SYNTHETIC LIQUID FUELS FROM HYDROGENATION OF CARBON MONOXIDE

Part 1.—Review of Literature; Bureau of Mines Research on Effect of Catalyst Preparation, Reduction, and Induction Procedures on Activity; Correlation of Physical Properties of the Catalysts with Their Activity [1]

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INTRODUCTION

The production of gasoline, Diesel oil, and wax by the catalytic hydrogenation of carbon monoxide was developed and applied on a large scale in Germany during the period 1932–45. In the United States during several years (1938–44) of industrial development work, the process was so greatly improved that, by the use of natural gas purchased at 3 to 5 cents per 1,000 cubic feet to produce the necessary hydrogen and carbon monoxide for the synthesis, gasoline could be obtained at an estimated cost not greater than that of current processes for converting petroleum to gasoline.

Although much basic information concerning the synthesis was obtained in the course of the industrial development, very large portions of the subject remain to be explored. Thus, there is a dearth of precise knowledge of the mechanism of the reaction, and several different modes of conducting the synthesis have received only very meager and hasty consideration in the industrial development work. Because of the importance of information on synthetic liquid-fuel processes in insuring an adequate supply of motor fuels and lubricating oils in the United States, the Bureau of Mines has been directed to do research and process development work on this synthesis.

This technical paper contains a detailed record of experimental work done in 1943 to 1946 on the effect of mode of catalyst preparation, reduction, and induction on activity in the synthesis and on boiling range of the product. The paper also includes data on the X-ray diffraction patterns, magnetic susceptibility, surface area, and porosity of the catalysts. Preceding the record of experimental work is a review of published information on the synthesis and the character and utilization of the products.

Process development and experimental work on the mechanism of the synthesis have been conducted for about 1 year. The results will

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be published in a separate technical paper when enough new information has been obtained.

Titles of footnote references enclosed in brackets are translations of the title from the language in which the work cited was published.

ACKNOWLEDGMENTS

The authors wish to acknowledge help given by many persons in the planning and execution of the catalyst-testing program. Cordial interest and administrative assistance were provided by the following Bureau of Mines workers: A. C. Fieldner, chief of the Fuels and Explosives Branch; W. C. Schroeder, chief of the Office of Synthetic Liquid Fuels; H. P. Greenwald, superintendent of the Central Experiment Station; L. L. Hirst, former, and M. A. Elliott, present assistant chief of the Synthetic Liquid Fuels Research and Development Division; and J. H. Crowell, head of the Gas Synthesis Section of the Research and Development Division.

The following Bureau of Mines workers were directly engaged in conducting the experiments of the catalyst-testing program: R. E. Solomon, A. Krieg, W. E. O'Neill, W. H. Tarn, G. E. Welch, L. Shaw, B. Seligman, and C. DeLeuze. W. K. Hall assisted in surface-area and porosity measurements; W. C. Peebles and W. E. Dieter assisted in obtaining X-ray diffraction patterns and measuring magnetic susceptibilities of catalysts; and J. T. McCartney prepared the electron micrographs of catalysts and other preparations. Gas analyses were made, using the mass spectrometer, under the direction of R. A. Friedel, by E. D. Glick, C. R. Humbert, H. R. Borgman, and S. Breakstone. Miscellaneous chemical analyses were done by M. E. Kundick, F. Jones, T. Horlenko, and W. Schoeneweis. Literature and patent abstracts were made by J. L. Wiley and H. C. Anderson. German documents were translated by M. Leva and W. Oppenheimer.

Many of the oil and gas companies in the United States and the British Fuel Research Laboratory in England supplied unpublished information and advice which were helpful in planning the catalyst-testing program.

REVIEW OF LITERATURE

INTRODUCTION

1913–28

The possibility of producing hydrocarbons other than methane by the catalytic reduction of carbon monoxide was disclosed by the Badische Anilin und Soda Fabrik in 1913[6] and by Fischer and Tropsch in 1923.[7] For several years these experimenters had been studying the reduction of carbon monoxide in the presence of alkali-iron catalysts at 400° to 450° C. and 100 to 150 atmospheres pressure.[8] "Synthol," which was the product of this reaction, consisted of a mixture of alcohols, aldehydes, fatty acids, and hydrocarbons.

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[6] Badische Anilin und Soda Fabrik [Hydrocarbons and Their Derivatives]: German Patent 293,787, Mar. 8, 1913.

[7] Fischer, F., and Tropsch, H. [The Preparation of Synthetic Oil Mixtures (Synthol) from Carbon Monoxide and Hydrogen]: Brennstoff Chem., vol. 4, 1923, pp. 276–285.

[8] Work cited in footnotes 6 and 7.

Fischer and his coworkers observed that the content of oxygenated compounds of synthol decreased with decreasing pressure and that the product obtained at pressures below about 7 atmospheres was mainly a paraffinic oil. Because the reaction velocity decreased rapidly with decreasing pressure, it was essential to look for more active catalysts. In 1925–26, Fischer and Tropsch[9] and Fischer[10] published results obtained by the use of more active catalysts prepared from iron or cobalt mixed with various supporting materials, and of mixtures of hydrogen and carbon monoxide at atmospheric pressure and at temperatures from 250° to 300° C. The product was almost free from oxygenated compounds and consisted largely of hydrocarbons ranging from ethane to solid paraffin. Fischer thought that a likely mechanism of this chemical reaction was the initial formation of metallic carbides and either water or carbon dioxide and subsequent production of paraffins by reaction between the carbides and hydrogen to produce methylene, which at once polymerized to higher hydrocarbons. Despite the fact that paraffinic hydrocarbons above methane could not be produced by passing hydrogen alone over the metal carbides, experimental work has provided considerable support for the reaction mechanism postulated by Fischer. Elvins and Nash[11] also reported the formation of oily material on a cobalt-copper-manganese oxide catalyst at atmospheric pressure and at temperatures from 245° to 284° C. The yields were small, and the product included some oxygen-containing compounds in addition to hydrocarbons. Subsequent work by Fischer and Tropsch[12] confirmed the presence of oxygenated organic compounds in the product from the atmospheric pressure synthesis and showed[13] that at 10 to 15 atmospheres pressure the products were intermediate in character. At atmospheric pressure the product consists largely of hydrocarbons, and at high pressures mainly oxygenated compounds are obtained.

1928–32

Smith, Davis, and Reynolds[14] reported the presence of olefinic as well as paraffinic hydrocarbons in the product. At about the same time Elvins[15] and Erdely and Nash[16] published the results of further work on the preparation and activity of various catalysts and on the

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[9] Fischer, F., and Tropsch, H. [Hydrocarbons]: German Patent 484,337, July 22, 1925. [The Synthesis of Petroleum at Atmospheric Pressures from Gasification Products of Coal]: Brennstoff Chem., vol. 7, 1926, pp. 97–104. [Direct Synthesis of Petroleum Hydrocarbons at Ordinary Pressure, Parts 1–2]: Ber. Deut. chem. Gesell., vol. 59B, 1926, pp. 830–831, 832–836. [Some Properties of the Synthetic Petroleum Hydrocarbons Prepared from Carbon Monoxide at Ordinary Pressure]: Ber. Deut. chem. Gesell., vol. 59B, 1926, pp. 923–925.

[10] Fischer, F., The Synthesis of Petroleum: Proc. First Internat. Conf. Bituminous Coal, 1926, pp. 234–246.

[11] Elvins, O. C., and Nash, A. W., Synthetic Fuel from Carbon Monoxide and Hydrogen: Fuel, vol. 5, 1926, pp. 263–265. The Reduction of Carbon Monoxide: Nature, vol. 118, 1926, p. 154.

Nash, A. W., Recent Developments in the Formation of Synthetic Fuel and Carbon Monoxide and Hydrogen: Chem. and Ind., vol. 45, 1926, pp. 876–878.

[12] Fischer, F., and Tropsch, H. [Hydrocarbons from Hydrogen and Oxides of Carbon]: German Patent 524,468, Nov. 2, 1926. [Reduction in Hydrogenation of Carbon Monoxide]: Brennstoff Chem., vol. 7, 1926, pp. 299–300.

Fischer, F. [The Synthesis of Petroleum and Hydrocarbons]: Brennstoff Chem., vol. 8, 1927, pp. 1–5.

Fischer, F., and Tropsch, H., with Ter-Nedden, W. [Synthesis of Paraffin Hydrocarbons of High Molecular Weight with Carbon Monoxide]: Ber. Deut. chem. Gesell., vol. 60B, 1927, pp. 1330–1334.

[13] Fischer, F., and Tropsch H. [The Formation of "Synthol" on Carrying Out the Petroleum Synthesis Under Pressure and the Synthesis of Hydrocarbons of High Molecular Weight from Water Gas]: Brennstoff Chem., vol. 8, 1927, pp. 165–167.

[14] Smith, D. F., Davis, J. D., and Reynolds, D. A., Synthesis of Higher Hydrocarbons from Water Gas: Ind. Eng. Chem., vol. 20, 1928, pp. 462–464.

[15] Elvins, O. C., Hydrocarbons Synthesis from Carbon Monoxide and Hydrogen: Jour. Soc. Chem. Ind., vol. 46, 1927, pp. 473T–478T.

[16] Erdely, A., and Nash, A. W., Catalysts Used in the Synthesis of Higher Hydrocarbons from Water Gas: Jour. Soc. Chem. Ind., vol. 47, No. 32, 1928, pp. 219T–223T.

character of the products obtained at atmospheric pressure and at 280° to 320° C. In 1928 Fischer and Tropsch [17] reported the results of an extensive examination of the gaseous and liquid hydrocarbon products of the synthesis at 190° C. on an iron-copper catalyst at atmospheric pressure. No hydrocarbons other than olefins and paraffins were found. The gaseous product contained C_2H_6, 42.5; C_3H_8, 19.5; C_4H_{10}, 2.0: C_2H_4, 6.0; C_3H_6, 21.0; and C_4H_8, 9.0 volume percent. The liquid product boiling between 60° and 185° C. contained 30 percent paraffins that were for the most part octane, nonane, and isononane, which were positively identified. The remaining 70 percent was olefins. No diolefins were present. No analytical work other than examination for unsaturates was done on the higher-boiling liquid product. Water-soluble oxygenated products amounted to 2 percent of the total products. In the same year (1928), Smith, Hawk, and Reynolds [18] presented detailed data 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 hydrocarbon product by Tropsch [19] and Tropsch and Koch [20] resulted in identification of various olefinic and paraffinic hydrocarbons; it showed the absence of napthenes, but small quantities of benzene and toluene were found.

The hydrocarbon fraction boiling below 100° C. was analyzed by Koch and Hilberath;[21] n-pentane, n-hexane, and n-heptane were the predominant n-paraffins. A few pure isoparaffins were isolated, and multibranched paraffins were present only in traces. The olefins consisted mainly of unbranched alpha- and beta-olefins.

Some additional work on the high-pressure synthesis was done by Audibert and Raineau [22] with catalysts such as iron phosphate or iron borate at about 150 atmospheres. The products were mixtures of hydrocarbons and oxygenated organic compounds, chiefly alcohols. Catalysts for the atmospheric-pressure synthesis were developed by Kodama,[23] who found that the activity of nickel and of cobalt catalysts is enhanced by the promoters Cu, ThO_2, and MgO. In looking for clues as to the reaction mechanism of the synthesis of hydrocarbons by

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[17] Fischer, F., and Tropsch, H. [The Composition of Products Obtained by the Petroleum Synthesis]: Brennstoff Chem., vol. 9, 1928, pp. 21–24.

[18] Smith, D. F., Hawk, C. O., and Reynolds, D. A., Synthesis of Higher Hydrocarbons from Water Gas. Part 2: Ind. Eng. Chem., vol. 20, 1928, pp. 1341–1348.

[19] Tropsch, H. [Composition of the Products Obtained in the Synthesis of Petroleum]: Ges. Abhandl. Kenntnis, Kohle, vol. 9, 1930, pp. 561–570.

[20] Tropsch, H., and Koch, H. [Synthetic Benzine from Water Gas]: Brennstoff Chem., vol. 10, 1929, pp. 337–346.

[21] Hilberath, F. [Composition of Synthetic Benzine from Carbon Monoxide and Hydrogen (Kogasin) and Suitability of Its Monoolefins for Production of Lubricating Oils]: Thesis, Kiel, 1940, 79 pp.

Koch, H., and Hilberath, F. [Hydrocarbons Boiling Below 100° in Synthetic Gasoline from Carbon Monoxide and Hydrogen (Kogasin)]: Brennstoff Chem., vol. 22, 1941, pp. 135–139, 145–152. [The Polymerization of Monoolefins to Viscous Oils]: Brennstoff Chem., vol. 23, 1942, pp. 67–73.

[22] Audibert, E., and Raineau, A. [Study of the Action of Iron Catalyzers on Mixtures of Carbon Monoxide and Hydrogen]: Ann. combustibles liquides, vol. 3, 1928, pp. 367–428. The Action of Iron Catalyst on Mixtures of Carbon Monoxide and Hydrogen: Ind. Eng. Chem., vol. 21, 1929, pp. 880–885.

[23] Kodama, S. [The Catalytic Reduction of Carbon Monoxide Under Atmospheric Pressure. Parts I and II. Studies by the Heating-Curve Method of the Catalytic Activity of a Few Metals]: Jour. Soc. Chem. Ind., Japan, vol. 32, 1929, Suppl. binding, pp. 4, 6, 23. [Catalytic Reduction of Carbon Monoxide Under Ordinary Pressure. Part III. Preparation of Liquid Hydrocarbons with a Cobalt-Copper-Thoria Catalyst]: Jour. Soc. Chem. Ind., Japan, vol. 32, 1929, Suppl. binding, pp. 285–286. [The Catalytic Reduction of Carbon Oxides under Atmospheric Pressure. Part IV. The Influence of Beryllium Oxide, Magnesium Oxide, Zinc Oxide, and Cadmium on the Cobalt-Copper Catalyzer]: Jour Soc. Chem. Ind., Japan, vol. 33, 1930, Suppl. binding, p. 60. [Catalytic Reduction of Carbon Monoxide Under Ordinary Pressure. Part V. The Influence of Titanium Oxide, Zirconium Oxide, and Cerium Oxide]: Jour. Soc. Chem. Ind., Japan, vol. 33, 1930, Suppl. binding, pp. 202–203. [Catalytic Reduction of Carbon Monoxide Under Ordinary Pressure. Part VI. The Action of an Iron Catalyst on Carbon Monoxide Formation]: Jour. Soc. Chem. Ind., Japan, vol. 33, 1930, Suppl. binding, pp. 399–400.

the reduction of carbon monoxide, Smith, Hawk, and Golden [24] found that ethylene reacts in admixture with CO and H_2 on a cobalt-copper-manganese oxide catalyst to form large quantities of higher hydrocarbons and oxygen-containing compounds. The latter dehydrate in the process to form hydrocarbons. The dehydration may be accompanied by polymerization. Alone, or in admixture with either CO or H_2, ethylene does not form higher hydrocarbons when passed over the Co-Cu-MnO catalyst at 200° to 250° C. and atmospheric pressure. These experimenters also found that the mechanism of hydrocarbon formation on an iron-copper catalyst differs essentially from that on a cobalt-copper-manganese oxide catalyst, as ethylene does not enter into reaction on the former catalyst. They also found that the iron-copper catalyst produces largely carbon dioxide along with the hydrocarbons instead of water, which is the main oxygenated product from the cobalt-copper-manganese oxide catalyst. Considerable experimental work on the properties of iron-copper catalysts was done by Kodama and Fujimura.[25] The latter experimenter [26] also studied the preparation and properties of copper-cobalt catalysts promoted with oxides of magnesium, thorium, tungsten, uranium, molybdenum, and chromium. Fischer and his coworkers [27] also studied nickel and cobalt catalysts, using thoria and manganese oxide as promoters. By improved methods of preparation the activity of these catalysts was increased until at about 200° C. a yield of liquid hydrocarbons of 100 to 153 cc. per cubic meter of gas mixture or 71 percent of theoretical was obtained. Fujimura and Tsuneoka [28] obtained 145 cc. per cubic meter, using a Cu-Co-Th-U (1 : 8 : 0.2 : 0.1) catalyst.

Fischer and his coworkers in 1932 considered their process sufficiently well developed on a laboratory scale to merit pilot-plant experimentation. The use of various technically available gas mixtures for the synthesis was examined practically and theoretically.[29] The most practical process at that time seemed to be conversion of coke-oven gas with steam-oven coke. Organic sulfur was removed by heating the synthesis gas to 400° C. in the presence of an iron catalyst and subsequent scrubbing with alkaline ferricyanide solution. The

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[24] Smith, D. F., Hawk, C. O., and Golden, P. L., Mechanism of the Formation of Higher Hydrocarbons from Water Gas: Jour. Am. Chem. Soc., vol. 52, 1930, pp. 3221–3232.

[25] Fujimura, K. [The Catalytic Reduction of Carbon Monoxide at Atmospheric Pressure. Part VIII. The Iron-Copper Catalyst]: Jour. Soc. Chem. Ind., Japan, vol. 34, 1931, Suppl. binding, pp. 136–138. [Catalytic Reduction of Carbon Monoxide Under Ordinary Pressure. Part IX. Additional Tests with a Co-Cu-MgO Catalyst]: Jour. Soc. Chem. Ind., Japan, vol. 34, 1931, Suppl. binding, No. 7, pp. 227–229.

Kodama, S. [Catalytic Reduction of Carbon Monoxide Under Ordinary Pressure. Part VI. The Hydrocarbon-Forming Action of Iron Catalysts]: Inst. Phys. Chem. Research (Tokyo), Sci. Papers, vol. 14, No. 269, 1930, pp. 169–183.

Kodama, S., and Fujimura, K. [Catalytic Reduction of Carbon Monoxide Under Ordinary Pressure. Part VII. Effective Alkalies on Iron-Copper Catalysts]: Jour. Soc. Chem. Ind., Japan, vol. 34, 1931, Suppl. binding, pp. 14–16.

[26] Fujimura, K. [Catalytic Reduction of Carbon Monoxide under Ordinary Pressure. Part X. The Influence of Certain Materials on the Catalytic Action of Cobalt-Copper-Magnesium Oxide Catalysts]: Jour. Soc. Chem. Ind., Japan, vol. 34, 1931, pp. 384–386. [Synthesis of Benzine from Carbon Monoxide and Hydrogen at Ordinary Pressure. Part XI]: Jour. Soc. Chem. Ind., Japan, vol. 35, 1932, Suppl. binding, pp. 179–182.

[27] Fischer, F. [The Development of the Benzine Synthesis from Carbon Monoxide and Hydrogen at Atmospheric Pressure]: Brennstoff Chem., vol. 11, 1930, pp. 489–500.

Fischer, F., and Koch, H. [New Developments in the Adaptation of Cobalt Catalysts to the Benzine Synthesis]: Brennstoff Chem., vol. 13, 1932, pp. 61–68.

Fischer, F., and Meyer, K. [The Applicability of Nickel Catalysts to the Benzine Synthesis]: Brennstoff Chem., vol. 12, 1931, pp. 225–232.

[28] Fujimura, K., and Tsuneoka, S. [Benzine Synthesis from Carbon Monoxide and Hydrogen at Ordinary Pressures. Part XII]: Jour. Soc. Chem. Ind., Japan, vol. 35, 1932, Suppl. binding, pp. 415–416.

[29] Fischer, F., Pichler, H., and Reder, R. [Survey of the Possibilities of Supply of Suitable Carbon Monoxide-Hydrogen Mixtures for the Benzine Synthesis on Grounds of the Present-Day Position of Science and Technic]: Brennstoff Chem., vol. 13, 1932, pp. 421–428.

catalyst was nickel-manganese oxide-aluminum oxide supported on kieselguhr and made by precipitating the nitrates with potassium carbonate and subsequent washing, drying, and reduction. The operating temperature was specified as 190° to 210° C., and the pressure was 1 atmosphere. The catalyst was revivified every 1,000 hours by extraction of the solid paraffin with gasoline. The catalyst chambers were narrow boxes, 1 by 10 by 500 centimeters in dimension, suspended in an oil bath for purposes of temperature control.[30] The gasoline product of the synthesis contained 15 to 38 percent of unsaturated hydrocarbons, the remainder being mainly straight-chain hydrocarbons; the octane number was 58. Sulfur and gumming compounds were absent. The fraction of the oil product boiling over 220° C. was better than gas oil for fuel work. The melting point of the solid paraffin was 48° C. These materials were produced [31] in the ratio of gasoline : oils boiling above 220° C. : paraffin=4 : 1 : 0.2.

INDUSTRIAL DEVELOPMENT

GERMAN EXPANSION OF COMMERCIAL PLANTS USING FISCHER-TROPSCH SYNTHESIS

The decade of research by Fischer and others outlined above improved the catalyst activity and increased the technical development of the synthesis of hydrocarbons from carbon monoxide and hydrogen so that in 1933 the Ruhrchemie A. G. undertook construction of a plant of 1,000 tons per year capacity.[32] This plant was erected in Oberhausen-Holten, Ruhr, Germany. It was designed to produce motor fuel and lubricating oil.[33] The synthesis gas, consisting of 1 part of carbon monoxide and 2 parts of hydrogen, completely (about 1 grain per 1,000 cubic feet) purified from sulfur, was passed over a nickel-aluminum-manganese-on-kieselguhr catalyst at 190° to 210° C. and atmospheric pressure. The estimated cost of the motor fuel was 22 pfennigs per kilogram.[34] At the time the first plant was erected, the following problems had to be solved if large-scale operations were to be successful: [35] (1) Prolongation of the life of the catalyst from 4 to 6 weeks to at least as many months; (2) cheap industrial design of contact chambers and sulfur-elimination plant; (3) industrial processes for the recovery of rare metals and oxides in the purest form from the exhausted catalysts; (4) conversion of Fischer's primary product, Kogasin, into marketable gasoline, because only the fraction boiling up to 140° C. had sufficient antiknock properties (without addition of tetraethyl lead) to be sold as motor fuel; and (5) preparation of cheap synthesis gas.

The laboratory research work leading to the solution of these problems will be outlined in subsequent sections of this paper. A comprehensive picture of the engineering and development work during the past decade has emerged only within the past year and is described in the next section.[36]

During the years following 1935 a number of general reviews of the process and of its industrial progress, particularly in Germany, were published.[37] At the end of 1936, the following plants, aggregating a total of 145,000 metric tons of primary oils a year, were completed or under construction: The Rheinpreussen colliery at Hamburg, 30,000 metric tons of primary products, produced from blast-furnace coke and coke-oven gas, consisting of gasoline, Diesel oil, soft and hard paraffin wax, oils for the production of fatty acids and for other chemical uses;[38] Ruhr Benzin A. G. (subsidiary of Ruhrchemie) at Oberhausen-Holten,[39] and the Viktor Colliery at Castrop-Rauxel,[40] each 30,000 tons of primary oil per year from coke; Braunkohle-Benzin A. G., known as "Brabag," at Ruhrland, north of Dresden, 25,000 tons of primary oils using synthesis gas produced by the gasification of brown-coal briquets;[41] Mitteldeutsche Triebstoff und Oel Werks (subsidiary of Wintershall A. G.) at Kassel, 30,000 tons of primary oils using synthesis gas resulting from the gasification of brown coal.[42]

Martin[43] [44] has published a general description of the early German plants and presented some information on the character of the products. The yield of primary product was about 125 grams per cubic meter of $2H_2+1CO$ gas, or about 60 percent of the maximum theoretical yield of 208 grams per cubic meter of $2H_2+1CO$ gas. This product included 8 percent of gaseous hydrocarbons, 60 percent gasoline (boiling to 200° C.), 22 percent gas oil, and 10 percent paraffin (melting

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[30] Fischer, F., Roelen, O., and Feisst, W. [The Present Technical Position of the Benzine Synthesis]: Brennstoff Chem., vol. 13, 1932, pp. 461–468.

[31] Fischer, F., and Koch, H. [The Chemism of the Benzine Synthesis and the Motor and Other Properties of Products Resulting Therefrom (Gas Oil, Benzine, Diesel Oil, Hard Paraffin)]: Brennstoff Chem., vol. 13, 1932, pp. 428–434.

Hartner-Seberich, R., and Koch, H. [The High-Boiling Oils (Kogasin II) Obtained in the Benzine Synthesis of Franz Fischer and Tropsch as Fuel for Diesel Motor Operation]: Brennstoff Chem., vol. 13, 1932, pp. 308–310.

Koch, H., and Horn, O. [Comparative Investigation of Motor Behavior of a Synthetic Naphtha (Kogasin I) by Franz Fischer-Tropsch and a Petroleum Naptha]: Brennstoff Chem., vol. 13, 1932, pp. 164–167.

[32] Iron and Coal Trades Review, Hydrocarbons from Water Gas—Germany: Vol. 129, 1934, p. 542.

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[33] Fischer, F. [The Synthesis of Fuels (Kogasin) and Lubricants from Carbon Monoxide and Hydrogen at Ordinary Pressure]: Brennstoff Chem., vol. 16, 1935, pp. 1–11.

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Koch, H. [Synthesis of Benzine from Carbon Monoxide and Hydrogen Under Atmospheric Pressure by the Method of Franz Fischer and Tropsch]: Glückauf, vol. 71, 1935, pp. 85–90.

Thau, A. [Motor Fuel from Coke]: Coll. Guard., vol. 150, 1935, pp. 335–337.

[34] Work cited in footnote 31.

[35] Martin, F., Oil from Water Gas: Ind. Chemist, vol. 13, 1937, pp. 320–326.

[36] Rose, H. J., Secrets of German Fuel Technology: Min. and Met., vol. 27, 1946, pp. 106–108.

[37] Bayer, O., Newer Large-Scale Technical Developments of the Chemistry of Aliphatic Compounds: Angew. Chem., vol. 54, 1941, pp. 353–356.

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Hugel, G. [Synthetic Petroleum and Its Derivatives]: Ann. combustibles liquides, vol. 11, 1936, pp. 719–733.

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Laneck, P., and Scheer, W. [Coal Improvement—Fischer-Tropsch Process]: Stahl u. Eisen, vol. 61, 1941, pp. 63–66, 86–90, 109–112.

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Sinnatt, F. S., Coal's New Industry—The Production of Oil: Gas Jour., vol. 212, 1935, pp. 711–712.

Thau, A., Synthetic Motor Spirit: Coal Carbonization, vol. 2, 1936, pp. 159–163.

[38] Gas Journal, Indirect Hydrogenation—Koppers: Vol. 215, 1936, p. 482.

Colliery Guardian, Indirect Hydrogenation—Koppers: Vol. 153, 1936, p. 419.

[39] Chemical Age, The Fischer Process: Vol. 35, 1936, p. 367.

[40] Colliery Guardian, Production of Oils from Coke Oven Gas: Vol. 153, 1936, pp. 380–381.

[41] Work cited in footnote 38.

[42] Chemical Trade Journal, Hydrocarbon Synthesis from Water Gas.: Vol. 99, 1936, p. 50.

[43] Work cited in footnote 35.

[44] Martin, F. [Industrial Synthesis of Benzine and Oil from Water Gas]: Oel, Kohle, Erdoel, Teer, vol. 13, 1937, pp. 691–697. [The Development of the Synthesis of Hydrocarbons from Water Gas]: Chem. Fabrik, vol. 12, 1939, pp. 233–240.

point, 20° to 100° C.). The gasoline fraction had a low octane number (about 40), and hence part of the oil was cracked to increase this number. The Diesel-oil fraction had a cetene number between 100 and 120 and was therefore a desirable blending constitutent for improving oils of low ignitibility. Excellent lubricating oils could also be synthesized from certain fractions of the primary product.[45]

During 1937 and 1938 the capacity of the German plants was increased, so that the total yearly oil and gasoline output in 1938, when Germany halted construction of Fischer-Tropsch plants and engineering development of the process in favor of coal hydrogenation, was 591,000 metric tons.[46] [47] During the war years, nine Fischer-Tropsch plants were in operation as follows: In the Ruhr, at Oberhausen-Holten, Ruhrchemie, 72,000 tons per year gasoline capacity; Gewerkschaft Viktor at Castrop-Rauxel, 40,000 tons; Rheinpreussen, at Moers-Meerbeck, 70,000 tons; Krupp Benzin at Wanne-Eickel, 60,000 tons; Essener Benzin at Bergkamen, 80,000 tons; and Hoesch Benzin, at Dortmund, 47,000 tons; Braunkohle-Benzin at Schwarzheide-Ruhland in Saxony, 170,000 tons; Schafgotsch Benzin, at Deschowitz in Silesia, 40,000 tons; Wintershall Lutzkendorf in Saxony, 82,000 tons. However, in 1943, only 368,000 tons were produced by the Fischer-Tropsch process as compared with 3,088,000 tons from the coal-hydrogenation process.[48] [49] In the commercial Fischer-Tropsch plants, synthesis gas consisting of 2 parts of hydrogen and 1 part of CO, prepared from coke, was passed over cobalt–thoria–magnesia–kieselguhr (100 : 5 : 8 : 180–200) catalyst at 200° C. in normal- and medium-pressure (10 atmospheres) reactors. No full-scale plants were operated with an iron catalyst during World War II, but plans had been projected to build a Fischer-Tropsch plant in Italy using an iron-copper-calcium oxide–kieselguhr (100 : 2.5–4 : 10 : 15) catalyst precipitated from the nitrates.

SPECIAL APPLICATION OF FISCHER-TROPSCH REACTION IN GERMANY

SYNTHESIS OF ISOPARAFFINS AND AROMATIC HYDROCARBONS

A process for the synthesis of isoparaffins, chiefly isobutane and isopentane, was developed on a laboratory scale at the Kaiser Wilhelm

Institut für Kohlenforschung in Germany.[50] [51] This process operated at 300 atmospheres pressure of $1H_2 + 1.2CO$ gas, and 400° to 450° C., using thoria–alumina and zinc oxide–alumina catalysts. Another process [52] using these same catalysts at 500° C. and 30 atmospheres pressure of $1CO + 1H_2$ gas was reported to produce aromatic hydrocarbons, but only poor yields were obtained. Both of these processes are at present of little industrial significance.

MANUFACTURE OF HIGHER ALCOHOLS IN GERMANY BY MODIFIED FISCHER-TROPSCH SYNTHESIS

Two new processes were developed in Germany for the manufacture of higher alcohols by the Fischer-Tropsch synthesis. The Synol process [53] [54] was operated at 18 to 25 atmospheres pressure, using a gas mixture of $0.8H_2 + 1CO$ and temperatures of 200° to 235° C. The catalyst consisted of granules of a fused mixture of Fe_3O_4–Al_2O_3–K_2O in the proportions of 97 : 2.5 : 0.4. Two stages of operation were used (single pass of synthesis gas through two sets of catalyst chambers), 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° to 350° C. The alcohols were chiefly normal, but there was some branching in the hydrocarbon product.

The second development, the OXO process, [55] [56] was initiated by Ruhrchemie. It was intended for the production of higher alcohols for use in detergent manufacture, particularly those in the group from C_{12} to C_{18}. In this process carbon monoxide and hydrogen were added to olefins, and the aldehydes thus produced were reduced to the corresponding alcohols. A narrow fraction of the olefins from the Fischer-Tropsch process, the C_{12} to C_{18} cut, was mixed with 3 to 5 percent of cobalt-thorium oxide-magnesium oxide-kieselguhr (in the proportions

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of 30 : 2 : 2 : 66) catalyst and reacted with a mixture of $1H_2 + 1CO$ gas at a pressure of 200 atmospheres and a temperature of 150° 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° C. The process may be carried out with ethylene for the production of lower aldehydes, particularly propionaldehyde. If the alcohol product obtained from a C_3–C_5 cut is dehydrated at atmospheric pressure and hydrogenated, the final product is of high octane number and suitable for aviation gasoline.[57]

FISCHER-TROPSCH PLANTS IN JAPAN

Reports [58] in 1938 indicated that two plants with an annual output of 150,000 tons per year were operating in Japan. Some development work done in a semiindustrial-size plant is also reported.[59] Tests made with 2.5-, 3.5-, and 5.5-centimeter catalyst tubes of 56 centimeters length, immersed in an oil bath and containing a Co–Cu–Th–U–kieselguhr catalyst, yielded 98, 78, and 40 cubic centimeters of oil (68.6, 54.6, and 28.0 grams, respectively, assuming an average density of primary Fischer-Tropsch oil of 0.7 gram per cubic centimeter) per cubic meter of synthesis gas. These tests indicate that narrow tubes are preferable, but the conclusion is not clear cut, as the space velocity varied greatly because the throughput was maintained constant at 100 liters per hour for all tests.

More recently it was reported [60] that in 1944 Japan was operating three Fischer-Tropsch plants whose total yearly capacity was about 110,000 tons of primary products and was constructing two additional plants with a total annual capacity of 28,700 tons. 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, fuel, and Diesel oils.

GREAT BRITAIN

In Great Britain an experimental plant of about 150 gallons per day capacity was constructed to test the Robinson-Bindley process,[61] which differs from the normal Fischer-Tropsch synthesis over cobalt catalysts in several respects, particularly in that it operates with a higher carbon monoxide : hydrogen ratio. A smaller experimental plant of about 4 gallons per day capacity was erected by the Fuel Research Board.[62] Experiments in these experimental plants during 1935 to 1939 were mainly concerned with design, erection, and operation of units based on the cobalt-thoria-kieselguhr (100 : 18 : 100) catalyst of Fischer. During the war years experimental work was restricted to a laboratory scale and directed toward a study of the variables affecting activity and life of cobalt catalysts for synthesis at atmospheric pressure and study of synthesis at medium pressure (5–20 atmospheres), using cobalt and iron catalysts.[63] [64] Results of work in these plants will be discussed in later sections of this chapter. There has been no commercial development of the Fischer-Tropsch process in Great Britain, but construction of commercial plants is recommended in several publications.[65]

ITALY, AUSTRALIA, SCOTLAND, SPAIN, AND CANADA

Elsewhere, writers in Italy,[66] Australia,[67] and Scotland [68] have advocated the introduction of Fischer-Tropsch plants in their countries. Reports of a 1938 drilling campaign indicate that a group of Scottish gas wells could supply more than 10 million cubic feet per day of methane-containing gas for the Fischer-Tropsch synthesis, while by horizontal drilling and vacuum extraction from coal seams, 1,000 cubic feet could be extracted per ton of coal.[69] Construction of a 100,000-metric ton-per-year synthetic gasoline plant, using local brown coal as starting material, was recently initiated at Escatron, in the Province of Zaragoza, Spain.[70]

In 1944, a laboratory project, begun by the Research Council in Alberta,[71] was concerned with the improvement and development of Fischer-Tropsch catalysts. Recent reports indicated that, by the end of 1946, a $100,000 pilot plant for making gasoline from natural gas will be in operation by a Calgary, Alberta, oil company.[72] The plant will have a capacity of 2 million cubic feet of gas per day, producing about 5 gallons of gasoline per 1,000 cubic feet. The process is said to be entirely original with the developing company.

Spillane [73] has patented a process for the production of hydrocarbons by the passage of a mixture of hydrogen and carbon monoxide at 250° to 450° C. and 18 atmospheres pressure through an alternating electric field of which the potential difference is maintained at 60,000 to 100,000 volts and the frequency is synchronized to the molecular

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oscillation of hydrogen and carbon monoxide—that is, 6,000,000 to 37,000,000 cycles per second. The catalysts were prepared by precipitation of the hydroxides from their respective mixed nitrate solutions with a boiling solution of sodium hydroxide and include the following: Beryllium : copper=2–5 : 100, manganese : copper=2.5 : 100 and 40 : 100, cerium : copper=2–300 : 100 or copper : zirconium =100 : 3–10.

UNITED STATES

In the United States, Bureau of Mines investigators resumed experimental work in 1942 after a lapse of 12 years.[74] Iron and cobalt catalysts were studied on a laboratory scale. An engineering laboratory, for development of process improvements and for pilot-plant operation on the scale of a few quarts of oil per day, was operated for about 8 months. As part of a 5-year Government program, begun in 1944 and devoted to research on the production of synthetic liquid fuels in the United States,[75] a pilot plant is under construction at Bruceton, near Pittsburgh, Pa., which will have a capacity output of 1½ barrels of Fischer-Tropsch oil per day. Carthage Hydrocol, Inc., will probably have the first commercial Fischer-Tropsch plant in the United States when it completes its projected building program at Brownsville, Tex., late in 1947.[76] This $15,000,000 plant is being engineered by Hydrocarbon Research, Inc., and has been designed to process 64,000,000 cubic feet of natural gas and 40,000,000 cubic feet of oxygen per operating day and to produce 1 barrel of oil per 10,000 cubic feet of gas. The product distribution is reported to be as follows: 5,800 barrels per day of 80-octane-number gasoline, 1,200 barrels of 45–50-cetane-number Diesel oil, and 150,000 pounds of crude alcohols (in water solution). The experimental phases (experimental plant 10 gallons per day, pilot plant 10 barrels per day, semicommercial plant 10+ barrels per day) of the work were carried out at Olean, N. Y., and Montebello, Calif. At the pilot plant, operations were carried out with (1) a continuously operated low-pressure oxygen plant with a capacity of approximately 10,000 cubic feet of oxygen per hour; (2) pressure generators for the burning of natural gas with oxygen to produce synthesis gas; (3) synthesis reactors, consisting of a fixed

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fluidized bed of iron catalyst with an internal heat exchanger, operated at 300° C., 20 atmospheres, and with some recycling of end gas; (4) product-recovery system; and (5) facilities for deoxygenating the gasoline produced.

Stanolind Oil & Gas Co.[77] is planning to construct a hydrocarbon-synthesis plant in the Kansas sector of the Hugoton field which will use 100,000,000 cubic feet of natural gas daily to produce 6,000 barrels of gasoline and 1,000 barrels of Diesel fuel per day. Extensive research and pilot-plant operations have been conducted at the company laboratories in Tulsa.

GENERAL REVIEWS

The Fischer-Tropsch process is a remarkable one because of its great flexibility, both as regards raw materials and products obtainable. A variety of types of coke and coal, as well as coke-oven gas and natural gas, may be used as raw materials for synthesis-gas production, and the proportion of gasoline and of other products may be varied considerably.[78] [79] Reviews [80] [81] of procedures and character of

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(Continued on p. 14)

products and descriptions of patents[82] published during the past few years provide an ample supply of general information concerning the Fischer-Tropsch process. In the following sections most of the available information is presented.

ENGINEERING DEVELOPMENT

The Fischer-Tropsch synthesis is accompanied by the evolution of a large amount of heat—namely, about 7,000 B. t. u. per pound of oil produced (4,000 gram-calories). The temperature of the reaction must be controlled within a narrow range of about 5° C. to avoid excessive methane production. Consequently, it is necessary to effect rapid and efficient heat transfer from the catalyst surface to some cooling medium, which may be in direct or indirect contact with the catalyst.

INDIRECT HEAT-TRANSFER REACTORS

The Fischer-Tropsch reactors in all the German commercial plants were of the indirect heat-transfer type. Prewar patents[83] specified a catalyst depth of not more than 10 millimeters, and the vaporization of water as the cooling mechanism, the water being contained in cooling jackets under 10 to 15 atmospheres pressure (see figs. 1 and 2). During World War II, German Fischer-Tropsch plants operated with two types of reactors—namely, normal- and medium-pressure ovens (10 atmospheres);[84] each chamber contained 1 metric ton of cobalt. Standard operating rate, to produce 150 grams (per cubic meter of $2H_2+1CO$ synthesis gas) of hydrocarbons ranging from propane-propylene to waxes of 2,000 molecular weight, was 1,000 cubic meters per metric ton of cobalt per hour in the first-stage chambers. As the catalyst became older, this rate was lowered until it was 800 cubic meters per ton per hour just before regeneration of the catalyst. The general policy of chamber rotation was to put fresh catalyst in the last stage in contact with older gas, while older catalyst was put into the first stage in contact with fresh synthesis gas.[85]

MULTISTAGE OPERATION

The desirability of operating the Fischer-Tropsch synthesis in two or more stages was soon recognized. Production in the two-stage process is increased by about 20 percent over the single-stage operation,

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[84] Atwell, H. V., Powell, A. R., and Storch, H. H., U. S. Government Technical Oil Mission Fischer-
Tropsch Report One: Technical Oil Mission Report 5, July 1945, 66 pp. Office of Publication Board Report
2051, 1945, 45 pp.

[85] No inventor given, Conversion of Carbon Monoxide with Hydrogen: U. S. APC TC 1,222, OZ 11,356,
German Appl. I–63,810.

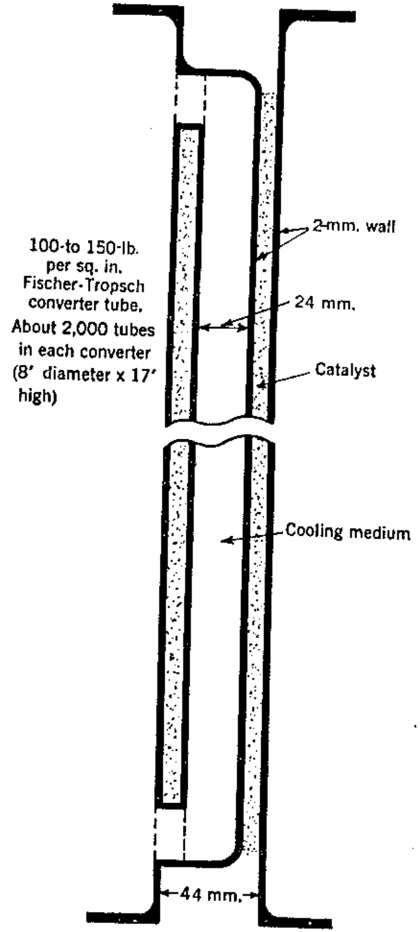

FIGURE 1.—100- to 150-pound-per-square-inch Fischer-Tropsch tube.

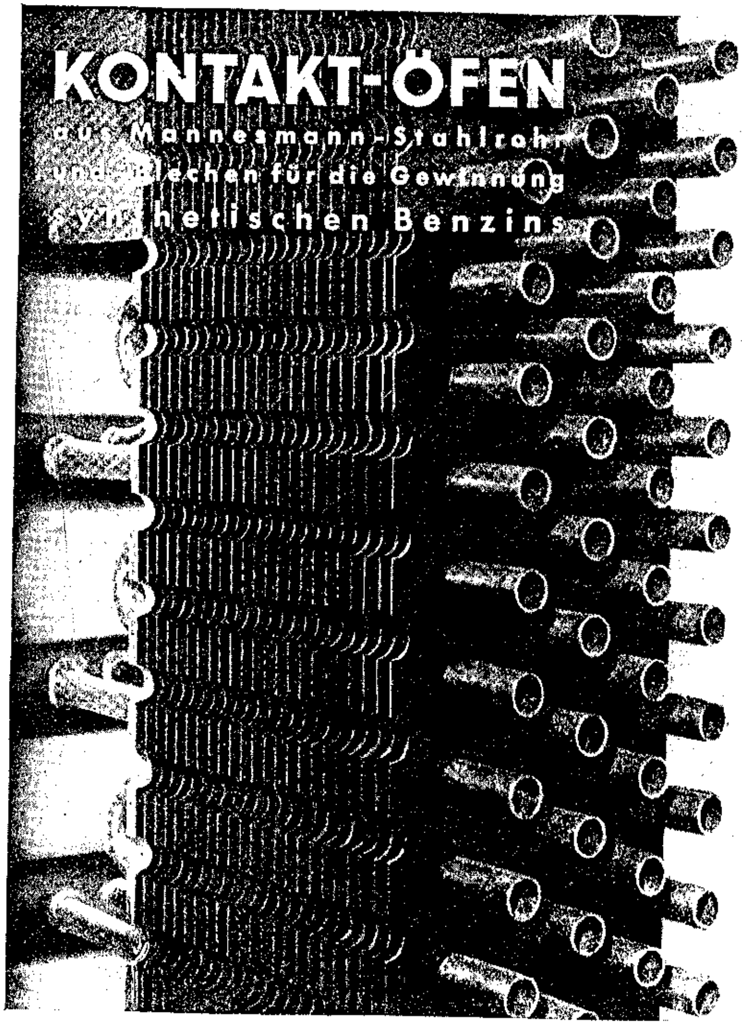

FIGURE 2.—Normal-pressure Fischer-Tropsch converter.

and the life of the catalyst is considerably increased.[86] [87] [88] [89] The so-called Robinson-Bindley process not only operates a multistage process but is also reported to have developed a special sulfur-resistant catalyst which is active in the synthesis of mono-olefins but only slightly active for hydrogenation.[90] The principal constituent of the catalyst used is cobalt to which a small amount of potassium carbonate has been added. Blue water gas ($1H_2+1CO$) containing appreciable quantities of sulfur was the synthesis gas used with this catalyst. Myddleton [91] stated that the fraction boiling up to 150° C. of the

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[87] Fischer, F., and Pichler, H. [Increasing Yields of Fluid Hydrocarbons by Performing the Benzine Synthesis of Fischer, F., and Pichler, H.]: Brennstoff Chem., vol. 17, 1936, pp. 24–29.
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[88] Synthetic Oils, Ltd., and Myddleton, W. W., Hydrocarbons: British Patent 491,778, Sept. 8, 1938. Hydrocarbons from Carbon Monoxide and Hydrogen: British Patent 519,722, Apr. 4, 1940.

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[90] The Chemical Trade Journal and Chemical Engineer, Robinson-Bindley Process: Vol. 104, 1939, p. 200.
Colliery Guardian, Robinson-Bindley Process: Vol. 159, 1939, p. 203.
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[91] Work cited in footnote 86, p. 16.

primary product of the Robinson-Bindley or Synthetic Oils procedure contained 70 percent of olefins and had an octane rating (motor) of 68, which could be raised to 80 by adding 4 cubic centimeters of tetraethyl lead per liter. However, no larger pilot or commercial-size plant has used this process, and there appears to be some question of the accuracy of the claims of the inventors.

Snodgrass and Perrin [92] have reported data obtained by the Ruhrchemie A. G. in Germany in a two-stage operation, the first stage being at atmospheric pressure and the second at several atmospheres. These data are given in tables 1 and 2. While very little paraffin wax is produced in the first stage, the second stage alone yields twice as much of this product as is reported by Fischer.[93] The second stage yields 43 percent of oil boiling above 300° C., whereas only 15 percent of the first-stage oil boils above that temperature. The olefin content of the second-stage gasoline from the charcoal scrubbers is lower than that of the first stage. The octane rating of the 30°–140° C. gasoline was 62 and of the 30°–110° C. was 67.

TABLE 1.—*Properties of products from two-stage operation*

Constituent	Boiling range, ° C.	Specific gravity	Olefins, volume percent		Percent by weight of total product	
			First stage	Second stage	First stage	Second stage
Gasol (C_3+C_4)			50	25–30	5	2
Gasoline to 150° C	30–150	0.66	35–40	20	26.5	8
Oil over 150° C	100–300	.74	12	12	26.5	11
Paraffin wax		.85				21

TABLE 2.—*Distillation of Kogasin from two-stage operation*

Temperature, ° C.	Volume, percent	
	First state	Second stage
30	0.0	0.0
50	8	3
100	29	14
150	47	24
200	60	35
250	75	48
300	85	57

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[92] Snodgrass, C. S., and Perrin, M., The Production of Fischer-Tropsch Coal Alcohol and Its Improvement by Cracking: Jour. Inst. Petrol. Technol., vol. 24, 1938, pp. 289–301.

[93] Great Britain Fuel Research Board, Synthesis of Hydrocarbons and the Production of Lubricating Oils: Report for the year ended Mar. 1938, His Majesty's Stationery Office, London, pp. 186–206.

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Tsuneoka, S., and Murata, Y. [Benzine Synthesis from Carbon Monoxide and Hydrogen at Ordinary Pressures. XXV. General Properties and Constituents of the Benzine Prepared with an Alloy Catalyst]: Jour. Soc. Chem. Ind., Japan, vol. 38, 1935, Suppl. binding, pp. 212–217.

In a modification of the multistage technique, iron catalyst is used in the first stage at 200° to 240° C. and cobalt catalyst in the second stage at 180° to 210° C., or vice versa. [94]

NORMAL-PRESSURE OPERATION

The German normal-pressure reactors (see fig. 2) were characterized by a system of hundreds of plates pierced by tubes filled with cooling liquid, contained in rectangular boxes. The Courrières-Kuhlmann Fischer-Tropsch plant at Harnes, France, was a typical normal-pressure synthesis plant. With a capacity of about 20,000 tons per year, it was brought into operation in June 1937 at only about half its full capacity.[95] During World War II the plant was operated by the Germans.[96] 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, 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 Fe_2O_3, and finally by passing the gas through an Fe_2O_3 catalyst containing about 25 percent Na_2CO_3 at 200°–300° C., to remove organic sulfur. The synthesis catalyst consisted of 18 percent cobalt, 1.8 percent magnesium oxide, 0.9 percent thorium oxide, and 79.3 percent kieselguhr. The reactors, operated at normal pressure (4 p. s. i. g.), were rectangular boxes about 20 feet long by 6 feet deep by 9 feet high and consisted of 600 2-millimeter sheets spaced 7 millimeters apart and pierced by 600 tubes filled with hot water fed by gravity in blocks of 2, 3, or 4 ovens from an overhead drum.[97] Each reactor had a total surface of 5,000 square meters and weighed 50 metric tons. The catalyst filled the voids between the baffles and tubes. Operation took place in 2 stages, 16 in the first stage and 8 in the second. Product was condensed after each stage. Considerable gasoline and butane were removed from the residual gas by an activated-charcoal recovery system. The methane production was 14 to 15 percent of the total product. The C_3 and C_4 fraction comprised 15 percent of the total

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[94] Heinrich Koppers Industrielle Maatschappij N. V. [Converting Carbon Monoxide and Hydrogen into Hydrocarbons]: French Patent 843,874, July 11, 1939. Manufacture of Hydrocarbons from CO and H_2: British Appl. 27,807, Sept. 23, 1938.

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[96] Schade, H. A., Foran, E., and Aldrich, R. C., Fischer-Tropsch Process: Technical Industrial Intelligence Committee Report 373. Nat. Petrol. News, vol. 37, No. 45, 1945, pp. R922–924.

[97] Alberts, L., Production of Hydrocarbons by Catalytic Hydrogenation of Carbon Monoxide: U. S. Patent 2,238,766, Apr. 15, 1941.

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Studien u. Verwertungs G. m. b. H. [Apparatus for the CO–H_2 Synthesis]: German Patent 708,889, July 31, 1941.

and consisted of 16 percent propylene, 49 percent propane, 26 percent butylenes, and 9 percent butanes. The remaining liquid consisted of 50 percent 160° C. end-point gasoline, 20 percent 160°–230° C. Diesel oil, 20 percent 230°–320° C. heavy oil, and 10 percent wax.

MEDIUM-PRESSURE OPERATION

The medium-pressure synthesis with the cobalt catalyst was developed in 1936 by Fischer and Pichler.[98] In the German commercial plants medium-pressure converters were double-tube reactors (see fig. 1), although there was no reason why the double-tube oven could not also be used in normal-pressure synthesis. Theoretically, it was superior to the multiplate reactor by providing a direct cooling surface. In the medium-pressure reactors, the catalyst lay in the annular space between the tubes. The outside shell was 2.7 meters internal diameter. Each shell contained 2,000 tubes of about 48 millimeters outside diameter by 44 millimeters inside diameter and about 4.5 meters in length, arranged on 54 millimeters triangular pitch. Water (or oil cooling medium) surrounded the tubes. Synthesis gas entered the reactor at the top and flowed downward through the catalyst. Four reactors arranged in a square were 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 released through a back-pressure regulator into the steam main. The temperature on the reactor was regulated by controlling the steam pressure in the drum.[99] One patent recommended that the reactor tubes be in horizontal position, in order to obtain more effective heat transfer and thus reduce methane formation.[1]

It was found that medium-pressure synthesis works best, from the point of view of smooth running and olefin production, with $1.5H_2 + 1CO$ synthesis gas. As it was desirable, on economic grounds, that the over-all synthesis gas have the ratio $2H_2 + 1CO$, medium-pressure synthesis was operated in several stages with adjustment of gas composition and product condensation between the stages.[2] Gasol hydrocarbons (C_3 and C_4) were adsorbed in an active carbon plant.

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[98] Sheer, W. [Franz Fischer and the Chemistry of Coal]: Glückauf, vol. 80, Nos. 7–8, 1944, pp. 76–78.

[99] Albert, W. [High-Pressure Converter for Benzine Synthesis]: German Patent 725,488, Aug. 6, 1942.

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No inventor given [Conversion of Carbon Monoxide with Hydrogen]: U. S. APC TC 1,142, OZ 11,324, Jan. 28, 1939, German Appl. I–63,658.

[1] I. G. Farbenindustrie A. G. [Catalytic Conversion of Carbon Oxides with Hydrogen]: TC 1,134, OZ 11,354, Feb. 10, 1939, German Appl. I–63,779.

[2] Hall, C. C., Craxford, S. R., and Gall, D., Interrogation of Dr. Otto Roelen of Ruhrchemie A. G.: British Intelligence Objectives Subcommittee Report 30/447, 1945, 50 pp.

The C_{3+} higher hydrocarbons product from medium-pressure synthesis included 10 percent C_3 and C_4 (40 percent olefins, 13 percent of C_4's being isobutane), 25 percent hydrocarbons boiling below 170° C. (24 percent olefins and about 45 octane number, motor method), 30 percent 170° to 280° C. (9 percent olefins), 20 percent 280° to 340° C. (soft wax), and 15 percent residue (hard wax, m. p. about 90° C.). Ten percent of the total hydrocarbon production was methane.

FLUIDIZED FIXED BED, INTERNAL HEAT EXCHANGER

Recent process designs by United States Oil Co. engineers specify a turbulent fixed bed of catalyst powder suspended in synthesis gas, heat removal being accomplished by indirect or direct means. In the former design heat-exchanger tubes are present in the catalyst bed; the latter design is described on page 24. The commercial plant under construction by Carthage Hydrocol, Inc., at Brownsville, Tex., will use a fixed fluidized bed of sintered iron and an internal heat exchanger. Numerous modifications of this technique have already been patented in the United States and Great Britain.[3]

LIGHT-HYDROCARBON-PRODUCT RECOVERY

In large-scale operation light hydrocarbons were adsorbed on active carbon and later recovered by steam distillation. For example, the active carbon plant at the Morpeth Gas Works had a capacity of 400,000 cubic feet of gas per day, using 3 hundredweight of carbon. A complete cycle of operation consisted of three periods—adsorbing, steaming, and drying—in the time ratio of 60 : 30 : 30. The efficiency of extraction was about 95 percent.[4]

RECYCLE OPERATIONS

Cobalt Catalysts.—Both Lurgi and Ruhrchemie did considerable experimental work on a recycle operation of the Fischer-Tropsch process, using normal cobalt catalyst in the conventional, externally cooled medium-pressure reactors connected in parallel in one stage, and recycling about 3 volumes of end gas per volume of fresh gas with product condensation after each cycle. The object of this method of operation was to increase the production of olefins by maintaining a high concentration of carbon monoxide in the synthesis gas charged to the reactors. Charging $1H_2 + 1CO$ gas mixture by this procedure resulted in a 20- to 55-percent increase in the liquid fractions of the

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[3] Campbell, D. L., and Barr, F. T., Treating Hydrogen with Oxides of Carbon for the Production of Products such as Methanol: U. S. Patent 2,266,161, Dec. 16, 1941.

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[4] Carbo-Norit-Union Verwaltungs G. m. b. H. [Hydrocarbons from the End Gases of Hydrocarbon Synthesis]: German Patent 737,620, June 10, 1943.

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Robson, G. W., Benzol Recovery by Active Carbon: Gas Jour., vol. 246, 1945, pp. 687, 689.

product. The use of $1H_2 + 1CO$ (that is, high CO concentration) gas in the older process without recycling resulted in low catalyst life because of carbon deposition. The recycle gases lowered the partial pressure of the carbon monoxide sufficiently so as to avoid excessive carbon formation. The reaction temperature for the recycle process was 200°–225° C., as compared to 180°–190° C. normally used. On a pilot-plant scale this development resulted in a 30-percent increase in 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. The products were 8 percent C_3 and C_4 (60–65 percent olefins), 30 percent gasoline C_5 to C_{10} (60–65 percent olefins), 28 percent middle oil C_{10} to C_{17} (40–65 percent olefins), and 34 percent wax C_{18+} (small quantity of olefins). The recycle-process gasoline had a 50 to 55 motor octane number, as compared with 40 for the older processes 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.[5] [6]

A variation in recycle technique specified vapor-phase reaction in the first pass and liquid-phase (powdered catalyst suspension in oil) operation in the second with intermediate product condensation.[7]

Iron Catalysts.—Lurgi and I. G. Farbenindustrie were interested in recycle operation in the externally cooled medium-pressure converters using moderately active iron catalysts and low recycle ratio. Michael's laboratory at I. G. Farbenindustrie A. G., Ludwigshafen/Oppau,[8] experimented with a precipitated iron oxide, mixed with 5 to 25 percent magnesium oxide or carbonate and 1 to 2 percent potassium carbonate or borate, pressed into pellets, sintered at 850° C., and then reduced with hydrogen after cooling to 350° to 450° C. The synthesis was conducted at 240° C. and 20 atmospheres pressure in the double-tube reactor. Using synthesis gas whose composition varied between $1.25H_2+1CO$ and $0.8H_2+1CO$, 70 to 80 percent conversion (by volume) was obtained and yields of 0.35 to 0.45 kilogram per liter of catalyst per day of the following products: Gasol hydrocarbons (C_3 and C_4), 10 percent (70 percent olefins); gasoline boiling to 200° C., 35 to 50 percent (70 percent olefins); gas oil boiling to 350° C., 25 to 35 percent (40 to 50 percent olefins); paraffin wax, 15 to 25 percent (60 percent boiling above 450° C.). The methane yield was about 10 percent of the total liquid and solid product.

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[5] Work cited in footnote 84, p. 15.

[6] Hall, C. C., and Haensel, V., Fischer-Tropsch Plant of Ruhrchemie A. G., Sterkrade-Holten: Technical Oil Mission Report 44, 1945, 97 pp.
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Herbert of the Lurgi Co.[9] [10] stated that the best iron catalyst had the composition $Fe : Cu : Al_2O_3 : K_2O : SiO_2 = 100 : 25 : 9 : 2 : 30$, precipitated from the nitrates by sodium carbonate, then mixed with kieselguhr and a small quantity of potassium carbonate. The dried granular product was reduced in hydrogen at 250° to 350° C. for 1 to 4 hours. Pilot-plant operation under conditions similar to those described above, using a recycle ratio of about 3 : 1, resulted in a yield of liquid, solid, and gasol hydrocarbons of 170 grams per normal cubic meter of $1H_2+1CO$ synthesis gas.

DIRECT HEAT-TRANSFER REACTORS

The conventional design of the German converters, in which the heat of reaction is withdrawn indirectly, requires very narrow layers of catalyst. Consequently, large amounts of steel (about 15 tons per barrel of oil per day) are necessary, and design improvement is limited. Contacting the catalyst directly with the cooling medium is a recent engineering development that will permit wide variation in design for improved efficiency of operation. The heat-transfer medium may be gas, liquid, or solid.

GASEOUS HEAT-TRANSFER OPERATION

Hot-Gas Recycle.—An I. G. Farbenindustrie A. G. hot-gas recycle process [11] [12] [13] developed by Michael was in pilot-plant operation at Ludwigshafen. It utilized as catalyst an iron powder obtained by thermal decomposition of iron carbonyl mixed into a paste with 1 percent of its weight of sodium borate in aqueous solution and extruded into granules that were dried and sintered in hydrogen for 4 hours at 850° C. During synthesis at 320° C., 20 atmospheres pressure, and ¾-second contact time the synthesis gas ($1H_2+1CO$ or $0.8H_2+1CO$) was passed through an external heat exchanger to remove heat of reaction and returned to the reactor. Conversion per pass was about 1 percent, so that about 100 volumes of recycle gas to 1 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 47–53 cetane number and minus 25° C. pour point, 11 percent; 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.

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[11] Work cited in footnote 84, p. 15.

[12] Work cited in footnote 8, p. 2.

[13] Brabag, No title: German Appl. B-178,085, Apr. 14, 1937. Office of Publication Board Report 412, May 15, 1945. No title, German Appl. B-181,705, Jan. 31, 1938. Office of Publication Board Report 412, May 15, 1945.
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Michael, W., and Planth, E., Synthesis of Hydrocarbons from Carbon Monoxide and Hydrogen: U. S, Patent 2,279,052, Apr. 7, 1942.

Fluidized Fixed Bed, External Heat Exchanger.—Heat of reaction may be removed from the fluidized fixed bed by a heat exchanger present in the catalyst bed (p. 21) or by a heat exchanger outside the reaction zone, the catalyst suspension in the synthesis-gas stream being passed from the converter through the heat exchanger and back into the converter.[14]

LIQUID HEAT-TRANSFER OPERATION

Foam Process.—Attempts are being made to solve the heat-transfer problem by conducting the synthesis in a liquid medium such as water or hydrocarbon oil in which the catalyst is suspended.[15] The heat of vaporization of the liquid removes heat rapidly from the catalyst surfaces. In 1939 to 1944 the I. G. Farbenindustrie was developing a liquid-phase operation in which iron powder prepared from iron carbonyl was mixed with oil and the gas contacted with this liquid suspension.[16][17] More Diesel oil (60–70 cetene number) was obtained by this process than by the hot-gas recycle process. The gasoline from the liquid-phase operation had a research octane number of 90. Up to 80 percent of the total product may be obtained in the Diesel fuel range by liquid-phase operation with iron or cobalt suspended catalysts, according to several International Hydrocarbon Synthesis Co. patents.[18]

Modified Foam Process.—Ruhrchemie[19] patented a modified liquid-phase process in which finely divided cobalt–thoria–magnesia–kieselguhr catalyst was suspended in oil boiling in the range between 240° and 300° C., into which water was injected and vaporized under reaction conditions to control the temperature. Operation with synthesis gas consisting of a mixture of $1CO$ and $2H_2$ at a pressure of 10 atmospheres, space velocity of 2.5 liters of synthesis gas per gram of cobalt per hour, and a temperature of 190° to 210° C. produced 172 grams of liquid and solid hydrocarbons per cubic meter. Ninety percent of the liquid product boiled below 300° C.

Disadvantage of Foam Process.—Processes in which catalyst powder was suspended in liquid were difficult to operate because the formation of high molecular weight products of limited solubility caused the catalyst particles to agglomerate and settle.[20]

A procedure[21] designed to facilitate removal of the reaction product was to pass the preheated synthesis gas into a 50-bubble tray tower at the rate of 1,000 cubic feet per hour. A catalyst suspension containing about ¾ pound of finely divided nickel catalyst activated with magnesium and aluminum oxides per gallon of sulfur-free paraffin wax was charged through the tower at the rate of 300 gallons per hour. The reaction produced about 1 gallon of liquid hydrocarbons for each 1,000 cubic feet of gas charged.

Duftschmid Process.—Another I. G. Farbenindustrie development[22][23][24] consisted of an oil recycle process in which a cooling oil was passed concurrent with the synthesis gas over granules of an iron catalyst (synthetic ammonia type, doubly promoted with aluminum and potassium oxides). Cooling was effected by recycling the heated oil through an external heat exchanger. The process was operated at a pressure of 20 to 25 atmospheres and a temperature of 260° to 300° C. in the first stage and 280° to 330° C. in the second stage. The throughput of $1.25CO + 1H_2$ synthesis gas was controlled to yield about 0.5 kilogram of total product per liter of catalyst per day. The yield of C_3 and higher hydrocarbons was about 150 grams per cubic meter of $1CO + 1H_2$ synthesis gas and was distributed as follows: 16 percent C_3 and C_4 (85 percent olefins), 40 percent gasoline boiling to 200° C. (50 percent olefins), 20 percent gas oil (25 percent olefins), 20 percent paraffin wax, and 4 percent alcohols, largely methanol and ethanol. The crude gasoline had a research octane number of 62 to 65 and the gas oil a cetane number above 70.

SOLID HEAT-TRANSFER OPERATION

Processes have been described in which synthesis gas is passed through a plurality of zones containing alternately catalyst and noncatalytic materials. The latter zone may contain granules of solid inert material or cooling liquid for removing the heat of reaction.[25]

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[23] Work cited in footnote 87, p. 16.

[24] Duftschmid, F., Linckh, E., and Winkler, F., Hydrocarbon Synthesis from Hydrogen and Carbon Monoxide: U. S. Patent 2,287,092, June 23, 1942. Synthesis of Hydrocarbons from Carbon Monoxide and Hydrogen: U. S. Patent 2,318,602, May 11, 1943. Catalytic Hydrogenation of Carbon Monoxide to Form Hydrocarbons: U. S. Patent 2,207,581, July 9, 1940.

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CATALYSTS

The most active catalysts for the synthesis of liquid and solid hydrocarbons from hydrogen and carbon monoxide are nickel, cobalt, iron, and ruthenium.[26] These metals alone or admixed with each other are used with activating materials such as aluminum, thorium, copper, or manganese oxides.[27] Catalysts are described in which cobalt, or iron and nickel together, is slowly precipitated at room temperature by potassium carbonate in the presence of about 8 percent of silver, based on the weight of cobalt or iron.[28]

NICKEL CATALYSTS

Nickel plus 20 percent of manganese oxide and 4 to 8 percent of thoria, alumina, tungstic oxide, or uranium oxide, mixed with 1.25 times its weight of kieselguhr, yields 100–160 cubic centimeters of liquid hydrocarbons per cubic meter of synthesis gas per pass at a space velocity (volumes of gas per volume of catalyst per hour) of about 150 and at optimum temperatures in the range 185°–210° C.[29]

Nickel catalysts were also studied by Russian investigators.[30] Nickel catalysts are best prepared by the addition of alkali carbonates to solutions of the metal nitrates in which the kieselguhr is kept in suspension by mechanical agitation; the mixture is then filtered, washed, and dried, whereupon it is obtained in friable cakes or in thin filaments, 1 to 3 millimeters in diameter, if the wet filter cake is forced through suitable, sized holes.[31]

The presence of ammonia during the precipitation of nickel-manganese-alumina catalysts increases the yield in subsequent gasoline synthesis and lowers the optimum reduction temperature from 450° to 300°–350° C.[32] Of a series of nickel catalysts produced from the oxalate and reduced at 200°, 230°, and 280° C., the one reduced at 230° C. was reported to give the highest conversion.[33]

COBALT–NICKEL CATALYSTS

One of the undesirable features of nickel catalysts is that, at operating pressures higher than 1 atmosphere, the catalyst deteriorates rapidly because of the formation of volatile nickel carbonyl. The use of cobalt in the catalyst overcomes this difficulty and generally results in a lower yield of methane and in a higher proportion of olefins in the liquid hydrocarbon product. Cobalt-nickel catalysts containing up to 50 percent nickel retain the important advantages of the cobalt catalysts.[34]

Tsutsumi [35] reported that a precipitated catalyst containing equal parts of cobalt and nickel without the addition of promoters such as thoria or alumina was a very poor one for the hydrocarbon synthesis. He stated that his most active catalyst was a mixture of equal parts of nickel and cobalt plus 20 percent manganese oxide, 20 percent uranium oxide, and 125 percent kieselguhr (the percentages are based on the amount of nickel plus cobalt present). Tsutsumi [36] also found that the best ratio of catalyst to kieselguhr was in the range 1 : 1 to 2 : 1. Katayama and his coworkers [37] reported that the activity of a cobalt-nickel (1 : 1) manganese–uranium–thorium oxides catalyst was increased by about 10 percent if it was oxidized at about 20° C. by a slow stream (space velocity per hour of about 150) of air before

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