EXPERIMENTAL PART

One of the principal objects of the present work was to establish a theoretical basis for the empirically determined conditions governing the Fischer-Tropsch synthesis on iron catalysts. With this in view, the behavior of iron catalysts during carburization and synthesis was studied by acid decomposition, reduction with hydrogen, and thermomagnetic analysis. A relationship was sought between chemical composition and activity of the catalyst in the gasoline synthesis, with particular emphasis on the formation of carbides. The mechanism of the Fischer-Tropsch process and the formation of free carbon on iron catalysts during pretreatment and medium-pressure synthesis were considered in the light of the results obtained.

CHEMICAL STUDY

CARBURIZATION OF IRON CATALYSTS PRIOR TO MEDIUM-PRESSURE SYNTHESIS

METHODS AND APPARATUS

The iron catalysts studied in the first part of this work were prepared in large batches in the usual way by precipitating a hot iron nitrate solution with sodium carbonate. The precipitate was washed and alkalized with potassium carbonate and then oven-dried at 105°C. After screening, a particle size of 1 to 5 millimeters was collected. The iron catalysts were treated with carbon monoxide in a standard aluminum block oven (fig. 2) which consisted of an aluminum heating block containing a copper-lined iron tube. This tube was used for experiments at high and low pressures.

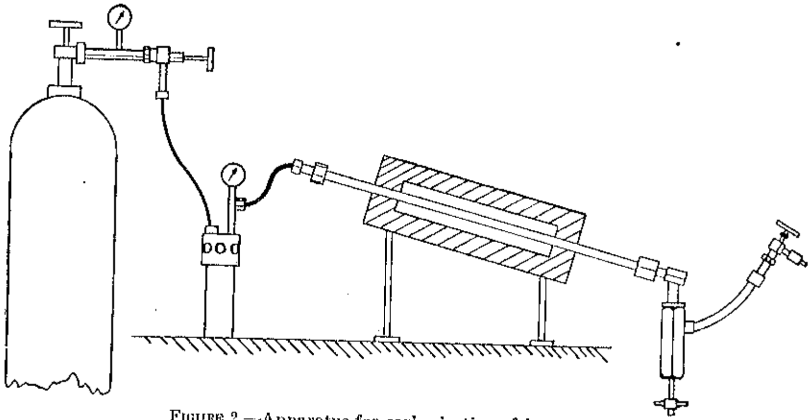

FIGURE 2.—Apparatus for carburization of iron catalysts.

An amount of catalyst corresponding to 10 grams of iron was placed in an iron boat and spread out over a length of 30 centimeters. The boat was placed in the center of the copper-lined iron tube. The system was flushed with carbon monoxide and then heated under a carbon monoxide pressure of 0.1 atmosphere. Temperature was maintained at 325° ± 1°C., by means of a thermostat. At the conclusion of the experiment, the aluminum heating block was cooled with wet cloths to reduce the temperature to below 200°C. within a few minutes. Thus no significant additional carburization occurred either during heating or cooling.

The carburized iron catalysts were markedly pyrophoric in air but not in water. Consequently, boiled distilled water was drawn through the cooled tube, making it possible to expose the catalyst to air without danger. The catalyst was stored in closed flasks under boiled distilled water. Since highly active catalysts evolved hydrogen on standing, it was necessary to use them immediately.

ACID DECOMPOSITION OF IRON CATALYSTS CARBURIZED UNDER VARIOUS CONDITIONS

METHOD AND APPARATUS

A number of methods are reported in the literature regarding the separation of carbidic carbon from free carbon by acid decomposition of the carbide. Decomposition of the carburized-iron catalysts with hydrochloric acid was carried out in the apparatus shown in figure 3. During decomposition, carbidic carbon produced gaseous hydrocarbons and the residual carbon was assumed to correspond to the amount of free carbon initially present in the catalyst.

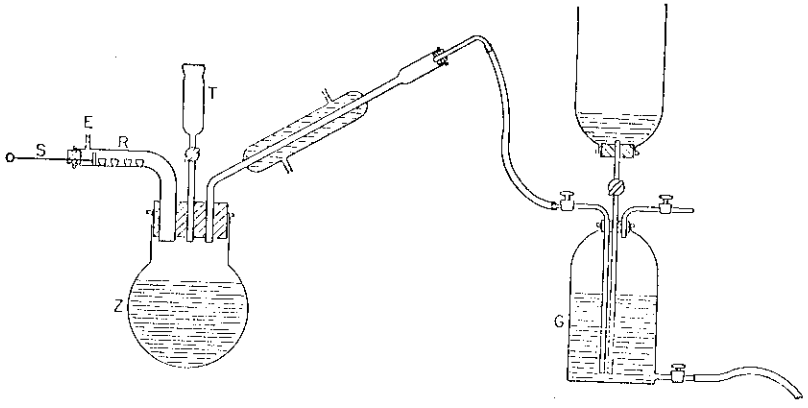

FIGURE 3.—Apparatus for acid decomposition of iron catalysts.

Conflicting data on the reaction of cementite (Fe_3C) with acids are reported in the literature. According to Hilpert,[2] cementite in steels is completely hydrogenated in the presence of strong acids. The carbonaceous deposits that originate from the decom-

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[2] Hilpert, S., and Dieckmann, T., work cited in footnote 9 (p. 3).

position of steels tempered at 200° to 600°C. are attributed to the decomposition of higher carbides. Schenck and Stenkhoff[3] have shown that acid decomposition of cementite can proceed according to two different reactions:

$$(1)\ Fe_3C + 6H^+ = 3Fe^{++} + CH_4 + H_2,$$
$$(2)\ Fe_3C + 6H^+ = 3Fe^{++} + C + 3H_2.$$

The course of the reaction is determined by the concentration of the acid, temperature, and concentration of ferrous ions. Reaction (2) occurs with weak acid and a high concentration of ferrous ions. Reaction (1) is favored by a lower concentration of ferrous ion and strong, hot acid. Work by Mittasch and Kuss[4] justifies the assumption that decomposition of cementite (prepared at 1,550°C.) may be effected according to equation (1).

The experiments described below were carried out in decomposition flask *Z* (fig. 3), containing 1 liter of 5N hydrochloric acid which was heated to boiling in a stream of nitrogen. The catalyst was placed in little glass dishes, which were introduced into glass tube *R*. A plunger, *S*, pushed the catalyst containers successively into the decomposition flask. This procedure corresponded to the conditions of acid decomposition of cementite used by Schenck. Since the quantity of iron used was only 2 or 3 grams, the formation of an undesirable concentration of ferrous ions was avoided and an excess of acid assured. Decomposition was very rapid and generally completed in a few seconds. The flasks were then filled with distilled water from the dropping funnel *T* almost to the opening of the inlet tubes, and the product gas was swept into gasometer *G* by a stream of nitrogen (introduced through tube *E*).

In addition to nitrogen introduced as described above, the product gas contained hydrogen and hydrocarbons in varying amounts. Carbon, originating from iron carbide and hydrogenated during acid decomposition, was determined by combustion of the hydrocarbons; in the following discussion it will be referred to as carbidic carbon. The elementary carbon was filtered off from the iron solution, dried, and burned. The residue contained small amounts of iron which could not be eliminated even by prolonged treatment with acid. The iron was determined by titration.

FREE CARBON

When carburized-iron catalysts undergo acid decomposition, free and carbidic carbon is always present. A study was made of the quantity of free carbon formed under different carburization conditions. The effect of the rate of flow of carbon monoxide on the formation of free carbon was examined first. In each case an amount of catalyst equivalent to 10 grams of iron was treated with 100 liters of carbon monoxide at 325°C. and 0.1 atmosphere pressure, the standard conditions of pretreatment. The carbon monoxide was first purified by passage through two columns containing soda lime and activated charcoal. The results obtained from this series of experiments are given in table 4.

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[3] Schenck, R., and Stenkhoff, R., work cited in footnote 26.
[4] Mittasch, A., and Kuss, E., work cited in footnote 86.

TABLE 4.—*Effect of rate of flow of carbon monoxide on formation of free carbon*
[Temperature, 325°C.; CO pressure, 0.1 atmosphere; Fe, 10 grams]

Experiment No.	Rate of flow (liters per hour)	Carburization time (hours)	Free carbon (grams)
1	100	1.0	0.56
2	40	2.5	.95
3	4	25.0	2.21

Table 4 shows that the quantity of elementary carbon increased as the rate of flow decreased, that is, as the contact time was prolonged. Similar results were observed when the throughput (liters of carbon monoxide per hour per gram of iron) was held constant and the pressure varied. The lower the pressure, the shorter was the contact time between catalyst and carbon monoxide and the smaller the amount of free carbon deposited. In an experiment similar to experiment (3) in table 4, carburization was carried out at 1 atmosphere instead of 0.1 atmosphere; 4.32 grams of carbon per 10 grams of iron was obtained.

Table 5 shows the effect of carburization temperature on free carbon deposition.

TABLE 5.—*Effect of carburization temperature on formation of free carbon*
[Rate of flow, 4 liters CO per hour per 10 grams Fe; pressure, 0.1 atmosphere; carburization time, 25 hours]

Experiment No.	Temperature (°C.)	Free carbon (grams)	Experiment No.	Temperature (°C.)	Free carbon (grams)
1	175	0.00	4	325	2.21
2	225	.07	5	425	10.02
3	275	.89			

No carbon deposition occurred at 175°C., but the catalyst turned black. Ferric oxide, Fe_2O_3, was reduced to magnetite even below 200°C. As the temperature was increased, the quantity of carbon deposited increased to 10.02 grams of carbon per 10 grams of iron at 425°C. The free carbon was large-grained and hard up to 325°C.; at 425°C. it was obtained in a fine, sooty powder. According to Hofmann,[5] the difference in properties of carbon deposited at different temperatures is determined by the orientation of the individual crystallites and by their regular increase in size as the temperature rises.

Table 6 shows the formation of free carbon as a function of time.

It will be seen from experiment 1 (table 6) that free carbon formed after only 4.5 minutes of carburization. This carbon had a flaky, voluminous appearance, whereas it was hard and granular after a longer period.

Figure 4 shows graphically the results listed in table 6. The rate of carbon formation reached a constant value after about 2.5 hours, the formation of free carbon being proportional to the

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[5] Hofmann, U., work cited in footnote 90.
Hofmann, U., and Groll, E., work cited in footnote 91.

TABLE 6.—*Effect of carburization time on formation of free carbon*

[Rate of flow, 40 liters CO per hour per 10 grams Fe; pressure, 0.1 atmosphere; temperature, 325°C.]

Experiment No.	Carburization time (minutes)	Free carbon (grams)	Experiment No.	Carburization time (minutes)	Free carbon (grams)
1	4.5	0.017	5	75	.49
2	9	.11	6	150	.95
3	18	.28	7	600	1.83
4	37.5	.41	8	1,500	3.23

carburization time. Even after 25 hours of carburization, and after 1,000 liters of carbon monoxide had flowed over the catalyst, there was no perceptible decrease in free carbon formation.

Next, the effect of activity of the catalyst upon the formation of free carbon was examined. Three iron catalysts of different origin were treated for 2.5 hours at 325°C. and 0.1 atmosphere with 40 liters of carbon monoxide per 10 grams of iron per hour. Catalyst *Z* 7 contained 0.81 gram of elementary carbon per 10 grams of iron, catalyst *Z* 4 contained 1.07 grams of carbon, and catalyst *Z* 3 contained 1.75 grams of carbon as shown in table 7. In the synthesis (15 atmospheres, 235°C.), all three catalysts showed satisfactory conversion (80 to 90 percent) of carbon monoxide on the first day of operation. After 6 to 10 days, conversion began to decrease for catalysts *Z* 7 and *Z* 4, but the activity of catalyst *Z* 3 was still unchanged after 35 days.

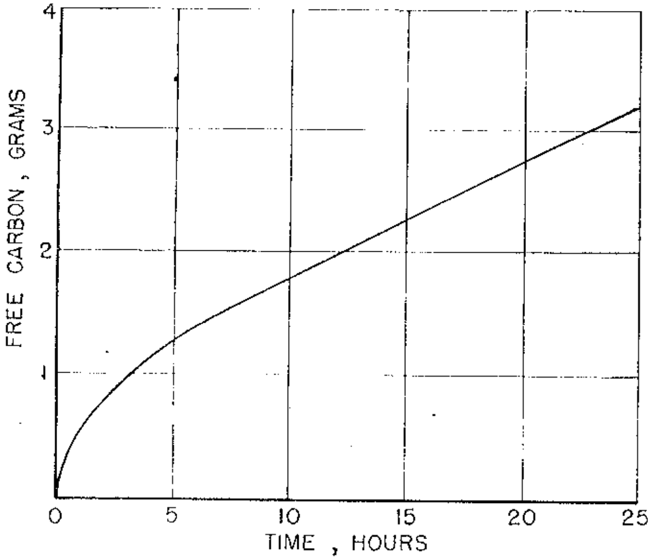

FIGURE 4.—Free-carbon deposition of alkalized-iron catalyst at 325°C. and 0.1 atmosphere, 40 liters of CO per hour per 10 grams of Fe.

TABLE 7.—*Effect of catalyst activity on formation of free carbon*

[Rate of flow, 40 liters CO per hour per 10 grams Fe; time, 2.5 hours; pressure, 0.1 atmosphere; temperature, 325°C.]

Catalyst	Free carbon, (grams)	Period during which catalyst showed full activity in synthesis (days)
Z 7	0.81	6–10
Z 4	1.07	6–10
Z 3	1.75	35+

CARBIDIC CARBON

The gas produced during acid decomposition of carburized catalysts was measured and calculated at standard conditions. In one sample unsaturated hydrocarbons were determined with concentrated sulfuric acid; hydrogen and saturated hydrocarbons were determined by fractional combustion. In a second sample, combustion of all the hydrocarbons was carried out in oxygen over a copper oxide catalyst at bright red heat, and the carbon dioxide evolved was determined.

An experiment was performed in which the total carbon content of a carburized catalyst was determined both by acid decomposition and by combustion in a current of oxygen. In the former case, the sum of free carbon obtained by acid decomposition and of carbidic carbon obtained by combustion of gaseous hydrocarbons was 0.448 gram per gram of iron. The total carbon obtained by combustion of the catalyst in oxygen amounted to 0.423 gram per gram of iron. These results were in satisfactory agreement within the limits of experimental error and showed that no liquid hydrocarbons were formed during acid decomposition.

The procedure for investigating the formation of free carbon was also used to study the effect of various carburization conditions on the formation of carbidic carbon. A quantity of catalyst equivalent to 10 grams of iron was treated with a current of carbon monoxide in a standard aluminum block oven under various conditions of rate of flow, temperature, pressure, and time. The effect of activity of the catalyst upon the formation of carbide was also studied.

Table 8 shows that the effect of the rate of flow of carbon monoxide on the formation of carbidic carbon was similar to that observed for free carbon (see table 4); however, combined car-

TABLE 8.—*Effect of rate of flow of carbon monoxide on the formation of carbidic carbon*

[Temperature, 325°C.; CO pressure, 0.1 atmosphere; Fe, 10 grams]

Experiment No.	Rate of flow (liters/hour)	Carburization time (hours)	Carbidic carbon (gram)
1	100	1	0.263
2	40	2.5	.436
3	4	25	.451

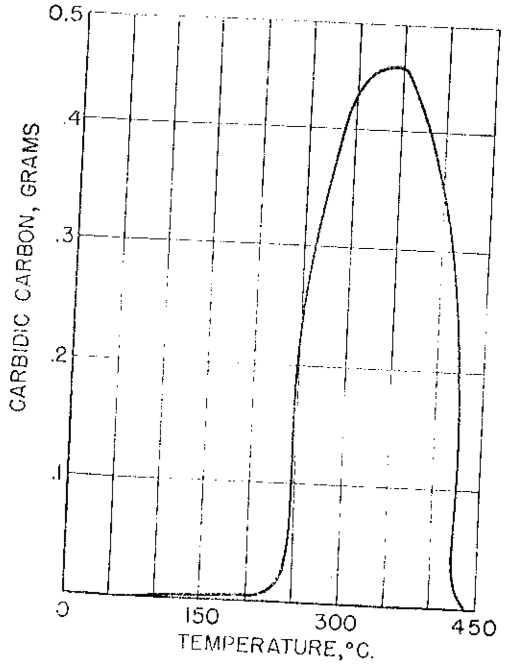

FIGURE 5.—Carbide formation on alkalized-iron catalysts during 25 hours carburization at 0.1 atmosphere, 4 liters of CO per hour per 10 grams of Fe.

bon reached a maximum value for a flow rate of 40 liters per hour, while the formation of free carbon continued to increase (table 4, experiments 2 and 3).

The following series of experiments show the effect of temperature on carbidic carbon (table 9 and fig. 5).

The quantity of carbidic carbon was still very small at 225°C., reached a maximum value at 325°C., and decreased abruptly at 425°C. These results show that, in the course of 25 hours, carburization produced considerable amounts of carbidic carbon only in a relatively narrow temperature range.

Table 10 shows the relationship between the formation of car-

TABLE 9.—*Effect of carburization temperature on the formation of carbidic carbon from carbon monoxide*

[Rate of flow, 4 liters CO per hour per 10 grams Fe; CO pressure, 0.1 atmosphere; carburization time, 25 hours]

Experiment No.	Temperature (°C.)	Carbidic carbon[a] (gram)	Experiment No.	Temperature (°C.)	Carbidic carbon[a] (gram)
1	175	0.003	4	325	0.454
2	225	.001	5	425	.017
3	275	.358			

[a] By acid decomposition.

TABLE 10.—*Formation of carbidic carbon from carbon monoxide as a function of carburization time*

[Rate of flow, 40 liters CO per hour per 10 grams Fe; CO pressure, 0.1 atmosphere; temperature, 325°C.]

Carburization time (minutes)	Carbidic C (gram)	Free C (grams)	H_2 (cc.)	CO_2 from hydrocarbons, (cc.)	$H_2 : CO_2$	Composition of evolved gas, volume percent					
						Unsaturated hydrocarbons "SKW"[a]	Saturated hydrocarbons	O_2	CO	H_2	N_2
4.5	0.001	0.017	—	—	—	—	0.4	5.0	0	0.8	19.1
9	.002	.11	2.6	2.9	0.9 : 1	—	1.4	5.4	0	1.0	23.3
18	.019	.28	72	35.4	2.0 : 1	0.6	.5	2.0	0	6.2	88.7
37.5	.085	.41	383	159	2.1 : 1	1.8	1.9	1.4	0	21.4	71.5
75	.201	.49	775	374	2.1 : 1	2.9	2.2	1.2	0	38.6	53.5
150	.436	.95	1,960	813	2.4 : 1	4.8	4.9	.7	0	57.5	32.4
600	.454	1.83	2,110	844	2.5 : 1	3.6	3.6	1.7	0	55.7	34.8
1,500	.457	3.23	2,110	855	2.5 : 1	1.7	3.7	1.2	0	54.0	37.1

[a] Determined with fuming H_2SO_4.

bidic carbon and contact time. Perceptible amounts of carbidic and free carbon were formed in the first 4.5 minutes of carburization. There was still little carbon after 9 minutes. After 150 minutes, carburization was almost complete under these conditions. In 1,500 minutes, carbidic carbon content increased only slightly. Prolonged carburization would be detrimental to activity in the synthesis since the free carbon which continues to form would block the active centers.

Column 6 of table 10 shows the ratio of hydrogen to carbon dioxide. Under the conditions chosen, the acid decomposition of cementite should proceed quantitatively according to the two following equations:

$$(1)\quad n\,Fe_3C + 6n\,HCl = 3n\,FeCl_2 + C_nH_{2n} + 2n\,H_2,$$
$$(2)\quad n\,Fe_3C + 6n\,HCl = 3n\,FeCl_2 + C_nH_{2n+2} + (2_{n-1})\,H_2.$$

Accordingly the hydrogen to carbon dioxide ratio should never exceed 2 : 1. Actually (according to table 10), exhaustive treatment with carbon monoxide resulted in a ratio of 2.5 : 1. The explanation will be discussed in connection with the thermomagnetic analysis.

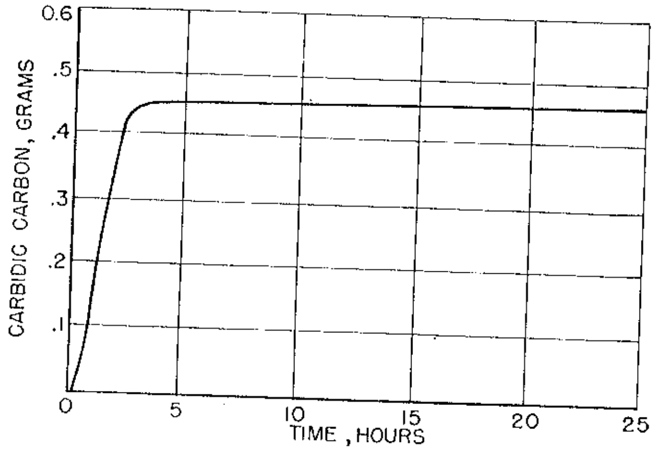

FIGURE 6.—Carbide formation on alkalized-iron catalysts at 325° C. and 0.1 atmosphere, 40 liters of CO per hour per 10 grams of Fe.

The data from table 10 summarizing the results of experiments on the formation of carbidic carbon as a function of the carburization time are graphically shown in figure 6. Comparison of figures 4 and 6 shows that the end of carbide formation could also be seen from the shape of the free-carbon deposition curve. Once the carbide content reached a constant value the free carbon curve became linear.[6]

The effect of varying the carbon monoxide pressure was studied (table 11); increase in pressure resulted in a decrease of carbidic carbon, in contrast to results obtained with free carbon.

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[6] Editor's note. The end of carbide formation did not coincide exactly with the beginning of the constant rate of free-carbon deposition. Dr. Pichler believed that this discrepancy was probably due to slight differences between the two samples used for these experiments.

TABLE 11.—*Effect of pressure on formation of carbidic carbon from carbon monoxide*

[Rate of flow, 4 liters CO per hour per 10 grams Fe; temperature, 325°C.; carburization time, 25 hours]

Catalyst No.	CO pressure (atmospheres)	Carbidic carbon (gram)	H_2 (cc.)
1	0.1	0.45	2,220
	1.0	.34	1,570
	15.0	.10	540
2	.1	.50	2,330
	15.0	.33	1,520

In order partly to characterize the hydrocarbons produced by acid decomposition of iron carbides, their carbon number was determined as follows: A sample of the gaseous hydrocarbon evolved was burned and the carbon dioxide measured. The volume of carbon dioxide produced by combustion of the saturated hydrocarbons was subtracted from this value. The difference, corresponding to the volume of carbon dioxide obtained by combustion of the unsaturated hydrocarbons, was divided by the volume of unsaturated hydrocarbons. The carbon number of the saturated hydrocarbons was determined similarly. Table 12 lists the carbon numbers obtained for different carburization times.

TABLE 12.—*Effect of carburization time on carbon number*

Carburization time (hours)	Carbon No.	
	Saturated hydrocarbons	Unsaturated hydrocarbons
1.25	2.2	4.7
2.50	1.7	4.5
10	1.9	4.3
25	1.7	—

The high carbon number for unsaturated hydrocarbons in table 12 indicated the probable presence of C_5 hydrocarbons. On the other hand, the carbon number of the saturated hydrocarbons was very low. There was apparently no correlation between carburization time and carbon number.

OXYGEN CONTENT OF CARBURIZED CATALYSTS

The next step in establishing the composition of carburized iron catalysts was to determine their oxygen content. The following solid phases can exist under carburization conditions: Fe_3O_4, Fe, Fe_3C, and C. In the presence of a carbon monoxide–carbon dioxide mixture the following reactions take place:

$$Fe_3O_4 + 4CO \rightleftarrows 3Fe + 4CO_2,$$
$$3Fe + 2CO \rightleftarrows Fe_3C + CO_2,$$
$$2CO \rightleftarrows CO_2 + C.$$

The volume of carbon dioxide present in the tail gas from carburization with carbon monoxide was determined. Table 13 shows the carbon dioxide to carbon monoxide ratios of the tail gas at different intervals.

TABLE 13.—*CO_2 : CO ratio in tail gas during carburization*

[Rate of flow, 4 liters CO per hour; temperature, 325°C.; pressure, 0.1 atmosphere]

Time (minutes)	CO_2 : CO (volume ratio)	Time (minutes)	CO_2 : CO (volume ratio)
25	1.92	365	0.458
55	.770	425	.348
75	.794	605	.144
115	.809	1,380	.073
165	.794	1,500	.068
305	.561		

After about 24 hours, the composition of the tail gas attained a constant ratio of carbon dioxide to carbon monoxide of 0.069 : 1. The equilibrium diagram for the system iron–carbon–oxygen shows that only Fe and Fe_3C are stable at 325°C. and in the presence of a gas of this composition.

The carbon dioxide : carbon monoxide ratio of the tail gas corresponded to the gas composition existing at the end of a 30-centimeter layer of catalyst. The carbon dioxide content decreased steadily toward the gas inlet so that these portions of the catalyst remained within the range in which free iron and iron carbide are stable.

The changes in carbon dioxide content of the carburization end gas are represented graphically in figure 7. The carbon dioxide content increased rapidly during the first 45 minutes and then decreased just as quickly to a value of 38.5 percent. This first rapid formation of carbon dioxide corresponded to the reduction of Fe_2O_3 to Fe_3O_4. It then increased again and reached a second maximum of 40.5 percent after carburization for 2 hours. This portion of the curve corresponds to the reduction of Fe_3O_4 to Fe and to the beginning of carbide formation (for a higher rate of flow, carbide formation had already started after a few minutes). Once reduction and carbide formation were completed, carbon dioxide formation reached a constant rate determined solely by the decomposition of carbon monoxide into carbon dioxide and free carbon.

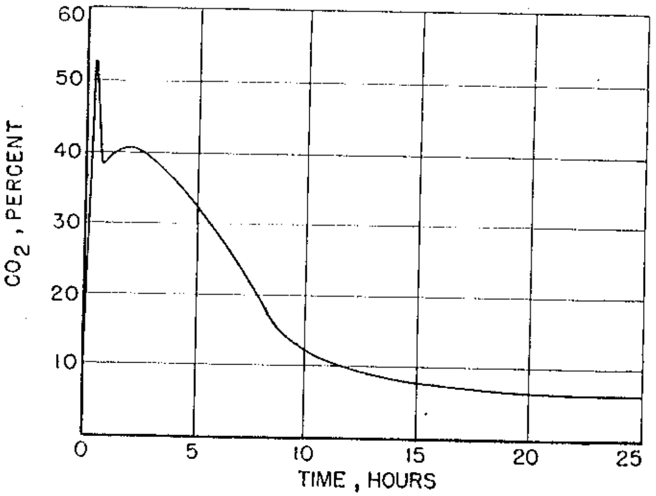

FIGURE 7.—Carbon dioxide content of tail gas during carburization of an alkalized-iron catalyst at 325° C. and 0.1 atmosphere, 4 liters of CO per hour.

In determining the oxygen content of the catalyst, the following procedure was used: The catalyst was dried at 250°C. in a current of oxygen-free nitrogen by placing the catalyst container in a hard glass tube and heating it in an electric oven. After drying, the catalyst was reduced at 600°C. with hydrogen that had been freed of oxygen by passage over a copper spiral at 400°C. and had been dried in a series of columns packed with calcium chloride. Water formed by reduction of iron oxides was absorbed in a U-tube filled with calcium chloride and weighed. To determine its iron content, the reduced catalyst was treated with hydrochloric acid until evolution of hydrogen had ceased. The iron content of the filtrate was determined by titration.

To check the procedure, the oxygen content of an uncarburized iron oxide sample was determined. Analysis showed 0.3870 gram of iron and 0.1648 gram of oxygen. Thus 100 grams of iron was present for 42.6 grams of oxygen; and in ferric oxide there is 100 grams of iron for 43.0 grams of oxygen. This determination also proved that the dried, precipitated catalyst contained almost pure trivalent iron, present as ferric oxide or its hydrates.

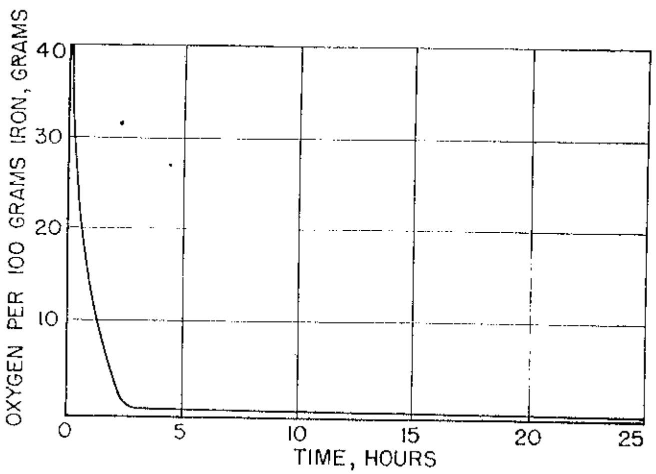

FIGURE 8.—Oxygen content of an alkalized-iron catalyst during carburization at 325° C. and 0.1 atmosphere, 40 liters of CO per hour.

The oxygen content was determined at intervals during carburization, to follow the course of catalyst reduction.

The low oxygen content of the catalyst after prolonged carburization (table 14 and fig. 8) indicates that only 1 percent of the iron was still present as magnetite after carburization was completed and that reduction was virtually complete after 2.5

hours of carburization. This is also shown by the fact that the carbidic carbon reached a maximum value after the same length of time (table 10 and fig. 6).

TABLE 14.—*Oxygen content of an iron catalyst as a function of carburization time*

[Rate of flow, 40 liters CO per hour; temperature, 325°C.; pressure, 0.1 atmosphere]

Carburization time (minutes)	Oxygen content (grams per 100 grams iron)	Carburization time (minutes)	Oxygen content (grams per 100 grams iron)
0	42.60	150	.59
9	30.95	600	.43
37	18.95	1,500	.39

The influence of the rate of flow of carbon monoxide on the reduction of iron catalysts was studied by a method analogous to that used in determining carbidic and free carbon. One hundred liters of carbon monoxide was passed over the catalyst at two rates of flow (table 15). For the same amount of gas, the higher rate of flow effected more extensive reduction. High rates of flow are thus necessary to prepare a catalyst virtually free of oxygen.[7]

TABLE 15.—*Oxygen content of an iron catalyst as a function of flow rate of carbon monoxide*

[CO pressure, 0.1 atmosphere; temperature, 325°C.]

Rate of flow (liters CO per hour)	Carburization time (hours)	Oxygen content (grams per 100 grams iron)
40	2.5	0.59
4	25	1.26

HYDROGEN REDUCTION OF A CARBURIZED-IRON CATALYST

Exhaustive reduction with hydrogen at atmospheric pressure was used to determine the composition of the iron carbides formed. This method has been used often to determine carbide in carburized iron. It is based on the fact that carbidic carbon can be hydrogenated to methane at lower temperatures than can free carbon. According to Bahr and Jessen,[8] carbidic carbon obtained during the carburization of iron oxides can be hydrogenated at temperatures as low as 280°C. These authors found that 260° to 265°C. was best for hydrogenation of carbidic carbon, since the results they obtained at higher temperatures were scattered. Any hydrogenation of free carbon seemed unlikely at this temperature, while the removal of carbidic carbon proceeds sufficiently fast.

An alkali-promoted catalyst was treated with a stream of carbon monoxide (40 liters per hour) for 8 hours in the aluminum block oven to ensure complete carbide formation. Then 0.8 liter per hour of electrolytic hydrogen was passed over the catalyst at 263°C. and atmospheric pressure. Hydrogen and methane were collected in a gas holder. Hydrogenation was interrupted every 24 hours and methane determined by passing the hydrogen–methane mixture over copper oxide at 280°C. until oxidation of the hydrogen was virtually complete. The residual gas was swept by carbon dioxide through a three-way stopcock into a second gas holder. The methane content was determined by combustion after removal of carbon dioxide.

This procedure not only gave more accurate results because of the concentration of methane, but permitted the determination of the rate of hydrogenation, as shown in figure 9. The experiment was interrupted after 408 hours, when 0.939 gram of carbon was reduced with hydrogen. The decarburized catalyst was dissolved with hydrochloric acid. The resulting gas contained no hydrocarbons, a proof of the complete hydrogenation of the carbidic carbon. The catalyst contained 10.060 grams of iron and 0.048 gram of oxygen. Assuming the oxide to be magnetite, 9.934 grams of iron combined with 0.939 gram of carbon—that is, a carbide containing 8.64 percent of carbon. This carbon content is lower than that of a carbide of formula Fe_2C (9.71 percent carbon), but appreciably higher than that of Fe_3C (6.68 percent carbon). Figure 9 shows the carbon content of Fe_2C and Fe_3C as dashed lines. The amount of carbidic carbon obtained by hydrogen reduction is indicated on the ordinate axis and the hydrogenation time on the abscissa. (With 0.9 liter of hydrogen per hour, the rate of decarburization attained its maximum value only after about 90 hours.) The horizontal portion of the decarburization curve lies between the two dashed lines; that is, the carbide seems to be a mixture of cementite and an iron carbide with a higher content of carbon.

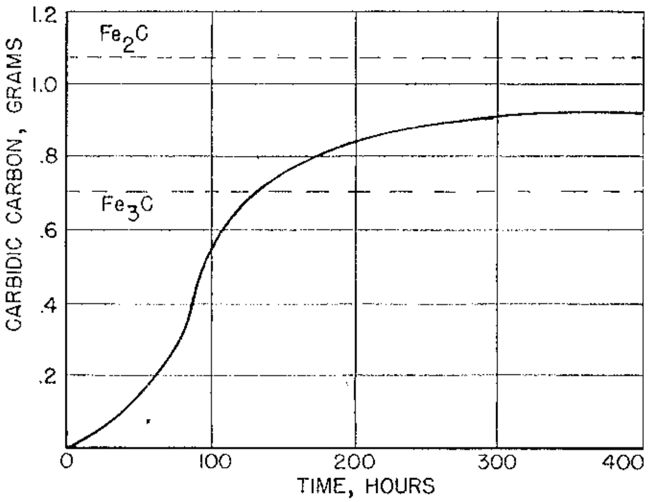

FIGURE 9.—Hydrogenation of 10.060 grams of a carburized, alkali-promoted (0.25 percent K_2CO_3) catalyst at 263° C. and atmospheric pressure, 0.8 liter of hydrogen per hour.

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[7] According to Hofmann, a product from which all oxygen has been eliminated may be obtained by using high temperatures and high rates of flow.

[8] Bahr, H. A., and Jessen, V., work cited in footnote 47.

Acid decomposition of the catalyst, after removal of carbidic carbon, gave the following result:

Carbidic carbon (gram)	Free carbon (grams)	Hydrogen (cc.)	Iron (grams)
0	1.4	3,800	10

The large amount of hydrogen is explained by the absence of carbidic carbon, which would have combined with a considerable amount of hydrogen upon reduction. Acid decomposition (without prior reduction) of a catalyst which had been carburized under the same conditions yielded 1.6 to 1.8 grams of free carbon per 10 grams of iron (see table 6), while only 1.4 grams of free carbon was present after hydrogenation.

SUMMARY

Carburization during pretreatment of iron catalysts was studied by means of acid decomposition. The formation of free carbon was favored by a higher temperature, higher carbon monoxide pressure, and higher catalytic activity. Carbide formation stopped after a relatively short period of carburization, as indicated by the low oxygen content of the catalyst. Exhaustive carbide formation occurred only at low carbon monoxide pressures within a narrow temperature range around an optimum value of 325°C. Oxidation-reduction equilibria between gas and solid phase were not attained.

A carburized-iron catalyst, reduced with hydrogen at atmospheric pressure and 263°C. until no more methane was formed, appeared to contain a carbide whose composition corresponded to the formula, $Fe_{2.28}C$. Acid decomposition yielded only half that value for carbidic carbon and produced hydrogen in excess of the calculated amount.

EFFECT OF CARBURIZATION OF IRON CATALYSTS UPON THEIR ACTIVITY DURING MEDIUM-PRESSURE SYNTHESIS

EFFECT OF CARBIDIC CARBON ON ACTIVITY OF IRON CATALYSTS

It was stated in the introduction that the carbides formed by the action of carbon monoxide on the metals of the iron group may be considered probable intermediates in the gasoline synthesis. After the conditions were examined under which such carbides are formed from iron catalysts, their behavior during synthesis was investigated. Deposition of carbon during this process was studied concomitantly. Carburized, alkalized iron catalysts were used. After operation under various conditions they were decomposed in the apparatus shown in figure 3. The deposit of high-boiling paraffins formed on the catalysts during synthesis was removed by exhaustive extraction with toluene. The extracted catalysts were washed with methanol to remove toluene, and then with water to remove methanol.

To determine whether any changes occur in the catalysts during extraction and washing, a used sample was decomposed with acid and compared with a second one which was extracted with toluene before acid decomposition. The results, as given in table 16, show that the effect of toluene extraction may be considered negligible.

TABLE 16.—*Effect of toluene extraction on analysis of a used iron catalyst*

[Analysis by acid decomposition]

Sample	Carbidic carbon, (gram)	Free carbon, (grams)	Hydrogen, (cc.)
Not extracted with toluene	0.430	5.75	2,104
Extracted with toluene for 16 hours	.426	5.85	1,945

In the first part of this paper it was shown that the composition of the catalyst (that is, the relative amounts of chemically combined carbon, free carbon, and magnetite) depends largely upon the carburization procedure. Table 17 shows the advantage of carburization at low pressures. Moreover, a smaller amount of free carbon was formed at low carbon monoxide pressures.

TABLE 17.—*Durability of catalyst as a function of carburization pressure*

CO pressure during pretreatment	CO conversion
2 mm. Hg	Maximum yield still obtained after 3 weeks
15 atm.	Completely inactive after 3 weeks

The experimental results of table 9 show the marked effect of temperature on carburization. Table 18 shows the relative durability of iron catalysts carburized at temperatures ranging from 255° to 450°C.

TABLE 18.—*Effect of carbiding temperature on the durability in the synthesis of an iron catalyst (copper-free)*

[Synthesis conditions: Temperature, 235°C.; pressure, 15 atmospheres; space velocity, 4 liters synthesis gas (NTP) per 10 grams Fe per hour]

Experiment No.	Carbiding temperature [a] (°C.)	Carbidic carbon content (grams per 100 grams Fe)	Period during which contraction was over 50% (days) [b]	Experiment No.	Carbiding temperature [a] (°C.)	Carbidic carbon content (grams per 100 grams Fe)	Period during which contraction was over 50% (days) [b]
1	255	0.6	2	5	325	4.6	365
2	285	3.8	10	6	355	4.2	20
3	305	4.2	24	7	450	.1	([c])
4	315	4.4	50				

[a] Carburization conditions: Pressure, 0.1 atmosphere; space velocity, 4 liters CO per 10 grams Fe per hour; time, 24 hours.

[b] This contraction represents the decrease in the volume of synthesis gas ($3CO + 2H_2$) resulting from the conversion of carbon monoxide and hydrogen into hydrocarbons. It was determined indirectly from the amount of nitrogen (which does not participate in the reaction) present before and after passage through the reactor. For almost complete carbon monoxide conversion, the maximum contraction obtained with iron catalysts was about 55 percent.

[c] Contraction never over 10 percent, heavy carbon deposition.

It will be seen from table 18 that preparations carbided at 255° and 450°C. were entirely unsuitable as catalysts. In the former case the initial contraction exceeded 50 percent, but decreased after 2 days; in the latter the catalyst was almost inactive. Both catalysts contained only small amounts of carbidic carbon as determined by acid decomposition. All of the other catalysts showed good initial activity, but their durability varied considerably. The catalyst that contained the largest quantity of carbidic carbon had the longest life.

To study the reasons for variations in catalyst activity, active catalysts (carburized as in experiment 5, table 18) were acid-treated after being operated for various periods. Table 19 presents data for five experiments in which conversion was still at a maximum after 7, 21, and 112 days.

TABLE 19.—*Acid decomposition of catalysts active in synthesis*

Experiment No.	Operating time (days)	Contraction (percent)	Carbidic carbon (percent)	H_2 (liters/100 grams Fe)	O_2 (grams/100 grams Fe)
1	0	----	5.04	23.2	0.59
	7	52	2.34	10.5	----
2	0	----	1.94	21.9	----
	7	53	3.53	14.7	----
3	0	----	4.14	17.9	----
	7	50	3.78	11.1	----
4	0	----	5.04	23.3	----
	21	52	3.01	14.4	----
5	0	----	4.23	15.5	----
	112	50	3.76	14.2	1.6

In each instance, catalyst samples were analyzed by acid decomposition at the beginning and at the end of the synthesis tests. All experiments showed that the amount of carbidic carbon of the catalysts as determined by acid decomposition decreased markedly after a few days of synthesis. After these few days, however, the value obtained for carbidic carbon showed no further decrease, even after months of operation. The catalyst that contained the highest amount of carbidic carbon before use in synthesis—that is, 5.04 grams per 100 grams of iron—reached the lowest value after 7 days (2.34 grams, experiment 1). The volume of hydrogen evolved during acid decomposition also decreased during the first days of operation and then remained approximately constant over a long period. The oxygen content of carburized catalysts, before they were used in synthesis, was discussed in the section on carburization. In experiment 1 it was 0.59 gram per 100 grams of iron. After 112 days of operation (experiment 5) it had increased to 1.6 grams per 100 grams of iron. The catalyst apparently suffered some oxidation during synthesis.

Table 20 shows the data obtained by acid decomposition of catalysts whose activity had decreased for various reasons. In all four experiments, diminished activity was associated with a decrease in the quantity of carbidic carbon and an increase in the oxygen content. When the synthesis temperature was too high the carbon dioxide, which amounted to 50 percent or more of the tail gas, appeared to oxidize the catalyst. In experiment 2, in which the synthesis gas was rich in hydrogen and the operating temperature was unusually low, the water formed in the reaction apparently was responsible for partial oxidation of the catalyst after a long operating period. A series of experiments with other catalysts with diminished activity showed a similar decrease in carbidic carbon to 1 gram or less per 100 grams of iron. A marked decrease in the volume of hydrogen evolved during acid decomposition was observed simultaneously. These results will be discussed further in the section on magnetic analysis.

TABLE 20.—*Acid decomposition of catalysts with diminished activity*
[Pretreatment: Temperature, 325°C.; CO pressure, 0.1 atmosphere]

Experiment No.	Synthesis conditions	Contraction (percent)	Carbidic carbon (grams/100 grams Fe)	H_2 (liters/100 grams Fe)	O_2 (grams/100 grams Fe)
1	548 operating days, S.G.[a] rich in CO, 15 atm., temp. progressively raised from 235° to 285°C. to maintain constant contraction.	50	2.00	3.9	13.8
2	150 operating days, S.G.[a] rich in H_2, 15 atm., temp. 210°C.	35	1.00	4.2	15.7
3	21 operating days, S.G.[a] rich in CO, 15 atm., temp. 235°C., with eventual overheating to 400°C.	40	.16	----	19.6
4	Normal catalytic activity decreased by prolonged overheating above 300°C.	40	.54	----	28.2

[a] S.G. = synthesis gas.

FORMATION OF FREE CARBON ON IRON CATALYSTS

The formation of free carbon on active unpromoted iron catalysts during the hydrocarbon synthesis has been a source of operating difficulties. Where horizontal reaction tubes were used in such a way that the catalyst did not occupy the entire volume of the tube, the synthesis proceeded for months and even years without interruption. When the catalyst was contained in vertical reaction tubes so as to leave relatively little void space, an increase in the internal resistance of the catalyst was observed, resulting in obstruction of the reaction tube after operating intervals which depended upon synthesis conditions.

Table 21 shows the amounts of free carbon (as determined by acid decomposition of the catalyst) formed after various intervals of synthesis.

In all the experiments, the quantity of free carbon increased with operating time. The increase in free carbon in experiment 3 may be caused to some extent by the increased temperature necessary for maintaining conversion. Contraction remained high in spite of dilution of the catalyst with embedded carbon. In experiment 4, only 40 percent contraction was obtained during 11 operating weeks. Very little free carbon was formed owing to the low activity of the catalyst.