catalysts at 245° to 265° C. as calculated by Eidus [92] was slightly higher than the value, 26–27, calculated by Weller [93] for cobalt–thoria–kieselguhr catalyst at 185° C. Other calculations have been performed by Myddleton,[94] who derived equations relating free energy of reaction to temperature in the Fischer-Tropsch synthesis. Molecular heat-temperature curves were drawn for each reactant and product in the range, 25° to 250° C. In analyzing the results, Myddleton attributed to special catalyst surface conditions the suppression of reactions in which carbon dioxide is formed, despite favorable free-energy changes; and to construction of hydrocarbon chains the appearance of only traces of ethylene in the synthesis products instead of the appreciable quantities predicted by free-energy relationships.

PROPERTIES OF FISCHER-TROPSCH SYNTHESIS PRODUCTS

Gasoline, Diesel fuel, paraffin wax, lubricants, alcohols, and fatty acids are the chief products obtainable from the Fischer-Tropsch synthesis.[95] The synthetic oils are also valuable as substitutes for glycerides in paints and sealing solutions.[96]

PRIMARY PRODUCTS

KOGASIN

The primary product of the Fischer-Tropsch synthesis, labeled "Kogasin" by Fischer, has been shown [97] to contain largely straight-chain paraffinic and olefinic hydrocarbons, with only very minor amounts of aromatic hydrocarbons, naphthenes, and oxygenated organic compounds.

Table 10 contains data on the boiling ranges and olefin contents of various fractions of the primary product obtained in Fischer's [97] laboratory from a cobalt catalyst. Gasoline boiling to 200° C. constitutes 60 percent of the total product.

TABLE 10.—*Composition of Kogasin*

Constituents	Percent by weight	Olefin content, volume percent
Gasol (C_3+C_4)	8	55
Gasoline to 150° C.	46	45
Gasoline 150°–200° C.	14	25
Diesel oil	22	10
Paraffin wax from oil (m. p., 50° C.)	7	
Paraffin wax from catalyst (m. p., 90° C.)	3	

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[92] Work cited in footnote 91, p. 37.

[93] Work cited in footnote 35, p. 44.

[94] Myddleton, W. W., Application of Free-Energy Equations to the Study of the Synthesis of Hydrocarbons from Carbon Monoxide and Hydrogen: Jour. Inst. Petrol., vol. 30, 1944, pp. 211–224, 248.

[95] Komarewsky, V. I., Production of Synthetic Liquid Fuel from Natural Gas: Petrol. Refiner, vol. 24, No. 5, 1945, pp. 96–98. Petrol. Eng., vol. 16, No. 12, 1945, pp. 202, 204, 206.

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[96] Williams, A. E., Synthetic Hydrocarbons from Water Gas: Paint Manuf., vol. 15, 1945, pp. 348–355.

[97] Work cited in footnote 93, p. 18.

The data of table 10 are in accord with the statement by Martin [98] that the average olefin content of the product obtained in the plants in operation up to August 1937, that used cobalt catalysts throughout, was 29 percent, the majority of the olefins being in the fraction boiling below 200° C. The olefin content in the low-boiling fraction could be increased to 50 to 80 percent, according to an I. G. Farbenindustrie A. G. patent, by operating with a 0.9–1.5 H_2+1CO gas mixture at atmospheric pressure and temperatures of 160° to 350° C.[99]

The gasoline fraction boiling from 30° to 200° C. is sometimes called Kogasin I. The rest of the liquid portion comprises a Diesel-oil fraction, Kogasin II, boiling between 200° and 320° C., and containing a certain amount of soft paraffin wax.

DIESEL OIL

The Diesel-oil fraction can be isolated from primary Kogasin by simple distillation and the acid components neutralized by percolating the oil at 120° to 150° C. through iron oxide.[1] The Diesel oil obtained has a boiling range of about 200° to 360° C., specific gravity (at 20° C.) 0.769, hydrogen content 15.2 percent, heat of combustion 10,470 to 11,300 kilocalories per kilogram (18,900–20,300 B. t. u. per pound), and a cetene value of over 100. This material, because of its high heat of combustion and high cetene number, is particularly suitable for mixing with and improving oils of lower ignitibility, such as tar oils,[2] and especially heavy petroleum oils. Generally, an addition of 30 to 40 percent of Fischer-Tropsch Diesel oil suffices. For example, if a Kogasin fraction with a cetene number of 120 is mixed with a tar oil of 20 cetene number in a 38 : 62 ratio, there is obtained a Diesel fuel of 60 cetene number equal in ignition qualities to commercial Diesel oil of petroleum origin.[3]

The increased olefin production in the Synthetic Oils process, which results in a higher octane rating for the gasoline produced, also causes the Diesel-oil fraction to have a lower cetene number, but the quality is still high; Myddleton [4] gives figures of 81 and 86 for the 200° to 300° C. and 200° to 290° C. fractions, respectively. Hydrogenation will, of course, increase the cetene number.[5]

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[98] Work cited in footnote 35, p. 7.

[99] I. G. Farbenindustrie A. G. [Producing Unsaturated Hydrocarbons]: French Patent 843,844, July 11, 1939.

[1] Pranschke, A. [Deacidification of Products Synthesized from CO and H]: German Patent 716,836, Jan. 8, 1942.

[2] Bristow, W. A., Coal and Oil. A Survey of New Facts and Future Possibilities: Gas World, vol. 118, No. 3065, Coking Sec., 1943, pp. 60–63.

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Kohle und Eisenforschung Gesellschaft [Diesel Fuel]: French Patent 877,257, Dec. 2, 1942.

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Martin, F., Roelen, O., and Schaller, P., Fuel for Diesel Motors: U. S. Patent 2,243,760, May 27, 1941.

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International Hydrocarbon Synthesis Co. [Diesel Fuel from Synthesis of Hydrocarbons]: Italian Patent 389,201, June 24, 1941.

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Pfirrmann, T. W., High Quality Benzine and Diesel Motor Fuels: U. S. Patent 2,232,673, Feb. 18, 1941.

Ruhrchemie A. G. [Diesel Fuel]: German Patent 726,894, Sept. 17, 1942.

Uhde, F., and Pfirrmann, T. W., Motor Fuel: British Patent 482,783, Apr. 5, 1938.

[3] Coke Smokeless-Fuel Age, Diesel Fuels from Coal: Vol. 2, 1940, pp. 70–71.

[4] Work cited in footnote 86, p. 16.

[5] Work cited in footnote 88, p. 16.

The yield of oils boiling in the Diesel-fuel range may be increased to 80 percent of the total synthesis products by liquid-phase operation.[6] A periodic alkali wash of the liquid medium decreases the rate of formation of solid paraffins. A Diesel fuel fraction of 85 cetene number can be prepared by cracking Fischer-Tropsch wax.[7]

PARAFFIN WAX

The solid portion of the primary product consists of hard wax, recovered from the catalyst by solvent extraction. Gross and Grodde[8] have shown that the solid product obtained is aliphatic, consisting of a mixture of normal and isoparaffins. Paraffin wax with melting points varying from 50° to 100° C. and with molecular weights up to 2,000 are produced on cobalt, nickel, or iron catalysts.[9] [10] In a study of the behavior of ruthenium, osmium, platinum, iridium, and palladium as catalysts, Pichler showed [11] that ruthenium is far more effective than iron, cobalt, or nickel in producing solid hydrocarbons. By a single pass of synthesis gas at 1 liter per gram of ruthenium per hour over the catalyst at 195° C. and 100 atmospheres pressure, 100 grams of solid paraffin and 50 grams of oil were obtained per cubic meter of gas. A 6-month test showed no appreciable change in catalyst activity. The solid paraffin was snow white in the crude state and melted to a clear liquid at 118° to 119° C.

With improved procedures, such as continuous removal of the paraffin formed during the reaction, high solid paraffin yields were obtained from cobalt catalysts at pressures of 5 to 20 atmospheres and increased contact time.[12]

By solvent extraction it was possible to isolate from the crude paraffin hitherto unknown solid paraffin hydrocarbons with melting points up to 132° C. and molecular weights of 7,000 to 9,000.[13] Additional information on the properties of the solid products obtained by the use of a ruthenium catalyst has been presented by Pichler and Buffleb,[14] who separated the solid paraffins by extraction with various solvents. The physical properties of the fractions are shown in table 11; the highest melting point was in the range 132° to 134° C. corresponding to an average molecular weight of 23,000.

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[6] Work cited in footnote 18, p. 24.

[7] National Petroleum News, Diesel Fuels from the Synthine Process: Vol. 36, No. 36, Technol. Sect.,
1944, p. R585.

[8] Gross, H., and Grodde, K. H. [Structure of Solid Hydrocarbons as Basis for Classification]: Oel u. Kohle,
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[9] Work cited in footnote 93, p. 18.

[10] Graefe, E., Wax from Fischer-Tropsch Synthesis: Jour. Inst. Petrol. Technol., vol. 23, 1936, p. 78A.
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from CO and H: British Patent 517,002, Jan. 17, 1940.

[11] Work cited in footnote 29, p. 43.

[12] Fischer, F., and Pichler, H. [Process for the Production of Paraffin]: German Appl. ST–56,469, July 30,
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OZ 11,312, 1939. German Appl. I 63,572.
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vol. 32, 1945, p. 149. Solid Paraffins from Carbon Monoxide and Hydrogen: British Patent 517,002, Jan.
17, 1940. Process for Producing Solid Paraffin: British Appl. 22,394, 1938.

[13] Deutsche Erdöl A. G. [Ceresin-Like Products]: French Patent 874,918, Aug. 28, 1941.

[14] Pichler, H., and Buffleb, H. [Properties of Some Solid Paraffins Produced from Carbon Monoxide and
Hydrogen at High Pressures on Ruthenium Catalysts, with Special Reference to the Previously Unknown
Highest-Melting Constituents]: Brennstoff Chem., vol. 21, 1940, pp. 285–288.

TABLE 11.—*Solvent extraction of solid paraffin obtained by use of a ruthenium catalyst at 1,000 atmospheres pressure* [1]

Fraction No.	Solvent	Extraction temperature, ° C.	Percent dissolved	Melting point, ° C.	Density		Average mol. wt.	Viscosity, centistokes, at—	
					20	150		150° C.	180° C.
1	n-pentane	34	30–33	51–57					
2	n-hexane	68	14–17	92.5–95		0.765	760	6	4
3	Kogasin frac	90	14–16	121–122.5	0.966	.778	1,750	29	17
4	n-heptane	98	20–25	129.5–130.4	.978	.783	6,750	870	410
5	Kogasin frac	121	12–15	132–134	.980	.786	23,000	35,600	15,800

[1] Work cited in footnote 14, p. 58.

FATTY ACIDS

The fatty acids formed in small quantities during the synthesis of Kogasin amount to about 0.35 percent by weight, referred to the main liquid hydrocarbon product. By fractionation, formic, acetic, propionic, and butyric acids were detected.[15] Two-thirds of the mixed, water-soluble fatty acids consisted of acetic acid. No unsaturated acids were found. The fatty acids dissolved in the Kogasin amounted to about 0.06 percent and consisted of acids of 5 to 10 carbon atoms per molecule, but acids of still larger molecular weight were detected in smaller quantities. Small amounts of fatty acids were isolated from the off-gases of a large-scale plant. They consisted chiefly of saturated monobasic acids of 5 and 6 carbon atoms and traces of unsaturated fatty acids.[16]

SECONDARY PRODUCTS

GASOL

The gasol fraction (C_3+C_4) can be liquefied by compression and sold for heating and lighting where coal gas or electricity is not available. Alternatively, it may be subjected to isomerization to convert butane to isobutane, followed by alkylation, whereby isobutane and butylene unite to form iso-octane.[17]

GASOLINE

Refining of Primary Gasoline.—For motor-fuel purposes it is essential in a Fischer-Tropsch plant to provide for refining, cracking, dehydrogenation, and re-forming of the primary synthesis products, using the techniques well-known to the petroleum industry for the produc-

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[15] Koch, H., Pichler, H., and Koelbel, H. [Fatty Acids from Fischer-Tropsch Synthesis]: Brennstoff Chem., vol. 16, 1935, pp. 382–387.

[16] Stinzendörfer, H. [Determination of the Constitution of the Fatty Acids Produced in the Fischer-Tropsch Synthesis]: Tech. Mitt. Krupp. Forschungsber., vol. 5, 1942, pp. 34–36.

[17] Kemp, L. C., Motor-Fuel: U. S. Patent 2,286,814, June 16, 1942.

tion of antiknock gasoline.[18] The primary gasoline fraction boiling to 150° C., collected by adsorption on active charcoal, has a density of 0.680 at 20° C.; and despite an olefin content of 45 percent, the octane rating is only about 55. Fischer [19] claims that this rating may be increased to 72 by the addition of 0.5 cubic centimeter of tetraethyl lead per liter of gasoline. The only refining necessary is a wash with alkali to remove traces of fatty acids.[20] Passage of synthetic gasoline over fuller's earth, silica gel, alumina, or active carbon was reported to result in improved octane rating, apparently as a result of isomerization.[21] When gasoline in the boiling range of 40° to 200° C. was passed at 180° to 200° C. over activated fuller's earth at the rate of 400 cubic centimeters per kilogram, per hour, the octane number was raised from 44 to 51.[22]

Cracking of Primary Liquid Products.—Investigations in Fischer's laboratory [23] and by Egloff and his associates [24] showed that yields of about 75 to 80 percent by weight may be obtained when the primary product boiling above 200° C. is cracked and the cracked gasoline mixed with 42 to 30 percent of the primary Kogasin boiling to 200° C. The finished gasoline has an octane rating of 63–70. According to Martin,[25] gasoline of 195° C. distillation end point, 68 octane number, and 0.728 density at 150° C. was obtained. Davies [26] describes a cracking plant designed by True Vapor Phase, Ltd., and erected alongside the Fischer-Tropsch plant at Oberhausen, Germany. Snodgrass and Perrin [27] present some data which were obtained with higher-boiling primary Fischer-Tropsch product in a True Vapor Phase control unit. These results are reproduced in table 12. The octane rating of the products is 62–75.

TABLE 12.—*Properties of gasoline obtained by cracking of Kogasin in True Vapor Phase operation* [1]

Charge	Reduced crude, sp. gr. 0.769			Untopped crude, sp. gr. 0.725	
Cracked gasoline:					
Yield, volume percent	81	75.5	65.2	70.6	65.2
Yield, weight percent	88	81.8	73	72	68.3
Specific gravity	.7079	.7906	.6876	.7114	.6920
End point, °C	200	197	168	197	160
Octane No. (motor)	62	68	75	67	73
$Pb(C_2H_5)_4$ to raise octane No. to 80, cc. per British gallon		3.5	1.3	3.7	1.7

[1] Work cited in footnote 92, p. 18.

Since 1938 a vast amount of literature concerning thermal and catalytic cracking of Fischer-Tropsch primary synthesis products has been published.[28] The amounts of gas and coke produced during cracking are greatly reduced, according to one patent,[29] if the primary product is first acid washed and treated with "bleaching earth". The formation of gaseous and low-boiling products is also suppressed by the addition of 10 to 20 percent of cyclic hydrocarbons or ash-free tar.[30] Pier and Simon [31] patented a method in which the use of a partly spent tungsten disulfide catalyst reduced gas formation during the cracking process. This catalyst was reported to crack a 200° to 235° C. oil to a 70-percent yield of gasoline with only 6-percent yield of hydrocarbon gas.

Storage Tests.—Storage tests on synthetic gasoline showed that exposure to light accelerated peroxide formation, which was accom-

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[18] Boyd, G. A., and Seeley, C. H., Hydrocarbon Conversion Process: U. S. Patent 2,253,607, Aug. 26, 1941.
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[19] Work cited in footnote 93, p. 18.

[20] Hanke, F. [Refining Synthetic Benzine Hydrocarbons]: German Patent 719,449, Mar. 12, 1942.
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[21] International Hydrocarbon Synthesis Co. [$CO-H_2$ Synthesis]: French Patent 860,383, Jan. 13, 1941.
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[24] Work cited in footnote 23, this page.

[25] Work cited in footnote 35, p. 7.

[26] Davies, V., Treating Fischer-Tropsch Gasoline: Ind. Chemist, vol. 13, 1937, pp. 442–446.

[27] Work cited in footnote 92, p. 18.

[28] Asbury, W. C., Motor Fuel from Carbon Monoxide and Hydrogen: U. S. Patent 2,264,427, Dec. 2, 1941.
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[30] Atwell, H. V., Gasoline from Gaseous Hydrocarbons: U. S. Patent 2,178,824, Nov. 7, 1939. Motor Fuel from Reaction Products of Carbon Monoxide and Hydrogen: U. S. Patent 2,258,839, Oct. 14, 1941.
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Martin, F., and Tramm, H., Synthetic Motor Fuel: U. S. Patent 2,368,939, Feb. 6, 1945. Production of Liquid Fuel: U. S. APC 60,192, Jan. 22, 1936.
Ruhrchemie A. G., No title: German Appl. R–105,615, July 7, 1939. Office of Publication Board Report 412, May 15, 1945. [Antiknock Gasoline Made from Hydrogenated Carbon Monoxide]: German Patent 726,197, Aug. 27, 1942.

[31] Pier, M., and Simon, W., Cracking or Pressure Hydrogenation of Hydrocarbons: U. S. Patent 2,224,003, Dec. 3, 1940.

panied by a decrease in octane number. o-Cresol inhibited peroxide formation almost completely during a storage period of 2 years. Evaporation losses to the extent of 2 percent by weight and a reduction in the Reid pressure of 0.04 caused a lowering of the octane rating.[32]

Determination of Octane Number.—A method for the analytical-arithmetical determination of the research octane number of gasolines from the Fischer-Tropsch synthesis was reported by Hammerich. The octane number $=0.7\times0.4\times$ (olefin index) $+0.69\times$ ("vaporizability"), the olefin index being equal to (iodine number $\times$ boiling index)/100, and "vaporizability" the mean of constituents boiling between 60° and 100° C.[33]

LUBRICATING OIL

The primary product of the Fischer-Tropsch synthesis does not contain any lubricating-oil fractions, but it does contain large amounts of olefins which can be readily polymerized to yield good lubricating oil.[34] Several possible procedures for the production of lubricating oil from the hydrocarbon synthesis products have been tested, namely: (1) Chlorination of the gas-oil fraction (boiling point, 200° C.) and mixing the products with aromatic hydrocarbons in the presence of aluminum chloride; (2) chlorination of the gas-oil fraction and polymerization without addition of aromatic hydrocarbons; (3) direct catalytic polymerization of the olefins produced in the synthesis; and (4) chlorination of the paraffin wax, followed by elimination of hydrochloric acid and polymerization of the resulting olefins. Of these procedures, the third has received most attention.[35] Pichler's results [35] show that oils prepared from the olefins in Kogasin by the action of anhydrous aluminum chloride had flat viscosity-temperature curves (viscosity index, 90–100); and for the same viscosity they had a higher mean molecular weight than paraffin-base mineral lubricating oils. The viscosities of the fractions and residue obtained on distillation of the oil *in vacuo* increased regularly with the molecular weight. The olefinic bonds in the lubricating oils were readily hydrogenated, for example, by the action of hydrogen at 180° C. and 100 atmospheres, in the presence of a nickel catalyst.

The lubricating oils were as stable toward air and light as mineral lubricating oils; their stability was increased by hydrogenation. Subjected to the British Air Ministry oxidation test, the oils showed a greater increase in viscosity but a smaller increase in Conradson

carbon than mineral lubricating oils. Similar results were obtained in tests on lubricating oils produced by polymerization of the 80° to 140° C.–Kogasin fraction made in the British Fuel Research Board Laboratories [36] and of the 150° to 200° C. fraction of the product obtained by Synthetic Oils, Ltd.[37] Aging by the Indiana oxidation test [38] showed that, as compared with natural products, a sample of the synthetic lubricating oil gave upon oxidation a large increase of viscosity that was associated with the formation of acidic and saponifiable substances, although the amounts of asphalt or coke formed were extremely small. According to Fischer,[39] very thorough hydrogenation of the synthetic oils increased the chemical stability so that no attack by oxygen or concentrated sulfuric acid could be detected, and no corrosion of motor metal parts was observable in a 6-months road test.

According to the Ruhrchemie A. G. patents,[40] it is advantageous, in the synthesis of lubricating oil from Kogasin, to use enough of the polymerizing agent (usually aluminum chloride) to effect complete reaction at a single temperature and to raise the temperature gradually during the process. The polymerizing agent may be used more than once. The properties of the lubricating oil obtained depend to a large extent on the boiling range and olefin content of the Kogasin fraction used. Koch's results [41] show that the higher-boiling Kogasin fractions yielded lubricating oils of highest viscosity index. Unfortunately, the yield is small because of the low olefin content of the high-boiling Kogasin fractions.

Koch [41] found that the synthetic lubricating oil contains one or two double bonds per molecule, and solvent extraction with acetone showed that the degree of unsaturation was about the same for all the fractions thus obtained. Analysis of the oil by Waterman's method showed the presence of about one naphthenic ring per molecule. Since this was true for all of the fractions selectively extracted by acetone, pure isoparaffins were present in only small proportions. Kreulen [42] determined the chemical and physical constants of two completely hydrogenated lubricating oils obtained by polymerization of Kogasin fractions and subsequent hydrogenation. He finds that about 50 percent of the carbon atoms in the synthetic oils occurred in branched paraffin chains. This is in marked contrast to Koch's [41] results with the same type of oils before hydrogenation. The hydrogenated oils, upon analysis by the Waterman method, showed 1.2 to 1.8 rings per molecule, but from parachor measurements the number of rings is 2.3 to 4.0.

Koch and Gilfert [43] and Koch and Hilberath [44] studied the properties of oils produced by polymerization of Kogasin fractions produced from $CO:H_2$ and from $CO:2H_2$. Fractions from the $CO:H_2$ Kogasin

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corresponding to C_5, C_6, and C_7 hydrocarbons and containing 70–75 percent of olefins gave about 65 percent (calculated on the olefin content) of lubricating oil of 1,110 to 1,550 centistokes viscosity at 20° C. and viscosity pole height of 1.88–2.33. The corresponding fractions from CO : $2H_2$ Kogasin contained 43–55 percent olefins and yielded only 35 to 55 percent of oils of viscosity 473 to 585 centistokes at 20° C. and viscosity pole height of 2.23–3.10; this lubricating oil was obviously much inferior to that from the CO : H_2 Kogasin. The lower yields from the CO : $2H_2$ Kogasin were not due to the lower olefin content of the raw material but to a difference in constitution of the olefins, particularly in the position of the double bond. The C_6 and C_7 fractions of the CO : H_2 Kogasin were refractionated into narrow cuts, from each of which a lubricating oil was synthesized. The viscosity of the oils from the C_6 fractions ranged from 2,277 (from 57.0° to 61.0° C. fraction) to 476 (from 67.5° to 69.0° C. fraction) centistokes at 20° C. The flattest viscosity-temperature curve (corresponding to a viscosity pole height of 1.77) was given by the oil from the 63.0° to 63.5° C. fraction, which was principally hexene–1. The steepest curve (corresponding to a viscosity pole height of 2.53) was obtained from the 67.5° to 69.0° C. fraction, which was principally hexene–2. The C_7 fractions showed similar but somewhat less marked differences. There was no apparent relation between the absolute viscosities of the oils and the viscosity pole height. The mean molecular weight of the lubricating oils ranged from 550 to 1,240.

By reducing the temperature of polymerization of a C_5 Kogasin fraction from 20° to 0° C., Koch and Gilfert[45] obtained a more viscous lubricating oil of the same viscosity index. All of the lubricating oils produced had one olefinic bond. Saturation of this bond with hydrogen resulted in a small increase in viscosity but no change in viscosity index. Examination by Waterman's method indicated the presence of one naphthenic ring per molecule.

Various catalytic polymerization procedures and their numerous modifications concerned with the synthesis of lubricating oil from Kogasin have been patented.[46] [47] For example, Imperial Chemical Industries, Ltd., has several patents covering the conversion of Kogasin by chlorination of the high-boiling fraction and of paraffin wax, followed by condensation with aromatic hydrocarbons using aluminum chloride as catalyst.[47] Two synthetic-lubricating-oil processes were operated in France by the Germans during World War II.[48] At Standard Kuhlmann-Lestaque, near Marseilles, highly paraffinic gas oil was chlorinated, and then reacted with benzol-dichlorethane mixture in the presence of aluminum chloride for 6 hours at 70° to 110° C. The products were roughly 20 percent recycle gas oil, 30 percent transformer oil, 30 percent turbine oil, and 20 percent steam-cylinder oil. At the Kuhlmann Co. at Harnes, Fischer-Tropsch gasoline was treated with 3 percent aluminum chloride for 5 hours at room temperature. The quality of the lubricating oils thus obtained was not good. The I. G. Farbenindustrie A. G. has patented a process for lubricating-oil production in which a Kogasin fraction boiling between 170° and 250° C. is subjected to high-frequency silent electric discharge, for example, 7,000 volts and 1,000 cycles, for 20 hours at a pressure of 2 to 5 millimeters of mercury.[49] Sustmann reported inconclusive results from an attempt to produce lubricating oil by polymerizing the unsaturates in a 50° to 250° C. fraction of Kogasin contained in a lead or zinc-plated lead tube under pressures of 5,000 and 11,700 kilograms per square centimeter.[50]

FATTY ACIDS AND RELATED PRODUCTS

Since 1936 there has been rapid development, particularly in Germany, of the art of production of fatty acids by the oxidation of the paraffin wax produced in the Fischer-Tropsch synthesis.[51] [52] In 1938 two plants, each of 20,000 tons per year, were reported.[53] During World War II more than 80,000 tons per year of synthetic fatty acids

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[45] Work cited in footnote 43, p. 63.

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were produced.[54] [55] The Markische Seifen-Industrie had an annual raw-material capacity of 40,000 tons. Three other plants had the following capacities: Oppau, 20,000 tons; Heydebrach, 20,000 tons; and Magdeburg, 12,000 tons. About 150 to 200 tons of fatty acids per month was the maximum used for the production of synthetic fats and margarine. The fatty acids were utilized as follows: Formic acid for treatment of fodder silos; acetic and butyric acids for esterification of cellulose; propionic acid, in the form of calcium salt, as bread preservative; C_5–C_9 acids for hydrogenation to the corresponding alcohols for glyptal-type resin production; C_7–C_9 acids for Foamite-type fire extinguishers; C_9–C_{11} acids for mineral flotation; C_1–C_{18} acids for soap production; and C_9–C_{16} acids for synthetic edible fats, which were of excellent quality.[56] [57] C_{18}–C_{24} acids were used in the form of salts for lubricating greases, softening agents for leather, and lubricants for plastic moldings; and the pitch residues after ketonization and hydrogenation for petroleum-jelly substitutes.

Other uses for the oxidation products of synthetic paraffin wax were as emulsifiers for the manufacture of cutting oils [58] and plasticizers [59]. Paraffins can be oxidized by air. The reaction is strongly exothermic, but when carefully controlled, mainly monocarboxylic acids are produced, along with minor amounts of alcohols. The addition of up to 50 percent by weight of partly oxidized paraffins to the raw material accelerates the reaction.[60] Paraffins with over 34 carbons are most suitable for the process. Operating conditions are 100° to 140° C., 1 cubic meter of air per kilogram of wax,[61] and the presence of catalysts such as manganese [62] [63] and other metal [64] salts of fatty acids. The crude saponification product is purified by treatment with steam [63] and by solvent extraction [64].

Jantzen and his coworkers [65] studied the composition of the fatty acids obtained from the oxidation of Fischer-Tropsch paraffin wax containing 27.4 percent of C_{16}–C_{19}, 31 percent of C_{19}–C_{22}, 23.7 percent of C_{22}–C_{25}, 11.7 percent of C_{25-27}, and 1.7 percent of C_{28} hydrocarbons. The oxidation product consisted almost entirely of saturated, normal, fatty acids of both the odd and even series, from which the acids from C_8 to C_{18} were separated and identified by fractionation of the methyl esters. Acids with less than 8 and more than 18 carbon atoms per molecule formed 7.4 and 18 percent, respectively, of the total product. The balance consisted of approximately equimolecular proportions of C_9 to C_{15} acids. Small amounts of unsaturated and of hydroxy acids were present. Studies in Germany during World War II devoted to the production of substitutes for the natural edible fats showed that even with an improved process, out of a total fatty acid yield of 55–60 percent, 20–25 percent consisted of fatty acids with carbon atoms ranging from 1 to 9, and of this latter amount one-half consisted of fatty acids ranging from formic to butyric. [66]

In a process patented by Martin [67] branched-chain fatty acids were produced by oxidation of the alcohols and aldehydes formed by the OXO process at 200° C. and 50 to 150 atmospheres pressure.

MISCELLANEOUS PRODUCTS

The oxidation of Fischer-Tropsch olefins containing more than 6 carbon atoms using hydrogen peroxide yields soap-forming carboxylic acids [68]. Recovery of higher oxygen-containing organic compounds from synthetic oils by extracting with isopentane-potassium carbonate mixture is reported.[69]

An important process was developed at the I. G. Farbenindustrie A. G. plant at Leuna for the production of 54,000 tons per year of Mersol, a soap substitute, which was manufactured from the C_{12}–C_{18} fraction of Fischer-Tropsch oil.[70] [71]

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Experiments on the cyclodehydrogenation of synthetic paraffin hydrocarbons were reported by several Russian investigators.[72] The C_7 to C_9 fraction of primary oil with Al_2O_3–Cr_2O_3–CoO and Cr_2O_3–CoO catalysts at 475° C. yielded products that were at least 50 percent aromatic. Combination of these aromatic products with the product resulting from polymerization and hydrogenation of the C_3 to C_4 fraction of the primary product yields high-grade fuels.[73]

The residual gas from the Fischer-Tropsch reactors containing about 21.3 percent carbon monoxide, 37.5 percent hydrogen, 23.6 percent methane, 8.1 percent carbon dioxide, and 8.5 percent nitrogen was mixed with water gas or coke-oven gas for utilization as illuminating gas.[74] [75]

FISCHER-TROPSCH COST ESTIMATES

Cost estimates based on the Ruhrchemie process as of 1938 and on prewar (1940) prices in the United States were presented by Williams[76] before a United States Senate subcommittee in 1943. These estimates, for a plant producing 2,424 barrels of primary product per day, from any one of three raw materials—coke, subbituminous coal, and natural gas—are summarized in table 13. The use of cheap subbituminous coals or lignites and modern continuously operating gas generators may reduce the cost of Fischer -Tropsch products from coal.[77]

TABLE 13.—*Cost estimates on Ruhrchemie process if operated in the United States in 1940, cents*

Raw material	Cost of synthesis gas per gallon of primary product	Cost of 1 gallon of primary product	Cost of 1 gallon of finished synthetic gasoline
Coke	12.2	18.6	24.4
Subbituminous coal	7.3	13.6	18.2
Natural gas	6.6	13.0	17.4

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[76] Williams, J. P., The Manufacture of Motor Fuels and Synthetic Petroleum, Especially from Coal. Synthetic Liquid Fuels Hearings Before a Subcommittee of the Committee on Public Lands and Surveys, U. S. Senate, 78th Cong., 1st Sess. on S. 1243, Aug. 3, 4, 6, 9, and 11, 1943: U. S. Government Printing Office, Washington, D. C., 1944, pp. 238–247.

[77] Miller, B., Synthetic Liquid Fuels and the Manufactured-Gas Industry: Gas Age, vol. 97, No. 4, 1946, pp. 19–21, 68.

Porter, H. C., Coal as an Auxiliary Source of Gasoline Supply: Chem. Eng. News, vol. 22, 1944, p. 901.

Farish[78] presented raw material and over-all steel requirements, as well as investment and operating costs for synthetic liquid fuel production from hydrogenation of both coal and carbon monoxide. The estimates based on 1942 prices in the United States are shown in table 14. Fieldner[79] reported that Bureau of Mines estimates for steel requirements are 8.8 and 14.3, whereas Farish's estimates are 14.1 and 8.9 tons per barrel per day for the hydrogenation of coal and of carbon monoxide (Ruhrchemie process), respectively.

The cost of gasoline production, using natural gas at 3 to 5 cents per 1,000 cubic feet as raw material and a radically new process designed by United States engineers, was reported by Russell[80] and Weil[81] to be close to the present cost of production of gasoline from petroleum. A summary of recent cost estimates was prepared by the Gulf Research & Development Co.[82] and is presented in table 15.

TABLE 14.—*Cost estimates on synthetic liquid-fuel processes if operated in the United States in 1942*

	Approximate plant investment per barrel of gasoline per day	Approximate tons of steel per barrel of gasoline per day	Approximate cost of gasoline per gallon without depreciation, cents	Approximate gasoline total cost including depreciation, cents
1. High-pressure coal hydrogenation	$12,800	14.1	15.9	22.6
2. Fischer process, European design, from coal	7,600	8.9	14.7	19.2
3. Fischer process, European design, natural gas at 5 cents per 1,000 cubic feet	4,750	6.5	6.0	8.8
4. Modern high-pressure hydrogenation of petroleum	1,150	1.4	4.8	5.5
5. Modern oil refinery crude at $1.20 per barrel, thermal cracking	700	.7	4.1	5.3
6. Modern oil refinery crude at $2.00 per barrel, thermal cracking	700	.7	8.3	8.5

Items 1 and 2 are for plants of 2,950 barrels and 3,960 barrels production capacity per day, respectively. For larger plants—for example, 30,000 tons—the costs would be slightly lower, probably about 15–16 cents per gallon and 15.5 cents per gallon, respectively.

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[78] Farish, W. S., Manufacture of Gasoline and Oil from Coal. Synthetic Liquid Fuels Hearings before a Subcommittee of the Committee on Public Lands and Surveys, U. S. Senate, 78th Cong., 1st Sess. on S. 1243, Aug. 3, 4, 6, 9, and 11, 1943: U. S. Government Printing Office, Washington, D. C., 1944, pp. 51–59.

[79] Fieldner, A. C., The Production of Liquid Fuels from Coal and Lignite. Synthetic Liquid Fuels Hearings before a Subcommittee of the Committee on Public Lands and Surveys, U. S. Senate, 78th Cong., 1st Sess., on S. 1243, Aug. 3, 4, 6, 9, and 11, 1943: U. S. Government Printing Office, Washington, D. C., 1944, pp. 168–178.

[80] Russell, R. P., Costs of Fischer-Tropsch Gasoline. Synthetic Liquid Fuels Hearings Before a Subcommittee of the Committee on Public Lands and Surveys, U. S. Senate, 78th Cong., 1st Sess., on S. 1243, Aug. 3, 4, 6, 9, and 11, 1943: U. S. Government Printing Office, Washington, D. C., 1944, p. 39.

[81] Weil, B. H., Fuels of the Future: Petrol. Eng., vol. 16, No. 5, 1945, pp. 156–166. Shale Oil and Other Substitutes for Petroleum: Nat. Petrol. News, vol. 35, No. 31, 1943, p. R348. Universal Oil Products Co., Lib. Bull., No. 33, 1943.

[82] Fieldner, A. C., and Schroeder, W. C., Oil and Gasoline from Oil Shale and Coal: Fuel, vol. 23, No. 2, 1944, pp. 34–36.

Fortune, Coming: Ersatz Gasoline: Vol. 31, March 1935, pp. 200, 203.

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Institute of Gas Technology, The Fischer-Tropsch Process: Report for the Technical Section Post-War Planning Cooperating Committee, Aug. 1945, pp. 19–33.

Weil, B. H., Economic Factors to Determine Fuels of the Future: World Petrol., vol. 16, No. 2, 1945, p. 49.

TABLE 15.—*General summary of cost data for synthetic liquid-fuels process*[1]

	From coal hydrogenation	From Fischer-Tropsch synthesis, using coal	From Fischer-Tropsch synthesis, using natural gas	From oil shales	From petroleum
Investment (dollars per daily barrel).	7,500–14,300	6,180–16,667[2]	2,200–4,767	375–3,000	700.
Operating costs[3] (cents per gallon).	15.5–25[2]	18.2–24.4[2]	4.8–17.4[2]	–10.7[1]	5–6.
Total raw materials required (tons per barrel).	*Coal.*—0.5–1.25.[2]	*Coal.*—0.7	*Natural gas.*—0.22–0.25.	*Oil shale.*—0.9–2.7.	*Crude oil.*—0.328.
Steel requirements (tons per barrel).	8.3–14.1	8.9–14	2.8–6.5	1.3–[1]	0.7.
United States reserves of raw material.	*Coal.*—3.2 trillion tons (3,000 years).	*Coal.*—3.2 trillion tons (3,000 years).	*Natural gas.*—85–170[2] trillion cubic feet (30 years).	*Shale oil.*—92 billion barrels (65 years).	*Oil.*—20–21 billion barrels (14 years).

[1] Data presented represent testimony extremes. In 2 cases, it appears that truly representative ranges were not given.

[2] Trend of testimony indicated that the most probable figure was of this order, although perhaps somewhat higher or lower. For operating costs by the first 2 methods, eventual estimates are somewhat lower.

[3] Including depreciation. Figures are presumably for 70–75 octane number gasolines.

Recent reports (1945–46)[83] state that 10,450 cubic feet of natural gas will yield 1 barrel of gasoline, which is equivalent to 4 to 6 gallons of gasoline per 1,000 cubic feet of raw gas. A plant capable of making 300,000 barrels per day (United States design) would cost 660 million dollars, as compared with a plant of German design at a cost of 1.4 billion. Using 5-cents-per-1,000-cubic-feet natural gas, 1 gallon of synthetic gasoline is estimated at 4.8 cents, including depreciation, but not taxes and profit. For the same conditions, refinery costs are 5.3 cents per gallon, starting from crude oil at $1.20 per barrel. However, Oberfell[84] has stated that the synthesis process using natural gas will not be able to compete with present refinery methods utilizing crude petroleum until the price of crude reaches $1.75 to $2.00 per barrel.

Keith[85, 86] has reported that fuel reserves in the United States as of January 1, 1946, if converted into crude oil, would make a total of 6,326 billion barrels, of which 21 billion are crude oil itself, 25 billion are obtained from natural gas, and 6,280 billion from coal synthesis. He reported that a Fischer-Tropsch plant now being designed by the Hydrocarbon Research Co., Inc., will produce gasoline at a cost of 5.25 cents per gallon, based on natural gas at 5 cents per 1,000 cubic feet and plant depreciation of 10 percent. He also predicted synthetic gasoline from coal at $2.00 per ton in the very near future. More conservative unpublished estimates on the process of Hydrocarbon Research, Inc., indicate a cost of about 7 cents per gallon of gasoline.

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[83] Alden, R. C., Conversion of Dry Natural Gas to Liquid Fuels: World Petrol., vol. 17, No. 4, 1946, pp. 46–49, 70.

Dotterweich, F. H., Report of Subcommittee. 1. On New Developments: Am. Gas Assoc. Proc., vol. 26, 1944, pp. 316–318.

Fieldner, A. C., Liquid Fuels from Sources Other than Petroleum. Hearings before a Special Committee Investigating Petroleum Resources, U. S. Senate, 79th Cong., 1st Sess., S. Res. 36: June 19–25, 1945, pp. 336–349.

Foster, A. L., Chemical Utilization of Natural Gas Limited Only by Commercial Demand: Oil and Gas Jour., vol. 44, No. 52, 1946, pp. 83, 84, 91.

Industrial and Engineering Chemistry, Gasoline from Natural Gas: Vol. 37, No. 7, 7 Adv. Sec., 1945, p. 5.

Schroeder, W. C., An Account of the German Synthetic Liquid Fuels Industry. Hearings before a Special Committee Investigating Petroleum Resources, U. S. Senate, 79th Cong., 1st Sess., S. Res. 36; June 19–25, 1945, pp. 349–360.

[84] Oberfell, G. G., Utilization of Natural Gas in the United States: Oil Gas Jour., vol. 44, No. 32, 1945, pp. 76–78. Petrol. Refiner, vol. 25, No. 1, 1946, pp. 94–101. Petrol. Eng., vol. 17, No. 4, 1946, pp. 158–178.

[85] Work cited in footnote 76, p. 12.

[86] Oil and Gas Journal, Natural Gas Investigation by the Federal Power Commission, Washington: Vol. 45, No. 8, 1946, pp. 60–61. High-Octane Motor Fuel from Natural Gas: Vol. 43, No. 36, 1945, pp. 48–49.

BUREAU OF MINES RESEARCH ON EFFECT OF CATALYST PREPARATION, REDUCTION, AND INDUCTION PROCEDURES ON ACTIVITY

CATALYST-TESTING EXPERIMENTS

INTRODUCTION AND SUMMARY

The results of the work done by Smith and his coworkers in the Bureau of Mines during the years 1928 to 1930 have been described. Because of lack of funds, this research was discontinued until 1942, when additional funds were allotted for the erection of a building to house catalyst-testing and engineering laboratories. Since the completion of these laboratories in January 1944, the catalyst-testing work summarized below was done.

(1) Active, durable, and easily regenerated iron catalysts can be prepared by observing special conditions of precipitation of iron hydroxide from ferric nitrate solutions. There is little, if any, advantage in two- or three-component iron catalysts, such as iron–copper or iron–copper–manganese.

(2) Excellent correlations have been observed between X-ray diffraction patterns, magnetic susceptibilities of the iron catalysts, and their activity in the synthesis. A comparison of the X-ray diffraction patterns of active and inactive iron catalysts (as freshly prepared and before use in the synthesis) with the diffraction patterns of the ferric oxide hydrates and hematite (αFe_2O_3) shows that the inactive catalyst contains $\beta Fe_2O_3 \cdot H_2O$ and the active catalyst contains either $\alpha Fe_2O_3 \cdot H_2O$ or αFe_2O_3, but no $\beta Fe_2O_3 \cdot H_2O$. Catalysts prepared from ferric chloride were all inactive, and it is probable that $\beta Fe_2O_3 \cdot H_2O$ is formed upon hydrolysis of ferric chloride.

The iron catalysts of high activity had high magnetic susceptibility and were ferromagnetic, while the inactive catalysts had only about one-half of the magnetic susceptibility of the active catalysts.

(3) Tests on the durability of iron catalysts showed that their useful life was only a few weeks at atmospheric pressure, but at least several months at pressures between 5 and 7 atmospheres.

(4) The X-ray diffraction pattern of cobalt–thoria–kieselguhr (diatomaceous earth) catalyst showed that the unreduced catalyst was almost completely amorphous, the sharpest line in the pattern being one due to β quartz from the kieselguhr. The reduced catalyst showed the lines of cubic cobalt crystals. As the cubic form is unstable at room temperature, it is likely that the thoria and possibly also the kieselguhr have an inhibiting effect on the conversion of cubic to hexagonal cobalt.

(5) Surface areas of unreduced cobalt–thoria–kieselguhr and cobalt–thoria–magnesia–kieselguhr catalysts range from 67 to 98 square meters per gram. Most of the area is due to the cobalt oxide-promoter complex and not to the kieselguhr. Some correlation exists between catalyst activity and total surface area for cobalt catalysts of the same type.

The presence of promoters in cobalt catalysts makes reduction more difficult and prevents sintering. The area of a cobalt–thoria–magnesia–kieselguhr catalyst reduced at 400°C. in a rapid stream of hydrogen for 2 hours was 36.9 square meters per gram.

(6) Unreduced iron catalysts (precipitated, gel-type) have a higher surface area than unreduced cobalt catalysts and usually have a gellike structure. Upon reduction at 360°C. the areas of the iron catalysts dropped to about 5 percent of that of the unreduced catalyst.

(7) Filter-Cel, a marine kieselguhr from Lompoc, Calif., and Portuguese kieselguhr (probably a fresh-water product) were found to be equally effective as carriers for the cobalt–thoria–magnesia catalyst, and both were definitely superior to "Hyflo Super Cel," which is prepared by alkali treatment and calcination of Filter-Cel.

(8) Three different modes of induction of the cobalt–thoria–magnesia–kieselguhr catalyst were tested. Induction at 100 pounds per square inch pressure of $2H_2 + 1CO$ resulted in a lower activity during the first 400 hours of operation as compared with similar induction at atmospheric pressure. Beyond 400 hours of operation the activity was the same for the two induction procedures. Use of a temperature or a contraction schedule in the induction procedures gave the same activity within the limits of reproducibility of the tests.

(9) Acid extraction and calcination of Filter-Cel and alkali extraction and washing of the magnesia used in preparation of the cobalt–thoria–magnesia–Filter Cel catalyst did not enhance its activity in the synthesis.

(10) Operation with the cobalt catalyst at atmospheric pressure for 1,500 hours was followed by an additional 800 hours at 100 pounds per square inch. The activity during the latter period was identical, within the limits of reproducibility of the tests, with that during the first 1,500 hours.

(11) In the catalyst tests a 15.8-millimeter internal-diameter catalyst tube containing a 6.4-millimeter outside-diameter thermocouple well was used. The thickness of the annulus containing the catalyst was 4.7 millimeters. In this apparatus it was found possible to increase the space velocity (volumes of synthesis gas per volume of catalyst per hour) to about 500 without damaging the catalyst by sintering. The operating temperature increased from about 180° C. at 100 to 205° C. at 500 space velocity. The space-time yield of oil plus wax increased from 10 kilograms per cubic meter of catalyst per hour at 100 space velocity to 42 kilograms at 500 space velocity.

(12) The temperature coefficient of the synthesis rate on the cobalt catalyst was measured by determining the space velocity necessary for about 70-percent contraction at several temperatures in the range 175° to 200° C. From the temperature coefficient the energy of activation was calculated to be 24 ± 2 kilocalories per gram molecular weight of $2H_2 + 1CO$ reacting. More precise values of the rate and temperature coefficient now are being measured and will be included in a later publication.

(13) The results of comparative pilot-plant tests on six iron catalysts made at Schwartzheide in Germany are included in this paper. The results of research at the Kaiser Wilhelm Institute for Coal Research on induction of iron catalysts using special carbiding procedures also are included.

CATALYST PREPARATION

Three methods for preparing catalysts were used—namely, precipitation as hydroxides or carbonates, impregnation of a carrier with the metal nitrates and subsequent roasting, and ignition of the nitrate or sulfate. The precipitation method was used in 80 percent of the

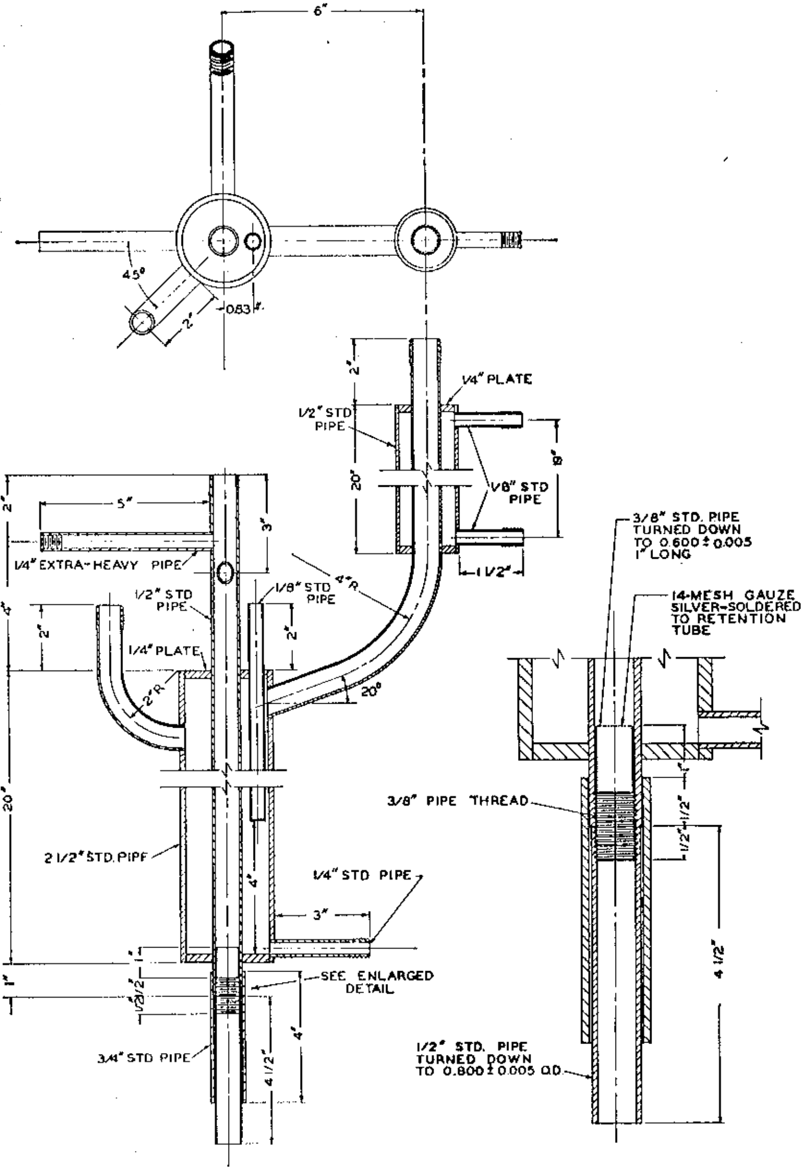


FIGURE 5.—Single-tube converter (modified Downs type), January 1944.

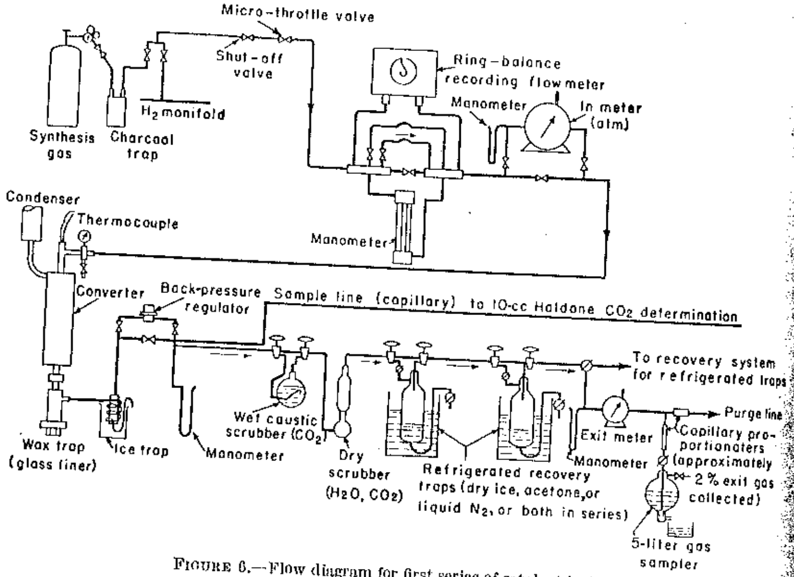
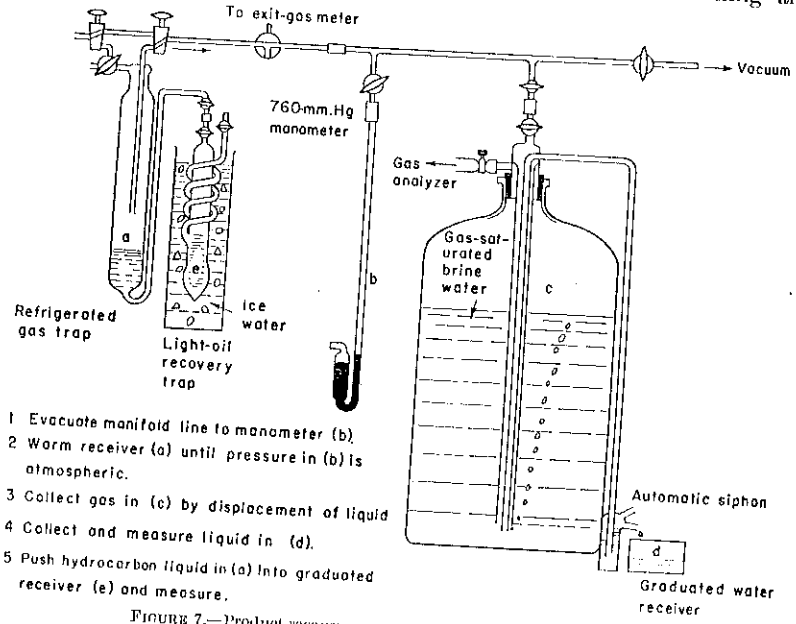


FIGURE 6.—Flow diagram for first series of catalyst tests.

preparations, and particularly for iron catalysts a study was made of the following variables: Nature of reagents, concentration of solutions, temperature of precipitation, method and extent of washing and drying, and method of forming particles of desired shape and size. The details of catalyst preparation are discussed in appendix 1, and the more important data are collected in tables 16 to 21, inclusive.



1 Evacuate manifold line to manometer (b).
2 Warm receiver (a) until pressure in (b) is atmospheric.
3 Collect gas in (c) by displacement of liquid
4 Collect and measure liquid in (d).
5 Push hydrocarbon liquid in (a) into graduated receiver (e) and measure.

FIGURE 7.—Product-recovery system in first series of catalyst tests.

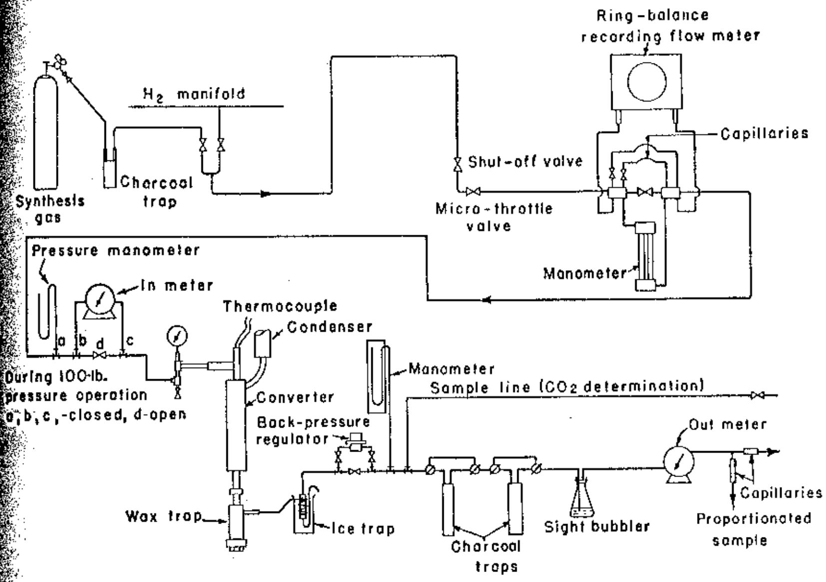


FIGURE 8.—Flow diagram for "X" series of catalyst tests.

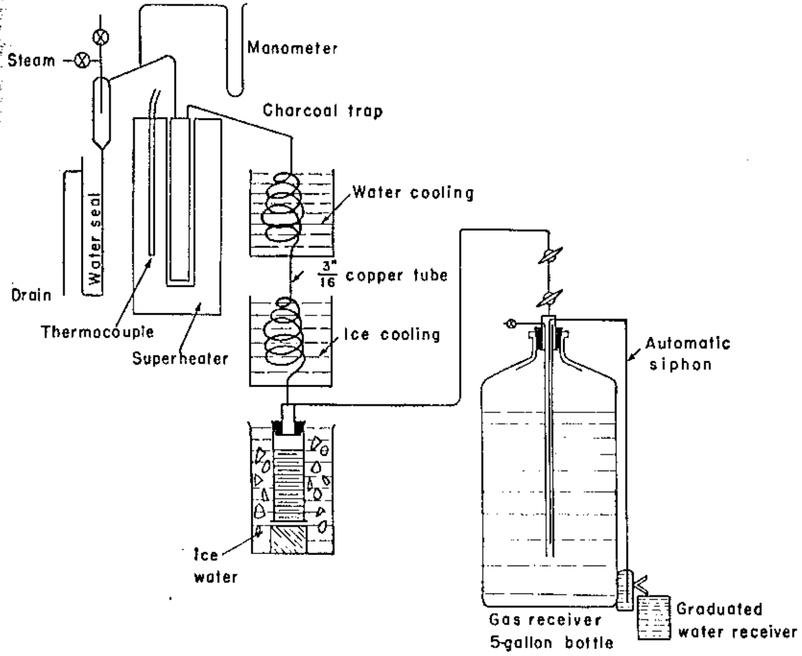


FIGURE 9.—Recovery of products in "X" series tests.

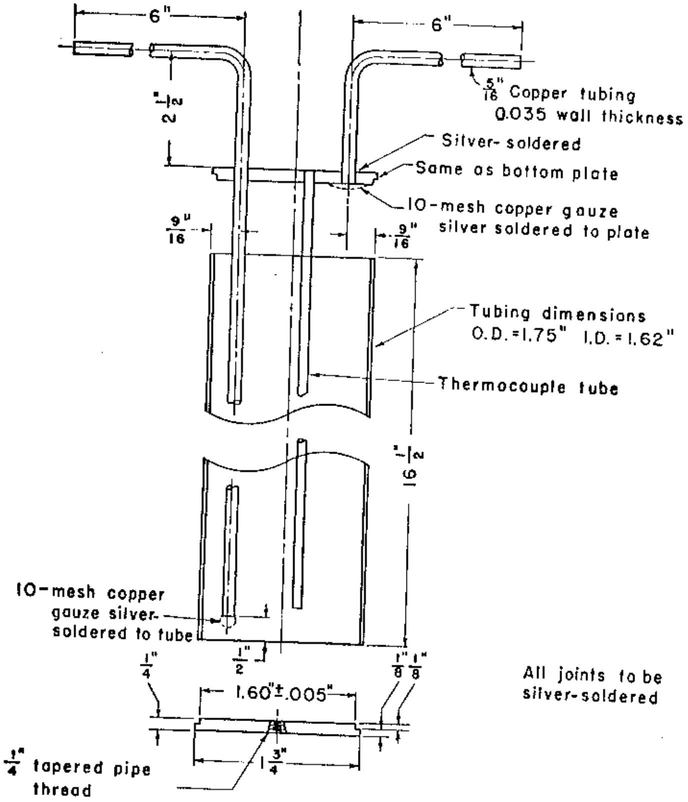


FIGURE 10.—Charcoal trap for "X" series of catalyst tests.

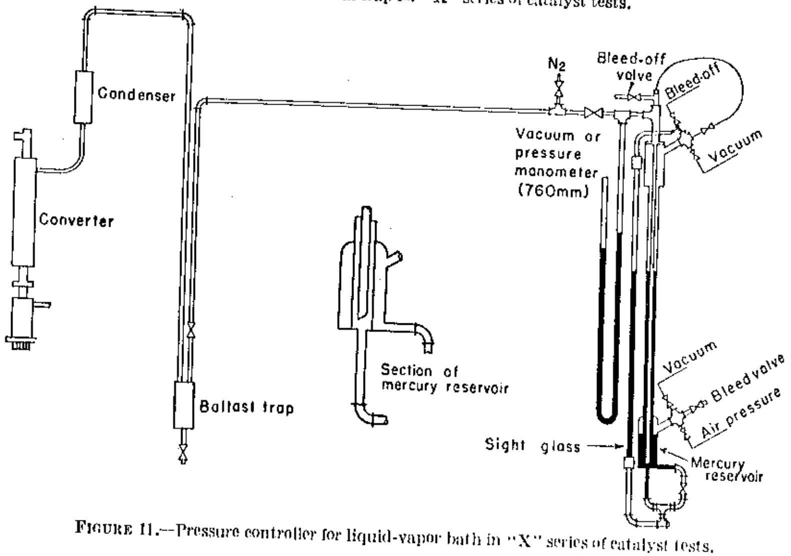


FIGURE 11.—Pressure controller for liquid-vapor bath in "X" series of catalyst tests.

DESCRIPTION OF APPARATUS

The reactor and auxiliary apparatus employed in the hydrogenation of carbon monoxide on a laboratory scale are shown in figures 5 to 11, inclusive, and photographs of the assembly of 12 units are shown in figures 12, 13, and 14. The converter proper consisted of half-inch standard black pipe welded into a jacket of 2½-inch standard pipe, the total converter length being about 50 centimeters. In the inner tube

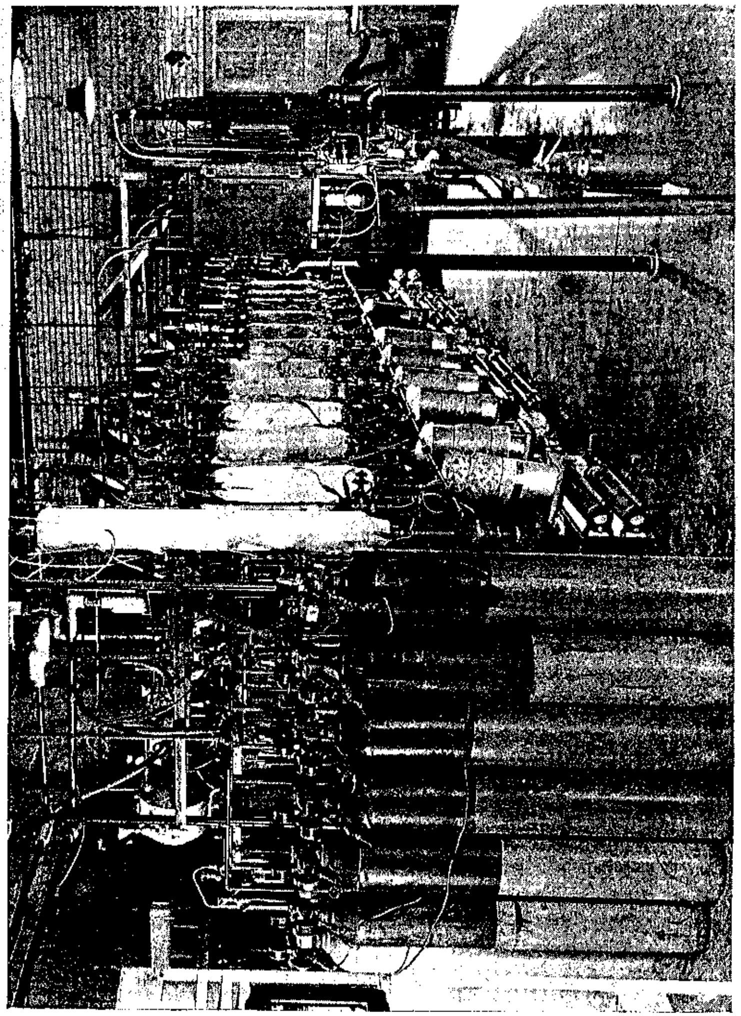


FIGURE 12.—Assembly of 12 laboratory-scale Fischer-Tropsch units.

of 11 of the units was a 30-centimeter catalyst bed, containing 45-50 cubic centimeters of catalyst supported about 6 inches from the bottom of the converter by a wire screen. The twelfth unit contained a catalyst bed 90 centimeters deep. The catalyst tubes were heated externally by a fluid, such as Dowtherm, boiling outside the catalyst tube under constant pressure, thus maintaining constant temperature

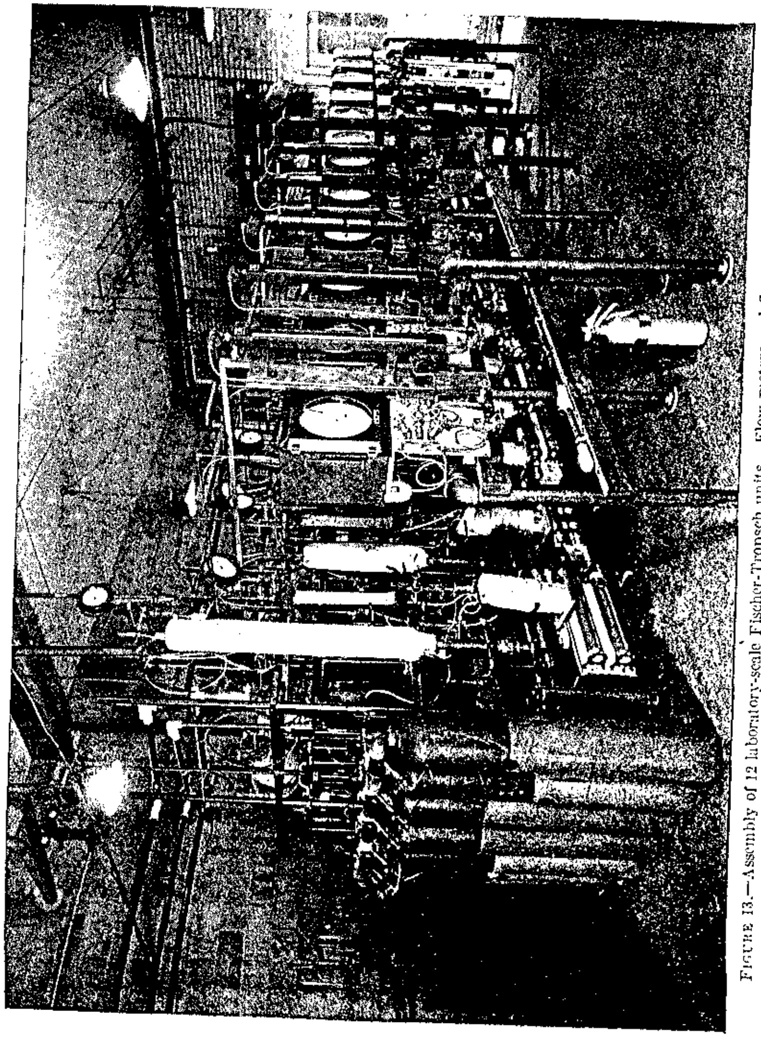


FIGURE 13.—Assembly of 12 laboratory-scale Fischer-Tropsch units. Flow meters and flow recorders in foreground.

in the catalyst. The liquid-vapor bath was heated electrically by a resistance winding on the outside of the 2½-inch jacket. The pressure above the liquid was automatically regulated by a boiler pressure controller, as shown in figure 11. Vertical temperature gradient for 30- and 90-centimeter catalyst depths are shown in figures 15 and 16, respectively.

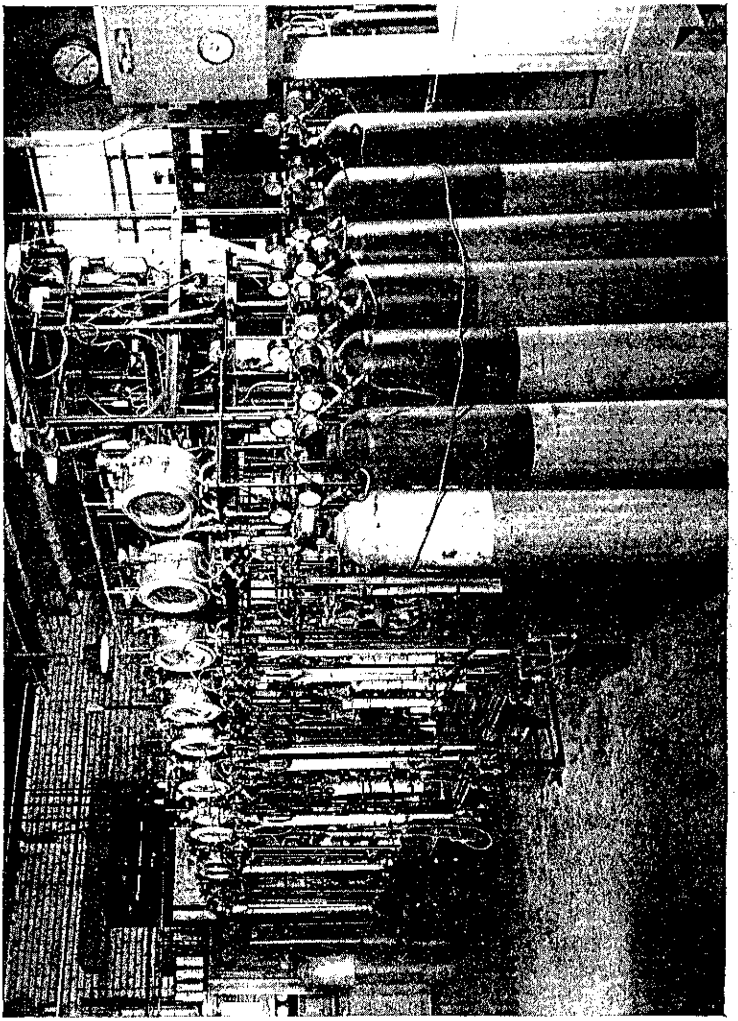


FIGURE 14.—Assembly of 12 laboratory-scale Fischer-Tropsch units. Rear view, showing end-gas meters.

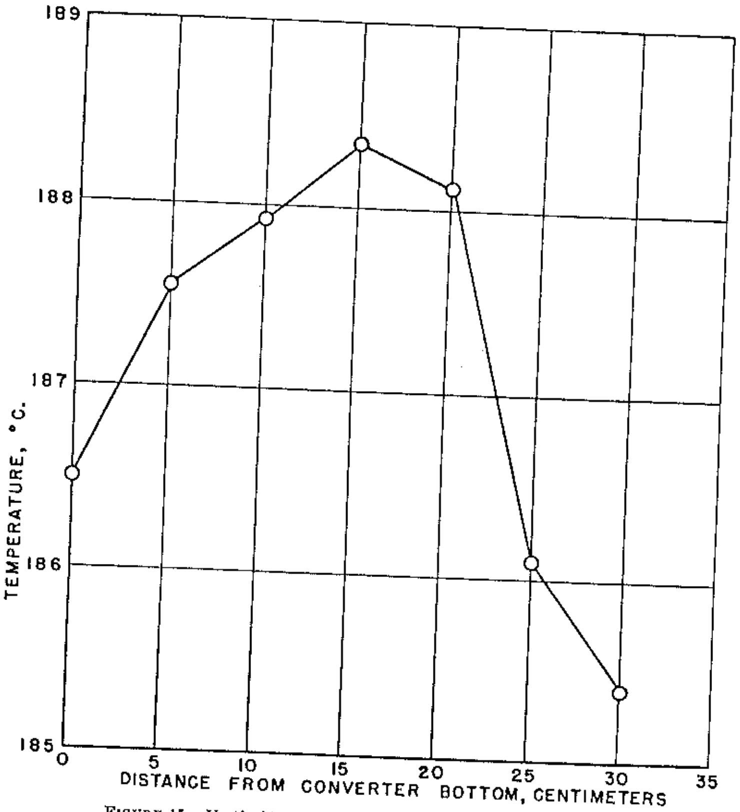


FIGURE 15.—Vertical temperature gradient in 30-cm. catalyst bed.

The auxiliary apparatus consisted chiefly of traps for collecting products and meters for measuring feed and exit gases and for regulating the flow of gases. Before entering the converter, the synthesis gas was scrubbed through a charcoal trap and metered through a flow meter. The heavy oil, wax, and water in the gas-liquid mixture issuing from the bottom of the converter dropped into the air-cooled wax trap just below the converter. The auxiliary ice trap next to the wax trap collected moisture and heavy hydrocarbons, which were not taken up in the wax pot, thus protecting the back-pressure regulator.

TABLE 16.—*Preparation of unpromoted iron catalysts; formation of ferric oxide*

Catalyst No.	Reagents				Temperature of precipitation, ° C.	Time of addition of precipitant, minutes	Potassium, percent [1]	Sodium, percent [1]	Appearance of precipitate	
	Source of iron	Concentration of solution, mols salt per liter water	Precipitant	Concentration of solution, mols salt per liter water					Color	Volume, liters per 100 grams Fe_2O_3
10A	$Fe(NO_3)_3$	0.6	K_2CO_3	4.1	80	25	0.073	0.014	Brown	2.2
10B	do	.8	do	4.1	70	25	.078	.003	Red-brown	1.8
10C	do	1.2	do	4.1	75	25	.055	.003	Choc.-brown	1.3
10D	do	1.1	do	4.1	83	30	.068	.005	Tan	1.7
10F	do	.6	do	3.3	68	<5	.005	.003	Red-brown	2.4
10K	do	.8	do	4.1	70	25	.042	.004	do	1.6
10M	do	.7	do	3.7	65	15	.067	.008	Choc.-brown	2.3
47A	$FeCl_3$	.8	do	4.0	75	35	.078	.005	Tan	1.8
47C	do	.8	do	3.4	72	<5	.015	.004	Choc.-brown	2.3
47D	do	.5	do	3.4	85	45	.046	.005	Light tan	1.4
47F	do	.8	do	3.4	76	<5	.017	.002	Choc.-brown	2.1
48A	$Fe(NO_3)_3$	.8	NaOH	11.8	73	30	.013	.067	do	1.8
49A	Sponge iron				Wetted with HNO_3.					
50A	Lavino oxide				Untreated.		.018	7.7		
50B	do				Untreated.					
50C	do				By ignition.					
68A	Limonite ore				Untreated.					
68B	do	.3	K_2CO_3	3.5	75	25			Choc.-brown	1.8
69A	$Fe_2(SO_4)_3$		Ignition		[2] 538					
70A	$Fe(NO_3)_3$		do		[2] 325		.028	.048		
80A	do	.6	KOH	9.0	83	35	.073	.006	Choc.-brown	1.9
81A	do	.5	Na_2CO_3	3.7	78	25			do	2.1

[1] Percent of dry unreduced catalyst, determined by use of flame photometer, after separation of most of the iron as ferric chloride by ether extraction.
[2] Temperature of ignition.

TABLE 17.—*Preparation of unpromoted iron catalysts; processing of ferric oxide*

Catalyst No	Washing				Drying				Final formulation	
	Number of decantation washes	Wash water: precipitate ratio, volumes	Total volume of wash water, liter per gram Fe_2O_3	Extent of washing	Temperature, °C.	Duration, hours per gram of final product	Dry cake yield,[1] percent	Appearance of dry cake	Appearance of granules[2]	Bulk density of granules, g./cc.
10A	12	1	0.35	NO_3 negative	23 105	0.2 .4	98.6	Black gel, conchoidal fracture	Pellets, hard dark brown	1.40
10B	16	1	.24	do	23	1.2	103.5	Black gel, conchoidal fracture	Pellets, hard dark brown	1.32
Part A					150	.3				
Part B					150	.3			Pellets, hard dark brown	1.30
Part C					150	.3			do	1.09
10C	16	1	.44	NO_3 negative	23 149	.4 .1	104	Black gel, conchoidal fracture	do	1.20
10D	16	1	.64	do	23 149	.7 .6	100	Dark brown gel, dull	do	1.23
10F	17	1	.34	do	23	.4	107	Black gel, conchoidal fracture	do	1.31
Part A					85	.2				
Part C					149	.2			Pellets, hard dark brown	1.30
10K	16	1	.24	NO_3 negative	23 148	1.1 .1	103	Black gel, conchoidal fracture	do	1.24
10M	16	1	.37	Cl positive	23 150	1.5 .2	105	Dark brown gel, dull	Granules 8-14 mesh, hard black Pellets, hard dark brown	1.17 .93
47A	17	1	.28	do	23 149	.4 .06	104	do	do	1.05
47C	18	1	.45	do	23 147	1.0 .1	105	do	do	1.20
47D	16	1	.53	do	23 150	.6 .4	105	Red-brown, nongel	Pellets, soft brown	1.04
47F	18	1	.50	do	23 150	.8 .4	101	Dark brown gel, dull	Pellets, hard dark brown	1.38
48A	17	1	.26	NO_3 positive	23 150	.4 .2	100	Brown, dull, somewhat hard	do	1.17
49A					23 150				Lumps, hard, 8-20 mesh	1.75
50A					149			Red-brown powder	Pellets, hard dark brown	1.16
50B			(3)	Cl, NO_3, SO_4 negative.	23 150			do	do	1.61
50C					85 151	.2 .2	74	Brown lumps	do	1.48
65A					150			Brown powder	do	1.75
68B	16	1.5	.53	NO_3 negative	23 149	1.4 .2	75	Black gel, conchoidal fracture	do	1.40
69A								Tan to red powder	Pellets, hard brown	1.30
70A							94	Red powder	Pellets, soft, dark red	1.40
80A	17	1	.56	NO_3 negative	23 150	.9 .1	107	Brown, dull, somewhat hard	Pellets	1.09
81A	16	1	.40	do	23 150	.9 .1	106	Black gel, conchoidal fracture	Pellets, hard dark brown	1.34

[1] Theoretical yield assumed to be Fe_2O_3, calculated from starting material.
[2] All pellets ⅛-inch in diameter by $\frac{5}{32}$-inch in length, with the following exceptions: 47F, 50A—⅛-inch x ⅛-inch.
[3] Water-soluble impurities removed by refluxing.

TABLE 18.—*Preparation of promoted iron catalysts; formation of iron + promoter oxides*

Catalyst No.	Composition of catalyst	Reagents					Temperature of precipitation, ° C.	Appearance of precipitate	
		Source of iron	Promoter	Total concentration of solution, mols salt per liter water	Precipitant	Concentration of solution, mols per liter water		Color	Volume, liters per 100 grams total oxides
1E	Fe : Cu :: 4 : 1	$Fe(NO_3)_3$	$Cu(NO_3)_2$	0.7	KOH	6.4	80	Chocolate brown	1.7
5A	do	$FeCl_3$	do	.6	do	7.3	80	Light brown	3.0
6A	Fe^{+3} : Fe^{+2} : Cu :: 8/3 : 4/3 : 1	$FeCl_3$, $FeSO_4$	do	.6	NaOH	6.7	80		2.5
9A	Fe : Cu :: 4 : 1	$Fe(NO_3)_3$		.6	NH_4OH	9.0	80		1.8
11A	do		do	.3	$(NH_4)_2CO_3$				
		do	do	1.0	NaOH		75		3.0
		do	do		$Na_2B_4O_7$	Sat.	23		
15A	FeO : ThO_2 :: 5 : 1	$FeSO_4$	$Th(NO_3)_4$	.4	NaOH	7.0	71		1.3
20A	Fe : Zn : Cu :: 4 : 1 : 1	$Fe(NO_3)_3$	$Cu(NO_3)_2$, $Zn(NO_3)_2$	.4	K_2CO_3	3.5	74	Brown	2.5
21A	Fe : Cu : Al :: 4 : 1 : 1	do	$Cu(NO_3)_2$, $Al(NO_3)_3$	.4	do	3.5	74	do	2.5
22A	Fe : Cu : Cr :: 4 : 1 : 1	do	$Cu(NO_3)_2$, $Cr(NO_3)_3$	.4	do	3.5	76	do	2.7
23A	Fe : Cu :: 4 : 1	$FeSO_4$	$CuSO_4$	.4	KOH	4.0	70	Black	.8
24A	do	do	do	.4	K_2CO_3	3.0	70	do	.8
24C	do	do	do	.6	do	3.0	81	do	.4
25A	do	$FeSO_4$	do	.4	NaOH		72		1.7
		do	do		$Na_2B_4O_7$	Sat.	23		
39A	Fe : Co : Cu : HSC[1] :: 4 : 1 : 1.25 : 8.25	$FeSO_4$	$Co(NO_3)_2$, $Cu(NO_3)_2$	.7	K_2CO_3	3.5	70	Black	.5
		do	do		$Na_2B_4O_7$	Sat.	23		
40A	Fe : Zn :: 4 : 1	$Fe(NO_3)_3$	$Zn(NO_3)_2$	.5	K_2CO_3	3.8	73	Red-brown	1.5
43A	Fe : Cu :: 4 : 1	$Fe_2(SO_4)_3$	$CuSO_4$	.4	do	3.8	71	Rust	.7
44A	Fe_2O_3 : CrO_3 : 1 : 4	$Fe(NO_3)_3$		.2	NaOH	5.5	75	Red	
			CrO_3						
51A	Fe : Th :: 5 : 1	do	$Th(NO_3)_4$	.4	K_2CO_3	3.5	75	Chocolate brown	2.5
67A	Fe : Co : Th :: 3 : 2 : 1	do	$Th(NO_3)_4$, $Co(NO_3)_2$	.4	do	3.0	73	do	2.5
85A	Fe : Cu :: 4 : 1	$FeCl_2$	$CuCl_2$	.6	do	3.0	82	Black	.4

[1] HSC=Hyflo Super-Cel.

TABLE 19.—*Preparation of promoted iron catalysts; processing of iron + promoter oxides*

Catalyst No.	Washing				Drying				Final formulation	
	Number of decantation washes	Wash water: precipitate ratio, volumes	Total volume of wash water, liter per gram metal oxides	Extent of washing	Temperature, °C.	Duration, hours per gram of final product	Dry cake yield,[1] percent	Appearance of dry cake	Appearance of granules[2]	Bulk density of granules, g./cc.
1A	14	1	0.29	NO_3 negative	23	0.1	104	Black gel, conchoidal fracture	Pellets, hard dark brown	1.31
					150	.3				
5A	17	1	.51	NO_3, Cl negative	23–150	.7	106	do	do	1.33
6A	19	1	.68	Cl, NO_3, SO_4 negative.	23–140	1.0	96	Dark brown gel, semifriable	do	1.39
9A	13	2	.46	NO_3 negative	23–145	.6	104	Black gel, conchoidal fracture	do	1.30
11A	9	1	.28	NO_3 positive	23–155	.4	111	do	do	1.20
15A	7	3	.25	SO_4, NO_3 positive	23	.4	112	Dark brown, soft, dense	do	1.49
					150	.1		do	do	
20A	8	1	.23	NO_3 positive	23	.3	111	Black gel, conchoidal fracture	do	1.34
					157	.1		do	do	
21A	11	1	.35	do	23	.1	108	do	do	1.29
					148	.3		do	do	
22A	12	1	.28	do	23	.5	106	do	do	1.28
					149	.1		do	do	
23A				SO_4 positive	23–150	.5	108	Dark brown, soft, dense	do	1.56
					150	.1		do	do	
24A	6	5	.28	do	23–146	.2	104	do	do	1.55
24C	15	6	.58	SO_4 negative	23	.6	94	do	do	1.42
					150	.2		do	do	
25A	7	2	.26	SO_4 positive	150	.1	90	do	do	1.60
39A	12	5	.30	SO_4 negative. NO_3 positive	150	.08	97		Pellets, soft black	.93
40A	16	1	.24	NO_3 negative	23	1.0	111	Black gel, conchoidal fracture	Pellets, hard dark brown	1.23
					150	.2		do	do	
43A	12	3	.24	SO_4 positive	23	.07	89	Rusts, nongel, friable	Pellets, soft light brown	.87
					150	.07		do	do	
44A					152	.1	89	Dark red, soft	Pellets, soft dark red	1.41
51A	16	1	.40	NO_3 negative	23	.7	111	Black gel, conchoidal fracture	Pellets, hard dark brown	1.38
					150	.1		do	do	
67A	15	1	.38	do	23	1.4	107		Pellets, soft black	1.23
					150	.1		do	do	
85A	17	6	.67	Cl negative	23	.4	111	Dark brown, soft, dense	Pellets, hard dark brown	.84
					111	.1			Granules 15 to 20-mesh soft, brown	.84

[1] Theoretical yield assumed to be mixture of completely dehydrated oxides.

[2] All pellets ⅛ inch in diameter by 5/32 inch in length, with the following exceptions: 43A, 39A—⅛ inch in diameter by 1/16 inch in length.

TABLE 20.—*Preparation of cobalt and nickel catalysts; formation of metal + promoter oxides + carrier*

Catalyst No.	Composition of catalyst	Reagents							Temperature of precipitaton, °C.
		Chief constituent	Promoter	Concentration of solution, mols salt per liter water	Carrier	Concentration of slurry, grams per liter water	Precipitant	Concentration of solution, mols salt per liter water	
2A	Co : ThO_2 : Celite :: 100 : 18 : 100	$Co(NO_3)_2$	ThO_2	0.4	H. S. C.[1] Celite		K_2CO_3	2.2	80
			$(Th(NO_3)_4)$	.07			(KOH)		80
12B	CoO : ThO_2 : Celite :: 82 : 18 : 100	do	$Th(NO_3)_4$	.3	H. S. C.[1] Celite		K_2CO_3	2.7	100
36A	CoO : NiO : MnO : Al_2O_3 : kieselguhr :: 40 : 40 : 16 : 4 : 100.	$Ni(NO_3)_2$, $Co(NO_3)_3$	$Mn(NO_3)_2$, $Al(NO_3)_2$	.6	Kieselguhr[2]		do	4.0	75
38A	NiO : MnO : $Na_2O{\cdot}Al_2O_3{\cdot}6SiO_2$ :: 83.2 : 16.8 : 100.	$Ni(NO_3)_2$	$MnSO_4$	2.4	$Na_2O{\cdot}AlO_3{\cdot}6SiO_2$		do		25
60A	NiO : CoO : ThO_2 : Celite :: 45.5 : 45.5 : 9 : 400	$Ni(NO_3)_2$, $Co(NO_3)_2$	$Th(NO_3)_4$		Type VIII Celite		Impregnation		90
61A	do	do	do	.4	Type III Celite		K_2CO_3	1.8	85
62A	NiO : ThO_2 : kieselguhr :: 91 : 9 : 100	$Ni(NO_3)_2$	do	.4	Kieselguhr[2]		do	1.5	80
64A	NiO : CoO : ThO_2 : Celite :: 46.36 : 46.36 : 4.60 : 100.	$Co(NO_3)_2$, $Ni(NO_3)_2$	do		Type VIII Celite		Impregnation		90
65A	NiO : CoO : ThO_2 : Al_2O_3 :: 20.1 : 20.1 : 4 : 100	do	do		Alumina pellets		do		90
89A	Co : ThO_2 : MgO : Celite :: 100 : 6 : 12 : 200	$Co(NO_3)_2$	$Th(NO_3)_4$, MgO	.8	H. S. C.[1] Celite	160	Na_2CO_3	.8	91
89B	do	do	do	.7	do[1]	160	do	.8	90
89H	do	do	do	.8	do[1]	170	do	.9	100
89I	do	do	do	.8	do[1]	160	do	.8	90
89J	do	do	do	.7	F. C.[3] Celite	130	do	.8	100
89K	do	do	do	.7	Portuguese kieselguhr	160	do	.8	100
89L	do	do	do	.8	H. S. C.[1] Celite	160	do	.8	90
89N	do	do	do	.8	do[1]	160	do	.9	100
89O	do	do	do	.8	Acid extracted F. C.[3] Celite.	160	do	.8	100
108B	Co : ThO_2 : Celite :: 100 : 18 : 100	do	$Th(NO_3)_4$	.6	F. C.[3] Celite		K_2CO_3	9.5	90

[1] H. S. C. = Hyflo Super-Cel.

[2] Origin of kieselguhr unknown.

[3] F. C. = Filter Cel.

TABLE 21.—*Preparation of cobalt and nickel catalysts; processing of metal + promoter oxides + carrier*

Catalyst No.	Washing				Drying				Final formulation	
	Number of decantation washes	Wash water: precipitate ratio, volumes	Total volume of wash water, liter per gram metal oxides + carrier	Method of washing	Temperature, ° C.	Duration, hour per gram of final product	Dry-cake yield,[1] percent	Appearance of dry cake	Appearance of granules [2]	Bulk density of granules, g./cc.
2A	7	2	0.34	Decantation	23	0.45	107	Tan to gray, soft, friable	Pellets, soft dark gray	0.69
					105	.14				
12B	16	2	.53	do	153	.16	108	Black, soft, friable	do	.98
					149	.68				
36A				Funnel	150	Constant weight	122	Gray, friable	do	.98
38A				do	150		117	Green gel	Pellets, dark green	.95
60A				None	140	Constant weight			Pellets, hard gray	.89
61A	12			Filtration [3]	140		107	Gray-green, friable	Pellets, soft dark gray	.88
62A	9		.55	do.[3]	150		103	Green, friable	Pellets, soft gray	.88
64A				None	140	Constant weight			Pellets, hard gray-green	1.09
65A				None	140	do			Pellets, hard gray	1.33
89A			.13	Funnel	115	.15	115	Tan to earth brown, friable	Pellets, soft earth brown	.82
89B			.13	do	115	.15	113	do	do	.78
89H			.13	do	120	.15 [4]	110	Tan, friable	Pellets, soft earth brown	.74
89I			.13	do	118	.15	113	Tan to earth brown, friable	Pellets, soft gray-brown	.79
									Granules, soft, tan to earth brown, 6- to 10-mesh.	
89J			.13	do	118	.15	113	Tan, friable	Pellets, soft, brown	.61
									Granules, soft, tan, 6- to 10-mesh	.23
89K			.13	do	118	.15	110	Tan to earth brown, friable	Pellets, soft, dark gray	.76
									Granules, soft, tan, 6- to 10-mesh	.35
89L			.13	do	113	.15	111	Gray to earth brown, friable	Pellets, soft, gray-earth brown	.84
89N			.13	do	120	.15	109	Dark gray, friable	Pellets, hard, gray	.82
89O			.13	do	123	.15	108	do	do	.60
108B			.02	do	103	(4)	113	Tan, friable	Pellets, hard, gray-brown	.77

[1] Theoretical yield assumed to be completely dehydrated oxides (CoO, NiO, MnO, Al_2O_3, MgO+carrier).

[2] All pellets ⅛ inch in diameter by 3/16 inch in length, with the following exceptions: 108B, ⅛ inch x ⅛ inch; 89L, ⅛ inch x 5/32 inch. Four percent graphite added as lubricant in all cases except 62A, where 5 percent graphite was used. Powdered graphite used in all cases except 108B, 89O, and 89L, where flake graphite was used.

[3] Filtration followed by reslurry and decantation.

[4] These catalysts dried in mechanical convection oven.

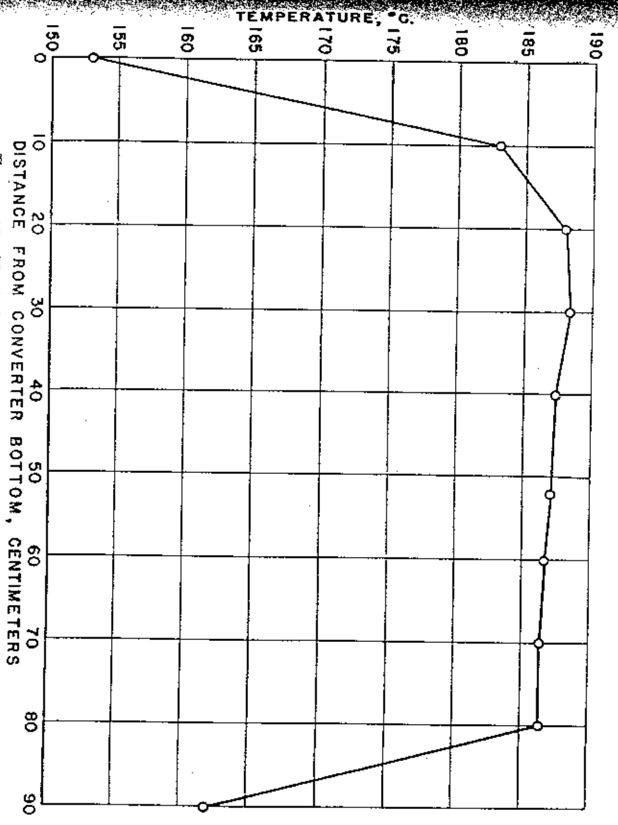


FIGURE 16.—Vertical temperature gradient in 90-cm. catalyst bed.

The vapors from the wax trap were passed through a caustic scrubber, which removed carbon dioxide, and through a soda-lime trap, which removed water and final traces of carbon dioxide; they were then directed into refrigerated glass traps in which hydrocarbon products were condensed. Prior removal of carbon dioxide and water vapor was necessary before the reaction products entered the refrigerated recovery traps, because both interfered mechanically with the recovery of the hydrocarbons liquefied by the cooling process. When the refrigerant was liquid nitrogen, all the hydrocarbon products (except for 1 percent CH_4) were collected at this point, the unreacted synthesis gas passing to the exit meter. When a carbon dioxide–acetone mixture was the refrigerant, pentane and the higher hydrocarbons were collected in the refrigerated traps, along with some of the gaseous hydrocarbons which were dissolved in the liquid hydrocarbons. The remaining gaseous hydrocarbons passed through the exit meter with the unreacted synthesis gas. The flow sheet (fig. 6) indicates the presence of two refrigerated traps in the system; usually one was in the system collecting products, while the other was being emptied of products.

The exit gases were metered and proportionated, so that a 2-percent fraction was continuously collected and stored in a sample vessel. The balance of the gases was discarded. The sampled gas was analyzed by a mercury Orsat apparatus when it consisted of unreacted synthesis gas and by a combination of mercury Orsat and low-temperature Podbielniak fractionation when the exit gas contained also a portion of the hydrocarbon product gases.

The hydrocarbon products were recovered from the refrigerator trap (as outlined in fig. 7) by low-temperature distillation. The