The action of CO upon the iron catalyst is fundamentally different from the action of H_2. First of all, the reduction into iron oxides proceeds differently than it does with H_2; secondly, by using CO, the catalyst structure is loosened because carbon is deposited within the lattice; and thirdly, carbides are formed when CO is used.

If one disregards diffusion, sintering, and carbon deposition, it is known from the literature that the reduction is accomplished faster with hydrogen that with CO. If one works with CO, however, the catalyst lattice is loosened up to such a degree that reduction processes can take place rapidly with CO.

The primary process during the reduction is the formation of ferromagnetic Fe_3O_4. It was formed during the reduction with CO as well as with H_2, and it may also be obtained by precipitating a mixture of ferri and ferro salts with alkalies and following dehydrogenation. However, it possesses no catalytic action in so far as the middle-pressure synthesis is concerned.

Next let us discuss the equilibrium conditions for the system iron, carbon, and oxygen. It depends on temperature, gas pressure, and the ratio of CO to CO_2 contained in the gas. Figure 5a refers to atmospheric pressure. This corresponds to results of investigations by R. Schenck (12). The dotted curves were obtained by J. Hofmann and J. Groll (13) through calculations. Figure 5 shows the equilibrium conditions for 1/10 atmosphere. The Fe_3O_4-Fe_3C curve was calculated by taking into consideration the pressure as a variable. The other curves were compiled through data by Schenck.

One can see from Figure 5 that at temperatures of below 550-560°C., no FeO is stable (Schenck termed this wuestit, because it always contains Fe_3O_4). At low temperatures therefore, the reduction of Fe_3O_4 may be accomplished without going through the FeO phase.

The metallic phase is only stable above temperatures of 550-600°C. (according to Schenck, it decomposes into oxoferrit containing oxygen and oxoaustenit containing oxygen and carbides). It is assumed therefore that at lower temperatures, the carbide is formed by the direction action of CO upon Fe_3O_4. This is believed to take place over unstable oxygen deficient in the immediate compounds. Hofmann and Groll made X-ray analyses of the bodies which one obtains from CO and iron. Below 655°C., they were only able to detect small quantities of free iron. We have found that the reduction of the higher to the lower oxides of iron is independent of pressure. It only depends on the ratio of CO to CO_2 and the temperature. Raising the pressure favors the formation of carbides and carbon.

In presence of 100 percent CO, as it may actually occur in some instances with high flow velocity, at one and at 1/10 atmospheres, only iron carbide is stable in the equilibrium.

If it is desired to come to equilibrium for the inter-action of pure CO upon metallic iron, first of all carbide has to be formed. At the same time, the CO_2 obtained exerts oxidizing influence upon the iron. It seems plausible that for the induction of an iron catalyst, low pressures and high CO velocities are advantageous, since these factors lower the CO_2 partial pressure and effect a rapid removal of the CO_2 from the catalyst.

a. (1 ATM.)

(Fe$_2$C)

Fe$_3$C

Fe$_3$C + CO$_2$

Oa

3Fe + 2CO ⇌ Fe$_3$C + CO$_2$

Of

Fe$_3$O$_4$ + 4CO ⇌ 3Fe + 4CO$_2$

Fe$_3$O$_4$ + 6CO ⇌ Fe$_3$C + 5CO$_2$

2CO ⇌ C + CO$_2$

Fe$_3$O$_4$ + CO ⇌ 3FeO + CO$_2$

W

Fe$_3$O$_4$

CO, PERCENT

80

40

0

Oa = Oxoaustenite
(oxide and carbide
containing metallic Fe)
3FeO + 5CO ⇌ Fe$_3$C + 4CO$_2$
Of = Oxoferrite
(O containing metallic
phase)
FeO + CO ⇌ Fe + CO$_2$
W = Wüstite
(Fe$_3$O$_4$ containing FeO
phase)

---- 2 CO ⇌ C + CO$_2$

—·— Extrapolated
equilibrium

b. (1/10 ATM.)

(Fe$_2$C)

Fe$_3$C

3Fe + 2CO ⇌ Fe$_3$C + CO$_2$

Oa

FeO/Fe$_3$C

Of

FeO/Fe

Fe$_3$O$_4$ + 4CO ⇌ 3Fe + 4CO$_2$

Fe$_3$O$_4$ + 6CO ⇌ Fe$_3$C + 5CO$_2$

2CO ⇌ C + CO$_2$

W

Fe$_3$O$_4$/FeO

Fe$_3$O$_4$

CO, PERCENT

80

40

0
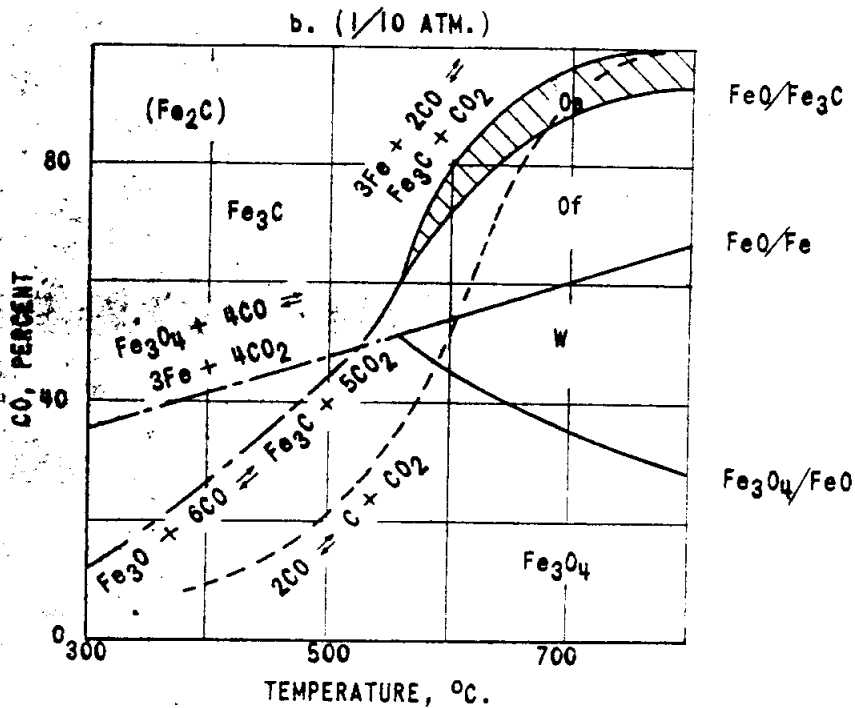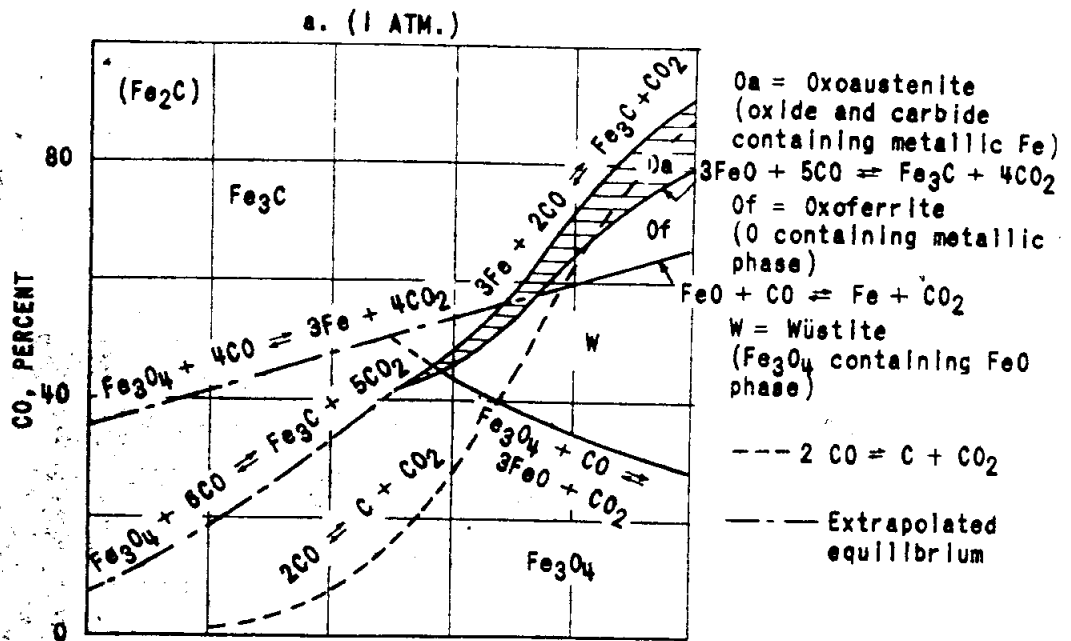300   500   700

TEMPERATURE, °C.

Figure 5. - Equilibrium conditions for
the system Fe-C-O.

In both figures the cementit (Fe_3C) has been recorded as carbides only, not however any higher carbides. Its existence was first assumed by Hilpert in 1915 (14). Fischer and his co-workers have repeatedly mentioned the formation of higher carbides as intermediate products during the benzine synthesis. Fischer and Bahr (15) also described such an iron carbide. Gluud and his co-workers (16) gave the formula Fe_2C to this iron carbide. The X-ray analyses of Hofmann and Grott have ascertained that at temperatures of over $400^{\circ}C$, this carbide becomes unstable because it splits off carbon. It is assumed that this decomposition occurs under the formation of cementit and free carbon.

Little can be said about equilibrium conditions of this or the higher carbides. Figure 5 therefore does not represent curves or areas referring to the existence of this carbide. It seems probable, however, that for their formation low temperatures and high CO concentrations are required. These conditions correspond to the optimum induction conditions for the iron synthesis. Therefore it appears very likely that the presence of these compounds in the catalyst is very essential for the degree of induction obtained and for the course of the synthesis to follow.

It is desirable of course that this carbide must be formed through a proper pretreatment before the synthesis is undertaken. Furthermore, in order to keep the synthesis going, this carbide should not be used up. Immediately after the induction the synthesis reaction proceeds satisfactorily even at low temperatures (for instance, below $220^{\circ}C$).

However, the conversion gradually decreases and may not even be maintained when the temperature is raised, for example at $230-240^{\circ}C$. If the temperature would have been $230-240^{\circ}C$ from the beginning, the catalyst would have continued to work at this temperature. It is believed that at the low temperatures the carbide was decomposed more rapidly by the hydrogen than it was re-formed by the action of the CO.

So far as the formation of free carbon is concerned, it may be assumed that this may be catalytically accelerated by the carbon-rich carbide. How far this undesirable decomposition of CO in presence of hydrogen may be prevented is still the subject of present investigations. However, it is definitely recognized that the formation of carbon may be suppressed by lowering the pressure and raising and increasing the flow velocity of the CO.

PART II
The Synthesis

A. The Synthesis Gas

The optimum synthesis gas composition corresponds to the ratio in which the reaction components CO and H_2 are used up. The only limitation is that the catalyst used for such theoretical mixture possesses a sufficiently high lifetime. The conversion on iron proceeds according to the general equation:

$$(1) \quad 2CO + H_2 \text{ equals } CH_2 + CO_2$$
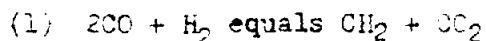
as a side reaction water is formed according to:

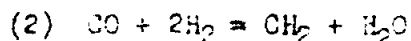$$(2) \quad CO + 2H_2 = CH_2 + H_2O$$

Figure 6 shows the formation of the reaction water (also contains water soluble organic compounds) at various pressures when a synthesis gas of composition $1CO + 2H_2$ is used at a temperature of 235°C. Between 0 and 20 atmospheres, the amount of reaction water increases from 14 to 60 per normal cubic meter of ideal gas.

Figure 7a and 7b show for 0 and 15 atmospheres, the portion of CO=O which at various synthesis gas compositions was converted to water and CO_2. At an initial content of 30 percent of CO in the starting gas and at atmospheric pressure, 7 percent of the CO=O are converted to water, whereas at 15 atmospheres 25 percent of CO=O are converter to water. With 60 percent of CO in the starting gas under atmospheric conditions, the process practically proceeds according to equation (1), whereas at 15 atmospheres, still 4 percent of the CO=O are used up for water formation. In addition to elevated pressures, an increase in the H_2 contents in the synthesis gas favors the water formation also.

Figures 8a and 8b show the influence of the synthesis gas composition upon the yields of solid and liquid and gasol hydrocarbons. The dotted straight lines show the calculated yields by assuming the reaction to proceed according to equation (1) over CO_2 formation. The dotted pointed curves show the corresponding results according to equation (2) with concurrent water formation. The solid curves show an actually obtained yield (4-weeks average). Theoretically it should be possible to obtain 208 g. of hydrocarbons with or without water formation for every normal cubic meter of synthesis gas. For atmospheric pressure and taking into consideration only the formation of CO_2 and still the theoretically best gas composition should be according to 2CO-1H_2, for 15 atmospheres, it should be 1.85 CO = 1 H_2 (apparently an error).

Fundamental differences exist between the synthesis carried out at atmospheric pressure and at 15 atmospheres. One cannot work at atmospheric pressure with the theoretical CO mixture because at these conditions, the activity of the catalyst decreased too rapidly. This is not the case for the middle-pressure synthesis. At one atmosphere synthesis pressure, a gas of composition $1CO + 2H_2$ behaves best. For the first 4 weeks of operation, it gave an average of 60 g. of solid and liquid and gasol hydrocarbons. These yields decrease rapidly during the fifth and sixth weeks.

It is possible to work well for many months with the theoretical gas mixture and obtain complete conversions. For the lower saturated homologs of methane, more hydrogen is required than equations (1) and (2) demand. Since the formation of methane is not entirely suppressed, CO and H_2 are not used up in the ratio of 1.85=1 but rather in the ratio of 1.6=1.8:1. Finally, it appears to be advantageous as regards the lifetime of the catalyst as the end-gas of the synthesis still contains a small excess of hydrogen. The ideal synthesis gas therefore contains 60 percent CO and 40 percent H_2 ($CO=H_2 = 1.5:1$). With such a gas mixture, it is possible to obtain 150-160 g. of solids, liquids, and gasol per normal cubic meter for many months when iron catalysts are used.
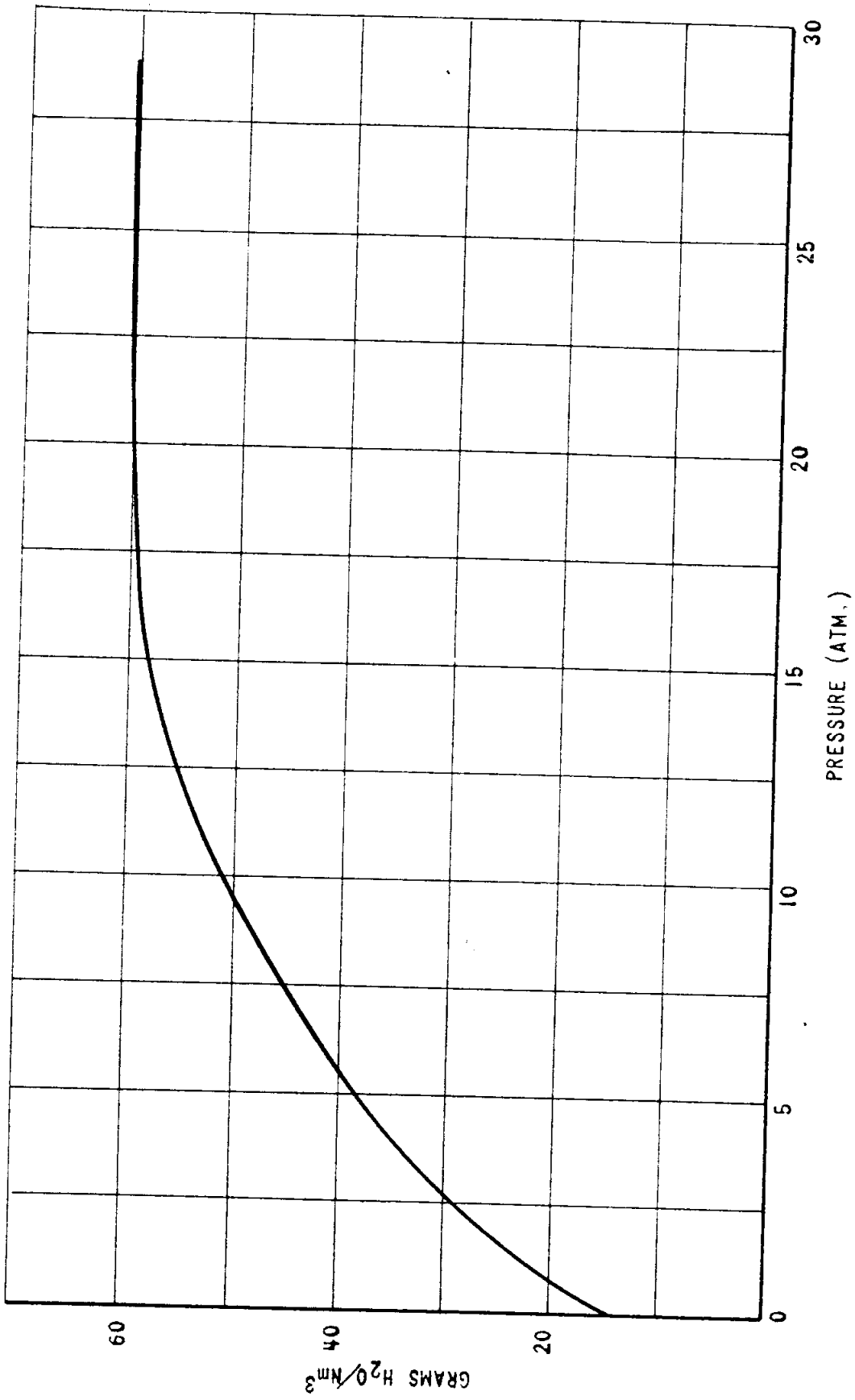
Figure 6. - Water formation at various pressures (synthesis gas composition CO:H₂ = 1).
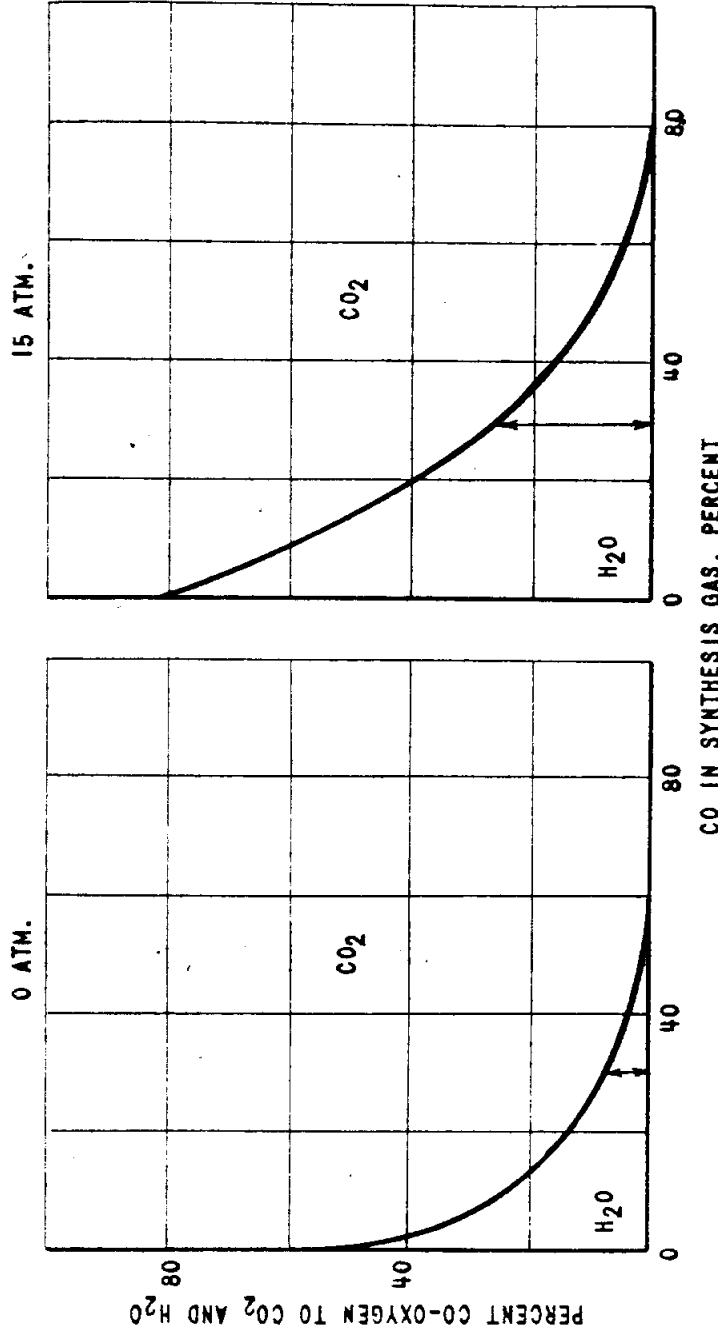
Figure 7. - Conversion of the CO-oxygen to CO_2 and H_2O, respectively, for various synthesis gas compositions at 0 and 15 atmospheres pressure.
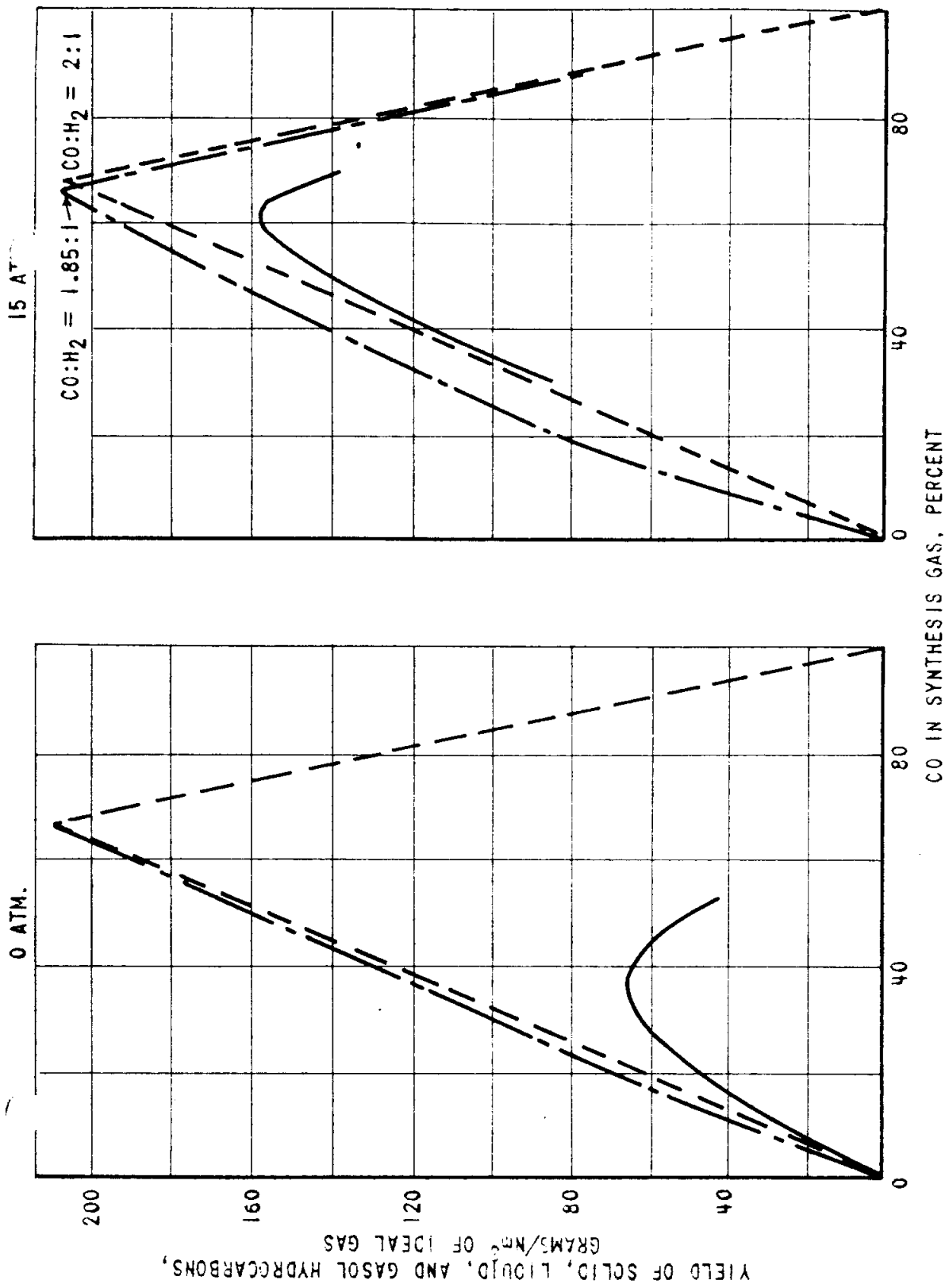
Figure 8. – Influence of synthesis gas composition upon the yields.

Table XI gives the ratio of CO and H_2 for a series of various synthesis conditions. It gives the ratio of the 2 components for the initial gas and also the usage ratio in which both components are used up during the synthesis.

During all the experiments slightly more CO was used than would correspond to the initial ratio of CO and H_2 in the starting gas. For experiments 1 and 2, the starting gas contained CO and H_2 in the ratios of 1.4-1 respectively 1.5:1. Both gases were used up in the ratio 0.54 to respectively 1.58:1.

Table XI
Ratio in which CO and H_2 are Used Up During the Synthesis for Various Conditions

Exp. No.	Catalyst type	Pressure, atm.	Temp., °C.	Days of operation	Percent Contraction	Ratio of CO and H_2 initial gas	Ratio of CO and H_2 used up
1	Fe-Normal catalyst	15	235	30	56	1.41:1	1.54:1
2	" " "	15	270	325	47	1.51:1	1.58:1
3	Fe-NH$_3$ precipitated 1/4% K_2CO_3	15	255	24	51	1.5 :1	1.7 :1
4	Fe-NH$_2CO_3$ precipitated 1% K_2CO_3	15	234	7	49	1.5 :1	1.59:1
5	" "	15	237	14	50	1.64:1	1.78:1
6	Fe-Normal catalyst	5	270	9	37	1.45:1	1.77:1
7	" " "	60	254	6	52	1.46:1	1.67:1
8	" " "	15	230	5	45	0.53:1	0.87:1
9	" " "	15	240	4	50	1.76:1	1.96:1
10	Fe-Na$_2CO_3$ precipitated 1% K_2CO_3	15	235	16	50	1.75:1	2.1 :1
11	Fe-Na$_2CO_3$ precipitated 5% K_2CO_3	15	238	7	49	1.76:1	2.08:1

With other experiments the difference was greater (experiment 3,6, and 7). Experiments 4,5, and 10 were carried out with a catalyst containing one percent K_2CO_3. For experiments 4 and 5, the CO-H_2 ratio was 1.5 respectively 1.64:1 for the initial gas. For the same experiments, the end-gas contained 1.59 respectively 1.78 CO to 1H_2. For experiment 10, the initial gas contains too much CO. The experiment points toward a carbon formation. The catalyst of this experiment only had about half as long a lifetime as the catalysts of experiments 4 and 5. The situation is similar for experiments 9 and 11. Experiment 8 was carried out with mixed gas (CO-H_2, 1.3-5.36:1). Hereto the ratio in which the components were used up was higher than the original and amounted to 0.87:1.

In order to get maximum yields, it is necessary to work with an initial gas containing both components in approximately the ratio in which they were used up. Initial gases which contain less CO than is required for the optimum conditions (1.4-1.6:1) are not capable of yielding maximum yields. This is because the end-gas contains an excess of H_2. Initial gases with too high a percent of CO increase the danger of carbon formation and shorten the lifetime of the catalyst. It is well to remember here that with increasing CO contents of the synthesis gas, the reaction temperature has to be higher for maximum yield.

B. The Synthesis Pressure

In the paragraph on synthesis gas, the reasons have already been explained why it is not practicable to work at atmospheric pressure when using iron catalysts.

Following are a few series of experiments carried out with catalysts having undergone different processes of induction. The experiments are designed to show the influence of the synthesis pressure upon the conversion.

First Series of Experiments. The catalyst used contained iron and copper in the ratio of 5:1. It was obtained from the solutions of ferrous chloride and copper chloride by precipitation with sodium carbonate. It had been alkalized by adding 1/8 percent K_2CO_3. This catalyst was subjected to an induction process at atmospheric pressure for 4 days at a temperature of $245°C$. (4 liters of mixed gas per 10 g. of iron per hour). After switching over to 15 atmospheres pressure, we carried out the synthesis by using 4 liters of synthesis gas ($CO + H_2 = 3:2$) per 10 g. of iron per hour. Table XII gives the results of this series of experiments. Contractions are recorded for 5, 15, 30, and 80 atmospheres and the necessary working temperatures. (The temperatures of this series of experiments, in general, were high as compared to the induction of the catalyst.)

Table XII

Reaction Temperature and Contraction at Various Pressures

Fe-Cu Catalyst Inducted with Mixed Gas at $245°C$. and One Atmosphere

Days of operation	5 atmospheres		15 atmospheres		30 atmospheres		80 atmospheres	
	Temp., °C.	Contraction percent	Temp., °C.	Contraction percent	Temp., °C.	Contraction percent	Temp., °C.	Contraction percent
10	257	44	257	42	263	50	270	38
20	265	45	265	50	275	50	286	49
30	270	42	270	53	280	48	300	13
40	272	45	274	53	287	52	302	50
50	275	45	275	55	289	52	-	-
60	285	48	272	52	290	49	-	-
90	278	50	281	51	-	-	-	-
120	-	-	285	49	-	-	-	-
150	-	-	290	47	-	-	-	-

For 5 atmospheres, the contractions obtained during 3 months of operation were between 45 to 50 percent. At 15 atmospheres and otherwise equal conditions, 50 to 55 percent contraction was obtained. Correspondingly at 15 atmospheres the yields of liquid and solid and gasol hydrocarbons were approximately 10 degrees higher than at 5 atmospheres. At 30 atmospheres, contractions of 50 to 52 percent could be reached too. However, at temperatures which were 10 to 15 degrees higher, and after the second month were 20 degrees higher than the temperatures required at 15 atmospheres pressure. When operating at 80 atmospheres, it was necessary to increase the temperature by 10 to 20 degrees over that at 30 atmospheres in order to obtain the same degree of conversion.

Table XIII shows the end-gas analyses obtained for a contraction of 50 percent at 5, 15, 30, and 80 atmospheres. The corresponding initial gas analyses of the runs carried out at 5 and 15 atmospheres contained 56 percent CO and 36.1 percent H_2; those carried out at 30 and 80 atmospheres, 55.5 CO and 35.5 H_2.

Table XIII

Reaction Gases at Various Pressures and Constant Contraction at 50 percent.

Pressure, atmos.	Days of operation	Temp., °C.	CO_2	sKW	O_2	CO	H_2	CH_4	N_2	N_2
5	6	257	53.8	3.4	0.2	12.3	13.3	7.0	1.9	10.0
15	3	252	55.5	3.0	0.2	11.5	11.6	8.0	1.8	9.4
15	23	267	51.4	3.8 ?	0.3	11.2	15.4	9.9	1.6	7.5
30	10	263	51.1	2.3	0.6	11.3	13.0	7.7	1.3	9.0
80	23	297	51.1	1.4	0.1	13.6	11.0	14.3	1.7	8.5

The end-gas analyses show that in spite of the various pressures and the correspondingly different temperatures, the course of the conversions does not change fundamentally. It had already been pointed out that at elevated pressures, the formation of reaction water increases at the expense of the formation of CO_2. Furthermore, it may be seen from the analyses, that at higher pressures, the quantities of unsaturated hydrocarbons decreases, and that the quantities of the saturated hydrocarbons increases correspondingly to the necessary higher reaction temperature. The increased consumption of H_2 is well expressed in the ratio in which CO and H_2 are used up. This usage ratio for the various pressures is as follows: For 5 atm., 1.7:1; 15 atm. 1.66:1; 30 atm. 1.6:1; 80 atm 1.44:1.

With respect to the lifetime of the catalyst at various working pressures, it should be pointed out that working temperatures above 290°C. should be avoided on account of the danger of carbon formation. The experiment carried out at 15 atmospheres showed that the catalyst had the longest lifetime. With the catalyst* used for this series of experiments, a temperature of 290°C. was required for 5 months operation and working at 15 atmospheres; the same temperature was required after 2 months when working under 30 atmospheres, and already during the first month when working under 80 atmospheres.

Second Series of Experiments. For this series of experiments, a copper-free so-called normal iron catalyst was used which had been inducted for 24 hours at 1/10 atmosphere and 325°C. with a CO-rich synthesis gas. Table XIV shows the results of experiments carried through at various pressures such as 1, 5, 10, 30, and 60 atmospheres. All the experiments were initially started at 235°C.

*The iron-copper catalyst used for this series really had a low activity if compared to the catalysts known at the present time. The influence of the pressure and the existence of an optimum pressure between 5 and 30 atmospheres, however, may even be observed from this catalyst.

Table XIV

Reaction Temperature and Contraction at Various Pressures
(Normal Iron Catalyst Inducted with CO-rich Gas at 325°C. and 1/10 Atmosphere)

Days of Operation	5 atmospheres		10 atmospheres		30 atmospheres		60 atmospheres	
	Temp., °C.	Contraction percent	Temp., °C.	Contraction percent	Temp., °C.	Contraction percent	Temp., °C.	Contraction percent
1	235	30	233	42	235	53	235	50
2	-	-	234	42	235	56	233	42
3	235	25?	235	48	234	57	235	40
6	250	38	238	50	-	-	254	52
9	270	37	239	50	-	-	-	-
12	-	-	237	50	-	-	-	-

This catalyst did not give a conversion at atmospheric pressure and 235°C., neither did it give a conversion on the second day at 250°C. (When we switched to 15 atmospheres and 235°C., this catalyst immediately gave a contraction over 53 percent.) At 5 atmospheres, the contractions lie somewhere between 30 and 40 percent. Hence the conversion was still incomplete. This did not improve even when the temperature was raised to 270°C. at the ninth day of operation. (When we went back to 15 atmospheres and 235°C., 50 percent conversion was obtained even then). At 10 atmospheres and 235°C., a contraction of 50 percent was reached. This was the case also at pressures of 30 and 60 atmospheres. However, in the case of the 30 atmosphere run, the conversion fell off sharply on the third day and for the 60 atmosphere run, it decreased rapidly already during the first day of operation. At 60 amospheres, a contraction of 52 percent could only be reached on the sixth day of operation when the temperature was raised to 254°C.

Here too, we found that an optimum pressure of somewhere between 10-30 atmospheres exists giving the highest yields and longest catalyst lifetime. (A comparison with experiments recorded in Table V for the same catalyst at 15 atmospheres shows that the optimum pressure is somewhere above 10 atmospheres)

Third Series of Experiments. A catalyst was used which was copper-free and had been precipitated with soda. One percent potassium carbonate was added, and the induction was carried out with CO at 1/10 atmosphere. The catalyst was prepared by a so-called inverted precipitation, that is, by running the iron solution (60°C.) into a boiling soda solution. We wanted to find out how long at 15, 20, 30, and 60 atmospheres at a reaction temperature of approximately 235°C. a contraction of more than 50 percent could be maintained. Table XV shows that for 15 atmospheres this time was 20 days, at 20 atmospheres, it was 9 days operation at 30 atmospheres, 5 days; and at 60 atmospheres, a contraction of more than 50 percent could be maintained only for one day.

Table XV

The Influence of the Synthesis Pressure Upon the Length of Time of Operation (Length of Time for Which a Contraction of 50% was Possible at 235°C., When Using an Iron Catalyst Alkalized with 1% K_2CO_3)

Days of operation	15 atmospheres		20 atmospheres		30 atmospheres		60 atmospheres	
	Temp., °C.	Contraction percent	Temp., °C.	Contraction percent	Temp., °C.	Contraction percent	Temp., °C.	Contraction percent
1	235	40	235	52	234	54	235	56
2	239	45	234	51	236	50	235	40
3	237	52	234	55	234	55	235	35
6	239	54	235	55	234	40	-	-
9	238	54	235	49	-	-	-	-
12	238	52	-	-	-	-	-	-
20	234	50	-	-	-	-	-	-
28	235	40	-	-	-	-	-	-

Results of Experiments Carried Out at Various Pressures

The optimum pressure of the middle-pressure synthesis for an iron catalyst lies somewhere between 10 and 20 atmospheres. (For most catalysts, the optimum pressure is most probably near 15 atmosphers). At lower or higher pressures, the conversion during the synthesis and the lifetime of the catalyst decreases.

C. The Reaction Temperature.

The temperature of the following work refers to the temperature recorded in the aluminum block.[*] Since both ends of the reaction tube stick out of the aluminum block inspite of good insulation with asbestos rope, heat is conducted towards the outside. As a consequence of that, the temperature in the interior of the tube is somewhat lower. Calibrations have shown that the temperature in the interior is approximately lower by 5 degrees. However, no temperature correction was taken into consideration, and the temperature of the block was taken as that of the synthesis.

We paid special attention to the temperature problem. We endeavored to keep the temperature for the iron middle-pressure synthesis as low as possible. This was necessary for economic reasons. On the large scale, the reactor is intended to be cooled with water and a small elevation in temperature would cause a considerable increase in steam pressure, and therefore increase the weight of the equipment.

[*]In the laboratory, we worked with pressure tubes which were embedded in a slanted position in the aluminum block furnace.

1. Influence of Induction.

It has been pointed out at another place that the induction temperature of the catalyst exerts an important influence upon the following synthesis. The curves shown in Figure 9, supplement the material already presented. The abscissas give the length of operation in months, the ordinates give the operating temperatures, and the steam pressure corresponding to these temperatures. All the experiments were carried out with a synthesis gas containing CO and H_2 in the ratio 3:2 (4 liters per 10 g. of iron per hour).

Curve 1 refers to a catalyst not previously inducted but taken into operation at 15 atmospheres immediately. In order to get maximum contraction, the temperature had to be raised to 290°C. The initial contraction was 45 percent, in the course of the second month of operation, the activity of the catalyst increased gradually so that a contraction of 50 percent was obtained. The temperature then could be lowered down to 280°C. without impairing the yield. During the fourth month of operation, however, it had to be raised again, and at the end of the fifth month it had reached 300°C.

Curve 2 shows the temperature relationships for an iron-copper catalyst which had acted upon a mixed gas for 3 days at 1 atmosphere and 240°C. (contraction 30 percent). Then it was switched to 15 atmospheres using the same synthesis gas. In order to get a maximum contraction of 50 to 55 percent (optimum conversion), the temperature had to be raised from 240 to 290°C. over the course of 5 months.

Curve 3 represents the temperature conditions for an experiment with a copper-free normal iron catalyst, which prior to the synthesis had been inducted at 1/10 atmosphere and 255°C. for 25 hours with pure CO. In order to get maximum contraction of 50 to 55 percent, the temperature had to be raised to 235-272°C. in the course of 8 months. The activity of the catalyst increased slowly at this temperature so that in the eleventh month, the temperature could be lowered again to 254°C. and still a contraction of 50 percent could be obtained. For the 15th and 16th months, the temperature was raised again to 265°C., and then lowered again to 259°C. Table XVI presents some end-gas analyses for this experiment.

Table XVI

End-gas Analyses of a Time-Test at Different Temperatures During 16 Months of Operation

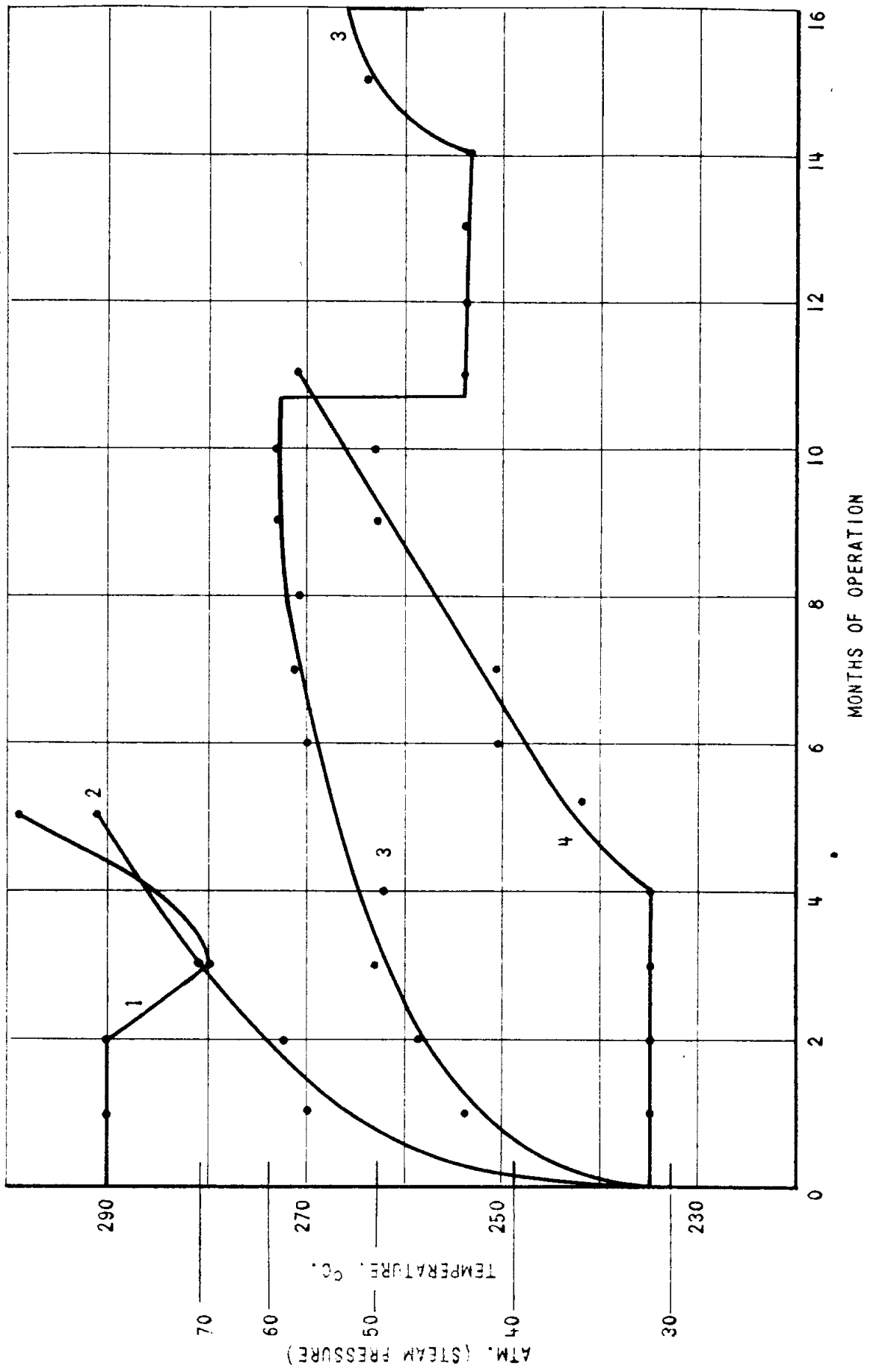| Months of operation	Temp., °C.	Contraction percent	End-gas composition in percent							
			CO_2	sKW	O_2	CO	H_2	KW	ΣyNo.	N_2
1	253	50	45.6	2.2	0.1	15.0	13.2	8.3	1.9	11.0
9	272	52	54.5	3.3	0.0	8.1	.7.4	11.2	1.8	15.5
14	254	50	50.1	2.8	0.2	11.9	11.9	7.3	1.7	12.8
16	266	48	53.5	3.1	0.1	8.2	10.6	11.9	1.9	12.6
16	259	48	51.2	3.2	0.2	9.9	12.6	10.4	1.8	12.5

Figure 9. – Influence of induction upon the synthesis temperature.

The table shows that by increasing the temperature, the quantity of gaseous hydrocarbons formed increases. On the whole, the end-gas analyses obtained from the synthesis gas do not differ too much for the 16 months of operation.

Curve 4 refers to a catalyst inducted at 325°C, with CO and 1/10 atmosphere. The induction at 325°C, facilitated operating at low temperatures for the first few months. The contraction remained constant at 50 to 54 percent through the course of 4 months at 235°C. After that, the temperature had to be raised. After one year, this iron catalyst did not show any advantages any longer as compared to a catalyst inducted at 255°C.

The curves of the figure bring out of what significance the pretreatment of the iron catalyst is to the synthesis temperature.

2. Influence of Gas Composition.

In Table XVII, comparative results are given for converstions of CO-rich and H2-rich synthesis gases at a reaction temperature of 205°C, (synthesis pressure 15 atmospheres).

Table XVII

Conversion of CO-rich and H2-rich Synthesis Gas at 205°C, and 15 Atmospheres

	CO_2	sKW	O_2	CO	H_2	KW	Cf	N_2	Contraction percent
CO-rich starting gas	2.2	0.0	0.2	58.9	33.9	0.2	1.0	4.6	20
end-gas	10.3	0.8	0.2	52.9	28.4	1.6	1.3	5.9	
H2-rich starting gas	1.2	0.0	0.0	.1.2	56.6	1.6	1.2	9.4	.1
	8.3	2.1	0.2	19.5	52.3	3.9	2.0	13.7	

Table XVIII shows the conversion of 3 different gases at 225.

Table XVIII

Conversion of CO-rich Gas, of water-gas, and of H2-rich Gas at 225°C, and at a pressure of 15 atmos.

	CO_2	sKW	O_2	CO	H_2	KW	cf	N_2	Contraction percent
CO-rich starting gas	2.3	0.0	0.0	8.8	33.4	0.4	1.0	5.1	45
end-gas	42.9	3.8	0.2	4.5	15.1	4.3	1.5	9.2	
Water-gas, starting	1.8	0.0	0.1	.6.4	43.4	0.8	1.0	7.5	52
end-gas	40.4	4.0	0.2	8.9	24.6	6.2	1.6	15.5	
H2-rich starting gas	0.6	0.0	0.1	.0.7	58.3	0.2	1.0		16
end-gas	22.6	1.6	0.1	0.0	43.8	13.1	1.7	18.3	

The analyses show that the reaction temperature can be lower if less CO is contained in the synthesis gas, that is, the less CO is converted. For the same temperature an increase in H2 contents in the synthesis gas, the percent contraction increases, (as long as the CO is not converted entirely as shown by the last experiment of Table XVIII), 0.66 respectively 0.71 liter of CO is converted per hour at 205°C (according to both experiments of Table XVII). According to Table XVIII, 1.8, 1.7, and 1.23 liters per hour of CO were consumed at 225°C. In the last experiment of this table, all of the CO was converted. As long as CO and H2 were present in the gas in sufficient quantity to react for the same temperatures and for the same length of time, the converted quantities of CO and CO-H2 ratio remained independent

3. <u>Effect of Too Low Starting Temperature.</u>

In general, the experiments were started at 225°C. to 235°C., although good con-version could have been obtained at lower temperatures immediately after the induction. Thus, with an experiment conducted with H_2-rich synthesis gas (CO-H_2 = 1:2), a contraction of 47 percent was still obtained at a temperature of 184°C. after the second day of operation. The ratio in which CO and H_2 were used up amounted to 0.7:1. This points to a reaction proceeding according to CO + $2H_2$ = CH_2 + H_2O. At such low reaction temperatures, the amount of con-version decreases after a few days and then the results are more unfavorable even after the temperature raised again, as compared to the results one would obtain if operation would have been commenced at the higher temperatures from the start. Table XIX brings this out too. This table contains the results of two comparative experiments using CO-rich synthesis gas and a normal iron catalyst. Experiment one is conducted at 235°C., experiment 2, at first, at 210°C.

Table XIX
Influence of Too Low a Reaction Temperature Upon the Stability of the Catalyst

Days of operation	Experiment 1		Experiment 2	
	Temp., °C.	Contrac-tion percent	Temp., °C.	Contrac-tion percent
1	235	56	210	42
2	"	52	"	31
3	"	51	"	27
4	"	51	–	–
5	"	52	220	21
6	"	55	235	36
7	"	55	250	45
8	"	55		
9	"	55		
10	"	57		
15	"	55		

The catalyst taken into operation at 235°C. gives constant contractions of 50 to 55 percent. The catalyst which was started at 210°C. gives contraction of 42 percent after one day of operation, after 2 days, it gave 31 percent, and after 3 days only 27 percent. When the temperature was then raised, the catalyst gave only 36 percent conversion at 235°C. and even at 250°C., 50 percent contraction could not be reached.

4. <u>Temperature and Reaction Products.</u>

It has been pointed out previously (for example, see Table XVI) that with raised temperatures the formation of the gaseous products increases. Table X shows average yields obtained on an iron catalyst containing 1/4 percent potassium carbonate, temperatures were 235, 270, and 280°C. When the temperature was raised from 235 to 270°C., the yields of solid paraffin dropped from 39 to 4 g. per normal cubic meter. The quantity of liquid and especially the volatile

- 26 -
2 6

liquid hydrocarbons and the gasol hydrocarbons increased at the same time. At 280°C, the paraffin yields were still lower, however, at this temperature, the yields of liquid and gasol hydrocarbons decreased also.

<div align="center">Table XX</div>

Reaction temperature, °C.	Yields (g./Nm^3 of Ideal Gas		
	Solid Paraffin	Liquid hydrocarbons	Gasol hydrocarbons
235	39	83	26
270	4	94	46
280	2	82	35

D. The Influence of Alkali Contents of an Iron Catalyst Upon Its Activity and Upon the Nature of the Reaction Products.

The preparation of the catalysts and the nature of the addition of alkali has been discussed earlier. In the following, an analysis is presented to show the influence of the alkali upon the course of the synthesis. The alkali additions indicated in the tables refer to potassium carbonate expressed as percent potassium carbonate referred to metallic iron. In the case of the other alkali salts (permanganate, fluoride, etc.) the notation "1 percent $KMnO_4$" is to signify that as much potassium was used in the formation of this salt as would correspond to one percent K_2CO_3. Table XXI, to start with, brings an experiment the catalyst of which was precipitated with ammonia and which did not contain any alkali. The testing of this catalyst was carried out at constant temperature (235°C.) with a CO-rich synthesis gas (CO-H_2 - 3:2, containing 8 to 10 percent inert ingredients). The pressure was 15 atmospheres.

<div align="center">Table XXI</div>
<div align="center">Activity of Various Alkalized Iron Catalysts</div>

Alkali addition		Days of operation								
		1	2	5	10	20	30	40	50	100
		Percent contraction at 235°C., and 15 atmospheres								
0		50	50	50	50	50	49	51	51	
0		53	50	48	49					
1/4%	K_2CO_3	47	50	50	51	55	56	54	54	53
1/2%	"	54	-	54	47	-	45			
1%	"	40	-	54	53	50				
1%	"	45	45	45	52	48	48	47		
2%	"	45	45	47	46	47	50			
5%	"	-	-	45	50	50	51	50	40	
10%	"	-	50	47	50	45	42	.		
1%	$KMnO_4$	40	-	50	51	55	50			
1%	K_2F_2	-	57	53	55	48				
1%	K_2SiO_3	-	54	53	46	50				
1%	K_2HPO_4	95	46	-	46	40				

The series of experiments shows that alkali addition to the catalyst is not required if one disregards the nature of the formed hydrocarbons. The catalyst

which was precipitated with ammonia and was entirely free of alkali was tested for 50 days and gave values of contraction which were not essentially below those obtained with a normal iron catalyst containing 1/4 percent K_2CO_3. We found that catalysts which contained up to one percent or more potassium carbonate showed a decrease in activity earlier than normal iron catalysts, namely, at 235°C., the decrease occurred between the 30th and 50th days. When we continued to operate and used catalysts which had been alkalized by salts other than potassium carbonate, no worth-while variations in the course of the synthesis could be observed during the first few weeks. However, the catalyst containing potassium permanganate showed very good conversion, whereas the one containing potassium phosphate was less stable.

Table XXII shows the quantity and the nature of the reaction products which were obtained with the various alkalized catalysts at 235°C. and 15 atmospheres synthesis pressure. The yields expressed in grams per normal cubic meter of ideal gas vary to some extent all through the first month of operation, corresponding to the not entirely uniform contraction obtained. Thus, we obtained between 150 to 160 grams per normal cubic meter of ideal gas. The alkali content of the catalyst exerts a very essential influence upon the nature of the reaction products. When no alkali was present only 12 percent of solid paraffin (referred to the total yields of solid, liquid, and gasol hydrocarbons) were obtained according to the Butanon method. When 1/4 percent potassium carbonate was added to the catalyst, this increased to 26 percent, for one percent potassium carbonate to 42 percent, for 2 percent to 43 percent, and at 5 percent potassium carbonate contents 45 to 46 percent of solid paraffins were obtained referred to the total yields. The quantity of liquid and gasol hydrocarbons correspondingly falls off as the alkali contents increases.

Table XXII finally brings out that it was unimportant what alkali salts had been added to the catalyst so far as the quantity and nature of the reaction products were concerned. The experiments conducted with a catalyst containing one percent potassium carbonate and the corresponding quantities of potassium manganate, potassium silicate, potassium fluoride, and potassium phosphate showed the same course of the reaction within limits of experimental error.

Table XXII
Yields With an Iron Catalyst Containing Various Amounts of Alkali Additions

Precip- itating agent	Alkali addition		Solid, Liquid, and gasol hydrocarbons g./Nm^3 of ideal gas	Paraffin percent	Liquid hydrocarbons percent	Gasol percent
NH_3	0		141	12	67	21
Na_2CO_3	1/4%	K_2CO_3	148	26	53	15
		0	140	13	67	23
Na_2CO_3	1%	K_2CO_3	157	42	47	11
	1%	$KMnO_4$	155	41	45	14
	1%	K_2SiO_3	158	43	41	16
	1%	K_2F_2	163	46	42	12
	1%	K_2HPO_4	154	33	52	15
Na_2CO_3	2%	K_2CO_3	143	43	44	13
	5%	"	161	45	43	12
	5%	"	155	46	44	10

E. Treatment with Hydrogen Before and After the Synthesis.

1. Pretreatment with hydrogen.

The normal iron catalyst instead of having been treated with CO was inducted with 6 liters per hour of H_2 at 1/10 atmosphere, 325°C. for 2-1/2 hours. When we switched over to CO-rich synthesis gas and operated at 15 atmospheres and 235°C., an end-gas analysis made after 1-1/4 hours showed 2 to 3 percent contraction, and another gas analysis made after 3-1/4 hours disclosed 4 percent contraction. The catalyst behaved in the same way as a non-inducted catalyst would have behaved. Nevertheless the catalyst after having been removed from the reaction tube was faintly pyrophoric and ferromagnetic. A comparative experiment which was run with a catalyst having been inducted with CO instead of H_2 prior to the synthesis gave a contraction of 54 percent from the very beginning.

In a further experiment we worked with a catalyst of somewhat lower activity, and we wanted to see whether a pretreatment with H_2 prior to the induction would result in an improvement. For this purpose, we worked for 6 hours passing 8 liters of H_2 per hour over the catalyst at 325°C. and 1/10 atmosphere. Then we passed 4 liters of CO per hour over the catalyst for 20 hours at 1/10 atmosphere and 325°C. Then we started to operate with CO-rich synthesis gas at 15 atmospheres. The contraction amounted to 42 percent on the second day at a temperature of 234°C., 45 percent on the sixth day, and 236°C., 47 percent on the eighth day and 238°C., and again 47 percent on the tenth day at 238°C. Comparing this data with the experiment conducted with a catalyst which was not pretreated with hydrogen, 42 percent contraction was obtained on the second day at 234°C., and 46 percent on the eighth day at 238°C. The hydrogen treatment prior to induction therefore was without influence upon the conversion.

2. Hydrogen Treatment Between Induction and Synthesis.

To start with, we passed 40 liters of CO for 2-1/2 hours at 325°C, and 1/10 atmosphere over the catalyst. Thereafter, we passed 6 liters of H_2 per hour over the catalyst at 325°C. Then we switched over to CO-rich synthesis gas at 15 atmospheres, and the activity was tested at 210°C. The contraction went up to 42 percent immediately. After one day, it was 43 percent. For a comparative experiment in which the H_2 pretreatment was omitted, the contraction after one day was 42 percent. The intermittent H_2 treatment was therefore of no influence upon the catalyst activity. (This result is surprising because one would expect that the H_2 would reduce the carbides having formed during the induction with CO).

3. Hydrogen Treatment During the Synthesis.

A catalyst which ordinarily should have been taken into operation at a somewhat higher temperature was tested at 235°C, and 15 atmospheres with 4 liters per hour of CO-rich gas. It gave 52 percent contraction on the first and second days (see Figure 10), 50 percent contraction after 2 days, and 47 percent contraction after 3 days. The dotted curve shows that the contraction should have arrived at 40 percent if the experiment could have been continued for one week at 235°C. However, after 3 days, a H_2 treatment was undertaken for 15 hours, using 8 liters per hour of H_2 at one atmosphere and 325°C. After this H_2 treatment, the contraction in the following synthesis amounted to 55 percent. It
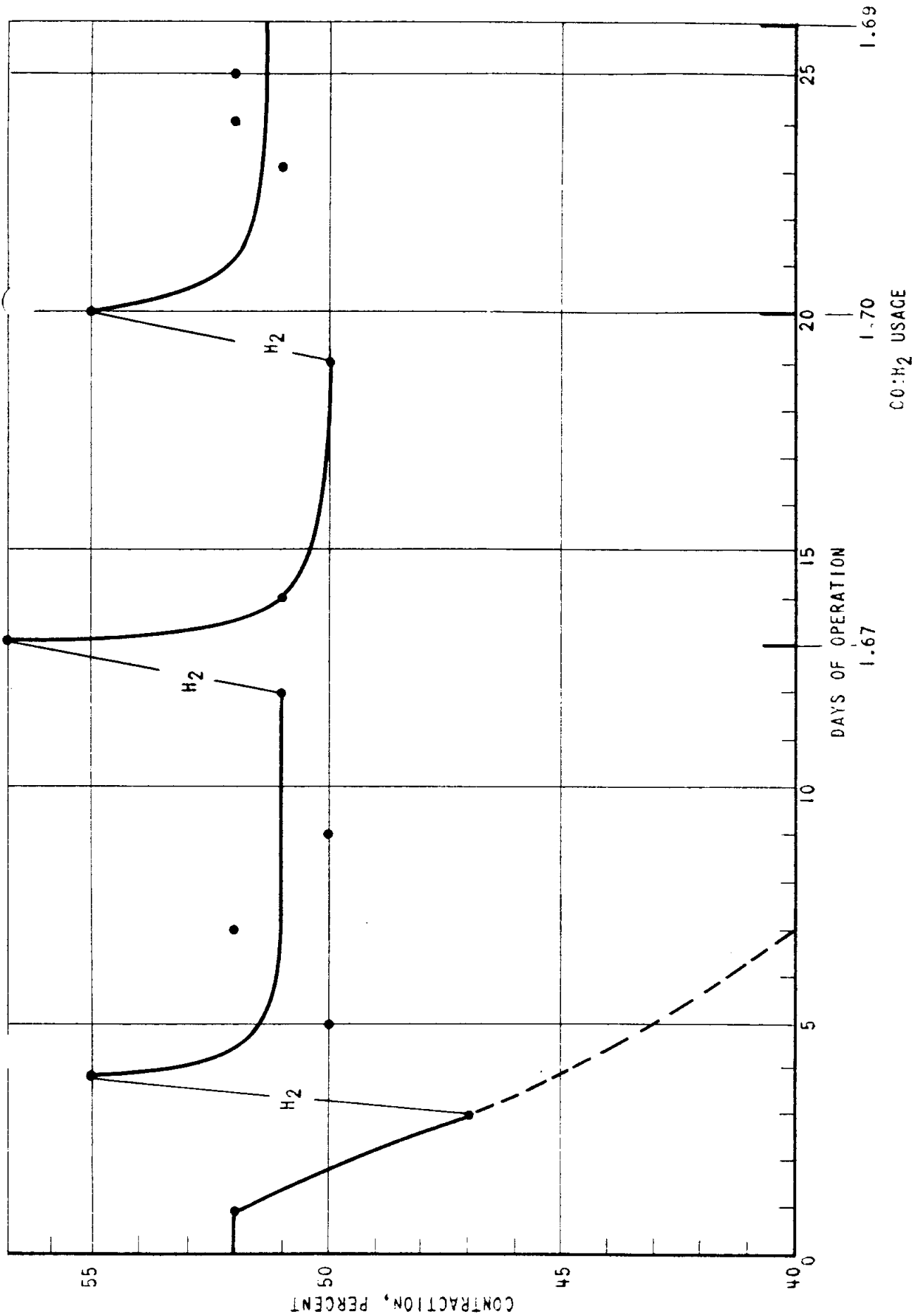
Figure 10. - Influence of a H_2 - pretreatment on the synthesis.