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UNITED STATES  
DEPARTMENT OF THE INTERIOR  
J. A. KRUG, SECRETARY

BUREAU OF MINES  
R. R. SAYERS, DIRECTOR

INFORMATION CIRCULAR

REVIEW OF FISCHER-TROPSCH AND RELATED PROCESSES  
FOR SYNTHETIC LIQUID FUEL PRODUCTION



BY

NORMA R. GOLUMBIC

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FOR SYNTHETIC LIQUID FUEL PRODUCTION<sup>1/</sup>

By Norma Columbic<sup>2/</sup>

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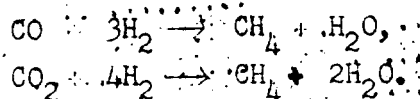
<sup>2/</sup> Technical assistant, Research and Development Division, Bureau of Mines, Central Experiment Station, Pittsburgh, Pa.

## HISTORICAL DEVELOPMENT

Gasoline and other liquid fuels may be obtained from coal by direct and indirect hydrogenation.<sup>3/</sup> The direct process, usually termed the coal-hydrogenation or the Bergius process, was patented in Germany by F. Bergius in 1914 and developed to a commercial stage by the inventor and I. G. Farbenindustrie. From a chemical point of view, the coal-hydrogenation process consists of adding hydrogen to the complex coal molecules and removing oxygen so that its chemical constitution is changed to that of petroleum, whereupon the coal substance liquefies, yielding an aromatic crude oil.

In the indirect-hydrogenation process, known as the Fischer-Tropsch process (invented by Franz Fischer and Hans Tropsch in Germany), coal, lignite, or natural gas is first converted to water gas, a mixture of carbon monoxide and hydrogen. This mixture of gases, in proper proportion and after suitable purification, is then passed over a solid catalyst at relatively low pressures (1 to 20 atmospheres) and temperatures ranging from 180° to 260° C. The products obtained are gasoline, Diesel oil, liquefiable gases, and paraffin wax.

Catalytic hydrogenation of the oxides of carbon has been actively studied for about 50 years. Sabatier and Senderens, who published their results in 1902,<sup>4/</sup> produced methane by passing a suitable mixture of hydrogen and carbon monoxide or dioxide over a reduced nickel catalyst at a temperature between 200° and 250° C. These reactions are represented by the following equations:



The relatively high temperatures and large hydrogen excess in the reacting gases favored the formation of methane rather than higher molecular weight hydrocarbons.

In 1913 the first liquid hydrocarbons were synthesized by the Badische Anilin und Soda Fabrik in Ludwigshafen, Germany, using catalysts consisting of the oxides of cobalt, osmium, or zinc, impregnated with alkali, a temperature about 350° C., and a pressure of 100 atmospheres.<sup>5/</sup> Some oxygenated organic compounds were also found to be present. After a lapse of some years during the First World War, work on the catalytic reduction of carbon monoxide was renewed in 1922 by Fischer and Tropsch, of the fuel-research laboratory of the Kaiser Wilhelm Institute in Berlin, Germany. Using as catalyst iron shavings impregnated with potassium carbonate, over which was passed a mixture of hydrogen and carbon monoxide, at 400° to 450° C. and 100 to 150 atmospheres pressure,

<sup>3/</sup> Hearings before a Subcommittee of the Committee on Public Lands and Surveys, United States Senate, 78th Congress, First Session on S-1243, August 3, 4, 6, 9, and 11, 1943, pp. 170, 172, 270-72.

<sup>4/</sup> Spencer, W. D., The Science of Coal-to-Oil Conversion. Part 4. Fischer-Tropsch Synthesis: Petroleum, June 1944, vol. 7, pp. 90-94.

<sup>5/</sup> See footnote 3.

a product called "Synthol" was obtained. This material contained no hydrocarbons, but only oxygenated compounds, such as alcohols, aldehydes, ketones, and acids.<sup>6/</sup>

Because of the low calorific value of the alcohols and other oxygenated compounds in comparison with hydrocarbons, which renders them unsuitable for use as motor fuels, a less highly oxygenated product was desirable. Fischer and his coworkers observed that reduction in pressure decreased the content of oxygenated compounds of synthol and that the liquid product obtained at pressures below about 7 atmospheres was mainly a mixture of olefinic and paraffinic hydrocarbons. As lower temperatures were also desirable for prolonging the life of the catalyst and for promoting liquid rather than gaseous hydrocarbon production, the reaction was investigated at decreased temperatures as well as pressures. As the rate of reaction decreased sharply with decreasing pressure and temperature, more active catalysts were essential.<sup>7/</sup>

In 1925-6, Fischer and Tropsch,<sup>8/</sup> using very active catalysts consisting of metals of the iron group plus various activating agents, obtained their first successful results with mixtures of hydrogen and carbon monoxide at atmospheric pressure and temperatures between 200° and 300° C. The organic product, named "Kogasin" by Fischer, was almost free from oxygenated compounds and consisted of gaseous, liquid, and solid hydrocarbons composed mainly of straight-chain paraffins and olefins. Its precise composition is a function of the catalyst employed and of the operating conditions.

In the interval from 1925 to 1933 active cobalt, nickel, and iron catalysts for this synthesis were developed by German, British, French, American, and Japanese chemists. Investigations were continued also on the technological development of the synthesis and on the mechanism of the reaction.

The British investigators, Elvins and Nash<sup>9/</sup> observed the formation of oily material on a cobalt-copper-manganese oxide catalyst at atmospheric pressure and at temperatures from 245° to 284° C. The products included some oxygen-containing compounds in addition to hydrocarbons. Smith, Davis, and Reynolds,<sup>10/</sup> of the U. S. Bureau of Mines, reported the presence of olefinic as well as saturated paraffinic hydrocarbons in the product. In 1928, Fischer and Tropsch<sup>11/</sup> disclosed the results of an extensive examination of the gaseous and liquid hydrocarbon products of the synthesis at 190° C. on an

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<sup>6/</sup> Leva, Max, Translations of German Documents on the Development of Iron Catalysts for the Fischer-Tropsch Synthesis-I; Lecture and Discussion on Iron Catalysts for the Middle Pressure Synthesis, Kaiser Wilhelm Institute for Coal Research, Muelheim-Ruhr by H. Fichler, Sept. 9, 1940, TOM Reel 101 Doc. PG-21574-NID: Bureau of Mines Inf. Circ. (in press).

<sup>7/</sup> See footnote 6.

<sup>8/</sup> Storch, H. H., Chemistry of Coal Utilization: National Research Council (H. H. Lowry, ed.), John Wiley & Sons, Inc. 1945, vol. 2, chap. 39, pp. 1797-1845.

<sup>9/</sup> See footnote 8.

<sup>10/</sup> See footnote 8.

<sup>11/</sup> See footnote 8.

iron-copper catalyst at atmospheric pressure. No hydrocarbons other than olefins and saturated paraffins were found. The liquid product boiling between 60° and 185° C. contained 30 percent saturated paraffins that were largely octane, nonane, and isononane which were positively identified. Olefins comprised the remaining 70 percent.

From 1928 to 1930 the Bureau of Mines developed an active iron-copper catalyst. Detailed data were presented by Smith, Hawk, and Reynolds<sup>12/</sup> on the yield of olefinic and paraffinic hydrocarbons by use of a cobalt-copper-manganese oxide catalyst at temperatures of 200° to 260° C. The lower hydrocarbons were analyzed completely. Further examination of the products of the synthesis on an iron-copper and on a cobalt-thoria-kieselguhr catalyst by the German experimenters Fischer, Tropsch, and Tropsch and Koch<sup>13/</sup> resulted in identification of various olefinic and paraffinic hydrocarbons; it showed the absence of naphthenes and diolefins, but small quantities of less than 0.5 percent of benzene and toluene were found.

The French workers Audibert and Raineau<sup>14/</sup> experimented with the high-pressure synthesis, using catalysts such as iron phosphate and iron borate at 150 atmospheres. The products contained chiefly alcohols. In hunting for clues to the reaction mechanism of the synthesis of hydrocarbons by the reduction of carbon monoxide, Smith, Hawk, and Golden<sup>15/</sup> working at the Bureau of Mines, found that on cobalt catalysts, ethylene when mixed with synthesis gas participated in the synthesis to form normally liquid hydrocarbons, whereas on an iron-copper catalyst the added ethylene appeared largely as ethane.

This difference in reaction indicated that the mechanism of hydrocarbon formation on an iron-copper catalyst is essentially different from that on a cobalt-copper-manganese oxide catalyst.

Japanese studies included experimental work on the properties of iron-copper catalysts and copper-cobalt catalysts promoted with oxides of magnesium, thorium, tungsten, uranium, molybdenum, and chromium. In Great Britain the fuel-research laboratory at Greenwich conducted extensive laboratory tests on the activity of cobalt catalysts and on the synthesis of lubricating oils from the lower boiling oils produced in the Fischer-Tropsch process.

#### INDUSTRIAL DEVELOPMENT

By 1932 Fischer<sup>16/</sup> and his coworkers had so improved the activity of the nickel and cobalt catalysts by better methods of preparation that a yield of liquid hydrocarbons of 100 to 153 cc. per cubic meter of gas mixture at 200° C. or 71 percent of the theoretical was obtained. Considering their process sufficiently well developed on a laboratory scale, they recommended pilot-plant experimentation.

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<sup>12/</sup> See footnote 8.

<sup>13/</sup> See footnote 8.

<sup>14/</sup> See footnote 8.

<sup>15/</sup> See footnote 8.

<sup>16/</sup> See footnote 8.

The catalyst employed in the pilot plant was nickel-manganese-aluminum oxide supported on kieselguhr and prepared by precipitating from the nitrates with potassium carbonate. Synthesis gas was prepared by conversion of coke-oven gas with steam over coke and freed from organic sulfur by heating to 400° C. in the presence of an iron catalyst and subsequent scrubbing with alkaline ferrocyanide solution. Operating conditions were specified as 1 atmosphere pressure and a temperature of 190° to 210° C. The catalyst was reactivated every 1,000 hours by extraction of the solid paraffin with gasoline. The catalyst chambers, suspended in an oil bath for temperature control, were narrow boxes 1.2 by 10 by 500 centimeters. The gasoline product of the synthesis consisted mainly of straight-chain hydrocarbons, of which 15 to 38 percent were olefins. The fraction of the oil product boiling over 220° C. was better than gas oil for Diesel fuel. The solid paraffin had a melting point of 48° C. These materials were produced in the ratio of gasoline: oils boiling above 220°: paraffin = 4:1:0.2.

In 1933 the Ruhrchemie A. G.<sup>17/</sup> undertook to construct a plant of 1,000 tons of oil a year capacity at Oberhausen-Holtien, Ruhr, Germany. It was designed to produce motor fuel and lubricating oil. The catalyst was a nickel-aluminum-manganese-on-kieselguhr preparation, over which synthesis gas, consisting of 1 part of carbon monoxide and 2 parts of hydrogen, completely purified from sulfur (to about 1 grain per 1,000 cubic feet) was passed at 190° to 210° C. and atmospheric pressure. Several plants were subsequently built in the Ruhr, using coke from bituminous coal as the source of synthesis gas. Other plants were erected in Central Germany and in Silesia. At the end of 1936 there were five Fischer-Tropsch plants in Germany, with a total capacity of about 145,000 metric tons of primary oils a year. These were the Rheinpreussisen Colliery at Homberg, 30,000 metric tons of primary products consisting of gasoline, Diesel oil, soft and hard paraffin wax, oils for the production of fatty acids and for other chemical uses, from blast-furnace coke and coke-oven gas; Ruhr Benzin A. G. (subsidiary of Ruhrchemie) at Oberhausen-Holtien and the Viktor Colliery at Castrop-Rauxel, each 30,000 tons of primary oil per year from coke; Braunkohle-Benzin A. G., known as "Brabag", at Ruhland, north of Dresden, 25,000 tons of primary oils using synthesis gas produced by the gasification of brown-coal briquets; and Mitteldeutsche Treibstoff und Oel Werke (subsidiary of Wintershall A. G.) at Kassel, 30,000 tons of primary oils using synthesis gas resulting from the gasification of brown coal.

The capacity of these plants was increased in 1937 and 1938 so that the total yearly oil and gasoline output was raised to 300,000 tons. Toward the end of 1938 additional plants were under construction that would increase the yearly output to a total of 525,000 metric tons.

In 1938 Germany halted construction of Fischer-Tropsch plants and engineering development of the process, in favor of coal hydrogenation. In April 1945<sup>18/</sup> members of the United States Technical Oil Mission inspected seven synthetic

<sup>17/</sup> See footnote 8.

<sup>18/</sup> Technical Oil Mission. Investigation of Ruhr Synthetic Oil Plants. T.I.I.C. Report 17: Natl. Petrol. News, vol. 37, No. 45, 1945, sec. 2, pp. R861-R864.

oil plants in the Ruhr Valley which used the Fischer-Tropsch process. These were: Sterkrade-Holten Ruhr-Benzin-Ruhrchemie A. G.; Gutehoffnungschutte A. G. - Sterkrade; Castrop-Rauxel Plant-Klocknerwerke A. G.; Wanne-Eichel Plant-Krupps; Hosch-Benzin and Kamen-Dortmund Plants; and Lurgi Frankfurt. The Ruhr plants used a cobalt-thoria-magnesia-kieselguhr catalyst in atmospheric and medium-pressure (10 atmospheres) reactors. The medium-pressure ovens consisted of a nest of pairs of vertical tubes, (fig.1), one inside the other, the catalyst lying in the annular space between the tubes. No full-scale plants were operated with an iron catalyst, but plans had been projected to build a Fischer-Tropsch plant in Italy that would use an iron-copper-calcium oxide-kieselguhr catalyst. Although the capacity of German Fischer-Tropsch plants was about 700,000 tons a year, in 1943 only 368,000 tons were produced<sup>19/</sup> as compared with 3,088,000 tons produced by the coal-hydrogenation process.

Ruhrchemie designed the Currieres-Kuhlmann Fischer-Tropsch plant at Harnes France,<sup>20/</sup> for a basic output of 20,000 tons a year. Basic raw material for this plant was coke from the high-temperature carbonization of French coal. The synthesis gas obtained had the following composition: carbon monoxide 27 percent, hydrogen 54 percent, carbon dioxide 14 percent, and nitrogen and methane 5 percent. Sulfur was removed by washing the gas with ammonia water to remove hydrogen sulfide, followed by scrubbing the gas with  $\text{Fe}_2\text{O}_3$ , and finally by passing the gas through an  $\text{Fe}_2\text{O}_3$  catalyst containing about 25 percent of  $\text{Na}_2\text{CO}_3$  at 200° to 300° C., to remove organic sulfur. The catalyst consisted of 18 percent cobalt, 1.8 percent magnesium oxide, 0.9 percent thorium oxide, and 79.3 percent kieselguhr. The reactors were rectangular boxes about 20 feet long by 6 feet deep by 9 feet high and consisted of 600 2-mm. steel sheets spaced 7 mm. apart and pierced by tubes filled with hot water. A cross-sectional view of one of these reactors is shown in figure 2. Each reactor had a total surface of 5,000 square meters and weighed 50 metric tons. The catalyst was placed in the voids between the baffles and the tubes. Synthesis took place in a two-stage operation. Two-thirds of the converters were used in the first stage. The effluent from the first stage was cooled and condensed and the resulting heavy product removed. The gases were next sent to the remaining one-third of the converters for the second pass. As before, the products were condensed and separated. The residual gas contained considerable gasoline and butane, which were collected in an activated charcoal system and later steam stripped. The average yield from the German Fischer-Tropsch plants was 150 grams (per cubic meter of  $2\text{H}_2$  plus 1CO synthesis gas) of hydrocarbons ranging from propane-propylene to waxes of 2,000 molecular weight.

It was reported that in 1944 Japan was operating three Fischer-Tropsch plants whose total yearly capacity was about 110,000 tons of primary products. Actual production amounted to only a small fraction of this figure. The peak production of the war years, reached in 1944, was 17,810 kiloliters (12,467 tons) of finished products (including gasoline, kerosine, fuels, and Diesel oils).

<sup>19/</sup> See footnote 8.

<sup>20/</sup> National Petroleum News, Fischer-Tropsch Plants Gave Nazis Diesel, Motor Fuels, Lubricants: Vol. 37, No. 45, sec. 2, p. R924.

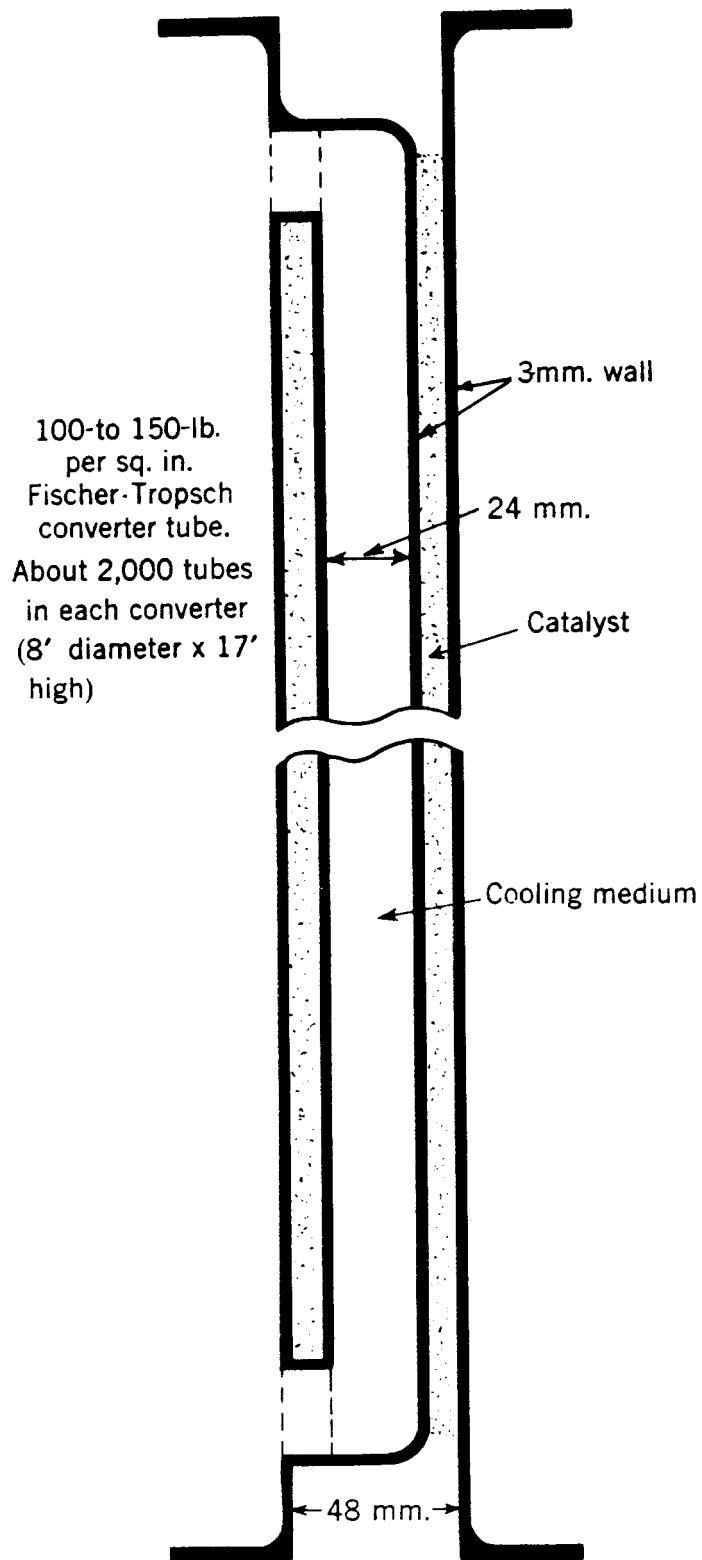


Figure 1. - 100- to 150-pound per square inch Fischer-Tropsch tube.



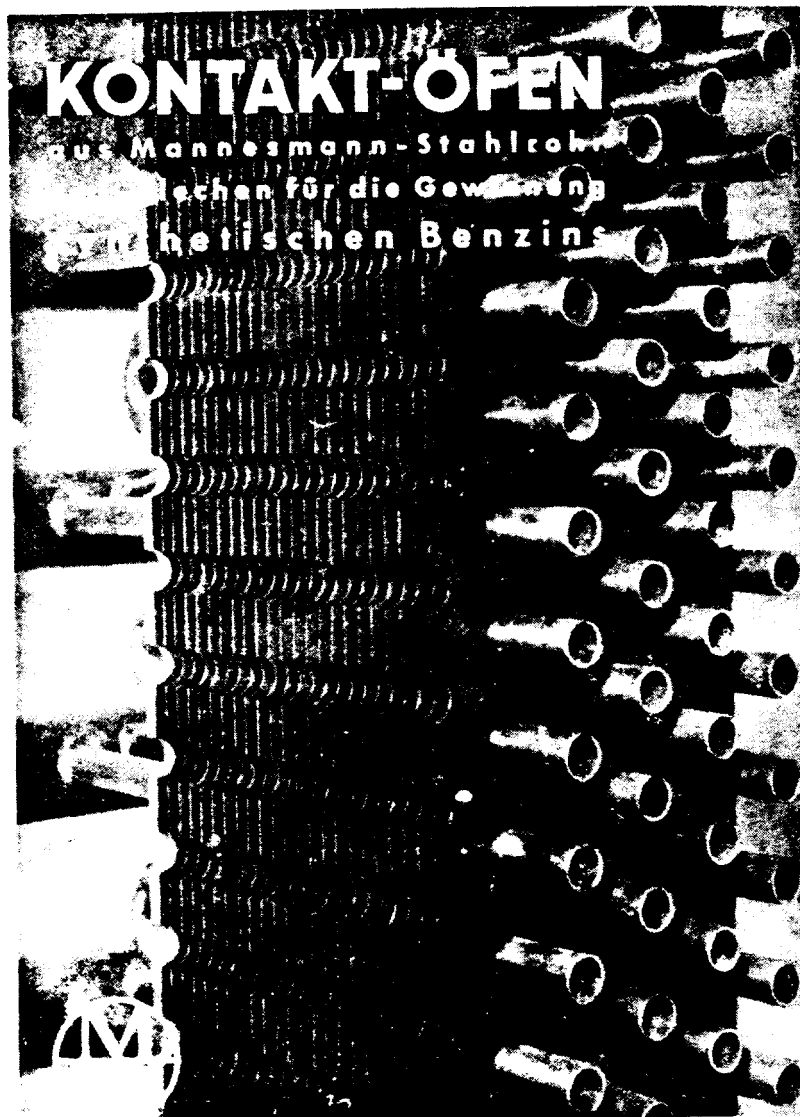


Figure 2. - Kontakt-Ofen (catalyst reactor).

In 1938 Great Britain was operating an experimental plant of 150 gallons per day capacity in which the Robinson-Bindley process was tested. It differed from the Fischer-Tropsch process in several respects and particularly in that it operated with a higher carbon monoxide:hydrogen ratio. A small experimental plant of about 4 gallons per day capacity was erected by the Fuel Research Board.

In the Bureau of Mines, United States Department of the Interior investigators resumed experimental work in 1942 after a lapse of 12 years. Iron and cobalt catalysts were studied on a laboratory scale. An engineering laboratory for developing process improvements and for pilot-plant operation on the scale of a few quarts of oil a day was operated for about 8 months. A pilot plant under construction at Bruceton, near Pittsburgh, will have a capacity output of  $1\frac{1}{2}$  barrels of Fischer-Tropsch oil per day.

The cost of production per gallon of gasoline and Diesel oil, with natural gas at 5 cents per 1,000 cubic feet, was given by the Standard Oil Co. of New Jersey in 1942 as about 9 cents.<sup>21/</sup> In some areas where natural gas may be obtained for less than 3 cents per 1,000 cubic feet, the cost per gallon of gasoline and Diesel oil should be about 8 cents. The cost of gasoline production, using natural gas at 3 to 5 cents per 1,000 cubic feet as raw material, was reported to be close to the present cost of production of gasoline from petroleum. Natural gas at 3 cents per 1,000 cubic feet is equivalent to coal at about 60 cents per ton. If and when natural-gas reserves are exhausted, coal could be substituted for natural gas with a gasoline cost of about 10 cents per gallon, exclusive of possible cost-lowering technological advances, according to an estimate by Hydrocarbon Research, Inc.<sup>22/</sup>

Hydrocarbon Research, Inc., headed by P. C. Keith,<sup>23/</sup> will probably have the first commercial-size Fischer-Tropsch plant in the country when it completes its projected building program at Brownsville, Tex. According to announced plans, ground for a \$15,000,000 plant was to be broken in February and operations were to begin some time in 1946. The plant will be designed to produce about 5,000 barrels per day of 80-octane number gasoline and 1,000 barrels per day of Diesel oil and is expected to turn out an additional 200,000 pounds of crude alcohols daily. Daily raw material requirements will include 65,000,000 cubic feet of natural gas and 40,000,000 cubic feet of oxygen. The large oxygen requirement results from the use of a controlled oxidation process rather than a modified water-gas reaction for producing the synthesis gas. By using heat from the exothermic synthesis reaction, steam is obtained to provide power for the compressors, and the oxygen is said to be produced for only 5 cents a thousand cubic feet. The experimental-plant (10 gallons a day) and pilot-plant (10 barrels a day) phases of the work were carried out at Olean, N. Y.

The pilot plant is reported to contain a fixed fluidized bed of iron catalyst with an internal heat exchanger, and the operating conditions are about 300° C., 20 atmospheres, and some recycling of end gas.

<sup>21/</sup> See footnote 3.

<sup>22/</sup> Collier's, Nov. 24, 1945, p. 26; Business Week, July 21, 1945, p. 74; Petrol. Refiner, vol. 25, March 1946, p. 142.

<sup>23/</sup> See footnote 22.

## PROCESS DEVELOPMENT IN GERMANY

The only outstanding process development during the Second World War using the cobalt catalyst consisted in recycling about 3 volumes of end-gas from the first stage per volume of fresh gas, with product condensation after each cycle.<sup>24/</sup> On a pilot-plant scale this development resulted in an increase of 30 percent in the throughput without sacrifice in yield or in an increase of the yield from 150 to 170 grams per cubic meter of  $2H_2 + 1CO$  gas at the same throughput. Using the recycle process and charging  $1H_2 + 1CO$  gas mixture, the olefin content was increased from 20 to 55 percent in the liquid fractions of the product. The use of  $1H_2 + 1CO$  gas in the older process without recycling resulted in a low catalyst life because of carbon deposition. The recycle gases lowered the partial pressure of the carbon monoxide sufficiently to avoid excessive formation of carbon. The recycle process gasoline had a 50 to 55 motor octane number as compared with 40 for the older process without recycle. Refining the gasoline from the recycle process by passage over activated clay increased the octane number to 70 without appreciable decrease in yields.

Process development using iron catalysts was under way in Germany. A pilot plant operated by I. G. Farbenindustrie utilized a hot-gas recycle process and a sintered-iron catalyst.<sup>25/</sup> Iron powder obtained by decomposition of iron carbonyl was made into a paste with a dilute solution of sodium borate, which was extruded into granules. The dried granules were heated at  $850^\circ C.$  in a hydrogen atmosphere for several hours before use in the synthesis, which was conducted at  $320^\circ C.$ , 20 atmospheres, and  $3/4$ -second contact time, with recycle of the gases through a heat exchanger to remove heat of reaction. Conversion per pass was about 1 percent, so that about 100 volumes of recycle gas to one of fresh gas entered the converter. The space-time yield was about 1 kilogram of product per liter of catalyst per day (this was three to five times that from the Ruhrchemie cobalt process). The distribution of products was as follows: Unrefined highly olefinic gasoline of 75 to 81 research octane number, 44 percent (yielding 40 percent of refined gasoline of 84-86 research octane number); Diesel oil of 47 to 53 cetene number and minus  $25^\circ C.$  pour point;  $C_4$ , 7 percent;  $C_3$ , 8 percent ( $C_4$  and  $C_3$  were 80 percent unsaturated);  $C_2H_4$ , 5 percent;  $CH_4 + C_2H_6$ , 17 percent; alcohols, chiefly ethanol and propanol, 7 percent; paraffin wax, 1 percent.

I. G. Farbenindustrie was also engaged in a liquid-phase operation in which iron powder prepared from iron carbonyl was mixed with oil and the gas contacted with this liquid suspension. More Diesel oil (60 to 70 cetene number) was obtained by this process than from the hot-gas recycle process. The gasoline from the liquid-phase process had a research octane number of 90. In another I. G. F. development a cooling oil was passed concurrent with the

<sup>24/</sup> Atwell, H. V., Powell, A. R., and Storch, H. H., (compilers), Fischer-Tropsch Report 1: TAC Report Sn MC-1, July 19, 1945; Hall, C. C., and Haensel, V. (compilers), The Fischer-Tropsch Plant of Ruhrchemie A. G., Sterkrade-Holteln, Ruhr: TAC Report Sn MC-11, July 5, 1945.

<sup>25/</sup> See footnote 24.

synthesis gas over granules of an iron catalyst (synthetic ammonia type, doubly promoted with  $\text{Al}_2\text{O}_3$  and  $\text{K}_2\text{O}$ ). The cooling was effected by recycling the heated oil through an external heat exchanger.

Lurgi development work involved recycle operation of the Fischer-Tropsch process, using a Ruhrchemie conventional, externally cooled 10 to 20 atmosphere converter and both cobalt and iron catalysts. Both the Lurgi and I. G. Farbenindustrie companies found that, by employing iron catalysts that were not highly active and operating with recycle at temperatures of  $275^\circ$  to  $320^\circ$  C., the proportion of gasoline in the product could be greatly increased and that of paraffin wax reduced to less than one percent. The gasoline was a highly olefinic one of about 75 motor octane number. In the United States similar processes have been developed using fluidized-iron catalyst systems.

Two new processes were developed for the manufacture of higher alcohols by the Fischer-Tropsch synthesis. The Synol process<sup>26/</sup> was operated at 18 to 25 atmospheres pressure, using a gas mixture of  $\text{CO} + 0.8\text{H}_2$  and temperatures of  $200^\circ$  to  $235^\circ$  C. The catalyst consisted of granules of fused  $\text{Fe}_3\text{O}_4\text{-Al}_2\text{O}_3\text{-K}_2\text{O}$  in the proportions of 97 to 2.5 to 0.4. Two stages of operation were used, each with a recycle of about 50 volumes of end-gas per volume of fresh gas. The products consisted of liquid hydrocarbons (50 to 65 percent) and alcohols (35 to 50 percent) boiling in the range  $50^\circ$  to  $350^\circ$  C. The alcohols were chiefly normal, but there was some branching in the hydrocarbon product.

The second development, the OXO process<sup>27,28/</sup> was developed by Ruhrchemie. It was intended for the production of higher alcohols for use in detergent manufacture, particularly those in the group from  $\text{C}_{12}$  to  $\text{C}_{18}$ . In this process carbon monoxide and hydrogen were added to olefins followed by reduction of the aldehyde thus produced to the corresponding alcohol. A narrow fraction of the olefins from the Fischer-Tropsch process, the  $\text{C}_{12}$  to  $\text{C}_{18}$  cut, was mixed with three to five percent of cobalt-thorium oxide-magnesium oxide-kieselguhr (in the proportions of 30 to 2 to 2 to 66) catalyst, and reacted with a mixture of  $\text{CO} + \text{H}_2$  gas at a pressure of 200 atmospheres and a temperature of  $150^\circ$  C. The product, consisting of 80 percent aldehydes and 20 percent alcohols, was hydrogenated over a nickel catalyst at the same pressure and somewhat higher temperature,  $170^\circ$  C.

A process for the synthesis of isoparaffins, chiefly isobutane and isopentane was developed on a laboratory-scale at the Kaiser Wilhelm Institute fur Kohlenforschung in Germany.<sup>29/</sup> This process operated at 300 atmospheres

<sup>26/</sup> Holroyd, R. (ed.), Report on Investigations by Fuels and Lubricant Teams at the I. G. Farbenindustrie A. G. Works at Leuna: Sept. 24, 1945.

<sup>27/</sup> See footnote 26.

<sup>28/</sup> Combined Intelligence Objectives Subcommittee, Report on Visit to Oil Targets in the Ruhr and Hanover Areas. I.I.I.C. Index No. 3; Nat. Petrol. News, vol. 37, No. 45, sec. 2, 1945, pp. R926-R930.

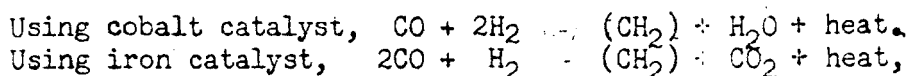
<sup>29/</sup> U. S. Naval Technical Mission in Europe, Wartime Research on Synthetic Fuels by the Kaiser Wilhelm Institute fur Kohlenforschung: Tech. Report No. 110-45, Oil and Gas Jour., vol. 37, Jan. 19, 1946, pp. 86-89.

pressure of  $1\text{H}_2 + 1.2\text{CO}$  gas, and  $400^\circ$  to  $450^\circ$  C., using thoria-alumina and zinc oxide-alumina catalysts. Another process using these same catalysts at  $500^\circ$  C. and 30 atmospheres pressure of  $1\text{CO} + 1\text{H}_2$  gas was reported to produce aromatic hydrocarbons, but only poor yields were obtained. Both of these processes now have little industrial significance.

#### DISCUSSION OF MECHANISM OF FISCHER-TROPSCH PROCESS

The main components of the Fischer-Tropsch catalysts that are active in the synthesis of liquid hydrocarbons from hydrogen and carbon monoxide are cobalt, iron, nickel, and ruthenium.

The reaction between hydrogen and carbon monoxide to form hydrocarbons may be represented empirically by means of the following equations:



in which the formula  $(\text{CH}_2)$  represents the hydrocarbons produced. The theoretical yield of primary liquid products from 1,000 cubic feet of  $2\text{H}_2 + 1\text{CO}$  synthesis gas is 2 gallons.<sup>30/</sup> However, as incomplete reaction and gas formation reduce the yield of the products, in practice the yield of hydrocarbons other than methane, ethane, and ethylene is 1.4 to 1.5 gallons per 1,000 cubic feet of synthesis gas. The heat to be removed is about 7,000 B.t.u. per pound of product, or 20 percent of the heat of combustion of the synthesis gas.<sup>31/</sup>

One of the most widely accepted explanations of the mechanism of the synthesis is that the reaction takes place by way of metal carbide formation.<sup>32/</sup> Iron and cobalt form relatively unstable carbides of nonionic crystal structure, when exposed to carbon monoxide in the temperature range of the synthesis. Below  $350^\circ$  C. these carbides react with hydrogen to yield quantitatively methane plus a few percent of ethane. Above  $350^\circ$  C. the carbides decompose to carbon. It is probably significant that the optimum temperature ranges in this synthesis --  $185^\circ$  to  $215^\circ$  C. for cobalt and  $240^\circ$  to  $320^\circ$  C. for iron catalysts -- are below  $350^\circ$  C. Reaction of the carbides with dilute acids results in the formation of normally liquid hydrocarbons.

In the synthesis when a freshly reduced catalyst is exposed to hydrogen and carbon monoxide the first hydrocarbon product is methane. However, within a few hours, higher molecular weight hydrocarbons appear. On the basis of the carbide theory, it appears that in the first stage of the process carbon monoxide is adsorbed on the catalyst, forming the carbide, and that hydrogen subsequently reacts with the carbide to form methylene  $(\text{CH}_2)$  groups which either

<sup>30/</sup> Komarewsky, V. I., Production of Synthetic Liquid Fuel from Natural Gas: Petrol. Refiner, Vol. 24, May 1945, pp. 96-98.

<sup>31/</sup> See footnote 4.

<sup>32/</sup> Storch, H. H., Catalysis in Synthetic Liquid Fuel Processes: Ind. Eng. Chem., Vol. 37, April 1945, pp. 340-351.

combine with hydrogen to give methane or polymerize, with the formation of higher hydrocarbons. Both reactions occur at the same time and at about the same rate. When the catalyst surface contains larger amounts of chemisorbed hydrogen, the methanization reaction is favored. In the early stages of operation with a fresh catalyst chemisorbed hydrogen is present in large amounts. Subsequently, carbide and hydrocarbon formation reduces the volume of active hydrogen on the surface. As long as the carbide is constantly regenerated, higher hydrocarbons can be produced. The absence of higher hydrocarbon formation during the initial period of operation with an active catalyst is explained by the time necessary for covering most of the catalyst surface with polymethylene groups to slow the reduction of methylene to methane.

Although both cobalt and iron form metal carbides; evidence exists that the mechanism of the synthesis on cobalt catalysts differs from that on iron catalysts. The first obvious difference is that during the synthesis water is the chief oxygenated product when cobalt catalysts are used and carbon dioxide is formed with iron catalysts. The ratio of the partial pressures of methane to ethane plus ethylene in the off-gases from the synthesis differs markedly for different catalysts, as shown in table 1. This ratio for cobalt is almost 20 times larger than that for iron-copper. This fact should be correlated with the discovery that ethylene reacts in admixture with carbon monoxide and hydrogen on a cobalt-copper-manganese oxide catalyst to form large quantities of hydrocarbons and of oxygen-containing compounds which dehydrate in the process to form hydrocarbons. Alone, or in admixture with either carbon monoxide or hydrogen, ethylene does not form higher hydrocarbons when passed over the same catalyst at 200° to 250° C. and atmospheric pressure, nor does ethylene enter into reaction on iron-copper catalysts. In the latter case the ethylene appears as ethane.

TABLE 1. - Bureau of Mines analyses of residual hydrocarbon gas from Fischer-Tropsch synthesis after one pass through catalysts (in percent by volume)

Catalyst	Co-ThO <sub>2</sub> -kieselguhr	Fe	Fe-Cu
Methane.....	76.0	66.0	20.2
Ethane.....	5.7	7.3	31.5
Ethylene.....	1.9	7.3	9.3
Propane.....	5.8	6.7	12.4
Propylene.....	8.6	11.0	21.2
Butanes.....	.7	-	1.5
Butenes.....	1.3	1.7	3.9
Ratio, C <sub>1</sub> :C <sub>2</sub> .....	10.0	4.5	.5

#### PRODUCTION OF SYNTHESIS GAS

The Fischer-Tropsch process uses as raw material mixtures ranging in composition from 1 part of carbon monoxide to 1 or 2 parts of hydrogen. A typical analysis of the synthesis gas used on the commercial scale by the Ruhrchemie A. G. in Germany is as follows: 55 percent hydrogen, 27.5 percent carbon