

Underground Gasification

The Bureau of Mines and the Alabama Power Co. cooperated in an experiment in gasifying coal in place underground, at Gorgas, Walker County, Ala.^{60,61} The objectives of this experiment were to determine whether combustion of coal in the bed could be maintained and controlled, whether the coal could be completely gasified, what effect the fire would have on the coal bed and the overlying strata, and the yield and quality of gas that could be obtained.

A portion of the Pratt coal bed which outcropped on three sides of an irregular shaped hill was isolated by a cut through the hill and coal bed on the fourth side. The development of a U-shaped experimental mine in the 35-inch-thick isolated portion of the bed was begun in November 1946, and on January 21, 1947, the mine was ignited with thermite bombs.

The direction of flow of air and gas in the mine was reversed periodically to provide uniform burning of the coal in the pillar between the entries. Tests were made with air, oxygen-enriched air, air-oxygen-steam, oxygen-steam, and steam alone during the 50-day period of forced burning of the coal.

The quality of the gas produced was affected by the physical conditions at Gorgas. For a burning face as long as that used, the air flow, which was limited by the size of blower used, should have been greater. This would have resulted in a higher rate of combustion, a longer hot zone, and better-quality gas. During a considerable period of fairly stable operation with air blast, the heating value of the gas averaged 46.8 B.t.u. per cu. ft. Heating value of the gas in short runs with steam averaged approximately 200 B.t.u. per cu. ft.; and with the air, oxygen, and steam mixtures averaged between the low value with air and the high with steam.

Combustion of the coal was easily maintained during the experiment. At the conclusion of the experiment, active combustion was stopped and the residue was cooled and examined. This examination showed that coal in place can be completely consumed, leaving only a residue of ash and clinker. Some 236 tons of coal were consumed, and no islands of unreacted coal or coke were found.

As a consequence of high temperatures developed at the burning face, the overlying strata of roof rock became plastic, expanded, and settled down on the mine floor directly behind the reacting coke face. This forced the air and gas to flow through the cracked and porous coke face, a very favorable development for the gasification process, as it filled the burned-out area and forced the air into intimate contact with the burning coke face.

⁶⁰/ Dowd, James J., Elder, James L., Capp, J. P., and Cohen, Paul, Experiment in Underground Gasification of Coal, Gorgas, Ala.: Bureau of Mines Rept. of Investigations 4164, 1947, 62 pp.

⁶¹/ McCabe, Louis C., Gasification of Coal Underground: Min. Cong. Jour., vol. 33, No. 8, August 1947, pp. 42-45.

This behavior of the cap rock confirmed a preliminary test made on a slab of the rock removed from the mine before firing and shipped to Pittsburgh for laboratory testing over a gas-fired test furnace. The similar behavior of the cap rock in the laboratory test and in the mine indicates that such preliminary laboratory tests may provide valuable prior evidence of conditions to be expected in a mine during underground gasification.

LIQUEFACTION

A report of Bureau of Mines progress in the Synthetic Liquid-Fuels Program has been given to Congress in accordance with the act authorizing the program.^{62/}

The authorization and objectives of the Synthetic Liquid-Fuels Program and the need for synthetic fuels, including raw materials and methods of converting, with a discussion of European developments and their application to American conditions, have been discussed.^{63/} The laboratories and demonstration plants and progress for their operation and the division of duties within the Bureau of Mines are given in that same publication.

In response to a request for information written in popular style, an article describing the production of gas for synthetic fuel, the synthesis of oil from this gas, and known plans for commercial development was issued.^{64/}

Facilities for Research and Development, Bruceton, Pa.

The buildings, including all services, are almost completed. An airplane view of the buildings is shown in figure 43. The center building, which houses the administrative offices, drafting room, instrument shop, store rooms, and cafeteria, was completed in May 1947. Occupation of the coal-hydrogenation building, which is the main building shown at the right of the photograph, was started in April 1947, when the experimental plant at Pittsburgh was dismantled and moved to Bruceton. The large building shown at the left of the group of main buildings houses the Fischer-Tropsch research and demonstration laboratories. The power plant and coal-washing laboratory are shown in the foreground of the picture immediately adjacent to the railroad siding. The sewage-disposal plant appears in the foreground of the picture, and the smaller buildings to the right of the main buildings are provided for oil storage and for the preparation of hydrogenation and carbon monoxide.

^{62/} Secretary of the Interior, Report on the Synthetic Liquid Fuel Act from January 1, 1946 to December 31, 1946: 82 pp.

^{63/} Fieldner, A. C., Synthetic Liquid Fuels Investigations of the Bureau of Mines: Science Counselor, March 1947, vol. 10, No. 1, pp. 8-10, 24-26.

^{64/} Newman, L. L., Synthetic Oil: Federal Sci. Prog., February 1947, pp. 11-13.

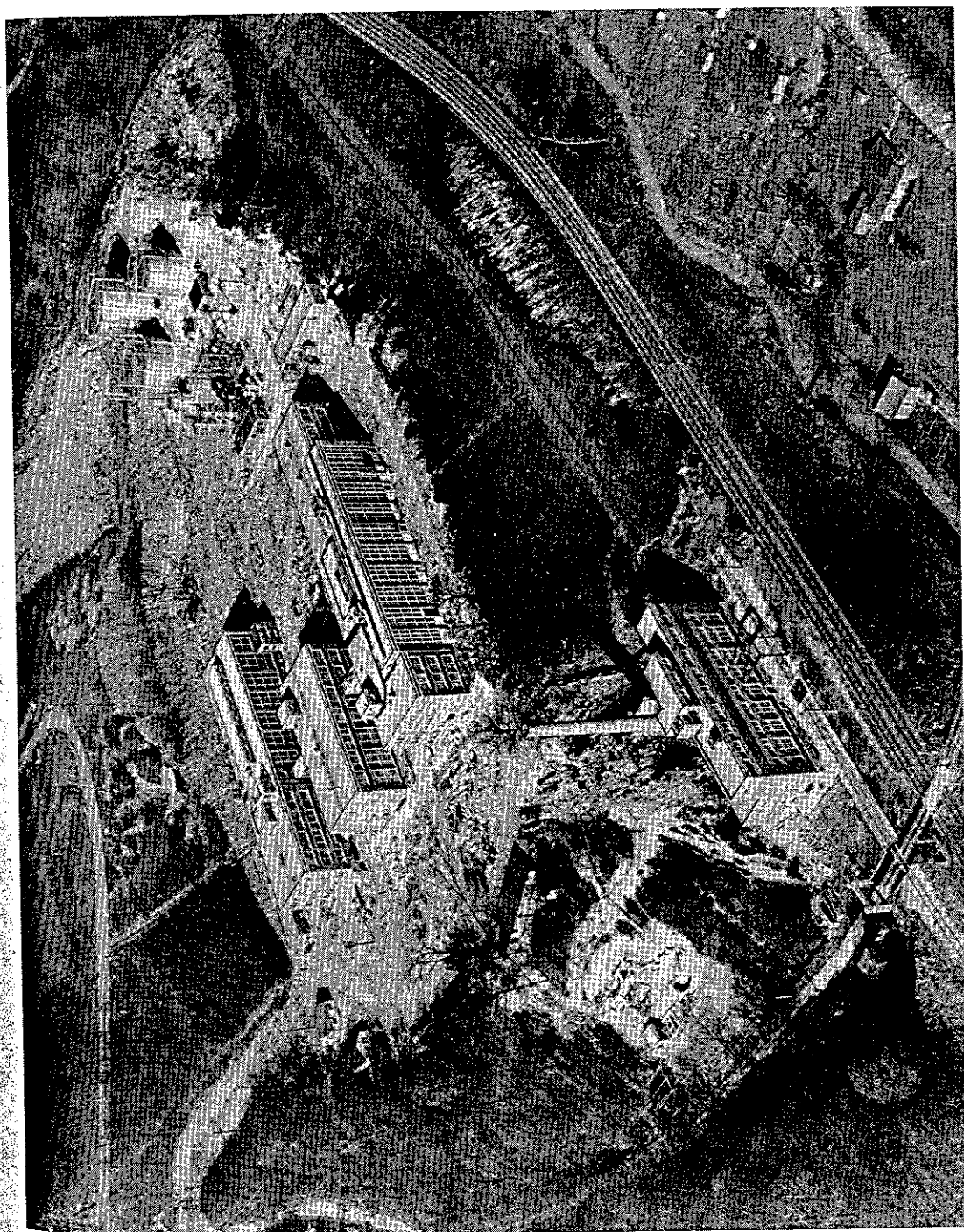


Figure 43. - Airplane view of synthetic liquid fuel laboratory and pilot-plant buildings at Bruceton, Pa.

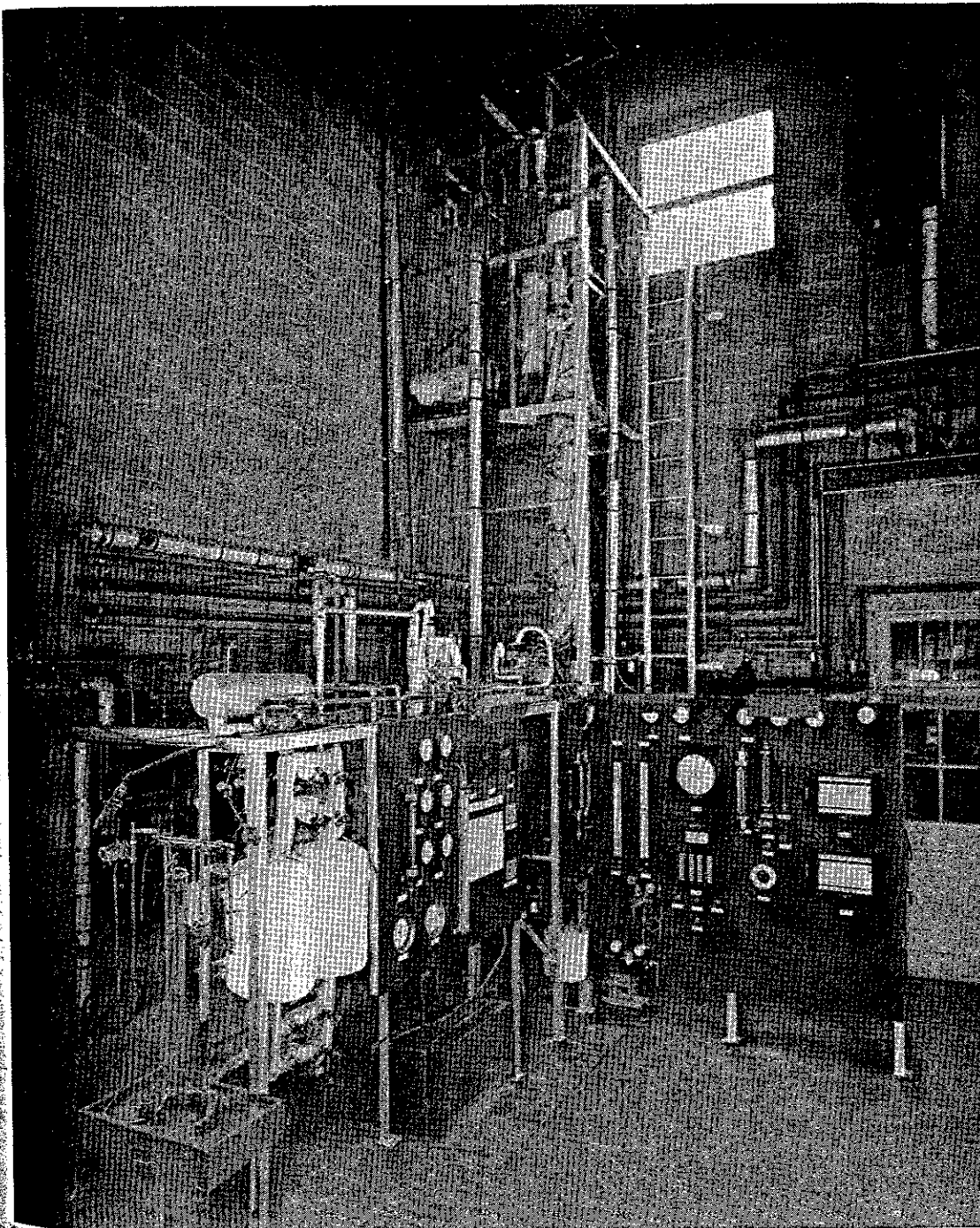


Figure 44. - Evaporative cooling pilot plant for synthesis of liquid fuel by hydrogenation of carbon monoxide.

Synthesis of Liquid Fuels from Hydrogen and Carbon Monoxide

Process Development; Pilot-Plant and Bench-Scale Tests

The preliminary work on the use of oil evaporation as cooling medium for the Fischer-Tropsch synthesis was described in last year's report.^{65/} The redesigned, internally cooled converter (by oil evaporation), built to accommodate a catalyst bed 3 inches in diameter by 8 feet deep, is shown in figure 44. Adequate control of all operating conditions such as pressure, temperature, rate of cooling oil circulation, space velocity, and rate of recycling of end gas was provided in the unit. In addition, provision was made for sample withdrawal and cooling oil injection at several points in the 8-foot column. About eight operations of 100 to 200 hours duration have been conducted with pelleted cobalt-thoria-Filter Cel catalyst since the unit was completed.

Experiments with countercurrent flow of cooling oil showed that the maximum space velocity (volumes of synthesis gas per volume of catalyst per hour) permissible without flooding is about 200; tests with cocurrent flow indicated that space velocities of 600 or greater could be used without flooding. The weight of oil obtained per unit volume of catalyst per day (space-time yield) increased two and one-half fold when the space velocity was increased from 100 to 300. The gaseous hydrocarbons, methane and ethane, constituted only 15 to 20 percent of the hydrocarbon product. The space-time yield increased three and one-half fold when the space velocity was increased from 100 to 450. A space velocity of 600 resulted in only a slight further increase in space-time yield.

The results thus far obtained indicate that it will be possible to obtain 3 to 5 times the weight of oil per unit volume of catalyst per day that is obtained in the Germany Ruhrchemie process, and it shows promise of equaling in industrial applicability the fluidized catalyst process recently developed by American oil-company engineers. The internally cooled converter process is more versatile than the fluidized-catalyst process in the respect that it is not limited to the use of only those catalysts that have certain critical fluidization characteristics. Additional extended operations are necessary with different modes of cooling-oil distribution, with a wider range of space velocities and at various operating pressures. It will be necessary also to determine the effect of recycling end gases and the ultimate yield, using multistage operation.

A modification of operating procedure tested recently was the complete submersion of the catalyst in cooling oil, the synthesis gas being introduced at the bottom of the converter. This procedure promises to eliminate the major source of trouble in the operation of the internally cooled converter - that is, variation in distribution of cooling liquid in the column, which results in formation of hot spots and overheating of the catalyst.

^{65/} Fieldner, A. C., and Ambrose, P. M., Annual Report of Research and Technologic Work on Coal, Fiscal Year 1946: Bureau of Mines Inf. Circ. 7417, 1947, 142 pp.

Experiments have been in progress for about 2 months using a pelleted iron-copper-potassium carbonate catalyst in the internally cooled converter. Operation with this catalyst has been much smoother than with cobalt, largely because of the wider temperature range that may be employed without excessive formation of methane.

The enlarged process development laboratory is continuing its exploratory "bench" or laboratory-size experiments on several processes. A view of this laboratory is shown in figure 45. Three processes are now under investigation. They are:

1. The liquid-phase catalyst suspension process, which was described in last year's report. The experimental converter is 3 inches in diameter with a maximum capacity of 2 liters of catalyst suspension. The operating pressure is in the range of 1 to 30 atmospheres. Porous disks fabricated of sintered iron powder are used for distributing the feed gas. Early results of the investigation of operating variables in this process show that high pressures, high concentrations of catalyst in the slurry, and high gas input favor the reaction by increasing the absorption rate of the synthesis gas. Studies of catalyst-conditioning (starting the synthesis) and reactivation procedures are in progress. Based on the results thus far obtained, a new reactor has been designed to obtain maximum gas to liquid interfacial area.
2. The hot-gas recycle process, in which all of the heat evolved during the synthesis is carried out of the synthesis vessel by the sensible heat of the gas. This process involves very large recycle rates of the order of 25 to 100 parts of recycle gas to 1 part of fresh gas. A cost estimate showed that such recycling would add about 1 cent per gallon to the cost of production, as compared with other processes in which only 2 to 5 parts of recycle gas to 1 part of fresh gas are used. Further analysis indicates that, with modification of catalyst shape and extent of recycle, the process may be economically feasible. Bench-scale equipment has been designed for some experimental work on this process.
3. Experiments on fluidized fixed-bed processes are currently directed towards a study of the factors controlling the rate of elemental carbon deposition on a fluidized iron catalyst. This problem now is of critical importance in the design of commercial plants using fluidized iron catalyst systems.

Preparation and Testing of Catalysts

X-ray diffraction patterns and magnetic susceptibility^{66/} of Fischer-Tropsch catalysts were reported.

In the preparation of large batches of precipitated iron catalysts under presumably identical conditions, it was observed that some were glossy black

^{66/} 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. Am. Chem. Soc., vol. 68, 1946, pp. 1953-1956.

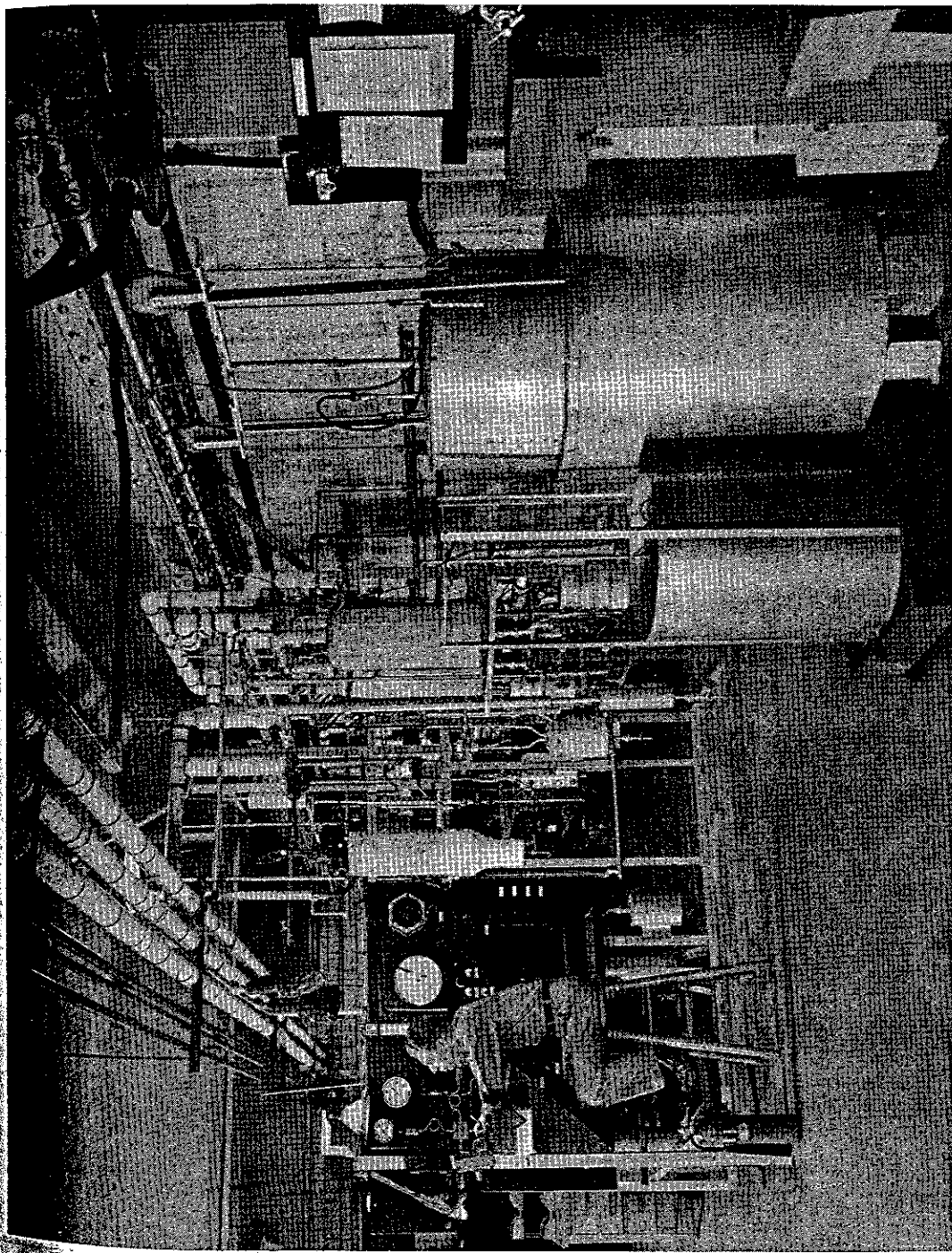


Figure 45. - Bench-scale unit for liquid-phase process for synthesis of liquid fuel by hydrogenation of carbon monoxide.

and others were brown and much less shiny. Surface areas of these preparations were measured by determining the nitrogen absorption isotherms at -195°C . of catalyst in the unreduced state and after induction at 230°C . in $\text{H}_2 + \text{CO}$ gas mixture. Chemisorption of carbon monoxide at -195°C . was measured to determine the fraction of metallic iron present on the catalyst surface. From the data shown in table 29, it was observed that both catalysts had a high surface area and small pore structure in the unreduced form. The isotherm of the black form of the catalyst was of the type observed in silica gels, but the brown form was unusual in being linear from a relative pressure of 0.1 to 0.7. When the catalysts were induced for 2 hours at 1 atmosphere pressure and 230°C . with $\text{H}_2 + \text{CO}$ gas, the areas dropped to 22.9 to 15.5 square meters per gram for the black and brown catalysts, respectively. These are consistent with other data upon the change in surface areas of gel-type iron catalysts.

TABLE 29. - Properties of Fe-Cu- K_2CO_3 catalysts

Catalyst			Unreduced		After induction			
No.	Appearance	Per-cent iron	Surface area m. ² /g.	Average pore diameter, Å	Weight loss, percent	Surface area m. ² /g.	V _{CO} chemi cc./g.	V _{Co} chemi V _m N ₂ /
<u>Composite</u>								
P-3003.03	(black)	56.7	303	28.0	10.3	22.9	0.93	0.18
P-3003.042								
P-3003.05								
P-3003.07	(brown)	59.5	135	41.6	5.9	15.5	.70	.20

1/ Calculated by the formula $d = \frac{4}{A} V_1$, where A is the surface area and V_1

the volume adsorbed at 0.98 relative pressure computed as liquid.

2/ Per gram of unreduced catalyst.

3/ V_{CO} chemi = volume of chemisorbed CO, V_m = cc. of N₂ in monolayer.

Dr. H. Pichler, after a visit in May 1947 to the Kaiser Wilhelm Institute, reports the results of a recent pilot-plant test made in one tube of the middle-pressure reactor using a catalyst prepared from a mixture of ferrous and ferric chlorides plus some copper as promoter. The catalyst was induced by treatment with $\text{H}_2 + \text{CO}$ gas at about 225°C . for 48 hours. Operation was then started at 10 atmospheres and 200°C . This catalyst was still at peak activity after 4-1/2 months of continuous operation; the present operating temperature is 205°C .

Data were obtained on various physical properties of unreduced-and reduced-cobalt catalysts and of different types of diatomaceous earth (kieselguhr) - namely, X-ray diffraction patterns, surface areas, and porosity.^{67/}

^{67/} Weller, S., Chemisorption of Gases: Jour. Chem. Phys., vol. 15, 1947, p. 336.

X-ray diffraction patterns of natural diatomaceous earths and of unreduced cobalt-thoria-natural diatomaceous earth catalysts showed them to be almost completely amorphous, the sharpest line in the pattern being that due to the quartz present in the diatomaceous earth; the pattern of alkali-treated and calcined diatomaceous earth showed a well-developed crystal structure. The X-ray pattern of reduced cobalt-thoria-kieselguhr and cobalt-thoria-magnesia-kieselguhr catalysts showed 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 on the conversion of cubic to hexagonal cobalt.

The total surface area of reduced and unreduced cobalt catalysts was measured by determining the nitrogen adsorption isotherms at -195°C . After reduction of the catalyst, the fraction of metallic cobalt in the surface was estimated by determining the carbon monoxide isotherm at -195°C . Figure 46 shows the nitrogen isotherms of kieselguhr and of an unreduced cobalt-thoria-magnesia-kieselguhr catalyst, and figure 47 shows the nitrogen adsorption isotherms for unreduced and reduced samples of the same catalyst. The isotherms are of 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 Ångstrom units in diameter. The nitrogen and carbon monoxide isotherms lie one above the other, the difference between them representing the quantity of chemisorbed carbon monoxide. Most of the area in the unreduced catalyst is provided by the cobalt oxide promoter-complex and only little by the kieselguhr. The surface areas of the catalysts are not additive with respect to the areas of the kieselguhrs used. Catalysts prepared from alkali-treated and calcined kieselguhr have lower areas than those prepared from natural kieselguhr; and in most cases the difference is greater than can be accounted for by assuming additivity of surface areas of the kieselguhr and the cobalt-promoter complex. Surface area measurements on cobalt-thoria-magnesia-diatomaceous earth catalysts showed that their activity in the synthesis varies directly with the surface area of the unreduced catalysts.

From the data shown in table 30, it was observed that upon reduction in a rapid stream of hydrogen at 400°C . for 2 hours, the surface area of the doubly promoted cobalt-thoria-magnesia-natural kieselguhr decreased to 75 percent of that of the unreduced catalyst, whereas the surface area of the singly promoted cobalt-thoria-natural kieselguhr catalyst decreased to 35 percent of that of the unreduced catalyst. Thus, the presence of promoters in cobalt catalysts makes reduction more difficult and prevents sintering. It is of interest to note that the surface area of the doubly promoted catalyst containing alkali-treated and calcined kieselguhr decreased to 55 percent of that of the unreduced catalyst.

Kinetic studies of rates of carbiding of cobalt and iron catalysts by carbon monoxide, of hydrogenation of the carbide, and of the synthesis have yielded some information concerning the temperature and pressure dependence of these rates. A general reaction-rate law, which was not restricted to constant pressure or constant volume and which was applicable to flowing

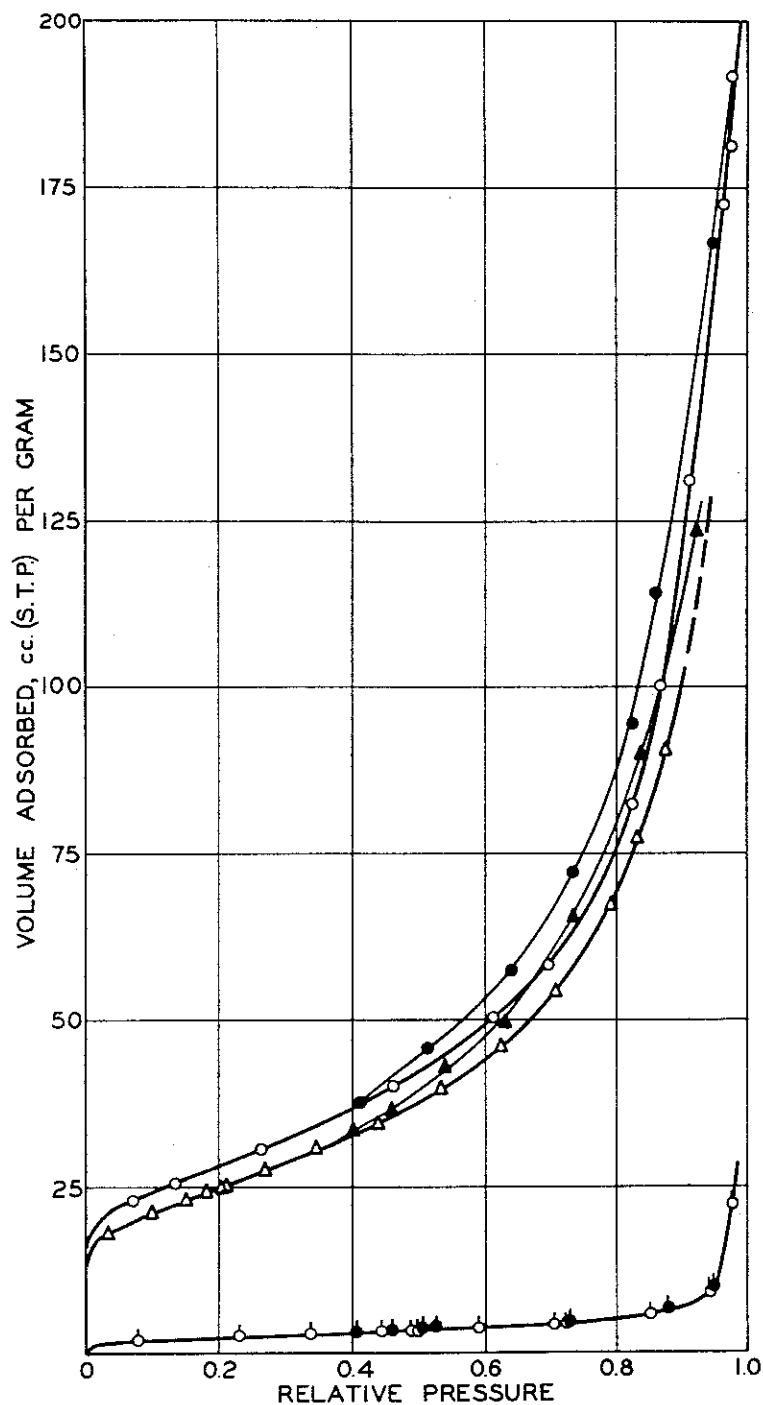


Figure 46. - Adsorption isotherms of nitrogen at -195°C . of unreduced cobalt Fischer-Tropsch catalyst 89J in granular and pelleted forms and kieselguhr used as catalyst support plotted for weight of kieselguhr per gram of catalyst. \circ represents 89J granules; Δ represents 89J pellets; and \circ represents kieselguhr. Adsorption points are open and desorption points solid.

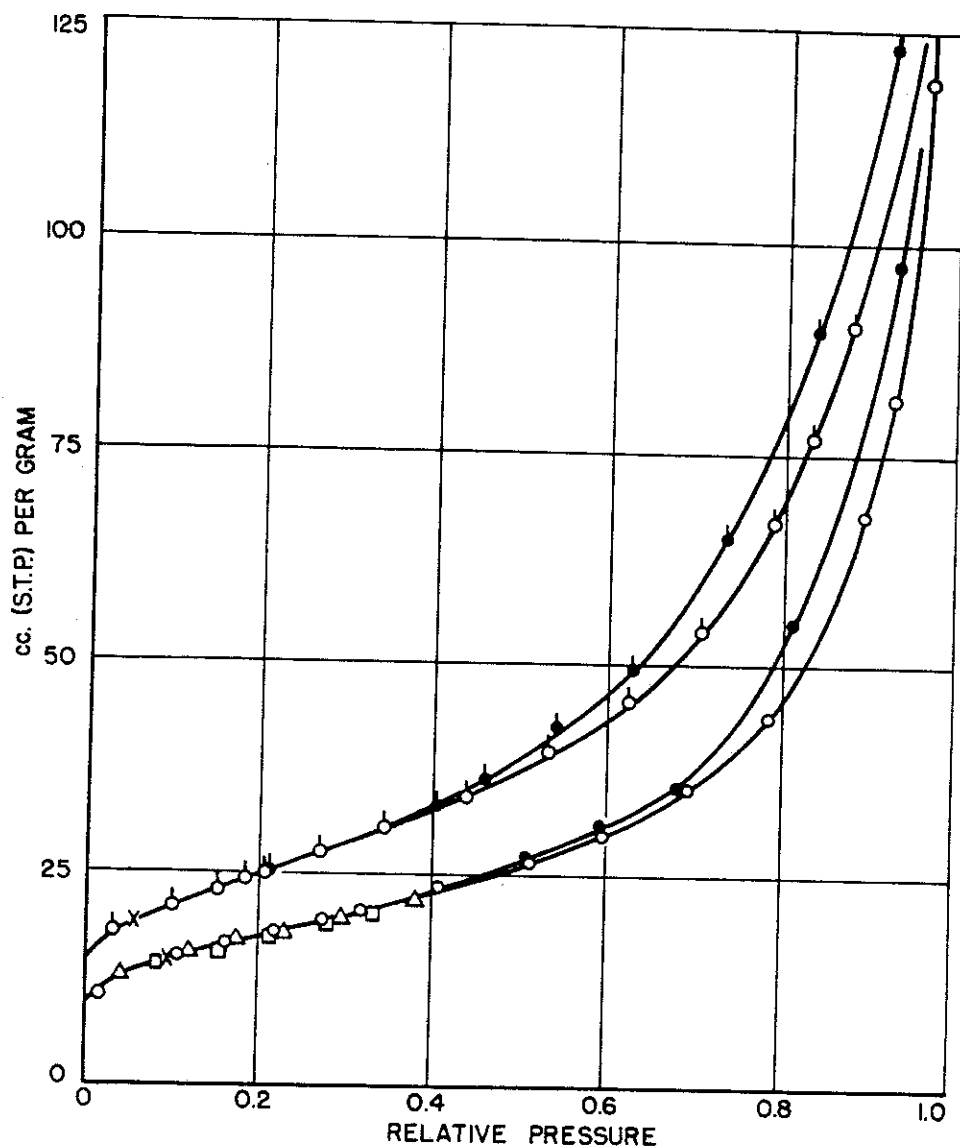


Figure 47. - Adsorption of nitrogen at -195°C . on unreduced- and reduced-cobalt catalyst 89J. \circ represents unreduced catalyst, and \circ , \square , and Δ represent different samples of reduced catalyst. Desorption points are solid, and volume of gas corresponding to a monolayer is represented by X.

systems, was obtained for homogeneous isothermal reactions in ideal systems.^{68/} Mention was made of modifications required for the consideration of systems that are nonisothermal. These results will be of value in the interpretation of data obtained experimentally in kinetic studies of the mechanism of the Fischer-Tropsch reaction.

TABLE 30. - Adsorption of nitrogen and carbon monoxide at -195° C. on unreduced- and reduced-cobalt catalysts and cobalt oxide

Catalyst	Reduction method			Loss, weight percent	Surface area, $m.^2/g.^2/$	V_m nitrogen, $cc./g.^2/$	V_{chemi} carbon monoxide, $cc./g.^2/$
	Temperature, $^{\circ}C.$	Hours	Space velocity, $hour^{-1}/$				
89H ^{3/}	-	-	-	0.0	67.2	15.4	0.0
89H	400	2	6,000	17.9	36.9	8.4	4.3
89J ^{3/}	-	-	-	.0	84.1	-	.0
89J	400	2	6,000	17.7	62.0	14.2	3.1
108B ^{4/}	-	-	-	.0	84.6	19.3	.0
108B	400	2	6,000	28.6	28.3	6.5	-
Co ₃ O ₄	-	-	-	.0	68.0	15.4	.0
Co ₃ O ₄	250	41	100	30.6	3.2	.74	.48

1/ Volumes hydrogen per bulk volume of catalyst per hour.

2/ All adsorption data per gram of unreduced catalyst.

3/ Cobalt-thoria-magnesia-kieselguhr.

4/ Cobalt-thoria-kieselguhr.

Rates of carbiding by carbon monoxide, of hydrogenation of the carbide, and of hydrocarbon synthesis from $2H_2 + 1CO$ gas mixture were measured for a cobalt-thoria-kieselguhr and a cobalt-thoria-magnesia-kieselguhr catalyst using an all glass apparatus, including a circulating pump. A similar investigation was begun for a precipitated iron catalyst. The gases were circulated over the catalyst and then through the liquid air traps so as to condense all products except about 1 cm. partial pressure of methane. The pressure was automatically adjusted to a constant value during each experiment, and the change in volume of the reactants was measured. It was found that the initial carbiding rate for cobalt catalysts was of the same order of magnitude as the synthesis rate, but that the subsequent "steady-state" rate of carbiding of the bulk of the catalyst was about ten times lower than the rate of the synthesis. The rate of hydrogenation of the carbide was very much faster than carbiding and synthesis at synthesis temperatures. Per unit of metal surface, carbiding of the iron catalyst proceeded about five times more quickly than the carbiding of the cobalt catalyst. However, hydrogenation of iron carbide proceeded more slowly than carbiding, at synthesis temperature. It was observed that the temperature and pressure dependence of the carbiding rate were essentially the same for cobalt and iron catalysts. The implication is that the same step is rate-determining for the carbiding of both metals.

^{68/} Brinkley, S. R., Jr., and Weller, S., Generalized Form of the Reaction-Rate Law for Homogeneous Reactions: Jour. Am. Chem. Soc., vol. 69, 1947, pp. 1319-1321.

An investigation of the role of cobalt and iron carbide in the Fischer-Tropsch synthesis is under way because the theory has long been popular that during the reaction these metal carbides are formed and subsequently reduced to methylene (CH_2) groups. The concept of metal carbide as a synthesis intermediate has been used rather loosely. Distinction has rarely been made between bulk carbide and "surface" carbide as a possible intermediate. The idea of "surface" carbide is elusive, since it is very difficult to distinguish between a "surface" carbide and adsorbed carbon monoxide. However, evidence has been accumulated which demonstrates that bulk carbide, in the case of cobalt catalysts, probably is neither an intermediate in the synthesis nor a catalytically active substrate for the synthesis.^{69/}

Recent work in the physical chemistry and catalyst-testing laboratories shows that the presence of extensive amounts of carbide in cobalt catalysts severely inhibits the Fischer-Tropsch synthesis. In one experiment, for example, a cobalt-thoria-magnesia-kieselguhr (100:6:12:200) catalyst was reduced with hydrogen at 400°C . and carbided with carbon monoxide for 20 hours at 200°C .; the volume of carbon monoxide reacted was equivalent to 70 percent conversion of the cobalt to Co_2C . Exposure of this carbided sample to circulating synthesis gas resulted in an over-all synthesis rate at 150°C . of $60\text{--}70 \times 10^{-4}$ grams of carbon per gram of cobalt per hour. After removal of the carbide by hydrogenation at $150^\circ\text{--}194^\circ\text{C}$. and reexposure of the sample of synthesis gas, a synthesis rate of $250\text{--}300 \times 10^{-4}$ grams carbon per gram cobalt per hour was observed, an increase of 400 percent. It may be noted that the distribution of synthesis products was about the same in both cases.

In another case, a sample of cobalt-thoria-kieselguhr (100:18:100) catalyst which had been completely carbided at 210°C . was found to exhibit no appreciable activity in the synthesis under conditions where a control sample, similarly reduced initially but not carbided, gave copious yields of oil and water. Partial hydrogenation of the carbided sample at 190°C ., with removal of 72 percent of the carbon which had been introduced, restored the activity to about one-half the normal value.

It was further shown that the loss of synthesis activity on carbiding can persist even when synthesis is continued for several days. Another sample of cobalt-thoria-kieselguhr catalyst was carbided for 24 hours at 200°C . after initial reduction. On exposure to flowing synthesis gas at 180°C ., the carbided sample originally showed no catalytic activity, as measured by the fractional decrease in gas volume (contraction) as the gas passed through the converter. During operation for one day at 180°C ., the contraction rose to 20 percent, but it did not increase further during another day of synthesis. Increasing the temperature to 190°C . increased the contraction only to 32 percent even after a period of a day. Subsequent hydrogenation of the sample at 210°C . and reexposure to synthesis gas resulted in a normal contraction of 60 percent at 180°C . Recarbiding of the

^{69/} Hofer, L. J. E., and Peebles, W. C., Preparation and X-ray Diffraction Studies of a New Cobalt Carbide: Jour. Am. Chem. Soc., vol. 69, 1947, pp. 893-899.

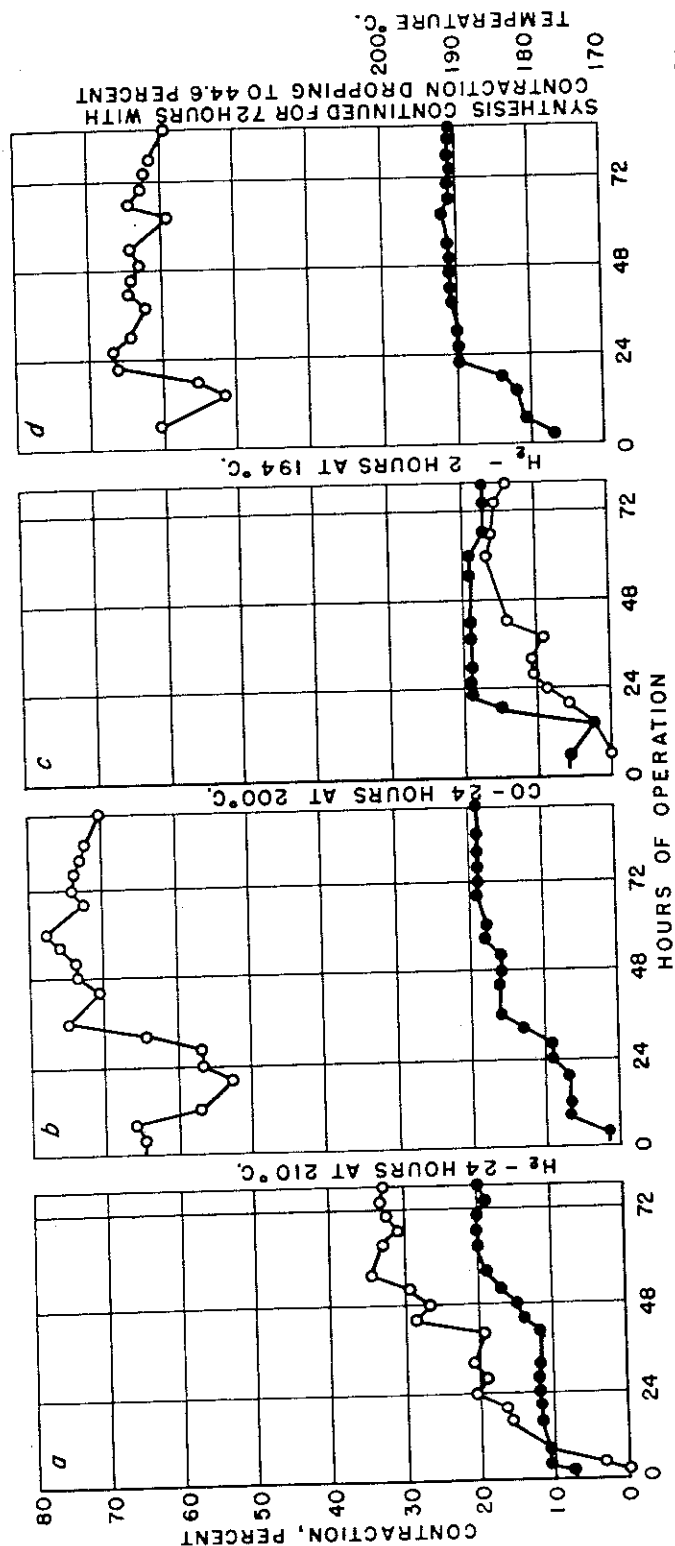


Figure 48. - Apparent contraction O and temperature of operation ● versus time for test 73 with cobalt catalyst 108B at atmospheric pressure. Catalyst was reduced in hydrogen at 360° C. and carburized with carbon monoxide at 200° C. for 24 hours prior to testing.

active catalyst for 24 hours at 200° C. again reduced the activity to the low value observed after the first carbiding, and rehydrogenation of the carbided sample again restored the normal activity. These results are graphically presented in figure 48.

It should be noted that this inhibitory effect of precarbiding before synthesis is not explainable as a poisoning due to free carbon deposited during the carbiding, since the effect is completely reversed by hydrogenation at temperatures where free carbon is not affected. These experiments show that bulk cobalt carbide is not a catalyst for the synthesis; this conclusion, furthermore, is contrary to that which would be expected if bulk carbide were an intermediate in the synthesis.

A second line of evidence which indicates that bulk cobalt carbide is not of importance in the synthesis is furnished by X-ray analysis of catalysts which have been used in the synthesis. It has previously been shown that on low-temperature carburization with carbon monoxide, reduced cobalt catalysts form a carbide, Co_2C , which has a characteristic X-ray diffraction pattern. This fact provides a means of identifying cobalt carbide in the catalyst. It was then observed by X-ray analysis that if catalyst samples were partly carbided before synthesis and then used in synthesis, carbide was still present in the samples, even after several days of synthesis. (In pure hydrogen, the carbide would have been completely removed as methane in several hours.) On the other hand, if the samples were used in the synthesis immediately after reduction (that is, no precarbiding), no carbide was ever found at the conclusion of the synthesis. In other words, bulk carbide is apparently not built up in appreciable quantity during steady-state synthesis, while carbide already present apparently is not removed at an appreciable rate during steady-state synthesis. Although quantitative determinations of the amount of carbide present under given conditions have yet to be made, the indication is that bulk carbide is neither formed nor destroyed as part of the synthesis process.

The final evidence to be adduced in connection with the role of bulk carbide is also based on X-ray analysis. It has been shown that cobalt in catalysts reduced at 360°-400° C. is present primarily as cubic cobalt. Cubic cobalt is thermodynamically unstable with respect to hexagonal cobalt at temperatures below about 360° C. Carbiding of the reduced sample and hydrogenation of the carbide, both at 200° C., always convert the cobalt to the low-temperature stable, hexagonal form. Now all samples of cobalt catalysts (not precarbided) which have been examined after use in the synthesis have given a diffraction pattern identical with that of the freshly reduced catalyst. If any appreciable amount of the cobalt had been through the cycle of carbiding and hydrogenation at any time during the synthesis, it would have appeared as hexagonal, not cubic, cobalt in the used catalyst sample. Since this did not occur, it follows that, within the limits of the X-ray method, the cobalt was not converted to bulk carbide and subsequently hydrogenated during the synthesis; that is, bulk carbide is not intermediate in the synthesis.