

Kaiser Wilhelm Institute for Coal Research  
Mulheim-Ruhr

Lecture and Discussion on Iron Catalysts for the Middle-Pressure Synthesis  
by

Dr. H. Pichler with a preface by Director Franz Fischer  
Mulheim-Ruhr, September 9, 1940

(Introduction of the Director to the lecture-discussion on iron catalysts for the middle-pressure synthesis on September 10, 1940)

On May 23 of this year, a lecture was held for the same body of men, and our Dr. Koch spoke on the production of special anti-knock benzines obtained from Kerasin. 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 here about the progress which has been made on this work at the Institute.

Hans Tropsch and myself have been concerned for more than 50 years with the production of gasoline from CO and H<sub>2</sub> by using iron catalysts. At that time, we examined the synthetic products which were obtained on alkalized iron shavings at pressures of 100 atm. 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 have identified a great number of the individual compounds, and we have termed the whole thing, Synthol. In the course of our investigations, we have discovered that iron catalysts have a tendency to give more hydrocarbons when the total pressure decreased. After we finally were able then to develop catalysts which would permit working at ordinary pressures and lower temperatures, since they differed from the alkalized iron catalysts by having a much higher activity, it could be demonstrated that almost exclusively hydrocarbons were obtained. 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. All three showed that they could be used for the synthesis. However, cobalt gave the best results. When I finally came to the decision many years later to investigate the Kerasin synthesis in the region between ordinary pressures and low temperatures and the region in which the synthol forms, namely over 100 atm. and higher temperatures, 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 Kerasin to Synthol. Instead we found that between 1 and 20 atm. pressure and at low temperatures using active catalysts, a mixed yield of solid paraffins could be obtained. At the same time, a maximum yield of total hydrocarbons resulted and the catalyst had its maximum lifetime. It was only natural that we wanted to see whether our experiences gained with cobalt also applied to nickel and iron. Nickel, however, had to be discounted because at the higher pressure and the higher temperature which are necessary for the synthesis it is being carried out of 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 lifetime of the catalyst was prolonged. About that, Dr. Pichler will report himself.

It is obvious that the further development of the Kogasin synthesis has to proceed over iron catalysts, that is, if the same yields can be expected than with cobalt, and if the lifetime of the iron catalyst is comparable to that of the cobalt catalyst.

This demand has not only been met, but has been surpassed. At least the same yields can be obtained as are with cobalt catalysts. The lifetime of the iron catalysts is a multiple of that of the cobalt catalysts. The lifetime of a year working at the highest capacity may easily be obtained, but on account of the cheapness, recovery, and regeneration of such catalysts is not even necessary any longer. The iron catalysts work at somewhat higher temperatures than the cobalt catalysts which call for stronger pressure vessels and thicker wall thicknesses of the apparatus than is required for the middle-pressure synthesis with cobalt. Against that, however, we have to take into account that the steam produced has a higher pressure and has 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 as is required for iron catalysts is just as easily produced as a 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 + H<sub>2</sub>, but also for mixtures of CO<sub>2</sub> + H<sub>2</sub>.

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

Lecture-Discussion  
The Middle-Pressure Synthesis with Iron Catalysts

Part I. Introduction

After we had recognized that the middle-pressure synthesis with cobalt catalysts had improved the yield of hydrocarbons and the lifetime of the catalysts as compared with the normal pressure synthesis, the question was asked whether the cobalt, which is hard to get in Germany, may be replaced by iron and if we still may expect 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 such catalysts which could do the work as well as cobalt and thorium and would be cheaper than those two metals. In 1923, Fischer and Tropisch passed water-gas over alkalized iron shavings at pressures of around 100 atm., and temperatures of 350-450°C. They observed the formation of oxygen containing organic compounds which they termed Synthol. Similar experiments of the Badischen Anilin- und Sodafabrik which date back to the year 1913, and where they used similar pressures and temperatures led to the synthesis of methanol in 1925. Fischer and Zerbe (4) also demonstrated, in 1923, that alkalized iron shavings used as catalysts at pressures below 100 atm. favored the formation of hydrocarbons, and suppressed that of oxygen containing compounds.

In 1926, Fischer and Tropisch report in their first publication on the petroleum synthesis that liquid hydrocarbons may be produced with iron catalysts from the CO and H<sub>2</sub> when working at temperatures of around 300°C. and above. On the basis of those experiments, we have tried in the past years over and over to change the

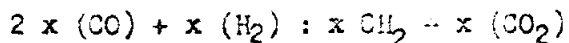
composition of the iron catalysts such as to increase the activity and thus lower the reaction temperature for the synthesis and improve the yield of liquid hydrocarbons. In 1928, we succeeded in obtaining 30 to 40 g. of benzene and oil per cubic meter of water-gas. The temperatures could be lowered to 240-250°C. The lifetime of the catalysts, however, was only a few days.

Fischer and Tropsch<sup>7/</sup> tried in 1927 to convert water-gas at 10-15 atm. and at 250-280°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<sup>3/</sup> reports in the lecture on the benzene synthesis, that at atmospheric pressure and the use of an iron catalyst, only 30-35 grams per cubic meter of mixed gas were obtained. (This corresponds to 40-45 grams per normal cubic meter of inert-free CO-H<sub>2</sub> mixture). Fischer added at that time, that the above yield cited, decreased by 20 percent within eight days.

Fischer and Meyer<sup>2/</sup> 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, 50-60 grams per cubic meter of gas were obtained with a maximum lifetime of the catalyst of 4 - 6 weeks.

Fischer and Ackermann<sup>10/</sup>, 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  $1CO + 2H_2$ , although one had 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  $2CO + 1H_2$  is used, the CO is converted only partly and a decrease in catalyst activity occurs quite rapidly.

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

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

We have succeeded to compound iron catalysts which will convert practically all of the CO-H<sub>2</sub> mixture at only slightly raised pressures over very long periods of time. Depending on working conditions, various 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 of the cobalt middle-pressure synthesis. Therefore, we were justified to consider the substitution of cobalt by iron. 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 benzine synthesis in order for them to check our results in their laboratories. Our researches, however, have been carried on, and especially a lot of work has 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 the year 1937 have been made under Ruhr-Chemie 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 about today will not be entirely new to you. However, since the development of the iron catalysts is one of such great importance, it seems desirable to have a discussion on the entire problem with you.

## Part II. The Catalyst

### A. Precipitation of the 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 alkalized, and dried.

After having been dried properly, the catalysts appeared black-brown or black.

It was desired to give sufficient rigidity to the catalysts. However, it was believed that pelleting would effect the activity. Therefore, certain precautions have to be taken during pelleting to prevent this. Pelleting will not be discussed here.

Furthermore, I shall limit myself to the discussion of pure iron catalysts only, or perhaps such catalysts which contain small additions of alkali. These are the catalysts which 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 ferri 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 pre-neutralize the iron solution in the cold, since without pre-neutralization on application of heat, or on standing for longer periods of time, insoluble salts precipitate out of the solution, which influence the reproducibility of a good catalyst considerably. Second, it is important to bring the iron precipitate to a boil prior to being filtered. This improves the activity and the lifetime of the catalyst.

### B. Pre-treatment of the Catalyst

The freshly precipitated and dried iron precipitate is entirely inactive as far as the conversion of CO and H<sub>2</sub> to hydrocarbons is concerned. In this respect, it is comparable directly to the non-reduced cobalt catalyst which is inactive too. 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 pretreating with hydrogen. For example, the trivalent iron is converted into  $Fe_3O_4$  when pretreated by hydrogen at 300-400°C. This  $Fe_3O_4$  is not in a position to catalyze the reaction between CO and  $H_2$ . However, if the iron catalyst is pretreated at certain working conditions by CO, the catalyst may be activated sufficiently to catalyze the synthesis. (Depending on the temperature, pretreatment with CO causes more or less the 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 "Forrierung" (induction).

1. Induction with mixtures of CO and  $H_2$  during the 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.

a. Experiments at atmospheric pressure.

Once more, let us recall the working conditions under atmospheric pressure. Fig. No. 1 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  $1CO + 2H_2$ , under atmospheric pressure, than 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% within 3 to 4 days. This time during which the catalyst by the action of the synthesis gas gradually acquires its activity, corresponds to the induction time (Figure 1, curve 1). For approximately 3 to 4 weeks, this catalyst induced 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- $H_2$  mixture which more nearly corresponds to the ratio in which the CO and  $H_2$  are used up during the reaction. How are the relationships then? Curves 2 to 4, Figure 1, show the results. It is seen from those curves that no improvement results; however, that the conversion is impaired. On using a CO-rich gas ( $3CO + 2H_2$ ) the contraction reached a value of 31 percent after operating for three days at 235°C. (Curve 2), when the temperature was 245°C., the contraction obtained was 36 percent after one day operation (Curve 3). When the operating temperature was 255°C., the percent contraction was only 33 percent after one day of 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 when it had to work with CO-rich gas under atmospheric pressure.

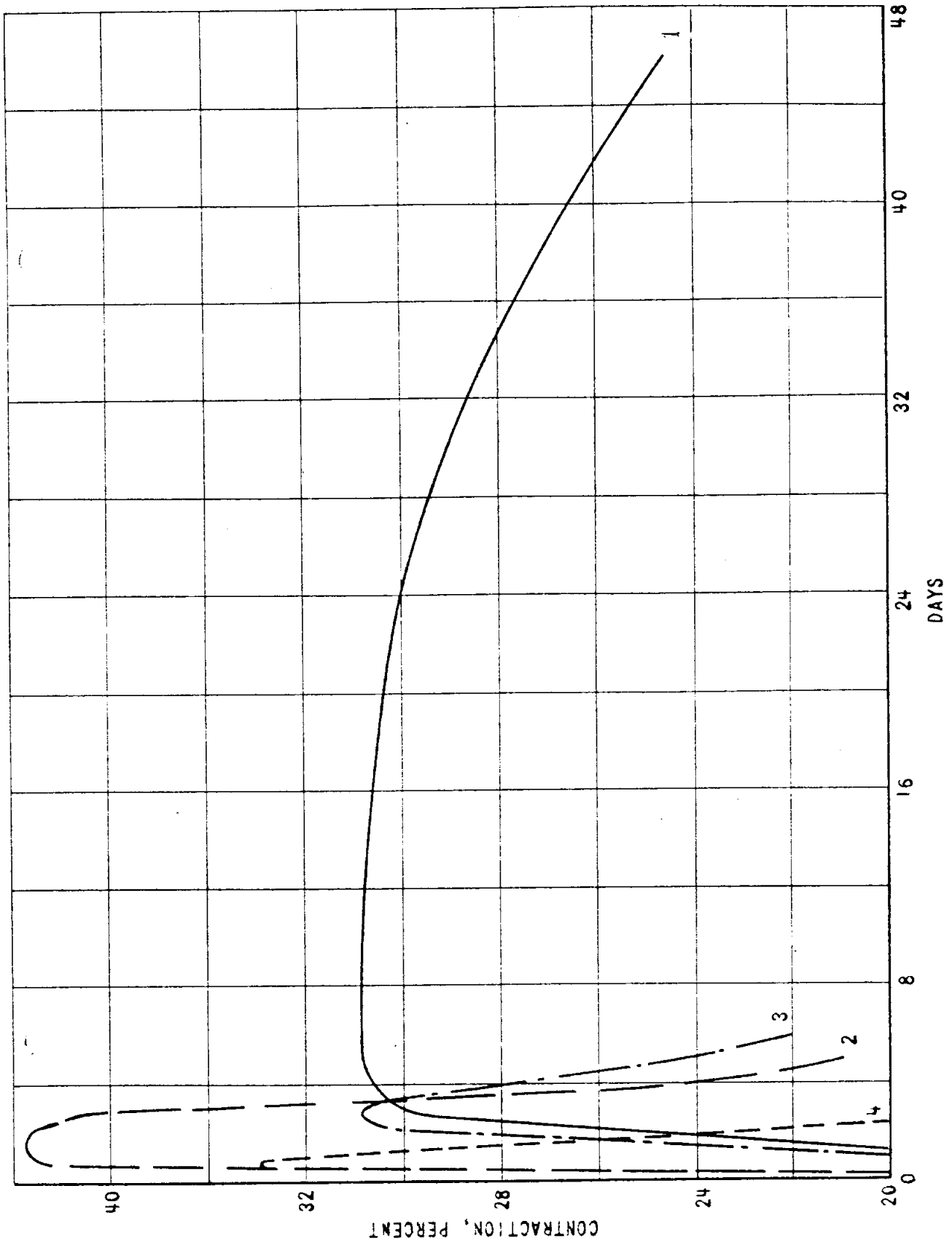


Figure 1. - Experiments at atmospheric pressure (decrease of contraction with duration of operation when various CO-H<sub>2</sub> mixtures are employed).

b. CO-rich gas and elevated pressure.

Table I brings the result of a run during which a normal iron catalyst was permitted to work for five months without interruption in the presence of CO-rich synthesis gas ( $3CO + 2H_2$ ). The catalyst was given no previous induction. The working pressure was 15 atmospheres. The gas velocity was 4 liters of synthesis gas referred to one atmospheric pressure per 10 grams of iron catalyst.

Table I.- Induction and Synthesis at a Pressure of 15 atm.

Days	Temp., °C.	Con- trac- tion, percent	Days	Temp., °C.	Con- trac- tion, 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			

At 245°C., and after one day of operation, the contraction was 4%, after 4 days the contraction 10% (as compared to 30-35% for the same time of operation at one atm. pressure). The temperature was gradually raised, and the increase of the contraction was observed. On the eleventh day, 24% contraction was observed at 260°C. An increase in temperature to 270°C. did not, at first, cause the yield to go up. At 270°C., 37% was observed, and at 280°C., 36%. Only when 290°C. was reached, did the contraction go up to 50%, which corresponded to a complete conversion of the CO to hydrocarbons and  $CO_2$ . Next we tried whether this conversion (50%) could be maintained if the temperature would be lowered. At 268°C., the contraction decreased to 37%. At 280°C., however, and in the third month of operation, a better degree of conversion was obtained than after one month. In the meantime, a slow induction of the catalyst had taken place. During the 4th and 5th month of operation the temperature had been increased again in order to keep the contraction between 40 and 50%. After five months operation, it was 300°C.

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

As compared to operations under atmospheric pressure, the 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 atm. 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 lifetime of the catalyst was still too small.

## 2. Induction of the Catalyst by a Separate Process Preceding the Actual Synthesis.

It was attempted to find out whether an increase in activity could be obtained by carrying through the induction in a step separate from the synthesis step. That is, for each induction and synthesis, the optimum conditions were to be found.

### a. Induction at ordinary pressure and synthesis at higher pressure.

Table II gives the result of an experiment which was carried through during the induction period with mixed gas at atmospheric pressure and 245°C.

Table II.- Induction at 1 Atm. Pressure, and Synthesis at 15 Atm.

Days	Pressure, atm.	Temp., °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 five days of operation, the contraction had reached a maximum value of 31 percent, we shifted to CO-rich synthesis gas at 15 atm. pressure. The contraction increased immediately from 31 to 55 percent. In order to obtain the highest yields and correspondingly the highest values of contraction (approximately 50%), 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 having been inducted at ordinary pressure and was used immediately at 15 atm. for the synthesis, it is clearly shown that the preliminary induction causes the synthesis temperature to be lower (approximately 30 to 40°C.). The increase in activity which resulted from carrying through the induction at the low pressure of one atm. remained intact for the whole duration of the experiment.

### b. 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 III. The induction was carried through at 255°C. for 20 hours with 4 liters of CO-rich gas (referred to one atmosphere per hour for 10 g. of iron) of composition  $3CO + 2H_2$ . Next we shifted



to the synthesis itself. Four liters per hour of  $\text{CO} + 2\text{H}_2$  per 10 g. of iron were used at atmospheric pressure for 1-1/2 hours at a temperature of  $255^\circ\text{C}$ .

Table III,  
Influence of the Induction Pressure  
Upon the Synthesis at One Atmosphere

Induction pressure, atms.	Synthesis Contraction, percent
9	5
3	12
1	28
0.1	30

The experiments show again that elevated pressures impede the process of induction. After induction at 9 atms., the contraction amounted to 5 percent, after an induction at 3 atms., 12 percent contraction was obtained, and after inducing the catalyst at one atm., 28 percent contraction was reached and 30 percent contraction resulted from a catalyst having been inducted at 0.1 atm.

c. Influence of the Induction Temperature Upon the Progress of the Synthesis.

After we had found out that a low pressure of induction favors the increase of the activity of iron catalysts, normal iron catalysts were inducted at 1/10 atms. with a  $\text{CO}$ -rich gas at different temperatures. The induction lasted for 25 hours, and the range of temperatures worked in was  $250$ - $350^\circ\text{C}$ . Then the catalysts were tested by acting on a gas of composition  $3\text{CO} + 2\text{H}_2$  at 15 atm., and  $235^\circ\text{C}$ . (4 liters of gas per 10 g. of iron per hour). (See Figure 2)

When the catalyst was inducted at  $255^\circ\text{C}$ ., the contraction decreased already below a value of 50 percent during the third day of operation, when the catalyst was inducted at higher temperatures, it was found that its lifetime was improved; thus, at an induction temperature of  $315^\circ\text{C}$ ., we could operate for an entire month without falling below 50 percent contraction. When the catalyst was inducted at higher temperatures, the activity decreased again.

Figure 3 shows an analogous series of experiments during which the induction was not carried through with a  $\text{CO-H}_2$  mixture, however, instead with pure  $\text{CO}$ .

When the catalyst was inducted with  $\text{CO}$  at 1/10 atm. and  $325^\circ\text{C}$ ., the conversion during the following synthesis remained constant for 4 months (at a temperature of  $235^\circ\text{C}$ ., and a pressure of 15 atm.). Hence the results obtained by carrying through the induction with  $\text{CO}$  are even better than those with  $\text{CO-H}_2$  mixtures.

3. The Influence of the Induction Upon the Synthesis Temperature.

Figure 4 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  $\text{CO} + \text{H}_2$  in the ratio, 3:2 (4 liters per 10 g. of iron per hour).

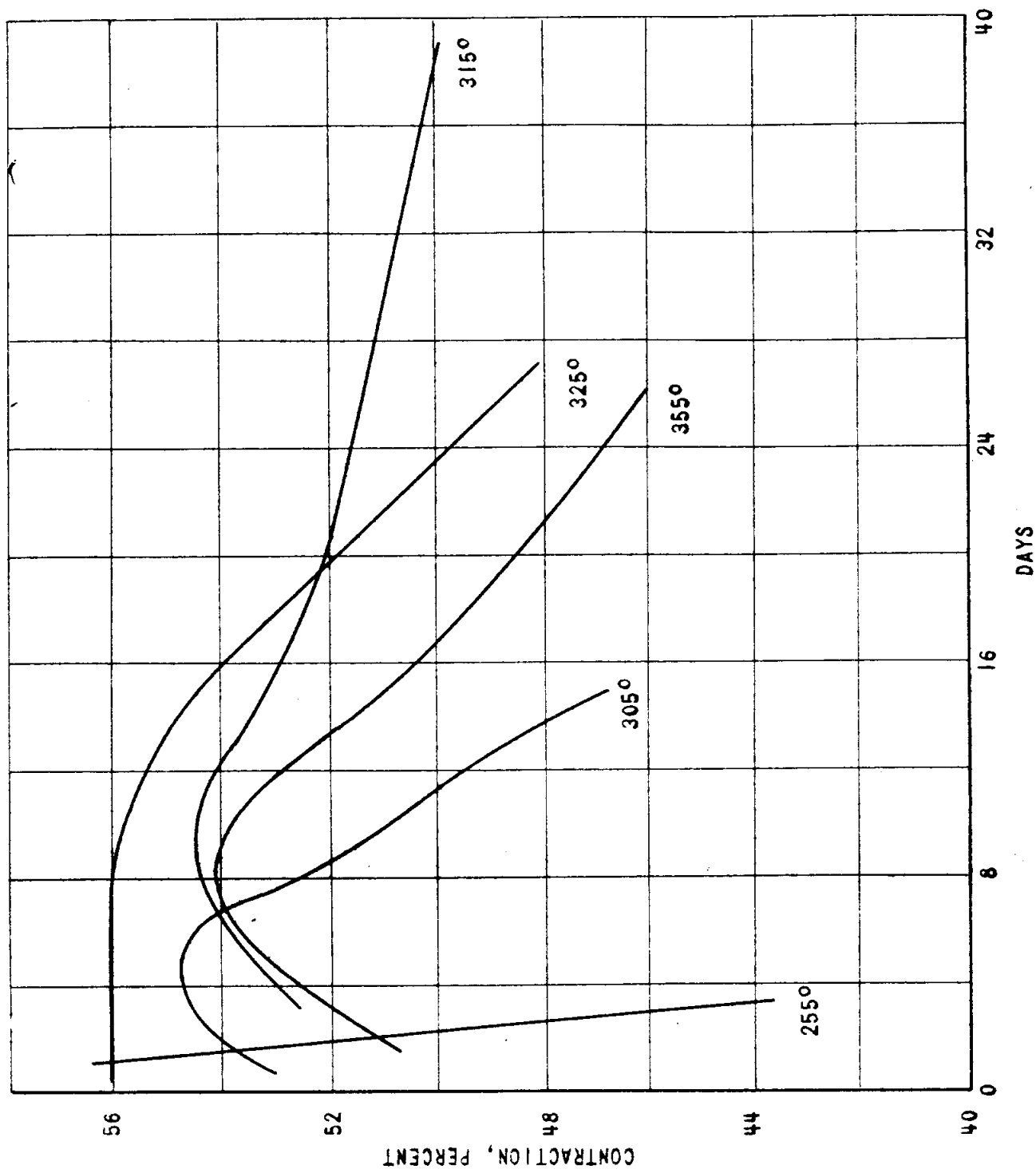


Figure 2. - Influence of induction temperatures of the catalyst upon the course of the synthesis (decrease of contraction with time of operation at 15 atmospheres and 2350 C.). Induction was carried out with a CO-rich synthesis gas at 1/10 atmosphere.

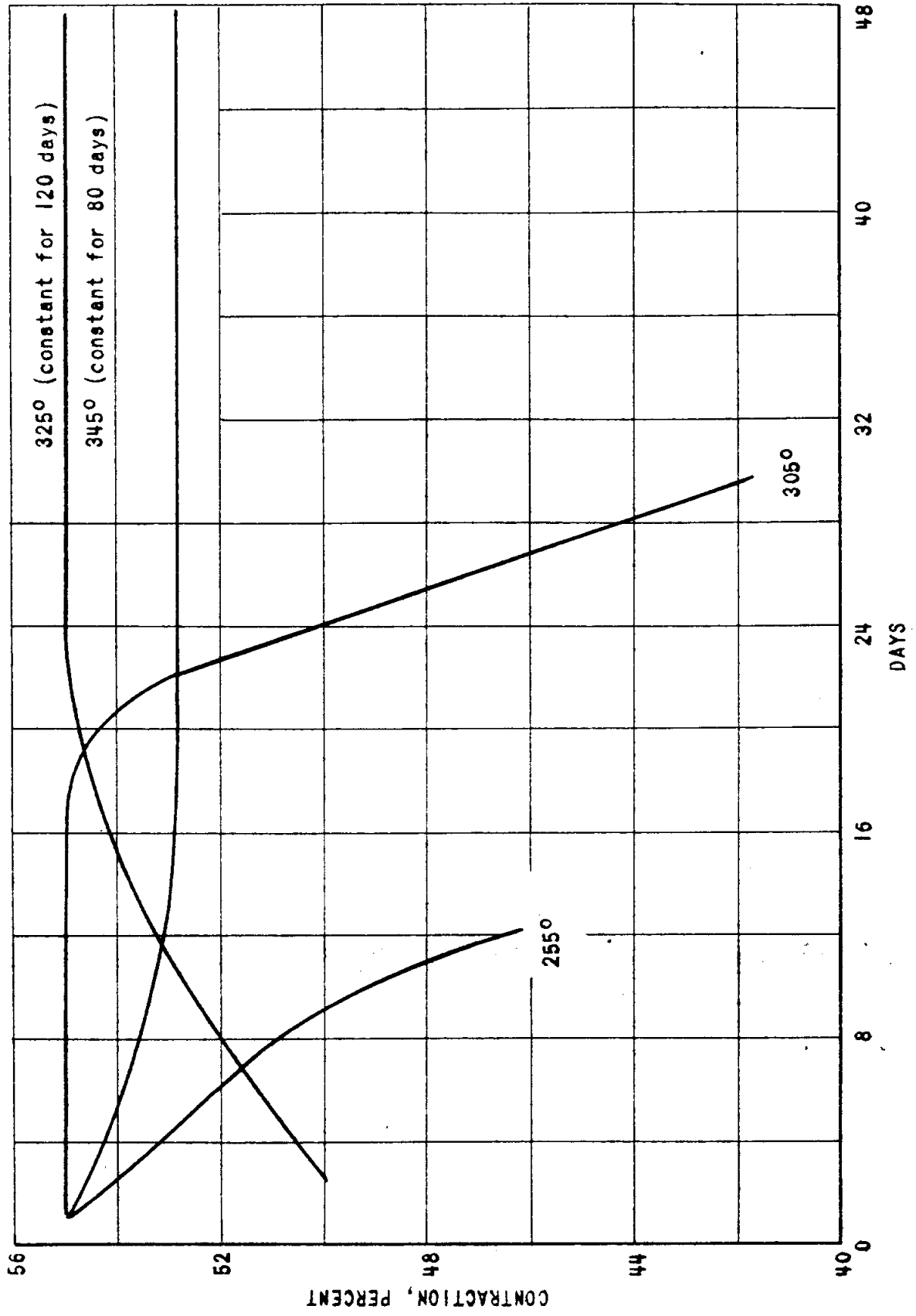


Figure 3. - Influence of the Induction temperature upon the course of the synthesis after an induction with CO at 1/10 atmosphere.

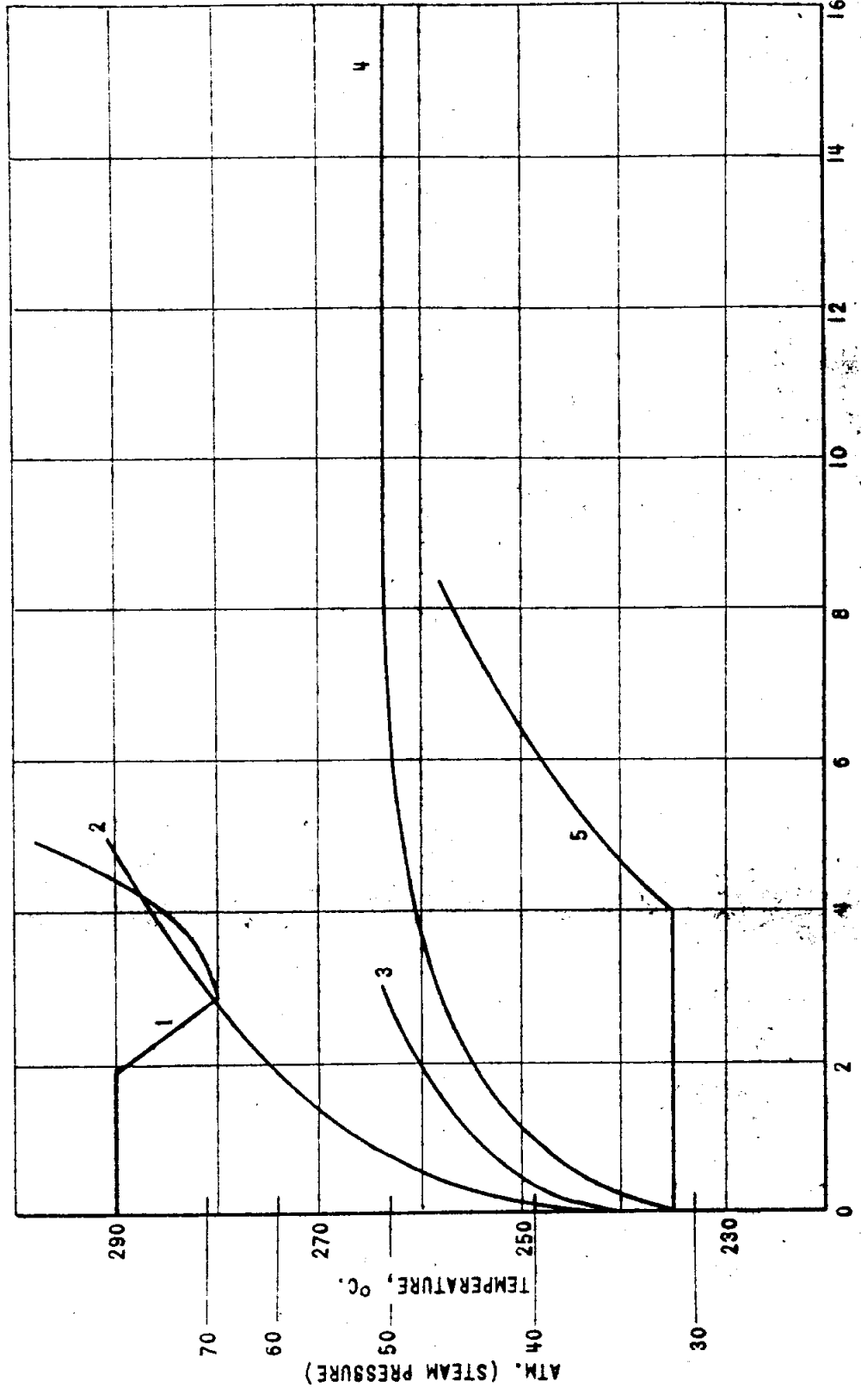


Figure 4. - Influence of induction upon the synthesis temperature.

Curve 1, refers to a catalyst which had not undergone induction but had been used directly for the synthesis at atmospheric pressure. In order 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 two months of operating, 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 one atm., and 240°C. (30% contraction), then the operation was switched over to 15 atm. pressure. In order 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 atm. pressure and 245°C., and was then used for the synthesis at 15 atm. (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 atm., and 255°C. This experiment still showed a contraction of 50 percent after 15 months of operation at 260°C.

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

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.

#### a. Time of Induction.

Not only pressure and temperature of the induction are important, however, the velocity with which the CO passes over the catalyst seems to be important too. Reductions and carbonizing processes occur during the induction which are responsible for the formation of CO<sub>2</sub>. Therefore, the progress of the induction can be judged by the formation of CO<sub>2</sub>. The induction is terminated when the CO<sub>2</sub> obtained has passed through a maximum and has reached a more or less constant minimum value (Figure 5). Any further formation of CO<sub>2</sub> 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 it does 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 following synthesis. Furthermore, it is advantageous to work with pure CO and at high gas velocities. During the induction process, equilibria between the solid phases adjust themselves. They depend on the composition of

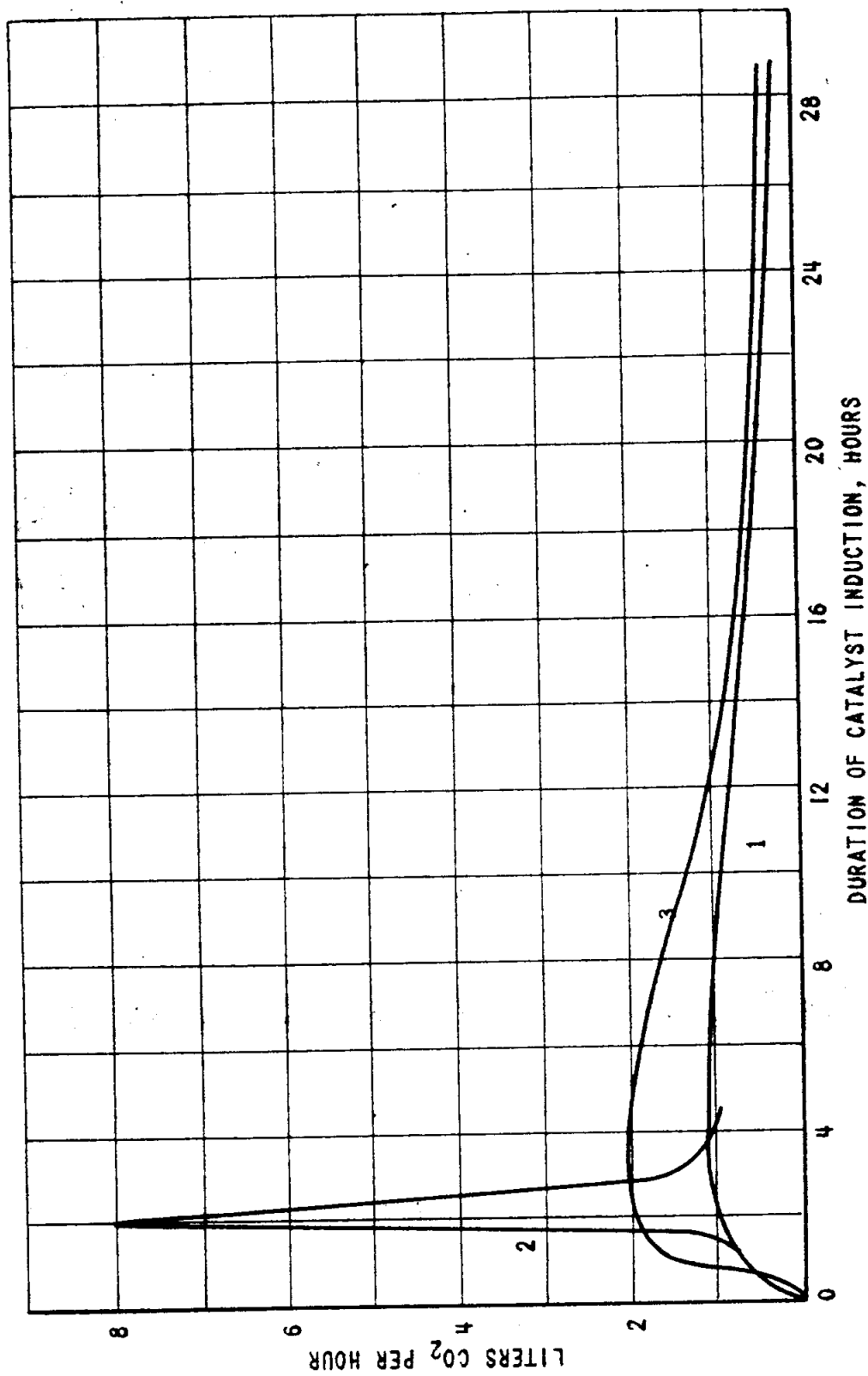


Figure 5. - CO<sub>2</sub> formation during the induction process.

the gas phase. If the  $\text{CO}_2$  content in the gas phase is kept low, the reduction of the iron oxide and the formation of carbides is favorable. This might be one way to explain the advantageous low induction pressures at high gas velocities.

Experiments are in the process of being studied dealing 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 which will permit us to obtain faster methods of determining the activity of the catalyst.

### Part III. The Synthesis

#### A. The Synthesis Gas.

The optimum synthesis gas composition is theoretically that which corresponds to the ratio in which CO and  $\text{H}_2$  are used up. It is assumed that the catalyst has a sufficiently long lifetime when it is used for such a theoretical mixture. The composition of such a theoretical mixture depends chiefly on the quantities of  $\text{CO}_2$  and water which are formed during the reaction.

Figure 6, shows for 0 and 15 atm., the portion of CO-oxygen which at various synthesis gas compositions is converted to water and  $\text{CO}_2$ . At a content of 30 percent of CO in the starting gas, 7 percent of the CO-oxygen are converted into water at one atmosphere pressure and 25 percent at 15 atmospheres. With 60 percent of CO in the starting gas and one atmosphere pressure, the conversion goes only to  $\text{CO}_2$ , whereas, at 15 atm. still 4 percent of the CO-oxygen goes to water. Not only higher pressures but also higher hydrogen contents in the synthesis gas favors the formation of water.

Figure 7a and 7 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  $\text{CO}_2$  formation. The dot-point curves show the corresponding yields when water formation is taken into consideration. The solid curves show the actually obtained yields (5-week average). Theoretically 208 g. of hydrocarbons may be obtained with or without formation of water for every normal cubic meter of synthesis gas. At atmospheric pressure, in taking into consideration the formation of  $\text{CO}_2$  and water, the theoretical optimum gas composition lies near a ratio of  $2\text{CO} + \text{H}_2$ , at 15 atm. at 1.85 CO to  $\text{H}_2$ .

The fundamental difference between the synthesis at one atmosphere and 15 atmospheres consists in 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 one atmosphere pressure, a gas of composition  $\text{CO} + 2\text{H}_2$  gives the best results. For the first 4 weeks of operation it gave an average of about 60 g. of solid liquid and gasol hydrocarbons. These yields, however, decreased rapidly during the 5th and 6th weeks of operation. At 15 atmospheres pressure, however, a yield of 150 g. was obtained for many months.