is converted to carbide, carbidic carbon is hydrogenated to methylene groups, and these CH_2 groups then polymerize to hydrocarbons. Bahr and Jessen established that carbides of iron, cobalt, and nickel could be produced by treating the metals with carbon monoxide at synthesis temperatures; the compositions but not the structures of the carbides were determined. Thermomagnetic studies by Pichler and Merkel indicated the existence of two carbides of iron, presumably of the approximate composition, Fe_2C (59). Indications of two carbides of iron were also obtained by X-ray diffraction studies of used iron catalysts at I. G. Farbenindustrie; however, no correlations were made between the thermomagnetic and x-ray studies.

In 1939 Craxford and Rideal (12) presented a carbide intermediate hypothesis for cobalt catalysts, essentially the same as that of Fischer and co-workers. In normal operation the catalyst surface was postulated to be carbide. At high temperatures, high conversions, or high ratios of hydrogen to carbon monoxide, all or part of the surface was assumed to be metallic cobalt. The metal surfaces were believed to be effective catalysts in the water-gas reaction, hydrocracking, and production of methane.

An oxygenated intermediate product was first postulated by Elvins and Nash (16). Methanol was suggested as a possible intermediate. The authors suggested that oxygenates and hydrocarbons may be produced by the same series of consecutive reactions or by simultaneous, independent reactions.

Workers at I. G. Farbenindustrie proposed a sequence of reactions involving an oxygenated intermediate, subsequently transformed to a methylene group, which then polymerized (37).

Smith, Hawk, and Golden of the Bureau of Mines studied the mechanism of the Fischer-Tropsch reaction with respect to possible reactions of hydrocarbons with synthesis gas on cobalt and iron catalysts at atmospheric pressure (71). They suggested that oxygenated molecules may be intermediates in the synthesis but that these are normally converted to hydrocarbons on the catalyst, so that virtually none of this material leaves the catalyst bed. Ethylene was incorporated in synthesis over cobalt but not over precipitated iron catalysts. This work may be considered a forerunner of the oxo synthesis.

Related Syntheses

About 1940 Roelen's studies of the effect of olefins in the feed gas led to discovery of the oxo synthesis. A mixture of hydrogen, carbon monoxide, and an olefin reacted over cobalt to form oxygenated compounds at 100° to 200° C. and 100 to 300 atmospheres. With primary olefins, about 60 percent branched- and 40 percent straight-chain aldehydes or alcohols were obtained. The form of the catalyst was not important in this process (62, 63, 77).

In the same year Pichler and Buffleb (58) reported the synthesis of high-molecular-weight hydrocarbons on ruthenium catalysts with $2H_2+1CO$ gas at pressures up to 1,000 atmospheres. At the higher pressures waxes with molecular weights up to 23,000 were obtained in sizable yields.

Pichler and Ziesecke (60) studied the hydrogenation of carbon monoxide on non-reducible oxide catalysts at higher temperatures and pressures than those normally used in the Fischer-Tropsch synthesis, i.e., 450° C. and 300 atmospheres. Thoria and mixtures of thoria and alumina or zinc oxide were the best catalysts. Large yields of branched-chain and cyclic hydrocarbons, as well as gaseous hydrocarbons, were produced, and hence the name "Isosynthesis" or "Isoparaffin synthesis" was given to this process (60).

Plant Developments

By 1944 most of the basic ideas for the design of Fischer-Tropsch reactors had been formulated and tested on a pilot-plant scale. As the major engineering problem is removal of the heat of reaction from the catalyst bed, processes were classified on this basis:

A. External cooling.
    1. Fixed bed.
        a. Plate type)
        b. Double tube) German commercial reactors in 1937-44
    2. Fluidized fixed bed.

B. Internal cooling.
    1. Oil as heat-transfer medium.
        a. Fixed-bed, oil-circulation process.
        b. Fluidized-bed, oil-slurry process.
    2. Gas as heat-transfer medium, hot-gas-recycle process.

Although standardization of apparatus for the German war effort required election of externally cooled, fixed-bed reactors, their inadequacy was real-zed and research on reactor design was continued. During 1938-44 three proc-sses were evolved: The oil-circulation process of I. G. Farbenindustrie; the il-slurry process of Rheinpreussen, Ruhrchemie, and I. G. Farbenindustrie; nd the hot-gas-recycle process of I. G. Farbenindustrie. Since 1940 fluid-zed catalyst techniques have been investigated by American companies, espe-ially the M. W. Kellog Co., Hydrocarbon Research, Inc., Standard Oil Co. Indiana), Standard Oil Development Co., and The Texas Co.

The basic operating features of Fischer-Tropsch reactors are depicted in igure 56. In the German fixed-bed reactors, the catalyst was maintained at istances no greater than 7 to 10 mm. from plates or tubes cooled by water der pressure. Fluidized fixed-bed reactors are large tubes cooled by iyonet-type heat exchangers hung from the top of the unit, and the reactor ; usually operated at high temperatures, 325° to 350° C. (617° to 662° F.),) prevent agglomeration of catalyst (72). In the oil-circulation process a ixed-bed catalyst is submerged in cooling oil. Synthesis gas and cooling oil :e passed cocurrently upward through the bed. The cooling oil flows out the)p of the reactor through a heat exchanger and reenters the bottom of the re-:tor. The temperature in the bed is regulated by the rate of circulation of oling oil. Variations of this process involve evaporative cooling (by vola-lization of cooling oil) and countercurrent flow of oil and gas (14, 15, 61, ., 74). In the slurry process a finely divided catalyst is suspended in cool-g oil, and both catalyst and oil are circulated through an external heat ex-anger. Heavy products are removed through sintered metal filters (17, 18,). The hot-gas-recycle process employs a fixed catalyst bed. A high rate recirculation of end gas is required (the ratio of end gas to fresh feed ing as high as 100) as the heat of reaction is dissipated by heating the s (72, 79).

In large-scale German atmospheric-pressure synthesis, paraffin wax re-ined on the cobalt catalyst and accumulated to 50 percent of the catalyst ight. Wax was one of the factors that caused a decrease in catalytic activ-y, and the catalyst was regenerated periodically by solvent extraction or drogenation. The average useful catalyst life was about 4 months, but this riod could be prolonged to 6 to 8 months by more frequent regenerations. At e end of that period the catalyst did not respond to further solvent extrac-ons and treatment with hydrogen at 200° C. Spent catalyst was dropped into trough under the converter and transported by chain conveyor to drums for ipment to the catalyst factory. Here it was processed to recover cobalt and oria.

Medium-pressure synthesis was preferred in Germany because of the appreci-ly higher yield of oil and wax per cubic meter of synthesis gas and the nger life (6 to 9 months) of catalyst without reactivation. Wax was continu-sly carried out of the converter by the solvent action of liquid products ndensed on the catalyst at 7 to 10 atmospheres.

Fresh and recycle gas

Steam

Cooling H$_2$O

To product recovery
and recycle

Double tube fixed-bed reactor

To product recovery
and recycle

Steam

Cooling H$_2$O

Cooling
bayonets

Fresh and recycle gas

Fluidized fixed-bed reactor

Fresh
gas
inlet

Recycle gas

Steam

To product
recovery
and purge

Gas
recycle
compressor

Heat
exchanger

Hot gas recycle process

To light product recovery
and recycle

Steam

Cooling oil

Heat
exchanger

Oil
circulation
pump

Fresh and recycle gas

Heavy product
removal

Oil circulation process

To product recovery
and recycle

Steam

Filter

Heavy
product
removal

Heat
exchanger

Slurry circulation pump

Fresh and recycle gas

Slurry process

Fixed-bed catalyst

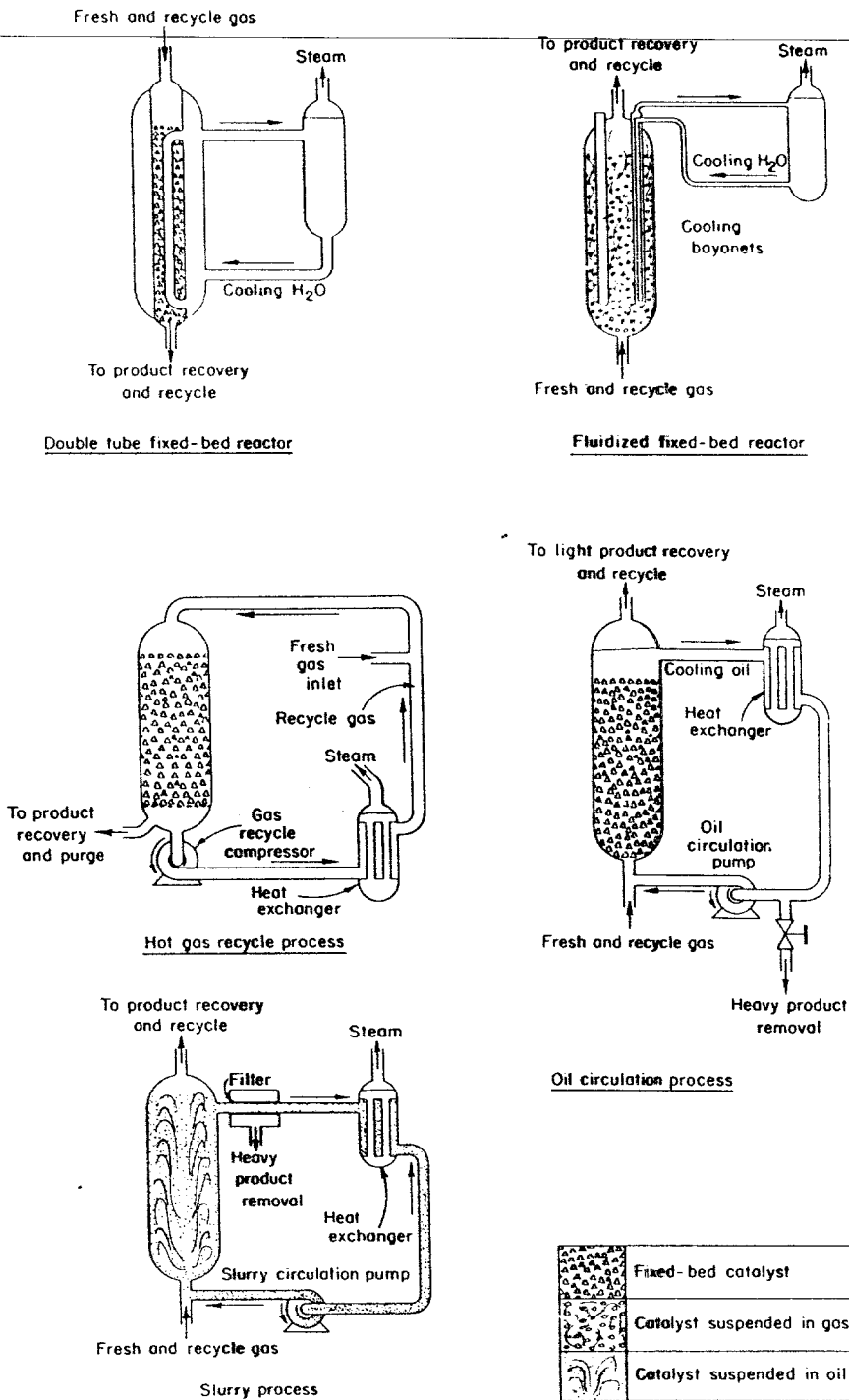Catalyst suspended in gas

Catalyst suspended in oil

FIGURE 56. - Schematic Flow Diagrams of Five Modifications of Fischer-Tropsch Process.

Bureau of Mines Contributions to Fischer-Tropsch Synthesis, 1944-55

Basic Research

Laboratory work on the hydrogenation of carbon monoxide was begun by the Bureau of Mines about 1925 with studies of the methanol, higher alcohol, and Fischer-Tropsch syntheses. This research was discontinued from 1930 to 1942. For the new laboratories at Bruceton, Pa., the catalyst-testing facilities were enlarged to include 16 semiautomatic reactors (fig. 57) and glass apparatus for studying physical and chemical properties of catalysts. The work was facilitated by well-equipped laboratories for chemical and physical characterization of catalysts and synthesis products, including X-ray diffraction, thermomagnetic analysis, and mass, infrared, and ultraviolet spectrometers.
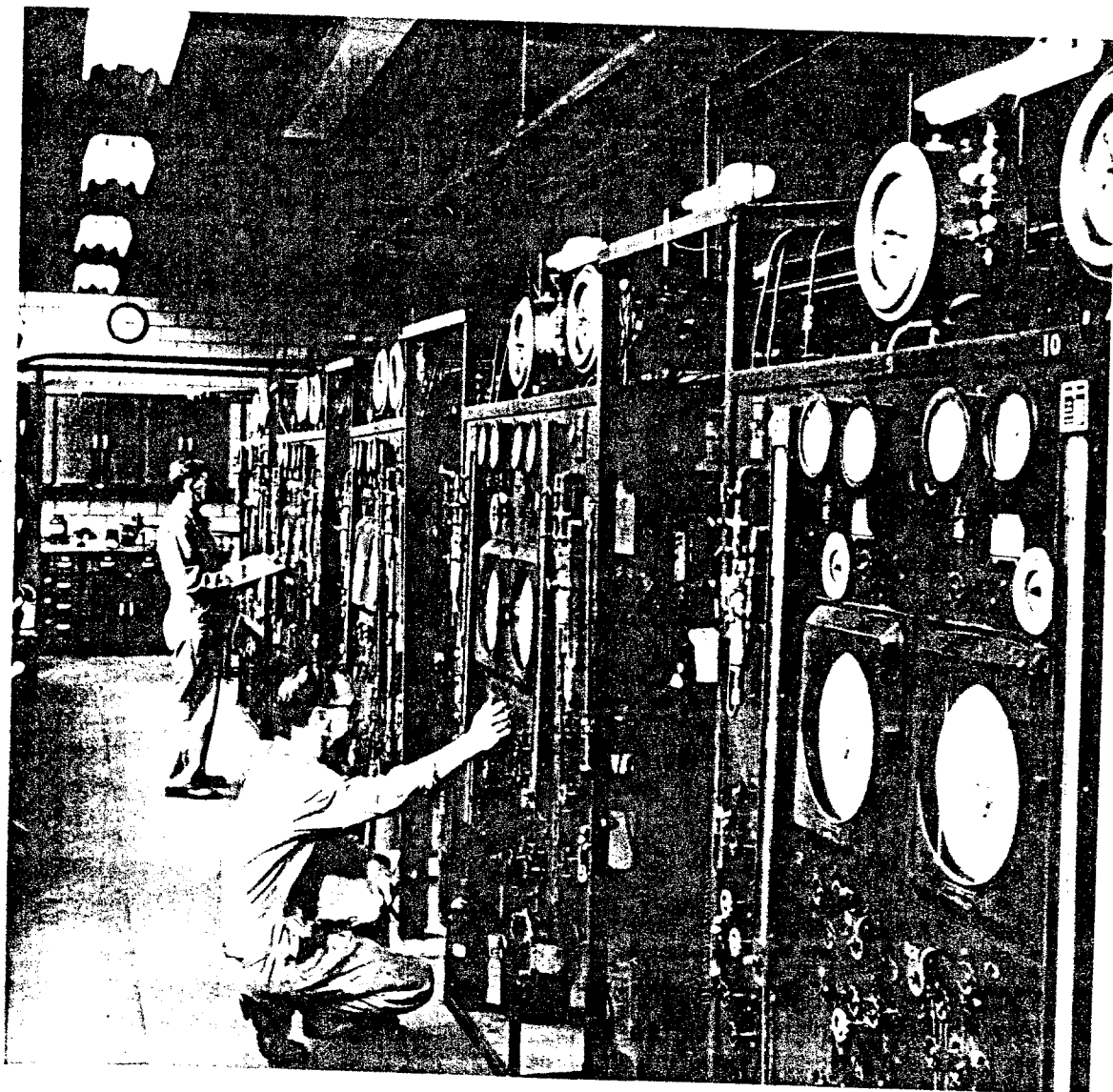

FIGURE 57. - Catalyst-Testing Reactors for Fischer-Tropsch Synthesis.