

UNITED STATES
DEPARTMENT OF THE INTERIOR
BUREAU OF MINES
OFFICE OF SYNTHETIC LIQUID FUEL 1294
LOUISIANA, MISSOURI

TOM Reel No. 49, Frames 541 - 662

T-424

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December 3, 1947

Report

On the Work of the Middle Pressure Synthesis

MIDDLE PRESSURE SYNTHESIS WITH IRON CATALYSTS

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Mulheim a. d. Ruhr, June 1940

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Summary

Literature

Introduction

We have published some time ago a paper under the title "Approximation to the Theoretically Possible Yields of the Fischer-Pichler Middle Pressure Synthesis" 1/. The experiments were conducted with cobalt-thorium catalysts. The yields in solid and liquid hydrocarbons (without counting about 13 g gasol) amounted under normal conditions to 150 g with a maximum of about 170 g/nbcm of the ideal gas. Under the most favorable conditions solid paraffines formed over 1/2 of the product.

Franz Fischer and his collaborators have tried ever since the beginning of their work on the synthesis of hydrocarbons from carbon monoxide and hydrogen to substitute cheaper catalysts for cobalt and thorium. Attempts to use iron catalysts were made repeatedly. In 1923 Franz Fischer and Tropsch 2/ have obtained a mixture of the most varied oxygenated compounds by conducting water gas over alkalized iron at pressures at about 100 atm and at 350 - 450°C, and have named the product obtained synthol. The Badische Anilin- and Soda-fabrik 3/ have worked since 1913 at similar pressures and temperatures and have succeeded in 1925 to synthesize methanol. Franz Fischer and Zerbe 4/ have shown, also in 1923 that when the pressure was reduced, the alkalized iron filings acted as a catalyst upon carbon dioxide and hydrogen passing through an intermediate formation of carbon monoxide and hydrogen with ever increasing amounts of hydrocarbons. Their work was done in a circulation apparatus at 410°C and at pressures down from 100 - 105 atm. At high pressures, only water soluble products were obtained, but at pressures of 7 atm, down to which the experiments were continued, some oil has been obtained, which, as has been shown in communications at that time, contained some 40 percent of products insoluble in concentrated sulfuric acid, and which were similar to petroleum in character.

Franz Fischer and Tropsch 5/ stated in 1926 in connection with their publication on the synthesis of petroleum, that at temperatures of 300°C and above and with iron catalyst, carbon monoxide and hydrogen can interact at atmospheric pressure with the formation of hydrocarbons. Starting with this fact, they have recently tried in the following years to increase the activity of the iron catalyst by changing the method of its preparation and by making certain additions to

it, and lower in this way the reaction temperature as well as raise the yield in liquid hydrocarbons. In 1928 6/ at atmospheric pressure, 30 - 40 g of gasoline and oil were obtained/cbm of water gas. The temperatures could be lowered to 240 - 250°C. The life of the catalysts amounted to a few days.

In 1927 Franz Fischer and Tropsch 7/ have also tried to convert water gas at 10 - 15 atm pressure and at 250 - 280°C. The iron-copper catalyst obtained by the ignition of the nitrates were put in operation directly with water gas. The reaction products obtained contained water-soluble and oily substance in proportion of 3 : 2 to 1 : 1. The authors have then stated that the results were poorer than when operating at atmospheric pressure. In the year 1934 Franz Fischer 8/ has however stated in a summarizing article on gasoline synthesis, that 1 cbm mixed gas at atmospheric pressure produced a maximum yield of 30 - 35 g with iron catalyst (which corresponds to about 40 - 45 g/cbm of carbon monoxide - water mixture), and they state further that this initial yield dropped by about 20 percent in 8 days.

In 1934 - 1936 Franz Fischer and Meyer 9/ have again tried to increase the liquid hydrocarbon yield by improving the activity of the iron catalyst. They used an iron-copper precipitated catalyst at atmospheric pressure and succeeded in obtaining 50 - 60 g/cbm yield with a maximum catalyst life of 4 - 6 weeks.

Franz Fischer and Ackermann 10/ have obtained in 1936 50 g of liquid hydrocarbons/cbm of mixed gas by following very definite conditions of precipitation of the copper-free catalyst and operating at atmospheric pressure. This yield began to drop off, however, after a few days, and they got less than 40 g during the third week.

The work then was done with a synthesis gas containing carbon monoxide and hydrogen in a proportion of 1 : 2, even though it had already been recognized that the conversion of carbon monoxide with iron catalyst proceeded entirely according to the empirical equation.



If the proportion of CO to H_2 in the synthesis gas used was 2 : 1, carbon monoxide was only partly converted, and the activity of the catalysts decreased extraordinarily rapidly.

Yields obtained in work up to this time were at most less than half as great as the yields of the industrial gasoline synthesis with cobalt catalysts, which prevented their introduction into the industry.

The present work is a report of means found recently of obtaining an almost complete utilization of a carbon monoxide-hydrogen mixture at a slightly increased pressure over extraordinarily long periods of time by a proper pretreatment of the iron catalyst. Different relative proportions of paraffin, gasoline and gasol hydrocarbons are formed depending on operating conditions. The total yields of this so called "iron middle pressure synthesis" is as great as in the synthesis with cobalt catalysts, permitting at present replacing cobalt with iron.

Towards the end of 1937 Dr. Fischer has already reported on the favorable course in our work on the synthesis with iron catalysts. It was intended at that time to give the opportunity to representatives of gasoline synthesis to verify rapidly in their laboratories the results obtained by us. The importance of replacing cobalt with iron in the synthesis was particularly great in Germany, and Dr. Fischer and myself and a number of collaborators have intensely followed up the work in this field in the meantime and in particular during the last year.

Patents on the important results published in the present paper have been applied for by us in the name of the Society for Study and Utilization (Studien- und Verwertungs - Gesellschaft). Applications dating back to 1937 have been turned over to the Ruhrchemie A.G. to apply for joint patents. In the meantime corresponding patents have also been obtained and published in a number of foreign countries.

I. The Catalysts

A. Precipitation of Catalysts.

We have started at first with the view point, that

variations in the method of preparation of iron catalysts or certain additions to them, could affect the course of reaction of synthesis at atmospheric pressure by increasing the yield of liquid hydrocarbons. Many hundreds of different iron catalysts have been prepared with a greatest variety of additions and by different methods of precipitation.

It has, however, been found in the course of our work that the required objectives could only be reached when operating under a slight pressure, but in that case the iron catalysts used could be prepared in a great variety of ways. If catalysts were subjected to a certain pretreatment (forming) before being put in operation with gases containing carbon monoxide under pressure, catalysts consisting of iron alone could be used for many months to synthesize a satisfactory yield of the required hydrocarbons from carbon monoxide and hydrogen.

1. Raw Material

Solutions of iron salts were generally used as raw material for the preparation of iron catalysts, and these solutions were prepared by dissolving a technical grade of iron. For comparison tests were made with the commercial C.P. grade of iron salts. Most of the tests were made with the following iron compounds.

a. Ferric nitrate (C.P.)

b. A solution of mostly tri-valent iron nitrate prepared from technical iron filings. For its preparation small proportions of iron filings were added to nitric acid of an original Sp. gr. of 1.18, without permitting the temperature to exceed 40 - 50°C (above 60 - 70°C the nitrate decomposes with the formation of insoluble compounds).

c. The ferrous nitrate solution was prepared by using a nitric acid of a maximum Sp. gr. of 1.05 and iron filings, maintaining the temperature at 35 - 40°C. (Higher acid concentration or higher temperatures resulted in conversion of the ferrous into the ferric form, in a violent reaction).

d. Ferrous chloride

concentration of the iron solution used in general 1 g of iron in solution (for divalent and trivalent catalysts) was first neutralized in the cold with a solution of sodium carbonate, until the precipitate redissolve. The ferric solutions were heated at 100°C, the ferrous solutions at a temperature of 70-75°C, using slight sodium carbonate. As a rule the solutions were of some to 8-10 ml of water. After the solution was briefly heated to precipitate and washed with hot distilled water from alkali. The moist precipitate was dried in distilled water, dried on a water bath homogeneous, and with the required amount of most cases potassium carbonate dissolved with steady stirring. Most of the water was removed on the water bath with continuous stirring. The precipitates were heated overnight in a drying oven, desiccated and freed from dust. The ferric catalysts were black-brown, rather hard, and crystalline structure. The ferrous catalysts were earth-brown.

Basic catalysts precipitated with sodium carbonate were used in general to be superior ferrous catalysts. For this reason catalysts and ferric nitrate solutions of technical grade were used in most tests and designated as iron catalysts.

Points in particular must be borne in mind in the preparation: 1. the preliminary neutralization of the solution must be done in the cold, since upon heating, or even after long standing, a precipitate forms in the solution because of deposition of salts, and this would affect the reputation of a good catalysts. 2. The boiling of the nitrate before filtration was important for the life of the catalysts. This can be seen in Table 1. These catalysts prepared under different conditions are compared with the contraction during synthesis (nitrogen-hydrogen mixture 3:2, 15 atm., 235°C), and measure of the activity after differently

long use.

The greatest possible contraction with an assumption of a 100-percent conversion to liquid hydrocarbons according to the equation $2\text{CO} + \text{Fe} = \text{CO}_2 + \text{C}_2\text{H}_6$ is 60 percent, with a synthesis gas containing 10 percent of inert constituents. Actual contractions of 50 - 55 percent were observed in the test yields.

Table 1.

Effect of Temperature of Precipitation upon the Activity of Iron Catalysts

Precipitation Temp. °C	Heated to boiling after precipitation	Alkali Content	Days of Operation					
			1	2	5	10	20	
			Contraction in percent					
20	"	"	45	-	44	43	-	-
60	"	"	50	-	43	20	-	-
20	short	"	20	-	43	51	-	-
20	"	"	-	50	48	51	-	50
20	1 minute	1/4	55	55	43	45	-	50
20	"	3/4	-	38	-	47	-	48
100	"	1/4	50	50	50	49	-	56

This table shows that the two catalysts not heated to boiling either failed to develop full activity or else lost it very rapidly. Catalysts heated briefly to boiling and those boiled for one minute were equally good. Longer heating brought no advantages. The last test where precipitation was done at the boiling point represents the normal iron catalyst.

3. Precipitation with Ammonia

A stream of ammonia was led into solution of ferric nitrate at 60°C containing 10g of iron/lit. The rate of flow of the gaseous ammonia was in general so regulated that the precipitation was complete in twenty minutes. Until the end of the precipitation, ammonia is quantitative absorbed. An equal volume of boiling distilled water was added to the party precipitate, the mixture filtered in the precipitate water five times with hot distilled water. The subsequent alkalization was done in the same way as with the catalysts precipitated with sodium carbonate. The iron catalysts precipitate with ammonia are black-brown, hard and have a vitreous fracture.

4. Addition of Kieselguhr

Iron-kieselguhr catalysts have been used in a number of tests. They will be discussed in a special section. In general the addition of kieselguhr was done after the alkalization, during the evaporation of the catalyst mass on the water bath. The previous dispersion of the kieselguhr in distilled water offers an advantage. It will prevent a too rapid elimination of water from the catalyst mass and the formation of non-homogeneous lumps.

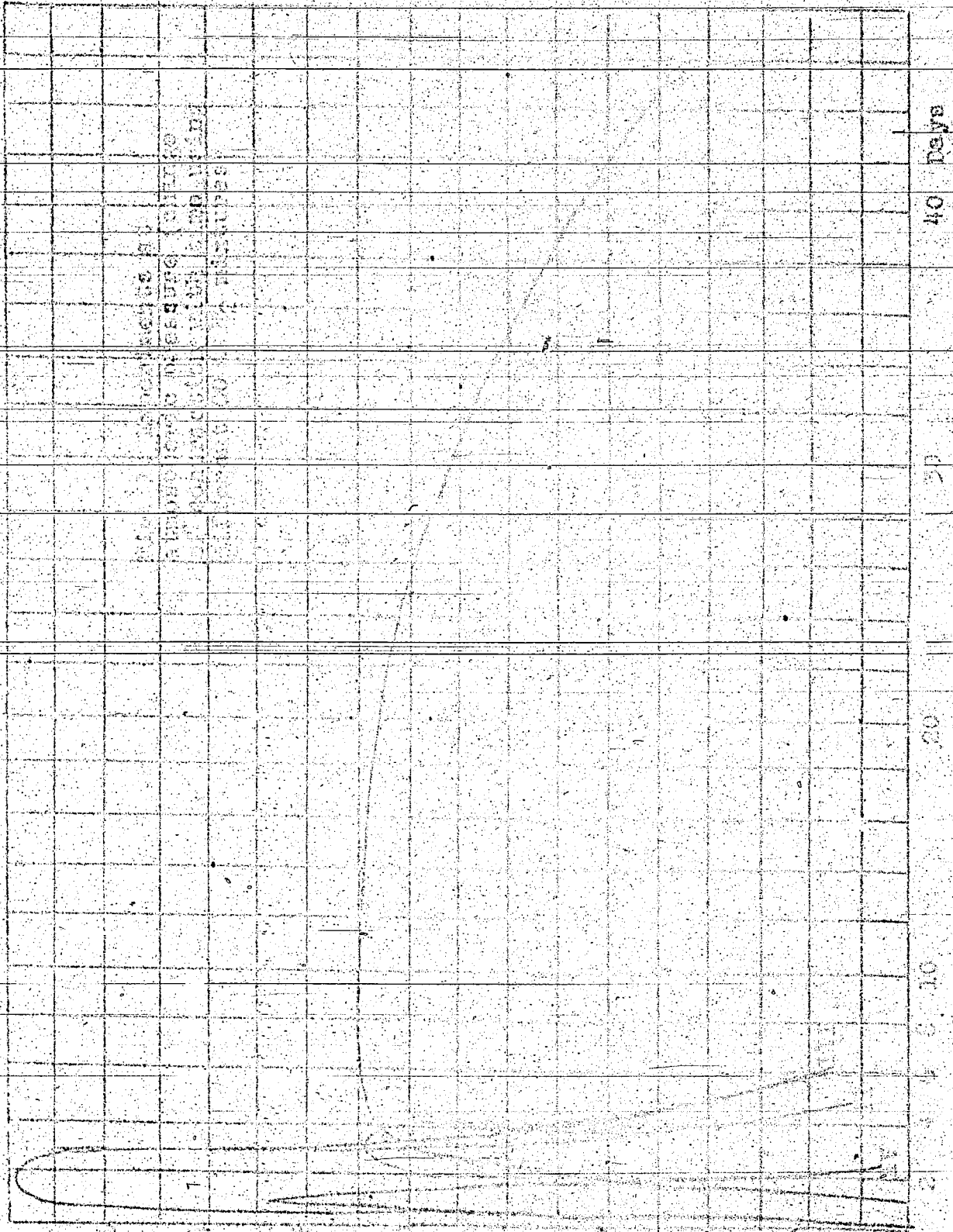
B. Preliminary treatment of the catalysts

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 Fe₃O₄, 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 : H₂ = 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 throughput of 4 li. mixed gas/h/10g of Fe.



5. Contraction

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 50 percent and with yields in liquid and solid hydrocarbons amounting to 50 g/gm. 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 51 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 (equivalent 25 - 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 by itself 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 contra- action	Days	Temp °C	percent contraction
1	245	4	69	268	37
4	245	10	75	280	47
5	250	15	90	280	49
7	253	17	93	285	44
11	260	24	106	285	43
13	270	24	130	285	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.	H ₂
Starting gas:	2.2	0.0	0.2	59.0	35.9	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/netm 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 catalyst 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 - 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 netm 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.

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a rapid dying-off of the conversion and would have been observed with each a time time almost 1 atm.

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

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

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

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 utilizing the full amount of iron for the two processes.

The effect of the pressure during forming upon the synthetic and other kinetic processes is shown in Table 2. The forming was done at 55°C. For twenty hours the reaction was carried out at 1 atm./a and /10g of iron; the gas was then at 1 atm. and the conversion was the following: respectively with the mixed gas (100 : 100) and with /10g of iron, the pressure was 1/5 hours after forming, and again at 55°C.

Table 2

The effect of pressure during forming upon synthesis and kinetic processes.

Forming pressure atm.	5.5	4.5	3.5	2.5	1.5	1	0.5	0.1
Conversion, percent	5	12	20	30	35	28	32	30

Tests show that high pressure interferes with the forming process. It is at the forming forming of better tests brought about the following improvements in the synthetic and kinetic processes.

4. Synthesis at Normal Pressure and Synthesis

at High Pressure

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

oxide. The catalyst precipitated with sodium carbonate was prepared by washing 4 lb/100g of a high carbon iron with 10% ammonia at 245°C for 21 1/2 hours. The catalyst precipitated with ammonia at the end of the pretreatment

was 100% active. The gas composition changed over to synthesis at 245°C. After changing over to pressure, the conversion immediately rose to 50 percent but

dropped to 30% at the end of synthesis and to 20% at the end of the run. The temperature of the catalyst was maintained at 245°C throughout the run.

The catalyst precipitated with ammonia was prepared by washing 4 lb/100g of a high carbon iron with 10% ammonia at 245°C for 21 1/2 hours. The catalyst precipitated with ammonia at the end of the pretreatment

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dropped to 30% at the end of synthesis and to 20% at the end of the run. The temperature of the catalyst was maintained at 245°C throughout the run.

Table 4.

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

Day	Temperature °C	Conversion percent
1	245	59
2	245	57
4	250	57
5	250	46
10	252	46
20	250	51
50	255	51
100	265	55

	CO ₂	H ₂ O	CO	H ₂	CH ₄	HCN	Other	Losses
	wt.-%	wt.-%	wt.-%	wt.-%	wt.-%	wt.-%	wt.-%	wt.-%
Starting	2.7	3.0	0.0	89.6	37.5	0.0	2	4.8
After 100 days	2.9	3.4	0.0	11.7	16.9	3.2	2.0	9.0

These tests gave 59 percent conversion on the first day of synthesis at 245°C. In order to obtain a maximum yield and conversion values corresponding to 50

days. 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 reduced pressure of 15 atm, showed that the preliminary forming at atmospheric pressure permitted a raising of the synthesis temperature by 50 - 40°C. The catalytic activity of the catalyst produced at the lower pressure of 1 atm was maintained during the whole testing period.

3. Forming at Reduced Pressure and Synthesis at
Highest Pressure

We now see the tests with various iron catalysts formed with carbon monoxide + ethylene (CO: C₂H₄) at 0.1 atm and at different temperatures. After forming, lasting for 25 hours at temperatures in the range of 250 - 355°C, the activity of the catalyst was tested over a longer time period by synthesis with a gas CO: C₂H₄ = 3:1, 15 atm and 235°C. Figure 2 shows the reduction in

the contraction with a constant synthesis temperature of 235°C (4.11 g_{cat}/10g_{Fe}/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 durability 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 225°C with synthesis gas

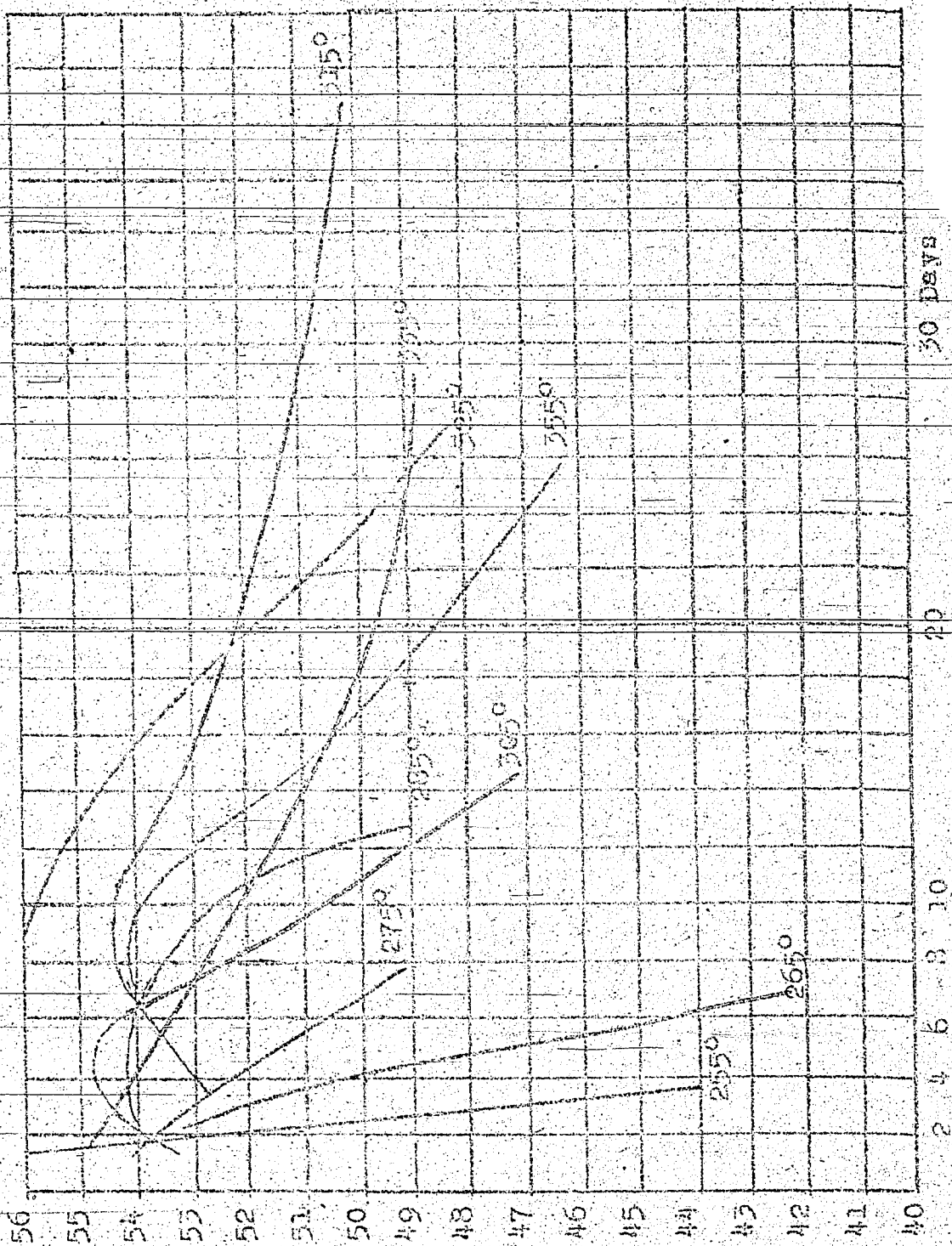
Forming: 30-min. g_{cat} .1 atm. 4.11/10g_{Fe}/h. 25 hours

Operating: 30-min. g_{cat} .1 atm. 4.11/10g_{Fe}/h. Temperature rising from 235°C

Day	Temp. °C	Contr. percent	Day	Temp. °C	Contr. percent
1	235	58	100	252	52
5	235	56	110	248	48
10	235	56	120	255	48
20	235	52	130	264	46
30	237	48	140	269	47
40	240	52	150	270	45
50	240	50	160	270	47
60	241	48	170	277	44
70	247	53	180	278	45
80	250	54	190	272	46
90	249	53	200	273	47

	CO ₂	Hydro- carbons	O ₂	CO	H ₂	Hydro- carbon number	Carbon number
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	0.5	1.0 5.9
End gas:	53.9	2.4	0.1	3.1	15.9	8.3	1.9 12.2
200th 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	13.4	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 275°C) after forming with carbon monoxide with gas at 1/10 atm.



% Contraction

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/normal 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 - 250°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 Pressures

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 (300 mmHg) 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.

3. Forming with Carbon Monoxide

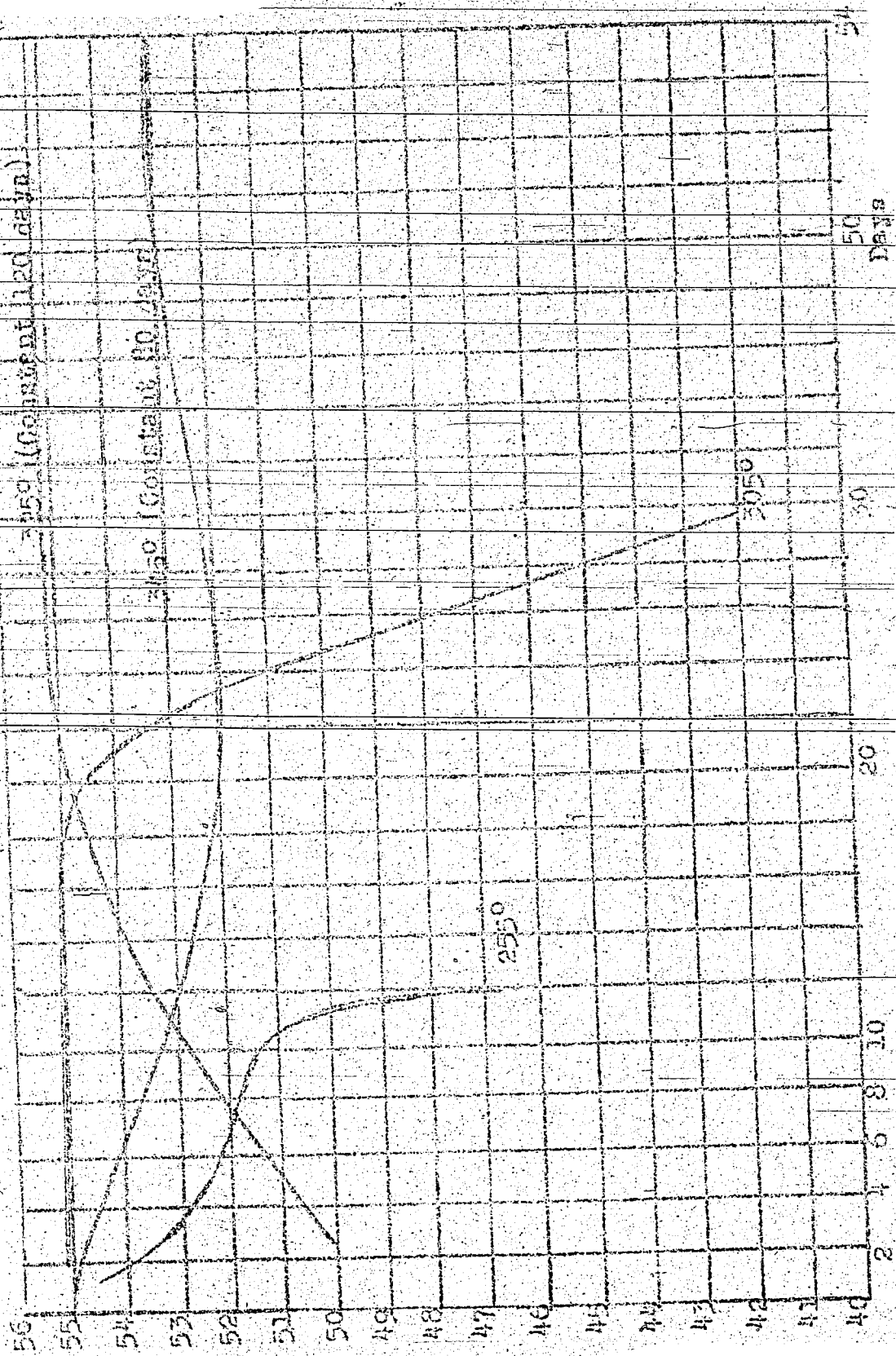
Hydrogen does not assist in the forming of an iron catalyst, and there is danger that products may be produced during forming which will coat the active spots of the catalyst, especially at forming temperatures of 300°C and above when carbon monoxide-hydrogen mixtures are used, and for that reason tests were run with hydrogen-free carbon monoxide.

a. Effect of the Forming Temperature at .1 atm Forming Pressure.

The optimum forming temperature was determined in a series of experiments analogous to those for forming with synthesis gas (v. figure 2). The forming was done for 25 hours with carbon monoxide at 0.1 atm and at different temperatures. The rate of supply of carbon monoxide was 4 l/10gFe/h (referred to 1 atm). The syntheses carried out for the testing of the catalysts were performed at 255°C with a high-carbon monoxide synthesis gas ($3CO + 2H_2$) at a pressure of 15 atm and a rate of flow of 4 l/10gFe/h. Figure 3 shows the behavior of the catalysts formed with carbon monoxide at 255, 305, 325, 345, and 400°C. The iron catalysts formed at 325°C acted best. During the first twenty hours of the synthesis the conversion rose gradually from 50 to 55 percent contraction. Up to the end of the four months the conversion remained constant at 235°C with a contraction of 55 percent. An iron catalyst formed at 345°C produced a contraction in excess of 50 percent for 80 days. Lower forming temperatures, e.g. 255 and 305°C, as well as higher, e.g. as 400°C, gave poorer results.

A comparison of figure 2 and 3 shows that at all forming temperatures the iron catalysts formed with pure carbon monoxide had a longer life than when treated with carbon monoxide-hydrogen mixtures. At 255°C the contraction dropped on the 12th day below 50 percent with a catalyst treated with carbon monoxide, while after pretreatment with synthesis gas it dropped on the third day; with a forming temperature of 305°C the corresponding drop occurred on the 25th. and 12th days respectively; and at 325°C after 120 days against 24 days. With a catalyst forming at 325°C the temperature was raised after 130 days of operation, and with the catalyst formed at 345°C after eight days. A few operating data of these tests are shown in tables 7 and 8.

Fig. 3 Effect of the temperature of forming on the course of synthesis after forming with Cu at 1/10 atm.



% Contraction

Table 7

Results with an Iron Catalyst Formed with Carbon Monoxide
at 325°C

Forming: Carbon monoxide, 1 atm & 11/10gFe/h, 25 hours
Synthesis: CO in rich gas, 15 atm & 11/10gFe/h,
temperatures rising from 235°C

Day	Temp. C	Concn. percent	Day	Temp. C	Concn. percent
1	235	47	140	245	49
2	"	50	160	250	49
5	"	50	180	251	50
10	"	51	200	250	44
20	"	55	250	265	50
50	"	54	300	265	45
100	"	53	350	270	40
130	"	47			

40th day	CO ₂	hydro- carbons	0	CO	H ₂	hydro- carbons	carbon number	2
Starting gas:	2.0	0.0	0.0	52.4	39.8	0.0	-	4.8
End gas:	57.0	2.6	0.1	6.3	14.6	8.9	2.0	10.5
70th day								
Starting gas:	2.5	0.0	0.2	54.7	37.9	0.2	1.0	4.5
End gas:	64.0	2.9	0.0	2.5	9.5	11.3	2.5	2.2
100th day								
Starting gas:	3.5	0.0	0.0	54.4	37.1	0.2	1.6	4.8
End gas:	61.2	3.5	0.1	5.2	11.2	9.0	1.9	10.0
300th day								
Starting gas:	2.0	0.0	0.2	56.6	34.8	0.2	1.0	6.2
End gas:	48.9	2.9	0.2	15.9	10.8	8.5	1.9	12.2

Yield/ncbm ideal gas, 40th day: 108 g liq. + sol.
hydroc. 44 g gasol.

Yield/ncbm ideal gas, 70th day: 105 g liq. + sol.
hydroc. 45 g gasol.

Yield/ncbm ideal gas 100th day: 110 g liq. + sol.
hydroc. 47 g gasol.

Yield/ncbm ideal gas 300th day: 110 g liq. + sol. gasol.

hydroc. not determined

The tests with the iron catalysts formed at 325°C were carried on for one year. After being kept for four months at 235°C with a constant conversion, the temperatures had to be raised to 270°C to maintain the same conversion. The yields remained approximately the same during the whole time of operation. They amounted to 105 - 110 g liquid and solid hydrocarbon and 40 - 47 g gasol hydrocarbon/normal ideal gas.

Table 8

Results with an Iron Catalyst Formed with Carbon Monoxide at 345°C

Forming: Carbon Monoxide, .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.	Day	Temp °C	Contr.
1	235	55	60	235	52
5	"	50	80	"	49
10	"	51	100	248	54
20	"	51	115	250	49
40	"	55			

	CO ₂	Hydro- carbons Heavy	O ₂	CO	N ₂	Hydro- carbons	Carbon number	N ₂
50 Day Starting gas	2.2	0.0	0.0	55.4	39.6	0.0	-	4.8
End gas	57.7	2.8	0.2	6.1	13.8	8.9	1.9	10.5

The yield with catalysts formed at 345°C at the end of the second month of operation at 235°C amounted to 110 g solids and liquids and 41 g gasol hydrocarbon/normal ideal gas. The temperature at the end of the second month was 250°C with a contraction still approximately 50 percent. The analysis of the end gas of the synthesis after forming with carbon monoxide at .1 atm and 325 - 345°C (cf table 7), corresponding to constant values of the contraction, remained without any important changes during many months of operation.

b. Effect of Forming Pressures

A series of tests were run with carbon monoxide, analogous to those for forming with synthesis gas

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(see table 6). Table 9 shows contractions after different lengths of synthesis with forming at 15 atm, 1 atm and 0.1 atm. The length of forming was again 25 hours (4.11/h) the forming temperature was 325°C. During the first days of operation the conversion was good with all three catalysts. However, it dropped during the fourth week with the catalysts formed at 15 atm, while with the catalysts formed at 0.1 atm, the conversion remained constant after three months.*

Table 9

Effect of the Forming Pressure (with a Forming Temperature of 325°C, with Carbon Monoxide used in Forming) upon the Course of Synthesis at 225°C.

Pressure	Days of Operation					
	1	10	20	25	30	60
	Contraction in percent					
15	58	52	48	40	-	-
1	58	57	53			
0.1	-	51	55	54	56	54

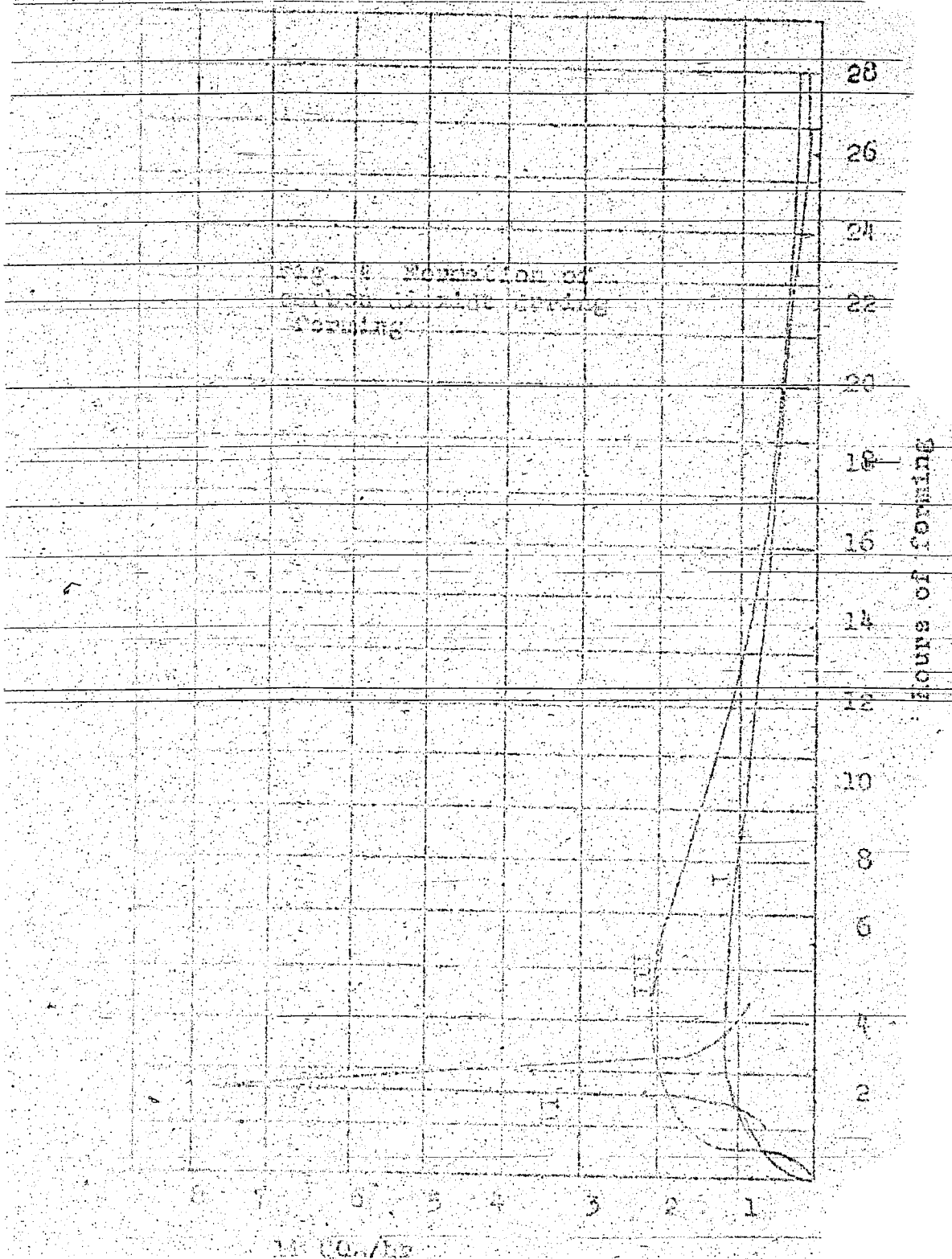
A comparison of the results of the different series of tests with those shown in table 6 leads us that forming at higher pressures with pure carbon monoxide gives better results than forming with carbon monoxide-hydrogen mixtures.

c. Rate of Forming

When forming at reduced pressures, about 100 ml of carbon monoxide were led over 10 g of Fe of the catalysts. The flow was relatively rapid, and only a small part of the gas was used up, and after eliminating the carbon dioxide the gas could be used again for the preparation of the iron catalysts.

As may judge the process of forming by the detection of the carbon dioxide formed during the process. Curves I and II in figure 4 show the amounts of carbon dioxide formed at 0.1 atm and 325°C/10 g Fe/h. The

* Relatively much carbon was deposited upon the catalysts when formed at higher pressures. Quantitative results on it are reported elsewhere.



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temperature of 525°C was reached in 2 1/2 hours in curve I, while 1 1/2 hours were required for curve II. During this preheating time the rate of flow of the carbon monoxide was 4 li/h. In the test curve I, the work was continued at the same rate of flow of gas, while in curve II it was increased to 40 li/h. With 4 li carbon monoxide/h at first more than 1 li of carbon dioxide/h was formed. The rate of formation of carbon monoxide gradually dropped. 25 hours after reaching the temperature of 525°C the carbon dioxide formation reached a certain minimum value 0.2 - 0.3 li/h. With 40 li/h the maximum carbon dioxide value amounted to 8 li/h, and became constant and equal to about 1 li/h after 2 1/2 hours. In both cases about 10 li of carbon monoxide were led over the catalysts before reaching the constant minimum value. The total amount of carbon dioxide formed in tests 1 up to this time was 10 li, in test 2 - 11 li. The forming with carbon dioxide represents a reduction process as well as the formation of the combined and free carbon according to the equation $2\text{CO} = \text{C} + \text{CO}_2$. Larger amounts of carbon were incorporated during the slow passage of gas in the test 1, than in test 2.

Table 10 summarizes 4 tests. Tests 1a and 1b correspond to the carbon dioxide formation of curve I, figure 4, tests 2a and 2b belong to the curve II.

The forming in test 1a lasted 25 hours with 4 li/h at 525°C , in the test 1b 2 1/2 hours, in the test 2a 2 1/2 hours with 40 li of carbon monoxide/h at 525°C , and in test 2b only 20 minutes. The time when forming was interrupted and the reaction with the synthesis gas was begun are shown with crosses on the curves of figure 4. The subsequent synthesis was carried out in all gases with a pressure of 15 atm and with a temperature of 235°C . Table 10 shows that in tests 1a and 2a, after passing 100 li of carbon monoxide, a good and permanent activity of the catalysts has been reached. Interruption of the forming before the dying down of the "carbon dioxide curve" (tests 1b and 2b) produced catalysts with good conversion at the beginning but which dropped off very rapidly.

Table 10

The Effect of the Rate of Flow of Carbon Monoxide and the Length of Forming upon the Amount of Synthesis

Tests	1a	1b	2a	2b
lit CO/h	4	4	40	40
Hours of forming	25	2.5	2.5	0.3
Total carbon monoxide passed	100	10	100	12
Contraction - percent during the Synthesis				
1 day	47	55	53	53
2 "	50	50	51	50
5 "	50	50	50	-
10 "	51	-	49	-
20 "	55	-	51	-
30 "	51	-	51	-

In the experiments with 4 lit of carbon monoxide/h and with 40 lit/h the rate of flow of the gas at a pressure of .1 atm was sufficiently great to remove the carbon dioxide which disturbs the forming process on the catalyst surface. In the test of forming during a shorter time (test 2a) 12% total carbon dioxide and therefore also less carbon was formed, which may represent in many cases an advantage, in spite of the same activity as in the test 1a.

values when forming at 1 atm (cf the results in table 9). Work was done with a rate of flow of carbon monoxide of 4 lit/h (like in curve I).

Curve III shows that with 1 atm pressure during the forming process, more carbon dioxide is formed than at reduced pressure, which indicates a higher formation of carbon.

d. Mixing Carbon Monoxide with other Gases.

Mixtures of carbon monoxide with hydrogen have already been discussed. The results were better especially when forming at normal or higher pressures, than were obtained with pure carbon monoxide, and this has been explained, by the formation of synthesis products on the catalyst surface which prevent action. The presence of carbon dioxide or steam hampers the reduction.

processes and therefore be avoided as much as possible during forming.

The presence of some amounts of inert gas, especially nitrogen, cannot be avoided in industrial operations. Larger amounts of inert gases interfere with forming. Results obtained with 0.1 atm pressure cannot be duplicated by working at atmospheric pressure with 0.1 atm partial pressure of carbon monoxide and 0.9 atm partial pressure of nitrogen. 25 hours forming under these conditions with 40 li carbon monoxide-nitrogen mixture (about 100 li carbon monoxide), produced a catalyst with only 37 percent contraction at 250°C. A 1:1 carbon monoxide-nitrogen mixture with a 10 atm partial pressure of carbon monoxide, produced an iron catalyst with about 40 percent contraction for three weeks at 250°C.

The results show that a pretreatment with carbon monoxide of the catalyst containing carbon monoxide at 250°C is necessary for the production of native iron catalysts. It is concluded that forming has to be carried out at temperatures lower than those used in the synthesis.

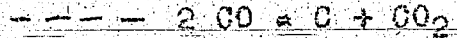
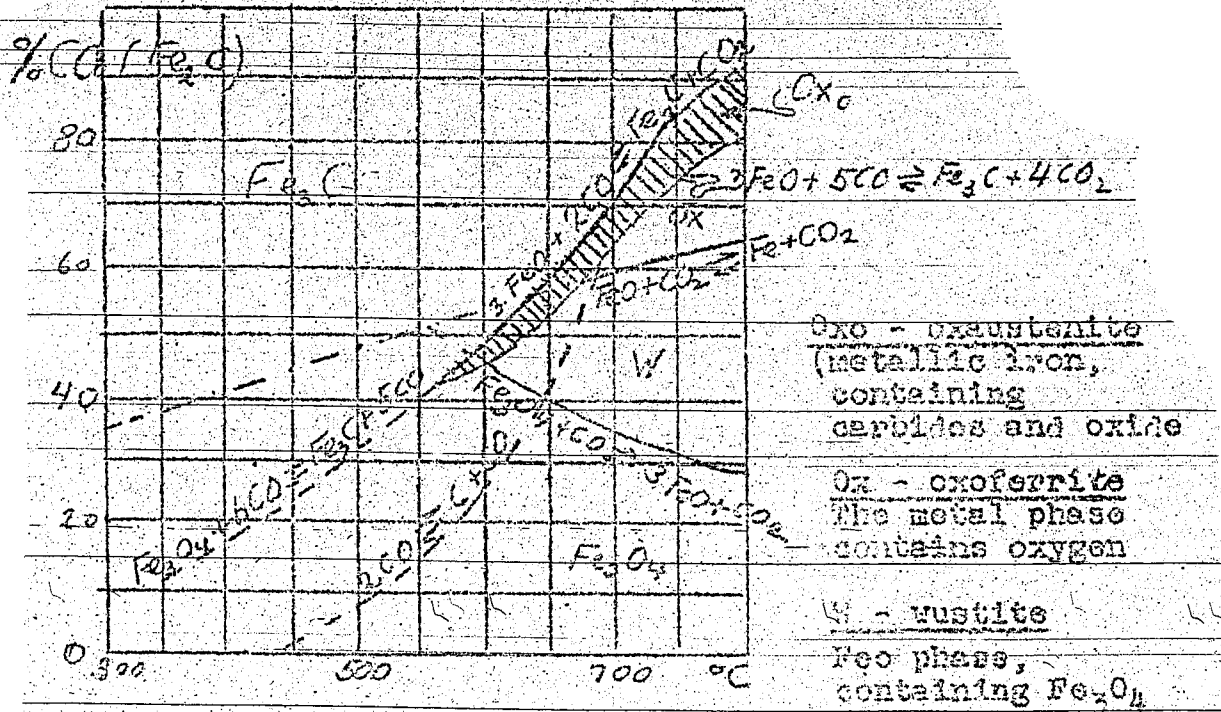
The results of the catalysts formed with carbon monoxide in the presence of nitrogen is somewhat lower than when formed with carbon monoxide alone, which was explained by the deposition of carbon monoxide with hydrogen on the surface of the catalysts, with formation of a layer which has a tendency to block pores or block the surface of the catalysts.

No sintering of the catalysts has been found possible.

The difference in the action of carbon monoxide and hydrogen may be based on the fundamental difference in the reaction processes of iron oxide, namely in the building up of the iron structure by the carbon intercalation during the reaction with carbon monoxide, and in the intercalation of oxygen by the treatment with carbon monoxide.

The reduction with hydrogen is more rapid than with carbon monoxide, if we disregard the diffusion, sintering and the deposition on catalyst, as is well known from data in literature. When operations are run under conditions

a) 1 atm



b) 1/10 atm

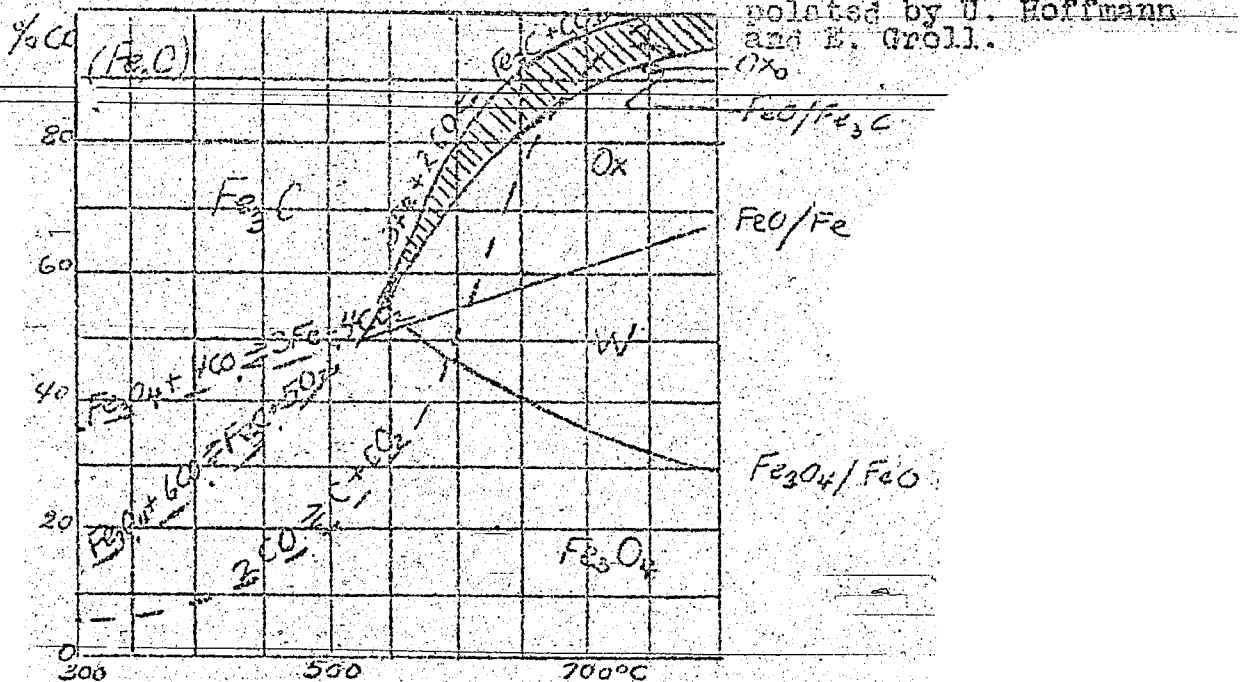


Fig. 5 Equilibrium conditions in the Fe-C-O system.

under which these above mentioned points must be considered, the reduction with carbon monoxide may proceed more readily because of the loosening up caused by the intercalation of carbon 11/.

The original process of the reduction is the formation of the ferromagnetic Fe_3O_4 . It is formed during the reduction with carbon monoxide as well as with hydrogen, and can be obtained by a precipitation of a mixture of ferrous and ferric salts with alkalis, followed by dehydration; it possesses, however, no catalytic properties for the middle pressure synthesis.

We may refer to the equilibrium conditions of the iron-carbon-oxygen system in our subsequent discussion of the course of the action of carbon monoxide. This equilibrium depends on the temperature, the gas pressure, and the proportion of carbon monoxide to carbon dioxide in the gas. Figure 5a refers to atmospheric pressure. It represents the results of investigations of R. Schenck 12/. The broken curves were obtained by U. Hoffmann and E. Crowl 13/ by computation. Figure 5b reproduces the equilibrium relationships at the pressure of 0.1 atm. The $Fe_3O_4-Fe_2O_3$ curve was calculated taking into consideration the relationship between pressure and equilibrium values, the other curves from results of Schenck in the work quoted above.

We may draw the conclusion from figure 5 that at temperatures below $550 - 560^\circ C$, FeO is unstable (according to Schenck, because it already contains Fe_3O_4 called by him "Wüstite"). The reduction of Fe_3O_4 proceeds therefore without passing through the FeO phase.

The metallic phase, which according to Schenck consists of oxygen-containing α -ferrite and the oxygen and carbides-containing α -austenite, and is in stable equilibrium only at temperatures above $550 - 600^\circ C$. At lower temperatures the carbide may therefore form by a direct interaction of carbon monoxide and Fe_3O_4 or by way of formation of unstable lower oxygen intermediate substances. U. Hoffmann and E. Crowl have subjected to X-ray analysis the substances formed by passing carbon monoxide over iron and found only a very slight amount of free iron at temperatures below $655^\circ C$.

The reduction of the higher oxides to the lower oxides or to metallic iron does not depend on the pressure, and therefore only on the proportion of carbon dioxide: carbon monoxide, and from the temperature; we may see, however, from the Figure 51 that the conversions during the formation of either the carbide or of carbon monoxide are displaced by lowering the pressure towards the carbon monoxide side. Raising the pressure will therefore favor the formation of carbides and of carbon.

When operations are conducted with a 100 percent carbon monoxide, as may be done when the carbon monoxide is conducted in a very rapid stream over the substance, only iron carbide is stable during equilibrium at 1 atm as well as 0.1 atm.

Should equilibrium become established during the action of pure carbon monoxide upon metallic iron, the carbide would form first, while the carbon dioxide formed acts as an oxidizing agent upon the metallic iron. This explains the fact that the forming of an iron catalyst is favored by lower pressures and the higher rates of carbon monoxide, because the process is a reduction process, and both these factors reduce the partial pressure of carbon dioxide and provide the rapid removal of the adsorbed carbon dioxide from the reacting surface.

In both diagrams the carbide is assumed to exist as cementite Fe_3C , and not as some higher carbide. Hilbert 14/ was the first to assume its existence in 1915. Franz Fischer and his collaborators have repeatedly referred to the formation of higher carbides as intermediate products of the gasoline synthesis. Franz Fischer and H. Bahr 15/ have even described such a carbide of iron. Glaud and his collaborators, 16/ have assigned the formula Fe_2C to this carbide. U. Hoffmann and E. Groll have reported in their work, cited above, on the interaction of carbon monoxide upon iron at below $400^{\circ}C$, the proof of the existence of such carbides from interferences in their X-ray investigations, and established that at temperatures over $400^{\circ}C$ this carbide disappears with a simultaneous increased deposition of carbon. It is assumed that during this deposition cementite and free carbon are formed.

Only little can be said at present about equilibrium conditions of this particular carbide or any possible higher carbides. The range of its existence could not

to what extent this undesired break-down of the carbon monoxide is interfered with by the simultaneous presence of hydrogen. It has, however, been already proven that the formation of carbon during forming is strongly repressed by lowering the pressure and by increasing the rate of flow of carbon monoxide.

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:

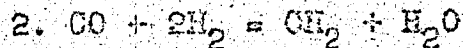
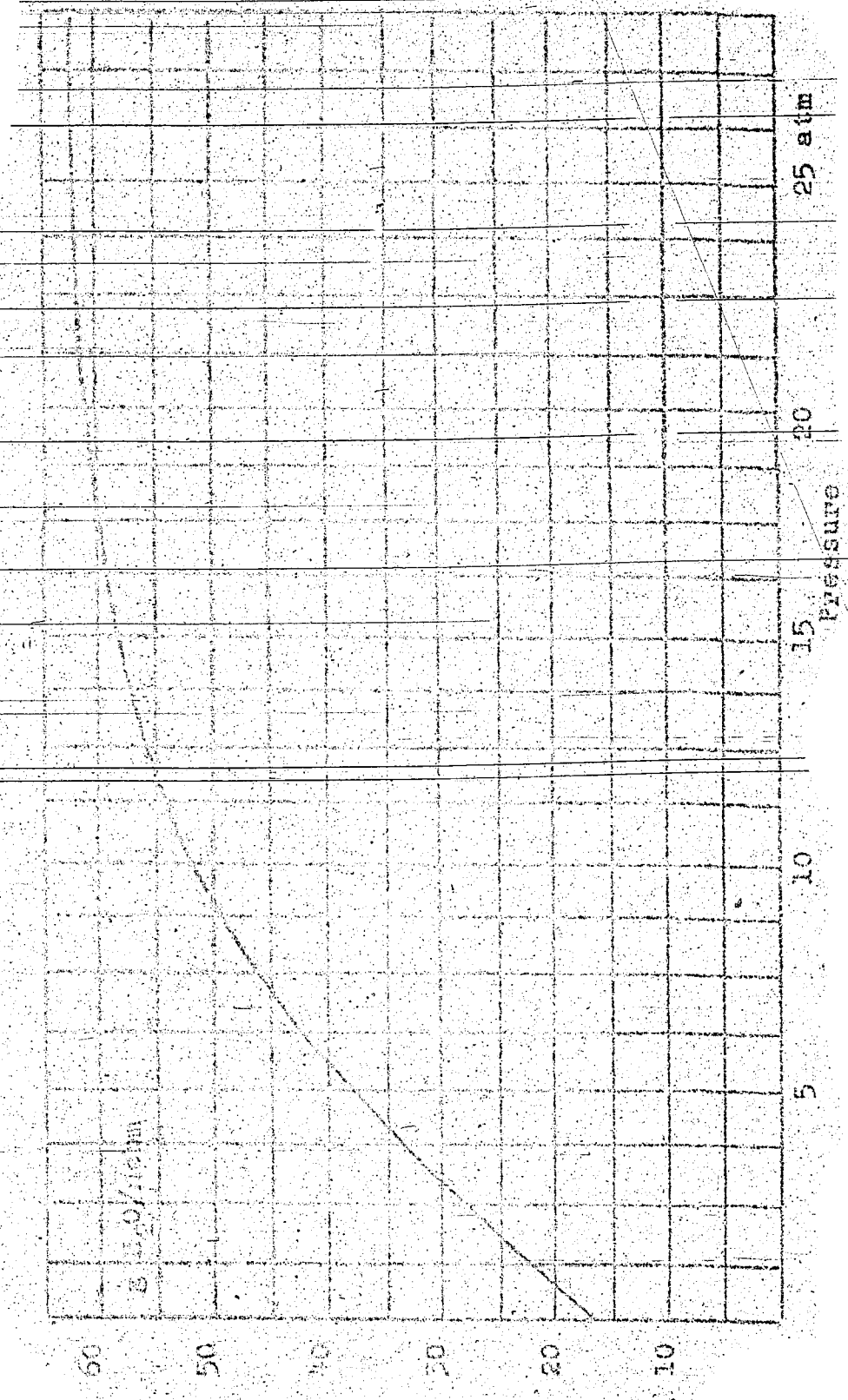


Figure 6 shows the forming of the water of reaction (containing also water soluble organic compounds) at different pressures with a synthesis gas with the carbon monoxide and hydrogen in proportion 1 : 2, and a reaction temperature of 235°C. The amount of water of reaction rises from 14 to 60 g/nobm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

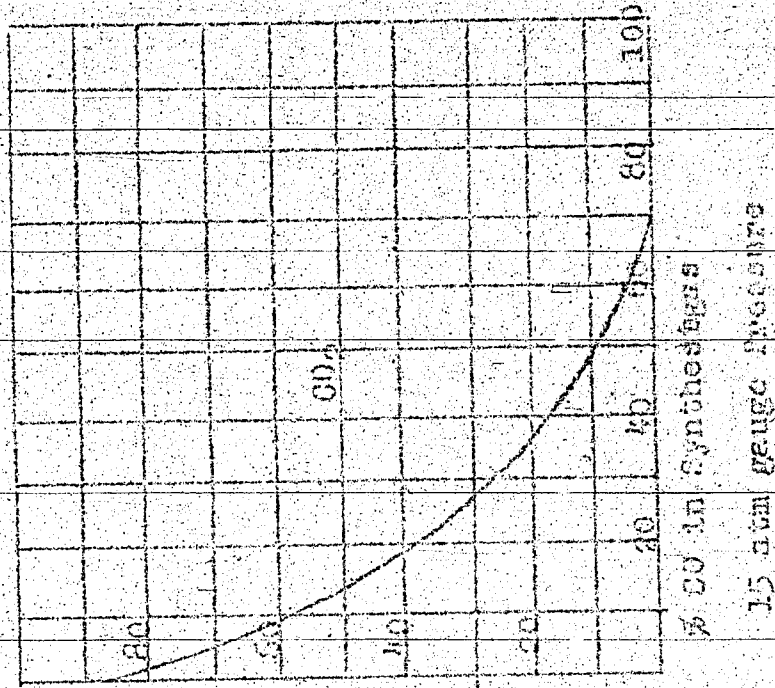
Figures 7a - 7b show the proportions of the oxygen of carbon monoxide in different synthesis gases converted into water and into carbon dioxide at 15 atm. With an initial content of 50 percent carbon monoxide in the starting gas and at atmospheric pressure, 7 percent of the oxygen of the carbon monoxide 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. 67. Formation of water vapor at different pressures
(Symbolic gas 00 1.1g)

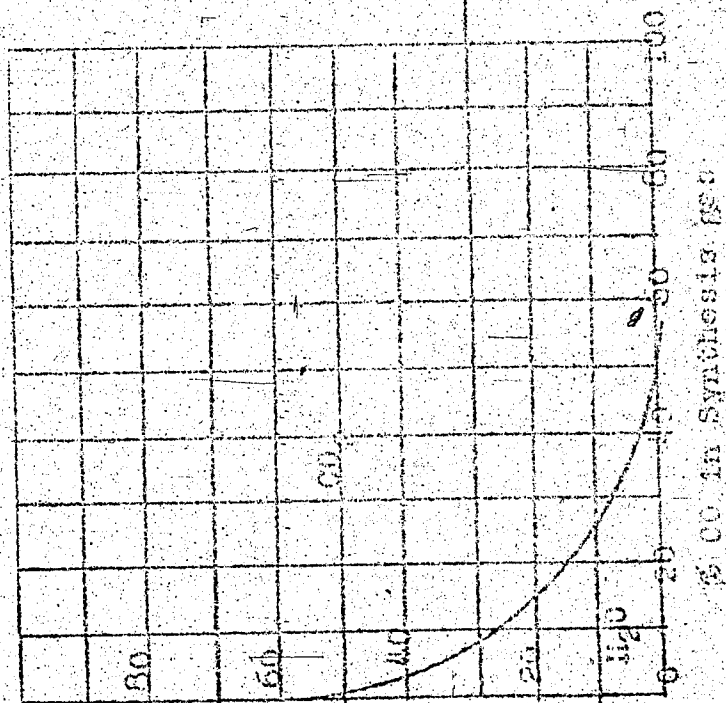


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% oxygen in CO converted to CO₂ + H₂O



% oxygen in CO converted to CO₂ + H₂O

Fig. 7. Conversion of the oxygen in CO into CO₂ and H₂O 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 200 g hydrocarbons/nbcm 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 "aging 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 1.05 : 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/nbcm on an iron catalyst for many months.

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



Fig. 2 Effect of composition of the synthesis gas on the yield

Effect of total liquid and gas on 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 ($0.34 : 1$).

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 minimum 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 degree of carbon formation which will affect the life of the catalyst; it must also be borne in mind that as the proportion of carbon monoxide increases, the rate of 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 disregarding 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 alkalinized with 1/8 percent K_2CO_3 . The catalyst was formed at atmospheric pressure for four days at 255°C with mischgas (4 l/10gFe/h). After forming, the synthesis was conducted with 4 l of gas ($\text{CO} : \text{H}_2 = 3 : 2$)/10gFe/h. Table I shows the results in this series of experiments. The operating temperatures are compared at 5, 15, 30 and 60 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 Mischas at 2350°C 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	255	50	270	38
20	265	45	265	50	274	50	286	42
30	270	42	270	55	280	48	300	48
40	272	45	274	55	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 gases in fact 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 Contractions of 50 Percent.

Pressure	Days of Oper.	Temp. °C	CO ₂	Hydro. carbons Heavy	O ₂	CO	H ₂	Hydro. carbons	Carbon Number	H ₂
5	6	257	53.8	3.4	0.2	12.5	13.3	7.0	1.9	10.0
15	3	252	55.3	3.8	0.2	11.5	11.6	8.0	1.8	9.4
15	27	267	51.7	2.5	0.2	11.2	16.4	2.9	1.6	11.5
30	10	263	51.1	2.3	0.1	11.3	18.0	7.7	1.8	9.0
80	27	297	51.1	1.4	0.1	13.6	11.0	14.3	1.9	8.5

The composition of the end gases above listed in spite of differences in pressure and correspondingly different temperatures, the contractions were not basically different. To have a better picture of the effect of the pressure we indicate, 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 unreacted hydrocarbons is reduced while the amount of hydrocarbons are increased because of the necessary high reaction temperatures. The increased hydrocarbon formation is reflected in the ratio of the consumption of carbon monoxide to hydrogen. It amounted to 5 atm to 1.7:1; at 15 atm to 1.65:1, at 30 atm to 1.63:1 and at 80 atm 1.41:1.

With respect to the life of the catalyst at different operating pressures we may say that the test carried out at 15 atm resulted in the longest operating times because of the longer life 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 normal iron catalyst, copper-iron, was used for forming for 24 hours at 1.5 atm and 275°C with carbon monoxide-rich synthesis gas. Table 1 shows the results with 1.5, 2.0, 3.0 and 5.0 atm. The reaction began at 275°C.

Reaction Temperature and Conversion of Catalyst
 Pressure (atm) and Days of Operation
 Rich Gas at 275°C

Days of Operation	1.5 atm		2.0 atm		3.0 atm		5.0 atm	
	°C	%	°C	%	°C	%	°C	%
1	275	10	275	15	275	20	275	25
2	275	15	275	20	275	25	275	30
3	275	20	275	25	275	30	275	35
4	275	25	275	30	275	35	275	40
5	275	30	275	35	275	40	275	45

50 percent conversion of catalyst at 275°C.

At atmospheric pressure, the reaction began with this catalyst at 275°C. However, the reaction after 24 hours at 1.5 atm and 275°C. At 5 atm the reaction began at 275°C. Conversion was 10% after 24 hours, even after increasing the temperature to the ninth day. (The catalyst was used at 1.5 atm, 2.0 atm, 3.0 atm, and 5.0 atm at 275°C. The reaction began at 275°C. The conversion was 10% after 24 hours at 1.5 atm, 15% at 2.0 atm, 20% at 3.0 atm, and 25% at 5.0 atm. In the operation of the catalyst at 275°C this series of experiments the conversion of 50 percent in the first 24 hours obtained with 50 atm. The reaction had been increased to 100%.

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 reverted 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	55
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 nickel 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.

C. The Reaction Temperatures

The temperature data in the present paper were obtained by measurements in an aluminum block. In spite of the good insulation of the two ends of the tubes protruding from the aluminum block with asbestos cord, the radiation from the ends of the tubes results in an around 5°C lower reading of temperature inside the tubes than the temperature of the aluminum block, as found in tests. On the other hand the catalyst temperatures are always somewhat higher than of the surrounding space because of the positive heat of the reaction, and both corrections were left out and the temperature of the block was given.

Special efforts were made during the work on the iron nickel pressure synthesis to lower the reaction temperature. This seemed to be important from purely economic considerations, because on an industrial scale the synthesis whenever possible is carried out in water cooled pressure tubes and every rise in temperature here would result in a rise of the steam pressure and will necessitate a strengthening of the reaction equipment.

M. Effect of Forging

It has already been mentioned elsewhere that the temperature required for synthesis was principally dependent on the temperature of forging of the iron catalysts to be used in that synthesis. The curves in figure 9 show the limitations in the contents already discussed. The months of operation are laid out on the abscissa, the temperatures on the ordinate, and the saturation pressures of steam at those temperatures are shown. All tests were now done with a synthesis gas with the partial composition and hydrogen in a proportion * The work was done in the laboratory in pressure tubes, heated in a standing aluminum block furnace.

of 3 : 2 (4 $11/10$ Fe/h).

Curve I refers to a catalyst which has been put in operation at 15 atm pressure without any previous forming. The temperature had to be raised to 290°C to produce a maximum contraction. At first the contraction amounted to 45 percent, in the course of the second month of operation the activity of the catalyst rose gradually and the contraction rose with it to around 50 percent. In further operations the temperature could be lowered without changing the conversion to 280°C. It had to be again raised during the fourth month, and at the end of the fifth month, a temperature of 300°C has been reached.

Curve II shows the temperature relationships with an iron-copper catalyst which was first operated at 1 atm and 210°C for three days with a miscogas (contraction 30 percent) and was changed over to synthesis gas at 15 atm pressure after three days. The maximum contraction of 50 - 55 percent (optimum conversion) was obtained by raising the temperature in the course of five months from 210°C to 290°C.

Curve III shows the changes in temperature in a test with a copper-free normal iron catalyst which was treated at 0.1 atm and 255°C for 25 hours with pure carbon monoxide. The maximum contraction of 50 - 55 percent was obtained by raising the temperature in the course of eight months from 225 to 275°C. At these temperatures the activity of the catalysts grew gradually and during the eleventh month the temperature could again be lowered to 255°C maintaining the contraction at 50 percent. During the fifteenth and sixteenth months the temperature had again been raised to 266°C and then lowered to 255°C. Table 16 gives the composition of some end gas obtained during this test.

Table 16

Composition of End Gases of Duration Experiment
Conducted at Different Temperatures During Sixteen
Months of Operation.

Months of Operation	Temp °C	Concn %	Composition of End Gas in Percent							
			CO ₂	Hydro- carbons Heavy	O ₂	CO	H ₂	Hydro- carbons	Carbon Number	N ₂
1	253	50	49.6	2.2	0.1	15.0	13.3	8.8	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	14.9	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	253	48	51.2	3.2	0.2	9.9	12.6	10.4	1.8	12.5

The table shows that as the temperature rises the amount of gaseous hydrocarbons is increased, but the composition of the end gas was generally very similar when considering a variation in the composition of the synthesis gas from the first to the sixteenth month.

Curve IV refers to a catalyst formed at 325° with carbon monoxide at 0.1 atm. Forming at 325° permitted operations at lower temperatures during the first month. The contraction remained constant at 50 - 54 percent for four months operation at 235°C. The temperature had then to be raised. After one year no more advantages could be found over the iron catalyst formed at 235°C.

The curves in this figure prove the importance of the proper pretreatment of the catalysts for the synthesis reactions.

2. Effect of the Composition of Gas

Table 19 shows the conversions obtained with high-carbon monoxide and high-hydrogen synthesis gas at a reaction temperature of 205°C (synthesis pressure 15 atm).

Table 17

Conversion of a Carbon Monoxide-Rich and a Hydrogen-Rich Synthesis Gas at a Reaction Temperature of 205°C and at 15 atm Pressure.

	CO ₂	Hydro- carbons heavy	O ₂	CO	H ₂	Hydro- carbons	Carbon Number	N ₂	Contr. %
CO-rich									
Start. gas	2.2	0.0	0.2	53.9	53.9	0.2	1.0	4.6	20
End gas	10.5	0.8	0.2	52.9	28.4	1.6	1.3	5.8	
H ₂ -rich									
Start. gas	2.2	0.0	0.0	51.2	55.6	1.6	1.2	9.4	31
End gas	8.5	2.1	0.2	19.5	52.5	3.9	2.0	13.7	

Table 18 shows conversions at 225°C with gases of three different compositions.

Table 18

Conversion of Carbon Monoxide-Rich Gas, Water Gas and Hydrogen-Rich Gas with a Reaction Temperature of 225°C and a Pressure of 15 atm.

	CO ₂	Heavy Hydro- carbons	O ₂	CO	H ₂	Hydro- carbons	Carbon Number	N ₂	Contr. %
CO-rich									
Start. gas	2.3	0.0	0.0	53.8	53.4	0.4	1.0	5.1	45
End gas	42.9	3.8	0.2	24.5	15.1	4.3	1.5	9.2	
Water gas	1.8	0.0	0.1	46.4	45.4	0.8	1.0	7.5	52
End gas	40.6	4.0	0.2	8.9	24.6	6.2	1.6	15.5	
H ₂ -rich									
Start. gas	0.6	0.0	0.1	50.7	58.3	0.2	1.0	10.1	46
End gas	22.6	1.6	0.1	0.0	43.8	13.1	1.7	18.8	

These analyses show that operations may be conducted at lower temperatures with low concentration of carbon monoxide in synthesis gas, i.e. with less carbon monoxide to be converted. At equal temperatures and with increasing hydrogen content in the synthesis gas the contraction values increase because of the simultaneous formation of water (instead of carbon dioxide), as long as the carbon monoxide is not completely converted, as it was in the last test, table 18. The hourly conversion of carbon monoxide in the two tests at 205°C, table 17 was 2.55 and 2.71 lb, at 225°C according to table 18 the hourly conversion of carbon monoxide was 1.8, 1.7 and 1.85 lb. In the last test on this table all the carbon monoxide had been converted. As long as carbon monoxide and hydrogen are present in sufficient amounts in the reacting gas, the amounts of carbon monoxide remains independent from the carbon monoxide; hydrogen ratio at temperature.

3. Operations at too low Starting Temperatures

Tests were usually begun at 225 - 235°C although a good conversion could be reached at a lower temperature. Thus with hydrogen-rich synthesis gas ($\text{CO} : \text{H}_2 = 1 : 2$) a conversion of 47 percent was measured on the second day of operation at 184°C. The proportion of carbon monoxide to hydrogen consumed was equal in that case to 0.7 : 1. This indicates a tendency for the reaction to proceed according to $\text{CO} + 2\text{H}_2 = \text{CH}_4 + \text{H}_2\text{O}$. At this low reaction temperature the conversion drops, however, in a few days, and the results are always less favorable when the temperature is then increased, than in experiments where higher temperatures were used from the start. This may be seen in table 19. Two remarkable tests were here recorded with a carbon monoxide-rich synthesis gas (normal iron catalysts) one of the tests starting at 235°C (test 1.) the other one at 210°C (test 2).

Table 19

Effect of Low Reaction Temperature Upon the Activity of the Catalysts.

Days of Operation	Test #1		Test #2	
	Temp °C	Contra %	Temp °C	Contra %
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 started at 235°C shows the constant contraction of 50 - 55 percent. The one started at 210°C produced a contraction of 42 percent after one day, 31 percent after two days, and 27 percent after three days. After the temperature was then raised only 36 percent were obtained at 235°C and even at 250°C only a contraction below 50 percent.

4. Temperature and Products of Reaction

It has already been mentioned (see o.g. table 16) that as the reaction temperature is raised the amount of gaseous reaction products is increased. Table 20 shows average yields with iron catalysts containing 1/4 percent potassium carbonate obtained at 235°C, 270°C and 280°C. Between 235°C and 270°C the solid paraffine yield dropped from 39 to 4 g/nbcm. The amounts of the liquid hydrocarbon, in particular of the volatile hydrocarbon, and of the gasol hydrocarbon increased simultaneously. At 280°C the paraffine yield was still smaller, and at this temperature the yields in liquid and gasol hydrocarbons were also smaller.

Table 20

The Character of the Reaction Products at Different Temperatures.

Reaction Temp. °C	Yields (g/nobm Ideal gas)		
	Solid Hydrocarbons	Liquid Hydrocarbons	Gasol
235	30	83	26
270	4	94	46
280	2	82	35

D. Effect of the Alkali Content of the Catalyst upon the Activity and upon the Nature of the Reaction Products.

We have already discussed in detail the preparation of the catalyst and the way alkalies are added. We shall show below the effect of the alkalies upon the course of the synthesis. The alkali additions shown in the table refer to percent by weight of potassium carbonate to the amount of the metallic iron. With the other alkali salts (potassium permanganate, fluoride etc.) the symbol "1 percent K_2O_2 " mean that the amount of potassium added corresponded to that in 1 percent of K_2CO_3 .

Table 21 shows first a test with a catalyst precipitated with ammonia and with no alkali addition. The activity was tested at a constant temperature of $235^\circ C$ with a high-carbon monoxide synthesis gas ($CO : H_2 = 3 : 2$, with 8 - 10 percent of inert constituents) and at a pressure of 15 atm.

Table 21.

The Activity of Different Alkalies Iron Catalysts.

Precipitating Agent	Alkali Addition	Days of Operation								
		1	2	5	10	20	30	40	50	100
		Percent contraction at 235°C and 15 atm.								
Nil ₃		0	50	50	50	50	50	49	51	51
Na ₂ CO ₃		0	53	50	43	49				
"	1/4 % K ₂ CO ₃		47	50	50	51	53	56	54	53
"	1/2 " "		54	-	54	47	-	45		
"	1 " "		50	-	51	50	50			
"	1 " "		45	45	45	52	43	48	47	
"	2 " "		45	45	47	46	47	50		
"	5 " "		-	-	45	50	50	51	50	40
"	10 " "		-	50	47	50	45	42		
K ₂ CO ₃	1 % KMnO ₄		40	-	43	51	55	50		
"	1 " K ₂ S ₂ O ₈		-	57	53	55	48			
"	1 " K ₂ S ₂ O ₃		-	54	53	46	50			
"	1 " K ₂ HPO ₄		55	46	-	45	40			

The series of the experiments shows that the alkali addition is not necessary for the preparation of active catalysts, if the character of the products obtained is left out of consideration. The ammonia precipitated catalyst, entirely free of alkali, produced contraction values after 50 days of operation which were not markedly below those with a normal iron catalyst containing 1/4 percent K₂CO₃. Tests with catalysts containing 1 percent and over of potassium carbonate show a drop of conversion sooner than with the normal iron catalyst, namely between the 30 and 50 days at 235°C. When potassium carbonate has been replaced by other alkali salts, no marked differences in the course of the reaction during the first weeks of operation were found. In these tests the catalysts with a potassium permanganate addition caused a good conversion, the catalysts with the potassium phosphate addition were less stable.

Table 22 shows the amount and nature of the reaction products obtained at 235°C and 15 atm synthesis pressure with differently alkalinized catalysts. The yields in g/norm ideal gas varied during the first month of operation between 140 and 160 g in line with the not entirely equal contraction. The amount of alkali has a very important effect upon the reaction products. The amount of solid paraffine determined by the butanone method (referred to the total yield of solid, liquid and gasol hydrocarbon) was 12 percent in the absence of alkali, 26 percent with the addition of 1/4 percent potassium carbonate, 42 percent with 1 percent potassium carbonate, 43 percent with 2 percent potassium carbonate and 45 - 46 percent with 5 percent potassium carbonate. The amounts of liquid and gasol hydrocarbons were correspondingly the lower the higher the alkali content.

The table 22 shows finally that the nature of the alkali salt added to the catalyst is unimportant for the amount and character on the reaction products during the first month of operation. Tests with 1 percent potassium carbonate and the corresponding amounts of potassium permanganate, potassium sulfite, potassium fluoride, and potassium phosphate show the same course of reaction inside the variations found in such tests.

Table 22

Yields with Different Alkali Additions to Iron Catalysts

Precipitating Agent	Alkali addition	g total hydrocarbons /norm ideal gas	Percent Paraffin	Percent liquid hydrocarbons	Percent Gasol
NH ₃	0	141	12	67	21
Na ₂ CO ₃	0	140	13	67	28
"	1/4% K ₂ CO ₃	148	26	56	18
Na ₂ CO ₃	1% K ₂ CO ₃	157	42	47	11
"	1% MnO ₂	155	41	45	14
"	1% K ₂ MnO ₄	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	145	42	44	13
"	5% " "	161	45	43	12
"	5% " "	155	46	44	10

E. Treatment with Hydrogen Before and During Synthesis.

1. Pretreating with Hydrogen

The normal iron catalyst was pretreated with 6 li of hydrogen/h at 0.1 atm and 325°C for 2 1/2 hours instead of the forming with carbon monoxide. The synthesis was next changed over to carbon monoxide-rich synthesis gas at 15 atm pressure and 235°C. An end gas analysis taken after 1 1/4 hours show the contraction of 2 - 3 percent and after 3 1/4 hours a 4 percent contraction. The behavior of the catalysts showed the effects of pretreatment. The catalyst, however, when taken out of the reaction chamber was slightly repolished and ferromagnetic. In a parallel test in which the catalyst was pretreated with carbon monoxide instead of hydrogen, with other conditions remaining the same, the contraction of 5 1/2 percent was obtained immediately after starting synthesis. In a subsequent experiment a catalyst of lower activity was used to see whether a pretreatment with hydrogen before forming would cause any improvement. For this purpose the catalyst was first treated for six hours with 2 li of hydrogen/h at 0.1 atm and 325°C and then for four hours with 4 li carbon monoxide/h, at 0.1 atm and 325°C, and was finally used with a high-carbon monoxide synthesis gas at 15 atm. On the second day the contraction at 235°C amounted to 42 percent, on the sixth day at 235°C it was 45 percent, on the eighth day 47 percent at 235°C and 47 percent on the tenth day at 235°C. Parallel tests made with a similar catalyst without pretreatment with hydrogen gave 42 percent at 235°C on the second day, and 46 percent on the eighth day at 235°C. The hydrogen treatment had therefore no effect upon the conversion.

2. Hydrogen Treatment Between Forming and Synthesis

The forming was first done for 2 1/2 hours at 325°C and 0.1 atm by passing 40 li of carbon monoxide over the catalyst. It was next treated for seventeen hours with 6 li of hydrogen/h at 325°C and atmospheric pressure. It was next tested with carbon monoxide-rich synthesis gas at 15 atm pressure and the activity found at 235°C, right after changing over, the conversion amounted to 42 percent, and 45 percent after one day. In a parallel test without

hydrogen pressure and contraction after one day
 week. (The results were explained in that one was justified
 to expect that the catalyst formed during forming and
 during treatment with hydrogen).

...with the catalyst...

A catalyst that had to be operated at a
 temperature several degrees higher to produce its
 maximum rate of reaction (2350°C under normal
 conditions (15 atm 5 l/100%₂H₂ gas/h). The contraction
 on the second day was 52 percent (see figure 10), 50
 percent after two days and 47 percent contraction
 after three days. The broken line figure 10 representing
 a parallel run shows that a contraction of 40 percent
 was reached after the first 24 hours of operation at 2350°C.
 However, after three days the contraction had risen to
 a higher value (55 percent, 5 l/100%₂H₂ gas/h).
 The contraction rose to 55 percent after the hydrogen
 treatment during the operation at 2350°C. The
 dropped after that but remained 50 percent on the
 second day. The contraction of
 hydrogen (under the same conditions) the contraction
 rose then to 57 percent and stayed at 57 percent on
 the second day. After a third two days of
 hydrogen the contraction rose to 58 percent and
 dropped to 55 percent after three days. The 55
 percent after four days. The contraction of this run
 at 2350°C remained at values of 50 - 55 percent for
 two months.

Figure 10 shows that a hydrogen...
 of this low...
 but results...
 carbon...
 of 1.07...
 not...
 carbon...

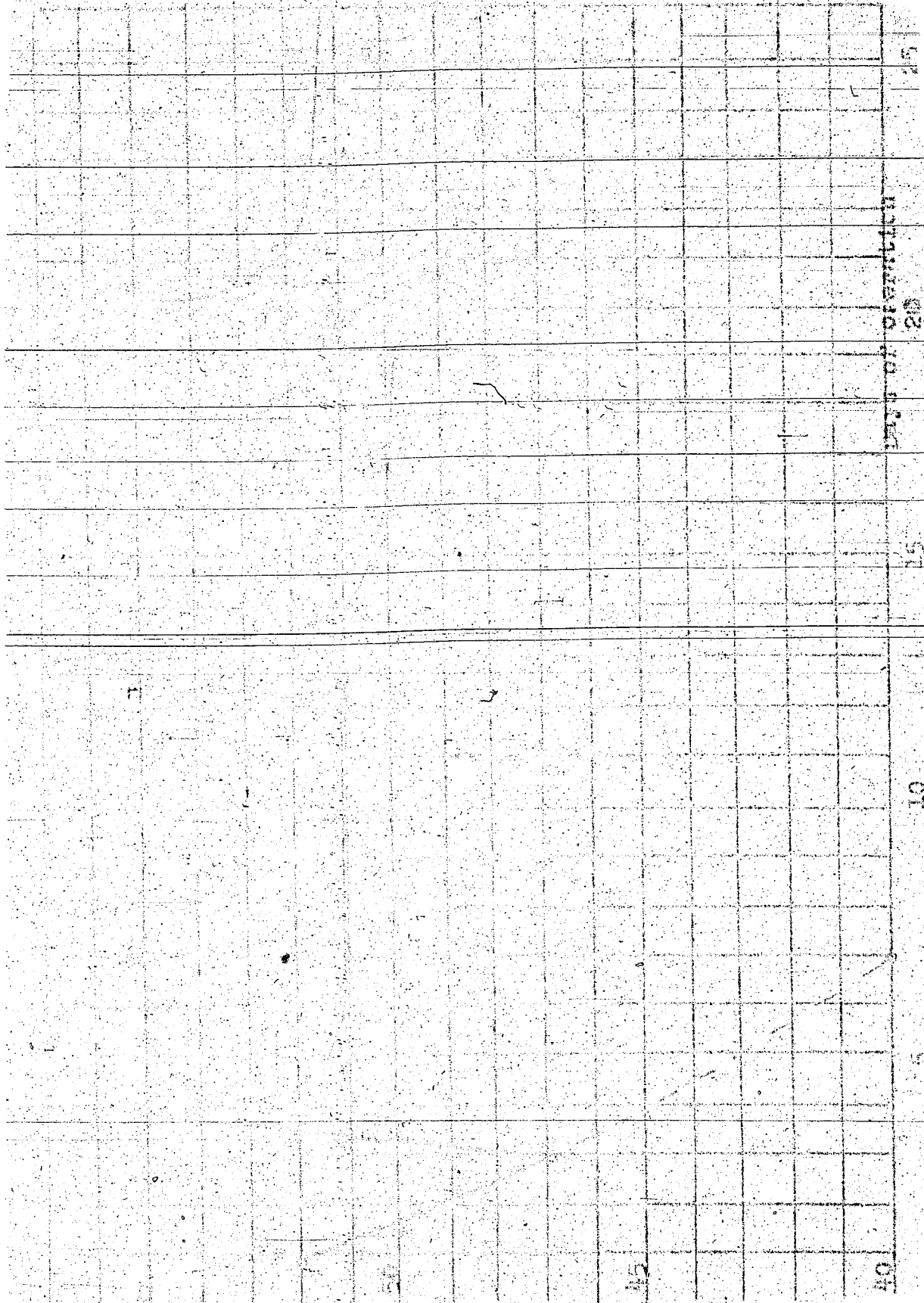


Fig. 10. Effect of treatment with hydrogen upon synthesis

iron catalysts already used for a long time which showed a marked drop in activity after reactivation after such a hydrogen treatment. How can such an improvement be obtained, even with carbon monoxide. The increase in the activity of the catalyst resulting from this treatment must be due to the effect of the traction to below 45 - 50 percent.

P. Catalysts Produced from Ferric

It has already been mentioned in the description of the preparation of the volumetric iron catalysts that the iron catalysts were made from ferric chloride and with a viscous fracture. The catalysts differ therefore in their appearance.

When operations with the catalysts were started without fouling (CO-rich gas), the results were as usual, as with other catalysts. (e.g., the catalysts produced on the first test) 30 percent conversion of the nitrogen at these conditions, the catalysts showed complete conversion of 30 percent.

Fouling with the nitrogen at 30 percent produced 43 percent conversion of the nitrogen (CO-rich gas), 40 percent conversion of the nitrogen and 47 percent conversion of the nitrogen.

Copper-free iron catalysts prepared from ferric chloride or ferric, heated with hydrogen at 0.1 atm and 525°C and then heated with CO-rich gas, had a great activity. However, began to drop after the first test.

Table 25 shows results of the first test. The conversion of the first test was on the third day from 37 to 34 percent. The test after heating to 30 percent conversion first set at temperatures lower than the possible damage to the catalyst through activity. At lower temperatures the activity dropped however, again. In the third test the catalyst prepared from ferric nitrate behaved differently.

Table 25

Test with "Ferrous Catalysts"

Catalysts Prepared From:	FeCl ₂		FeCl ₂		Fe(NO ₃) ₂	
	Temp °C	Concn %	Temp °C	Concn %	Temp °C	Concn %
1	235	57	235	56	235	56
2	235	57	225	56	235	57
3	235	34	225	49	235	40
4	235	30	215	38		
5			225	35		
6			225	29		

The optimum operating conditions given for the "ferrous catalysts" (prepared from solutions of ferric sulfate) show that the "ferrous catalysts" performed about equally poorly.

In the tests on Table 19, iron-copper catalysts were 99% FeCl₂ - copper chloride were used. They were loaded with nischgas at atmospheric pressure. The table states that these "ferrous catalysts" effected a complete conversion for several months in accordance with the conditions of their forming, but only at temperatures of 260°C and higher.

Table Effect of Additions of Copper

Evans, Fischer, Ackermann, and Meyer 17/, have shown that the activity of copper-containing iron catalysts was superior to the copper-free catalysts at atmospheric pressure. Table 27 shows the best results obtained with the two types of catalysts at atmospheric pressure. The reaction temperature was 230 - 235°C, with 4 li nischgas/h and per 10 g of Fe during the conversion.

Table 24

The Effect of Copper Addition upon the Synthesis

Catalysts:		Fe : Cu = 5 : 1	Fe (no Cu)	
Operating days:		2 days	4 - 7 days	
Days of Synthesis	Conv.	Yield g/100 g g/100 g	Conv. %	Liquid product g/100 g
1	30	56	32	55
5	30	52	31	50
10	30	55	30	48
20	30	52	27	38
30	30	50	25	34
40	27	46		

The copper-containing catalysts requires less time to produce the maximum contraction of around 30 percent. The maximum yield was about the same at the beginning of synthesis in both cases, but the copper-containing catalysts requires the maximal work to be done, while the copper-free catalysts lost their activity in a few days.

When synthesis was carried out at a pressure of 15 atm (without previous heating at lower pressures), catalysts without as well as with copper additions (5Fe : 1 Cu) produced a contraction of 40 - 44 percent only at 280 - 270°C. Without addition of copper a contraction of 30 percent was reached at 280 - 260°C and kept there for several months, while the activity of the copper-containing catalysts fell off rapidly at these temperatures.

Table 25 shows two pairs of tests with catalysts made from ferric salt solutions and loaded with carbon monoxide at 0.1 atm and 225°C. The synthesis was carried out with CO-rich gas at 15 atm. The results are compared of synthesis at 225 and 205°C with and without copper.

Table 25

The Effect of Copper Addition upon the Activity of Iron Catalysts

Days of operation	235°C		225°C	
	Fe, no Cu	Fe-Cu 5 : 1	Fe, no Cu	Fe-Cu 5 : 1
1	55	54	52	55
2	55	56	-	54
3	55	-	50	50
4	55	50	-	-
5	55	50	45	50
10	54	52	-	-

The above data show that the addition of copper to iron catalysts resulted in no advantages in middle pressure synthesis of ammonia, or in forming at 225°C.

The Effect of Addition of Nickelium

The addition of nickelium to cobalt catalysts has been found to be constant for the synthesis of hydrocarbons. This reaction in liquid and solid hydrocarbons has not been studied with catalysts containing nickel.

In high pressure synthesis, on the other hand, the addition of nickelium to iron catalysts resulted in a decrease of activity invariably lower in activity than when cobalt catalysts was used. 50 - 55 g liquid hydrocarbons were found in a few cases, but the life of these catalysts was only a few days.

Recently tests have been undertaken on middle pressure synthesis with iron catalysts in which nickelium was added. These tests were intended to determine the leaching up of the catalysts would reduce their stability in the vertical reaction. It was a hope to improve the iron catalysts in the synthesis of hydrocarbons. (see part IV of this work).

The following experiments at the different stages of the catalyst preparation. The following experiments might be mentioned:

Experiment 11, 4 g nickelium were added to 10 g of Fe before the precipitation from the iron solution.

Experiment #2, 4 g kieselguhr/10gFe were added to the sodium hydroxide solution before the precipitation.

Experiment #3, 4 g kieselguhr/10gFe were added to the moist catalysts paste after alkalizing (see part I, preparation of catalysts).

Experiment #4, The possibility of adding dry kieselguhr to a ready catalyst is excluded if a hard grainy catalyst is being prepared.

The results obtained in experiments 1 - 3 are summarized in table 26, experiment 3a was conducted at synthesis temperature of 235°C, 3b at 225°C. The contractions found after different operations time are recorded. In all cases forming was done for 24 hours with 4 l carbon monoxide/10g/h at 0.1 atm and 325°C, and the synthesis then performed with a carbon monoxide-rich gas (300 : 200) at 15 atm.

Table 26

The Effect of the Addition of Kieselguhr to Catalysts.

Part of Operation	Exper #1		Exper #2		Exper #3a		Exper #3b	
	Temp °C	Contr %	Temp °C	Contr %	Temp °C	Contr %	Temp °C	Contr %
1	235	53	234	55	235	54		
2	235	50	234	53	235	54	225	56
3			234	51			225	56
4			234	50			225	56
5			235	49	235	54	225	54
6	234	45	236	50	235	54	225	54
8			235	49	235	56	225	54
9			234	40	235	55	225	50
10					235	54	225	46
20					235	54		
30					235	52		
40					235	52		
50					235	50		
60					235	50		

Table 26 shows that results obtained in experiment 3a are best. In this case kieselguhr had been added after alkylating. The contraction remained over 50 percent (without reactivation) after two months of operation. At 225°C (experiment 3b) the contraction dropped to below 50 percent after ten days.

Table 27 shows the composition of the reaction gas with a contraction of 53 - 54 percent. Experiment 3a produced the most gaseous hydrocarbons. Catalysts prepared with kieselguhr present during the precipitation which had a chance to become saturated with alkali (experiments 1 and 2) as well as the experiment 3b catalyst at 225°C produced considerably less gaseous hydrocarbon. (The normal iron catalysts under analogous conditions produces a reaction gas with 6 - 8 percent saturated gaseous hydrocarbons).

Table 27
Analysis of Reaction Gases of the Kieselguhr Catalysts
with a contraction of 53 - 54 percent

	CO ₂	Heavy Hydro- carbons	O ₂	CO	H ₂	Hydro- Carbon carbons	Carbon Number	N ₂
Test 1	59.1	3.5	0.2	6.3	12.9	4.7	1.8	13.3
Test 2	55.2	4.4	0.1	5.4	11.1	6.1	1.7	12.7
Test 3a	64.8	3.0	0.1	1.3	6.0	11.4	1.9	13.4
Test 3b	55.9	2.6	0.2	8.8	9.9	7.7	2.1	14.2

The analysis of yield in experiment 3a gives 87 g of solid and liquid hydrocarbons and 30 g gaseous hydrocarbons /normal ideal gas.

The liquid hydrocarbons contained at first 3 percent solid paraffin, 12 percent after four weeks and 14 percent after six weeks. (This catalyst was alkalinized with 1 percent potassium carbonate. The paraffin formation is therefore considerably less than with the clean kieselguhr-free iron catalysts).

The products obtained were colorless and their composition is described elsewhere.

A catalyst prepared in accordance with experiment 3 was used in filling a vertical apparatus with 18 tubes (18 catalyst fillings for 10 g of Fe). The forming with carbon monoxide preceded in the usual

way at 0.1 atm and 325°C and operations were then started with carbon monoxide-rich gas at 15 atm and 225°C. The contraction dropped in the course of six days from 54 to 50 percent, the catalysts was then reactivated at the same temperature with hydrogen. On the eighth day the contraction was 52 percent, on the tenth day 47 percent. After a second treatment with hydrogen at 230°C the operations were conducted at 232°C. The contraction again dropped to 48 percent on the seventeenth day. After a repeated hydrogen treatment the test was continued for one week at 236°C etc. (see Figure 11).

In comparison with corresponding tests in horizontal or weakly inclined tubes showed that the experiment 5 in table 26 in a vertical apparatus proceeded less uniformly. Nevertheless with repeated hydrogen treatment a contraction of around 50 percent could be maintained. (The apparatus is discussed in greater detail in part IV).

III Products of Reaction

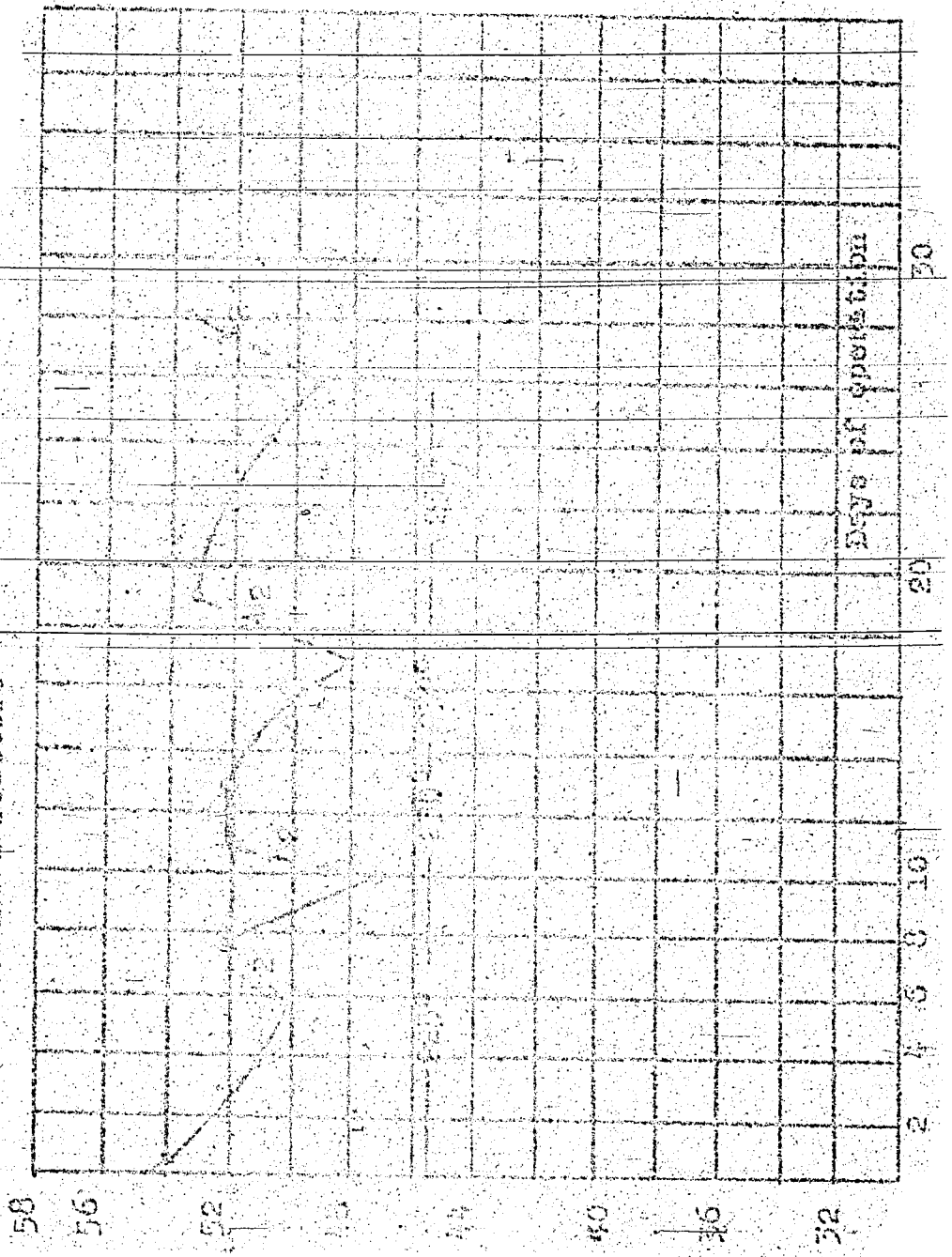
Paraffin and olefine hydrocarbons of different molecular weights, from methane and lower gaseous hydrocarbon to the high molecular weight solid paraffins are formed during the middle pressure synthesis with iron catalysts. Table 28 gives the yields in solid, liquid products and gasol hydrocarbons under a few varying reaction conditions, collected from current experiments.

Table 28

Solids, Liquid and Gases Hydrocarbons, under Different Reaction Conditions.

Catalysts	Percent K ₂ CO ₃	Starting Temp. °C	Paraffin percent	Liquid Hydro- carbons	Gasol percent
Fe(Na ₂ CO ₃ precipitant)	1/2	270	3	65	32
Fe - Cu	1/8	260	4	76	20
Fe-Kieselguhr	1	235	8	63	29
Fe(NH ₃ precipitant)	0	235	12	67	21
Fe - Normal	1/4	235	26	56	18
Fe(Na ₂ CO ₃ precipitant	1	235	42	47	11
Fe(Na ₂ CO ₃ precipitant	5	235	46	44	10

Fig. 11. Tests with Fe - Niobium catalyst in vertical reactors



We can see from this table that the total paraffin contents in these test varied from 3 - 46 percent of the total reaction products. These amounts referred to solid and liquid products correspond to 5 - 51 percent. The proportion of liquid hydrocarbons varies between 44 to 76 percent of the reaction products, the proportion of gasol between 10 and 32 percent. Catalysts which produce good yields for particularly long times, especially those precipitated with sodium carbonate (at 235°C) and with ammonia (at 235°C) produce a proportion of solid, liquid and gasol hydrocarbons represented by the average of the values mentioned above; in general, a lowering of the reaction temperature and an increase in the alkali content changes the nature of the reaction products toward higher molecular weights. The iron-kieselguhr catalysts do not fall into this series.

The proportion of unsaturated hydrocarbons in the liquid products as well as in gasol was different under different reaction conditions, just like the boiling point variations. High melting paraffin is a by-product obtained during synthesis.

In addition oxygenated organic compounds are formed similar to the synthols described by Franz Fischer and Tropach, 18/.

The iron catalysts may finally be used under certain conditions for the production of city gas conforming to specifications.

The middle pressure synthesis with iron catalysts permits one in particular to alter the production to form primarily one or another reaction products. No predications could be made in the normal and middle pressure synthesis with cobalt catalysts about the direction of the reaction, for regulating the formation of any individual type of hydrocarbons, nor the formation of any definite products, because of the great variability of these syntheses.

A. Liquid Hydrocarbon

The crude liquid products are not as a rule entirely colorless, but are slightly yellowish. Distillation produces water-clear gasoline, and smaller amounts of a yellowish oil is left in the residue. The gasoline is stable and remains colorless even after storage for many months.

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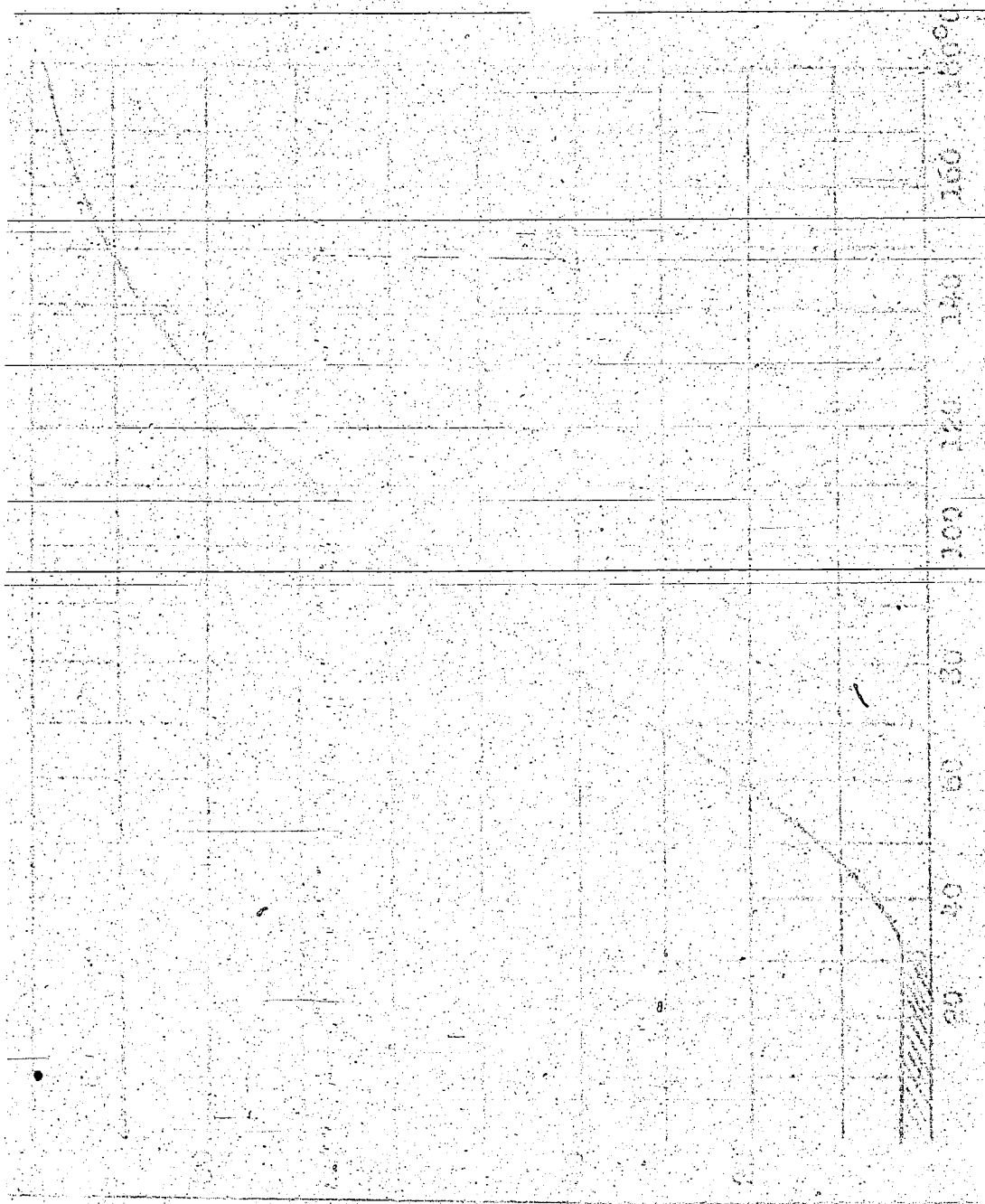


Fig. 15. Engler distillation of a gasoline

The proportion of liquid hydrocarbons boiling below 180°C to the total liquid hydrocarbons depends on experimental conditions. A catalyst precipitated with ammonia (with 1/4 percent K_2CO_3 , at 250°C) gave 55 percent of a distillate -180°C , and with an iron-copper catalyst operated at 250°C , 80 percent of a distillate -180°C was obtained.

Figure 15 shows a Engler distillation of a gasoline produced with a normal iron catalyst at 250°C and boiling -180°C . 50 percent of this gasoline boiled -28°C , 60 percent -100°C . The boiling curve of the gasoline can be strongly affected by changing the operating conditions.

Table 29 shows the gravity, olefine content, boiling data and octane number of a few gasolines produced with some iron catalysts.

Table 29
Properties of Gasolines Obtained with Iron Catalysts

Number	Washed with NaOH	Grav.	Olef.	S.P. Analysis			Grav.	O.N.
				Start	10%	50%		
1	yes	0.695	64	30°	46°	88°	0.54	61
2	"	0.673	65	30°	38°	75°		62
3	no	0.633	58				0.48	63

Sample number 1, table 29 was obtained with a catalyst precipitated with ammonia, sample number 2 from an experiment with an iron-copper catalyst and sample 3 in a test with an iron-kieselguhr catalyst.

The gravity of the gasoline -180°C was 0.7. Phosphorus pentoxide-sulfuric acid extracted 64, 65 and 58 percent by volume respectively from the three gasolines. The octane number by the motor method of the three stabilized gasolines varied from 61 - 63.

The possibilities of further raising the knock resistance of gasoline obtained from middle pressure synthesis are discussed in a special section on the subsequent working up of the primary products.

A comparison of the fractions removed with phosphorus-pentoxide-sulfuric acid from the gasoline with their octane numbers show that the latter does not depend entirely on the olefine content.

The synthol like organic compounds found in the reaction products of iron chloride pressure synthesis are of importance. Their amount and nature varies greatly with the operating conditions. Table 30 gives the acid, ester, saponification and hydroxyl numbers of some synthesis products.

Table 30

Chemical Analysis of the Reaction Products of the Iron Chloride Pressure Synthesis

Reaction conditions	Boiling point	acid no.	ester no.	saponification no.	hydroxyl no.
FeCl ₃ 10% K ₂ CO ₃	30 - 150				
FeCl ₃ 10% K ₂ CO ₃	over 150	0.2	0.2	0.5	2.3
FeCl ₃ 10% K ₂ CO ₃	over 150	1.8	2.1	3.9	7.0
FeCl ₃ 10% K ₂ CO ₃	30 - 150	1.4	15.0	16.4	
FeCl ₃ 10% K ₂ CO ₃	over 150	0.2	2.0	2.2	
FeCl ₃ 10% K ₂ CO ₃					

The table shows that large amounts of esters and alcohols, together with small amounts of free acids can be produced during synthesis and this applies not only to low molecular weight esters and alcohols occurring in gasoline, but also to those of higher molecular weight with boiling points above 150°C. The formation of these products, is strongly favored by the alkalizing of the iron catalyst. When the total products obtained with the iron chloride catalyst are washed with 50 percent aqueous chlorine solution, 2.5 percent were dissolved in the water solution, and 0.8 percent of alcohol were dissolved in the subsequent washing with carbon tetrachloride.

The ultimate analysis of the total reaction products obtained with three different iron catalysts are shown in table 31.

Table 21

The Chemical Analysis of Synthetic Products in the Series

Product	Carbon	Hydrogen	Oxygen
1	78.5	10.5	11.0
2	78.5	10.5	11.0
3	78.5	10.5	11.0
4	78.5	10.5	11.0
5	78.5	10.5	11.0
6	78.5	10.5	11.0
7	78.5	10.5	11.0
8	78.5	10.5	11.0
9	78.5	10.5	11.0
10	78.5	10.5	11.0
11	78.5	10.5	11.0
12	78.5	10.5	11.0
13	78.5	10.5	11.0
14	78.5	10.5	11.0
15	78.5	10.5	11.0
16	78.5	10.5	11.0
17	78.5	10.5	11.0
18	78.5	10.5	11.0
19	78.5	10.5	11.0
20	78.5	10.5	11.0
21	78.5	10.5	11.0
22	78.5	10.5	11.0
23	78.5	10.5	11.0
24	78.5	10.5	11.0
25	78.5	10.5	11.0
26	78.5	10.5	11.0
27	78.5	10.5	11.0
28	78.5	10.5	11.0
29	78.5	10.5	11.0
30	78.5	10.5	11.0
31	78.5	10.5	11.0
32	78.5	10.5	11.0
33	78.5	10.5	11.0
34	78.5	10.5	11.0
35	78.5	10.5	11.0
36	78.5	10.5	11.0
37	78.5	10.5	11.0
38	78.5	10.5	11.0
39	78.5	10.5	11.0
40	78.5	10.5	11.0
41	78.5	10.5	11.0
42	78.5	10.5	11.0
43	78.5	10.5	11.0
44	78.5	10.5	11.0
45	78.5	10.5	11.0
46	78.5	10.5	11.0
47	78.5	10.5	11.0
48	78.5	10.5	11.0
49	78.5	10.5	11.0
50	78.5	10.5	11.0

The melting points were obtained. The oxygen content of the high boiling product is higher than in the lower product.

When 5 g of the product of the solid and liquid reaction products consist of paraffin (determined by the hydrogen method). This paraffin-rich synthesis product is white to colorless, with carbon monoxide-rich gases and nitrogen containing one percent percent of potassium carbonate is yellow to yellow-brown. The coloring is due to the presence of small amount of high boiling oils and is removed by oxidation or by accelerated hydrogenation.

The melting point of the paraffin extends over the whole range of the known paraffins. The total product contains practically high boiling constituents, and melts only at a relatively high temperature. A monomer formed at 300°C in the melt, that takes with a paraffin, when from 100°C hydrogenation by means of cobaltine, then produces with catalyst containing 1/4 percent cobalt, and at 100°C after the catalyst consists of nickel.

The product obtained when an 11% - 1 percent 100% extract of 5% percent soluble in boiling ether. The product was obtained with methyl alcohol melted completely in boiling point tubes between 60 and 70°C. 11 percent were insoluble in ether (24 hours extraction in Soxhlet, using boiling hexane). Their melting point was between 90 and 100°C. The remaining 9 percent

of the hexane-insoluble paraffin had an end melting point of 122°C.

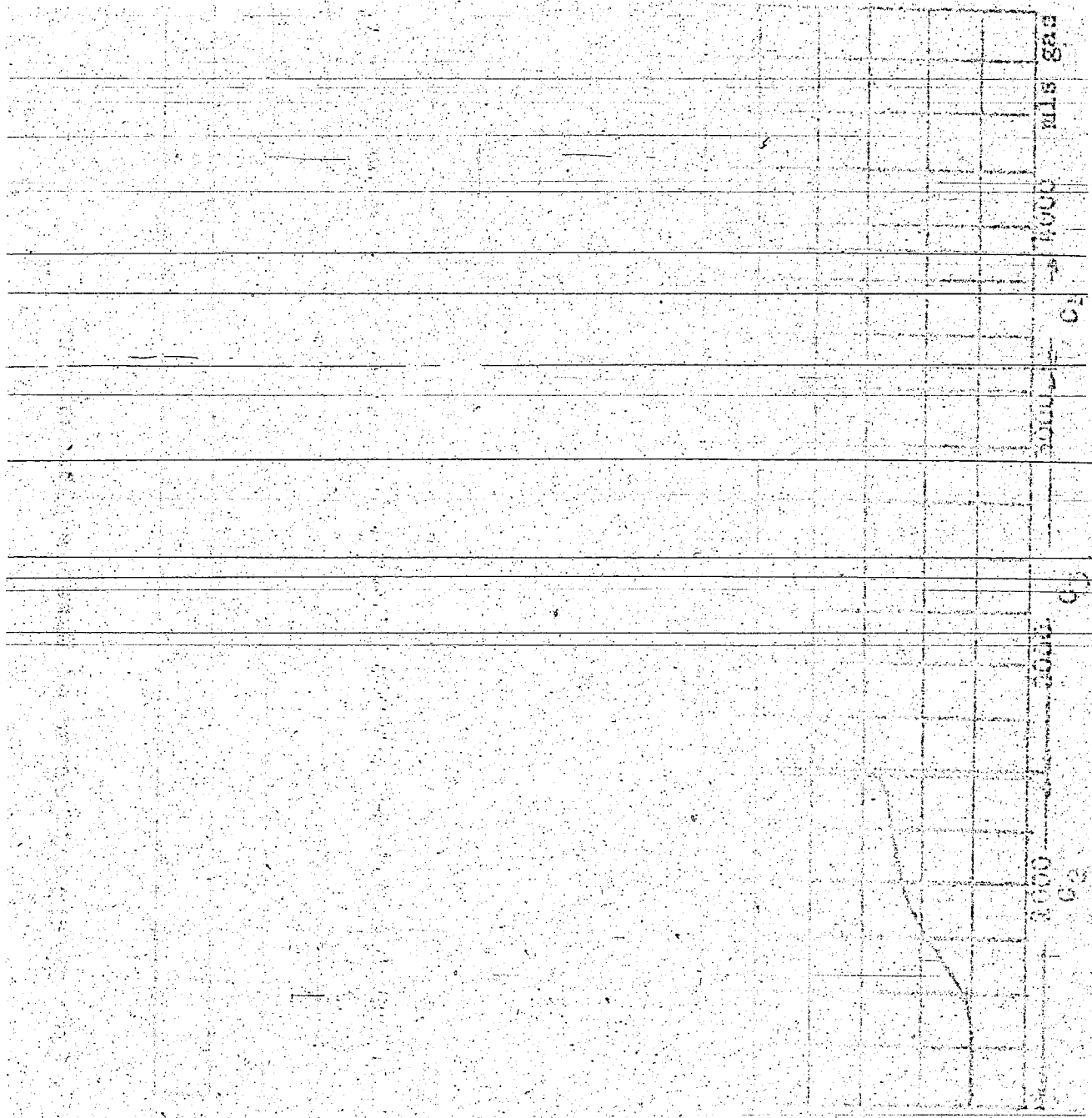
The so-called catalyst paraffin obtained when an iron catalyst was fractionally extracted in boiling benzol, leaving some insoluble residue which was soluble in boiling toluol and melted at about 125°C.

C. Gasol

Table 28 shows that 10 to 30 percent of the reaction products of synthesis consist of gasol hydrocarbon ($C_2 + C_4$). Ethylene is a product of the iron-catalyzed pressure synthesis. Figures 14 and 15 show the results of low temperature distillation made at the Institute by F. Weinrotter. The gaseous reaction products of a synthesis (iron catalyst with 1 percent H_2O_2) were led through a trap cooler with liquid air gasoline and all hydrocarbons except some of the methane are condensed in the trap. The $C_2 - C_4$ fraction of a sample distilled up to room temperature is shown in figure 14 (distillation I). The gasoline remaining in the trap still contained considerable amounts of C_4 hydrocarbons. They were removed by distillation. The C_2 fraction obtained is shown in figure 15 (distillation II). No isobutylene has been found in the two distillations.

Table 32 summarizes the results of the low temperature distillation. The distillation I was recalculated to the amount of gasol corresponding to that of the distillation II. The proportion of unsaturated hydrocarbon in the different fractions was determined with mercuric nitrate.

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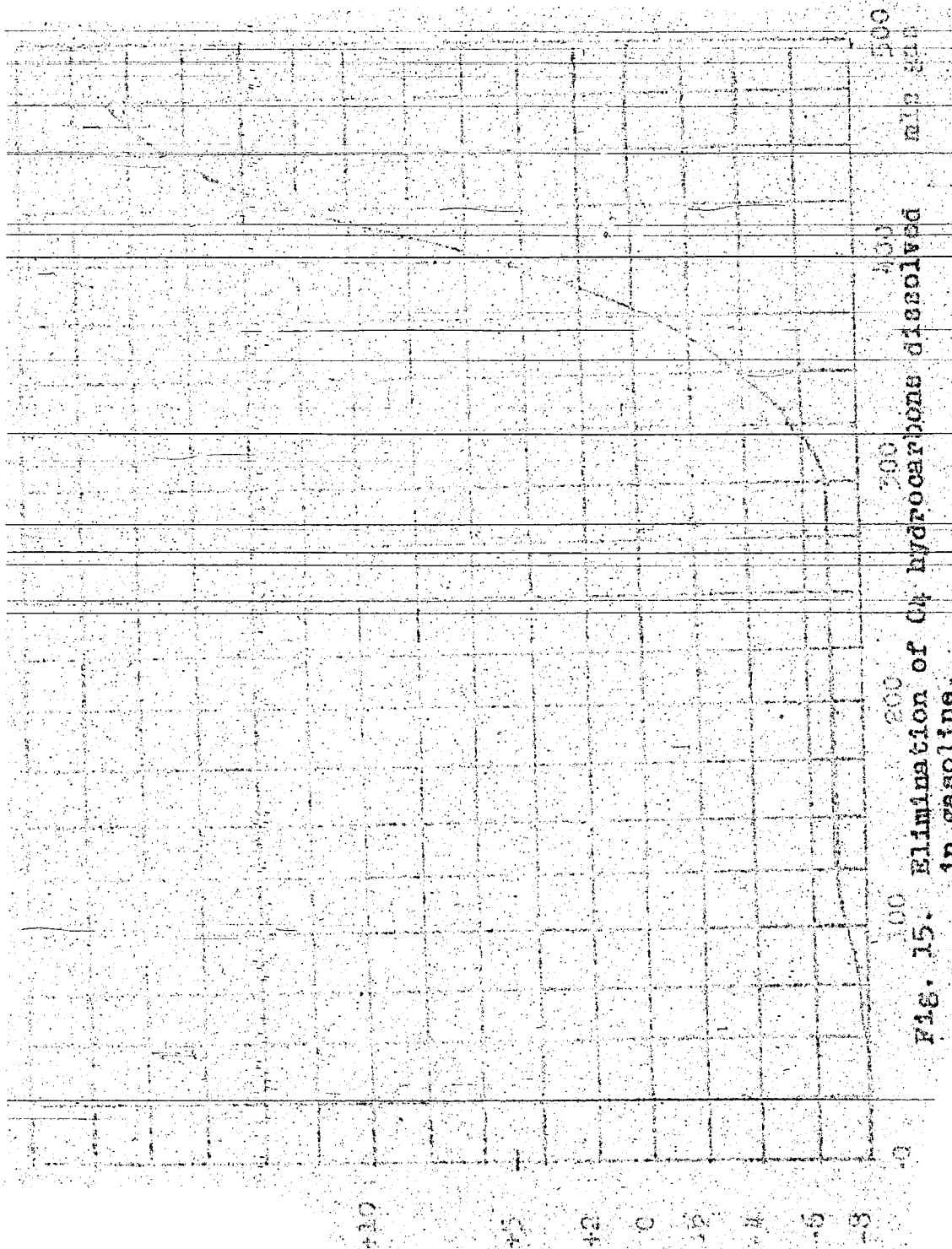


FIG. 15. Elimination of C4 hydrocarbons dissolved in gasoline.

at a synthesis temperature of 235°C and with an iron catalyst precipitated with ammonia or with some the amount of gasol hydrocarbon/nobn fuel the amount to 20 - 30 g, with 75 - 80 percent of unsaturated hydrocarbons. The amount of gasol hydrocarbons was still higher at higher reaction temperatures, but their hydrogenation as well as their formation were both favored, so that the amount of unsaturated hydrocarbon/nobn of the gasol obtained at the reaction temperature of 270°C amounts to amount 20 g.

The gasol hydrocarbons obtained with the iron-hydroxide catalyst differ quantitatively from those obtained with a catalyst free from kieselguhr. Just as in the case with gasoline, the gasol obtained with the iron-hydroxide catalyst containing a small proportion

Reaction-Containing Products

Reaction-Containing Water

About 15 g of aqueous products were obtained from gasol 235°C , 90 - atm gas, 15 atm, with an iron-hydroxide catalyst. They contained acid (the test for formic acid was negative, for acetic acid was positive), aldehydes (positive test with Schiff's reagent), esters (determined by saponification, 0.5 g calculated to ethyl acetate/lit of the reaction mixture), also alcohols (small amount of methyl alcohol, ethyl alcohol determined by boiling point and the chemical reaction). The reaction water was distilled in a microstill on a rotating band. Figure 15 shows the boiling point analysis of a fraction boiling below 50°C (20 percent of the total reaction

The boiling point curve shows distinctly the ethyl alcohol fraction, it represented 7.5 percent of the total volume of reaction.

Reaction-Containing Products

Figure 16 shows that the reaction products boiling below 100°C as well as those boiling above 100°C contained varying amounts of synthol-like products depending on the reacting conditions. The presence of organic acids, esters and alcohols has been ascertained. Investigations of the composition of the higher alcohols and esters are at present in progress, and will be published separately.

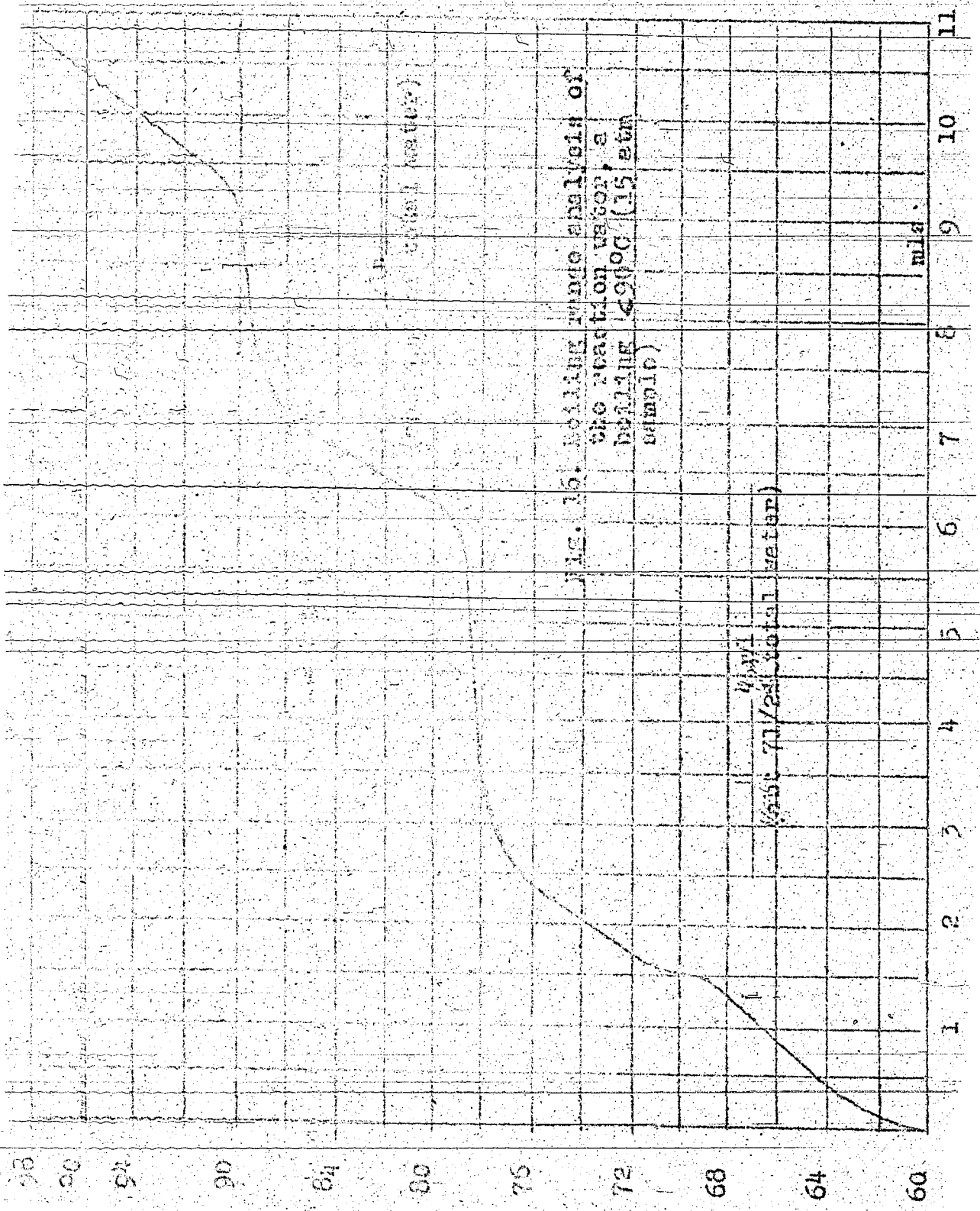


FIG. 10. Boiling range analysis of the reaction vapor, a boiling 69/00 (15 atm sample)

We will discuss briefly the products obtained by extraction of a 180°C b.p. gasoline obtained with an iron-catalyst (total 5.5 percent of the gasoline) with a 30 percent calcium chloride solution of the products. Figure 17 shows the distillation (similar to figure 16) of a water solution distilled to 95°C.

E. City (Illuminating) Gas

As a result of the present shortage of coke oven gas, the question is frequently asked about the possibility of preparing a suitable city gas from coke. The heating value of water gas is too low and to obtain the required heating value hydrocarbons would have to be made by synthesis. This is readily possible with nickel or cobalt catalysts. It was necessary to find out whether the production of such a gas was also possible by way of the iron nickel pressure synthesis. Under normal pressure iron catalysts do not produce a gas with a sufficiently high heating value.

According to specifications 19/ for the properties of this gas, the following properties had to be met:

I. Combustion properties

1. Heat of combustion (upper heating value)
4,200 to 4,600 kcal/cbm.
2. Density (Air = 1) = 0.4 - 0.5
3. Gas pressure over 50 mm
4. Flash point (Oetzahl) 60 - 100

II. Purity

1. Oxygen less than 0.5 percent
2. Hydrogen sulfide less than 2 g/100 cbm.
3. Ammonia less than 0.3 g/100 cbm.
4. 5 to 10 g/100 cbm at atmospheric pressure
5. Organic sulfur less than 25 g/100 cbm,
Hydrogen cyanide less than 15 g/cbm, nitric oxide 0.2 ml/cbm.

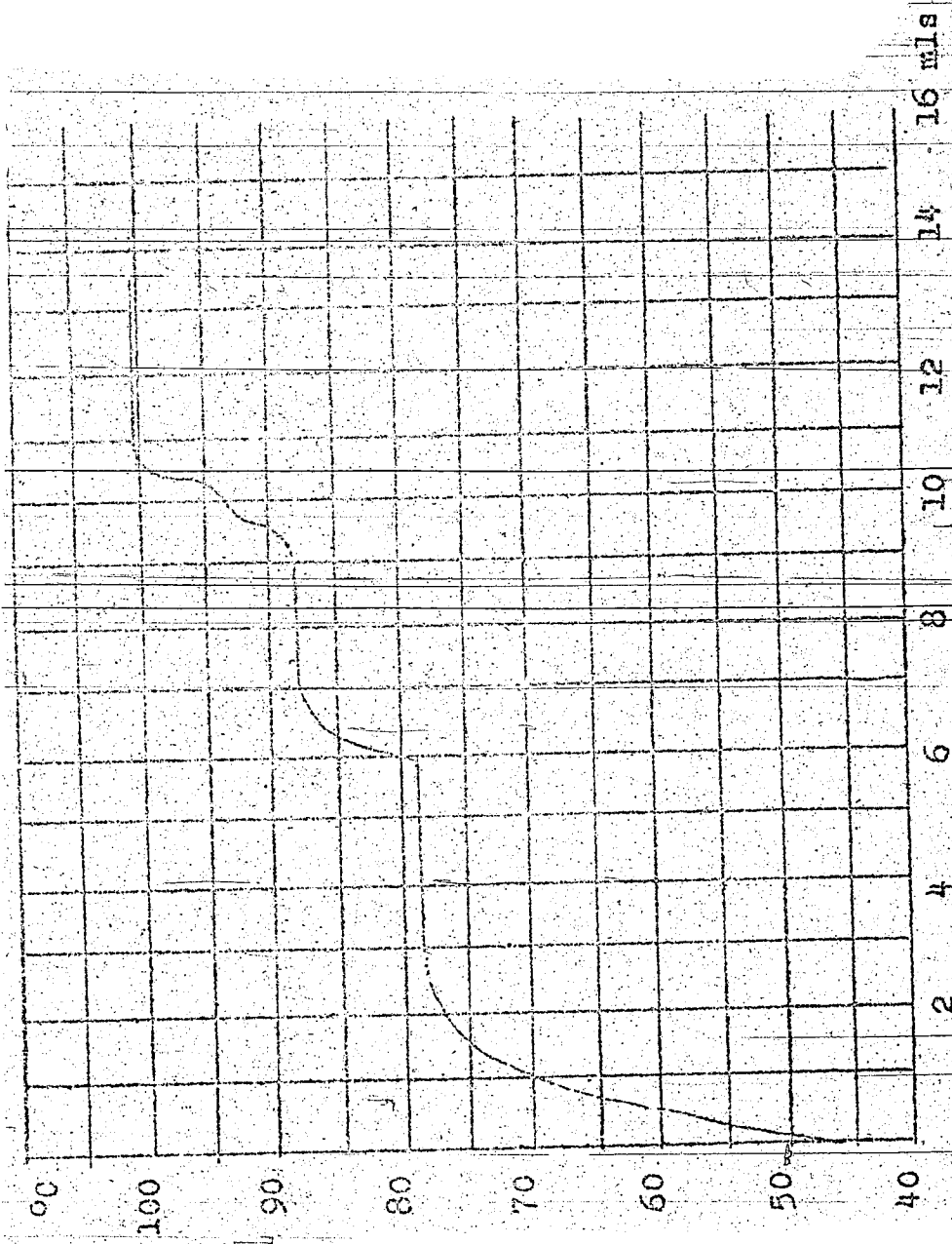


Fig. 17, Distillation of the water fraction of the liquid reaction products (14 ml sample)

6. Practically tar-free

III. Final Purification

1. Any possible corrosion is considerably reduced by lowering the values under II, using final purification methods. Points I - III are not specifications but only directions for having a gas operating perfectly in the gas equipment. These specifications do not contain the formerly common limits of content of inert constituents.

Bruckner and Weissen 20/ have suggested the addition of propane, formed during synthesis, to water gas. They have shown that mixtures of propane and water gas containing 6 - 7 1/2 percent of propane had heating values of 4,200 - 4,500 kcal/norm. Such gas would have however, too high density (0.61 - 0.65) and too low flash point (40 - 46).

A gas satisfying the specifications can be readily obtained by mixing water gases or hydrogen-carbon monoxide mixtures with the total hydrocarbons of the synthesis gas obtained by removal of the liquid reaction products and the major part of the carbon dioxide, and containing the hydrocarbons $C_1 - C_4$.

City gas can also be obtained in the gasoline production by converting a carbon monoxide - hydrogen mixture 1 : 3 with iron-catalyst at about 10 atm pressure.

The formation of the higher hydrocarbons is greatly reduced by using an ammonia precipitated iron-catalyst, free from alkalis. Forming and thruputs were the same as usual. The initial temperature was 235°C, 250°C after one month of operation, 265°C after two months and 270°C after three months. A gas of constant composition was obtained through the whole operation period. Table 34 shows the initial and end gas composition of this synthesis.

Table 34

Preparation of Gas Conforming to the Specifications

Catalysts: alkali free iron-catalysts

Synthesis gas: $\text{CO} : \text{H}_2 = 1 : 3$

Pressure 10 atm

Temperature 255 - 270°C

	CO_2	heavy hydro-carbons	O_2	CO	H_2	Hydro carbons	Carbon number	N_2
Starting gas:	0.0	0.0	0.0	25.5	73.5	0.0	-	3.0
End gas:	10.9	0.2	0.1	1.0	69.8	13.1	1.8	4.9

The gas produced has a heating value of 4,154 kcal/norm (Junkers calorimeter), density of 0.425 (effusion method), flash number of 70 - 71. When somewhat lower nitrogen gas is used the heating value can be raised by about 100 kcal without affecting the other constituents.

The gas thus meets the specification requirements, and is moreover sufficiently pure because of the final purification necessary for synthesis.

According to our more recent experience, the iron-kieselguhr catalyst is particularly well suited as a catalyst for the preparation of city gas because of its specific tendency to form gaseous hydrocarbons.

IV. General ProblemsA. Manufacture of Synthesis Gas.

The best results in synthesis with iron catalysts are obtained with a gas in which carbon monoxide and hydrogen are in the proportion of 3 : 2, as has already been shown. This gaseous mixture was manufactured in our experimental installation at the institute using the usual water gas producer 21/ by passing steam and carbon dioxide over glowing coke. This method of preparation might also be suitable occasionally to a large scale industrial production, because much more carbon dioxide is formed during the synthesis with iron-catalysts than is required for the manufacture of synthesis gas. With normal conversion, 250 li of carbon dioxide is formed/cbm of synthesis gas with $\text{CO} : \text{H}_2$ ratio of 3 : 2, while only 100 li of

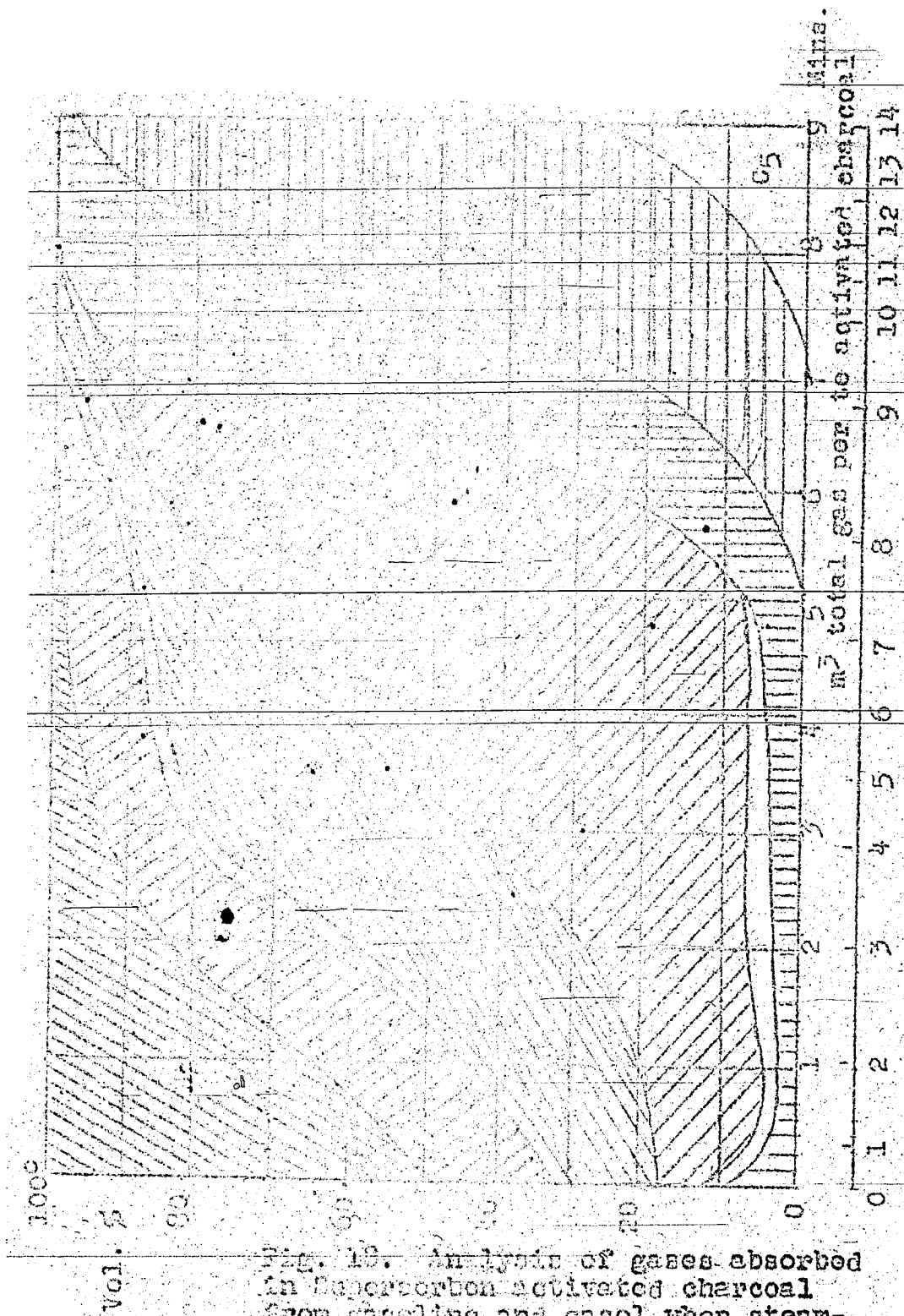


Fig. 18. Analysis of gases absorbed in Superporon activated charcoal from gasoline and gasol when steaming it out (instantaneous values after 1,2, mins) (Herbert and Ruping)

carbon dioxide are necessary/cbm of carbon monoxide - rich gas according to the equation $5C + 4H_2O + CO_2 = 6CO + 4H_2$. Even a partial scrubbing out of the carbon dioxide from the end gas, and its return into the gas producer would cover the increased requirements of carbon dioxide against normal water gas.

The separation of carbon dioxide may be done with activated charcoal. Herbert and Ruppig 22/ reported briefly on such a method of operations for the separation of carbon dioxide from gasol in the Fischer-Tropsch synthesis. In this synthesis (with cobalt catalysts) almost no carbon dioxide is formed, but if a synthesis gas be used, obtained by a partial conversion of water gas and containing CO_2 , a reaction gas with 35 - 40 percent carbon dioxide is formed resulting from the contraction of the gas during synthesis. If activated charcoal saturated with this reaction gas is steamed out in the reverse direction to the direction of changing it, the different gases are set free one after the other (as shown in figure 18), and methane and carbon dioxide can to a great extent be separated from the $C_2 - C_4$ hydrocarbons.

If the methane present together with carbon dioxide in the reaction gas (5 to 10 percent) and the unconverted carbon monoxide and hydrogen (10 - 15 percent combined) or passed with steam through the gas producer, the additional conversion would increase the synthesis yield to a value approaching more nearly to the theoretical (208 g/hydrocarbons/normal ideal gas).

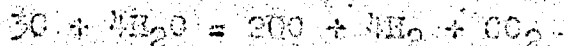
We will compare below the theoretical conversions during the production of water gas, michegas ($CO : H_2 = 1 : 2$) and carbon monoxide - rich gas ($CO : H_2 = 3 : 2$) used in the middle pressure synthesis with iron catalysts.

1. Water Gas



267 g carbon, 500 ml steam and 350 kcal of heat are used up per cbm of water gas (without regard to the efficiency of the gas producer).

2. Hydrogen-rich Michegas



2. Space-Time Yields and Questions of Equipment Construction.

In most of the laboratory tests described, pressure tubes with an internal diameter of 12 - 13 mm were used for reactor tubes. The catalyst was uniformly distributed in an iron or copper boat, and the boat was pushed into the middle of the tube (arranged at some slant for the partial draining of the paraffin formed). The normal catalyst charge was 10 g of Fe, which corresponds to 15 - 16 ml of a freshly prepared so-called "normal catalyst". The empty space in the reaction zone of the tube (30 centimeters in length) amounted to about 35 ml. When considering the space occupied by the boat, 25 ml of this reaction space or about 1/2 of the space was filled with the catalysts, while the upper half remained free. The scheme I, figure 19 was drawn to illustrate these conditions.

... synthesis gas per unit ... catalyst exchanged as ... to be kept the ... converted in a unit ... 20, a 50 percent con- ... throughput of only 1.7 li ... 220°C; at 233°C ... 240°C - 8 li/hr, and at 275°C

In another test 1000 cc/hr were passed over the catalyst at 200°C at 40 li/hr at 200°C, to produce a contraction of ...

It is preferable to conduct a synthesis at the lower temperatures as long as possible, which will result in a greater life of the catalyst, higher hydrocarbons, and for industrial considerations; on the other hand it would be preferable for space-time yields to operate at higher temperatures and use higher temperatures. With hourly gas thruputs of 10 - 20 li/hr 10 g Fe, the heat removal on a large scale industrial ... when trying to avoid ... deposition of carbon, ... of the activity ... for selecting an ... of synthesis gas per hr ... shown in figure 19, ... one to two years without ... and producing a

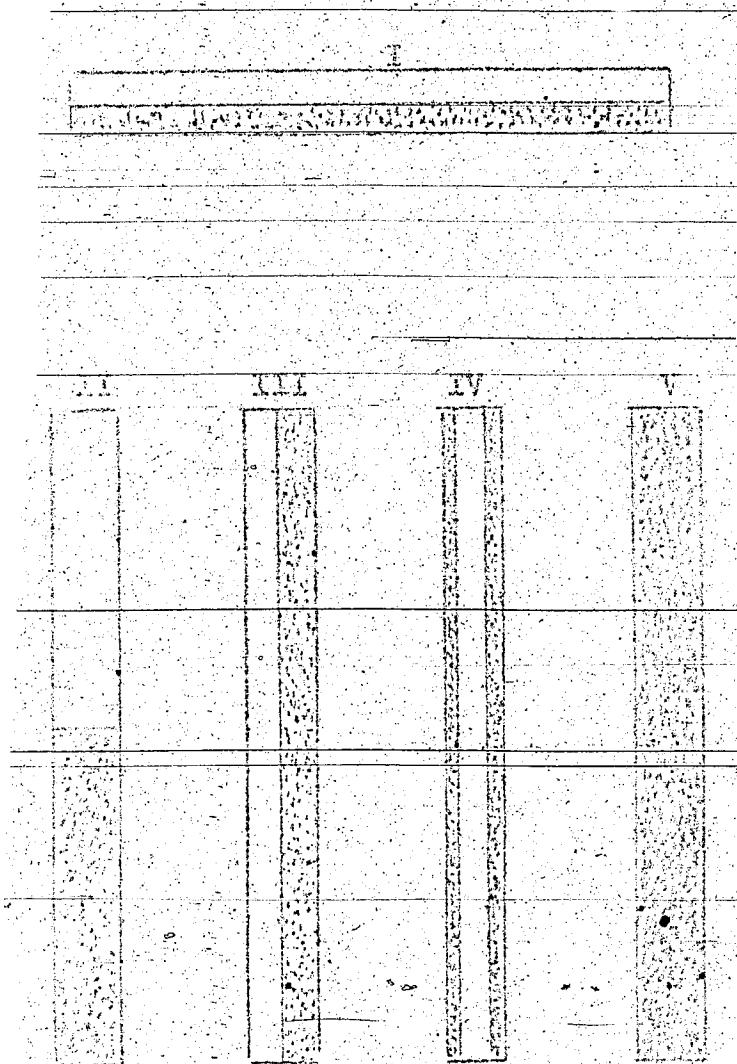


Fig. 10 Schematic representation of various filled catalyst tubes.

Relative humidity against temperature and
dew point for 100% relative humidity

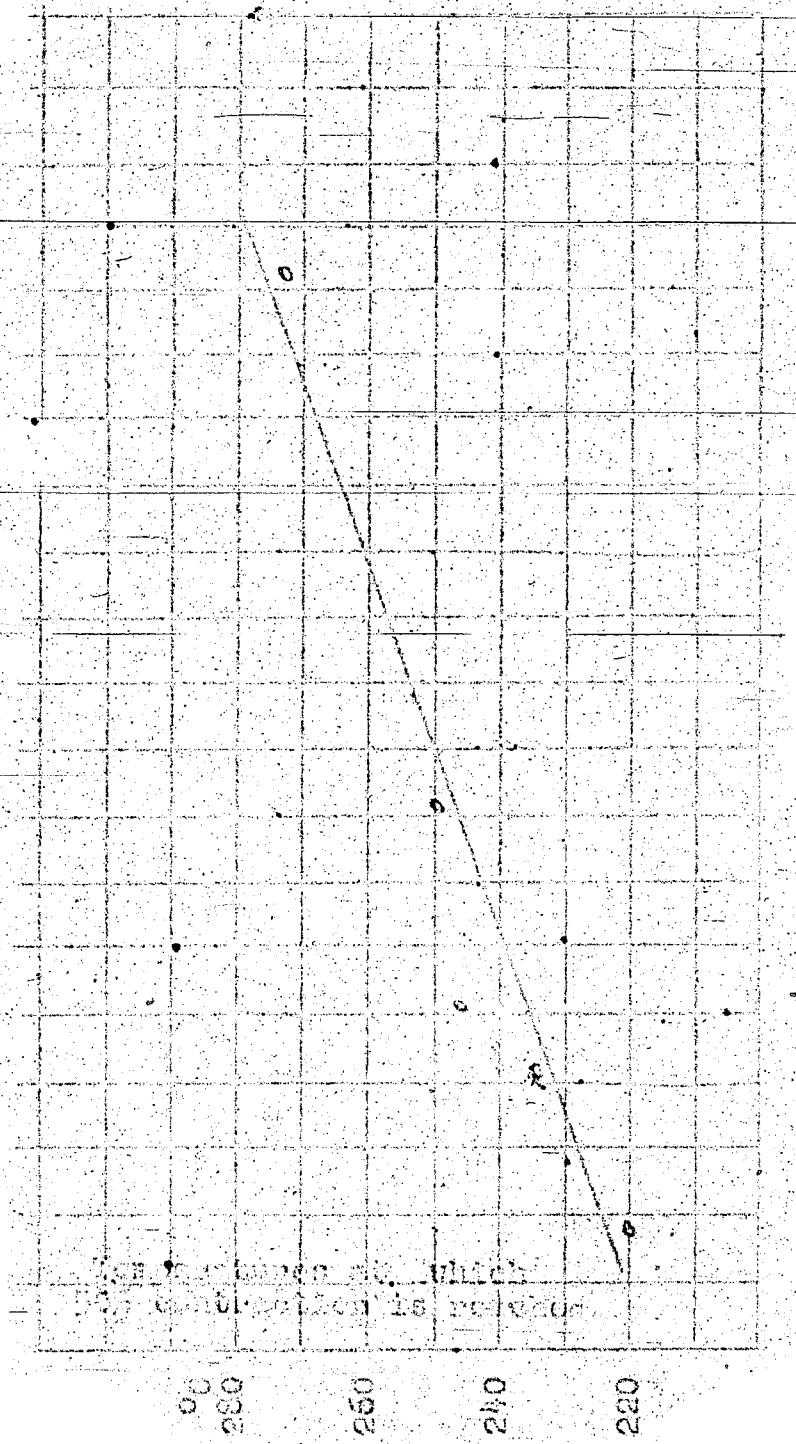


Fig. 11. Relative humidity vs. temperature

Temperature at which
the condensation is reached

It has also been shown in the iron middle pressure synthesis, that without increasing the pressure, the gas thruput, i.e. the weight of gas converted per unit weight of the catalysts, could not be increased. Many processes occur on the surface of the catalysts (the transportation of the participant and products of the reaction to and from the catalysts, etc.) and the processes which determine the rate of the reaction are not accelerated by increasing the pressure.

When the reaction tube is set vertically (figure 19, scheme 2), then the catalysts distributed in a layer 30 centimeters long becomes compressed to 10 - 15 centimeters, and the gas which travelled relatively long over the catalysts passes now more rapidly through the narrower channels between the grains of the catalysts. The empty space available to gas in the region of the catalysts in the two schemes, I and II, is therefore in proportion of about 3 : 1. The relationship between the gas thruput and the temperature shown in figure 20 may be understood to mean that equally good results can not be obtained according to scheme II as to scheme I. There is a further difficulty in that the volume of the catalysts increases as a result of the absorption of reaction products and of carbon. This results in a further shortening of the residence time of the gases because of the narrowing of the hollow spaces inside the catalysts.

It may be impossible industrially to avoid using vertical reactors, and a solution of the problem was at first sought according to schemes III and IV. The broken lines represent perforated sheets. In case 3 a perforated sheet separates the reaction tube into two equal parts, in case 4 a second tube made of perforated sheets is set inside the reaction tube. The catalyst here is placed between the two tubes. In both cases the length of the layer, the space filled by the catalyst and the empty space correspond to the proportion in case 1. The results were also at first similar. The perforated sheets caused no noticeable slowing down of the conversion. (The catalyst was formed in a separate apparatus and the catalyst was transferred in an atmosphere of carbon dioxide). After a few weeks of operation a retardation of conversion was observed in methods III and IV in comparison with the method according to scheme I. The reason for it may be in the chance for the catalysts in case I to expand

during synthesis, which could happen in cases III and IV only at the expense of the empty spaces between the catalyst grains.

The scheme shown in drawing V figure 19 was based on the addition of a substance tending to increase the porosity of the catalyst, e.g. of kieselguhr. 4 g of kieselguhr was normally used with 10 g of iron, in which case the iron-kieselguhr catalyst fills 12 to 13 mls of space in the reaction tube to a length of approximately 30 centimeters. The free gas space is smaller than in the case I by the space occupied by kieselguhr, but the increased porosity of the catalysts resulted in a considerable increase of its activity. A relatively smaller percent increase in the iron volume through absorption of carbon can no longer affect the process as adversely in case 5 as in cases 2 and 4. A test run in this way (figure 11) proceeded satisfactorily for several weeks.

We may in general point out that the volume increases distinctly observable in tests II and IV were not observed in all cases. Thus an iron catalyst precipitated with ammonia and formed with nitro gas at atmospheric pressure, and used in vertical reaction tubes could be used in the temperature range from 240 - 260°C for three months with out reactivation and with a good conversion. Tests to explain these results are still in process.

It must be mentioned with reference to the iron-kieselguhr-catalysts that the space-time yields obtained with them were approximately the same as with the cobalt catalysts. With this catalyst the same industrial equipment could be used as in the cobalt synthesis. In the laboratory, water cooled tubes could be used. The steam pressure was naturally higher because of the higher reaction temperatures. It was equal to 30 - 50 atm, depending on the length of operation.

C. Forming the Catalysts

The iron catalysts described in the first part of this paper and precipitated by sodium carbonate from ferric nitrate solution as well as the catalysts precipitated with ammonia from ferric-nitrate solution were hard after drying and broke with a lustrous fracture, and their strength satisfied industrial requirements.

Tests were nevertheless made of grinding the iron catalysts and compressing them into tablets.

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The brownish - black color of the grains of the catalysts are changed during grinding into a reddish brown color which is retained by the compressed tablets. It has been found that the activity of the original catalysts was not always retained in the tablets. This may have been connected with the heating during compression, and from phenomena produced by a pressure during the tableting.

Iron catalyst tablets of very good activity and life have been prepared when paraffin was added to the catalysts powder to be pressed. Synthetic paraffin, shaved to fine scales was used in these tests.

Test 1 table 35 shows a test with tablets which contained 25 percent paraffin referred to iron. Test 2 has been performed for the sake of comparison without any addition of paraffin. Paraffin does not interfere with the forming and can also be mostly recovered during that step. The tablets retained their shape even after many months of synthesis.

Table 35

Experiments with Catalysts Compressed into Tablets

Days of operation	Experiment 1		Experiment 2	
	Temp. °C	Contr. %	Temp. °C	Contr. %
1	235	54	234	57
2	235	54	235	56
10	235	51	235	54
16	234	53	236	50
20	235	52	235	49
25	235	47	240	48
31	235	46	243	47
47	240	49		
60	240	45		

	$^{12}C_2$	Heavy hydrocarbons	O_2	CO	H_2	Hydrocarbons number	Carbon No.
Experiment 1							
Starting gas:	2.3	0.0	0.2	53.3	25.7	0.2	2.0
End gas:	3.7	3.9	0.1	1.1	19.2	7.0	1.0
Experiment 2							
Starting gas:	2.1	0.0	0.1	53.7	23.0	0.4	1.9
End gas:	3.6	3.5	0.0	1.3	19.2	7.0	1.8

The conversion at the start of the operation was practically the same in the two series of tests (as may be seen from the two parallel gas analyses printed at the bottom of the table). However, the catalyst tablets prepared without paraffin addition required a more rapid rise in temperature after a few weeks, than the tablets made with paraffin. The activity of the catalyst in series 1 is the same after fifty days of operation as after twenty-five days of operation of the catalyst 2.

An improvement in the catalytic behavior of the catalysts tablets was also found upon the addition of 5 and 10 percent of paraffin.

D. On the Subsequent Working up of the Primary Products.

Great variety of reaction products was obtained in the middle pressure synthesis with iron catalysts, as has already been discussed in a special section. In most cases they could be used for the same purpose as the products of synthesis with cobalt catalysts. It remains to discuss a little more closely the possibilities of the utilization of the products. The products of the iron-synthesis differ naturally in certain respects from those of the cobalt synthesis. One such instance is the formation of the synthack-like by-products, such as the different alcohols, and another one is the increased formation of unsaturated hydrocarbons. The oxygen-containing and the unsaturated compounds produce a higher knock resistance in the iron gasolines. These compounds show no tendency to form gum. The gasoline formed with iron-catalysts remains completely colorless and clear after months of storage.

The amount of unsaturated gaseous hydrocarbons is greater in the middle pressure synthesis with iron-catalysts; they may permit a polymerization to the knock-resisting liquid hydrocarbons, which appears to indicate that the iron catalysts synthesis is suited for the production of high grade gasoline.

We have performed a few tests on the catalytic polymerization of the olefin hydrocarbon which has been primarily developed by Ipatiev of the Universal Oil Products Company and his collaborators 23/ who worked on the problem of a combination of synthesis and polymerization. A special phosphoric acid catalyst, namely $\text{Cd}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$, was used for that purpose.

The calcium phosphate $\text{Ca}_3(\text{PO}_4)_2$ was used as a carrier and was obtained by precipitation of calcium nitrate solution at the boiling point with a calculated amount of Fe_2HPO_4 and NaOH . It was washed with hot water and mixed while still moist with the calculated amount of the 89 percent phosphoric acid, evaporated, dried, and granulated.

When a gasol containing 35 to 40 percent of unsaturated hydrocarbons (obtained in cobalt synthesis) led over this catalyst (1.11 gaseous gasol/hr/10g catalyst), under a pressure of 7 atm 80 percent of the unsaturated hydrocarbons were converted at 140°C , 60 percent at 160°C and 70 - 80 percent at 120°C . A polymere gasoline was formed which was distilled, and 10 - 20 percent of compounds boiling $180 - 200^\circ\text{C}$ were separated and found to have an octane number of 97 to 99 without the addition of any volatile hydrocarbons, with a Reid vapor pressure of 0.1 to 0.2 atm., and without any additional hydrogenation.

Tests were carried out in which the total reaction gas of the iron middle pressure synthesis was led into a second stage synthesis under pressure with phosphoric acid catalysts, after separating the products condensable at room temperature. About equal volumes of catalysts were used in the synthesis and the polymerization. The synthesis was in operation for about two months before the different tests were started. An ammonia precipitated iron catalyst with $1/4 \text{ FeCO}_3$ was used after being formed with mischgas at atmospheric pressures. The yield of solid, liquid and gasol hydrocarbons amounted to about 140 g per norm of the ideal gas. Table 36a shows a few analyses of the reaction gases after the synthesis and after the polymerization. This series of experiments was run at pressures of 15 atm. The temperatures of the synthesis were at 250°C , of polymerization at $200 - 220^\circ\text{C}$.

Table 36

Composition of the Reaction Gases after Synthesis and after Polymerization.

CO_2	Heavy hydrocarbons	$\text{C}_2 \text{ G}$	C_3	H_2	Hydrocarbons	Carbon number	N_2
a 58.3	3.7	0.2	8.7	12.8	8.7	1.6	9.6
b 59.8	1.1	0.2	9.1	13.0	6.2	1.7	10.6
a 62.9	3.7	0.2	7.0	10.1	7.7	1.8	8.4
b 64.8	1.2	0.3	7.1	10.0	7.6	1.8	9.0
a 58.4	4.2	0.0	10.9	5.1	6.4	1.7	15.0
b 60.6	1.2	0.4	10.8	5.0	6.0	1.8	16.0

Analyses show that 2/3 to 3/4 of the heavy hydrocarbons disappeared during polymerization.

Table 27 shows the number of g of solid, liquid and gasol hydrocarbons per mole ideal gas produced during synthesis with and without polymerization. The top values represent an average of three weeks of operation, the bottom series is an average of the next week of operation during which the polymerization step was omitted. The AK gasoline was obtained only once at the end of the conversions (that is not between the synthesis and the polymerization stages).

Table 27
Comparison of Synthesis and Polymerization

Poly- merization of the liq- uid hydro- carbons (including paraffin)	Yield g/norm Wt. percent	% of liquid hydrocarbons by wt.			
		Gasol (after Syn- thesis)	70 after Poly- meri- zation	20 after Poly- meri- zation	10 As AK gasoline
With	125	14	70	20	10
without	105	30	85	0	15

139 g of liquid and gasol hydrocarbons (including paraffin) were formed in the synthesis during the first period, 135 g/norm during the second period (without polymerization). The synthesis therefore produced about 5 percent more products during the first period, while the amount of liquid hydrocarbons was 19 percent greater, largely produced from gasol by polymerization. In the containers cooled to room temperature, 70 percent of the liquid products separated in the polymerization experiment after the synthesis and 20 percent after the polymerization, with 10 percent as AK gasoline. The so-called AK gasoline obtained during synthesis and not condensed in the first container, was led with the reaction gases over the phosphoric acid catalyst and polymerized part of the unsaturated gasoline hydrocarbons. While the amount of gasol hydrocarbons was reduced from 30 to 14 g/norm by polymerization, the proportions of the AK gasoline was reduced only from 16 to 13 g/norm. We may explain this by assuming that the olefinic hydrocarbons of the C_4 hydrocarbons are more readily polymerized than the hydrocarbons with lower or higher molecular weights which

react at a slower rate. For this reason the dimers of olefins are largely formed in this polymerization over phosphoric acid esters.

Unlike the "open gasoline", the polymer gasoline can be advantageously hydrogenated, and it would therefore be preferable to remove as perfectly as possible the synthetic gasoline from the reaction gas before the polymerization stage.

It becomes therefore possible to complete the working up of the reaction gases of the middle pressure synthesis with the iron catalysts for the manufacture of polymer gasoline in one continuous operation. It will have to be left to practical experience whether such a process is more economical than a recent polymerization stage of the gasol hydrocarbons freed from the other gases.

A closer connection between synthesis and polymerization might be obtained by mixing the synthesis catalysts with the one used in polymerization, but it results in a gradual weakening of both processes especially if the contact of the two types of the catalysts is very intimate (by the interaction of the acid phosphoric acid catalysts and iron).

Tests in which acid iron phosphate was used for polymerization instead of calcium phosphate produced similar results.

The gasolines obtained by stabilization and washing of the two liquid reaction products in table 37 with sodium hydroxide have been tested for knock resistance in the I. G. test motor. About 2/3 of the total liquid products in this test boiled within the range of 50 - 180°C. Table 1 shows:

1. Gasoline not followed by polymerization:
2. Gasoline 180°C obtained in a combination of synthesis and polymerization:
3. Gasoline b.p. 150°C obtained by polymerization following synthesis:

The density, olefin content, boiling point curve and vapor pressures at 37.8°C as well as the octane numbers are given for all three samples.

Table 38

Effect of Additional Polymerization upon the Properties
of Gasoline Obtained in Middle Pressure Synthesis.
Boiling Range

No.	d ₁₅	Olef. %	Start. b.p.				P 37.9° C.M.	O.N.
			°C	10% °C	50% °C	90% °C		
1	0.695	64	30	45	88	145	0.54	61
2	0.705	65	32	53	100	150	0.48	67
3	0.700	65	34	50	95	130	0.55	71

An octane number of 61 was obtained without additional polymerization of olefines (table 38 #1). Octane number 67 was obtained with polymerization (#2). When the gasoline was cut at 150°C (#3) the octane number was equal to 71.

The addition of 0.7 alc of tetramethyl lead to #2 gasoline raised the octane number to 79, #2 and to 80 in gasoline #3.

Summary

A review is given of the work on middle pressure synthesis with iron catalysts. It includes investigation of the precipitation, alkalization and forming of the catalysts, the finding of the optimum synthesis conditions (composition of gas, pressure, temperature, additions, catalysts reactivation etc.); the third topic was a discussion of the reaction products and the fourth was treatment of general problems such as the production of synthesis gases, equipment construction problems, tabling the catalysts and the subsequent treatment of the original products.

The principal results of these investigations are the following:

1. Precipitation of the iron catalysts:

The catalysts were generally produced by precipitation of iron with sodium carbonate or ammonia from ferric nitrate solution, obtained by solutions of technical grade of iron in dilute nitric acid. The catalysts precipitated from ferric solutions were

superior to those obtained from ferrous solutions.

2. Alkalinization of the Catalysts:

The presence of alkalis is not necessary for synthesis, nor does it regulate the amount of conversion. However, the presence of increasing amounts of alkalis favors the formation of higher molecular weight hydrocarbons. The addition of alkali is therefore important for the production of solid paraffin. Potassium carbonate was generally used but different alkali salts produced the same results.

3. Forming the Catalysts:

Forming (pretreating the catalysts with gases containing carbon monoxide, best with pure carbon monoxide) is necessary for the production of active catalysts. Forming is conducted at pressures below the synthesis pressure, e.g. at atmospheric pressure, but best at a reduced pressure.

The gas used for forming is best conducted at a high rate and at temperatures over 250°C , best at 300 to 350°C , until the carbon dioxide formed in the reaction passes through a maximum and then reaches an approximate constant minimum value.

4. Synthesis:

The optimum proportion of carbon monoxide to hydrogen in the synthesis gas is 3 : 2. The optimum synthesis pressure is between 10 and 20 atm. The optimum synthesis temperatures are between 230 and 240°C . At the start catalysts synthesized the gas at considerably lower temperatures. This is not however, of advantage to the life of the catalysts, nor are temperatures in excess of 230°C (the latter because of a deposition of carbon).

The addition of kieselguhr (after alkalinizing) results in a considerable increase in the activity of the catalysts.

No advantages were found in treating catalysts with hydrogen before synthesis, but an occasional treatment with hydrogen during the synthesis results in a reactivation of the iron catalysts.

5. Optimum Yields:

The best yields in solids, liquid and gasol hydrocarbons amounted to about 150 g/nccm ideal gas. The longest life was obtained with a catalyst which still brought about a conversion of 140 g/nccm gas at a temperature of 620°C after 1 1/2 years of operation.

6. Reaction Products:

The nature of the reaction products can be modified within wide limits by changing the operating conditions.

5 to 50 percent of the total solid and liquid hydrocarbons were solid paraffin. Low melting point paraffins are formed as well as particularly high melting paraffins with melting points up to 125°C.

The liquid reaction products differ from those obtained with the cobalt catalysts by their increased content of unsaturated hydrocarbons and by their content of synthol-like products among which alcohols and esters of different molecular weights have been proven.

The octane number of the 130°C cuts of primary gasoline is 60 to 63. It can be increased further 10 octane numbers by combining synthesis with the polymerization of the gasol hydrocarbons, and the addition of 0.7 ml of tetraethyl lead per li of gasoline will increase it by an additional 10 O.N.

10 to 30 percent of the solids, liquids and gasol hydrocarbons consist of gasol. Its olefin content reaches 80 percent. When the temperature or the activity of the catalyst are increased, the total gasol yield is increased, but its olefin content is lowered.

Iron catalysts have been found suitable also for the production of a gas meeting specifications of the gas manufactures.

7. Production of Synthesis Gas:

A synthesis gas with the carbon monoxide and hydrogen in proportion of 3 : 2 is obtained by a simultaneous conversion of carbon dioxide and steam in a water gas producer, with the carbon dioxide required obtained from the synthesis products. Another

suitable synthesis gas is obtained by gasification of coke or coal with oxygen.

8. Equipment Construction:

Connections between the parts of the equipment and the life and activity of the catalyst has been discussed. The best results are obtained in horizontal or slightly inclined reactor. The removal of the positive heat of the reaction with water requires steam pressures of 30 to 50 atm on the water side of the reactor.

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July 1, 1940

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