

PROPERTIES AND USES OF PRODUCTS

Primary Products

The primary products of the Fischer-Tropsch synthesis consist chiefly of straight-chain paraffinic and olefinic hydrocarbons ranging from methane

36/ Reichl, E. H., Work cited in footnote 12.

37/ Weir, H. M., The OXO Process for Alcohol Manufacture from Olefins: Technical Oil Mission Report 6, 1945, 28 pp.; PB2,047.

38/ Gordon, K., Work cited in footnote 11.

to high molecular weight paraffins (see tables 2, 3, and 4). The small quantities (10 to 15 percent) of branched-chain hydrocarbons contain only a single methyl group in the 2 or 3 position.

Hydrocarbons from Fischer-Tropsch Process

The gaseous hydrocarbons C_3 and C_4 were liquefied by compression and sold for fuel. Gasoline (C_5 -170°C.) and Diesel fuel (170°-280°C.) were obtained by refining the liquid hydrocarbon fractions.

The solid fraction from the conventional Fischer-Tropsch synthesis comprises paraffin waxes whose melting points range from 40° to 110°C. and whose molecular weights range up to 2,000. At the Ruhrchemie works at Holten, the residue above 320°C. from the distillation of the primary product of the medium-pressure synthesis was separated by vacuum fractionation into two distillates and a residue distilling above 460°C. (760 mm.). The first fraction was "sweated" to give "soft wax" (m.p. 40°C.); the second fraction was sweated to m.p. 50-52°C. to yield "slab wax." The residue (crude "hard wax") m.p. 90°C. was refined with bleaching earth and sold as "refined wax." By blending 30 parts of this wax with 70 parts soft wax, a product sold as "refined plastic wax" was obtained. By similar treatment of the residue above 320°C. obtained from distillation of products from the normal-pressure process and the wax extracted from the catalyst by solvent, further quantities of soft wax and a moderately hard wax sold as "catalyst wax" were obtained. Table 9 shows the properties of the Ruhrchemie Fischer-Tropsch waxes.^{39/}

TABLE 9. - Properties of Ruhrchemie Fischer-Tropsch waxes^{1/}

Properties	Soft wax	Slab wax	Catalyst wax	Refined plastic wax	Refined hard wax
Setting point, °C. (rotating thermometer)	42.5	50-52	87-91	75	90
Melting point, °C.	44.0	53	-	About 85	110
Flow point, °C.	40.2	48-49	-	77	98
Drop point, °C.	41.8	49-50	-	79	99
Iodine No.	-	2.5	3.5	2.0	2.0
Acid No.	0.14	0.03	-	0.05	0.1
Saponification No.	0.35	0.6	1.0	0.9	0.8
Penetrometer No.	-	35.0	About 30	17.0	4.0
Mean molecular weight	-	380	-	500	600
Mean carbon No.	-	27	-	36	43

^{1/} Footnote 36.

The bulk of the soft wax, or "Gatsch", was oxidized to fatty acids at the Deutsche Fettsauere Werke, Witten, for use in the production of soap and edible fats. A part of these waxes was also used in the manufacture of lubricating oils. The hard wax and slab wax were used in the manufacture of polishes, candles, and explosives. The "plastic wax" was used for impregnation of paper and cardboard.

^{39/} Gordon, K., Work cited in footnote 11.

Waxes from the ruthenium synthesis melt in the range 50° to 135° C. and have molecular weights as high as 23,000. Solvent extraction by Pichler and Buffleb^{40/41/} of the solid product obtained from the ruthenium synthesis at 1,000 atmospheres resulted in the fraction described in table 10. One-third of the product had an average melting range of 51° to 57° C.; 14 to 17 percent, 92.5° to 95° C.; and approximately half above 120° C. The high-melting waxes from ruthenium catalyst were not considered commercially feasible because of the extreme scarcity of ruthenium and small commercial demand.

TABLE 10. - Solvent extraction of wax from ruthenium synthesis at 1000 atmospheres^{1/}

Extraction conditions			Melting range, °C.	Physical properties				
Solvent	Temperature, °C.	Percent soluble		Density		M.W. Average	Viscosity, 150°C.	Centistokes, 180°C.
				20°C.	150°C.			
n-Pentane.....	34	30-33	51-57	-	-	-	-	-
n-Hexane.....	68	14-17	92-95	-	.765	760	6	4
Product fraction.	90	14-16	121-122	.966	.778	1,750	29	17
n-Heptane.....	98	20-25	129-130	.978	.783	6,750	870	410
Product fraction.	121	12-15	132-134	.980	.786	23,000	35,600	15,800

^{1/} Footnote 41.

By-product Oxygenated Compounds from Fischer-Tropsch Process

In 1943, the combined yield of primary products, including C₃ and C₄ gases, from the nine German Fischer-Tropsch plants, was 569,179 tons, or approximately 1.4 billion pounds.^{42/} About 1 percent or less of the total products consisted of oxygenated compounds.

The by-product water from the normal-pressure synthesis contained about 0.35 percent by weight, based on the liquid hydrocarbon product, of the lower fatty acids.^{43/} Acetic acid comprised two-thirds of these water-soluble fatty acids. The oil-soluble fatty acids from the normal-pressure synthesis comprised 0.06 percent of the liquid hydrocarbon product and consisted of C₅ to C₁₀ acids. Slightly larger quantities of fatty acids, up to about 1 percent of the total products, were produced in the medium-pressure synthesis.^{44/45/} About half of these fatty acids were present in

^{40/} 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.

^{41/} Pichler, H., Work cited in footnote 9.

^{42/} Gordon, K., Work cited in footnote 11.

^{43/} Koch, H., Pichler, H., and Koelbel, H., [Fatty Acids from Fischer-Tropsch Synthesis]: Brennstoff-Chem., vol. 16, 1935, pp. 382-387.

^{44/} Gordon, K., Work cited in footnote 11.

^{45/} Hall, C. C., and Haensel, V., The Fischer-Tropsch Plant of Ruhrchemie, A. G., Sterkrade-Holteln, Ruhr: C. I. O. S. File XXVII-69, Item 30, 1945, 97 pp.; PB 415.

the Diesel oil fraction, and at Sterkrade-Holton about 72,000 pounds per year of C₁₁ to C₁₈ acids were recovered and converted into soap. Small amounts of the lower alcohols, ethyl, propyl, and butyl alcohols also were produced in the medium-pressure synthesis. At the Hoesch-Benzin works, about 700,000 pounds per year were recovered from the condensate water.

When the fluidized iron-catalyst process is put into commercial operation, a large by-product yield of oxygenated chemicals is anticipated.^{46/} The total weight of products from one hydrocarbon synthesis plant, such as is to be constructed for Carthage Hydrocol at Brownsville, Tex., will approach one billion pounds annually, and a considerable fraction of the product will be organic chemicals. Approximately 15 percent of the total products will comprise the water-soluble oxygenated compounds of low molecular weight. Oil-soluble oxygen-containing chemicals are said to be present in amounts about equal to the water-soluble by-products; these will not be recovered.

The water-soluble organic chemicals that will result as by-products of the Hydrocol process are estimated at 152,450,000 pounds per year (table 11). These products may become the principal source of many basic organic chemicals, particularly those used in the cellulose plastics and fibers, acetate rayon, and aliphatic solvents industries.

TABLE 11. - Estimated production of water-soluble oxygenated chemicals from Carthage Hydrocol Plant, Brownsville, Tex.

	Estimated production, 1,000 lb./year	Percent of total oxygenated product
Methyl alcohol	730	0.48
Ethyl alcohol	63,680	41.8
n-Propyl alcohol	14,400	9.45
n-Butyl alcohol	4,370	2.85
n-Amyl alcohol	1,060	0.7
Acetaldehyde	9,100	5.98
Propionaldehyde	1,930	1.27
n-Butyraldehyde	2,750	1.8
Acetic acid	24,700	16.2
Propionic acid	8,700	5.7
n-Butyric acid	4,200	2.74
Acetone	11,200	7.34
Methyl ethyl ketone	4,780	3.14
Methyl propyl ketone	600	0.39
Methyl n-butyl ketone	250	0.16
	152,450	100.0

^{46/} Oil and Gas Journal, Work cited in footnote 14.

Oxygenated Compounds from Related Processes

The synol process was designed for the production of straight-chain primary alcohols for use as chemical intermediates.^{47/48/49/50/} The liquid product from the synol process consisted chiefly of alcohols and hydrocarbons in the ratio of about 60 to 40. The alcohol content was largely in the range boiling between 150° and 200° C. The ester content of the product increased with the boiling range of the fraction. Lower aldehydes could be extracted with bisulfite solution.

The OXO synthesis was designed for the production of C₁₂ to C₁₈ alcohols for use in detergents.^{51/52/53/54/} For this purpose, long-chain olefins in the C₁₀ to C₂₀ range produced directly by the Ruhrchemie olefin synthesis (page 20) or by mild thermal cracking of Fischer-Tropsch wax were used as raw material. Reduced pressure distillation of the filtered product from the hydrogenation stage yielded alcohols of 98 percent purity, unreacted hydrocarbons, and 5 to 15 percent (based on the alcohols) of heavy oil consisting of ketones, condensed aldehydes, and hydrocarbons. The unreacted hydrocarbons were to be returned to Ruhrchemie as Diesel oil. The alcohols are all primary, but are mixtures of isomers.

Separation of the alcohols from both processes could be carried out by the boric acid esterification method; ketones, olefins, and paraffins remained in the neutral oil. The crude product was separated into fractions in a 50° to 60° C. boiling range, each of which was treated separately. Low-boiling alcohols up to C₆ from the synol process were removed from the distillate by extraction with water-methanol solution. The higher-boiling product was esterified with a slight excess of solid boric acid at 95° to 120° C. and atmospheric pressure. The water of reaction and lower-boiling hydrocarbons were continuously removed as overhead. The product of the reaction was distilled at atmospheric pressure, or under vacuum, if necessary, to avoid decomposition of the boric acid ester. The esters are stable at temperatures up to 300° C. at atmospheric pressure. The separation of the alcohols and hydrocarbons is not difficult as esterification raises the boiling point of the alcohol about 120° C.

^{47/} Storch, H. H., Work cited in footnote 7.

^{48/} Gordon, K., Work cited in footnote 11.

^{49/} Reichl, E. H., Work cited in footnote 12.

^{50/} Holroyd, R., editor, Report on the Investigation of Fuels and Lubricants Teams at the I. G. Farbenindustrie A. G. Leuna Works, Merseburg, Germany: Bureau of Mines Inf. Circ. 7370, 1946, 135 pp.; PB 6,650.

^{51/} Gordon, K., Work cited in footnote 11.

^{52/} Reichl, E. H., Work cited in footnote 12.

^{53/} Wender, I., and Orchin, M., Critical Review of Chemistry of OXO Synthesis for Production of Alcohols from Olefins, Carbon Monoxide, and Hydrogen, with Discussion of Reaction Mechanism for OXO and Related Synthesis: Bureau of Mines Rept. of Investigations 4270, 1948, 26 pp.

^{54/} Holroyd, R., Work cited in footnote 50.

The separated esters were then mixed with recycle dilute boric acid solution and hydrolyzed by heating to 95°-120°C. The hot mixture of alcohols and boric acid solution (16 to 17 percent H₃BO₃) separated into two layers, and the upper alcohol layer was washed with water and redistilled. The boric acid solution was cooled to 5°C., the boric acid crystals were filtered off for recirculation to the esterification stage, and the filtrate was recycled to the hydrolysis stage.

Germany's main interest in the higher alcohols from a commercial standpoint from 1940 onward was apparently for the production of washing and wetting agents obtainable by sulfonating alcohols.^{55/} It was believed that the mixture of OXO alcohols was better than any of the individual alcohols when converted to detergents. Test proved that OXO alcohols were better for this purpose than the corresponding fraction of synol alcohols containing a similar number of carbon atoms. Sulfonation of the OXO alcohols with chlorosulfonic acid produced the alcohol sulfate RCH₂CH₂OSO₃H. The resulting "soaps" were fine white powders forming clear colorless solutions when 5 percent was dissolved in water at room temperature. These products met requirements of storage stability, wetting power, and foam propensity. They were excellent for washing both wool and cotton, including "fine washing." One advantage of deriving washing materials from the OXO process is the choice possible between soaps prepared by oxidizing the aldehydes to fatty acids and by sulfonating alcohols, prepared by reduction of the aldehydes to the alcohols and treatment with sulfuric acid. The sulfonated alcohols give greater washing power per hydrocarbon unit.^{56/}

The C₇-C₁₀ OXO and synol alcohols can be esterified with acids of equal chain length (produced from the same alcohols) and used as plasticizers. Plans had been made in 1943 for the Ruhrbenzin to deliver 6,000 tons a year of a C₇-C₁₀, 80° to 175°C. primary fraction, containing at least 35 percent olefins, which was to be sent through the OXO process at Leuna. The crude alcohols were to be shipped to Schkapau (site of an I.G. Farbenindustrie rubber-manufacturing plant). The alcohols were to be esterified in the presence of the neutral oils. C₃-C₈ synol alcohols were esterified to yield lacquer solvents. C₉-C₁₄ synol alcohols were esterified with adipic acid to produce excellent lubricants.

Some of the pilot-plant products from the further processing of OXO alcohols included cutting oils, lubricating oils, Diesel oils, and hydraulic fluids. Very good lubricating oils with pour points of -70°C. and below were made by preparing acids and alcohols from suitable olefins and uniting the two to form esters. This technique applied to olefins of lower molecular weight gave good hydraulic fluids. Diesel oil with a cetene number of 280 was made by converting a range of OXO alcohols to their nitric acid esters; this oil was under consideration during the war as a cold-starting aircraft fuel. Roelen had used propionaldehyde, prepared by subjecting ethylene to the OXO reaction, in making a synthetic drying oil. I.G. Farbenindustrie prepared a nC₉-C₁₀ alcohol mixture from a dimethylhexadiene that could be substituted for rose essence in perfumes. The OXO process has almost unlimited synthetic possibilities.

^{55/} Wender, I., and Orchin, M., Work cited in footnote 53.

^{56/} Hall, C. C., Craxford, S. R., and Gall, D., Interrogation of Dr. Otto Roelen of Ruhrchemie A. G.: B. I. O. S. Final Report 447, Item 30, 1946, 63 pp.; FB 77,705.

Secondary Products from Fischer-Tropsch Process

The discussion in this section will not be concerned with such products as lubricating oils and high-grade motor fuel, that are the principal industrial secondary products of the Fischer-Tropsch process, but rather with those that are of interest as source materials for chemical synthesis.

Use of Gasol Fraction

In 1940, Rheinpreussen built a plant to produce propyl and butyl alcohols from the olefins present in the C_3+C_4 fraction of the primary products.^{57/} The C_3+C_4 feed containing 30 percent olefins was mixed with 58° Be' sulfuric acid in a water-jacketed vessel at a temperature not exceeding 45°C. After settling, the lower acid layer was removed and treated with water. The upper layer of polymers thus formed was separated, and the lower layer, containing the esters was hydrolyzed with steam in four stages. The dilute sulfuric acid was concentrated and returned to the esterification stage; the distillate, consisting of a 50-percent aqueous solution of alcohols, was treated in a series of 6 fractionating columns to produce pure isopropyl alcohol and a mixture of secondary and tertiary butyl alcohols. The hydrocarbon layer from the esterification reactors was distilled, the unreacted C_3 and C_4 hydrocarbons were recovered as bottled gas, and the small amount of polymer residue, together with that obtained by treating the acid layer with water, was blended with motor fuel. From a daily input of 26 to 28 tons of C_3-C_4 fraction, the production of isopropyl alcohol was 2.0 to 2.1 tons and of mixed butyl alcohols 3.2 to 3.5 tons.

Use of Liquid Hydrocarbon Fractions

Because of the acute shortage of soap during the war, the heavy oil (b.p. 230°-320°C.) fraction was used in the manufacture of "Mersol" detergents.^{58/} At the I.G. Farbenindustrie Leuna plant, the Fischer-Tropsch oil containing 5 to 12 percent of olefins was hydrogenated at 200 to 230 atmospheres pressure, using a nickel-tungsten sulfide catalyst. This treatment converted the olefins to saturated compounds. At room temperature and atmospheric pressure, the oil was then treated with chlorine and sulfur dioxide for 12 to 16 hours in the presence of ultraviolet light. The product remaining after the removal of hydrogen chloride by blowing with air or nitrogen consisted of 82 percent sulfonyl chlorides and 18 percent unreacted paraffins. This product, known as Mersol D, was sent to soap manufacturers for saponification to the sodium sulfonate Mersolate, used mainly as a soap powder in admixture with water glass or Tylose (a cellulose product). The Mersolates were believed to have a peacetime future for wool-washing and as polymerization emulsifier in Buna rubber manufacture. The longer-chain Fischer-Tropsch soft wax would have been a superior raw material for this process but was not available, because it was used in fatty-acid production.

^{57/} Gordon, K., Work cited in footnote 11.

^{58/} Holroyd, R., Work cited in footnote 50.

Ruhrchemie developed a process for the production of toluene by the catalytic cyclization of the heptane-heptene fraction of Fischer-Tropsch primary products. The C₇ fraction containing 15 to 20 percent olefins was vaporized and preheated to 400° C. and passed at a rate of 0.15 to 0.20 cubic meter of liquid feed per cubic meter of catalyst per hour through a bed of Al₂O₃-Cr₂O₃ catalyst (containing 20 percent Cr₂O₃), maintained at 480°-530° C. by the heat produced in burning off the deposited carbon with air during the preceding regeneration stage. The time cycle was:

	Minutes
Cyclization.....	30
Purging with flue gas.....	3
Regeneration with air.....	15
Reduction in hydrogen.....	5
Switching.....	4

In pilot-plant tests, a 90 to 92 percent recovery of liquid products containing 50 percent by weight of toluene was obtained, and carbon formation amounted to 1.5 to 1.8 percent of the feed. The catalyst life was reported to be 2 years, but during this period the operating temperature had to be increased by 30° C., the yield of recovered product fell to about 85 percent, and the proportion of toluene to 44 percent. The total liquid product was fractionated in a column equivalent to 45 theoretical plates. The toluene fraction, containing 3 to 5 percent olefins, was acid-washed and redistilled to a nitration-grade toluene. Construction of a plant to produce 24,000 tons per year was begun but was abandoned on Government orders when only 20 percent complete.

Olefin-rich liquid hydrocarbons are of great value as charging stock in certain syntheses. Lower and middle-oil olefins were polymerized to synthetic lubricating oil; C₁₁ to C₁₇ olefins were used in the OXO synthesis.

Use of Solid Paraffin Fraction

Crude soft wax was oxidized to fatty acids in a large-scale operation at the Deutsche Fettsauere-Werke of Witten, Ruhr.^{59/} In the process for obtaining C₁₀ to C₂₂ fatty acids, batches of 8 to 20 tons of C₂₀-C₄₀ wax (b.p. 320° to 450° C.) were oxidized in aluminum vessels at a temperature of 110° to 120° C. by blowing with air at a rate of 50 cubic meters of air per ton of wax per hour in the presence of 0.2 percent of potassium permanganate in 15 percent aqueous solution, for 20 to 24 hours. The wax charge consisted of one part of fresh wax to 1.8 parts of recycle unsaponifiable material. The process was stopped when the acid number reached 70-80 (saponification number 135-140), and the product was washed with hot water to remove potassium permanganate and water-soluble

^{59/} Baldeschwieler, E. L., Report on Production of Synthetic Fatty Acids and Edible Fats; Deutsche Fettsauere-Werke and Markische Seifenfabrik, Witten, Ruhr, Germany: PB 225, 1945, 7 pp.

acids. The product was then neutralized with sodium carbonate and saponified with 38 percent caustic soda solution at 100°C. The undissolved layer was returned to the oxidation vessels, and the crude soap solution was heated to 170° to 180° C. at 25 atmospheres for 1 hour. After the separation of a further quantity of unoxidized material (returned to the oxidation stage), the soap solution was passed through a pipe still at 320°C., and the resulting anhydrous liquid soap was run into water, treated with sulfuric acid, and the free fatty acids were liberated. In the pipe still, further small quantities of unsaponifiable material were steam-distilled off and returned to the oxidation stage. The free acids (acid number 340, saponification number 350) were fractionated at 3 to 4 mm. pressure. The yields of the four fractions (based upon wax converted) and their properties are shown in table 12.

TABLE 12. - Fatty acids from the oxidation of synthetic paraffin wax

	Light fraction	Main fraction	Heavy fraction	Residue
Temperature, °C.	< 120	120-270	270-315	> 315
Yields, percent of wax oxidized ^{1/}	16	45	10	9
Molecular weight.....	< C ₈ -C ₁₀	C ₁₀ -C ₂₀	C ₂₁ -C ₂₈	> C ₂₈
Acid No. ^{2/}	450-460	245	155-160	80-90
Saponification No. ^{2/}	450-460	255	175-180	110-120
Esterification No. ^{2/}	0-1	10	20	30
Esterification No. for edible fats	-	1.5	10	-
Unsaponifiable matter, percent	0	1.5	10.0	-
Unsaponifiable matter for edible fats, percent	-	about 1	-	-

^{1/} Total yield of fatty acids was 80 percent of the wax charged to reactor.

^{2/} Expressed in milligrams of potassium hydroxide per gram of sample.

The Witten plant treated 40,000 tons per year of Fischer-Tropsch wax and produced 32,000 tons of fatty acids. I.G. Farbenindustrie had wax-oxidation plants, using an almost identical process, at Oppau and Heydebreck, each of 20,000 tons per year throughput. The raw material in these cases was partly Fischer-Tropsch wax and partly wax from the hydrogenation of brown coal.

The main fraction of fatty acids, with the properties shown in table 12, was converted into soap in the adjacent Markische Seifen-Fabrik. The product had excellent lathering properties but suffered from the disadvantage of leaving an unpleasant odor on the skin after use. For this reason, in the preparation of toilet soaps not more than 30 percent of the total fatty acids used was synthetic.

If the acids were to be used in the production of edible fats, a higher temperature (380°C.) was used in the pipe still, and the raw acids before distillation had a lower ester number (acid number 380, saponification number 382). The fraction employed was similar in length to that used

for soap; that is, C₈ to C₂₀. The acids were esterified to the triglycerides with natural glycerine at 200°C. and 2 mm. pressure, using 0.2 percent metallic tin as catalyst. A 3- to 4-percent excess of acids over the theoretical amount was used. The product was washed with alkali, treated with alkali and bleaching earth, filtered, and then steam-distilled at 200°C. and 2 mm. pressure. The refined fat was emulsified with 20 percent water, chilled, and milled with the incorporation of carotene.

At Witten, the output of finished edible fat was 150 tons per month. This synthetic fat was officially approved as fit for human consumption by the German Health Office, but the work of certain university biochemists, which was suppressed by the Nazi Government, threw considerable doubt on the suitability of this fat. The fat always contains some esters of branched-chain fatty acids, and certain of these have been shown to be toxic. The appearance and tests of the synthetic edible fats were similar to oleomargarine. At least 90 percent of these fats can be assimilated by the body. However, these differ from natural fats (which always contain even numbers of carbon atoms) in containing odd and even numbers of carbon atoms.

The lower- and higher-boiling fatty acids found various uses. Formic acid was used for treatment of fodder silos; acetic and butyric, for the esterification of cellulose; and propionic (as calcium propionate), as a preservative in bread. C₅-C₉ acids were hydrogenated to the corresponding alcohols, which upon reaction with phthalic acid, yielded alkyd resins; C₇-C₉ acids were used in fire extinguishers of the foamite type; C₉-C₁₁ acids were used for the separation of minerals by flotation; C₁₈-C₂₄ acids were employed in greases, as softening agents for leather (in combination with triethanolamine), and as lubricants for plastic moldings (as zinc, magnesium, and calcium soaps). From the distillation residue (table 12), molding agents for foundry cores, "artificial petrolatum", and softeners for plastics have been produced.