IV — REACTION CONDITIONS

The Effect of Reaction Temperatures

The Fischer-Tropsch reaction takes place in a fairly narrow temperature range. The reaction occurs very slowly below 350°F. (110), even with the most active nickel or cobalt catalysts. With the same catalysts above 440°F., the yield of liquid hydrocarbons diminishes rapidly and the yields of methane increase correspondingly (123, 124). At higher temperatures, 575 - 600°F., methane production predominates (113) and the oxygen in the synthesis gas appears in the product in the form of CO_2.

Each catalyst has a unique optimum operating temperature. The range, however, is narrow in all cases. The optimum temperature for a cobalt cata-lyst is 180 - 200°C. The activity of the cobalt decreases at 207°C. and is permanently impaired at temperatures above 218°C. (130). For an iron cata-lyst, this optimum temperature is 465°F. (240.5°C.) (114). An increase in the operating temperature may decrease the activity of the catalyst because of sintering and carbon deposition (130). The temperature coefficient of the rate of synthesis on cobalt and iron catalysts is about 1.6/10°C. in the range of 191 - 207°C. (110, 120).

Although the nature of the reaction product depends, to a large extent, upon the catalyst and the reaction pressure, it is also influenced by the

reaction temperature. Thus, in general, the reaction of hydrogen with carbon monoxide produces straight-chain hydrocarbons at relatively low temperatures, alcohols in the range 575 - 750°F. (302 - 399°C.), isoparaffins in the range 575 - 885°F. (399 - 474°C.) and aromatic hydrocarbons in the range 885 - 930°F. (474 - 499°C.) (104, 111). The Hydracol process which uses an iron base catalyst in a fluidized reactor operates within the temperature range 550 - 700°F. (288 - 371°C.) (105).

The Effect of Reaction Pressure

In general, the use of elevated pressure in the Fischer-Tropsch process favors the formation of oxygenated compounds and of high molecular weight hydrocarbons. This reduces the yield of liquid hydrocarbons (106, 107, 110). The use of moderate pressures (75 - 220 psi) has shown definite advantages in its effect on the total yield as well as on the composition of the product. Fischer and Pichler (108) working with a Co-ThO$_2$-kieselguhr catalyst (which was not regenerated during its one-month period of usage) found that, 1) the total yield increased with increasing pressures up to about 75 psi, 2) the yield of paraffin wax increased with pressure up to about 220 psi and 3) the active life of the catalyst was greatest when moderate pressures were used. Similar results were reported by Martin (115) for a two-stage operation. The effect of the pressure upon the yield and type of product is given in Table I.

Table I

Effect of Pressure on Yield and Types of Product Yield (108)
(Pounds per 1000 cu. ft. of Synthesis Gas)

P psi/g	Total Solid and Liquid	Paraffin Wax	Liquid Above 390°F.	Gasoline Below 390°F.	Hydrocarbon Gases C_1-C_4 Inclusive
0	7.28	0.62	2.36	4.30	2.37
22	8.16	0.93	2.68	4.55	3.12
73.5	9.35	3.74	3.18	2.43	2.06
220	9.03	4.36	2.24	2.43	2.06
735	8.59	3.36	2.30	2.93	1.31
2200	6.48	1.68	2.12	2.68	1.93

Just as each catalyst has an optimum operating temperature, so it has also an optimum working pressure. For iron, the optimum pressure is in the region of 10 - 20 atmospheres, whereas the cobalt has a maximum life and capacity at 5 - 15 atmospheres (110, 121). At pressures above 30 atmospheres the durability of iron and cobalt catalysts decreases due to the formation of the carbonyl (130). Fischer and Pichler (108) compared the yields given by a Co-ThO$_2$-kieselguhr catalyst at atmospheric and medium pressures. At pressures of 75 - 220 psi, the total yield of liquid and solid hydrocarbons was 9.35 pounds per 1000 cu. ft. of synthesis gas on fresh catalyst and it still exceeded 6.24 pounds after 26 weeks of operation without regeneration. However, at atmospheric pressure, the initial yield was 8.11 pounds and this decreased to 6.24 pounds after only one month of operation. For a ruthenium catalyst, no conversion takes place below 10 atmospheres pressure. Its optimum pressure is 300 atmospheres at which the conversion is 95% (121).

Below one atmosphere, for all catalysts, greater amounts of the catalyst were required to produce an equivalent conversion although there was

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no change in the chemical composition of the product (119).

Most of the Fischer-Tropsch plants in Germany used a multi-stage process. For the normal pressure process, two stages were used. The conversion in the first stage was 50% and in the second stage 41%. For the medium pressure process (in all cases a Co-ThO$_2$-kieselguhr catalyst was used), three stages were used with the following conversions, 66%, 21% and 7% respectively. The pressure was 9 - 11 atmospheres gauge pressure (112). The American Hydracol process operates at 200 - 500 psi, thus making this process very productive per unit volume of the catalyst (105). The use of moderate pressures offers the practical advantage of reduction in plant size for a given output (118).

Wanatabe (127) found that the relation $x = a\,p^b$ holds between the reaction pressure, p, and x, which represents the yield of oil or the contraction of the gas volume. The quantities a, and b, are constants. This equation is of the same form as the Freundlich absorption isotherm $y = ap^n$. It appears, thus, that there is a direct relationship between the consumption of CO and absorption of CO.

The Effect of the Throughput Rate

In general, reducing the space velocity has a similar effect on the products as an increase in pressure with the difference that a low space velocity decreases the output of the plant and a high pressure increases it (118). As the space velocity is increased, the contact time is decreased. The contact time, θ, is given in terms of space velocity by the equation (119):

$$\theta = \frac{1}{S} \cdot \frac{P}{P_{std.}} \cdot \frac{T_{std.}}{T}$$

where S is the space velocity.

Fischer and Pichler (108), by using a Co-ThO$_2$-kieselguhr (100:18:100) catalyst in a two stage process at a pressure of 150 psi, found that the yield of the solid paraffin as well as the total yield of the higher hydrocarbons decreased with an increase in the rate of the throughput. At a throughput of 3.2 cu. ft. per hour per pound of cobalt in the catalyst, they obtained a yield of about 11.8 pounds of primary product per 100 cu. ft. of synthesis gas. Of this, 48% was solid paraffins, 44% was liquid hydrocarbons and 8% was C$_3$-C$_4$ hydrocarbons. Upon increasing the throughput to 32 cu. ft./hr. the yield of primary product fell to 9 pounds per 1000 cu. ft. of synthesis gas, of which, 14% was solid paraffins, 73% was liquid hydrocarbons and 13% was C$_3$-C$_4$ hydrocarbons.

With an increase in the throughput rate, higher temperatures are required to maintain good yields. This increase in reaction temperature leads to the formation of methane. However, for an isothermal process, the yield falls rapidly with an increase in the throughput rate. This is illustrated in Table II which shows the results obtained with a cobalt catalyst at 390°F. and 220 psi. Japanese (122) and British (103) investigators have reported similar results.

Using a lower throughput than Fischer and Pichler, Tsuneoka and Nishio (126) have observed that the yield rises to a maximum as the throughput is

Table II

The Effect of Increased Throughput on
Yields at Constant Temperature

Throughput (cu. ft./hr./lb. Co)	18.4	37.0	57.6	160.
Total yields (lbs./1000 cu. ft. of synthesis gas)	6.30	5.30	3.74	1.03

increased before it falls off. For a cobalt catalyst, the maximum yields are observed at 4 l/hr./g. Co, and for a ruthenium catalyst, the maximum occurs at 9 l/hr./g.Ru. (121). With a Ni-Al$_2$O$_3$ catalyst at 200°C., it was found that the highest yield was obtained at a space velocity of 100. Upon increasing the space velocity to 177, the total yield decreased. With a decrease of the space velocity to 57, the yield of the lighter hydrocarbons increased (117).

The Effect of the Hydrogen-Carbon Monoxide Ratio

The composition of the synthesis gas may have an H$_2$:CO ratio which varies from 2 to less than 1. By increasing the relative amount of carbon monoxide to hydrogen, a more olefinic product is produced and an increase in the amount of CO$_2$ formed (128). A high H$_2$:CO ratio produces a saturated product and favors the formation of methane. It has been found that the amount of olefins in the reaction product is inversely proportional to the hydrogen content of the synthesis gas (116). With the conventional cobalt catalyst, a ratio of 2:1 is considered the optimum for obtaining the maximum total yield of hydrocarbons (110, 122). For a cobalt catalyst, a reduction of the H$_2$:CO ratio to 1:1 brings about the deposition of carbon, decreasing thereby the life of the catalyst. For an iron catalyst, the optimum ratio is 1:1.7 for the medium pressure process. An increase in the amount of CO requires an increase in the reaction temperature (110). As the H$_2$:CO ratio increases, for the conventional catalyst, the synthesis rate increases and then falls (121).

As stated before, the Fischer-Tropsch synthesis can be carried out with a synthesis gas containing 10 - 12% inerts. The dilution of the synthesis gas mixture with inert materials such as CO$_2$, N$_2$, CH$_4$ tends to decrease the initial formation of methane by lowering the temperature of the catalyst bed. At atmospheric pressure, the addition of an inert diluent, does not increase the percent of conversion (121).

Wanatobe, Morikawa and Igawa (129) compared the results of adding saturated and unsaturated hydrocarbons to the synthesis gas mixture. They found that with the addition of a saturated hydrocarbon, the rate of consumption of CO and formation of CO$_2$ decreased, and the formation of olefins increased slightly. With an increase in molecular weight of the saturated hydrocarbon which was added, the number of carbon atoms in the gaseous saturated hydrocarbon product was increased. When the diluent was an unsaturated hydrocarbon, the consumption of carbon monoxide was lowered, but the production of oil was not decreased. About 50% of the olefin which was added was hydrogenated and 30% of it took part in the polymerization.

V - HEAT REMOVAL

The Fischer-Tropsch synthesis is a highly exothermic reaction. The temperature of the reaction must be controlled within a narrow range of about 5° so as to avoid excessive methane formation. For this reason, methods for the rapid and effective removal of heat from the reaction zone have been of great interest. The transfer of heat from the catalyst surface to the cooling medium may be effected by direct or indirect contact with the catalyst.

All of the German plants brought about the heat transfer by the indirect method. The catalyst was limited to a very shallow layer (not more than 10 mm.) (151) and the heat was removed by the vaporization of water which was circulated through a series of pipes around the catalyst bed (139, 142). The normal pressure reactors were characterized by a system of hundreds of plates pierced by tubes filled with cooling liquid contained in rectangular boxes. The reactors at the Courrieres-Kuhlmann plant at Harnes, France, each had a total surface of 5,000 square meters. The catalyst filled the voids between the baffles and the tubes (145, 149). In the medium pressure synthesis, the cooling was effected by means of a double-tube reactor. The catalyst lay in the annular space between the tubes. The outside shell was 2.7 meters internal diameter. Each shell contained 2000 tubes of about 48 mm. outside diameter by 44 mm. inside diameter and about 4.5 meters in length. Water or oil surrounded the tubes and served as a cooling medium. Four such reactors arranged in a square operated as a unit. The shell side of the four reactors was connected to an overhead steam separating drum. Boiler water was fed to the steam drum and the steam generated was released into the steam main. The temperature on the reactor was regulated by controlling the steam pressure on the drum (131, 135, 146, 148, 150). One patent (143) recommended that the reactor tubes be in a horizontal position in order to obtain more effective heat transfer. Recent process designs by the United States Oil Company specify a turbulent fixed bed of catalyst suspended in synthesis gas, heat removal being accomplished by indirect or direct means. In the former, heat exchanger tubes are present in the catalyst bed (138, 140, 155, 158).

The design of the German converters, in which the heat of reaction is withdrawn indirectly, requires very narrow layers of catalyst and consequently large amounts of steel are required. Heat removal by the direct contact of the catalyst with the cooling medium is a recent developement which will permit wide variation in design for improved efficiency of operation. The heat-transfer medium may be gas, liquid, or solid. The I. G. Farbenindustrie A. G. used a hot-gas recycle process in which the synthesis gas was passed through an external heat exchanger and then returned to the reactor (132, 137). The heat of reaction may be removed from a fluidized fixed bed by a heat exchanger present in the catalyst bed or outside of the reaction zone. The catalyst, suspended in the synthesis gas, is passed from the converter through the heat exchanger and back into the converter.

There are several processes in which the reaction is carried out in a liquid medium such as water or oil in which the catalyst is suspended (136, 144). The I. G. Farbenindustrie was developing (1939-44) a liquid phase operation in which the powdered iron catalyst was suspended in oil and the synthesis gas contacted with this liquid suspension (147, 153). The heat of vaporization of the liquid removes heat rapidly from the catalyst surface. Ruhrchemie (132) patented a modified liquid-phase process in which a mixed

cobalt catalyst was suspended in oil into which water was injected and vaporized under the reaction conditions to control the temperature. The liquid-phase processes were difficult to operate because the formation of high molecular weight products of limited solubility caused the catalyst particles to agglomerate and settle (141). The Duftschmid process which was used by the I. G. Farbenindustrie (156) consisted of an oil recycle process in which a cooling oil was passed concurrent with the synthesis gas over the catalyst. Cooling was effected by recycling the heated oil through an external heat exchanger.

Several processes have been described for the solid heat-transfer operation (152, 154, 159). In these, the synthesis gas is passed through a plurality of zones containing, althernately, catalytic and non-catalytic materials. The latter may contain granules of solid inert material or cooling liquid for removing the heat of reaction.

A mathematical treatment has been given by Brinkely (134) for the heat transfer between a fluid and a porous solid. It is shown that the equations which are developed can be applied to the catalytic formation of hydrocarbons from carbon monoxide and hydrogen.