

STANDARD OIL DEVELOPMENT COMPANY

Translation of Oil Mission Reel No. 101.

ft.21, fr.5 to ft.23, fr.4

German Item No. 21574

"Iron Catalyst in Medium Pressure Synthesis" by H.Pichler, with an introduction by F.Fischer (Kaiser-Wilhelm Institut fur Kohlenforschung), dated 10 Sept. 1940.

Pages 9-19 of the original, comprising "a discussion of the theory of activation of the catalyst" have been translated.

B. Preliminary Treatment of Catalyst

The freshly prepared and dried iron precipitate is, just like a cobalt catalyst, completely inactive at first as catalyst for the conversion of carbon monoxide and hydrogen. However, while in the case of cobalt an extensive reduction to metal is effected by treatment with hydrogen at about 360°C. and concurrently therewith takes place an activation of the catalyst for the hydrocarbon synthesis at low temperatures, an iron catalyst cannot be brought into a suitable condition for the synthesis at low temperatures by a preliminary treatment with hydrogen. The trivalent iron is converted by a preliminary treatment with hydrogen at about 300-400° into black ferromagnetic Fe_3O_4 which does not catalyze as yet the conversions of carbon monoxide with hydrogen. By preliminary treatment with carbon monoxide, however, the iron catalyst may be brought into a highly active form for the synthesis as long as certain working conditions are observed. (It is known that the carbon monoxide causes, along with a more or less extensive reduction according to the temperature conditions, also the formation of carbides and a loosening of the iron structure by the interposition of carbon). Herein below, the preliminary treatment with carbon monoxide or with gases containing carbon monoxide will be designated as formation.

I. Formation by means of carbon monoxide - hydrogen mixtures during synthesis.

It seems expedient to distinguish between a formation which takes place under the conditions of the synthesis and a formation which is carried out under special conditions prior to the start of the synthesis.

a) Experiments at atmospheric pressure.

First, the relationships in working under atmospheric pressure should be pointed out again. Fig. 1 shows the increase and decrease of the value of contraction (as a measure of conversion) plotted against time when using synthesis gas high in hydrogen or high in carbon monoxide.

When iron catalysts of the precipitation type are started upon a gas mixture ($\text{CO}:\text{H}_2 = 1:2$) at atmospheric pressure, the contraction rises at 235°C . (and at a thruout rate of 4 ltrs. of gas mixture per hr. and 10 g. iron) to 30% within three to four days. This period of time, during which the catalyst is gradually brought up to full activity by the action of the synthesis gas, corresponds to the formation period (Fig. 1, curve 1). At atmospheric pressure it is possible to work for three to four weeks at a maximum contraction of about 30% with average yields of liquid and solid hydrocarbons of 30 g/m^3 . The carbon monoxide of the gas mixture is almost used up, while a large excess of hydrogen remains in the end gas.

If, instead of running the iron catalyst on a gas mixture high in hydrogen, it is run on a carbon monoxide - hydrogen mixture whose composition corresponds better to the ratio in which the components react with each other, then no increase but a decrease in the conversion rate occurs at atmospheric pressure, as is shown in curves 2 - 4. Using a gas rich in carbon monoxide ($3 \text{ CO}:2 \text{ H}_2$), the contraction rose to 31% at 235° within three days (curve 2), to 38% at 245° within one day (curve 3), and to 33% at 255° within one day (curve 4). In all three cases, the conversion decreased rapidly after reaching these maximum values. The effectiveness of the catalyst when operating at atmospheric pressure was impaired by the gas rich in carbon monoxide.

b) Gas rich in carbon monoxide and increased pressure.

Table 1 shows a continuous experiment carried on for 5 months with an ordinary iron catalyst used directly with a synthesis gas rich in carbon monoxide ($3 \text{ CO}:2 \text{ H}_2$), i.e. without previous formation, at a pressure of 15 atm. (4 ltr. synthesis gas, based on 1 atm., flowed over the catalyst per each 10 g. of iron),

TABLE 1

Formation and Synthesis at a Pressure of 15 Atm.

Day	Temp. °C.	Contr. %	Day	Temp. °C.	Contr. %
1	245	4	69	268	37
4	245	10	75	280	47
5	250	13	90	280	49
7	253	17	98	283	44
11	260	24	106	285	43
13	270	24	130	288	43
14	275	37	140	292	44
28	280	36	150	298	47
60	290	50			

The contraction was 4% at 245°C. after one day and 10% after four days. (compared to 30-35% after the same time at 1 atm.). The temperature was gradually increased and in every case the increase of contraction was observed for several days. 24% contraction was reached on the eleventh day at 260°C. No further increase in conversion was reached by increasing the temperature to 270°C., 37% was measured at 275°C. and 36% at 280°C., 50% contraction was reached only at 290°C., corresponding to almost complete conversion in the direction of formation of hydrocarbons and carbon dioxide. Thereafter an attempt was made to determine whether or not this conversion, once reached, will remain constant after lowering the temperature. The contraction decreased again to 37% at 268°C.; at 268°C. however, a better conversion was noted in the third month of the experiment than after the first month. Meantime a slow formation of the catalyst had taken place. In order to maintain a contraction of 40-50% in the fourth and fifth month of the experiment, the temperature had to be increased again. After completion of the experiment (after five months) it amounted to 300°C.

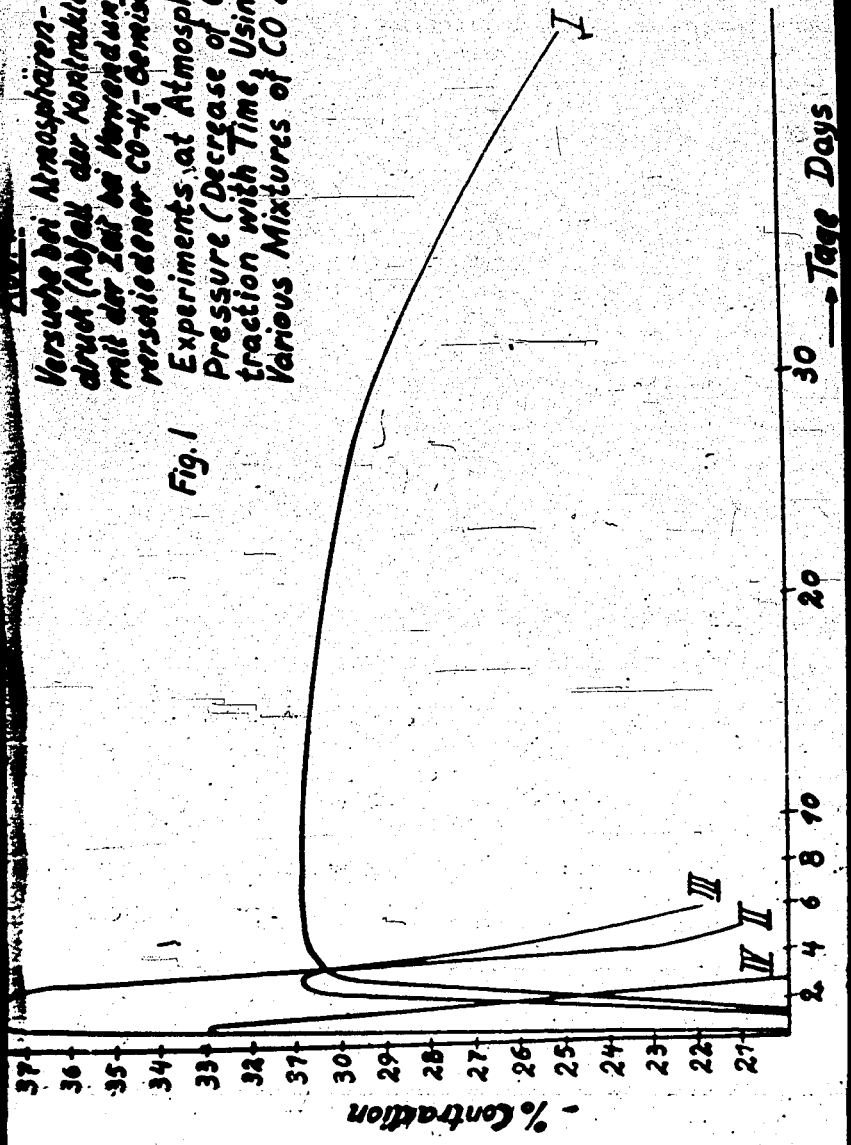
A determination of the yield, carried out in the third month at 280°C., showed 3 g. solid paraffin, 93 liquid hydrocarbons and 32 g of C₃-C₄ hydrocarbons (gasol) per normal m³ of ideal gas.

In contrast to synthesis at atmospheric pressure, the starting up of the catalyst directly at elevated pressure retards the formation process,

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

Experiments at Atmospheric
Pressure (Decrease of Con-
traction with Time, Using
Various Mixtures of CO & H₂)

Fig. 1



particularly when the reaction is initiated at low temperatures. On the other hand the temperature can be increased to 280-290°C. at a synthesis pressure of 15 atm. when using synthesis gas rich in carbon monoxide, without causing rapid inactivation of the catalyst due to this increase of temperature as would be the case at 1 atm. For synthesis on an industrial scale, the temperatures seem too high and the life span of the catalyst seems to be still too short

II. Formation in a separate process from the synthesis.

It was investigated whether or not an increase in the activity of the catalyst could be accomplished by carrying out formation and synthesis separate from each other. The optimum conditions for both processes were determined.

a) Formation at ordinary pressure and synthesis at elevated pressure.

Table 2 shows results of an experiment carried out during the period of formation with gas mixtures at atmospheric pressure and at 245°C.

TABLE 2

Formation at 1 atm. and synthesis at 15 atm.

Day	Pressure Atm.	Temperature °C.	Contraction %
1	1	245	15
2	1	245	22
3	1	245	28
4	1	245	30
5	1	245	31
	15	245	55
6	15	245	48
8	15	250	53
9	15	250	49
14	15	252	46
24	15	256	51
50	15	255	51
100	15	265	55

When a maximum value of contraction of 31% has been reached after five days, conditions were changed to 15 atm. and a synthesis gas rich in

carbon monoxide was used. The contraction increased at once from 31% to 55%. In order to maintain highest yields and corresponding contraction values of about 50%, the temperature was increased gradually. After 100 days of the experiment a contraction of 55% was still obtained at 265°C.

A comparison of this series of experiments with the former ones in which operation started directly at 15 atm. without previous formation at ordinary temperature, shows that by the previous formation at atmospheric pressure it was possible to decrease the average synthesis temperature by 30-40°C. The increase in activity of the catalyst, effected by the formation at the low pressure of 1 atm., was maintained during the entire experiment.

b) Formation at various pressures and synthesis at ordinary pressure.

In order to test the influence of the formation pressure on the synthesis at atmospheric pressure, we refer to the series of experimental data reproduced in Table 3. Formation was accomplished at 255°C. in 20 hours with 4 liters (based on 1 atm., per hour and 10 iron) of gas rich in carbon monoxide (3 CO:2 H₂). The extent of conversion in the subsequent synthesis carried out with the gas mixture (1 CO:2 H₂, 4 liters/hr./10g iron) at atmospheric pressure was measured 1-1/2 hours after the switch-over, likewise at 255°C.

TABLE 3

Influence of the formation pressure on the synthesis at 1 atm.

<u>Formation Pressure</u> <u>(atm.)</u>	<u>Synthesis Contraction</u> <u>(atm.)</u>
9	5
3	12
1	28
0.1	30

The experiments show again that elevated pressure retards the progress of formation. The contraction was 5% after formation at 9 atm., 12% after formation at 3 atm., 28% after formation at 1 atm. and 30% after formation at 0.1 atm.

c) Influence of temperature of formation on the progress of synthesis.

Ordinary iron catalysts were formed with a gas rich in carbon monoxide at 1/10 atm. and various temperatures after it had been found that a low formation pressure has a beneficial effect on the activity of the iron catalyst. After formation for 25 hours at temperatures in the range of 250-350°C., the activity of the catalyst in the synthesis ($\text{CO:H}_2 = 3:2$, 15 atm. and 235°C.) was measured during long intervals of time. Fig. 2 shows the decrease in contraction with time at a constant synthesis temperature of 235°C. (4 liters of gas/10g iron/hr.).

The contraction dropped below 50% already on the third day of the synthesis after a formation at 225°C. With rise in formation temperature, the life of the catalyst increased. With a formation temperature of 315°C. the contraction dropped below 50% not until after more than 1 month's time. The stability of the iron catalyst decreased at higher formation temperatures.

Fig. 3 shows an analogous series of experiments in which the formation was carried out with pure carbon dioxide in place of the mixture of carbon monoxide and hydrogen.

After formation with carbon monoxide at 1/10 atm. and 325°C., the conversion in the subsequent synthesis remained constant throughout 4 months (at a temperature of 235°C. and a pressure of 15 atm.). The results are therefore even better than those for formation with mixtures of carbon monoxide and hydrogen.

e) Influence of formation or synthesis temperature.

A comprehensive picture of the influence of formation on the course of the synthesis is given in Fig. 4. With the time of experiment in months as abscissa, the working temperatures and the water vapor saturation pressures corresponding to these temperatures are plotted as ordinates. All experiments were carried out with a synthesis gas containing carbon monoxide and hydrogen in the proportion of 3:2 (4 liters /10g iron/hour).

Curve I refers to an iron catalyst used directly at a pressure of 15 atm., without previous formation. In order to obtain a maximum contraction, the temperature had to be raised to 290°C. The contraction was at first 45%. In the course of the second month of the experiment, the activity of the catalyst gradually increased and with it the contraction rose to about 50%. The temperature could be lowered to 280°C. in the further course of the experiment while maintaining a constant conversion rate. However, in the fourth month it already had to be increased again, and at the end of the fifth month a temperature of 300°C. was reached.

Titles of Diagrams 1 thru 5

1. Experiments at atmospheric pressure (decrease of contraction with time, using various mixtures of CO and H₂).
2. Influence of formation temperature on the synthesis process (decrease in contraction with time at 15 atm. and 235°C.) after formation with synthesis gas rich in carbon monoxide at 1/10 atm.
3. Influence of the formation temperature on the synthesis process after a formation with carbon monoxide at 1/10 atm.
4. Influence of the formation on synthesis temperature.
5. Production of carbon dioxide during the formation process.

Curve II shows the temperature conditions with an iron-copper catalyst which operated at first at 1 atm. and at 240°C. for three days on a gas mixture (contraction 30%) and then was switched over to synthesis gas at 15 atm. In order to reach a maximum contraction of 50-55% (optimum conversion), the temperature had to be raised gradually from 240 to 290°C. over a period of 5 months.

Curve III refers to a catalyst free of copper, which was formed first at atmospheric pressure and 245°C. for five days and then put in operation at 15 atm.

Curve IV shows the temperature changes in an experiment using likewise a copper-free catalyst, a so-called ordinary iron catalyst, which was treated beforehand with pure carbon monoxide under at 1/10 atm. pressure and 255°C. for 25 hours. This experiment produced a contraction of 50% even after 16 months at 260°C.

Curve V refers to a catalyst pretreated with carbon monoxide at 1/10 atm. and 325°C. Formation at 325°C. made possible an unusually smooth operation at low temperatures during the initial months. The contraction remained constant at 50-54% through 4 months at a temperature of 235°C. Thereafter the temperature had to be increased.

The above curve shows the importance of the pretreatment of iron catalysts for the reaction temperature in the synthesis. This influence of the formation remains even after many months of operation.

a) Formation time.

In addition to pressure and temperature, the velocity with which the carbon monoxide passes over the catalyst and the time of formation are of importance. Since the reduction and carbonation processes concurrent with the formation are connected with the production of carbon dioxide, the course of the formation process may be observed by determining the carbon dioxide content of the end gas of the formation. The formation is completed when production of carbon dioxide after passing through a maximum reaches an approximately constant minimum value (see Fig. 5). Further production of carbon dioxide corresponds to a production of free carbon which should be prevented as far as possible. This production of carbon is larger with high flow velocities of carbon monoxide than with low ones.

As a summary of the work on pretreatment or formation of iron catalysts it may be stated that this pretreatment must be carried out at low pres-

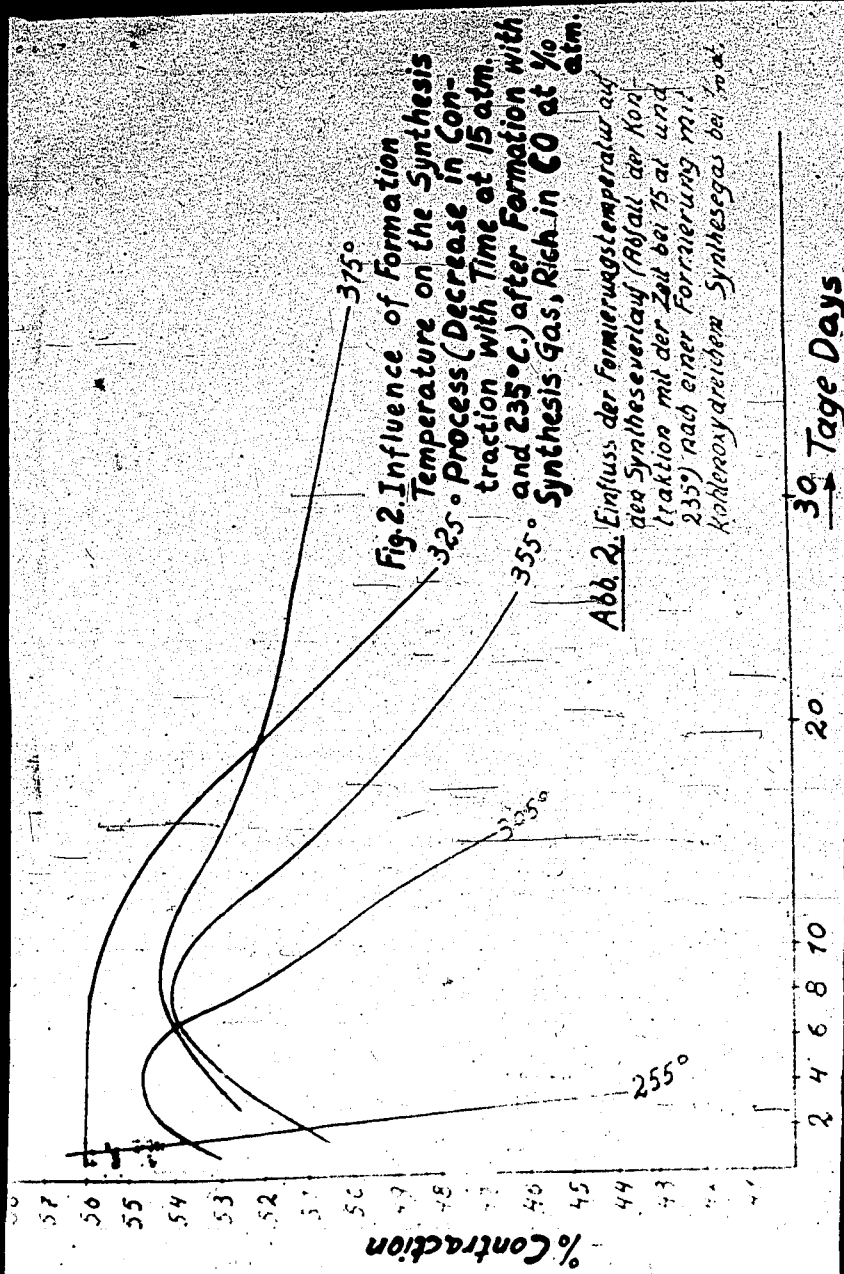


Fig. 2. Influence of Formation Temperature on the Synthesis Process (Decrease in Contraction with Time at 15 atm. and 235°C.) after Formation with Synthesis Gas, Rich in CO at 1/10 atm.

Abb. 2. Einfluss der Formierungstemperatur auf den Syntheseverlauf (Rückfall der Kontraktion mit der Zeit bei 15 at und 235°) nach einer Formierung mit kohlenoxytreichem Synthesegas bei 1/10 atm.

tures but higher temperatures than the subsequent synthesis. It is expedient to work with pure carbon monoxide and high gas velocities. During the formation process, certain states of equilibrium are reached in the solid phase. They are dependent on the composition of the gaseous phase. The lower the carbon dioxide concentration in this phase, the more favorable it is for the reduction of iron oxide and the production of carbides. The beneficial effect of a low formation pressure and high gas velocities may be thus explained.

Investigations of processes occurring in the solid phase, that is in the catalyst during formation and synthesis, are in progress. We hope that they will furnish a valuable contribution to the practical aspects of the synthesis, especially for a more rapid determination of the activity of the catalyst.

Translated by:
Standard Oil Dev. Co., Library
ml/mt
3/29/46