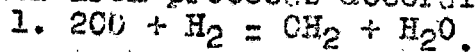


II. The Synthesis:

A. The Synthesis Gases

Theoretically the best composition of synthesis gas is in the proportion of the consumption of the participants of the reaction, carbon monoxide and hydrogen. We may stipulate that the life of the catalysts when using such "theoretical mixture" is sufficiently long. As a general rule the conversion with iron proceeds according to the equation



Side by side with this reaction is one involving the formation of water:

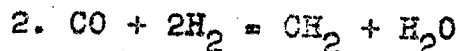
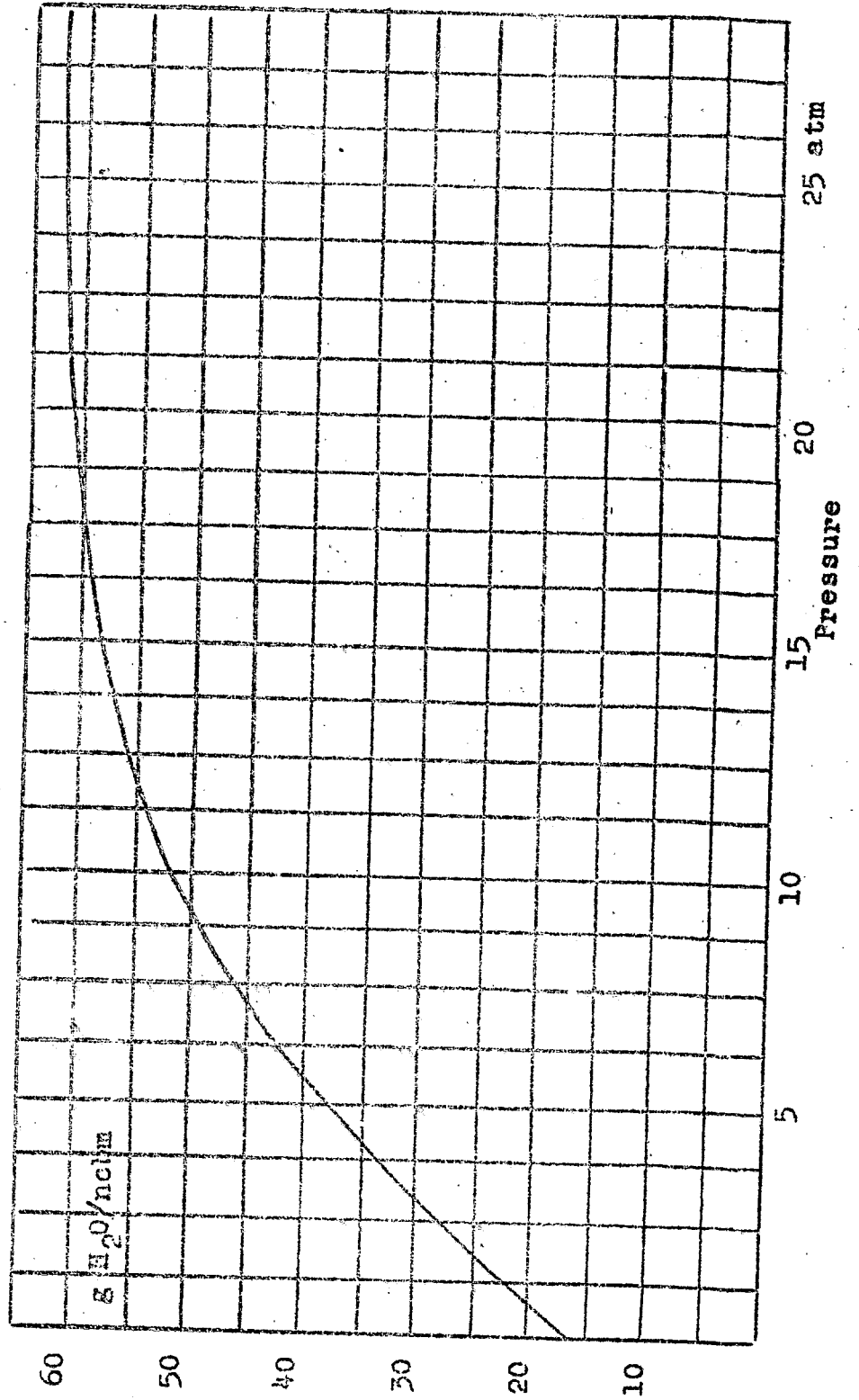


Figure 6 shows the forming of the water of reaction (containing also water soluble organic compounds) at different pressures with a synthesis gas with the carbon monoxide and hydrogen in proportion 1 : 2, and a reaction temperature of 235°C. The amount of water of reaction rises from 14 to 60 g/ncbm of ideal gas when the pressure is increased from 0 to 20 atm gauge pressure.

Figures 7a - 7b show the proportions of the oxygen of carbon monoxide in different synthesis gases converted into water and into carbon dioxide at 15 atm. With an initial content of 30 percent carbon monoxide in the starting gas and at atmospheric pressure, 7 percent of the oxygen of the carbon monoxide is converted into water, and at 15 percent pressure the conversion reaches 25 percent. When the carbon monoxide content in the starting gas is 60 percent, the reaction proceeds practically quantitatively according to the equation 1 at atmospheric pressure, while at 15 atm 4 percent of the oxygen of the carbon monoxide is still used up in the formation of water. The formation of water is therefore favored by increasing the hydrogen content of the synthesis gas as well as by raising the pressure.

Fig. 6. Formation of water at different pressures
(Synthesis gas CO : H₂ = 1 : 2)



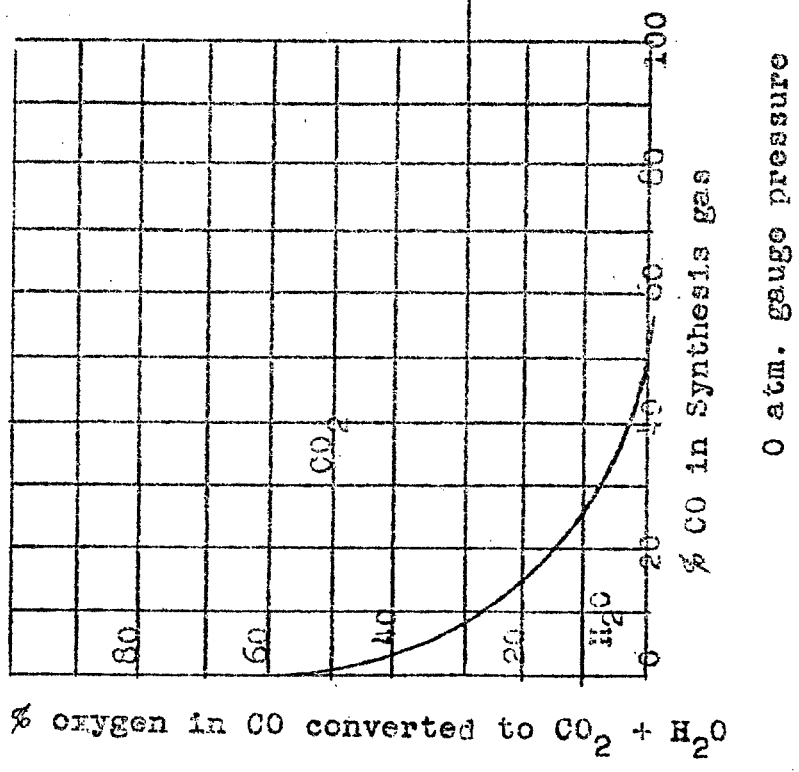
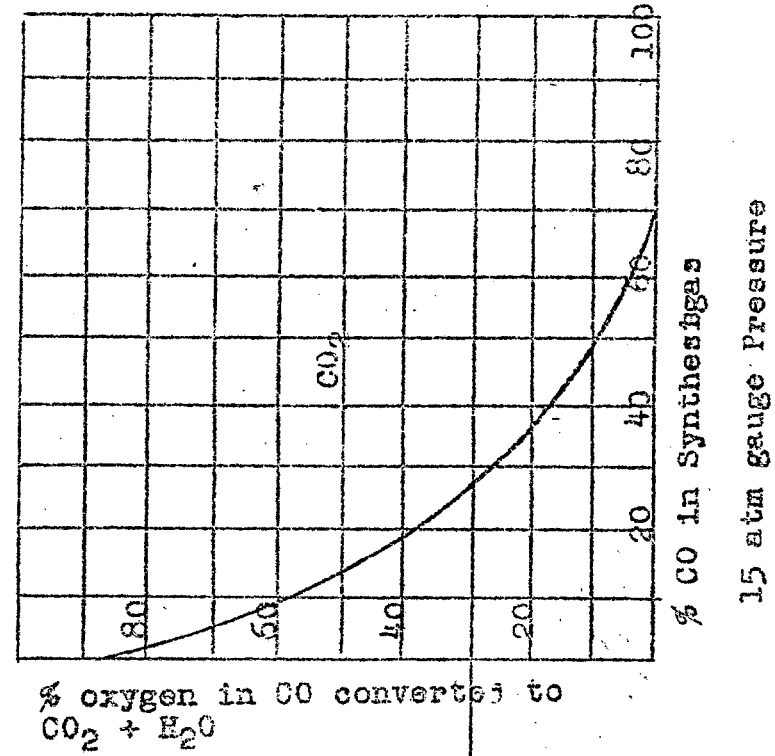


Fig. 7. Conversion of the oxygen in CO into CO_2 and H_2O with different compositions of the synthesis gas at 0 and 15 atm gauge pressure.

Figures 8a and 8b show the effect of the composition of the synthesis gas upon the yields of solid, liquid and gasol hydrocarbons. The broken straight lines show the calculated yield on the basis of formation of only carbon dioxide according to equation 1. The dash-point-dash line shows the corresponding results according to equation 2 with the formation of water. The solid curves are actually obtained yields (average for four weeks operation). We may see from the diagram that 208 g hydrocarbons/ncbm synthesis gas could theoretically be obtained with or without the formation of water. At atmospheric pressure, considering only the formation of carbon dioxide or of water, the optimum composition of the gas would be with carbon monoxide to hydrogen proportion of 2 : 1, at 12 atm with 1.85 : 1.

There exists a fundamental difference between work at atmospheric pressure and at 15 atm in that work cannot be done at atmospheric pressure with the theoretical mixture of carbon monoxide and hydrogen, because such a gas will very readily cause the dying-off of the activity of the catalysts, which does not happen in middle pressure synthesis. At 1 atm gauge pressure a synthesis gas with 1 CO : 2H₂ acted best. It produced on the average during the first four weeks of operation around 60 g of solid, liquid and gasol hydrocarbons. These yields dropped greatly during the 5th and 6th weeks.

At a synthesis pressure of 15 atm the theoretically required gas mixture may be used for a complete conversion with the same yields maintained during many months of operation. The lower saturated homologs of methane require more hydrogen than corresponds to the equations 1 and 2, and the formation of methane cannot be completely suppressed, and the carbon monoxide and hydrogen are not used up therefore in the proportion 1.85 : 1 but in the proportion 1.6 - 1.8 : 1. It finally appears to be advantageous for increasing the life of the catalyst to have the end gas still contain a slight excess of hydrogen. The synthesis gas is composed accordingly of 60 percent CO - 40 percent H₂ (CO : H₂ = 1.5 : 1). Such mixture permits to obtain 150 - 160 g solid, liquid and gasol hydrocarbons/ncbm on an iron catalyst for many months.

Table 11 contains the proportion of carbon monoxide and hydrogen of the starting gas and the proportion

in which the two components were used up during the synthesis for a series of different syntheses in the current tests.

Somewhat greater amount of carbon monoxide was consumed in all the experiments than corresponded to the carbon monoxide - hydrogen proportion in the starting gas. In the experiments 1 and 2 the proportion of carbon monoxide to hydrogen was 1.41 and 1.51 : 1 while they were consumed in the proportions 1.54 and 1.58 : 1

Table 11

Proportion in which Carbon Monoxide and Hydrogen are Consumed during Synthesis under Different Conditions

Expr. No.	Cat. type	Press. atm.	Temp. °C	Days Oper.	% Contr.	Proportion CO : H ₂ in start gas	Proportion CO : H ₂ converted gas
1	Normal iron cat.	15	235	30	56	1.41 : 1	1.54 : 1
2	" "	15	270	325	47	1.51 : 1	1.58 : 1
3	NH ₃ precipitated Fe cat. with 1/4 percent K ₂ CO ₃	15	255	24	51	1.5 : 1	1.7 : 1
4	Na ₂ CO ₃ precipitated Fe cat. with 1 percent K ₂ CO ₃	15	234	7	49	1.5 : 1	1.59 : 1
5	" " " "	15	237	14	50	1.64 : 1	1.78 : 1
6	Normal Fe cat.	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	Na ₂ CO ₃ precipitated Fe cat. with 1 percent K ₂ CO ₃	15	235	16	50	1.74 : 1	2.1 : 1
11	Na ₂ CO ₃ precipitated Fe cat. 5 percent K ₂ CO ₃	15	238	7	49	1.76 : 1	2.08 : 1

In the other experiments the difference was still greater (tests 3, 6 and 7). Tests 4, 5 and 10 were run with a catalyst containing 1 percent K₂CO₃. In tests 4 and 5 the ratios of carbon monoxide to hydrogen were 1.5 and 1.64 : 1 in the starting gas, and in the end gas 1.59 and 1.78 : 1. Too much carbon monoxide was present in the starting gas in experiment 10, and the

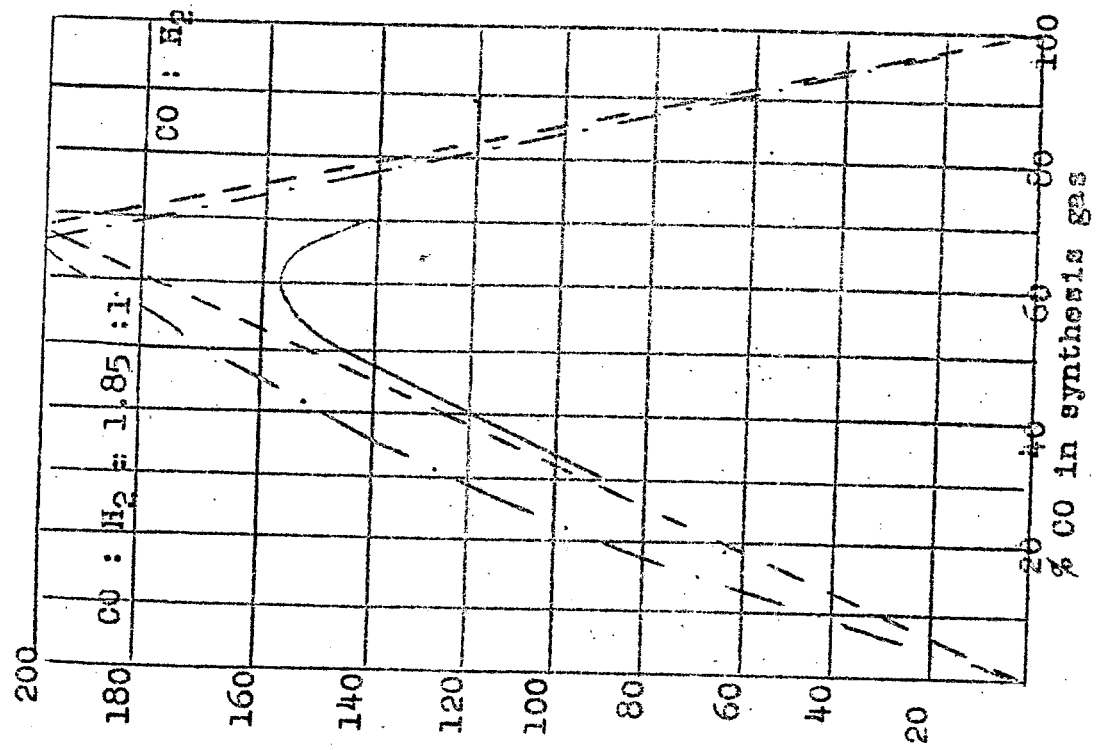
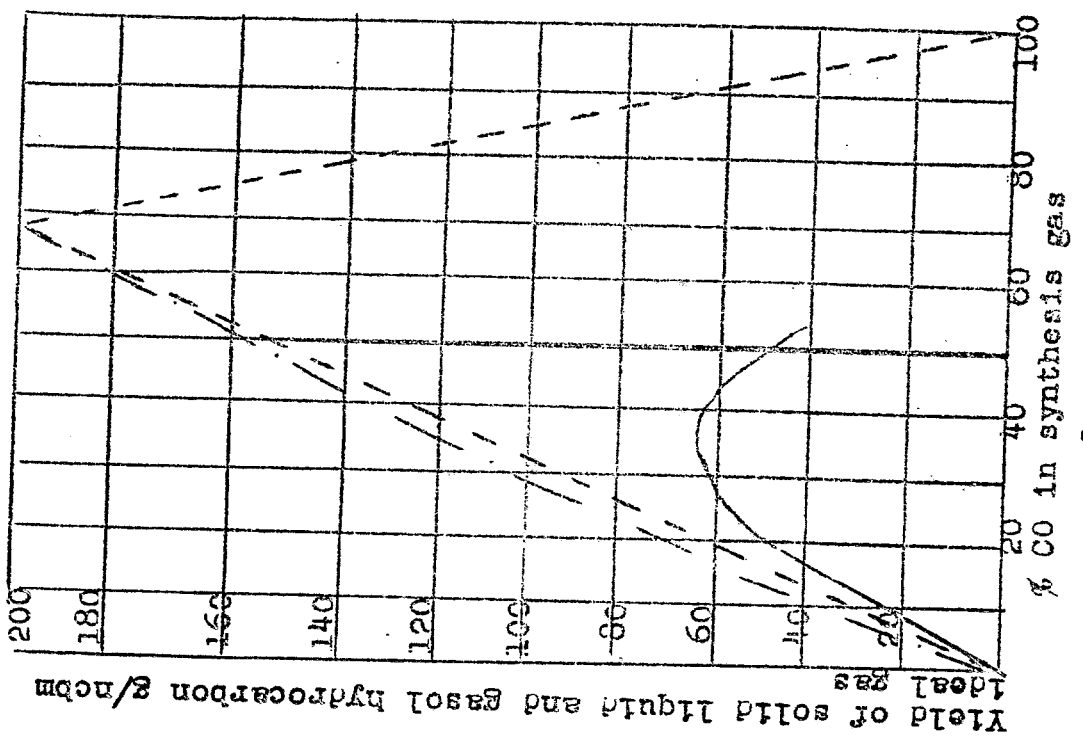


Fig. 8 Effect of composition of the synthesis gas on the yield

conversion points to a formation of carbon. The catalyst used in this test had only half the life of that in the experiments 4 and 5. Conditions were similar in experiments 9 and 11. Experiment 8 was used with "mischgas" ($\text{CO} : \text{H}_2 = 0.53 : 1$). Here again the consumption was in a higher proportion (0.87 : 1).

Operating conditions must be selected for maximum production, with the proportions in the starting gas and converted being nearly alike. Starting gases with little carbon monoxide in the optimum proportion 1.4 - 1.6 : 1 do not produce maximum yields and the end gases contain an excess of hydrogen. A high carbon monoxide content in the starting gases causes a greater danger of carbon formation which will affect the life of the catalysts; it must also be borne in mind that as the proportion of carbon monoxide increases, a definite conversion can only be obtained by raising the reaction temperature.

B. The Synthesis Pressure

We have already presented in the section on the synthesis gas the reason for practically discarding synthesis of hydrocarbons with iron catalysts at atmospheric pressure. We will summarize below a few series of experiments with differently prepared or formed catalysts, which show the effect of synthesis pressure on the conversion.

First Series: Iron and copper were in a proportion of 5 : 1 in the catalyst. It was prepared from a solution of ferrous chloride and copper chloride by precipitation with sodium carbonate, and alkalized with 1/8 percent K_2CO_3 . The catalyst was formed at atmospheric pressure for four days at 235°C with mischgas (4 li/10gFe/h). After forming, the synthesis was conducted with 4 li of gas ($\text{CO} : \text{H}_2 = 3 : 2$)/10gFe/h. Table 12 shows the results in this series of experiments. The operating temperatures are compared at 5, 15, 30 and 80 atm to obtain the same contraction values. Because of the manner of forming the catalyst, the temperatures in this series of experiments were in general high.

Table 12

Reaction Temperatures and Contractions at Different Pressures (Fe - Cu catalysts, Formed with Mischgas at 2350C and 1 atm)

Days of operation	5 atm		15 atm		30 atm		80 atm	
	Temp °C	Contr. %	Temp °C	Contr. %	Temp °C	Contr. %	Temp °C	Contr. %
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	48
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	-	-	-	-

The values for contraction were 45 - 50 percent during the three months of operation at 5 atm. With other conditions remaining the same the contraction was 50 - 55 percent at 15 atm. The yields at 15 atm in solids, liquids and gasol hydrocarbons were correspondingly higher by 10 percent when operating at 15 atm than at 5 atm. Operating under 30 atm, a contraction of 50 - 52 percent could also be obtained, but at temperatures from 10 to 15°C higher, and even 20°C higher by the end of the second month, than with a pressure of 15 atm. With 80 atm the same conversion was obtained with temperatures again raised 10 - 20°C in comparison with those at 30 atm pressure.

Table 13 gives the end gas analyses of runs at 5, 15, 30 and 80 atm operated with the same contraction of 50 percent. The corresponding starting gas analysis during operations at 5 and 15 atm contained 56.0 percent CO and 36.1 percent H₂, in runs at 30 and 80 atm they contained 55.5 percent CO and 39.3 percent H₂.

Table 13

End Gases Obtained at Different Pressures and with the Same Contraction of 50 Percent.

Press- ure	Days of Oper.	Temp °C	CO ₂	Hydro- carbons Heavy	O ₂	CO	H ₂	Hydro- carbons	Carbon Number	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	3.8	0.2	11.5	11.6	8.0	1.8	9.4
15	23	267	51.4	3.3	0.3	11.2	16.4	9.9	1.6	7.5
30	10	263	51.1	2.3	0.6	11.3	18.0	7.7	1.8	9.0
80	23	297	51.1	1.4	0.1	13.6	11.0	14.3	1.9	8.5

The composition of the end gases shows that in spite of differences in pressure and correspondingly different temperatures, the conversion was not basically different. We have already pointed out that when the pressure was increased, a reaction of water formation was favored at the cost of formation of carbon dioxide. The analyses show further that at high pressures the amount of the unsaturated hydrocarbons is reduced while the saturated hydrocarbons are increased because of the necessary higher reaction temperatures. The increased hydrogen consumption is expressed in the proportion of consumption of carbon monoxide to hydrogen. It amounted to 5 atm to 1.7:1, at 15 atm to 1.66:1, at 30 atm to 1.65:1 and at 80 atm 1.41:1.

With respect to the life of the catalysts at different operating pressures we may say that the test carried out at 15 atm resulted in the longest operating times because of the danger of the formation of carbon at temperatures of 290 - 300°C. The temperature of 290°C was reached with 15 atm after the 5th. month of operation, with 30 atm after the 2nd month and with 80 atm during the first month using the same catalyst in the test*.

* The iron-copper catalyst used in these experiments was less active than those used today. The effect of the pressure and the existence of an optimum pressure between 5 - 30 atm is, however, well illustrated in the results obtained with this catalyst.

The Second Series of Experiments: the so-called normal iron catalyst, copper-free, was used after forming for 24 hours at .1 atm and 325°C with a carbon monoxide-rich synthesis gas. Table 14 shows the results with 1, 5, 10, 30 and 60 atm. All were begun at 235°C.

Table 14

Reaction Temperature and Contraction at Different Pressures (Normal Iron Catalysts, Formed with CO-rich Gas at 325°C and .1 atm).

Days of Operation	5 atm		10 atm		30 atm		60 atm	
	Temp °C	Contr. %	Temp °C	Contr. %	Temp °C	Contr. %	Temp °C	Contr. %
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	-	-	-	-

* After changing over to 15 atm 50 percent contraction was obtained at 235°C.

At atmospheric pressure no conversion was obtained with this catalyst at 235°C nor on the second day at 250°C. (This experiment produced a 53 percent contraction after changed conditions to 15 atm and 235°C). At 5 atm the contraction was 30 - 40 percent and the conversion was therefore incomplete, and remained such even after increasing the temperature to 270°C on the ninth day. (In this case again changing over to 15 atm, a 50 percent contraction was already obtained at 235°C) a 50 percent contraction was found at 10 atm and 235°C. Such was also the case at 30 and 60 atm, but at 30 atm and 235°C there was a strong drop in the conversion on the third day. With 60 atm pressure and 235°C this already took place after one day. A contraction of 52 percent on the sixth day could be obtained with 60 atm pressure only after the temperature had been increased to 254°C.

An optimum pressure between 10 and 30 atm could be established with this catalyst as well as in the first series of experiments. (A comparison of the same catalysts at 15 atm shown in table 5 proves that the optimum pressure is at about 10 atm).

The Third Series of Experiments: this series was run with copper-free iron catalyst precipitated with sodium carbonate and containing 1 percent potassium carbonate, formed at .1 atm with carbon monoxide. This catalyst was prepared by the so-called reversed precipitation, i.e. by pouring a solution of iron heated to 60°C into a boiling solution of sodium carbonate. It has been tested at 15, 20, 30 and 60 atm for as long as the reaction temperature of around 235°C could be maintained with a contraction exceeding 50 percent. Table 15 shows that with the catalysts used at 15 atm, operations were possible for twenty days, with 20 atm for nine days, at 30 atm for five days, with 60 atm for only one day.

Table 15

The Effect of Synthesis Pressure on the Length of Operation (Tests During which a Contraction of 50 percent was Obtained at 235°C using an Iron Catalyst Containing 1 percent K_2CO_3)

Days of Operation	15 atm		20 atm		30 atm		60 atm	
	Temp °C	Contr %	Temp °C	Contr %	Temp °C	Contr %	Temp °C	Contr %
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 at Different Pressures: the optimum range of pressures in middle pressure synthesis with iron catalysts is between 10 and 20 atm. (For most catalysts the optimum is most probably about 15 atm synthesis pressure) the conversion and the life of the catalyst are less at lower or higher pressures.