TABLE 4. - Space-time yield of various Fischer-Tropsch processes

Catalyst	Temperature, °C.	Pressure, atmosphere	Space-time yield of C_3+, kg./m³/hr.	Liquid product distribution				Steel in converter, tons/bbl./day
				Gasoline	Diesel	Wax	Alcohol	
			Ruhrchemie					
Co	175-200	1	8	56	33	11	V.S.	2.7
Co	175-200	10	10	35	35	30	V.S.	2.4
			Fluidized iron catalyst					
Fe	300-320	20	65	75	15	1	9	0.6
			Internally-cooled converter					
Co	175-225	7	40	35	35	30	V.S.	0.8
Fe	240-260	20	40	40	26	24	10	0.6
Fe	270-290	20	60	60	15	15	10	0.6

EFFECT OF VARIABLES UPON PRODUCTS

Considerable variations in the quantity and types of products are obtained under different reaction conditions. The boiling range of the products and the relative quantity of unsaturated compounds depend chiefly on the composition and age of the catalyst, pressure, temperature, gas throughput, and composition of the synthesis gas.

Catalyst

The most active catalysts for the synthesis of liquid and solid hydrocarbons from hydrogen and carbon monoxide are nickel, cobalt, iron, and ruthenium. The basic catalytic metals used by Fischer and Tropsch in their early experiments were iron and cobalt.[16] At temperatures below 300° C. and atmospheric pressure, Fischer and Tropsch found that these catalysts yielded products that consisted almost exclusively of saturated and unsaturated aliphatic hydrocarbons ranging from methane to high molecular weight waxes.[17] Nickel is essentially a methanization catalyst, but in combination with other catalytic materials is active in the hydrocarbon synthesis. However, it deteriorates rapidly because of the formation of volatile nickel carbonyl at operating pressures higher than one atmosphere. Cobalt catalysts are more durable and produce lower yields of methane and higher proportions of olefins in the liquid hydrocarbon product. The percentage of olefins decreases in the order iron, cobalt, nickel (60, 40, and 5 percent, respectively, of olefins in the product), when these are used as catalysts. Pichler[18] observed that a precipitated ruthenium catalyst operated at high pressure and a temperature of 200° C. surpassed all other catalysts for the synthesis of higher hydrocarbons. Many of these hydrocarbons were pure white, even in the crude state, and had melting points of 130° C. and higher.

16/ Weil, B H., and Lane, J. C., Synthetic Petroleum from the Synthine Process: Remsen Press, Brooklyn, N. Y., 1948, 303 pp.
17/ Pichler, H., Work cited in footnote 9.
18/ Pichler, H., [The Discovery and Synthesis of New Paraffins of Very High Molecular Weight] : Brennstoff-Chem., vol. 19, 1938, pp. 226-230.

The standard cobalt catalyst, which was used in the German commercial plants, was precipitated Co-ThO$_2$-MgO-Kieselguhr (100:5:8:200 parts by weight). The catalyst used in early work by Fischer, 100Co:18ThO$_2$:100 Kieselguhr, produced more paraffin wax and the same quantity of middle oil. The purpose of magnesia was solely to increase the hardness of the resulting catalyst and thus reduce its tendency to disintegrate in the converters.[19] Experiments with catalysts containing more cobalt (Co:Kg> 1) produced liquids and solids containing 50 to 55 percent of solid paraffin and 25 percent of Diesel oil. With a cobalt-manganese catalyst, Roelen (Ruhrchemie) obtained liquid and solid products containing 64 percent of solid paraffins at the exceptionally low reaction temperature of 165° to 168° C. and 10 atmospheres.[20]

Before being used in the hydrocarbon synthesis, cobalt catalysts are conditioned by reduction. Complete reduction results in too high an initial activity and short catalyst life. The optimum degree of reduction is 60 percent; the residual oxide is useful in preventing further sintering. In the German commercial plants, the catalyst granules, 1 to 3 mm. in size, were reduced at 350° to 450° C. in a stream of dry, carbon dioxide-free hydrogen flowing at a space velocity of 3,000 to 4,000 volumes per volume of catalyst per hour.

Although the best cobalt catalyst is prepared by precipitation, iron catalysts may be prepared in a number of ways, according to the operating conditions to be used and the products desired. Precipitated catalysts are usually highly active, giving good yields of hydrocarbons at low temperatures. At the Kaiser Wilhelm Institute for Coal Research, precipitated iron catalysts containing little (1 percent) or no copper were pretreated with carbon monoxide at 1/10 atmosphere and 325° C. before use in the hydrocarbon synthesis. With copper-containing (10 to 20 percent) catalysts, best results were obtained by pretreatment with 2H$_2$+1CO or 2H$_2$+3CO gas at atmospheric pressure and 220° to 240° C.

Moderately active iron catalysts are prepared by decomposition of iron nitrate mixed with appropriate promoters, by sintering the iron powder obtained from the decomposition of iron carbonyl, or by fusing iron with various promoters to produce fused catalysts of the synthetic ammonia catalyst type. A characteristic difference between fused and precipitated catalysts is that the former produce smaller middle-oil fractions and larger light and heavy fractions.

The addition of promoters is desirable as a means of controlling the type of products obtained. The presence of alkali promotes the formation of high molecular weight products but reduces the durability of cobalt catalysts. In tests at the Kaiser Wilhelm Institute, it was observed that the addition of alkali did not affect the activity of iron catalysts, but only the distribution of products. The Kaiser Wilhelm Institute results showed that ammonia-precipitated iron catalysts without subsequent addition

19/ Weil, B. H., and Lane, J. C., Work cited in footnote 16.
20/ Pichler, H., Work cited in footnote 9.

of potassium carbonate were as durable as those precipitated with sodium carbonate to which 0.25 percent potassium carbonate was subsequently added. A larger percentage of paraffin wax in the product was characteristic of the catalysts containing added potassium carbonate. Increasing the alkali content from 0.25 to 5 percent of potassium carbonate caused the yields of paraffin wax to increase from 26 to 46 percent, based on the total yield of solid, liquid, and gasol ($C_3 + C_4$) hydrocarbons. Increasing the alkali content also promotes formation of oxygenated and olefin products.

Pressure

The early work of Fischer and coworkers showed that pressures above 1 atmosphere favor the formation of oxygenated organic compounds and of high molecular weight hydrocarbons, and reduce the yield of normally liquid hydrocarbons per cubic meter of synthesis gas.[21] Pressures lower than atmospheric necessitated proportionately greater amounts of catalysts for equal conversion to hydrocarbons, although the average molecular weight and chemical composition of the product were unaffected by the reduced pressure[22]. Weller[23] studied the pressure dependence of the synthesis over a cobalt-thoria-kieselguhr catalyst at about 1 atmosphere pressure, using very short contact times, so that the concentration of synthesis products was very low. Under these conditions, the synthesis rate increased approximately as the square root of the synthesis gas pressure.

For the cobalt catalyst, maximum life is obtained at 5 to 15 atmospheres pressure of $2H_2+1CO$ gas. A study of the effect of pressures above atmospheric was made by Fischer and Pichler.[24] Table 5 shows the results of their work. As the pressure was increased above atmospheric, the yield at first increased and then (at about 15 atmospheres) decreased. Only a few weeks of operation at higher pressures of 50 to 150 atmospheres sufficed to cause a large decrease in catalyst activity. A cobalt-thoria-kieselguhr catalyst and a constant throughput of 1 liter (measured at atmospheric pressure) per hour of $2H_2+1CO$ gas per gram of cobalt metal were used. The data are averages for 4-week operation. Only a single pass of the gas through the catalyst was made, and there was no catalyst regeneration.

21/ Fischer, F., and Kuster, H., [The Influence of Pressure and Temperature Upon the Synthesis of Benzine and Synthol in Liquid Medium]: Brennstoff-Chem., vol. 14, 1933, pp. 3-8.

22/ Fischer, F., and Pichler, H., [The Influence of Pressure Upon Several Conversions of Water Gas] : Brennstoff-Chem., vol. 12, 1931, pp. 365-372.

23/ Weller, S., Kinetics of Carbiding and Hydrocarbon Synthesis with Cobalt Fischer-Tropsch Catalysts: Jour. Am. Chem. Soc., vol. 69, 1947, pp. 2432-2436.

24/ Fischer, F. and Pichler, H., [The Synthesis of Paraffin from Carbon Monoxide and Hydrogen Upon Cobalt Catalysts (Medium-Pressure Synthesis)]: Brennstoff-Chem., vol. 20, 1939, pp. 41-48.

TABLE 5. - Effect of pressures above atmospheric

(Yield data in grams per cubic meter of synthesis gas)

Pressure, atmosphere	Total solid and liquid hydro-carbons	Paraffin wax	Oil boiling above 200°C.	Gasoline boiling below 200°C.	Gaseous hydro-carbons C_1 to C_4
1.0	117	10	38	69	38
2.5	131	15	43	73	50
6.0	150	60	51	39	33
16.0	145	70	36	39	33
51.0	138	54	37	47	21
151.0	104	27	34	43	31

Table 6[25] contains the results of laboratory tests at 1 atmosphere and 7 atmospheres pressure, using the standard German commercial catalyst. In the medium-pressure range, the total yield of hydrocarbons containing more than three carbon atoms per molecule and the yield of saturated hydrocarbons are higher than in atmospheric-pressure operation.

TABLE 6. - Product from 100Co:5ThO$_2$:7.5MgO:200 Kieselguhr catalyst at 175°-200°C. and at (A) atmospheric, (B) 7 atmospheres pressure of 2H$_2$+1CO gas, 18-20 percent inerts. No recycle.

Fraction	Ideal gas, g./m3		Weight percent of liquids plus solids		Density, 150°C.		Olefins, volume percent		Pour point, °C.		CFR octane number		Cetene number	
	A	B	A	B	A	B	A	B	A	B	A	B	A	B
C_1 + C_2....	26	21												
C_3 + C_4....	24	17					50	30						
C_4 to C_{10}..	70	51	56	35	0.689	0.685	37	20			52	28		
C_4 to C_{11}..	77	58	62	40	.693	.689	34	18			49	25		
C_{11} to C_{18}.	41	51	33	35	.760	.760	15	10	-18	-7			100	100
C_{12} to C_{19}.	34	51	27	35	.766	.766	13	8	- 9	-2			100	105
Soft wax...	10	36 to 43	8	25 to 30	.900	.900								
Hard wax...	4				.930									

1/ Higher percentage of wax may be obtained from Co-Mn catalysts at 165°-168°C. and 10 atmospheres but with no increase in Diesel oil yield.

Iron catalysts usually are much less durable at atmospheric pressure than are cobalt catalysts. As with the cobalt catalyst, it is possible, however, by frequent flushings with hydrogen, to keep a carefully prepared and pretreated iron catalyst active at atmospheric pressure for 6 to 12 months. The pressure coefficient of the synthesis on iron catalysts decreases with decreasing operating temperature and at about 175°C. probably would be close to that of a zero order reaction, as found for cobalt catalysts.

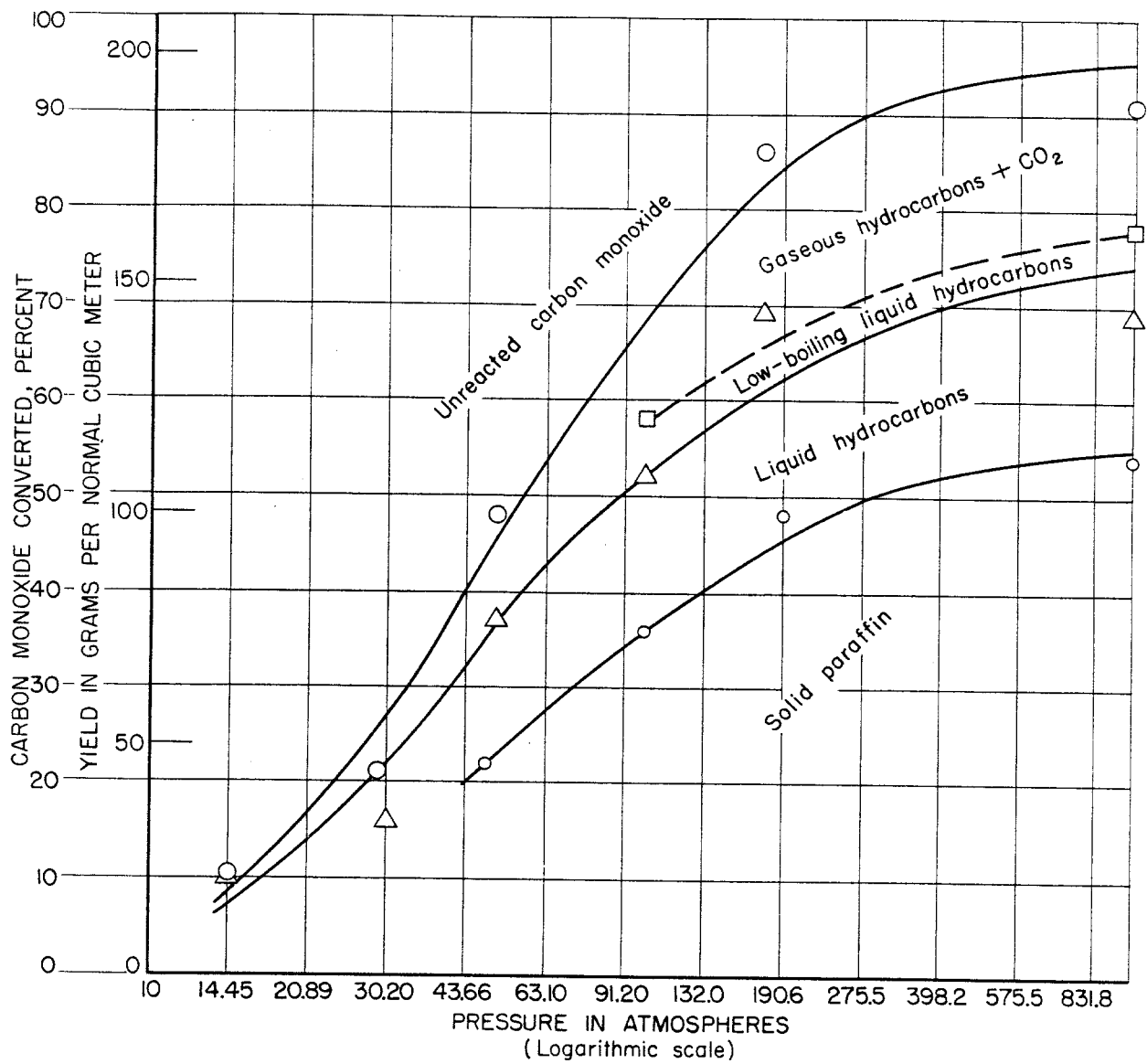25/ Pichler, H., Work cited in footnote 9.

CARBON MONOXIDE CONVERTED, PERCENT

YIELD IN GRAMS PER NORMAL CUBIC METER

100 — 200
90 —
80 —
70 — 150
60 —
50 — 100
40 —
30 —
20 — 50
10 —
0 — 0

10 14.45 20.89 30.20 43.66 63.10 91.20 132.0 190.6 275.5 398.2 575.5 831.8

PRESSURE IN ATMOSPHERES
(Logarithmic scale)

Unreacted carbon monoxide

Gaseous hydrocarbons + CO_2

Low-boiling liquid hydrocarbons

Liquid hydrocarbons

Solid paraffin

Figure 1. — Yield and character of products at 180° C. and various pressures, with ruthenium catalyst.

Medium-pressure operation of iron catalysts raises the boiling range of the products. Data showing this effect are given in table 7.[26]/[27]/

TABLE 7. - Effect of operating pressure upon boiling range of product from an iron catalyst

(Data cited by E. H. Reichl)

Pressure, atmospheres	1	5	20
CO conversion, percent	95	70	75
Yield of liquid plus solid products, g./m^3	90	86	120
Gasoline, percent	57	30	22
Diesel oil, percent	24	25	22
Wax, percent	19	45	56
Olefins in gasoline, percent	68	63	63
Olefins in Diesel oil, percent	41	49	46

The optium pressure for operation of iron catalysts is 10 to 20 atmospheres of $2H_2+3CO$ gas. At higher pressures, above about 30 atmospheres, the decreased durability of both iron and cobalt catalysts may be caused by corrosion by metal carbonyl formation.

On ruthenium catalysts, at pressures below 10 atmospheres and temperatures of 200° or lower, no appreciable conversion of carbon monoxide and hydrogen to higher hydrocarbons results. Figure 1 shows the results obtained by Pichler and Buffleb[28]/ in experiments at pressures from 15 to 1,000 atmospheres and at a temperature of 180°C. Three grams of ruthenium catalyst was used, and the flow of $2H_2+1CO$ synthesis gas was so adjusted that 1 liter of effluent gas was obtained per hour. The throughputs of $2H_2+1CO$ (calculated from the nitrogen contents of the ingoing and effluent gases) were 1.08, 1.16, 1.79, 2.57, 5.0, and 5.26 liters per hour per 3 grams of ruthenium for 15, 30, 50, 100, 180, and 1000 atmospheres, respectively. The conversion to hydrocarbons increased rapidly with increasing pressure up to about 300 atmospheres and more slowly above this pressure. At all pressures, solid paraffinic hydrocarbons constituted about 60 percent of the total yield of liquid + solid hydrocarbons. At 1,000 atmospheres and 180° C., 57 percent of the carbon monoxide charged to the converter and 71 percent of the liquid + solid product was solid paraffin wax. The fraction of gaseous hydrocarbons in the products was approximately 25 percent for all pressures. After 560 days, when the temperature had been raised to 215° C., at 100 atmospheres the yield was 140 grams per cubic meter, only 10 percent below the initial value. It is interesting to note that whereas for a cobalt

[26]/ Reichl, E. H., Work cited in footnote 12.

[27]/ Storch, H. H., Anderson, R. B., Hofer, L. J. E., Hawk, C. O., Anderson, H. C., and Golumbic, N., Synthetic Liquid Fuels from Hydrogenation of Carbon Monoxide. Part I: Bureau of Mines Tech. Paper 709, 1948, 213 pp., 47 figs.

[28]/ Pichler, H., and Buffleb, H., [Synthesis of Paraffin Wax on Ruthenium Catalysts at Pressures up to 100 Atmospheres]: Brennstoff-Chem., vol. 21, 1940, pp. 257-264.

catalyst about 95 percent conversion is reached at 15 atmospheres, for a ruthenium catalyst 95 percent conversion necessitates a pressure of about 300 atmospheres.

Temperature

The temperature range for the synthesis of hydrocarbons from hydrocarbons from hydrogen and carbon monoxide is quite narrow. Even for the most active catalysts, the reaction is very slow below 175° C.; above 250° C. the rate of production of liquid hydrocarbons decreases, and methane formation and carbon deposition predominate. To compensate for gradual decrease in activity during synthesis, the reaction temperature must be raised progressively for all catalysts to maintain the rate of conversion. The temperature coefficient for the temperature ranges 197° to 207° C. and 191° to 207° C. are 1.4 and 1.67 per 10° C., respectively; these values were calculated from some data of Aicher and coworkers,[29] who used a nickel catalyst. These coefficients correspond to an activation energy per mole of about 20 kcal., as calculated from the Arrhenius equation. The temperature coefficient in Weller's tests[30] corresponded to an activation energy of 26 kcal. per mole. Storch and his coworkers[31] obtained a value of 25 kcal. per mole at long contact times corresponding to the Ruhrchemie process.

The optimum synthesis temperature for cobalt catalysts lies between 180° and 200° C. In Bureau of Mines tests on cobalt-thoria-magnesia-kieselguhr, the catalyst activity decreased when the temperature reached 207° C. and was permanently impaired at temperatures over 218° C.

The activity of the iron catalyst is to a great extent dependent upon the operating temperature. At high temperatures, carbon and methane are produced; at low temperatures, the conversion of carbon monoxide and hydrogen is poor. For optimum conversion, the choice of catalyst should depend upon the conditions of operation. For low-temperature synthesis, very active catalysts are necessary; for high-temperature synthesis, less active iron catalysts can be used. Where high yields of solid paraffins are required, the operating temperature must be kept low. If low-boiling gasoline hydrocarbons are to be the main product, operation at higher temperatures is desirable. The diagram in figure 2 shows the relationship that exists between the reaction temperature and the catalyst.[32]

Hydrogen:Carbon Monoxide Ratio

In the conventional cobalt synthesis, a ratio of $2H_2:1CO$ is optimum for obtaining maximum yields of hydrocarbon.[33] A higher concentration

[29] Aicher, A., Myddleton, W. W., and Walker, J. J., The Production of Hydrocarbon Oils from Industrial Gases: Jour. Soc. Chem. Ind., London, vol. 54, 1935, pp. 313-320 T.

[30] Weller, S., Work cited in footnote 23.

[31] Storch, H. H. et al., Work cited in footnote 27.

[32] Pichler, H., Work cited in footnote 9.

[33] Tsuneoka, S., and Fujimura, K., [Benzine Synthesis from Carbon Monoxide and Hydrogen at Ordinary Pressure. XIX. The Ratio of $CO:H_2$ in the Initial Gas Mixture]: Jour. Soc. Chem. Ind., Japan, vol. 37, 1934, suppl. binding, pp. 463-467.
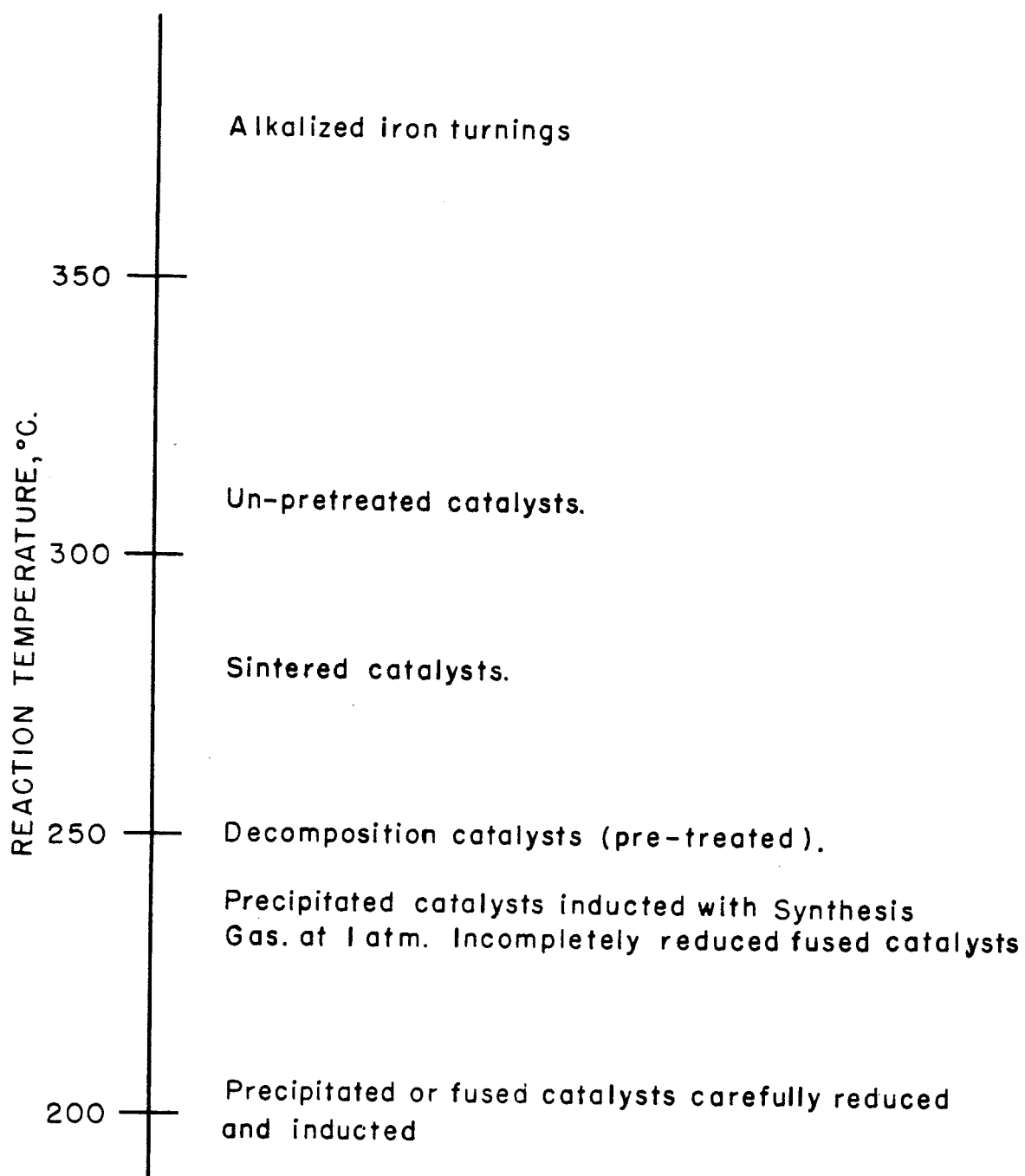
Alkalized iron turnings

REACTION TEMPERATURE, °C.

350 —

Un-pretreated catalysts.

300 —

Sintered catalysts.

250 — Decomposition catalysts (pre-treated).

Precipitated catalysts inducted with Synthesis
Gas. at 1 atm. Incompletely reduced fused catalysts

200 — Precipitated or fused catalysts carefully reduced
and inducted

Figure 2.— Initial reaction temperature for various iron
catalysts.

of carbon monoxide in the gas mixture had the effect of increasing the olefin content of the products. However, when water gas ($1H_2$:1CO) is used, a low catalyst life results because of carbon deposition. The development of a process by the Ruhrchemie, in which water gas was charged to the medium-pressure reactor and three volumes of end gas from the first stage per volume of fresh gas, with product condensation after each cycle, was recycled through the system, resulted in an increase in olefin content from 20 to 55 percent in the liquid fractions of the product. The recycle gases lower the partial pressure of the carbon monoxide sufficiently to avoid excessive carbon formation. The recycle-process gasoline has a 50 to 55 motor octane number, as compared with 45 for the older process without recycle.

Over iron catalysts the optimum ratio is $1H_2$:1.7CO in the medium-pressure synthesis.[34] Carbon monoxide-rich synthesis gas requires the use of higher synthesis temperatures.

DESCRIPTION OF PROCESSES RELATED TO FISCHER-TROPSCH SYNTHESIS

Synol

The "synol" process for the production of alcohols is identical with the Fischer-Tropsch synthesis using an iron catalyst, differing from it only in space velocity of feed gas and operating temperature.[35] Passage of $1CO:0.8H_2+20$ to 50 volumes of recycle gas at 18 to 25 atmospheres and 190°-200°C., over a catalyst which was a fused mixture of 97 percent Fe_3O_4, 2.5 percent Al_2O_3, and 0.5 percent K_2O previously reduced with hydrogen at about 450°C., yielded about 160 grams per cubic meter of fresh gas of a mixture of hydrocarbons and alcohols. Space velocity was 2,500 to 5,500 volumes total gas per volume catalyst per hour. The boiling range and composition of the product are given in table 8.

TABLE 8. - Composition of synol products

Boiling range, °C.	Percent of total product	Percent in fraction			
		Alcohol	Aldehydes	Fatty acids	Esters
34-105	29.7	1/20	4	0.2	2
105-150	19.7	55	6	0.7	2.5
150-175	5.0	44	8	0.3	4.5
175-218	12.7	55	4	0.3	8
218-255	9.2	55	2	0.4	10
255-290	6.4	49	3	0.5	15
290-320	5.5	45	3	0.5	19.5
320-360	4.8	35	4	0.6	20
over 360	2.1				

1/ Low, because of solubility in reaction aqueous phase.

34/ Leva, M., Translations of German Documents on the Development of Iron Catalysts for the Fischer-Tropsch Synthesis, Part I (Technical Oil Mission Reel 101, Document PG-21,559-NID, Report on the Middle Pressure Synthesis with Iron Catalysts, June 1940): Office of Synthetic Liquid Fuels Report, Pittsburgh, Pa., 1947, p. 18.
35/ Reichl, E. H., Work cited in footnote 12.

The reaction was tested in both tubular and plate-type reactors using diphenyl as cooling medium, but difficulty had been experienced in removing spent catalyst. Production of synol alcohols at I.G. Farbenindustrie A.G. Leuna Works had been on a pilot-plant scale of 3 to 5 tons per month of liquid products.

OXO

The "OXO" process consists in reacting olefins with carbon monoxide and hydrogen to produce aldehydes and subsequent reduction of the aldehydes with hydrogen to alcohols.[36]/[37]/[38]/ A slurry of liquid olefin plus 3 to 5 percent reduced Fischer-Tropsch cobalt-thoria-magnesia-kieselguhr catalyst, which is pumped along with $1H_2+1CO$ gas (about 0.2 cubic meter per liter of olefins) through a preheater ($150°-160°C.$) into the reactors at 200 atmospheres pressure, produced a mixture consisting of 80 percent aldehydes (about one-quarter of this is polymerized aldehyde) and 20 percent alcohols. Because hydrogenation of the aldehydes is retarded by carbon monoxide, the first-stage product must be let down to atmospheric pressure. The second stage is operated with hydrogen at $170°-195°C.$ and at 200 atmospheres pressure. Fischer-Tropsch cobalt catalyst or copper chromite may be used in the second stage. If the former is used, some carbon monoxide is formed by hydrogenation of cobalt carbonyl, and the exit gas is passed over an iron catalyst at $250°C.$ to convert the carbon monoxide to methane whose concentration, up to about 10 percent, is of only slight importance. The second stage is otherwise identical with the first. The first stage is not affected by sulfur compounds, but the second is quite sensitive; if sulfur compounds are present, sulfide catalysts (such as a mixture of nickel and tungsten sulfides) must be used.

The basic reaction was discovered by the Ruhrchemie, and a full-scale plant had been erected at Holton, but never operated, to produce 12,000 tons per year of OXO alcohols by batch-type operation. A large-scale continuous process resulted from cooperative effort of Ruhrchemie and I.G. Farbenindustrie, operating under similar conditions but permitting a throughput 9 to 10 times greater than the Ruhrchemie batch process for the same degree of conversion (95 percent reaction). This process had been operated on a pilot-plant scale with an output of 40 to 50 tons of alcohols per month.

The OXO reaction was found to take place with a wide variety of pure compounds and technical materials containing ethylenic double bonds. It is clear that almost limitless possibilities are available for further processing of the aldehydes first formed, either by aldol condensation or conversion to the corresponding acids, in addition to conversion to alcohols, as in the "parent" process described above.