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IRON CATALYSTS FOR MIDDLE-PRESSURE SYNTHESIS

PREFACE BY FRANZ FISCHER^{a/} (24)

On May 23 of this year, a lecture was given for the same body of men, and our Dr. Koch spoke on the production of special antiknock gasolines obtained from Kogasin. At that time I announced the coming lecture on iron catalysts for the middle-pressure synthesis which has for its purpose to inform our body of men about the progress which has been made on this work at the Institute.

Hans Tropsch and I have been concerned for more than 50 years with the production of gasoline from CO and H₂ by using iron catalysts. At that time we examined the synthetic products which were obtained on alkalized iron shavings at pressures of 100 atmospheres and above and at relatively high temperatures somewhere in the neighborhood of 400°C. Contrary to statements in the literature, we made the fundamental observation that, under those conditions, no hydrocarbons were formed; however, only oxygen-containing products appeared. They consisted of alcohols, aldehydes, ketones, and acids. We identified a great number of the individual compounds, and we termed the whole product Synthol. In the course of our investigations, we discovered that iron catalysts tend to give more hydrocarbons when the total pressure decreased. After we finally developed more active catalysts that would permit working at ordinary pressures and lower temperatures, it was demonstrated that hydrocarbons were obtained almost exclusively. The three metals which we have recognized as being the active ingredients of the catalysts in the course of our studies were iron, nickel, and cobalt. However, cobalt gave the best results. When I came to the decision many years later to investigate the Kogasin synthesis in the region between ordinary pressures (and low temperatures) and the high pressure region in which synthol forms, the work on the middle-pressure synthesis using cobalt catalysts was started in Pichler's division. To our great surprise, we found at that time that with respect to the products no gradual change occurred from Kogasin to Synthol. Instead, we found that between 4 and 20 atmospheres pressure and at low temperatures using active catalysts, a mixed yield of solid paraffins could be obtained. At the same time, a high yield of total hydrocarbons resulted and the catalyst had its maximum life. It was only natural to try to apply the experiences gained with cobalt to nickel and iron. Nickel, however, had to be discounted because at the higher pressure and the higher temperature necessary for the synthesis it was removed from the reaction vessel in the form of nickel carbonyl. In contrast to nickel, however, iron could be used. In the case of iron, also, a higher yield resulted, and the life of the catalyst was prolonged. About that, Dr. Pichler will report himself.

It was obvious that further development of the Kogasin synthesis with iron catalysts was necessary if yields and catalyst durability were to compare with cobalt catalysts.

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This demand was not only met but surpassed. At least the same yields can be obtained as with cobalt catalysts. The life of the iron catalysts is many times that of cobalt catalysts. A life of 1 year working at highest capacity may easily be obtained with iron catalysts, and it is not even necessary to regenerate them, because of their low cost. The iron catalysts work at somewhat higher temperatures than the cobalt catalysts and require stronger pressure vessels and thicker wall thicknesses of the apparatus than are necessary for the middle-pressure synthesis with cobalt. However, we have to take into account that the steam produced has a higher pressure and greater availability. The starting gas for the iron catalysts has to contain more CO than the starting gas for cobalt catalysts, but such a gas is just as easily produced as 2:1 gas. The iron catalysts seem to have also the ability, at least to a small degree, to produce higher hydrocarbons, not only for mixtures of CO + H₂ but also for mixtures of CO₂ + H₂.

Approximately 3 years ago, I discussed the question of iron catalysts briefly in your circle. Today, however, Dr. Fichler will speak in detail on the whole problem and especially will point out the progress which has been made in the last three years. Let me introduce Dr. Fichler.

LECTURE-DISCUSSION BY H. FICHLER

INTRODUCTION

After we had recognized that the middle-pressure synthesis with cobalt catalysts had improved the yield of hydrocarbons and the life of the catalysts as compared with the normal-pressure synthesis, the question was asked whether the cobalt, which is hard to get in Germany, could be replaced by iron and still retain all the good features which we obtain with the cobalt. Ever since Franz Fischer developed his synthesis of hydrocarbons we have tried in our Institute to find catalysts that could do the work as well as cobalt and thorium and would be cheaper than those two metals. In 1923, Fischer and Tropsch passed water gas over alkalinized iron shavings at pressures of around 100 atmospheres and temperatures of 350°-450°C. They observed the formation of oxygen-containing organic compounds which they termed Synthol. Similar experiments of the Badische-Anilin- und Sodafabrik, which date back to 1913, where they used similar pressures and temperatures, led to the synthesis of methanol in 1925. Fischer and Zerbe (27) also demonstrated, in 1923, that alkalinized iron shavings used as catalysts at pressures below 100 atmospheres favored the formation of hydrocarbons and suppressed that of oxygen-containing compounds.

(28)
In 1926, Fischer and Tropsch reported in their first publication on the petroleum synthesis that liquid hydrocarbons could be produced with iron catalysts from CO and H₂ at temperatures of around 300°C. and above. On the basis of those experiments, we have tried in the past years to change the composition of the iron catalysts so that the activity is increased and the reaction temperature for the synthesis lowered, improving the yield of liquid hydrocarbons. In 1928, we succeeded in obtaining 30 to 40 grams of gasoline and oil per cubic meter of water gas. The temperatures could be lowered to 240° to 250°C. The life of the catalysts, however, was only a few days.

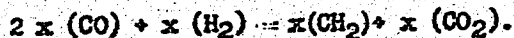
Fischer and Tropsch (30) tried in 1927 to convert water gas at 10 to 15 atmospheres and at 250° to 280°C. The iron-copper catalysts were obtained by roasting the nitrates, and they were employed as such with water gas. The products

obtained consisted of watery and oily substances in the ratio of 3:2 and 1:1. The authors reported at that time that the results of their pressure experiments were not as good as those of the atmospheric experiments. Still, in 1934, Fischer (31) reported in the lecture on the gasoline synthesis that, at atmospheric pressure and with the use of an iron catalyst, only 30 to 35 grams (per cubic meter of mixed gas) were obtained. (This corresponds to 40 to 45 grams per normal cubic meter of inert-free CO-H₂ mixture.) Fischer added at that time that the yield cited above decreased by 20 percent within 8 days.

Fischer and Meyer (32) attempted in 1934 to 1936 to improve the activity of the iron catalysts, and thus raise the yields of liquid hydrocarbons. By using precipitated iron-copper catalysts at atmospheric pressure, 50 to 60 grams per cubic meter of gas were obtained with a maximum lifetime of the catalyst of 4 to 6 weeks.

Fischer and Ackermann (33) in 1936 obtained 55 grams of liquid hydrocarbons per cubic meter of mixed gas when they worked with a carefully compounded, precipitated iron catalyst which did not contain copper. This yield, however, diminished after a few days and in the third week was only 40 grams.

At that time they used a synthesis gas of composition 1CO + 2H₂, although it had been recognized that iron catalysts require a different gas and that with iron catalysts the CO conversion proceeds almost entirely according to



However, when a synthesis gas of 2CO + 1H₂ was used, the CO was converted only partly, and catalyst activity decreased quite rapidly.

Until that time, the work with iron catalysts gave maximum yields only about half as high as the yields from the cobalt catalysts used on the technical scale and for that reason an economic application of the synthesis with iron catalysts was not possible.

The task that confronted us in 1936 was therefore to double the yield of liquid hydrocarbons and to improve the life of the iron catalysts by a multiple. It was furthermore desirable to find a way to lower the reaction temperature and finally to find a possible way to control the nature of the products of the reaction.

We have succeeded in compounding iron catalysts that will convert virtually all of the CO-H₂ mixture at only slightly raised pressures over very long periods. Depending on working conditions, varying amounts of paraffins, liquid hydrocarbons, and gasol hydrocarbons may be obtained. The total yields obtained now in the iron middle-pressure synthesis are of the same order of magnitude as those from the cobalt middle-pressure synthesis. Therefore, we were justified in considering the substitution of iron for cobalt. At the end of 1937 Fischer had already reported to us on the favorable course which our work on the iron catalysts and the synthesis using iron catalysts seemed to take. At that time, it was decided to acquaint other interested parties with our new developments in the gasoline synthesis to permit them to check our results in their laboratories. Our researches have been continued, and a lot of work has especially been done in the last year. The essential parts of this work were patented under the name "Studien und Verwertungs-Gesellschaft. m.b.H."

The applications going back to 1937 have been made under Ruhrchemie A.G. At the same time a number of companies in foreign countries have been used as patent assignees. Those developments are responsible for the fact that some of the things which I am going to report today will not be entirely new to you. However, since the development of the iron catalysts is so important, it seems desirable to have a discussion of the entire problem with you.

THE CATALYST

Precipitation of Catalyst

As starting material for the production of iron catalysts, generally iron-salt solutions were used. The iron-salt solutions were made by dissolving technical iron in nitric acid. Most of the time the iron was precipitated with soda ash or with ammonia. The precipitate was filtered hot, washed, perhaps alkalinized, and dried. After having been dried properly, the catalysts appeared black-brown or black. Although it was desired to give rigidity to the catalysts, it was believed that pelleting would affect the activity. Therefore, certain precautions must be taken during pelleting to prevent this. Pelleting will not be discussed here.

I shall limit myself to the discussion of pure iron catalysts only or perhaps to catalysts that contain small additions of alkali. These are the catalysts that have the greatest prospect of being used on a technical scale. In general, we have found that catalysts prepared by precipitation of ferric iron with sodium carbonate solutions are superior to those obtained by precipitation of ferrous iron with sodium carbonate solution. These ferric catalysts have been used for most of the experiments, and we called them normal iron catalysts.

In their production two points had to be observed carefully: First, it was necessary to preneutralize the iron solution in the cold, since without preneutralization, on application of heat, or on standing for longer periods, insoluble salts precipitated out of the solution, which considerably influenced the reproducibility of a good catalyst. Secondly, it was important to bring the iron precipitate to a boil before being filtered. This improves the activity and increases the life of the catalyst.

Pretreatment of Catalyst

The freshly precipitated and dried iron precipitate is entirely inactive as far as conversion of CO and H₂ to hydrocarbons is concerned. In this respect, it is comparable directly to the nonreduced cobalt catalyst, which is also inactive. However, cobalt may be activated by treating it with hydrogen at 360°C. The hydrogen reduces the cobalt compounds to the metallic state, and in this state the cobalt catalyst can form hydrocarbons at low temperatures. However, an iron catalyst may not be activated by pretreatment with hydrogen. For example, the trivalent iron is converted into Fe₃O₄ when pretreated by hydrogen at 300° to 400°C. This Fe₃O₄ cannot catalyze the reaction between CO and H₂. However, if the iron catalyst is pretreated under certain conditions by CO, the catalyst may be activated sufficiently to catalyze the synthesis. (Depending on the temperature, pretreatment with CO causes more or less formation of carbides, which cause also a reduction and a loosening of the catalyst structure, because carbon is deposited inside of the catalyst mass.) The pretreatment with CO or CO-containing gases is referred to in the following as "Formierung" (induction).

Induction with Mixtures of CO and H₂ During Synthesis

It is well to distinguish here between two different ways of carrying through the induction. There is an induction which takes place under conditions of the synthesis, and there is another induction which may take place under special conditions before the synthesis is begun.

Experiments at atmospheric pressure.—Once more, let us recall the working conditions under atmospheric pressure. Figure 11 shows the variation in percent contraction (as a measure of the conversion) with time when working with a hydrogen-rich synthesis gas and a CO-rich synthesis gas. If the precipitated iron catalysts are permitted to work on mixed gas of composition $1\text{CO} + 2\text{H}_2$, under atmospheric pressure, then at a temperature of 235°C., an initial gas rate of 4 liters of mixed gas per hour per 10 grams of iron, the contraction increases to 30 percent within 3 to 4 days. This time, during which the catalyst gradually acquires its activity by the action of the synthesis gas, corresponds to the induction time (Fig. 1, curve 1). For approximately 3 to 4 weeks, this catalyst inducted in the manner just described will continue to give 30 percent of maximum gas contraction with an average yield of 50 grams of liquid and solid hydrocarbons per cubic meter of synthesis gas. The CO of the mixed gas has almost all been converted, whereas a large excess of hydrogen remains in the end gas.

Let us consider the case where we permit the iron catalyst to act on a CO-H₂ mixture which more nearly corresponds to the ratio in which the CO and H₂ are used up during the reaction. How are the relationships then? Curves 2 to 4, Fig. 1, show the results. It is seen from these curves that no improvement results; indeed, the conversion is impaired. On using a CO-rich gas ($3\text{CO} + 2\text{H}_2$) the contraction reached a value of 31 percent after operating for 3 days at 235°C. (curve 2); when the temperature was 245°C., the contraction obtained was 38 percent after 1 day's operation (curve 3). When the operating temperature was 255°C., the contraction was only 33 percent after 1 day's operation (curve 4). In all three cases, it was observed that the conversion dropped off very rapidly after having reached the peak. The catalyst was therefore being damaged by CO-rich gas at atmospheric pressure.

CO-rich gas and high pressure.—Table 39 shows the result of a run during which a normal iron catalyst was operated for 5 months without interruption in the presence of CO-rich synthesis gas ($3\text{CO} + 2\text{H}_2$) at 15 atmospheres. The catalyst was given no previous induction. The gas velocity was 4 liters of synthesis gas referred to 1 atmosphere pressure per 10 grams of iron catalyst.

Table 39.—Induction and synthesis at a pressure of 15 atmospheres

Operation, days	Temperature, °C.	Contraction, percent	Operation, days	Temperature, °C.	Contraction, percent
1	245	4	69	268	37
4	245	10	75	280	47
5	250	13	90	280	49
7	253	17	98	283	44
11	260	24	106	285	43
13	270	24	130	288	43
14	275	37	140	292	44
28	280	36	150	298	47
60	290	50			

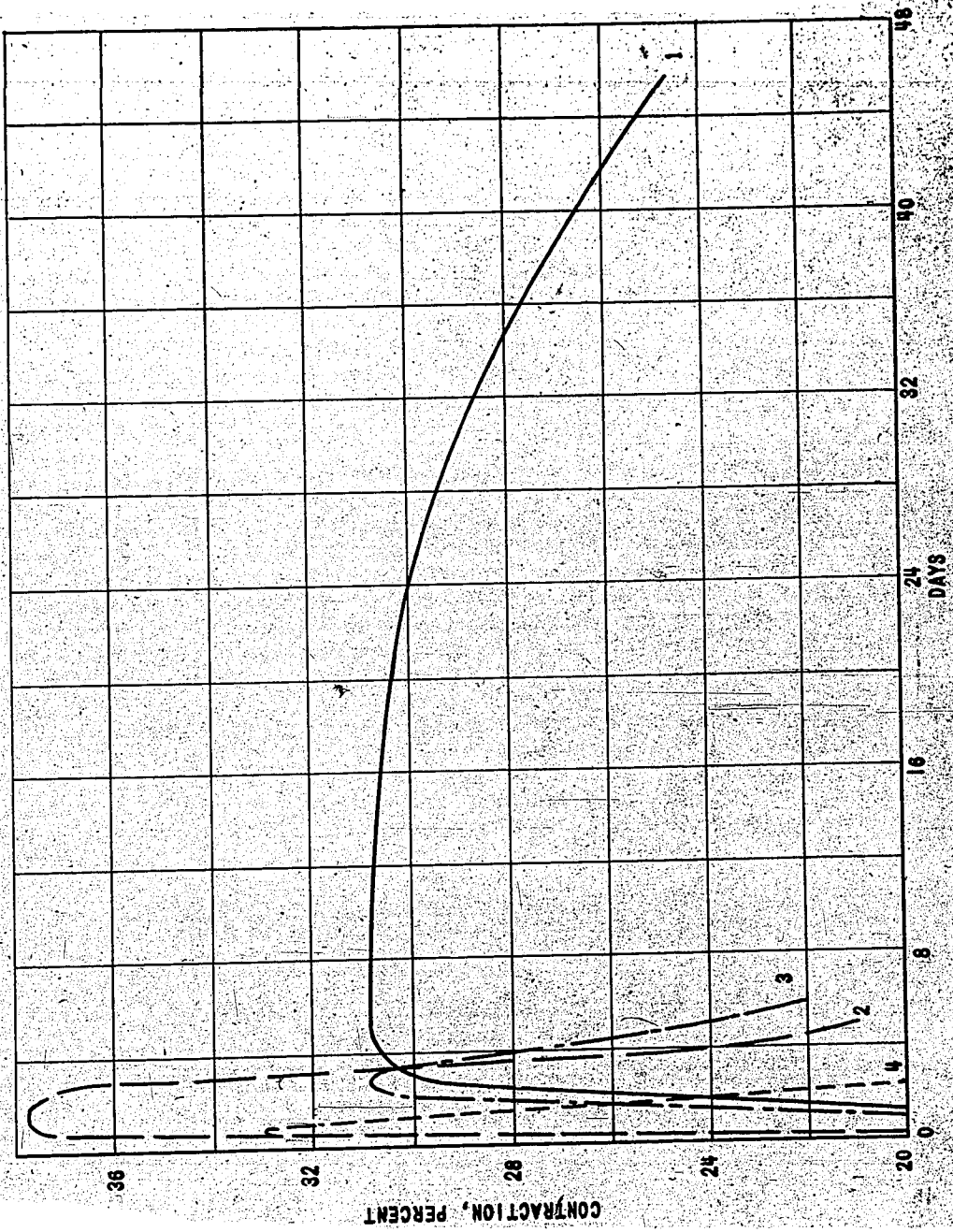


Figure 21.- Experiments at atmospheric pressure (decrease of contracton with duration of operation when various CO-H₂ mixtures are employed)

At 245°C. and after 1 day of operation, the contraction was 4 percent, and after 4 days the contraction was 10 percent, as compared to 30 to 35 percent for the same time of operation at 1 atmosphere pressure. The temperature was gradually raised, and the increase in the contraction was observed. On the 11th day, 24-percent contraction was observed at 260°C. An increase in temperature to 270°C. did not, at first, cause the yield to rise. At 270°C., 37 percent was observed, and at 280°C., 36 percent. Only when 290°C. was reached did the contraction go up to 50 percent, which corresponded to a complete conversion of the CO to hydrocarbons and CO₂. Next we tried to determine whether this conversion (50 percent) could be maintained if the temperature were lowered. At 268°C. the contraction decreased to 37 percent. At 280°C., however, and in the third month of operation, a better degree of conversion was obtained than after 1 month. Meanwhile, a slow induction of the catalyst had taken place. During the 4th and 5th months of operation the temperature had been again increased to keep the contraction between 40 and 50 percent. After 5 months' operation, it was 300°C.

During the third month, an operation was carried out at 280°C. which gave a yield of 3 grams of solid paraffins per normal cubic meter of gas, 93 grams of liquid hydrocarbons, and 32 grams of gasol hydrocarbons, all referred to 1 cubic meter of ideal gas.

As compared to operation under atmospheric pressure, induction of the catalyst did not proceed so well for the runs under pressure, and if the catalyst was inducted during the synthesis under pressure, the yield at low temperatures was very low. On the other hand, working under 15 atmospheres pressure and using a CO-rich synthesis gas, the temperature could be raised to 280° to 290°C. without decreasing the activity of the catalyst as rapidly as it would decrease if the pressure of the operation were atmospheric. For a large-scale operation, however, the temperatures appeared to be still too high and the life of the catalyst was still too brief.

Induction of Catalyst by a Separate Process Preceding Actual Synthesis

The attempt was made to find out whether an increase in activity could be obtained by carrying through the induction in a step separate from the synthesis. The optimum conditions were to be found for both induction and synthesis separately.

Induction at ordinary pressure and synthesis at higher pressure.—Table 40 gives the result of an experiment with induction at atmospheric pressure and 245°C. using mixed gas.

Table 40.—Induction at 1 atmosphere pressure and synthesis at 15 atmospheres

Operation, days	Pressure, atmospheres	Temperature, °C.	Contraction, percent
1	1	245	15
2	1	245	22
3	1	245	28
4	1	245	30
5	1	245	31
—	15	245	55
6	15	245	48
8	15	250	53
9	15	250	49

14	15	252	46
24	15	256	51
50	15	255	51
100	15	265	55

When, after 5 days of operation, the contraction had reached a maximum value of 31 percent, we shifted to CO-rich synthesis gas at 15 atmospheres pressure, the contraction increased immediately from 31 to 55 percent. To obtain the highest yields and correspondingly the highest values of contraction (approximately 50 percent), the temperature was raised gradually. After 100 days of operation, a contraction of 55 percent was still obtained at 265°C.

When one compares the results of these experiments with the earlier ones where a catalyst was used without induction at ordinary pressure but was used immediately at 15 atmospheres for the synthesis, it is clearly shown that the preliminary induction causes the synthesis temperature to be lower (approximately 30° to 40°C.). The increased activity which resulted from carrying through the induction at the low pressure of 1 atmosphere remained intact for the duration of the experiment.

Induction at different pressures and synthesis at ordinary pressures.— In order to examine what influence the induction pressure has upon the synthesis at atmospheric pressure, let us refer to table 41. The induction was carried through at 255°C. for 20 hours with 4 liters of CO-rich gas (referred to 1 atmosphere per hour for 10 grams of iron) of composition $3CO + 2H_2$. Next we shifted to the synthesis itself. Four liters per hour of $1CO + 2H_2$ per 10 grams of iron were used at atmospheric pressure for 1-1/2 hours at a temperature of 255°C.

Table 41.—Influence of induction pressure upon synthesis at 1 atmosphere

Induction pressure, atmospheres	Synthesis contraction, percent
9	5
3	12
1	28
0.1	30

The experiments again show that high pressures impede induction. After induction at 9 atmospheres, the contraction amounted to 5 percent; after an induction at 3 atmospheres, 12-percent contraction was obtained; after inducting the catalyst at 1 atmosphere, 28-percent contraction was reached; and 30-percent contraction resulted from a catalyst having been inducted at 0.1 atmosphere.

Influence of induction temperature upon progress of synthesis.—After we had found out that a low pressure of induction favors increased activity of iron catalysts, normal iron catalysts were inducted at 1/10 atmosphere with a CO-rich gas at different temperatures. The induction lasted 25 hours, and the range of temperatures worked in was 250° to 350°C. Then the catalysts were tested by acting on a gas of composition $3CO + 2H_2$ at 15 atmospheres and 235°C. (4 liters of gas per 10 grams of iron per hour). (See Fig. 23)

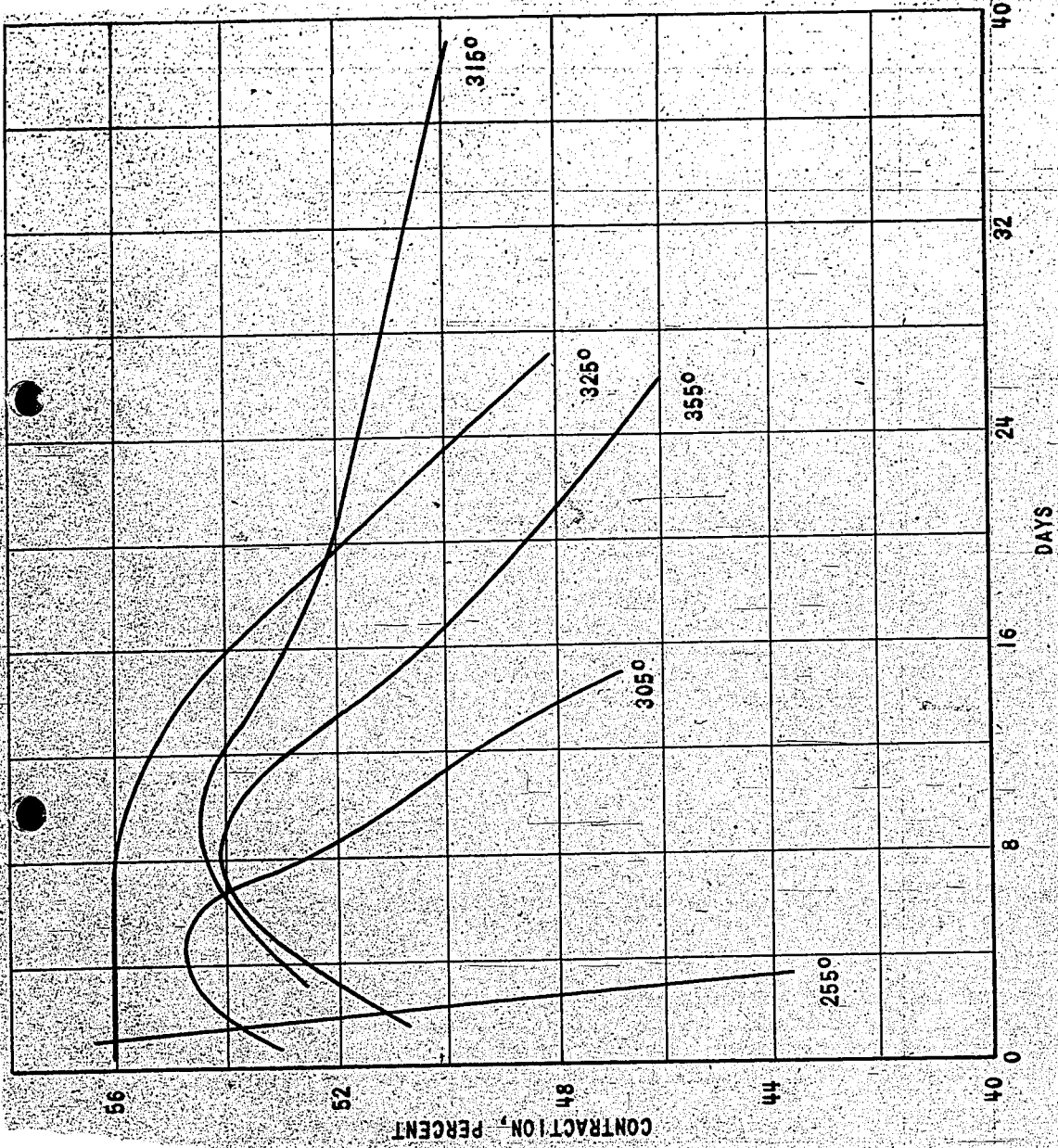


Figure 22.- Influence of induction temperatures of the catalyst upon the course of the synthesis (decrease of contraction with time of operation at 15 atmospheres and 2350 C.). Induction was carried out with a CO-rich synthesis gas at 1/10 atmosphere.

When the catalyst was inducted at 255°C., the contraction decreased below 50 percent; during the third day of operation, when the catalyst was inducted at higher temperatures, it was found that its life was improved. Thus, at an induction temperature of 315°C., we could operate for an entire month without falling below 50-percent contraction. When the catalyst was inducted at higher temperatures, the activity again decreased.

Figure 23 shows an analogous series of experiments during which the induction was not carried through with a CO-H₂ mixture but with pure CO.

When the catalyst was inducted with CO at 1/10 atmosphere and 325°C., the conversion during the following synthesis remained constant for 4 months (at a temperature of 235°C. and a pressure of 15 atmospheres). Hence the results obtained by carrying through the induction with CO are even better than those with CO-H₂ mixtures.

Influence of Induction Upon Synthesis Temperature

Figure 24 gives a comprehensive picture of the influence of the induction on the course of the synthesis. The abscissa reads in months of operation; the ordinate is calibrated in operating temperatures and the corresponding steam pressures. All experiments were carried through with a synthesis gas containing CO + H₂ in the ratio, 3:2 (4 liters per 10 grams of iron per hour).

Curve 1 refers to a catalyst that had not undergone induction but had been used directly for the synthesis at atmospheric pressure. To reach a maximum degree of contraction, the temperature had to be raised to 290°C. At first, the contraction was 45 percent. In the course of the 2 months of operation, the activity of the catalyst improved gradually, and the contraction went up to 50 percent. The temperature could be lowered gradually to 280°C. During the 4 months of operation, however, it was necessary to raise the temperature again, and at the end of the fifth month, the temperature of 300°C. was required.

Curve 2 shows the temperature relationships with an iron-copper catalyst which was allowed to act upon a mixed gas for 3 days at 1 atmosphere and 240°C. (30 percent contraction); then the operation was switched over to 15 atmospheres pressure. To obtain the highest contraction of 50 to 55 percent, the temperature had to be raised gradually in the course of 5 months from 240° to 290°C.

Curve 3 refers to a copper-free iron catalyst which had been inducted for 5 days at atmospheric pressure and 245°C. and was then used for the synthesis at 15 atmospheres.

Curve 4 reports the temperature relationships for an experiment with another copper-free so-called normal iron catalyst which had been treated for 25 hours with pure CO under a pressure of 1/10 atmosphere and 255°C. This experiment still showed a contraction of 50 percent after 16 months of operation at 260°C.

Curve 5 refers to a catalyst pretreated with CO at 1/10 atmosphere and 325°C. The induction at 325°C. made possible very uniform working conditions at low temperatures during the first month. The contraction remained constant at 50 to 54 percent for 4 months at 235°C. Then the temperature had to be increased.

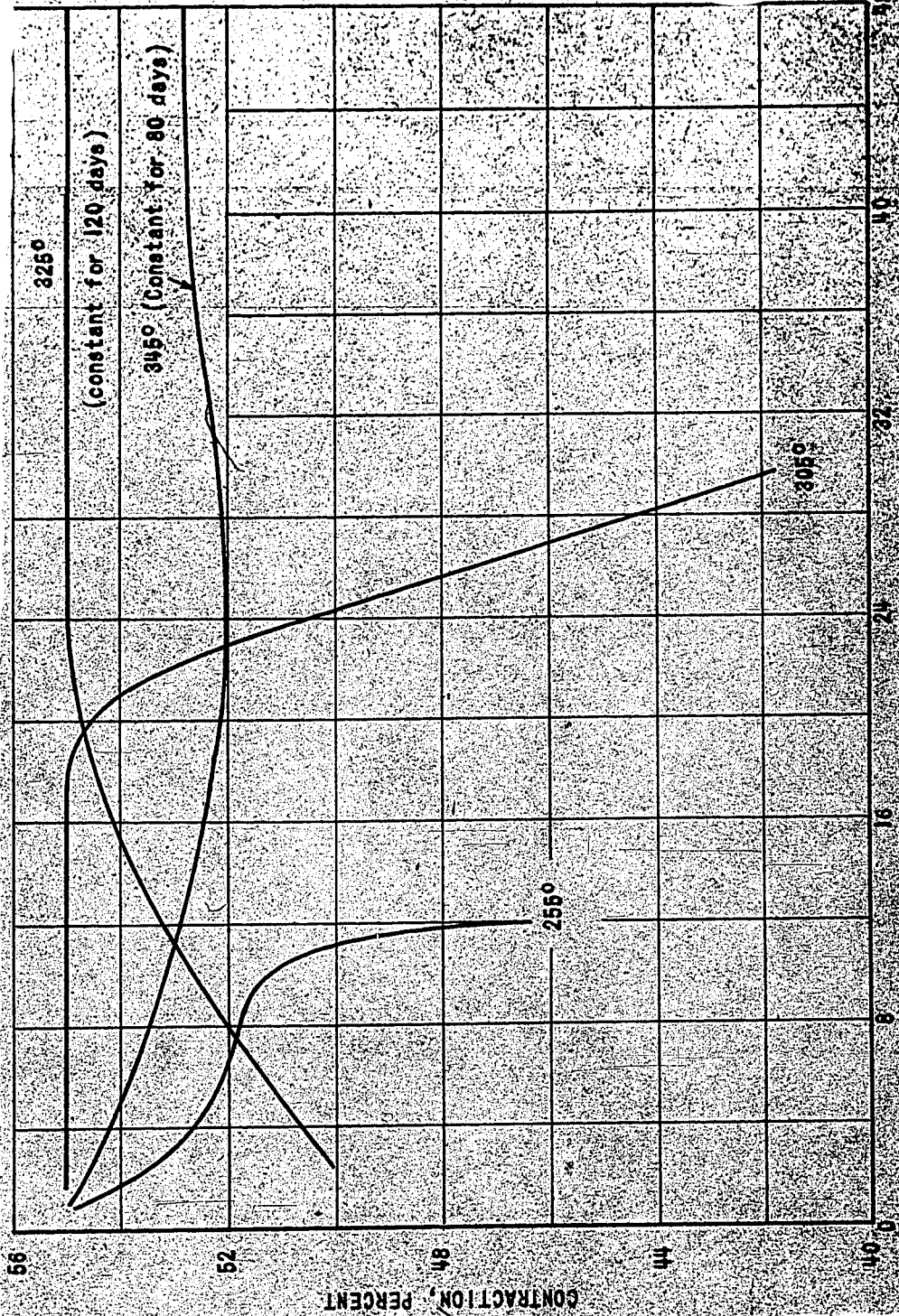


Figure 23. Induction period of the induction temperature upon the course of the synthesis of a polymer with CO_2 at 1/10 atmosphere pressure.

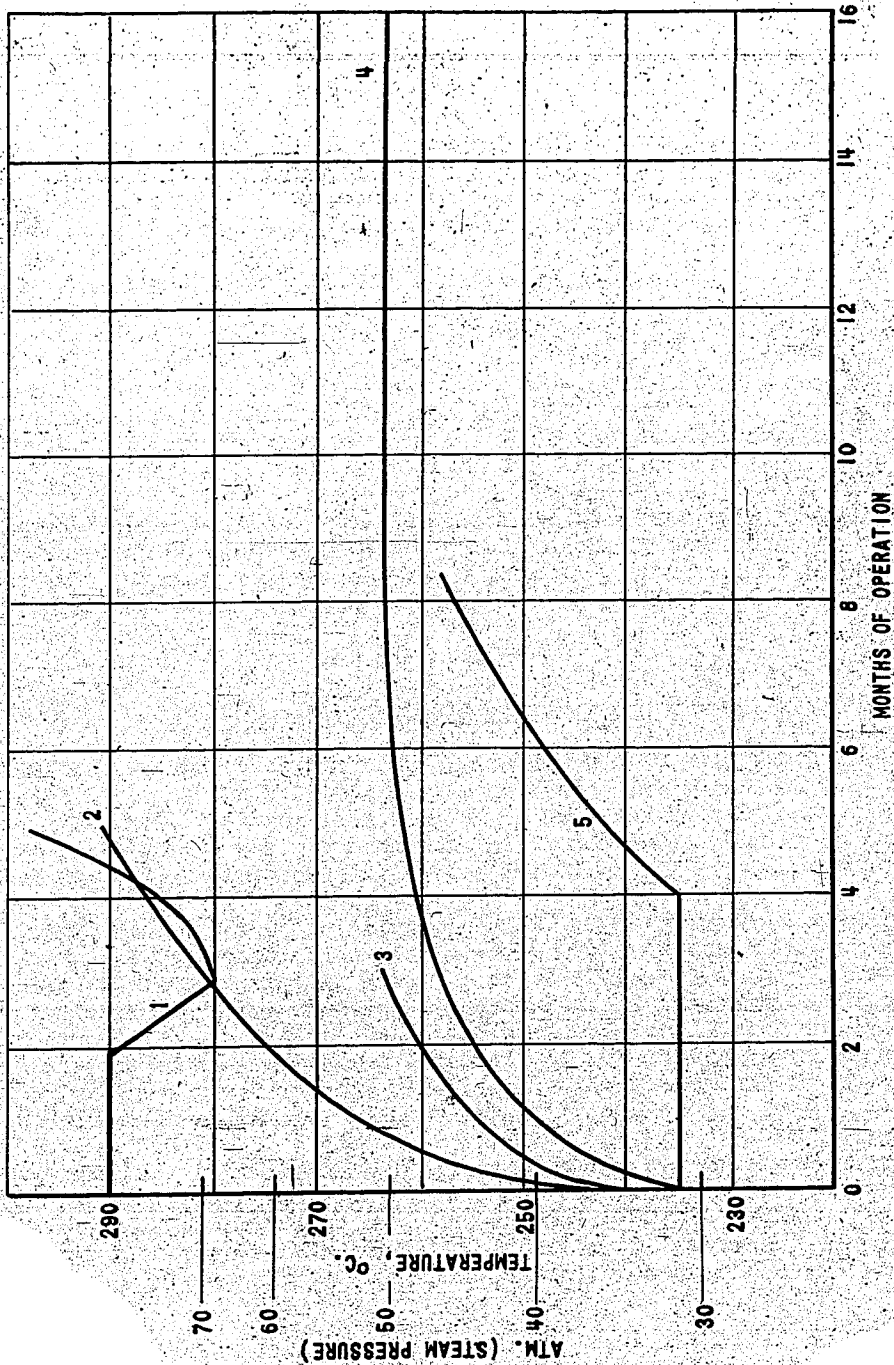


Figure 24.- Influence of induction upon the synthesis temperature.

The curves show very well the significance of the pretreatment of iron catalysts and what influence this pretreatment has upon the reaction temperature. This influence of the induction remains noticeable even after many months of operation.

Time of induction.—Not only pressure and temperature of the induction are important, but also velocity with which the CO passes over the catalyst. Reduction and carburization occur during induction and are responsible for the formation of CO₂. Therefore, the progress of the induction can be judged by the formation of CO₂. The induction is terminated when the CO₂ obtained has passed through a maximum and has reached a more or less constant minimum value. (Fig. 26). Any further formation of CO₂ corresponds to the formation of free carbon, which should be avoided if possible. This carbon formation takes place to a lesser degree at high flow velocities of CO than at low flow velocities.

To summarize the work on the induction of iron catalysts, it may be said that the induction may be carried through at lower pressures and higher temperatures than the synthesis which follows. Furthermore, it is advantageous to work with pure CO at high gas velocities. During induction, equilibria between the solid phases adjust themselves. They depend on the composition of the gas phase. If the CO₂ content in the gas phase is kept low, the reduction of the iron oxide and the formation of carbides are favorable. This might be one way to explain the advantageous low induction pressures at high gas velocities.

Experiments are in the process which are concerned with the solid phase, that is, processes which occur within the catalyst during the induction as well as the synthesis. We hope that these experiments will give results that will permit us to obtain faster methods of determining the activity of the catalyst.

THE SYNTHESIS

The Synthesis Gas

The optimum synthesis-gas composition is theoretically that which corresponds to the ratio in which CO and H₂ are used up. It is assumed that the catalyst has a sufficiently long life when it is used for such a theoretical mixture. The composition of such a theoretical mixture depends chiefly on the quantities of CO₂ and water formed during the reaction.

Figure 26 shows for 0 and 15 atmospheres the portion of CO-oxygen which at various synthesis-gas compositions is converted to water and CO₂. At a content of 30 percent of CO in the starting gas, 7 percent of the CO-oxygen is converted into water at 1 atmosphere pressure and 25 percent at 15 atmospheres. With 60 percent of CO in the starting gas and 1 atmosphere pressure, the conversion goes only to CO₂, whereas at 15 atmospheres 4 percent of the CO-oxygen still goes to water. Not only higher pressures but also higher hydrogen content in the synthesis gas favor the formation of water.

Figure 27, a and b, shows the influence of the synthesis-gas composition upon the yield of liquid and solid and gasol hydrocarbons. The dotted straight lines show calculated yields on the basis of exclusive CO₂ formation. The dot-point curves show the corresponding yields when water formation is taken into consideration. The solid curves show the yields actually obtained (4-week average).

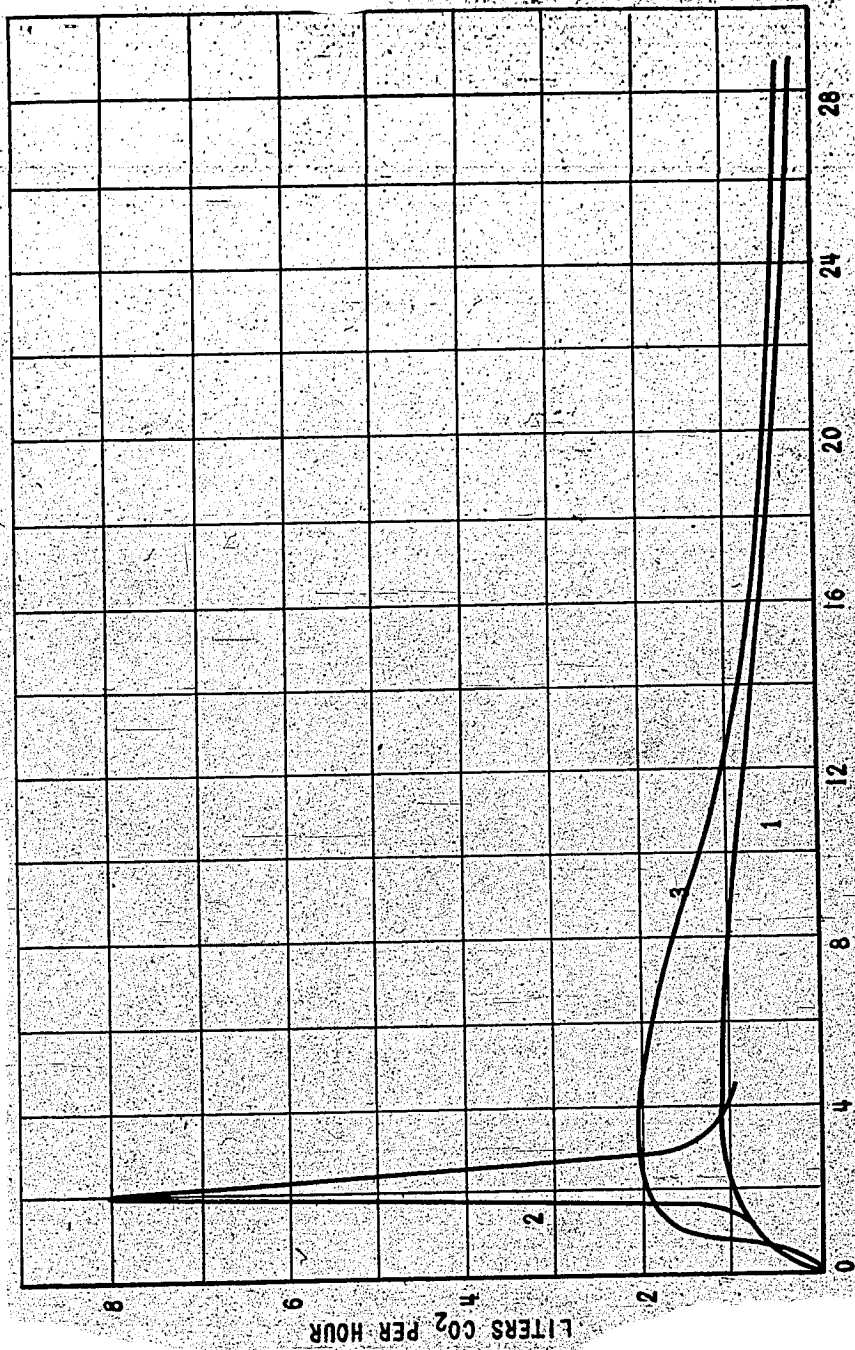


Figure 25.-CO₂ formation during the induction process.

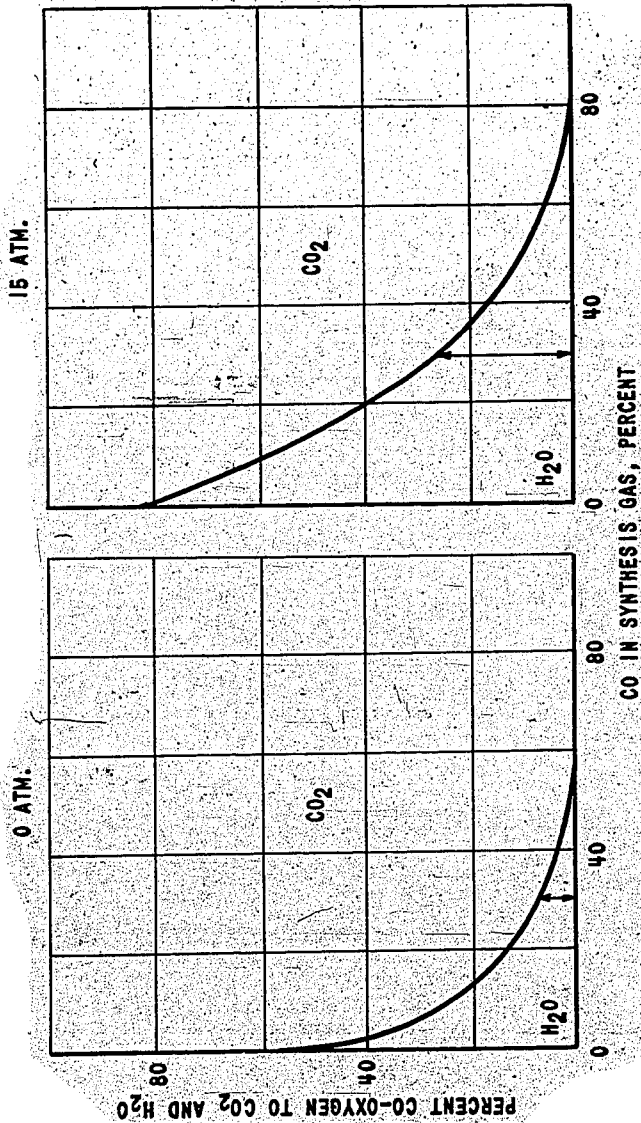


Figure 26. - Conversion of the CO-oxygen to CO₂ and H₂O, respectively, for various synthesis gas compositions at 0 and 15 atmospheres pressure.

15 ATM.

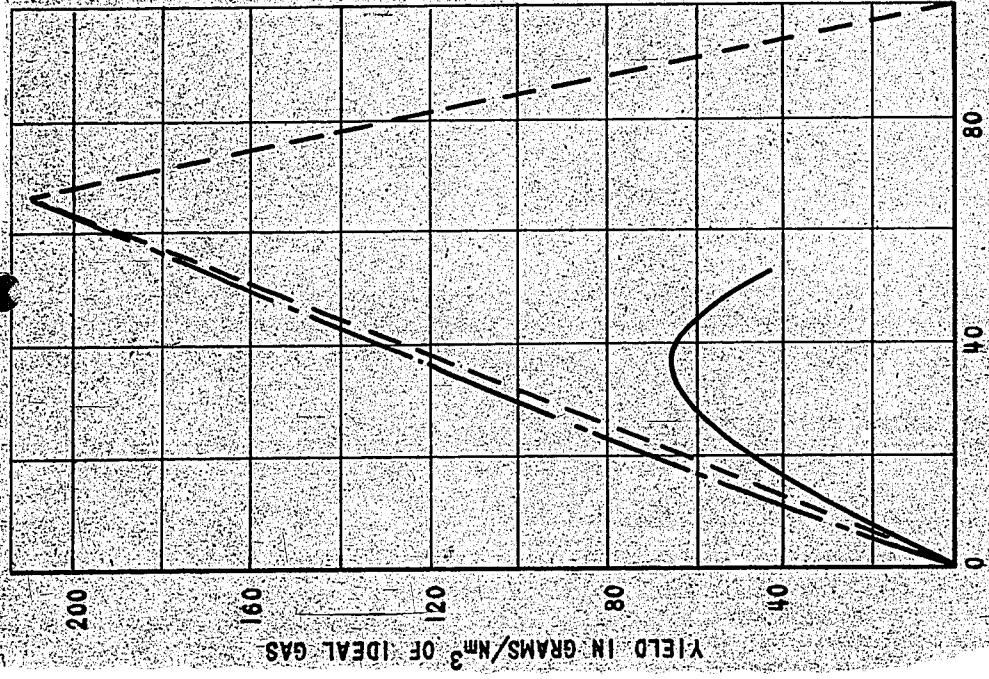
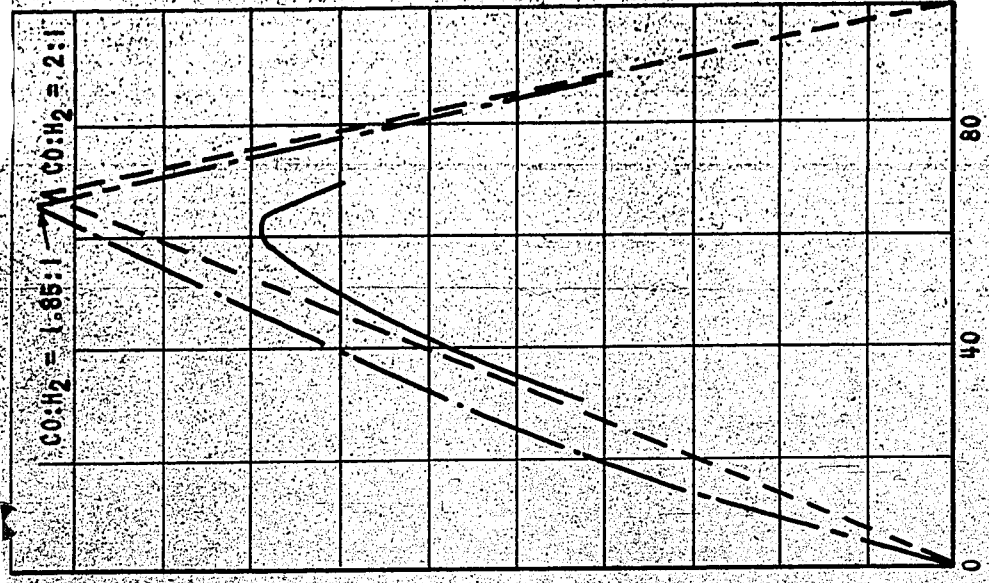


Figure 27. - Influence of synthesis gas composition upon the yields.

Theoretically 208 grams of hydrocarbons may be obtained with or without formation of water for every normal cubic meter of synthesis gas. At atmospheric pressure, taking into consideration the formation of CO_2 and water, the theoretical optimum gas composition lies near a ratio of $2\text{CO} + 1\text{H}_2$, at 15 atmospheres at $1.85 \text{ CO}_2:\text{H}_2$.

The fundamental difference between the synthesis at 1 atmosphere and 15 atmospheres is that one cannot work at atmospheric pressure with the theoretical $\text{CO}:\text{H}_2$ mixture because it causes the activity of the catalyst to decrease too rapidly. This, however, is not the case for the middle-pressure synthesis. The figure shows that, at 1 atmosphere pressure, a gas of composition $2\text{CO} + 1\text{H}_2$ gave the best results. For the first 4 weeks of operation it gave an average of about 60 grams of solid, liquid, and gaseous hydrocarbons. These yields, however, decreased rapidly during the 5th and 6th weeks of operation. At 15 atmospheres pressure, however, a yield of 150 grams was obtained for many months.

For the formation of CH_2 hydrocarbons, less hydrogen is required than for the formation of CH_4 . Finally it seems to be advantageous for the activity of the catalyst if the final gas still contains a small excess of hydrogen. The ideal synthesis gas, therefore, contains 60 percent CO and 40 percent H_2 . At this point let us mention something about the production of synthesis gas. In the Institute, this gas mixture was generated in a normal gas generator. CO_2 and steam were passed over hot coke. Such a process could be recommended in some instances for large-scale operation, since the synthesis carried out with the iron catalysts forms far more CO_2 than would be required for production of the synthesis gas. From 1 cubic meter of synthesis gas with a ratio of $3\text{CO}:\text{H}_2$, normally 250 liters of CO_2 are obtained, whereas according to $5\text{C} + 4\text{H}_2\text{O} + \text{CO}_2 = 6\text{CO} + 4\text{H}_2$ only 100 liters of CO_2 are required per cubic meter of CO -rich gas. Partial scrubbing of the CO_2 from the end gas and addition of same to the gas generator could fulfill all the CO_2 needs of the generator.

The carbon requirement as shown by the above equation is no larger than that for the production of normal water gas.

The production of CO -rich gas in the water-gas generator of the Institute and purification of the gas has been taking place in the Institute for years at the rate of 100 cubic meters per hour. If one could utilize not only the CO_2 but also the methane (5 to 10 percent) and the unreacted CO and H_2 (10 to 15 percent) one could approach the theoretical yield of 208 hydrocarbons per normal cubic meter of gas.

Another way to make synthesis gas is by the well-known gasification of coke or coal with the addition of oxygen. It is unnecessary to elaborate on this.

Synthesis Pressure

In the chapter on the synthesis gas, we have already explained the reasons why, in the hydrocarbon synthesis on iron catalysts, work at atmospheric pressure is not practicable. Table 42 shows some comparative experiments in which synthesis took place with the same catalyst at various elevated pressures. We used a number of iron catalysts which had been inducted for 24 hours at $1/10$ atmosphere and 325°C . with a CO -rich synthesis gas. Table 42 shows the results of experiments completed at 5, 10, 30, and 60 atmospheres. All of these experiments were conducted at 235°C . At 235°C . the catalysts did not give any conversion at atmospheric pressure; neither did they give a conversion on the second day at 250°C . (after switching, however, to 15 atmospheres and 235°C ., the catalysts gave a contraction of 53 percent).

Table 42.—Reaction and contraction at various temperatures
(Normal iron catalysts inducted with CO-rich gas at
325°C. and 1/10 atmosphere)

Operation, days	5 atmospheres		10 atmospheres		30 atmospheres		60 atmospheres	
	Tem- pera- ture, °C.	Con- trac- tion, percent	Tem- pera- ture, °C.	Con- trac- tion, percent	Tem- pera- ture, °C.	Con- trac- tion, percent	Tem- pera- ture, °C.	Con- trac- tion, percent
1	235	30	233	42	235	53	235	50
2	-	-	234	42	235	56	238	42
3	235	25	235	48	234	37	235	40
6	250	38	238	50	-	-	254	52
9	270	37	239	50	-	-	-	-
12	-	-	237	50	-	-	-	-

At 5 atmospheres the contraction was 30 to 40 percent; hence the conversion was still incomplete. This remained so even after the temperature was raised to 270°C. on the ninth day (a switch-over to 15 atmospheres caused a 50-percent contraction even here when the temperature was 235°C.). At 10 atmospheres a 50-percent contraction was reached at 235°C. This was the case also at 30 and 60 atmospheres. However, when working at 30 atmospheres and 235°C., after the third day a considerable decrease in the amount of conversion occurred. For the 60-atmosphere run, this decrease set in after two days of operation. When the operating temperature was 254°C., the decrease in conversion did not set in earlier than the sixth day, when a maximum of 52 percent had been reached.

The optimum pressure is found to lie between 10 and 30 atmospheres or somewhere around 15 atmospheres. (When operating under 15 atmospheres, the same catalyst operating at 237°C. still gave the same conversion after a whole month of operation, that is, approximately 50-percent contraction.)

Reaction Temperature

Special attention was given the reaction temperature. We tried a lower reaction temperature in the middle-pressure synthesis. This was important not only from a chemical but from an economic viewpoint as well. On a large scale, the reaction is kept at a uniform temperature by cooling with water; hence, lowering the reaction temperature will cause a lowering of the steam pressure, and, consequently lower cost for equipment.

The influence of induction upon synthesis temperature has been discussed in detail.

The influence of the gas composition is such that H₂-rich gases permit a lower working temperature than the CO-rich gases.

For example, an experiment with a hydrogen-rich synthesis gas of composition 1CO + 2H₂ yielded 47-percent contraction at a temperature of 184°C. after the second day of operation. The usage ratio of CO and H₂ pointed toward the formation of hydrocarbons and water. At low reaction temperatures, the conversion, however, decreases after a very few days, and it is interesting to note that even if the temperature is raised thereafter, the results do not improve. It is better to initiate the experiment at the high temperatures.

With a gas containing CO + H₂ in the ratio 1:2, it was possible, however, to operate for several months at 200°C. and practically convert the entire CO with an average contraction of 47 percent and a yield of 90 grams per normal cubic meter of gas. The liquid and solid products obtained were entirely colorless. Essentially larger yields cannot be obtained on iron catalysts when such a gas is used.

When we used the CO-rich gas we usually initiated the experiment at 225° to 235°C. (in order to get good time yields). We did this in spite of the fact that a good degree of conversion could have been obtained if we had operated at 210° to 220°C.

The temperature of the reaction influences the nature of the reaction products. Table 43 shows average yields obtained from iron catalysts containing 1/4 percent of potassium carbonate and operating at 235°, 275°, and 280°C. The yield of solid paraffins was 39 grams per normal cubic meter of gas for 235°C. and only 4 grams for 270°C. As the solid paraffins decreased when the temperature was raised, the liquid and especially the volatile hydrocarbons and the gasol hydrocarbons increased in quantity. At 280°C., the paraffin yields were even less, but at this temperature the yields of liquid and gasol hydrocarbons started to decrease also.

Table 43.—Nature of reaction products for various temperatures

Reaction temperature, °C.	Yields, grams per normal cubic meter of ideal gas		
	Solid paraffin	Liquid hydrocarbons	Gasol
235	39	83	26
270	4	94	46
280	2	82	35

Influence of Alkali Contents on Iron Catalysts

The method of producing the catalyst has been discussed. The following table 44 shows the influence of the addition of alkali to the catalyst upon the synthesis.

The indicated quantities of potassium carbonate added to the catalyst are based on the content of iron metal. In the case of the other alkalinized salts (permanganate, fluorides, etc.) the notation "1 percent KMnO₄" indicates a quantity equivalent to 1 percent K₂CO₃.

Table 44 shows the yield and nature of the reaction products obtained from catalysts containing different amounts of alkali. The temperature was 235°C. and the pressure 15 atmospheres. The yields, indicated as grams per normal cubic meter of ideal gas, are not quite constant for the first month of operation because of varying percent contraction. The yields are approximately 140 to 160 grams for this first month. If the nature of the products formed is disregarded, we see that the alkali addition to the catalyst has no important effect on the total yield. The alkali-free catalyst precipitated with ammonia gave yields that were not essentially below those obtained from catalysts containing 1/4 percent K₂CO₃.

The alkali content of the catalyst, however, had a very marked influence upon the nature of the reaction products. When no alkali was present, the Butanone method revealed approximately 12 percent of paraffins in the product. When 1/4 percent potassium carbonate was added to the catalyst the paraffins was 26 percent; with 1 percent potassium carbonate the products contained 42 percent of paraffins; with 2 percent potassium carbonate, 43 percent; and with 5 percent potassium carbonate, the final product contained 45 to 46 percent paraffins. The yield of liquid and gasol hydrocarbons decreases with increasing alkali content of the catalyst.

Table 44.—Yields obtained from various iron catalysts containing different amounts of alkali

Precipitant	Alkali addition percent	Solid, liquid and gasol hydrocarbons, grams per normal cubic meter of synthesis gas	Paraffin, percent	Liquid hydrocarbons, percent	Gasol, percent
NH ₃	0	141	12	67	21
Na ₂ CO ₃	0	140	13	67	20
Na ₂ CO ₃	1/4 K ₂ CO ₃	148	26	56	18
Na ₂ CO ₃	1 K ₂ CO ₃	157	42	47	11
Na ₂ CO ₃	1 KMnO ₄	155	41	45	14
Na ₂ CO ₃	1 K ₂ SiO ₃	158	43	41	16
Na ₂ CO ₃	1 K ₂ F ₂	163	46	42	12
Na ₂ CO ₃	1 K ₂ HPO ₄	154	38	52	10
Na ₂ CO ₃	2 K ₂ CO ₃	143	43	44	13
Na ₂ CO ₃	5 K ₂ CO ₃	161	45	43	12
Na ₂ CO ₃	5 K ₂ CO ₃	155	46	44	10

Table 44 shows further that the quantity and the nature of the reaction products were not affected by the type of alkaline salt added to the catalyst. No essential difference was discovered when the catalyst was alkalinized by 1 percent potassium carbonate or an equivalent quantity of potassium permanganate, potassium silicate, potassium fluorides, or potassium phosphate.

The life of the catalyst is longer at a low alkali content (for example, 1 percent K₂CO₃) than it is at higher alkali content.

Treatment of Catalyst with Hydrogen

We have already pointed out that hydrogen may not be substituted for CO in the induction of the catalyst. Catalysts pretreated with hydrogen—that is, reduced iron catalysts—are inactive at low temperatures. If the catalyst was pretreated with hydrogen before it was subjected to the action of CO, no improvement resulted. Neither did improvement result if the catalyst was treated with hydrogen between the induction period and the synthesis proper.

The treatment with hydrogen, however, had a different result if carried out on an iron catalyst during the synthesis. The situation was then similar to that of cobalt catalysts. To demonstrate this, we carried out the following experiment. We had available a catalyst which, in order to give the best results, should have been employed at a temperature a few degrees higher than 235°C. (at

15 atmospheres and 4 liters of CO-rich gas per hour). We operated this catalyst at 235°C. During the first and second days of operation, we observed a contraction of 52 percent (see Fig. 28). After the second day, the contraction was 50 percent, and after 3 days, 47 percent. From the dotted curve (Fig. 28) we are able to see that the contraction would have fallen to 40 percent had we continued to operate for a week at 235°C. However, after the third day of operation, the catalyst was treated with hydrogen for 15 hours with 8 liters per hour at 1 atmosphere and 325°C. After this hydrogen treatment, the catalyst caused a contraction of 55 percent in the following synthesis. It decreased slowly thereafter; however, it remained above 51 percent up to the 12th day. On the 12th day, the hydrogen treatment described above was repeated. The contraction rose again to 57 percent and after 19 days of operation decreased to 50 percent. After the third treatment with hydrogen, 55 percent contraction was observed, which decreased to 51 percent after 3 days and after 4 days to 52 percent. When the synthesis was continued for 2 months thereafter at 235°C., the contraction remained near 50 to 53 percent.

Figure 28 shows that an increase in catalyst activity resulted when the synthesis was interrupted and a hydrogen treatment performed. This increased activity was especially pronounced during the first few hours of the hydrogen treatment, and it also stabilized the catalyst thereafter. When the activity of the catalyst was at a maximum after the hydrogen treatment, the usage ratio of CO and H₂ was no different from that of the normal synthesis occurring with 50 to 52 percent contraction. In both cases CO and H₂ were used up in the ratio 1.67-1.70:1. It is therefore obvious that no carbon formation occurred during the time of optimum activity of the catalyst.

Iron catalysts that had been used for a long time or had decreased in activity to a great extent did not show lasting improvement when treated with hydrogen. Lasting improvement may not be obtained even if another induction is given with CO. If it is desired to perform a hydrogen treatment and produce good results, the catalyst must be subjected to hydrogen before it gives a contraction of 45 to 50 percent.

I want to point out once more that we have operated with iron catalysts for several months, even up to 1 year, and it was not necessary to carry out one single regeneration of the catalyst.

Effect of Adding Kieselguhr

We have discussed the effect of alkali when added to the catalyst; let us mention briefly the effect of kieselguhr when mixed into the catalyst. It is well known that kieselguhr is an essential constituent of cobalt catalysts and that good yields are obtained only when kieselguhr is used as a carrier for those catalysts.

This is not so with iron catalysts. The best results were obtained with catalysts free of kieselguhr. However, it might be desired to add kieselguhr to the catalysts for various reasons, such as, for instance, loosening of the iron catalyst or decreasing the danger of carbon formation. In general, the addition of kieselguhr to iron catalysts causes an improvement in activity in the sense that more lower-boiling and gaseous hydrocarbons are formed.

Construction of Apparatus

The discussed time tests were carried out in horizontal, slightly tilted reaction tubes. A slight expansion of the catalyst may thus take place due to carbon deposition without serious damage (Fig. 29, schematic drawing 1). If the reaction tube is vertical, expansion of the catalyst causes a restriction between the catalyst granules and hence a shortening of the contact time of the gases passing over them (Fig. 29, schematic drawing 2). To eliminate any possible disturbances from the viewpoint of construction, we are still in the process of

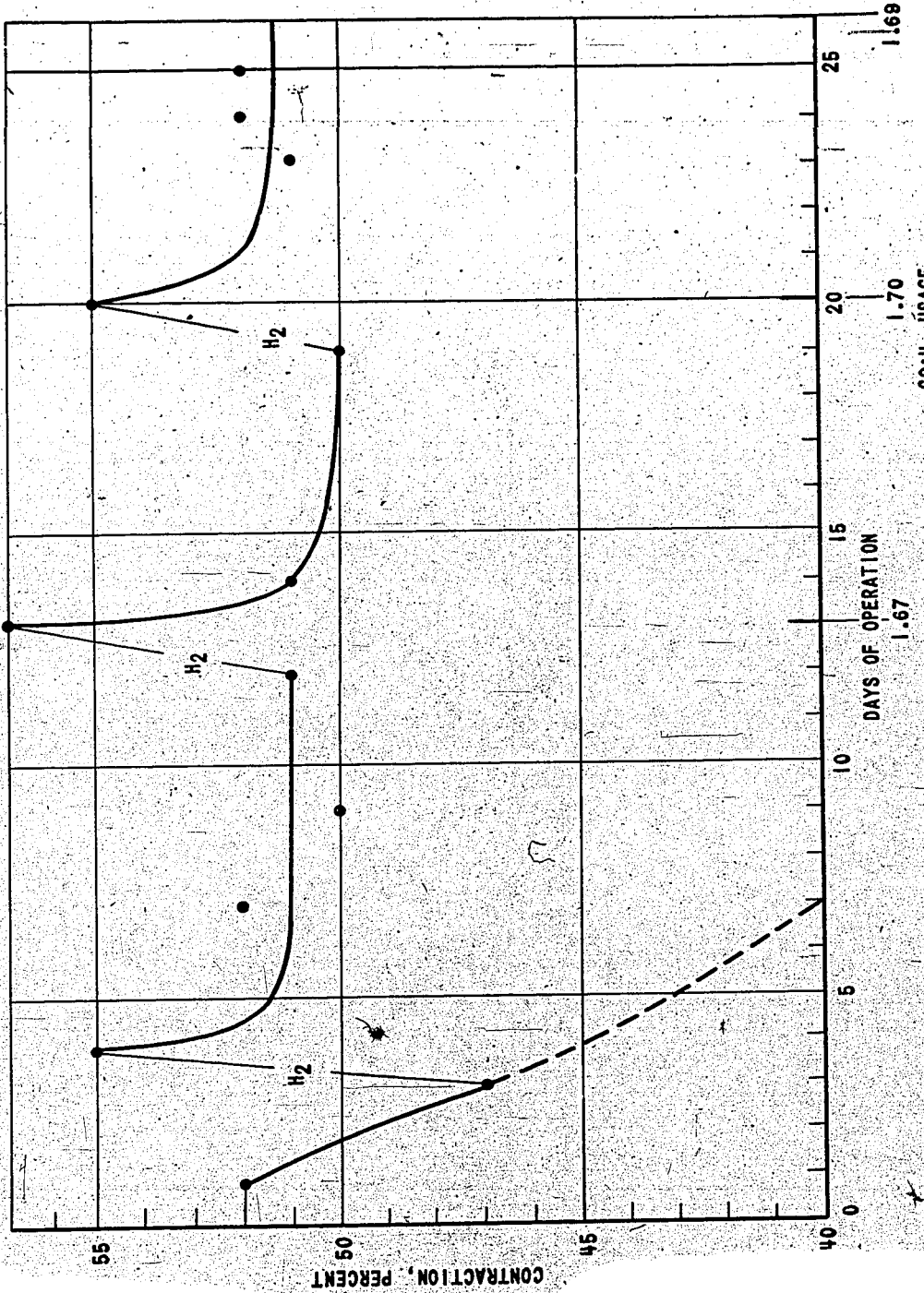


Figure 28.- Influence of a H₂ - pretreatment on the synthesis.

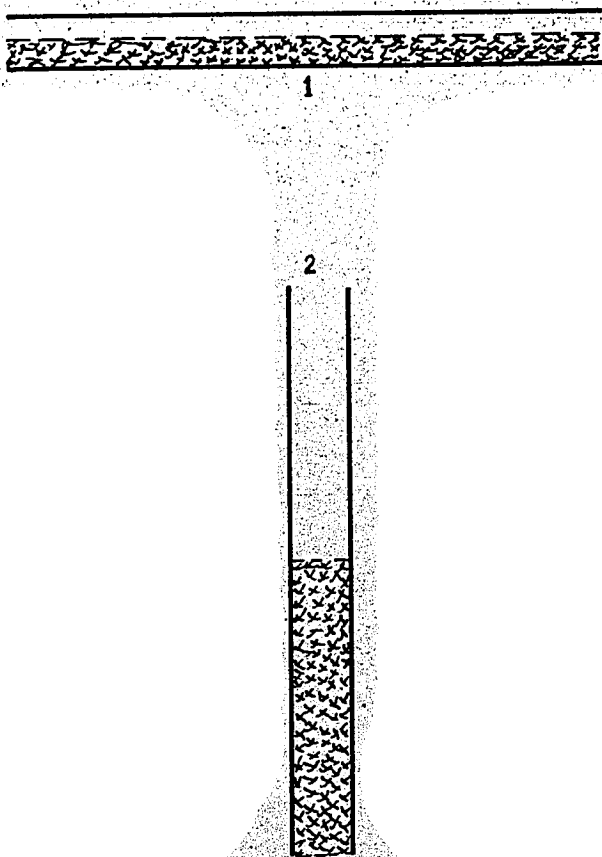


Figure 29.- Schematic representation of positions of reaction tubes.

carrying out experiments dealing with this subject. According to Fig. 29 (schematic drawing 2), at a gas rate of 4 liters of synthesis gas per hour per 10 grams of iron, the space-time yield is approximately twice that of a normal cobalt-kieselguhr catalyst. The apparatus is cooled by water and has to withstand a pressure of 50-60 atmospheres. If salt solutions were used instead of water, the necessary steam pressures could be reduced somewhat.

PRODUCTS OF REACTION

When the iron catalyst is used in the middle-pressure synthesis, paraffin and olefin hydrocarbons of varying molecular weights are produced, as well as methane and lower gaseous hydrocarbons. It is possible to regulate the course of the reaction to form certain products in preference to others. In addition to the products listed above, oxygen-containing organic compounds are produced, products similar to the Synthol described by Fischer and Tropsch several years ago.

Liquid Hydrocarbons

The crude total liquid product obtained from CO-rich gases and alkali catalysts, in general, is not quite colorless but has a greenish-yellow tinge. After a distillation, however, one obtains a water-clear colorless gasoline; whereas small traces of the formed oil remain as a yellow residue. The gasoline is stable and remains colorless even after months of storage.

The quantity of the fraction boiling up to 180°C.—in other words, the gasoline fraction (varying in amount in each case depending on working conditions)—may be 80 percent or 40 percent or even less, based on the total liquid and solid hydrocarbons produced.

Table 45 shows the properties of the stabilized gasoline washed with sodium hydroxide. Its knocking properties were determined in the I.G. testing engine. Approximately two-thirds of the total liquid product boiled in the range of 30° to 180°C. Table 45, No. 1, corresponds to the primary gasoline. Its octane number is 61.

Table 45.—Properties of gasoline obtained in the middle-pressure synthesis with iron catalysts (with and without additional polymerization)

No.	d ₁₅ ^o	Olefins, percent	Boiling characteristics				P _{37.8} ^o	Octane No.
			0 °C.	10% °C.	50% °C.	90% °C.		
1	0.696	64	30	46	88	145	0.54	61
2	.705	65	32	53	100	150	.48	77
3	.700	65	34	60	95	130	.55	71

The two gasolines listed under 2 and 3 are only mentioned briefly here. During the synthesis, the total end gas (which includes the CO₂) was passed over a phosphoric catalyst at 15 atmospheres pressure. The unsaturated hydrocarbons contained in the gas furnished primary polymer gasoline, which was mixed with the primary gasoline. Such mixed gasoline boiling to 180°C. had an octane number of 77 (gasoline 2). If the distillation was interrupted at 150°, the octane number was only 71 (gasoline 3). If 0.7 cc. of tetraethyl lead per liter was mixed into gasoline 2, its octane number improved to 79; if the same quantity of tetraethyl lead was added to gasoline 3, its activity went up to 83.

If the gasoline is not subjected to washing with sodium hydroxide, a higher octane number is obtained in the primary gasoline also. If washing is not carried out with sodium hydroxide, acid constituents are left in the gasoline in addition to water-soluble oxygen-containing organic compounds such as alcohols. The high content of unsaturated hydrocarbons is very favorable for the antiknock properties of the gasoline. Should it be desired to produce lubricants from the unsaturated constituents, then it would be necessary to rework the oil in order to remove all traces of oxygen-containing constituents, which normally would disturb the polymerization with aluminum chloride.

Paraffin

The solid and liquid products of the liquid, according to the Butanone method, contain approximately 5 to 50 percent of solid paraffin. The paraffin is white to brownish-yellow when hydrogen-rich synthesis gas and alkali-deficient catalysts are used. If a CO-rich gas and an alkalinized catalyst containing up to 1 or more percent potassium carbonate catalyst are used, the paraffins are both yellow to dark yellow. The coloring matter may be due to iron compounds. In general, however, the coloring matter is due to small quantities of higher-boiling oils, which may be removed by extraction or by hydrogenation.

The melting points of the paraffins range over the whole region of the known paraffin hydrocarbons. The paraffin which remains behind in the catalyst contains constituents of especially high melting points.

The uses of the paraffins are very many. It is not necessary here to discuss them. We did not think too much about oxidizing them to fatty acids used in the soap industry. The paraffins obtained from iron catalysts are not as ideal for fatty acid production (as in the soap industry) as are the paraffins manufactured with cobalt catalysts. To make those paraffins available for the soap industry, they have to undergo a special treatment. It has not been shown whether the "iron paraffin" contains a greater number of branched-hydrocarbons than the "cobalt paraffin".

Gasol

Quantity and composition of the gaseous hydrocarbons are also functions of the nature of the catalyst and the reaction temperature. Table 46 shows yields of gasol hydrocarbons with their content of unsaturated constituents produced under various synthesis conditions. All experiments refer to a synthesis gas of composition $3CO + 2H_2$ and a synthesis pressure of 15 atmospheres. The gasol yields are essentially larger here than with cobalt catalysts.

Table 46.--Yields of gasol hydrocarbons with different catalysts

Catalysts	Tempera- ture, °C.	Grams of gasol per normal cubic meter of gas	Percent of unsatu- rated hydrocarbons in gasol
Fe, NH ₃ precipitated, 0% K ₂ CO ₃	235	30	70
Fe, Na ₂ CO ₃ precipitated, 0% K ₂ CO ₃	235	28	80
Fe, Na ₂ CO ₃ precipitated, 1/4% K ₂ CO ₃	235	26	76
Fe, Na ₂ CO ₃ precipitated, 1% K ₂ CO ₃	235	17	80
Fe, Na ₂ CO ₃ precipitated, 1/4% K ₂ CO ₃	270	46	47
Fe-kieselguhr, 1% K ₂ CO ₃	235	36	35

With the iron catalysts precipitated with ammonia or soda ash at a synthesis temperature of 235°C., 20 to 30 grams of gasol hydrocarbons per normal cubic meter of gas were obtained, with a total of 70 to 80 percent of unsaturated constituents. With increasing alkali content and with all other conditions the same, the quantity of gasol produced decreases. With higher reaction temperatures the quantity of gasol hydrocarbons increased, but their hydrogenation was favored too, so that at a temperature of 270°C. the same amount (grams per normal cubic meter of ideal gas) of unsaturated hydrocarbons were obtained, namely, 20 grams per normal cubic meter of ideal gas.

When the iron catalyst contains kieselguhr, the gasol hydrocarbons produced at 235°C. differ from those of a catalyst without kieselguhr in that they contain a smaller amount of unsaturated hydrocarbons.

Iron catalysts not only produce gasol hydrocarbons containing 3 and 4 carbon atoms to the molecule but also form C₂ hydrocarbons. The gases from one experiment were subjected to a low-temperature distillation, and the following constituents were obtained: Eleven grams per normal cubic meter of propylene, 6 grams per normal cubic meter of butylene, and 5 grams per normal cubic meter of ethylene. The relatively high yields of unsaturated gasol hydrocarbons are especially favorable if one considers further processing for high-octane gasoline.

Products Containing Oxygen

At 235°C. and with a CO-rich gas at 15 atmospheres, we obtained 13 grams of aqueous products with the iron-kieselguhr catalyst. They contain acids, aldehydes, and esters (the test for formic acid was negative, that for acetic acid was positive; the test for aldehydes was positive when fuchsine-sulfurous acids were used; and esters were present (saponification)). The aqueous compounds also contain alcohols, such as ethyl and a little methyl alcohol. Figure 30 shows a distillation analysis of the constituents of the reaction water which boiled below 90°C. (28 percent of the total reaction water). The distillation was carried out by a microcolumn.

The boiling-point curve shows distinctly the ethyl alcohol fraction. It represents 7.5 percent of the total reaction water. The second constant temperature corresponds to the azeotropic mixture of propyl alcohol and water (87.7°C. and 28.3 percent of water).

Not only did we find synthol-like compounds in the reaction water, but in the hydrocarbons. They could be found in the low-boiling and in the high-boiling fractions. The oxygen determined by analysis varied between 0.2 and 2 percent. The lower-boiling fractions contained more oxygen than the higher-boiling fractions. Alkali-deficient iron catalysts produce only small quantities of products containing oxygen. More alkalinized catalysts produced higher quantities. The normal iron catalyst produces, at 180°C., a gasoline which contains 1 to 2 percent of water-soluble products. Other iron catalysts yield 5 percent or more. The acid number of products below 180°C. is 1; that above 180°C. is 0.1. The corresponding esterification values are 1.6 and 0.5, respectively, and the saponification values are 2.6 and 0.6, respectively. Among others we were able to prove the presence of esters and alcohols. More detailed analytical information is left for a future report.

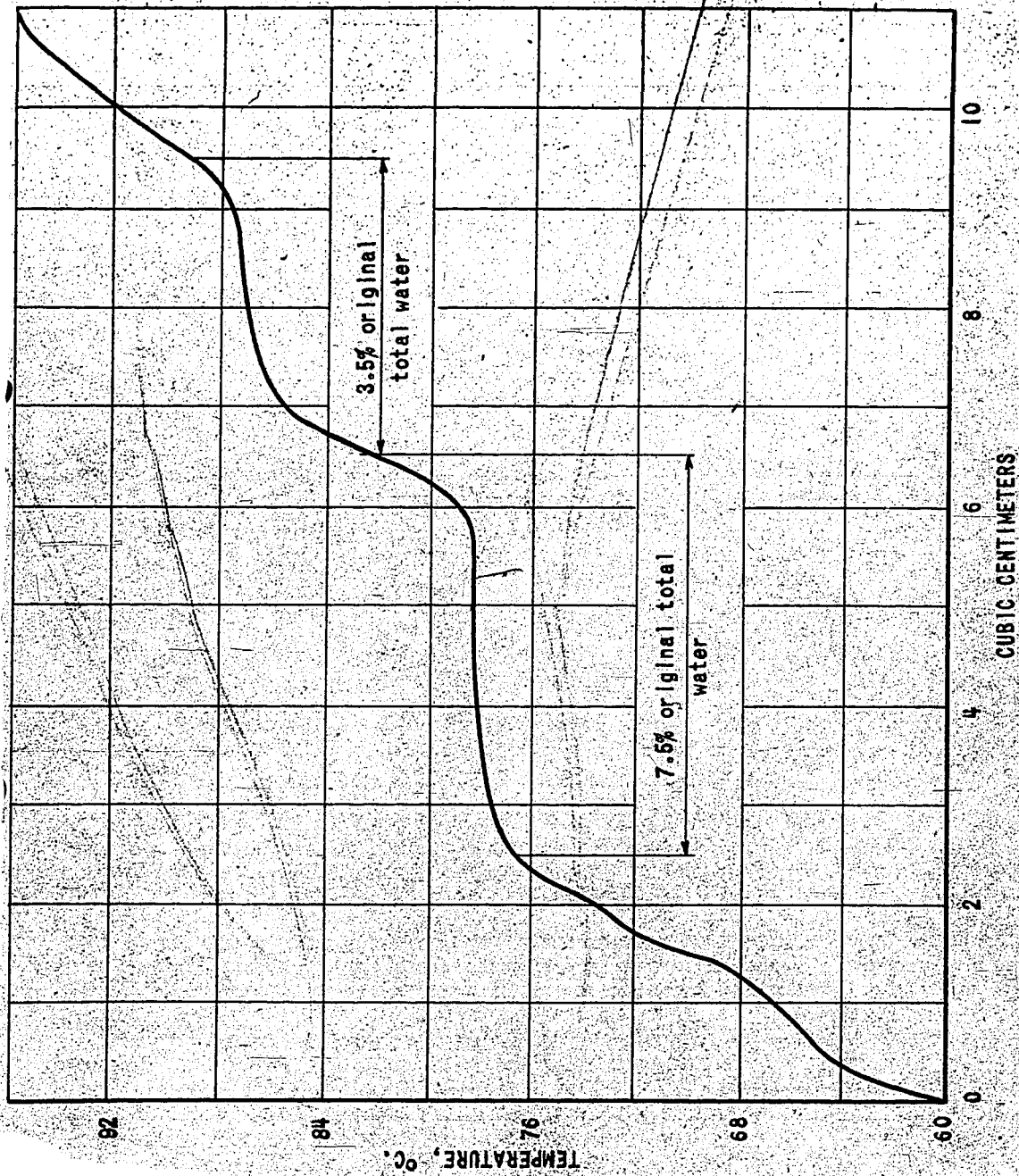


Figure 30. - Boiling point analyses of the reaction water boiling below 90° C. (charge 15 cc.).

City Gas

Before I end my discussion on the reaction products, I want to mention here that, according to our newest experiences, the iron catalysts are well-adapted for production of a standard city gas from water gas.

CONCLUSION

The following may be said about the iron middle-pressure synthesis. The yields of solid, liquid, and gasol hydrocarbons are between 130 and 160 grams per normal cubic meter of ideal gas. The longest life obtained for the catalyst was 1-1/2 years without any regeneration at a temperature of 260°C. At the same time it still gave a yield of 140 grams per normal cubic meter.

The stability of the iron catalysts over long periods may be observed from the end-gas analyses, which are summarized in table 47.

Table 47

Operation, months	Tem- pera- ture, °C.	Con- trac- tion, percent	CO ₂	Olefins	O ₂	CO	H ₂	Hydro- carbons	Carbon No.	N ₂
A. End-gas analysis of an experiment at 255°C., iron catalyst inducted with CO at 1/10 atmosphere:										
1	235	50	49.6	2.2	0.1	15.0	13.3	8.8	1.9	11.0
14	254	50	50.1	2.8	.2	14.9	11.9	7.3	1.7	12.8
B. End-gas analysis of an experiment with a catalyst inducted at 325°C., 1/10 atmosphere:										
1	235	54	57.0	2.6	0.1	6.3	14.6	8.9	2.0	10.5
3-1/2	235	52	61.2	3.3	.1	5.2	11.2	9.0	1.9	10.0

Table 47 concerns a catalyst inducted at 255°C. with CO at 1/10 atmosphere. It shows the same conversion for 14 months of operation uninterruptedly operated at 253° to 254°C at the same charge of gas through the converter of 400 liters of synthesis gas per kilogram of iron.

Table 47 also covers a catalyst inducted at 325°C. at 1/10 atmosphere with CO. This catalyst yielded virtually the same degree of conversion and optimum yields of 150-160 grams per normal cubic meter of gas after four months of operation.

The iron catalysts are not only superior to the cobalt catalysts on account of their lower cost, but also for the less expensive apparatus which they require and for the more even life they exhibit. It should be added that the antiknocking properties of the iron gasoline are better than those of the cobalt gasoline and that the unsaturated gasol hydrocarbons obtained with iron catalysts can be used to greater advantage for production of high-quality gasoline.

The following disadvantages are presented by iron catalysts: They work at higher temperatures, hence require greater steam pressure, if it is desired to cool with water, than cobalt catalysts. Iron catalysts have a greater tendency to form carbon than cobalt catalysts.

The problem of using iron catalysts for the synthesis of hydrocarbons has been discussed. It all was conceived through the efforts of Dr. Fischer and his previous work.

The developments which I have told you about today on the iron middle-pressure synthesis are the result of the last 4 years of research. We have succeeded in raising the yield two- to three-fold as compared to the earlier experiments with cobalt, and we have succeeded in lengthening the life of the catalysts 10 to 20 times. Hence, the total yield improved 20 to 60 times. We succeeded in the following:

1. We used iron catalysts pretreated with CO.
2. We maintained the synthesis-gas pressure at the same optimum as that of cobalt middle-pressure synthesis, namely, 10 to 20 atmospheres.
3. We used a ratio of $H_2 + CO$ best suited for the synthesis.

At the end of 1937, Dr. Fischer reported to you the developments of iron catalysts. Today, we can say that a great significance is attached to the middle-pressure synthesis with iron. I want to express my thanks to Dr. Fischer who has assisted us with his counsel and advice in all this work. Finally, I want to express my thanks to all my coworkers who have helped in the same effort.