natural gas-steam mixture. Because of uncertainties concerning reaction velocity and amount of carbon that might be deposited, the laboratory study was undertaken. Experiments were done in the temperature range 1,225° to 1,516° C. with steam-natural gas ratios of 1.5 to 5 and contact times in the range 0.21 to 4.6 seconds.[78] Even at the high temperatures, long contact times, and steam-natural gas ratio of 5, there is some carbonization of the natural gas. The extent of carbonization is dependent upon temperature, contact time, and partial pressure of steam.

Catalysts in Synthetic Liquid-Fuel Processes

A literature review was presented of the development of catalysts for the hydrogenation of carbon monoxide to yield hydrocarbons[79] and for the hydrogenolysis of coal and oil.

The chief aim of the Bureau of Mines catalyst testing program is to determine the influence on catalyst activity of conditions of catalyst preparation, pretreatment (such as reduction and carbiding), and mode of induction (starting the synthesis) for iron and cobalt catalysts. The tests were conducted in small converters containing about 45 cc. of catalyst in the shape of 1/8 by 1/8-inch pellets or granules. Figure 26 is a photograph of a battery of 12 units. At the right side of the photograph are the flowmeters that control and record the rate of flow of synthesis gas to the converters. The latter consist of 1/2-inch iron pipe filled to a depth of 12 inches with catalyst. The catalyst temperature was maintained by boiling Dowtherm in an electrically heated jacket surrounding the tube and controlling (automatically) the pressure on the Dowtherm.

The results of the catalyst-testing program are summarized as follows:

1. Active, durable, and easily regenerated iron catalysts can be prepared by maintaining special conditions of precipitation of iron hydroxide from ferric nitrate solutions and providing a small concentration (about 0.1 percent) of alkali, preferably potassium carbonate, in the finished catalyst. There is little if any advantage in two or three component iron catalysts such as iron-copper or iron-copper-manganese. This conclusion was arrived at also by the Kaiser-Wilhelm Institute für Kohlenforschung in Germany in publications cited later. (See Foreign Fuels, footnote 95.)

2. Excellent correlations have been observed between the X-ray diffraction patterns, magnetic susceptibilities of the iron catalysts, and their activity in the synthesis.[80] A comparison (see table 23 and figure 27) of the X-ray diffraction patterns of unreduced ferric oxide catalysts with

[78] Gordon, A. S., Uncatalyzed Reaction of Natural Gas and Steam: Ind. and Eng. Chem., vol. 38, 1946, pp. 718-20.

[79] Storch, H. H., Catalysis in Synthetic Liquid Fuel Processes: Ind. and Eng. Chem., vol. 37, No. 4, April 1945, pp. 340-351.

[80] Hofer, L. J. E., Peebles, W. C., and Dieter, W. E., X-ray Diffraction and Magnetic Studies of Unreduced Ferric Oxide Fischer-Tropsch Catalysts: Jour. Amer. Chem. Soc., vol. 68, No. 10, 1946, pp. 1953-1956.

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the diffraction patterns of the ferric oxide hydrates and of hematite (αFe_2O_3) showed that the inactive catalysts (with the exception of 47F) in the unreduced state, before use in the synthesis, all contained $\beta Fe_2O_3 \cdot H_2O$, and the active catalysts contained either $\alpha Fe_2O_3 \cdot H_2O$ or αFe_2O_3, or both, but no $\beta Fe_2O_3 \cdot H_2O$. Catalysts prepared from ferric chloride (the 47 series) or from ferric nitrate mixed with an appreciable quantity of potassium chloride (catalyst 10M) contained $\beta Fe_2O_3 \cdot H_2O$ and were inactive, whereas those prepared from pure ferric nitrate (the 10 series excepting 10M) were active. Catalyst 47F, which contains no $\beta Fe_2O_3 \cdot H_2O$ despite its preparation from ferric chloride, was inactive. It was shown that in this case $\beta Fe_2O_3 \cdot H_2O$ was initially present but that prolonged washing caused aging and conversion to αFe_2O_3. Comparisons of intensities (height of vertical lines) and wave lengths (Angstrom units on horizontal axis) given in figure 27 form the basis for the conclusions outlined above.

It should be noted that none of the iron oxides mentioned in the preceding paragraph is stable under the conditions of the Fischer-Tropsch synthesis on iron catalysts. The deactivating effect of precipitation in the presence of chloride ion is not due, therefore, to the presence of $\beta Fe_2O_3 \cdot H_2O$ itself, but to some characteristic which it imparts to the finished catalyst. Although chloride ion seems to have a small deleterious effect (see Foreign Fuels, footnote 95), the presence of $\beta Fe_2O_3 \cdot H_2O$ at any stage of the catalyst preparation greatly accentuates this deactivating effect. Active catalysts were obtained by precipitation from solutions containing cupric nitrate and ferric chloride; cupric chloride and ferrous chloride; and only ferrous chloride; but in each of these cases the precipitate at no stage contains any $\beta Fe_2O_3 \cdot H_2O$, as the presence of the bivalent ion insures a crystalline form other than $\beta Fe_2O_3 \cdot H_2O$.

The magnetic susceptibility of the catalysts was determined by measuring the force acting upon a sample suspended between the poles of an electromagnet with specially designed pole faces so as to obtain a uniform gradient between them. The magnetic balance used is shown in figure 28. It was calibrated at several field strengths with Mohr's salt (ferrous ammonium sulfate, hydrated crystals), the susceptibility of which at 27° C. was taken as 31.6×10^{-6}. The probable error of the measurements is in all cases $\pm 0.5 \times 10^{-6}$. All of the measurements were made at a field strength of 2,120 gausses. The magnetic susceptibility data of table 23 show that all the active 10-series catalysts, with the exception of 10M, and all the 80-series catalysts (prepared from ferric nitrate by precipitation with KOH solution instead of K_2CO_3 solution, as in the 10 and 47 series), had higher magnetic susceptibilities than the inactive 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 of 5 to 7 atmospheres. The Kaiser-Wilhelm Institute experiments cited later (see Foreign Fuels, footnote 95) include tests that show that active iron catalysts have a useful life of more than 1 year at 15 atmospheres pressure.
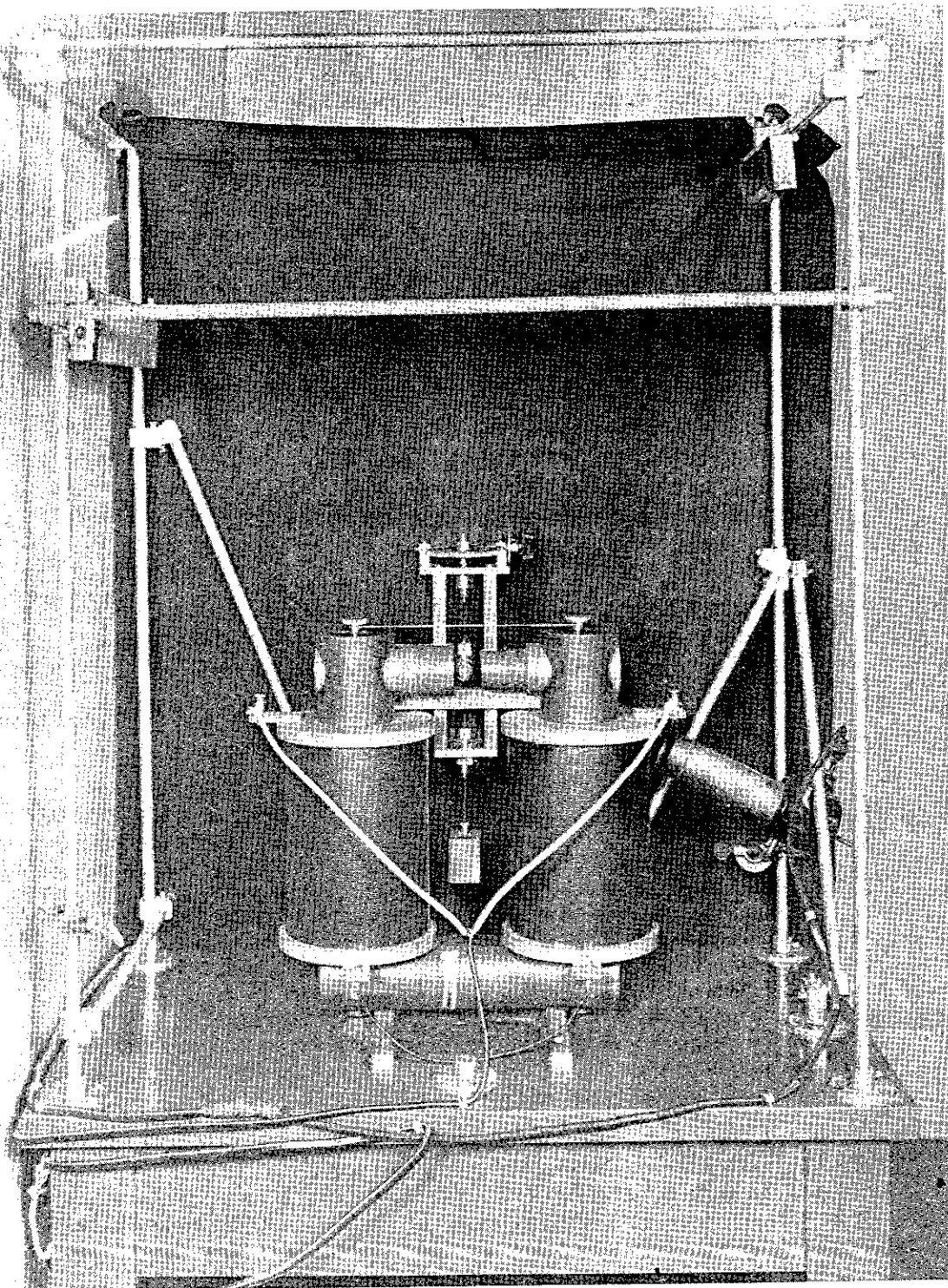
Figure 28. - Magnetic balance.

TABLE 23. - X-ray diffraction, magnetic susceptibility, and activity data on unreduced iron catalysts

Catalyst	X-ray diffraction		Magnetic suscepti-bility $\times 10^{-6}$	Activity			Operating pressure gage, p.s.i.
	Phases	Diffuse-ness[1/]		Weeks tested	Optimum week	Yield[2/]	
10A + 10B	α Fe$_2$O$_3$ (probably)	X	150	15	2d	48.4	0
10B (pt. b)	α Fe$_2$O$_3$	B	160	1	1st	16.7	0
10B (pt. c)	α Fe$_2$O$_3$	B	150	2	1st	21.0	0
10C	α Fe$_2$O$_3$; (α Fe$_2$O$_3$.H$_2$O)	B	135	{5	3d	70.6	135
				1}	1st	27.9	0
10D	α Fe$_2$O$_3$; α Fe$_2$O$_3$.H$_2$O	B	210	4	1st	62.8	100
10E	α Fe$_2$O$_3$	B	220	-	-	-	-
10F (pt. a)	α Fe$_2$O$_3$	D	130	1	1st	34.5	0
10F (pt. c)	α Fe$_2$O$_3$	D	180	3	1st	52.6	100
10G	α Fe$_2$O$_3$	D	170	-	-	-	-
10H	α Fe$_2$O$_3$	D	170	-	-	-	-
10I	α Fe$_2$O$_3$; α Fe$_2$O$_3$.H$_2$O	B	140	-	-	-	-
10J	α Fe$_2$O$_3$; α Fe$_2$O$_3$.H$_2$O	B	180	-	-	-	-
10K	α Fe$_2$O$_3$	C	170	-	-	-	-
10L	α Fe$_2$O$_3$	B	170	-	-	-	-
10M	β Fe$_2$O$_3$.H$_2$O	B	43	1	1st	<2	100
10O	α Fe$_2$O$_3$; α Fe$_2$O$_3$.H$_2$O	B	130	-	-	-	-
47A	β Fe$_2$O$_3$.H$_2$O	B	44	1	1st	<2	0
47B	β Fe$_2$O$_3$.H$_2$O	C	56	1	1st	<2	-
47C	β Fe$_2$O$_3$.H$_2$O	C	61	1]	1st	<2	0
47D	β Fe$_2$O$_3$.H$_2$O	C	61	1	1st	<2	100
47E	β Fe$_2$O$_3$.H$_2$O	C	40	1	1st	<2	0
47F	α Fe$_2$O$_3$	A	130	1	1st	<2	0
47G	β Fe$_2$O$_3$.H$_2$O	C	56	-	-	-	0
80A	α Fe$_2$O$_3$; α Fe$_2$O$_3$.H$_2$O	A	140	3	1st	63.9	-
80B	α Fe$_2$O$_3$; α Fe$_2$O$_3$.H$_2$O	A	210	-	-	-	100

1/ A = sharp lines; B = diffuse; C = very diffuse; D = very, very diffuse; X = undecipherable.
2/ Grams of liquid hydrocarbons per cubic meter of synthesis gas.

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4. X-ray diffraction patterns of cobalt-thoria-kieselguhr catalysts show that the unreduced catalyst is almost completely amorphous, the sharpest line in the pattern being that due to the quartz present in the kieselguhr. The X-ray pattern of the reduced catalyst shows the lines of cubic cobalt crystals. As the cubic form is unstable at room temperature, it is likely that the thoria and magnesia have an inhibiting effect upon the conversion of cubic to hexagonal cobalt.

5. A study was made of the porosity and surface areas of unreduced and reduced cobalt-thoria-magnesia-kieselguhr catalysts and of different types of kieselguhr.[81] Total surface area was measured[82] by determining the nitrogen absorption isotherms at -195° C. The number of molecules required to form a monolayer was calculated from the Brunauer, Emmett, and Teller Equation (Jour. Amer. Chem. Soc., vol. 60, 1938, p. 309), taking 16.2 Angstroms as the average cross-sectional area of the nitrogen molecule.[83] The nitrogen isotherms of unreduced cobalt catalysts are the usual S-shaped type, with only a slight amount of hysteresis, indicating that the pore structure consists of capillaries, most of which are larger than 500 Angstrom units in diameter. Most of the area is provided by the cobalt oxide-promoter complex and only little by the kieselguhr.

Kieselguhr, or diatomaceous earth, is a mineral composed of the skeletons of diatoms, which are microscopic plants. This residuum is essentially hydrous-amorphous silica. Table 24 presents data on surface areas and porosity of various kieselguhrs.

TABLE 24. - Properties of kieselguhrs

	Surface areas, m^2/gram	Pore volume, cc./gram		
		Micro	Macro	Total
German	14.9	3.22	3.62	6.85
Portugese	17.5	1.47	0.90	2.40
Filter Cel	22.2	2.81	3.32	6.13
Johns-Manville II	5.5	2.43	2.12	4.57
Hyflo Super Cel	1.9	2.32	1.77	4.09
Dicalite 911	29.3	2.22	1.41	3.63

Filter Cel, a marine diatomaceous earth from Lompoc, Calif., and Portugese kieselguhr (probably a fresh-water product) were found to be equally

81/ Anderson, R. B., Hall, W. K., Hewlett, H. D., and Seligman, B., Studies of the Fischer-Tropsch Synthesis. Part II. Properties of Unreduced Cobalt Catalysts: Jour. Amer. Chem. Soc. (In press.)
    Anderson, R. B., Hall, W. K., Krieg, A., and Seligman, B., Studies of the Fischer-Tropsch Synthesis, Part III. Properties of Reduced Cobalt Catalysts: (In preparation.)
82/ Anderson, R. B., Improved Absorption Vessel: Ind. and Eng. Chem., Anal. ed., vol. 18, 1946, p. 156.
83/ Anderson, R. B., Modifications of the Brunauer, Emmett, and Teller Equation: Jour. Amer. Chem. Soc., vol. 68, 1946, pp. 686-90.

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.

The surface areas of the catalysts are not additive with respect to the areas of the kieselguhrs used. Catalysts prepared from Hyflo Super Cel have lower areas than those prepared from natural kieselguhr, and in most instances the difference is greater than can be accounted for by assuming additivity of surface areas of the kieselguhr and the cobalt-promoter complex.

The bulk densities of the catalysts reflect the bulk density of the kieselguhr used in them. In granular catalysts, the bulk density varies directly with the bulk density of the kieselguhr, whereas the densities of the pelleted catalysts appear to be functions of the kieselguhr and of the pelleting, which is not always reproducible. It is interesting to note that the bulk volume occupied by an amount of granular catalyst containing 1 gram of kieselguhr is nearly equal to bulk volume of a gram of kieselguhr. When the catalyst is pelleted, the bulk volume is less than that of the kieselguhr that it contains.

In table 25 are given the surface areas and pore volumes of several unreduced cobalt catalysts in the granular and pelleted form. In every instance, the surface areas of pelleted catalysts are less than the corresponding granules. When the filter cake was slugged, that is, pressed into a very large pill, which was then ground and repelleted to produce harder and more reproducible pellets, the area dropped further. For example, $84.1 \, m^2/g.$ for 108B granules, $76.0 \, m^2/g.$ for small pellets, and $66.5 \, m^2/g.$ for slugged pellets. These results are different from those found for the surface area of a rigid gel - such as silica-alumina used as an oil cracking catalyst - which was not changed by pelleting. The average pore diameter calculated for cylindrical pores from the pore volume divided by surface area are about 250 $\overset{o}{A}$ for pellets and 800 $\overset{o}{A}$ for granules. The MC15, which contains no kieselguhr, has pores of 330 $\overset{o}{A}$ diameter in a granular form. From the data presented, and others, the following picture of a cobalt catalyst is presented. The kieselguhr in a catalyst acts as a "brush pile" into which the cobalt complex may be placed without increasing the bulk volume. The cobalt complex is composed of clusters of much smaller particles than the kieselguhr, and these particles probably almost completely cover the kieselguhr, so that the total surface may be cobalt complex. Many of the pores are of the order of 200 to 1,000 $\overset{o}{A}$ in diameter.

As shown in table 25, the surface areas of unreduced cobalt catalysts are in the range 67 to 98 for the pellets and 84 to 110 square meters per gram for the granules. The activity of the catalysts listed in table 25 varies directly with the surface area of the unreduced catalyst. 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 37 square meters per gram. Approximately 40 percent of this surface was cobalt metal.

TABLE 25. - Properties of unreduced cobalt Fischer-Tropsch catalysts

Catalyst	Form[1]	Kieselguhr	Area of kieselguhr, m²/g.	Area of catalyst, m²/g.	Percent cobalt	d_{Hg}[2]	d_{He}[2]	Pore volume, cc./g.
Fischer (Cobalt-thoria-Kieselguhr):								
108B	G	Filter Cel	22.2	84.1	-	0.481	3.08	1.76
	P	Filter Cel	22.2	71.6	34.0	1.13	3.08	.56
	LP	Filter Cel	22.2	66.5	34.0	1.51	3.08	.34
Hall (Cobalt-Thoria-Magnesia-Kieselguhr):								
MC15	G	None		149.0		.676	3.80	1.22
89I	G	Hyflo Super Cel	1.9	83.6		.51	2.75	1.60
	P	Hyflo Super Cel	1.9	75.2	23.7	1.27	2.75	.43
89J	G	Filter Cel	22.2	104.1		.43	2.76	1.97
	P	Filter Cel	22.2	88.7	24.5	.97	2.77	.67
89K	G	Portugese	17.5	101.1		.61	2.75	1.28
	P	Portugese	17.5	98.2	24.6	1.20	2.75	.47
89U	G	German	14.9	109.3		.445	2.75	1.89
	P	German	14.9	86.2		1.10	2.75	.55
89V	G	D-911	29.3	101.9		.544	2.75	1.47
	P	D-911	29.3	77.6		1.31	2.75	.40

[1] G = granulated, P = pelleted, and LP = large pellets.
[2] d_{Hg} = specific gravity in mercury; d_{He} = specific gravity in helium.

Unreduced iron catalysts prepared by precipitation by alkali from aqueous solution have a higher surface area than unreduced cobalt catalysts and usually are of a gel-like structure. Upon reduction at 360° C., the areas of such iron catalysts decrease to about 5 percent of that of the unreduced catalyst.

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

7. Several modes of induction (starting the synthesis after reduction of catalyst) of the cobalt-thoria-magnesia-kieselguhr catalyst were tested. No significant differences were observed owing to changes in starting temperature (usually 150° C.) or rate of increase of temperature. Induction at 100 pounds per square inch pressure of 2H₂+1CO resulted in lower activity during the first 400 hours of operation, as compared with similar induction at atmospheric pressure. Beyond 400 hours, the activity was the same for the inductions at the two pressures.

8. Operation at atmospheric pressure of the synthesis on a Co-ThO$_2$-MgO-kieselguhr catalyst, for 1,500 hours, was followed by an additional 800 hours at 100 pounds per square inch pressure. The activity of the catalyst during the latter period was identical, within the limits of reproducibility of the tests, with that during the first 1,500 hours.

9. In the catalyst tests, a 15.8-mm. internal-diameter catalyst tube containing a 6.4 mm. outside diameter thermocouple well was used. The thickness of the annulus of catalyst was 4.7 mm. and its height was 30 cms. 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 increased from 10 kilograms per cubic meter of catalyst per hour at 100 space velocity to 42 kilograms at 500 space velocity.

In general, pelleted catalysts produce more methane, C$_1$-C$_4$ and carbon dioxide than the granules (dry filter-cake, crushed and screened), as indicated in table 26 for runs 18 and 19 and 21 and 26. It will be noted that the temperature of operation at a given space velocity is considerably lower than for the pelleted catalyst, although when the temperatures are compared at a given flow _per gram_ of catalyst the granules operate at slightly lower temperatures. It may be concluded that the variation of activity between pellets and granules is due to the decrease in surface area during pelleting. The change in the distribution of products is significant, but not too great. In most instances it would probably be desirable to pellet the catalyst to achieve the increased throughput, as the improved mechanical properties usually outweigh the undesirable effect of pelleting upon product distribution.

TABLE 26. - Granules vs. pellets data

Average temperature, °C.	Contraction, percent	Space[1]/ velocity	Products in grams per cubic meter				
			CH$_4$	C$_1$-C$_4$	CO$_2$	H$_2$O	Liquids plus solids
	Run 21, pelleted 89J, 30.5 g. of catalyst						
186	72.0	112.0	20.4	33.0	7.9	190.6	101.4
	Run 26, granular 89J, 11.0 g. of catalyst						
194	63.0	97.4	15.4	28.0	5.2	158.5	84.6
	Run 19, pelleted 89K, 38.8 g. of catalyst						
176	72.7	101	21.6	37.0	12.7	180.7	90.8
	Run 18, granular 89K, 16.0 g. of catalyst						
188	73.5	100	17.6	30.2	8.0	177.4	89.5

1/ Volumes of synthesis-gas per volume of catalyst per hour.

10. Studies of the rates of carbiding of cobalt catalysts by carbon monoxide, of hydrogenation of the carbide, and of the synthesis have yielded

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