

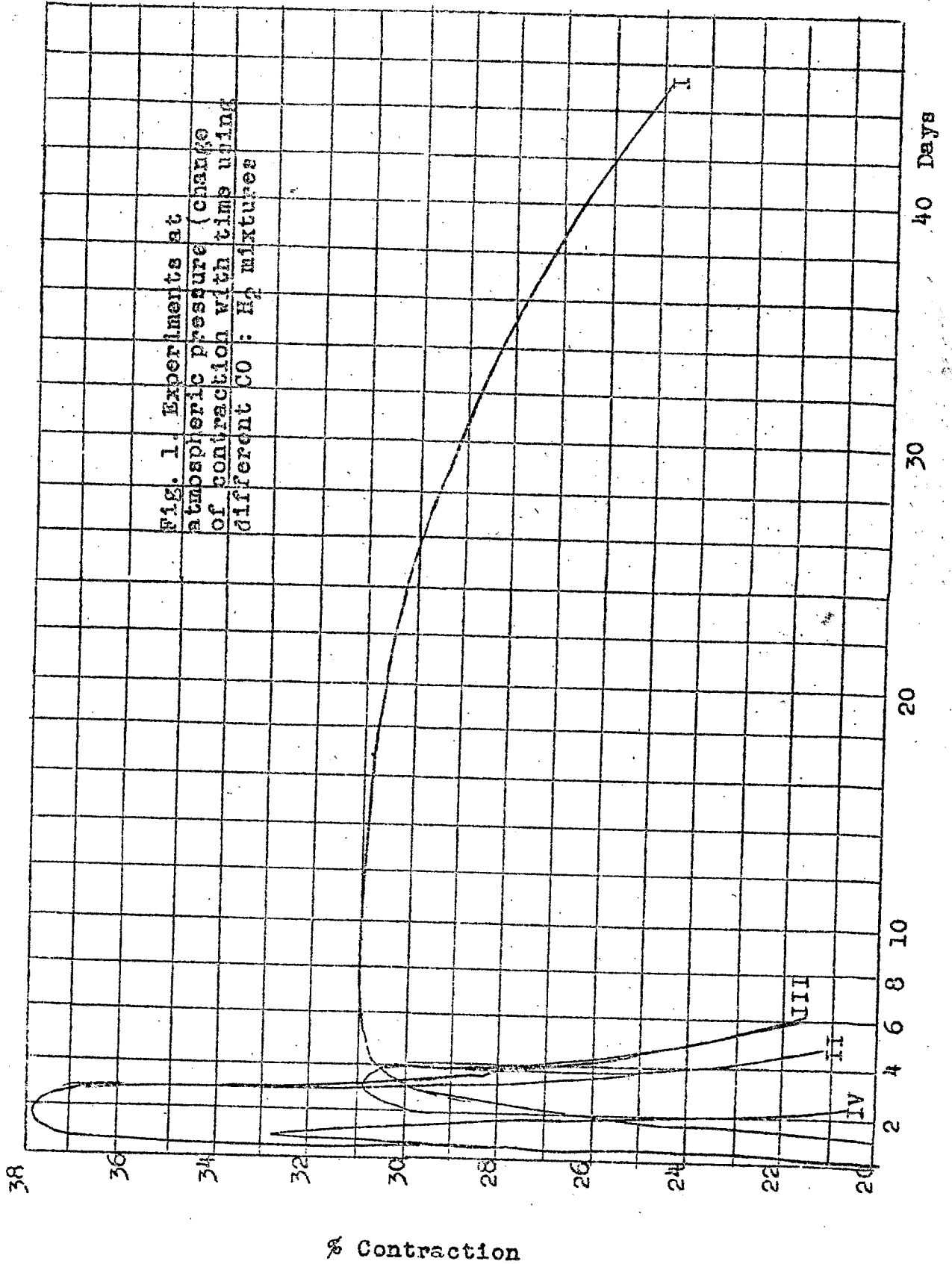
B. Preliminary treatment of the catalysts

The freshly precipitated, dried iron precipitates, like the unreduced cobalt catalysts are entirely inactive as catalysts in the conversion of carbon monoxide with hydrogen. However, when cobalt is treated with hydrogen at about 360°C the reduction to metal proceeds to quite an extent, and the material becomes active as a catalyst for the hydrocarbon synthesis at lower temperatures. The iron catalysts are not converted, however, to a suitable form by a preliminary treatment with hydrogen. When iron is pretreated with hydrogen at some temperature like 300 - 450°C, it is converted into a black ferromagnetic Fe_3O_4 , which does not catalyze the reaction of carbon monoxide with hydrogen. If, however, pretreated with carbon monoxide, which, as commonly known, not merely reduces the oxides, but also forms carbides, with a loosening up of the structure by intercalation of the carbon, the iron catalysts are converted into their most active form for synthesis. We have called the pretreatment with carbon monoxide or with gases containing carbon monoxide the "forming".

1. Forming with Carbon Monoxide - Hydrogen Mixture During Synthesis.

a. Mixed gas and atmospheric pressure.

When iron catalysts produced by precipitation are started in operation with the mixed gas ($CO : H_2 = 1 : 2$) this should be done at 235 - 250°C. Under conditions of the normal pressure synthesis the contraction rises in the course of 3 - 4 days to 30 percent at a temperature of 235°C and a thruput of 4 li mixed gas/h/10g of Fe.



During this time the catalysts are gradually improved to their full activity by the action of the synthesis gas, and this corresponds to the forming period. Synthesis may be continued at atmospheric pressure for 3 - 4 weeks with a maximum contraction of around 30 percent and with yields in liquid and solid hydrocarbons amounting to 50 g/cbm. The carbon monoxide of the mixed gas is approximately used up, while a large excess of hydrogen remains in the end gas. (Figure 1, Curve 1 shows the course of the observed contraction changes during conversion).

b. CO - Rich Gas and Atmospheric Pressure

If a carbon monoxide-hydrogen mixed gas is used during the reduction of carbon monoxide-hydrogen in proportion closer to that in which they interact, instead of the hydrogen in proportion of the rich mixed gas, no improvement in conversion is found when operating at atmospheric pressures. The forming period lasts about three days at 235°C. A maximum contraction of 31 percent has been reached (Figure 1, Curve 2). At 245°C the maximum contraction of 38 percent was reached after one day (Curve 3), while at 255°C a maximum of 33 percent has been reached after one day (Curve 4). The conversion value dropped rapidly after reaching the maximum. The dying-off shows that catalysts are harmed by the hydrogen-carbon monoxide gas during synthesis at atmospheric pressures.

c. CO - Rich Gas and Higher Pressures

Table 2 shows a duration test over 5 months with a normal catalyst which has been started directly in operation at 15 atm. with a synthesis gas, in which carbon monoxide and hydrogen was in the approximate proportion of 3 : 2. 4 li of the synthesis gas were passed per 10 g of Fe of the catalysts, the gas being measured at atmospheric pressure. At 245°C the contraction reached 4 percent after one day, 10 percent after 4 days (against 30 - 35 percent after the same length of time at 1 atm). The temperature was now gradually raised and the contraction observed after every few days. At 260°C the contraction amounted to 24 percent on the 11th. day. Raising the temperature to 270°C at first brought no corresponding increase in conversion. At 275°C, 37 percent has been measured and at 280°C, 36 percent, while only at 290°C did the contraction reach 50 percent.

Forming and Synthesis at a Pressure of 15 Atm.

Days	Temp °C	percent contr- action	Days	Temp °C	percent contraction
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			

Determinations of yield in the 3rd. month of operation at 280°C

	CO ₂	Heavy hydro- carbons	O ₂	CO	H ₂	Hydro- carbons	C- No.	N ₂
Starting gas:	2.2	0.0	0.2	59.0	33.9	0.2	1.0	4.5
End gas:	55.5	3.4	0.2	11.5	11.7	9.3	1.7	8.4

Yield/ncbm ideal gas: 3 g paraffin, 93 g liquid hydrocarbons, 32 g gasol hydrocarbons

Tests were next run to find out if this maximum conversion would remain after lowering the temperature. The contraction dropped again to 37 percent at 268°C, but at 280°C a better conversion has been found after the third month of operation than after the first month. A slow forming of the catalysts has taken place in the meantime. During the 4th. and 5th. months of operation the temperature had again to be raised to maintain a contraction of 40 - 50 percent. At the conclusion of the tests (after the fifth month) the temperature of 300°C had to be maintained.

A determination of yield at 280°C made during the third month gave results shown at the bottom of table 2. Yield per ncbm of ideal gas (starting gas free from inerts) 3 g solid paraffin yield was obtained, 93 g liquid hydrocarbon and 32 g of gasol hydrocarbons (C₃ + C₄).

Compared with the synthesis at atmospheric pressure, when catalysts are put in operation at a higher pressure, the process of forming, and particularly the starting of the reaction at lower temperature, are interfered with. On the other side, higher-carbon monoxide synthesis gas could be used at a pressure of 15 atm. with the temperature raised to 280 - 290°C, without observing.

a rapid dying-off of the conversion as would have been observed with such a temperature rise at 1 atm.

These results have been obtained with iron catalysts obtained in the greatest variety of ways (ferrous and ferric catalysts) with or without additions of copper.

2. Forming with Carbon Monoxide-Hydrogen Mixtures in a Process Separate from the Synthesis.

A. Forming at different pressures, and syntheses at normal pressures.

Tests were made in order to observe whether the activity of the catalysts could be increased by separating the forming and the synthesis processes and selecting the optimum conditions for the two processes.

The effect of the pressure during forming upon the synthesis and atmospheric pressure is shown in table 3. The forming was done at 255°C for twenty hours by passing 4 li. of gas (measured at 1 atm)/h and /10g of Fe; the gas was high in CO (300 : 2H₂). The conversion during the following synthesis with the mixed gas (100 : 2H₂, 4 li/h/10g Fe) was measured 1 1/2 hours after changing, and again at 255°C.

Table 3
The Effect of Pressure During Forming upon Synthesis at Atmospheric Pressure.

Forming pressure atm.	8.5	4.7	2.9	2	1.5	1	0.5	0.1
Contraction, percent	5	12	12	28	25	28	32	30

Tests show that high pressures interfered with the forming process. The pressure during forming of below 1 atm brought about material improvements in the synthesis at atmospheric pressure.

B. Forming at Normal Pressure and Synthesis at Raised Pressure. *

This method of operation was tested with an iron catalyst precipitated with sodium carbonate and the test for the life of the catalyst with an iron catalyst precipitated with ammonia. Both catalysts were prepared as described above and contained 1/4 percent of potassium carbonate.

The iron catalyst precipitated with sodium carbonate was "formed" by passing 4 l/10gFe/h of a high carbon monoxide gas at 1 atm and 245°C for 21 1/2 hours. The contraction of this gas at the end of the pretreatment was 33 percent. It was then changed over to synthesis gas (15 atm and 235°C). After changing over to pressure, the contraction immediately rose to 50 percent but was only 33 percent on the 2nd day of synthesis and only 30 percent on the 3rd day. The temperature of 235°C was too low to maintain a 50 percent contraction with this catalyst. After pretreating the same iron catalyst with mixed gas at atmospheric pressure and 245°C (contraction 30 percent) and changing over to 15 atm of high-CO gas, 43 percent contraction has been obtained at 235°C and 47 percent at 250°C. To maintain a contraction of 45 - 50 percent the temperature had to be raised in the course of 15 days to 257°C. The iron catalysts precipitated with ammonia was formed at 245°C and atmospheric pressure. The contraction rose in the course of 5 days to 51.5 percent. It was then changed over to a high-CO synthesis gas (3CO:2H₂) at 15 atm pressure. Table 4 shows the contraction after different operating periods and the composition of the synthesis gas and reaction gas obtained at 250°C (on the 4th day)

* This has been tested under suitable synthesis conditions in the experiments on the effect of the forming process upon the activity of the catalysts. The effect of different synthesis conditions will be discussed under "synthesis".

Synthesis at 15 atm. with Iron Catalysts Precipitated
with Ammonia and Formed at 1 atm.

Day	Temperature °C		Contraction percent					
1	245		59					
2	245		48					
4	250		53					
5	250		49					
10	252		46					
20	256		51					
50	255		51					
100	265		55					
	CO ₂	Hydro- carbons Heavy	O ₂	CO	H ₂	Hydro- carbons	Carbon number	N ₂
Starting gas: --	2.7	0.0	0.0	55.8	37.3	0.0	-	4.2
End Gas:	53.8	3.4	0.0	11.4	16.2	6.2	2.0	9.0

These tests gave 59 percent contraction on the first day of synthesis at 245°C. In order to obtain a maximum yield and contraction values corresponding to 50 percent and over, the temperature was gradually raised. A complete conversion could be maintained for three months. The temperature after 100 days of operation was 265°C.

A comparison of this series of experiments with those shown in table 2 where the catalyst was used without a preliminary forming at a starting pressure of 15 atm, showed that the preliminary forming at atmospheric pressure permitted a lowering of the synthesis temperature by 30 - 40°. The increased activity of the catalyst produced at the lower pressure of 1 atm was maintained during the whole testing period.

C. Forming at Reduced Pressure and Synthesis at
Raised Pressure

We now record tests with normal iron catalysts formed with carbon monoxide - rich gas (3CO:2H₂) at 0.1 atm and at different temperatures. After forming, lasting for 25 hours at temperatures in the range of 255 - 355°C, the activity of the catalyst was tested over a longer time period by synthesis with a gas CO:H₂ = 3:2, 15 atm and 235°C. Figure 2 shows the reduction in

the contraction with a constant synthesis temperature of 235°C (4 li gas/10gFe/h). After forming at 255°C the contraction dropped to below 50 percent already on the third day of the synthesis, with an increased forming temperature the life of the catalyst was increased; at a forming temperature of 315°C the contraction became less than 50 percent only after one month of operation. At still higher forming temperatures the stability of the iron catalyst became less.

Table 5 shows the results of a test with a catalyst formed at 325°C and at .1 atm. Temperatures and contractions for 200 days are plotted, as well as the starting and end gas analysis on the 10th, 100th, and 200th. days of operation. Operations were conducted at 235°C as long as the contraction remained above 50 percent, the temperature then was slowly raised, and always only enough to get the maximum contraction. The temperature had to be raised to only 240°C after two months of operation, and after three months to only 250°C

Table 5

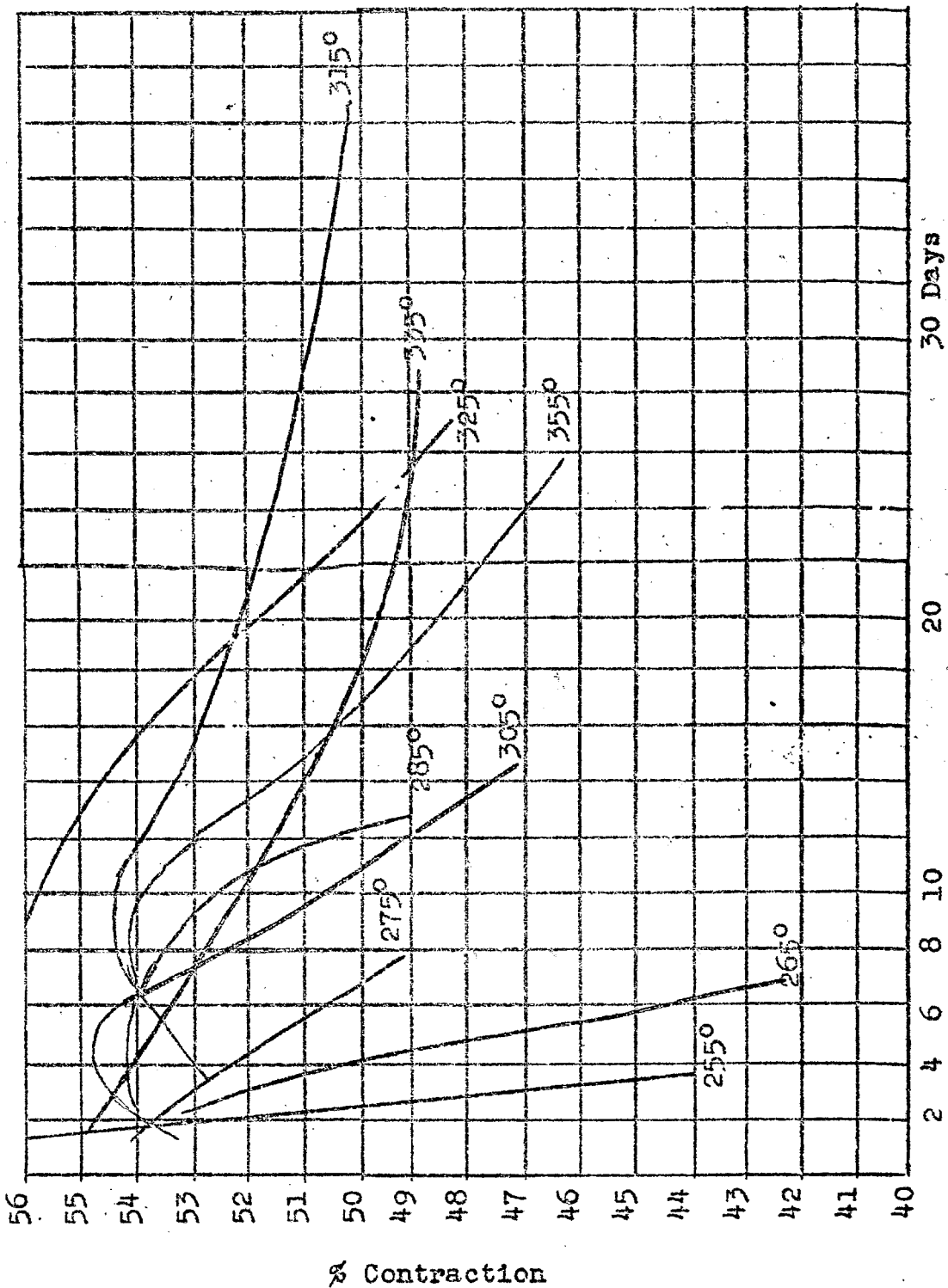
Results with Iron Catalysts Formed at 235°C with Synthesis Gas

Forming: CO-rich gas .1 atm, 4 li/10gFe/h, 25 hours
 Synthesis: CO-rich gas 15 atm. 4 li/10gFe/h, temperature rising from 235°C.

Day	Temp. °C	Contr. percent	Day	Temp °C	Contr. percent
1	235	56	100	252	52
5	235	56	110	248	48
10	235	56	120	256	48
20	235	52	130	264	46
30	237	48	140	269	47
40	240	52	150	270	43
50	240	50	160	270	47
60	241	48	170	277	44
70	247	53	180	278	43
80	250	54	190	272	46
90	249	53	200	273	47

	CO ₂	Hydro- carbons Heavy	O ₂	CO	H ₂	Hydro- carbons	carbon number	N ₂
10th. day								
Starting	2.4	0.0	0.1	52.5	37.6	0.0	-	6.3
End gas:	61.8	2.8	0.0	1.6	12.2	7.2	1.9	14.4
100th day								
Starting	2.0	0.0	0.2	53.6	37.0	0.3	1.0	5.9
End gas:	53.0	2.4	0.1	8.1	15.9	8.3	1.9	12.2
200 th day								
Starting	2.3	0.0	0.2	57.0	31.3	0.2	1.0	7.6
End gas:	48.3	2.8	0.1	15.4	13.4	5.6	1.9	14.4

Fig. 2 Effect of forming temperature on the course of the synthesis (Drop of contraction with time at 15 atm and 235°C) after forming with carbon monoxide with gas at 1/10 atm.



% Contraction

30 Days

20

10

8

6

4

2

The contraction dropped during 200 operating days, from 56 to 47 percent. The composition of the end gas changed but little except for the peak value for carbon dioxide during the first days. Solid, liquid and gasol hydrocarbon/nobm ideal gas were found during a yield determination in the course of the second week of operation. The proportion of gasol hydrocarbon amounted here to 31 g.

A comparison of results obtained with forming the catalysts at .1 atm and 325°C forming temperature with those obtained when forming at 1 atm and 245°C forming temperature (table 4) as well as with those obtained after forming at 15 atm pressure (table 2) shows that during the first month the synthesis temperature required for a 50 percent contraction was 235°C after forming at .1 atm, 245 - 255°C after forming at 1 atm, and at 280 - 290°C after forming at 15 atm.

D. Effect of Forming Pressure at a Forming Temperature of 325°C upon Synthesis at Higher Pressure.

The forming pressure of .1 atm and a forming temperature of about 325°C has been found to be best and the forming pressure at this temperature was re-determined. Table 6 presents the results obtained. Forming was always done for 25 hours with a high - CO synthesis gas and the catalyst was then tested at 235°C with synthesis gas (3CO:2H₂) at 15 atm.

Table 6
Effect of Forming Pressure (at a Forming Temperature of 325°C and Using Synthesis Gas for Forming) upon the Course of Synthesis at 235°C.

press- ure at	Days of operation					
	1	2	4	10	20	30
15	30	24	15	-	-	-
1	56	54	55	50	49	50
0.1	56	56	56	56	52	48

The table shows that the activity of the catalyst formed at 15 atm and 325°C is but slight and becomes rapidly worse. Forming at 1 atm or .1 atm at 325°C resulted in equal conversions during one month of synthesis.