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

TABLE OF CONTENTS

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(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 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 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_2 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 too 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 Kogasin 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 Kogasin to Synthol. Instead we found that between 4 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 than 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 $CO + H_2$, but also for mixtures of $CO_2 + H_2$.

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 Tropsch 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 Tropsch report in their first publication on the petroleum synthesis that liquid hydrocarbons may be produced with iron catalysts from the CO and H_2 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 benzine 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[7] 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[8] reports in the lecture on the benzine 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_2 mixture). Fischer added at that time, that the above yield cited, decreased by 20 percent within eight days.

Fischer and Meyer[9] 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[10] 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

$$2 \times (CO) + x (H_2) : x CH_2 + x (CO_2)$$
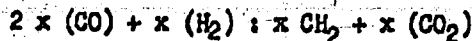
However, when a synthesis gas of 2CO + 1H_2 is used, the CO is converted only partly and a decrease in catalyst activity occurs quite rapidly.

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_2 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. These 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. Pretreatment of the Catalyst.

The freshly precipitated and dried iron precipitate is entirely inactive as far as the conversion of CO and H_2 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 catalyst 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 "Formierung" (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 38 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.

b. <u>CO-rich gas and elevated pressure.</u>

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.

<u>Table I.- Induction and Synthesis at a Pressure of 15 atm.</u>

Days	Temp., °C.	Contraction, percent	Days	Temp., °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			

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 $245^{\circ}C$.

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

Days	Pressure, Atm.	Temp., $^{\circ}C$.	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 $265^{\circ}C$.

When one compares the results of those 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 $40^{\circ}C$.). 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 $255^{\circ}C$. 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 1CO + 2H₂ per 10 g. or iron were used at atmospheric pressure for 1-1/2 hours at a temperature of 255°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 atmos., 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 CO-rich gas at different temperatures. The induction lasted for 25 hours, and the range of temperatures worked in was 250-350°C. Then the catalysts were tested by acting on a gas of composition 3CO +2H₂ at 15 atm., and 235°C. (4 liters of gas per 10 g. of iron per hour).

When the catalyst was inducted at 255°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°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 CO-H₂ mixture, however, instead with pure CO.

When the catalyst was inducted with CO at 1/10 atm. 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 atm.). Hence the results obtained by carrying through the induction with CO are even better than those with CO-H₂ 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 CO + H₂ in the ratio, 3:2 (4 liters per 10 g. of iron per hour).

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 atmos., 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 16 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_2. Therefore, the progress of the induction can be judged by the formation of CO_2. The induction is terminated when the CO_2 obtained has passed through a maximum and has reached a more or less constant minimum value (Figure 5). Any further formation of CO_2 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

the gas phase. If the 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 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 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 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 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 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 (4-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 CO_2 and water, the theoretical optimum gas composition lies near a ratio of $2CO + 1H_2$, at 15 atm. at 1.85 CO to $1H_2$.

The fundamental difference between the synthesis at one atmosphere and 15 atmospheres consists in that one cannot work at atmospheric pressure with the theoretical $CO:H_2$ 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 $1CO + 2H_2$ 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.

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 occasion let us mention something about the production of synthesis gas. In the Institute, this gas mixture was generated in a normal gas generator. We conducted CO_2 and steam over hot coke. Such a process could even 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 the production of the synthesis gas. From one cubic meter of synthesis gas with a ratio of $3CO:2H_2$, normally 250 liters of CO_2 are obtained, whereas according to $5C + 4H_2O + CO_2$ is equal to $6CO + 4H_2$ only 100 liters of CO_2 are required per cubic meter of CO-rich gas. Already a partial scrubbing of the CO_2 from the end-gas and addition of same to the gas generator could account for all the CO_2 needs of the generator.

The carbon requirement demanded 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 the purification of the gas is taking place in the Institute already for years at the production rate of 100 cubic meters per hour. If one would work off 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 along with the addition of oxygen. It is unnecessary to elaborate on this.

5. The 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 IV brings some comparative experiments for which the synthesis was undertaken 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 atm., and $325°C$. with a CO-rich synthesis gas. Table IV 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 IV.- Reaction and Contraction at Various Temperatures
(The normal iron catalysts were inducted with
CO-rich gas at 235°C., and 1/10 atmosphere)

Days of operation	5 atm.		10 atm.		30 atm.		60 atm.	
	Temperature, °C.	Contraction, percent	Temperature, °C.	Contraction, percent	Temperature, °C.	Contraction, percent	Temperature, °C.	Contraction, 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 atm. the contraction amounted to 30 - 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 atm. a 50 percent contraction was reached at 235°C. This was the case also when working with 30 and 60 atms. However, when working at 30 atm. and 235°C. already after the third day, a considerable decrease in the amount of conversion occurred. For the 60 atm. 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).

C. The Reaction Temperature.

Special attention was given the reaction temperature. We attempted to succeed with a lower reaction temperature in connection with iron catalysts to be used in the middle-pressure synthesis. This no only was important from a chemical viewpoint but economical as well. On the 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. This will cheapen the equipment materially.

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

The influence of the gas composition is such that H_2-rich gases permit a lower working temperature than the CO-rich gases.

For example, an experiment performed with a H_2-rich synthesis gas of composition 1CO + 2H_2 still yielded 47 percent contraction at a temperature of 184°C. after the second day of operation. The usage ratio of CO and H_2 pointed towards the formation of hydrocarbons and water. At those 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 any longer. It is more favorable to initiate the experiment at the high temperatures from the beginning.

With a gas containing $CO + H_2$ 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 g. per normal cubic meter of gas. The liquid and solid products obtained were entirely colorless. Essentially larger yields may not be obtained on iron catalysts when using such a gas.

When we used the CO-rich gas, we initiated the experiment usually 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 would have operated at 210 to 220°C.

The temperature of the reaction exerts an essential influence upon the nature of the reaction products. Table V shows average yields which were obtained from iron catalysts carrying 1/4 percent of potassium carbonate and operating at 235, 275, and 280°C. The yield of solid paraffins amounted to 39 g. per normal cubic meter of gas for 235°C. and only 4 g. 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 V.- Nature of the Reaction Products for Various Temperatures

Reaction Temperature, °C.	Yields, g. per normal cubic meter of ideal gas		
	Solid Paraffin	Liquid Hydrocarbons	Gasol
235	39	83	26
270	4	94	46
280	2	82	35

D. The Influence of the Alkali Contents on the Iron Catalysts.

The method of production of the catalyst has been discussed at the beginning. The following table shows what influence the addition of alkali to the catalyst has upon the catalyst.

Precipitant	Alkali addition		Solid and Liquid and Gasol HC g. Nm^3 of synthesis gas	Paraffin percent	Liquid HC percent	Gasol percent
NH$_3$	0		141	12	67	21
Na$_2$CO$_3$	0		140	13	67	20
"	1/4%	K$_2$CO$_3$	148	26	56	18
Na$_2$CO$_3$	1%	K$_2$CO$_3$	157	42	47	11
"	1%	KMnO$_4$	155	41	45	14
"	1%	K$_2$SiO$_3$	158	43	41	16
"	1%	K$_2$F$_2$	163	46	42	12
"	1%	K$_2$HPO$_4$	154	38	52	10
Na$_2$CO$_3$	2%	K$_2$CO$_3$	143	43	44	13
"	5%	"	161	45	43	12
"	5%	"	155	46	44	10

The indicated quantities of potassium carbonate added to the catalyst are based on the iron metal contents. In the case of the other alkalized salts (permanganate, fluorides, etc.) the notation "1% KMnO$_4$" is to indicate that such a quantity was used which would be equivalent to one percent K$_2$CO$_3$.

Table VI shows the yield and nature of the reaction products which were obtained from catalysts containing different amounts of alkali. The temperature was 235°C. and the pressure 15 atm. The yields indicated as g. per Nm^3 of ideal gas are not quite constant for the first month of operation. This is due to the 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 yield as such. The alkali-free catalyst precipitated with ammonia showed yields which were not essentially below those obtained from catalysts containing 1/4 percent K$_2$CO$_3$. The alkali contents of the catalyst, however, has a very marked influence upon the nature of the reaction products. When no alkali was present, the Butanon method revealed approximately 12 percent of paraffins in the product. When 1/4 percent potassium carbonate was added to the catalyst the paraffins amounted to 26 percent, with one percent potassium carbonate the products contained 42 percent of paraffins, with two 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 VI shows furthermore that the quantity and the nature of the reaction products was not effected by the type of alkaline salt added to the catalyst. No essential difference was discovered when the catalyst was alkalized by one percent potassium carbonate or the equivalent quantities of potassium permanganate, potassium silicate, potassium fluorides, or potassium phosphate.

The lifetime of the catalyst is longer at a low alkali content (for example, 1% K$_2$CO$_3$) than it is at higher alkali contents.

E. Treatment of the Catalyst with Hydrogen.

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

The treatment with hydrogen, however, has a different result if it is carried out on an iron catalyst during the synthesis. The situation is 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 atm. and 4 liters of CO-rich gas per hour). We allowed this catalyst to work at 235°C. During the first and second days of the operation, we observed a contraction of 52 percent (see Figure 8). After the second day, the contraction was 50 percent, and after three days, 47 percent. From the dotted curve, Figure 8, 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 one atmosphere and 325°C. After this hydrogen treatment, the catalyst caused a contraction of 55 percent in the following synthesis. It slowly decreased thereafter, however it remained above 51 percent up to the 12th day. On the 12th day, the same hydrogen treatment as 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, 52 percent. When the synthesis was continued for two months thereafter at the temperature of 235°C., the contraction remained near 50 to 53 percent.

Figure 8 shows that an increase in catalyst activity results when the synthesis is interrupted and a hydrogen treatment is performed. This increase in activity was especially pronounced during the first few hours of the hydrogen treatment, and it also caused a better stability of the catalyst thereafter. When the activity of the catalyst was at a maximum after the hydrogen treatment, the usage ratio of CO and H_2 was no different from that of the normal synthesis occurring with 50 to 52 percent contraction. In both cases CO and H_2 were used up in the ratio 1.67-1.70:1. It is, therefore, noticeable that no carbon formation occurred during the time of optimum activity of the catalyst.

Iron catalysts which had been used for a long time already or which had decreased in activity to a great extent did not show a lasting improvement when treated with hydrogen. A lasting improvement may not be obtained even if another induction is given with CO. If it is desired to perform a hydrogen treatment, and if it is expected that the hydrogen pretreatment produces good results, the catalyst must be subjected to hydrogen before it gives as low a contraction as 45-50%.

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

F. The Effect of Addition of Kieselguhr.

We have discussed the effect which alkali has when added to the catalyst; let us shortly mention the effect of Kieselguhr when mixed into the catalyst. It is well known that Kieselguhr is an essential carrier with cobalt catalysts. Good yields are only obtained with cobalt catalysts 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.

G. The Construction of the Apparatus.

The discussed time-tests were carried out in horizontal respectively, slightly tilted reaction tubes. A slight expansion of the catalyst may thus take place due to carbon deposition without any serious dangers of causing damages. (Fig. 9, Schematic Drawing 1). If the reaction tube is in a vertical position, the expansion of the catalyst causes a restriction between the catalyst granules and hence a shortening of the contact time of the gases passing over it. (Fig. 9, Schematic Drawing 2). In order to eliminate any possible disturbances from the viewpoint of construction, we are still in the process of carrying out experiments dealing with this subject. According to Figure 9, Schematic Drawing 2, (at a gas rate of 4 liters of synthesis gas per hour and 10 b. or iron), the space-time yield is approximately twice that of a normal cobalt-Kieselguhr catalyst. The apparatus is cooled by water and has to stand a pressure of 50-60 atm. (See Figure 4) If salt solutions would be used instead of water, the necessary steam pressures could be reduced somewhat.

Part IV

The Products of Reaction

When the iron catalyst is used in the middle-pressure synthesis, paraffin and olefin hydrocarbons of various 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 as well, products something similar to the Synthol having been described by Fischer and Tropsch several years ago.

A. Liquid Hydrocarbons.

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

The quantity of the fraction boiling up to 180°C., in other words, the benzine fraction (slightly different in each case depending on working conditions varies in amount according to working conditions) may amount to 80 percent, or 40 percent or even less than that as referred to the total liquid and solid hydrocarbons produced.

Table VII shows the properties of the stabilized benzine washed with sodium hydroxide. Its knocking properties were determined in the I.G. testing engine. Approximately 2/3 of the total liquid product boiled in the range of 30-180°C. Table VII, No. 1, corresponds to the primary benzine. Its octane number is 61.

<div align="center">Table VII.</div>

Properties of the Benzine Obtained in the Middle-Pressure Synthesis with Iron Catalysts (with and without additional polymerization)

| No. | $d_{15°}$ | Olefins percent. | Boiling Characteristics | | | | $p_{37.8°}$ | Octane No. |
			0 °C.	10% °C.	50% °C.	90% °C.		
1	.696	64	30	46	88	145	0.54	61
2	.705	65	32	53	100	150	0.48	77
3	.700	65	34	60	95	130	0.55	71

The two benzines listed under 2 and 3 are only shortly mentioned here. During the synthesis, the total end-gas (that includes the CO_2) was conducted over a phosphoric catalyst at 15 atm. pressure. The unsaturated hydrocarbons contained in the gas furnished primary polymer benzine, which was mixed in with the primary benzine. Such mixed benzine boiling up to 180°C. had an octane number, 67 (Benzine 2). If the distillation was interrupted at 150, the octane number was only 71 (Benzine 3). If 0.7 cc. lead tetra-ethyl per liter were mixed into Benzine 2, its octane number improved to 79, if the same quantity of lead tetra-ethyl was added to Benzine 3, its activity went up to 83.

If the benzine is not subjected to washing with sodium hydroxide a higher octane number is obtained too in the primary benzine. If washing is not carried out with sodium hydroxide, acid constituents are left in the benzine in addition to water soluble oxygen containing organic compounds such as alcohols. The high contents of unsaturated hydrocarbons is very favorable for the antiknock properties of the benzine. 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.

B. Paraffin

The solid and liquid products of the liquid according to the Butanon 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 alkalized catalyst up to one or more percent potassium carbonate catalyst is 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 point of the paraffins range over the whole region of the known paraffin hydrocarbons. The so-called contact paraffin which remains behind in the catalyst contains constituents having an especially high melting point.

The usefulness of the paraffins is very great. 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 which are obtained from iron catalysts are not as ideal for fatty acid production as used in the soap industry as are the paraffins manufactured with cobalt catalysts. In order 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".

C. Gasol.

Quantity and composition of the gaseous hydrocarbons is also a function of the nature of the catalyst, and the reaction temperature. Table VIII shows yields of gasol hydrocarbons with their contents 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 in the case of the cobalt catalysts.

Table VIII.- Yields of Gasol Hydrocarbons with Different Catalysts

Catalysts	Temp., °C.	Grams of gasol per Nm³ of gas	Percent of gasol of unsaturated HC
Fe NH₃ precipitated, 0% K₂CO₃	235	30	70
Fe, Na₂CO₃ precipitated 0% K₂CO₃	235	28	80
Fe, " " , 1/4% "	235	26	76
Fe, " " 1% "	235	17	80
Fe, " " 1/4% "	270	46	47
Fe-kieselguhr 1% "	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 contents and with all other conditions remaining the same, the quantity of the gasol produced decreases. With higher reaction temperatures, the quantities of gasol hydrocarbons increased, but their hydrogenation was favored too so that at a temperature of 270°C., the same amount (g_0/Nm^3 of ideal gas) of unsaturated hydrocarbons were obtained, namely, 20 g_0/Nm^3 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 they also form C_2 hydrocarbons. The gases from one experiment were subjected to a low-temperature distillation, and the following constituents were obtained: 11 g_0/Nm^3 of propylene, 6 g_0/Nm^3 of butylene, and 5 g_0/Nm^3 of ethylene. The relatively high yields of unsaturated gasol hydrocarbons are especially favorable if one considers the further processing for high octane benzine.

D. Oxygen-containing Products.

At 235°C. and working with a CO-rich gas at 15 atmospheres, we obtained 13 grams of acqueous 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 aldehydes showed a positive when fuchsine-sulphurous acids were used, and the esters could be demonstrated (saponification)). The acqueous compounds also contain alcohols, such as ethyl and a little methyl alcohol. Figure 10, shows a boiling point 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 micro-column.

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 they were also present in the hydrocarbons. They can be found in the low-boiling as well as the high-boiling fractions. The oxygen determined by analysis varies between 0.2 and 2 percent. The lower-boiling fractions contain more oxygen than the higher-boiling fractions. Alkali-defficient iron catalysts produce only small quantities of oxygen-containing products. More alkalized catalysts produced higher quantities. The normal iron catalyst produces at 180°C., a benzine which contains one to 2 percent of water soluble products. Other iron catalysts yield 5 percent or more. The acid number of products below 180°C. is one, that above 180°C. is 0.1. The corresponding esterification values are 1.6 respectively 0.5 and the saponification values are 2.6 respectively 0.6. Amongst others we were able to prove the presence of esters and alcohols. More detailed analytical information is left for a future report.

E. 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.

Part V

Conclusion

The following may be said about the iron middle-pressure synthesis. The yields of solid, liquid, and gasol hydrocarbons are somewhere near 130 to 160 normal cubic meters of ideal gas. The longest lifetime obtained for the catalyst lasted for 1-1/2 years without any regeneration at a temperature of 260°C. At the same time it still gave a yield of 140 g./Nm^3.

The evenness with which iron catalysts are capable of working for long periods of time may be observed from the end-gas analyses which are summarized in Table IV.

Table IX

Months of operation	Temp., °C.	Contraction percent	CO2	sHC	O2	CO	H2	HC	-	N2
A. End-gas analysis of an experiment performed 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	0.2	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 atm.										
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	0.1	5.2	11.2	9.0	1.9	10.0

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

Table IX refers to a catalyst inducted at 325°C. at 1/10 atm. with CO. This catalyst yielded practically the same degree of conversion and optimum yields of 150-160 g./Nm^3 of gas, after 4 months of operation.

The iron catalysts are not only superior to the cobalt catalysts on account of the cheapness, but also for the cheaper apparatus which they require and for the more even lifetime which they exhibit. It should be added that the antiknocking properties of the iron benzine are better than those of the cobalt benzines, and that the unsaturated gasol hydrocarbons obtained with iron catalysts can be used to greater advantage for production of high quality benzine.

The following disadvantages come in with iron catalysts: They work at higher temperatures, hence greater steam pressure, if it is desired to cool with water, than in the case of cobalt catalysts. Furthermore the iron catalysts have a greater tendency to form carbon than the cobalt catalysts.

Gentlemen, 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 threefold as compared to the earlier experiments with cobalt, and we have succeeded in improving the lifetime ten to twenty times. Hence, the total yield improved 20 to 60 times. We succeeded in the following:
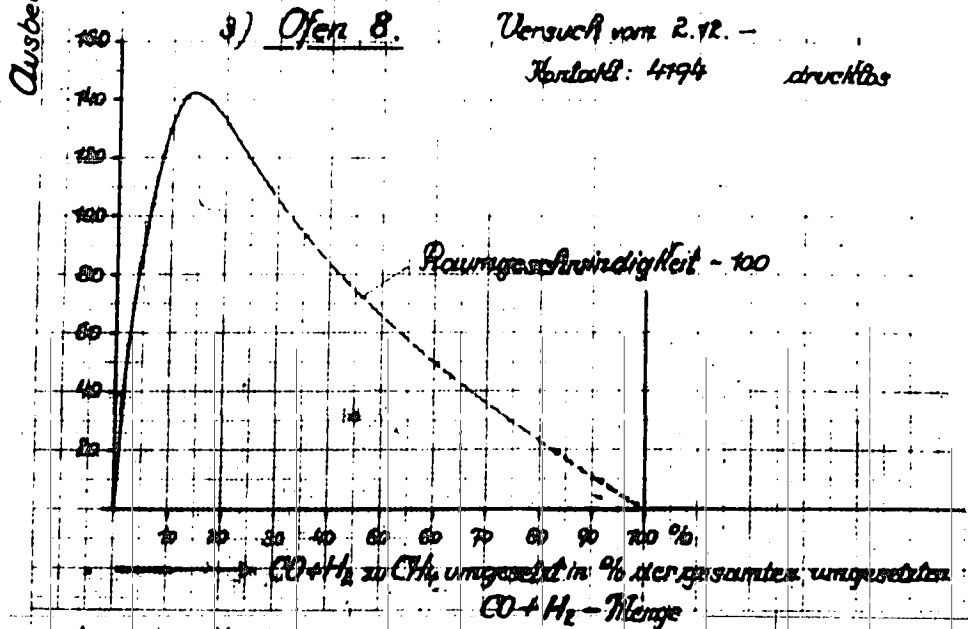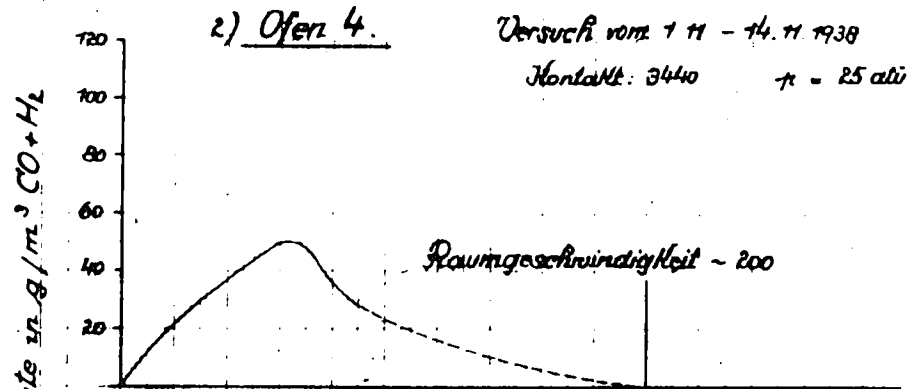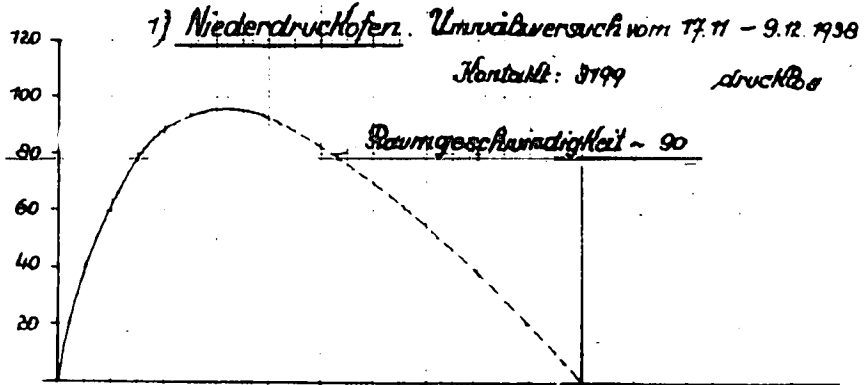
1. We used iron catalysts which were pretreated by CO

2. We maintained the synthesis gas pressures at the same optimum as that of cobalt middle-pressure synthesis, namely, 10 to 20 atmospheres.

3. We used a ratio of H2 + CO which was most ideally suited for the synthesis.

Already at the end of 1937, Dr. Fischer has 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 council and advice in all this work. Finally, I want to express my thanks to all my co-workers who have helped in the same effort.

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Ausbeute als Funktion des gebildeten Methans.

1) Niederdruckofen. Umwälzversuch vom 17.11 – 9.12.1938

Kontakt: 8199   drucklos

Raumgeschwindigkeit ~ 90

2) Ofen 4.   Versuch vom 1.11 – 14.11.1938

Kontakt: 3440   p = 25 ати

Raumgeschwindigkeit ~ 200

3) Ofen 8.   Versuch vom 2.12. –

Kontakt: 4194   drucklos

Raumgeschwindigkeit ~ 100

(y-Achse) Ausbeute in g/m^3 $CO+H_2$

(x-Achse) $CO+H_2$ zu CH_4 umgesetzt in % der gesamten umgesetzten $CO+H_2$ – Menge

10   20   30   40   50   60   70   80   90   100 %

Me 431- SK 929 c
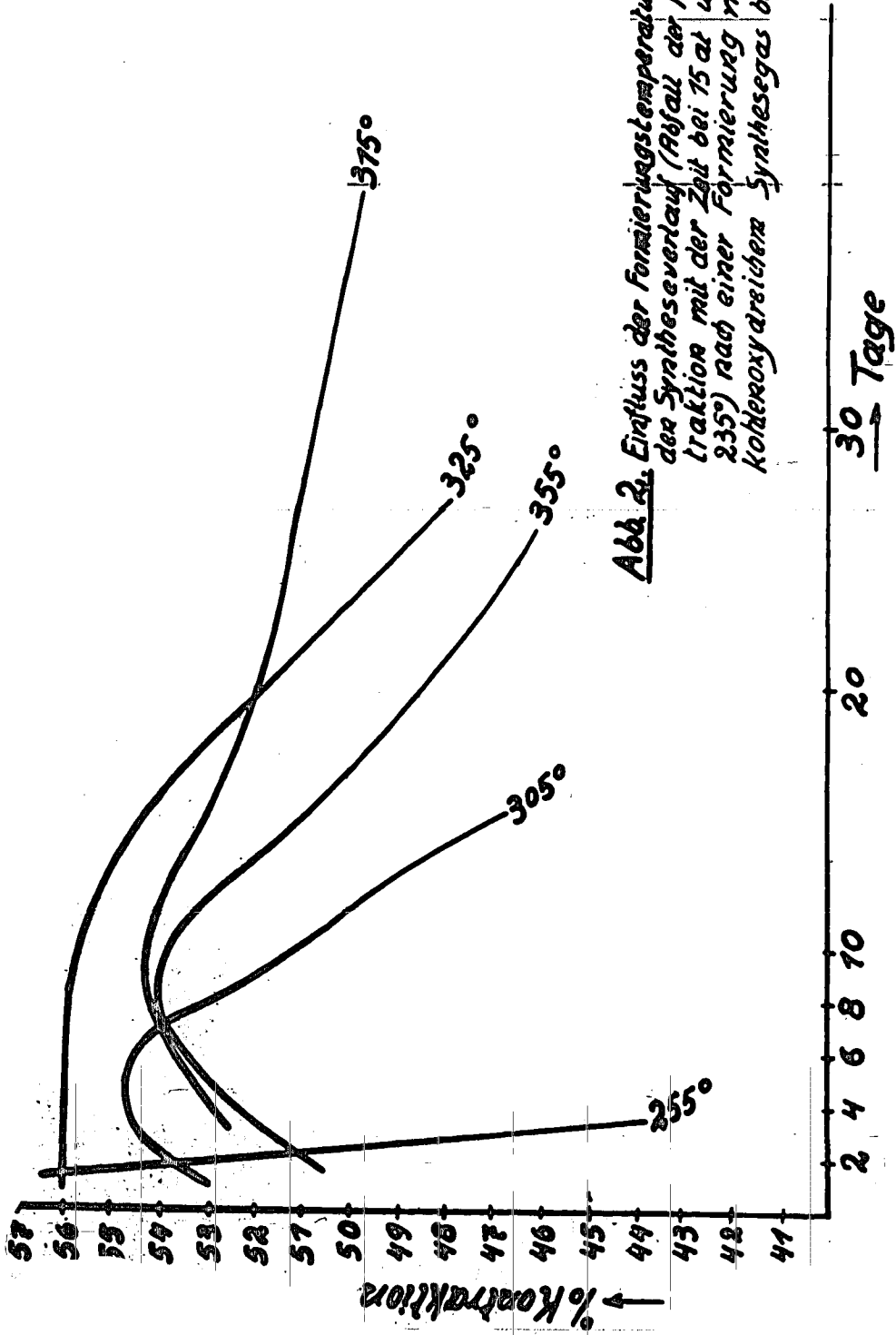
Abb. 2. Einfluss der Formierungstemperatur auf den Syntheseverlauf (Abfall der Kontraktion mit der Zeit bei 15 at und 235°) nach einer Formierung mit kohlenoxydreichem Synthesegas bei 7/0 at.

325°(120 Tage konstant)

345°(80 Tage konstant)

305°

255°

Abb.3. Einfluß der Formierungs-
temperatur auf den Synthese-
verlauf nach einer Formierung
mit Kohlenoxyd bei 1/10 at.

% Kontraktion →

Tage →

57 56 55 54 53 52 51 50 49 48 47 46 45 44 43 42 41

2 4 6 8 10 20 30

Versuche bei Atmosphären-
druck (Ablauf der Kontraktion
mit der Zeit bei Verwendung
verschiedener CO-H₂-Gemische)

→ Tage

% Kontraktion →

Abb. 4. Einfluß der Formierung der Synthesetemperatur auf die Syntheseapparatur

— Monate Betriebsdauer
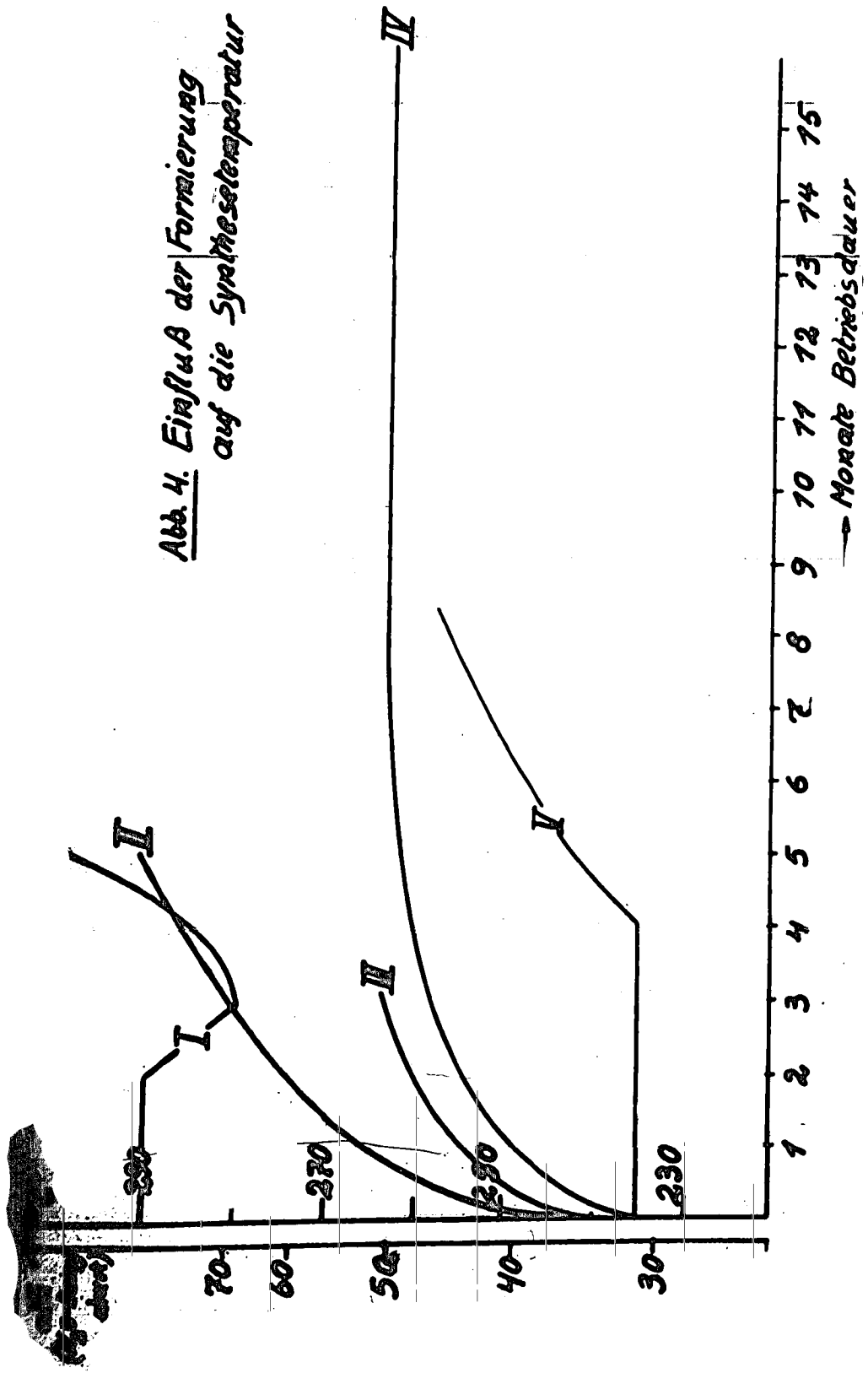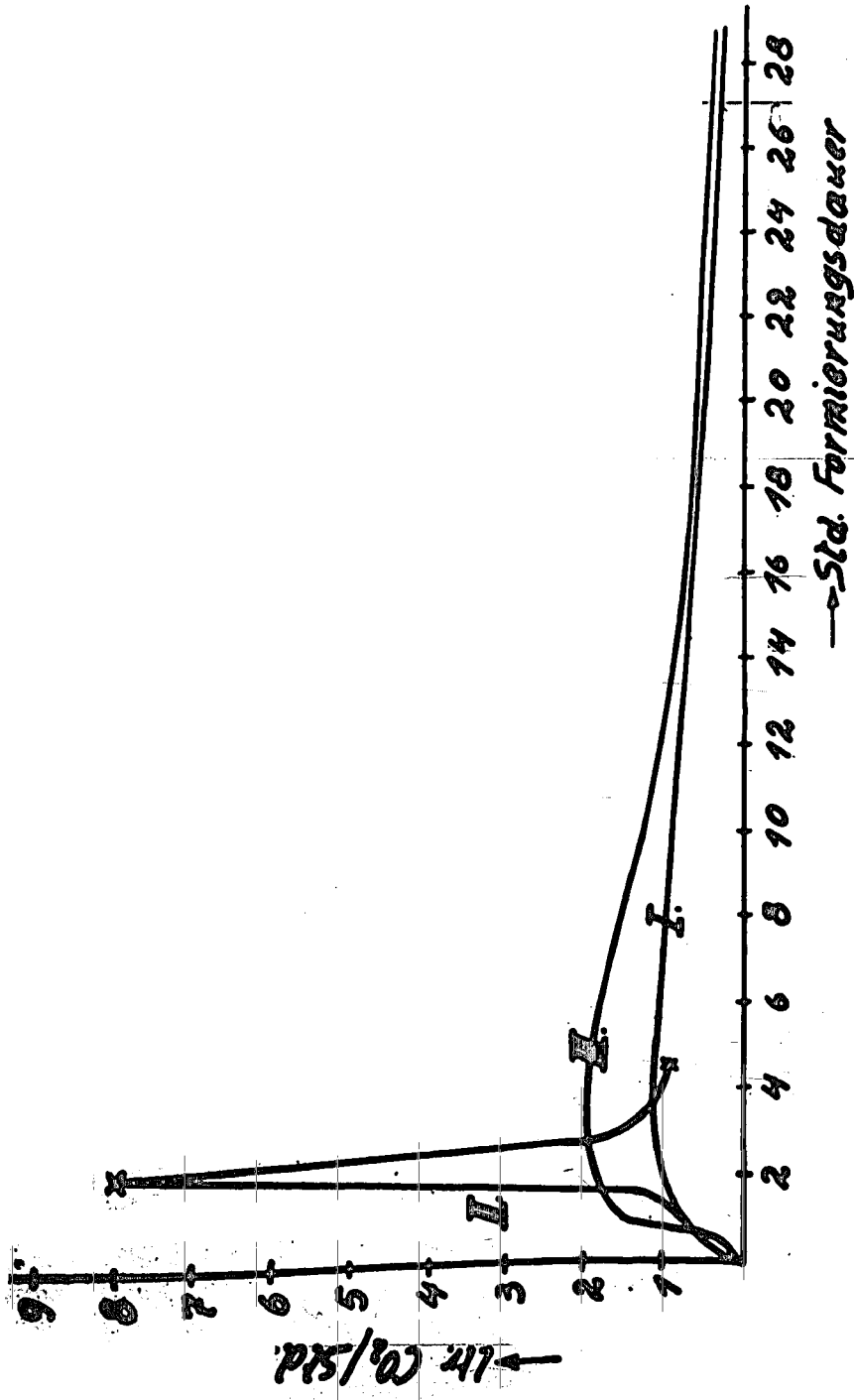
Abb. 5. Kohlensäurebildung während des Formierungsvorganges
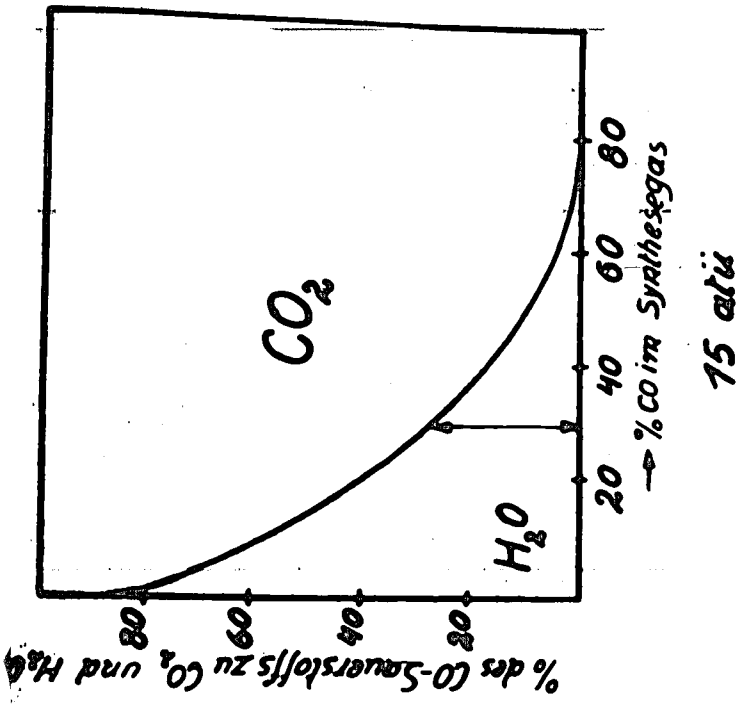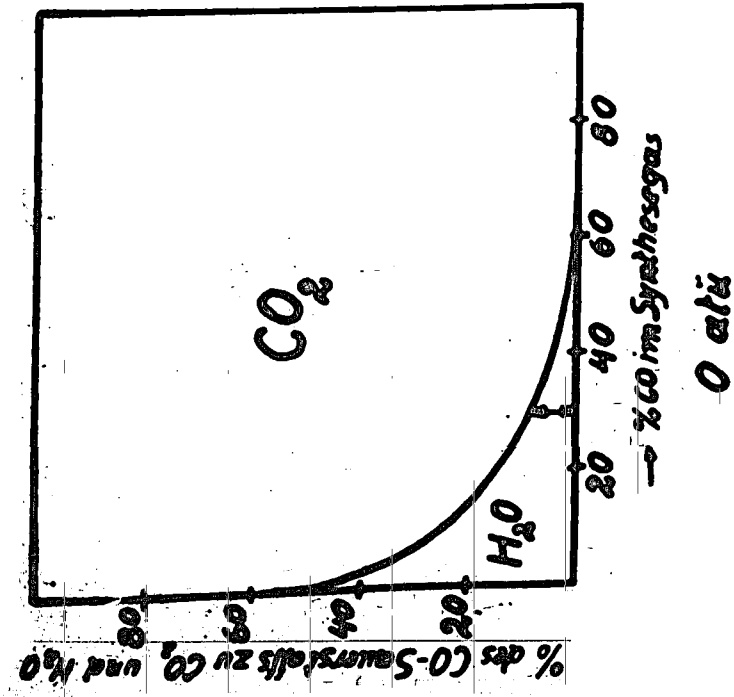
Abb. 6. Umsetzung des Kohlenoxydsauerstoffs zu CO_2 bzw. H_2O bei verschiedener Synthesegaszusammensetzung bei 0 u. 15 atü
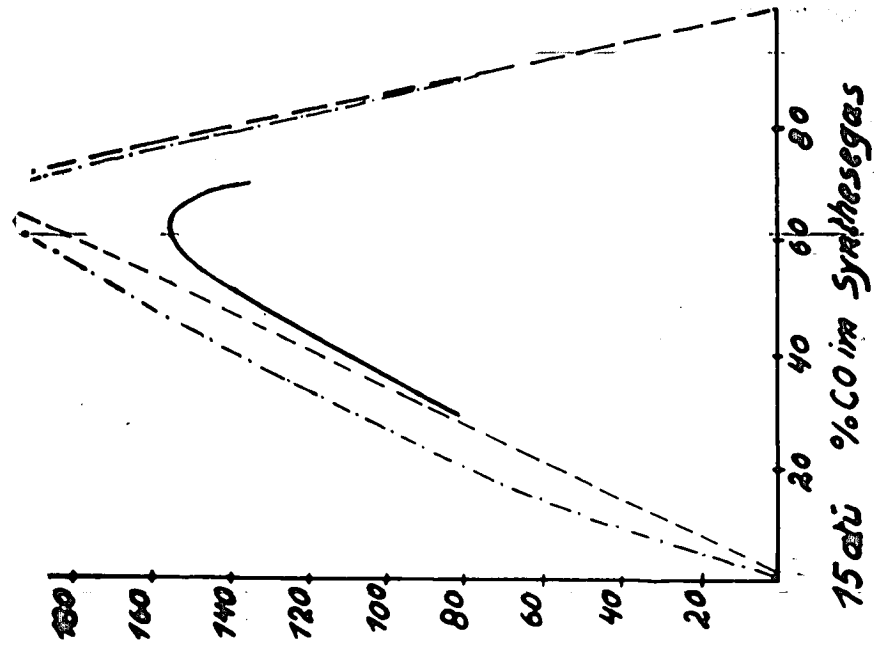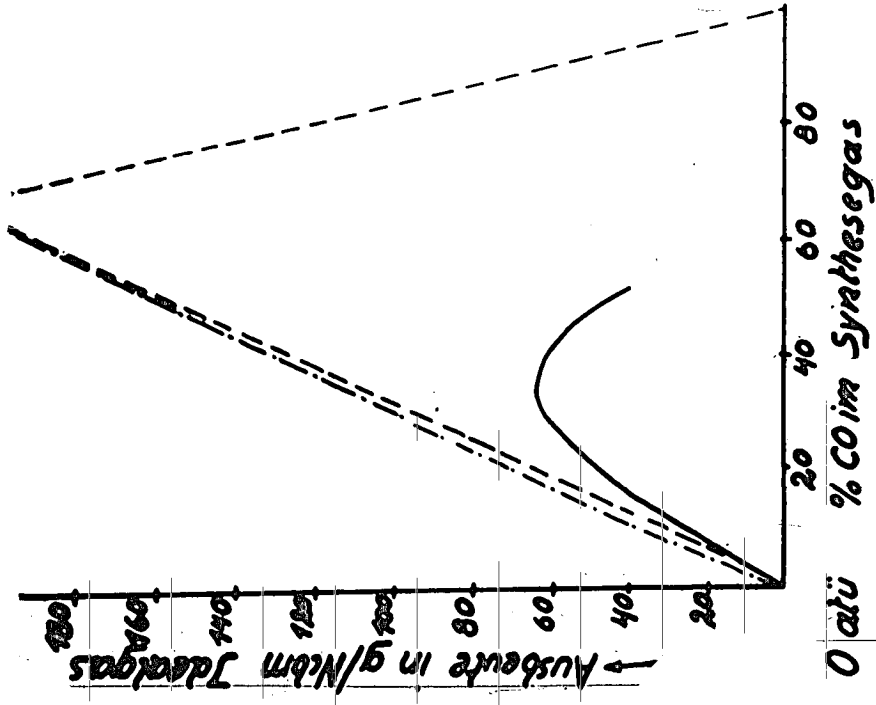
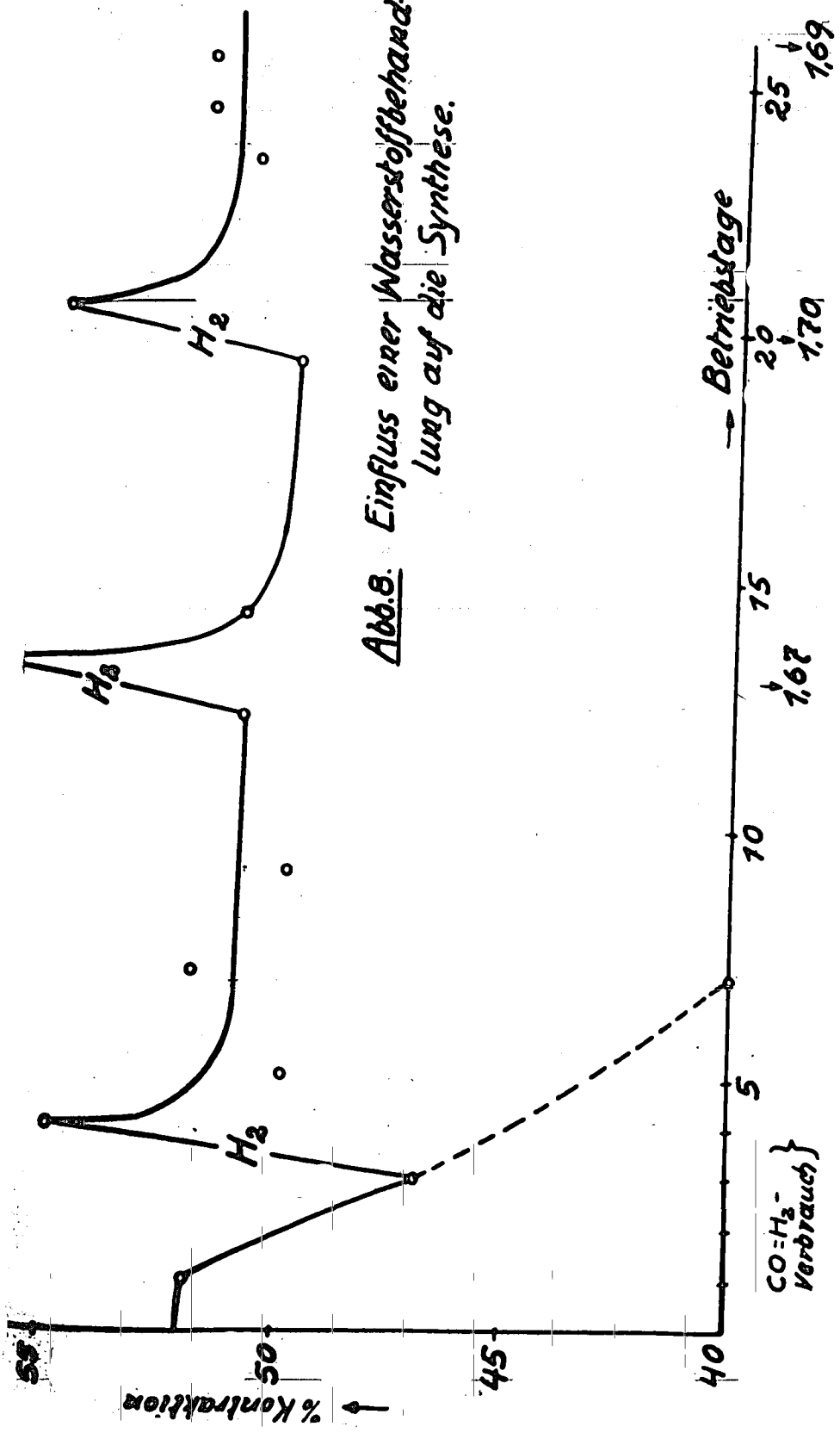Abb. 7: Einfluß der Zusammensetzung des Synthesegases auf die Ausbeuten.

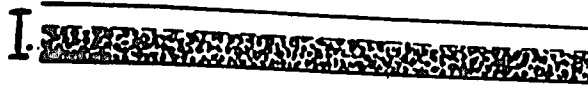Abb.8. Einfluss einer Wasserstoffbehand-
lung auf die Synthese.

I.

II.

Abb. 9

Schematische Darstellung
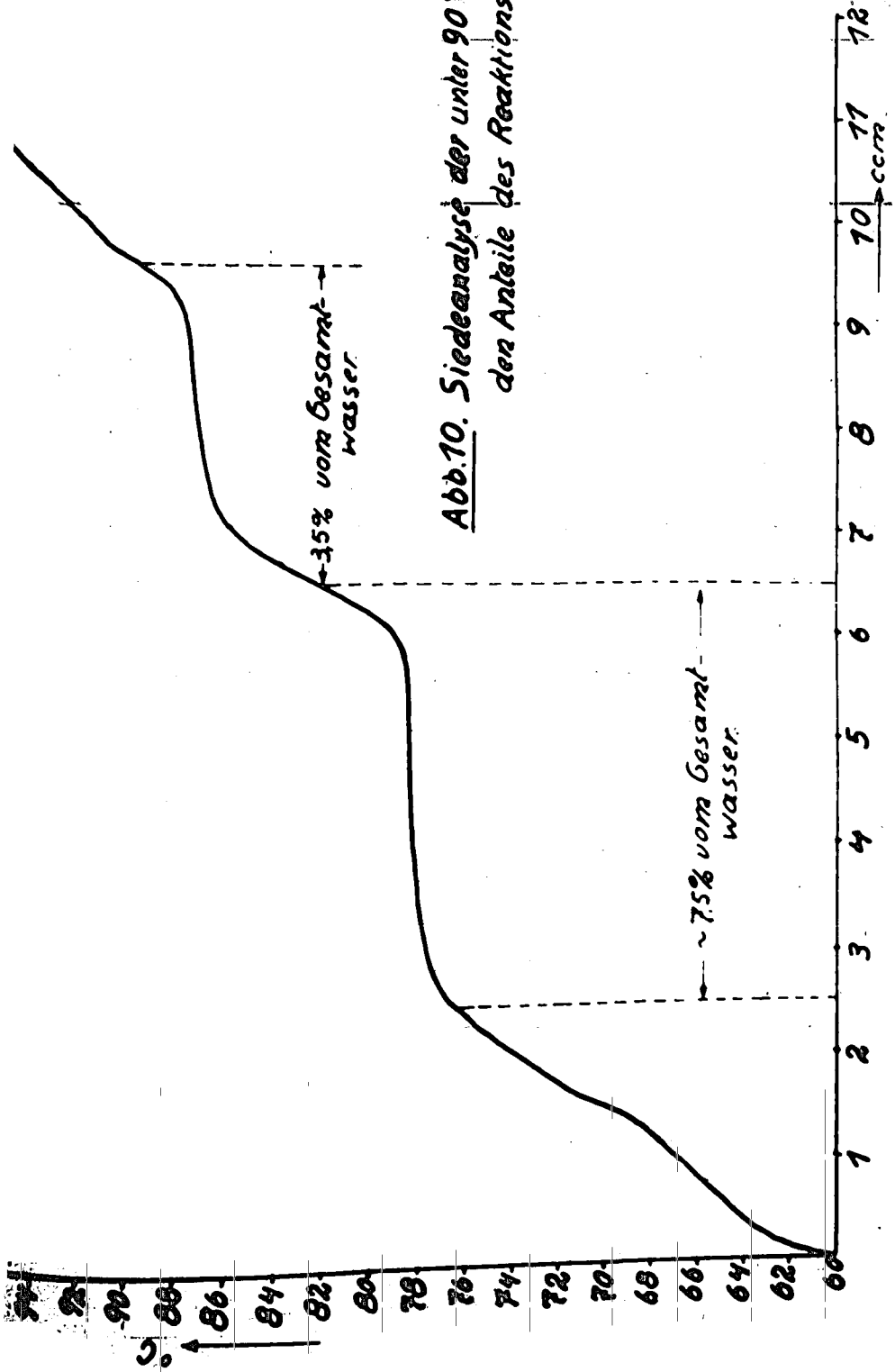verschieden gefüllter
Kontaktrohre.

Abb. 10. Siedeanalyse der unter 90° siedenden Anteile des Reaktionswassers.