

## INTRODUCTION

Some time ago we published an article entitled, "The Approach of Actual Yields to the Theoretical Yields of the Fischer-Pichler Middle-Pressure Synthesis." (1)<sup>a</sup> The experiments were carried out with cobalt-thorium catalysts. The yields of solid and liquid hydrocarbons (with approximately 15 grams of gasol) amounted to 150 grams to 170 grams maximum per normal cubic meter of ideal gas. Of this, more than 50 percent constituted paraffins when the most favorable reaction conditions were provided.

Ever since Fischer and his coworkers perfected the synthesis of hydrocarbons from CO and H<sub>2</sub> using cobalt-thorium catalysts, the desire was foremost in our minds to use cheaper catalytic agents which would give the same or similar products. We kept on working with iron catalysts. In 1923, Fischer and Tropsch (2) obtained the so-called Synthol when they passed water gas over alkalinized iron shavings at approximately 100 atmospheres pressure, and 350° to 450°C. The Badische Anilin- und Sodafabrik (3) worked with similar pressures and temperatures in 1913, and in 1925 they arrived at the synthesis of methanol. Fischer and Zerbe (4) showed, in 1923, that alkalinized iron shavings acting on CO<sub>2</sub> and H<sub>2</sub> will lead to the formation of hydrocarbons. They observed that, with decreasing pressure, a tendency exists to form hydrocarbons rather than oxygen-containing compounds. They worked in a circulating apparatus at 410°C., and 100-150 atmospheres pressure. They observed that, at higher pressures, only water-soluble products were formed, but at around 7 atmospheres, some oil was obtained which contained approximately 40 percent of petroleum products soluble in concentrated sulfuric acid.

In 1926, Fischer and Tropsch (5) reported that, at a temperature of 300°C. and above and using iron catalysts on CO and H<sub>2</sub>, even under atmospheric pressure, hydrocarbons are obtained. On the basis of these experiments and results, we have tried repeatedly to introduce iron catalysts and at the same time reduce the reaction temperature and improve the yield of liquid hydrocarbons. In 1928 (6), 30 to 40 grams of gasoline and oil were obtained at atmospheric pressure for every cubic meter of water gas. The temperatures could be lowered to 240°-250°C. The lifetimes of the catalysts amounted to several days.

Fischer and Tropsch (7) had attempted in 1927 to use water gas at 10 to 15 atmospheres pressure and 250°-280°C. They worked with fused iron oxide catalysts with a small addition of copper, and they worked with water gas directly under pressure. Their products consisted of aqueous and oily substances in the ratio 3:2 to 1:1. At this time, the authors revealed that their results were not as good as with atmospheric pressure. In 1934, Fischer (8) gave a lecture on the gasoline synthesis in which he reported a maximum yield of 30 to 35 grams per cubic meter of mixed gas when using an iron catalyst under atmospheric pressure (this corresponds to approximately 40 to 45 grams per Nm<sup>3</sup> of CO-H<sub>2</sub> mixture). He also added that the initial conversion decreased by 20 percent in the course of 8 days.

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<sup>a</sup> Figures in parentheses refer to items in the Bibliography at the end of this article (p. 168).

Fischer and Meyer (9) attempted in 1934-1936 repeatedly to improve the yields of liquid hydrocarbons by increasing the activity of the iron catalysts. By using iron-copper precipitated catalysts, they succeeded in getting 50 to 60 grams per normal cubic meter of gas at a maximum lifetime of the catalyst of 4 to 6 weeks.

Fischer and Ackermann (10), in 1936, obtained 55 grams of liquid hydrocarbons per normal cubic meter of mixed gas when they used certain copper-free iron catalysts produced under certain conditions. They worked at atmospheric pressure. This yield, however, started to decrease after very few days and in the third week amounted to less than 40 grams.

At this time, they used a synthesis gas which contained CO and H<sub>2</sub> in the ratio of 1:2, although they had recognized that on iron catalysts the CO conversion proceeds almost entirely according to the equation:



When they used a synthesis gas mixture of 2CO + 1H<sub>2</sub>, the CO was used up only partly, and the activity of the catalyst decreased rapidly.

In every one of the experiments cited, the maximum yields obtained were less than half those obtained with cobalt catalysts on industrial scale. Therefore, we could not consider the use of iron on a large scale at that time. The result of the work which we are going to discuss here will show that if we operate in a certain manner, using iron catalysts at high pressures, the CO-H<sub>2</sub> mixture may be virtually entirely converted into hydrocarbons. According to synthesis conditions, one gets various quantities of paraffins, gasoline, and gasol hydrocarbons. The total yields of this so-called iron middle-pressure synthesis compare closely to those of the synthesis using cobalt catalysts, so that now we can consider replacing cobalt by iron.

Toward the end of 1937, Fischer reported on the favorable course of our work on the synthesis with iron catalysts. We intended, at that time, to make our results public and inform those parties which would be interested for the commercial application. Because we recognized the importance of being able to substitute iron for cobalt, since Germany has only little cobalt available, Fischer and a series of his coworkers have intensified their work in the last years.

The essential content of the present work has been assigned to Studien und Verwertungs Gesellschaft. The assignment which goes back to the year 1937 was communicated to Ruhrchemie for patent purposes. In the meantime, several patents had been applied for in foreign countries.

## THE CATALYST

### Precipitation of Catalyst

At first we believed that variation in the production methods of the iron catalysts and also that certain additions to the iron catalysts would improve the yields of liquid hydrocarbons at atmospheric pressure. For this purpose, we produced many hundreds of different iron catalysts whereby we tested the various additions and various modes of precipitation.

In the course of our researches we recognized, however, that we could only reach our aim by working at a slightly positive pressure, and the catalyst characteristics could vary considerably. When we worked with a pure iron catalyst which had been inducted with CO before the atmospheric synthesis, we found that we obtained satisfactory yields for many months thereafter.

#### Starting Material

As starting material for the production of the iron catalysts, we generally used iron-salt solutions. These solutions were obtained by dissolving commercial iron directly. For the sake of comparison we also used chemically pure iron. The majority of experiments were carried out with the following iron samples:

- a. Ferric nitrate (commercial).
- b. Iron nitrate solutions obtained by dissolving technical iron shavings in nitric acid. The iron was chiefly present as trivalent iron. The iron shavings were introduced in small portions into nitric acid of an initial density of 1.18, and the temperature was kept below 40° to 50°C. (Above 60° to 70°C., a decomposition of the nitrates occurs, with the formation of an insoluble precipitate.)
- c. For the production of ferrous nitrate solutions, nitric acid with a maximum density of 1.05 was allowed to act upon iron shavings at 35° to 40°C. (A higher acid concentration or a higher temperature caused a violent reaction which forms ferric salts instead of ferrous salts.)
- d. Ferrous chloride (commercial).

#### Precipitation with Sodium Carbonate

The concentration of the iron solutions used for precipitation generally corresponded to 1 kilogram of iron per 30 liters of the solution (with catalysts based on bi- and trivalent iron). The solution was preneutralized in the cold with the solution of sodium carbonate, and care was taken to assure enough alkalinity that no permanent precipitate remained in existence. The ferric solutions usually were precipitated at 100°C., whereas the ferrous solutions were precipitated at a maximum of 70°-75°C.; in both cases a small excess of sodium carbonate was used. The sodium carbonate solutions generally contained 1 kilogram of soda for every 8 to 10 liters of water. After precipitation, the mixture was brought to a boil for a few minutes, filtered, and washed free of alkali with hot, distilled water. The moist precipitate was repulped in distilled water and made to a uniform slurry on the water bath; and under constant stirring, the desired quantity of alkali (mostly potassium carbonate dissolved in water) was added. The chief quantity of water was evaporated off on the water bath; after this the catalyst was put into a dry oven overnight at 110°C. and thereafter was pelleted and freed of all dust. The ferric catalysts are blackish-brown, rather solid, and mostly show a glassy fracture. The ferrous catalysts are voluminous and earth brown.

The ferric catalysts precipitated with sodium carbonate generally proved to be superior to the ferrous catalysts. The ferric catalysts obtained from technical iron over a ferric nitrate solution were used more frequently than the ferrous catalysts, and therefore we termed the ferric catalysts normal iron catalysts.

Two points had to be observed carefully in their preparation:

a. The preneutralization of the iron solution had to be carried out in the cold, because at high temperatures a precipitate of insoluble salts forms which makes it difficult to get reproducible results.

b. It is important that the iron precipitate be brought to a boil before filtering. This was found to increase the activity and the lifetime of the catalyst. Table 1 shows that plainly. In this table, catalysts prepared under different temperature conditions are compared with one another. We used the degree of contraction occurring during the synthesis as a measure of the catalyst activity (CO-H<sub>2</sub> mixture, 3:2, 15 atmospheres, 235°C.). Thus, comparative activity data are given for various lengths of operation. The highest possible contraction amounted to 60 percent if we assumed the conversion to liquid hydrocarbons to proceed according to the equation, 2CO + H<sub>2</sub> = CO<sub>2</sub> + CH<sub>4</sub>. In actual practice, the best yields are obtained at a contraction of 50 to 55 percent.

Table 1.—Influence of precipitation temperature upon activity of iron catalysts

Precipitating temperature, °C.	Raised to boiling after precipitation	Alkali content, percent	Operation, days				
			1	2	5	10	20
			Contraction, percent				
20	No	1	43	—	44	43	—
60	No	1	50	—	33	20	—
20	Short	1	50	—	48	51	—
20	Short	1/4	—	50	48	51	50
20	1 minute	1/4	55	55	48	48	50
20	5 minutes	1/4	—	56	—	47	48
100	1 minute	1/4	50	50	50	49	56

The table shows that the catalysts which were not brought to boil did not come up to full activity or that they lost their activity rapidly. The catalysts that were boiled for a short time and those that were boiled for 1 minute showed equally good results. Heating longer than 1 minute showed no advantage. The last experiment listed in the table, where the catalyst was precipitated at boiling temperature, corresponds to a normal iron catalyst.

#### Precipitation with Ammonia

At 60°C., a stream of ammonia gas was conducted into a ferric nitrate solution containing 100 grams of iron per liter. The flow velocity of the gaseous ammonia, in general, was regulated so that the precipitation was terminated after 20 minutes. The ammonia was absorbed quantitatively up to the end of the precipitation. An equal volume of boiling distilled water was added to the precipitate, then it was filtered and washed five times with hot, distilled water. The eventual alkalization was carried out as described earlier for the catalysts precipitated with sodium carbonate. The iron catalysts precipitated with ammonia are blackish-brown, solid, and show a glassy fracture.

## Addition of Kieselguhr

For a series of experiments, we used iron-kieselguhr catalysts. These are discussed in a special chapter. Kieselguhr generally was added after alkalization and during evaporation of the water from the catalyst over the water bath. It is practicable to suspend the kieselguhr in distilled water before adding to the catalyst. By doing this, one prevents a too rapid removal of water from the catalyst mass and hence the formation of non-homogeneous lumps.

## Pretreatment of Catalyst

The freshly precipitated and dried iron precipitate is entirely inactive as a catalyst for the conversion of CO and H<sub>2</sub> into hydrocarbons. In this it is similar to the unreduced cobalt catalyst. In order to activate the cobalt catalyst sufficiently to serve as a good agent in the hydrocarbon synthesis, it is usually only necessary to treat the unreduced oxides with hydrogen at 360°C. If the same treatment is given to the still inactive iron catalyst, no improvement in activity is observed. When the iron is treated with hydrogen at 300°-450°C., it is converted into a black substance which is ferromagnetic and has the composition, Fe<sub>3</sub>O<sub>4</sub>. This substance does not catalyze the reaction between CO and H<sub>2</sub>. However, if the catalyst is pretreated with CO, its activity may be increased enormously, and in that form, the catalyst is well suited for the synthesis. When CO is used for pretreatment, the catalyst is more or less reduced, depending on the temperatures at which the treatment is carried through; at the same time, carbides are deposited within the catalyst, which causes the granules to loosen. The treatment with CO or CO-rich gases in general is called induction of the catalyst.

## Induction with CO-H<sub>2</sub> Mixture during Synthesis

Mixed gas and atmospheric pressure.—If the precipitated iron catalysts are inducted with mixed gas (CO-H<sub>2</sub> = 1:2), this is best done at atmospheric pressure and at 235°-250°C. Under the conditions of the normal pressure synthesis, the contraction reaches a value of 30 percent after operating for 3 or 4 days at 235°C. with 4 liters of mixed gas per hour per 10 grams of iron. The time necessary to bring the catalyst to its full activity through the action of the synthesis gas corresponds to the induction period. At atmospheric pressure, one can obtain as much as 50 grams of liquid and solid hydrocarbons per cubic meter of gas at average contraction of 30 percent, and for a length of time of 3 to 4 weeks. The CO of the mixed gas is approximately all used up, but a large excess of hydrogen remains in the end-gas. (Fig. 1, curve 1, shows the observed contractions for this conversion.)

CO-rich gas and atmospheric pressure.—If the iron catalyst is allowed to work in presence of a CO-H<sub>2</sub> mixture of such a composition that it corresponds more closely to the ratio in which the two components combine with one another at atmospheric pressure, no improvement in the degree of conversion may be observed. At 235°C. the induction period lasted approximately 3 days. A maximum contraction of 31 percent was obtained (Fig. 1, curve 2). At 245°C. the highest contraction, namely 38 percent, was reached after 1 day of operation (curve 3), whereas at 255°C., after 1 day of operation, the maximum contraction obtained was only 33 percent (curve 4). After having reached the highest contractions, the conversion decreased very rapidly. This decrease shows that the catalyst had been damaged during the synthesis at atmospheric pressure with CO-rich gas.

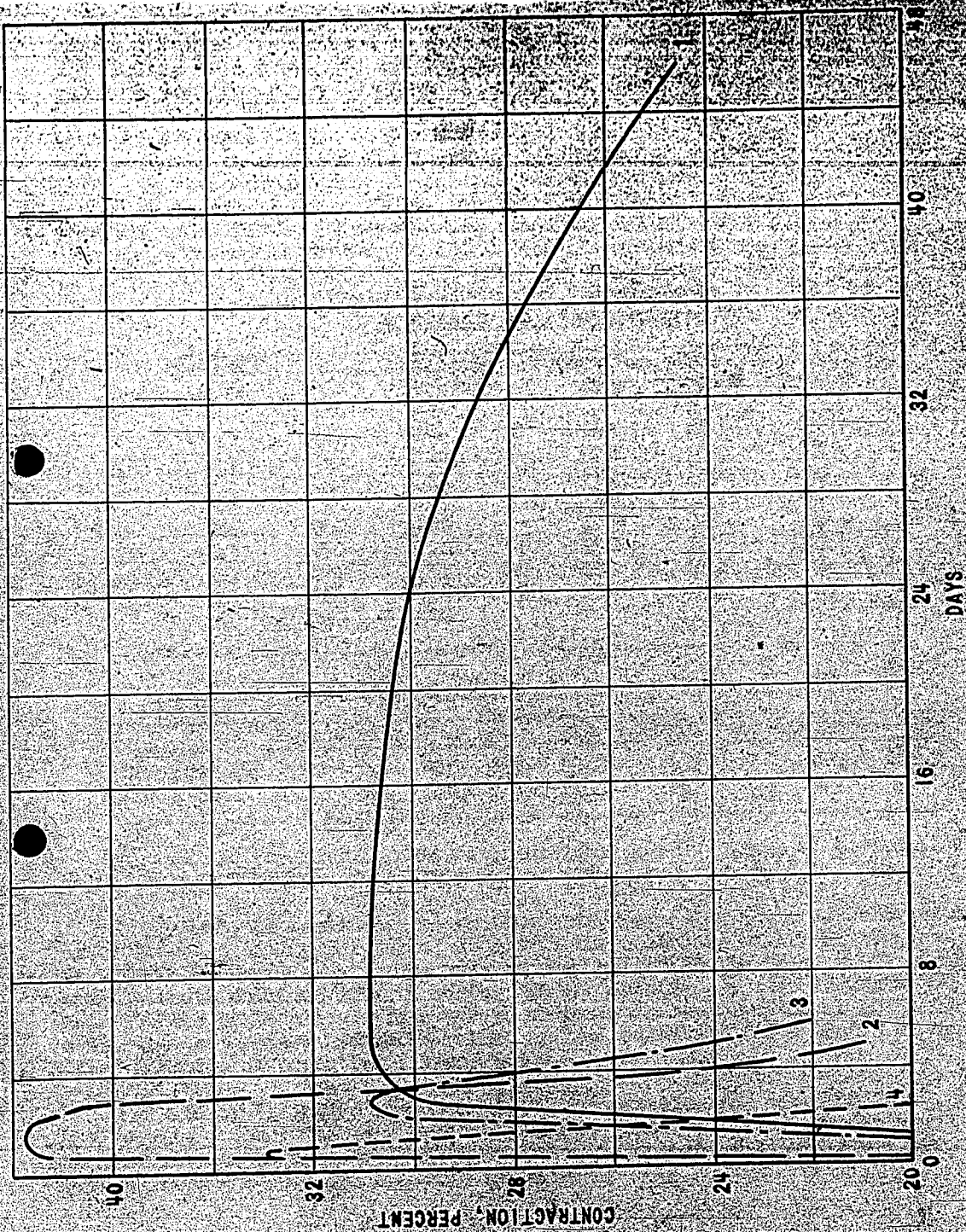


Figure 1. - Experiments at atmospheric pressure (decrease of contraction with duration of operation when various CO-H<sub>2</sub> mixtures are employed).

CO-rich gas and high pressure.—Table 2 shows a time test for which a normal catalyst was allowed to work on synthesis gas at 15 atmospheres pressure. The gas had an approximate composition of  $3CO + 2H_2$ . Four normal liters of this gas were used for every 10 grams of iron. At  $245^\circ C$ . the contraction was only 4 percent after 1 day; after 4 days it was 10 percent (as compared to 30 to 40 percent for the same period at 1 atmosphere). After the fourth day, the temperature was gradually raised, and the increase in contraction was observed through several days. On the eleventh day, 24-percent contraction was reached at  $260^\circ C$ . When the temperature was raised to  $270^\circ C$ ., at first no further increase in conversion occurred. At  $275^\circ C$ ., 37 percent was measured, and at  $280^\circ C$ ., 36 percent. Only when the temperature went up to  $290^\circ C$ . did the contraction go up to 50 percent.

Table 2.—Induction and synthesis  
at a pressure of 15 atmospheres

Operation, days	Temp., °C.	Contraction, percent	Operation, days	Temp., °C.	Contraction, Percent
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			

Yield determination for 3d month of operation at  $280^\circ C$ .

	CO <sub>2</sub>	Olefins	O <sub>2</sub>	CO	H <sub>2</sub>	Hydrocarbons	Carbon No.	N <sub>2</sub>
Starting gas	2.2	0.0	0.2	59.0	33.9	0.2	1.0	4.5
Final gas	55.5	3.4	.2	11.5	11.7	9.3	1.7	8.4

Yield per normal cubic meter of ideal gas: 3 grams of paraffin, 93 grams of liquid hydrocarbons, 32 grams of gasol hydrocarbons.

Next, we wanted to see whether this conversion could be obtained again after lowering the temperature. At  $268^\circ C$ . the contraction fell to 37 percent. At  $280^\circ C$ ., however, a better conversion was noticed in the third month of operation than was obtained after 1 month. In the meantime, a slow induction of the catalyst had taken place. In order to maintain the contraction at 40 to 50 percent, the temperature had to be raised in the fourth and fifth months of operation. After 5 months of operation, it was  $300^\circ C$ .

After the third month, a yield determination for a run at  $280^\circ C$ . gave the results shown in table 2. Three grams of solid paraffins were obtained per normal cubic meter of ideal gas (inert-free), 93 grams of liquid hydrocarbons, and 32 grams of gasol hydrocarbons ( $C_3 + C_4$ ).

When the catalyst was subjected to working conditions at higher pressures from the beginning, the process of induction was inhibited and the catalyst was incapable of working at low temperatures. On the other hand, at a pressure of 15 atmospheres with a CO-rich synthesis gas, the temperature of the reaction could be raised to 280°-290°C., without causing a rapid decrease in catalyst activity, such as was observed at 1 atmosphere pressure.

These results were obtained with iron catalysts which had been prepared in different ways (ferrous and ferric catalysts). Some of them contained copper, others did not.

### Induction with CO and H<sub>2</sub> Mixtures in a Process Separate from that of Synthesis

Induction at various pressures and synthesis at ordinary pressure.—It was attempted to find out whether an increase in activity of the catalyst could be reached by carrying the induction through independently of the synthesis. We wanted to find the optimum conditions for both the induction and the synthesis. In order to investigate what effect pressure had upon the synthesis at atmospheric pressure, the experiments listed in table 3 were undertaken. We inducted for 20 hours at 255°C. with 4 liters of normal gas per hour per 10 grams of iron. The gas had a composition of 3CO + 2H<sub>2</sub>. Then we used this catalyst in a synthesis with a gas of composition 1CO + 2H<sub>2</sub>. Four liters per hour per 10 grams of iron were employed at atmospheric pressure. The extent of conversion during this reaction was measured after 1-1/2 hours at 255°C.

Table 3.—Influence of induction pressure upon  
synthesis at atmospheric pressure

Induction pressure, atmospheres	8.5	4.7	2.9	2.0	1.5	1	0.5	0.1
Synthesis, contraction percent	5	12	12	28	25	28	32	30

The results showed that high pressures impede the induction. When the induction pressures were below 1 atmosphere, no essential improvement could be noticed during the synthesis at atmospheric pressure.

Induction at ordinary pressure and synthesis at high pressure.—For this experiment we worked with an iron catalyst which was precipitated with sodium carbonate and another iron catalyst precipitated with ammonia. Both catalysts were described earlier and contained 1/4 percent potassium carbonate. (During the experiment it was intended to study the influence of induction upon activity of the catalyst. The synthesis conditions under which the catalysts were examined are discussed in the section on "Synthesis.")

The normal iron catalyst, which was precipitated with soda was allowed to work on the CO-rich gas at a rate of 4 liters per hour per 10 grams of catalyst at 1 atmosphere and 245°C. The experiment lasted 21-1/2 hours. This gas yielded a contraction of 33 percent at the end of the pretreatment. Then we switched to 15 atmospheres and 235°C. Immediately, the contraction went up to 50 percent; however, on the second day, it was only 33 percent, and on the third day, 30 percent. The temperature of 235°C. proved too low to maintain a contraction of 50 percent with this catalyst. Next, we pretreated the same iron catalyst with mixed gas at atmospheric pressure and 235°C. The contraction at the end of the pretreatment was 30 percent. Then we switched to 15 atmospheres and



a CO-rich gas. At 235°C., 43-percent contraction was obtained, and 47-percent at 250°C. To maintain the contraction at 45 to 50 percent, the temperature had to be raised to 257°C. within 14 days.

The iron catalyst, which was precipitated with ammonia, was inducted with mixed gas at atmospheric pressure and 245°C. The contraction reached 31.5 percent after 5 days of operation. Then we switched to CO-rich synthesis gas ( $3CO + 2H_2$ ) and operated at 15 atmospheres pressure. Table 4 shows the contraction after some time of operation and the composition of the synthesis gas and of a product gas obtained at 250°C. (4th day).

Table 4.—Synthesis at 15 atmospheres with iron catalyst precipitated with ammonia and inducted at 1 atmosphere

Operation, days	Temperature, °C.	Contraction, percent
1	245	59
2	245	48
4	250	53
5	250	49
10	252	46
20	256	51
50	255	51
100	265	55

	CO <sub>2</sub>	Olefins	O <sub>2</sub>	CO	H <sub>2</sub>	Hydrocarbons	Carbon No.	N <sub>2</sub>
Starting gas	2.7	0.0	0.0	55.8	37.3	0.0	—	4.2
Final gas	53.8	3.4	.0	11.4	16.2	6.2	2.0	9.0

This experiment gave a contraction of 59 percent on the first day of operation and at 245°C. To maintain the highest possible yields and a contraction of 50 percent or above, the temperature was gradually raised. This degree of conversion could be maintained for more than 3 months. After 100 days of operation, the temperature had risen to 265°C.

This experiment showed that the reaction temperature could be lowered by 30° to 40° when the catalyst was inducted at atmospheric pressure, as compared to the temperature of the reaction when the induction was carried out at 15 atmospheres. The enhanced activity which the catalyst acquired during induction at 1 atmosphere remained intact for the duration of the experiment.

Induction at reduced pressure and various temperatures, synthesis at high pressure.—Following is the description of an experiment during which normal iron catalysts were inducted with CO-rich gas ( $3CO + 2H_2$ ) at 1/10 atmosphere and various temperatures. The induction lasted for 25 hours and was carried out between 255° to 355°C. The activity of the catalyst was tested with the synthesis gas of composition CO-H<sub>2</sub> = 3:2. The pressure during the synthesis was 15 atmospheres, and the temperature 235°C. Figure 2 shows the decrease of contraction with time at a constant synthesis temperature of 235°C. (4 liters of gas per 10 grams of iron per hour). When the induction was carried out at 255°C., the contraction dropped below 50 percent; on the third day of the synthesis, as the induction temperature was raised, an increase in the catalyst lifetime was observed.

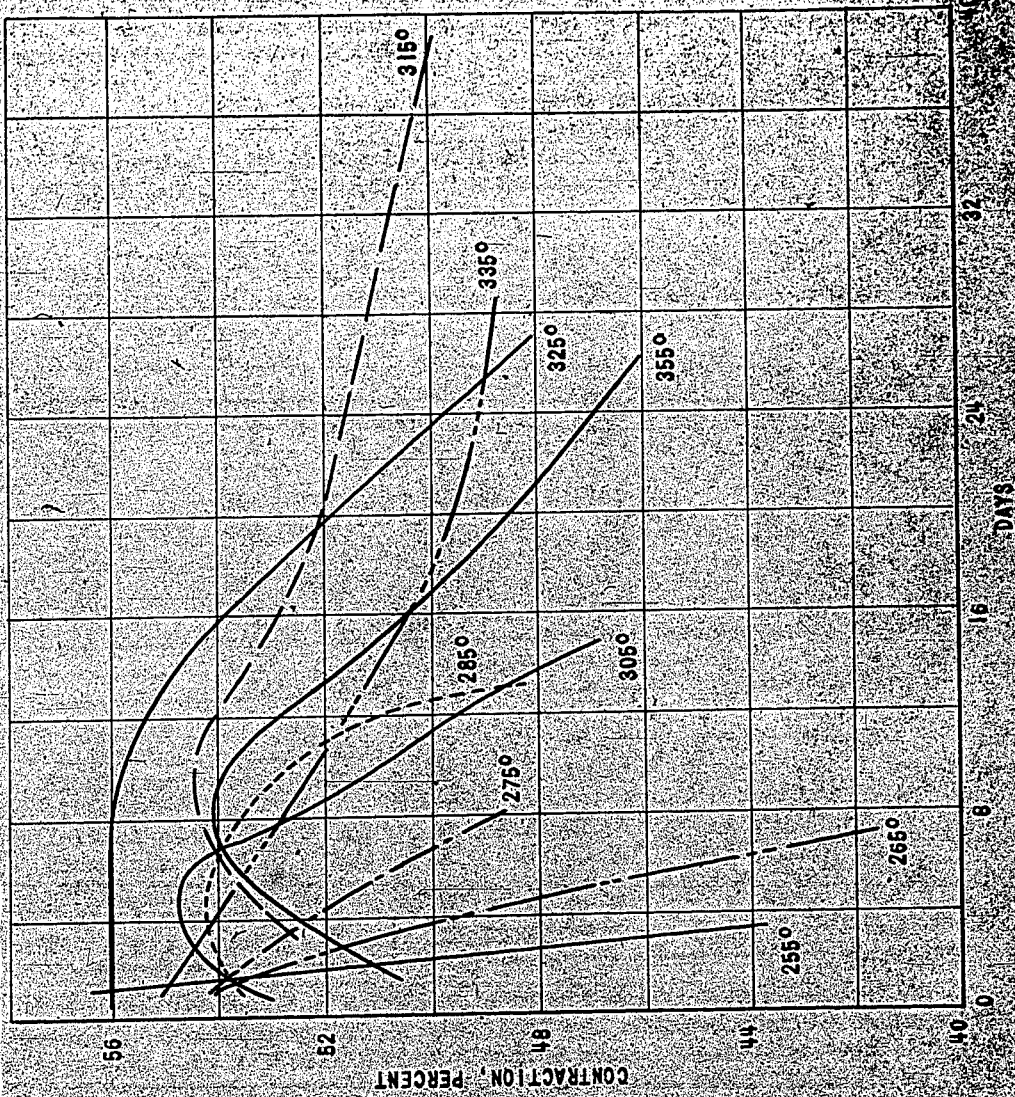


Figure 2. - Influence of Induction temperature of the catalyst upon the course of the synthesis (decrease of contraction with time of operation at 15 atmosphere and 2450 C.). Induction was carried out with a CO-rich synthesis gas at 10 atmosphere.

When the induction temperature was 315°C., the limit of 50-percent contraction was passed only after more than a month of operation. When the induction was carried out at higher temperatures, the lifetime of the iron catalyst decreased.

Table 5 shows an example where a catalyst was inducted at 325°C. and 1/10 atmosphere. The table gives temperatures and contractions for 200 consecutive days of operation. Besides, it also gives the initial and final gas analysis on the 10th, 100th, and 200th days of operation. The synthesis was continued at 235°C. as long as the contraction did not fall below 50 percent; as soon as it did, the temperature was slowly raised and only raised enough to assure a maximum contraction. Only after operating for 2 months did the temperature go above 240°C. and after 3 months, above 250°C.

**Table 5.—Results of an iron catalyst inducted at 325°C. with synthesis gas**

Induction: CO-rich gas, 1/10 atmosphere, 4 liters per 10 grams of iron per hour, 25 hours. Synthesis: CO-rich gas, 15 atmospheres, 4 liters per 10 grams of iron per hour, temperature, 235°- up

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

	CO <sub>2</sub>	Olefins	C <sub>2</sub>	CO	H <sub>2</sub>	Hydrocarbons	Carbon No.	N <sub>2</sub>
<u>10th day</u>								
Initial gas	2.4	0.0	0.1	52.5	37.6	0.0	—	6.3
Final gas	61.8	2.8	.0	1.6	12.2	7.2	1.9	14.4
<u>100th day</u>								
Initial gas	2.0	.0	.2	53.6	37.0	.3	1.0	5.9
Final gas	53.0	2.4	.1	8.1	15.9	8.3	1.9	12.2
<u>200th day</u>								
Initial gas	2.3	.0	.2	57.0	31.3	.2	1.0	7.6
Final gas	48.3	2.8	.1	15.4	13.4	5.6	1.9	14.4

The contraction decreased during the 200 days of operation from 56 to 47 percent. The composition of the final gas changed sharply during the first few days but only a little during the following longer-time operation. One hundred and forty grams of solid and liquid and gasol hydrocarbons were obtained at the end of the second week of operation. Of this, 31 grams constituted gasol hydrocarbons.

From tables 2 and 4, it may be observed that a contraction of 50 percent results from a catalyst which was inducted at 1/10 atmosphere and 325°C., when the reaction temperature is 235°C. When the catalyst was inducted at 1 atmosphere and 245°C., a 50-percent contraction resulted at 245° to 255°C. For a catalyst inducted at 15 atmospheres pressure, a temperature of 280° to 290°C. was required to produce a 50-percent contraction.

Influence of the induction pressure upon synthesis at high pressure (induction temperature, 325°C.).—After we had found that, for an induction pressure of 1/10 atmosphere, the optimum induction temperature was 325°, we once more investigated the effect of pressure upon the induction at that temperature. Table 6 shows these results. The induction was carried out in each case for 25 hours with a CO-rich synthesis gas, and the catalyst was tested at 235°C. with a gas of composition  $3CO + 2H_2$  at 15 atmospheres.

Table 6.—Influence of induction pressure upon course of synthesis at 235°C. (at induction temperature of 325°C. and use of synthesis gas for induction)

Pressure, atmospheres	Operation, days					
	1	2	4	10	20	30
	Contraction, percent					
15	30	24	15	—	—	—
1	56	54	55	50	49	50
0.1	56	56	56	56	52	48

The table shows that the catalyst possessed only slight activity when inducted at 15 atmospheres and 325°C. Whatever little activity it had, it lost rapidly. When the induction was carried out either at 1 or at 1/10 atmosphere and 325°C., the same degree of conversion was obtained for the first month of the synthesis.

#### Induction with CO

It was recognized that hydrogen alone cannot be used for the induction of iron catalysts. When CO-H<sub>2</sub> mixtures are employed (and especially is this true for temperatures of 300°C. and above), the danger exists that during the induction, products are formed that will block the active centers of the catalyst. For these reasons, we have experimented with hydrogen-free CO.

Influence of induction temperature at 1/10 atmosphere pressure.—In order to find the optimum induction temperature, a series of experiments was undertaken which were analogous to that when synthesis gas was used for the induction (compare Fig. 2). The induction was carried out for 25 hours at 1/10 atmosphere and different temperatures, using CO. Four liters per hour of CO referred to 1 atmosphere pressure were used for every 10 grams of iron. The synthesis which followed the induction was carried out with a gas of composition  $3CO + 2H_2$  at a temperature of 235°C., and pressure of 15 atmospheres. The flow velocity of the synthesis gas was 4 liters per 10 grams of iron per hour. Figure 3 shows the behavior of the catalysts which were inducted at 255°C., 305°C., 325°C., 245°C., and 400°C., using CO. The catalyst which had been inducted at 325°C. proved to be the best one.

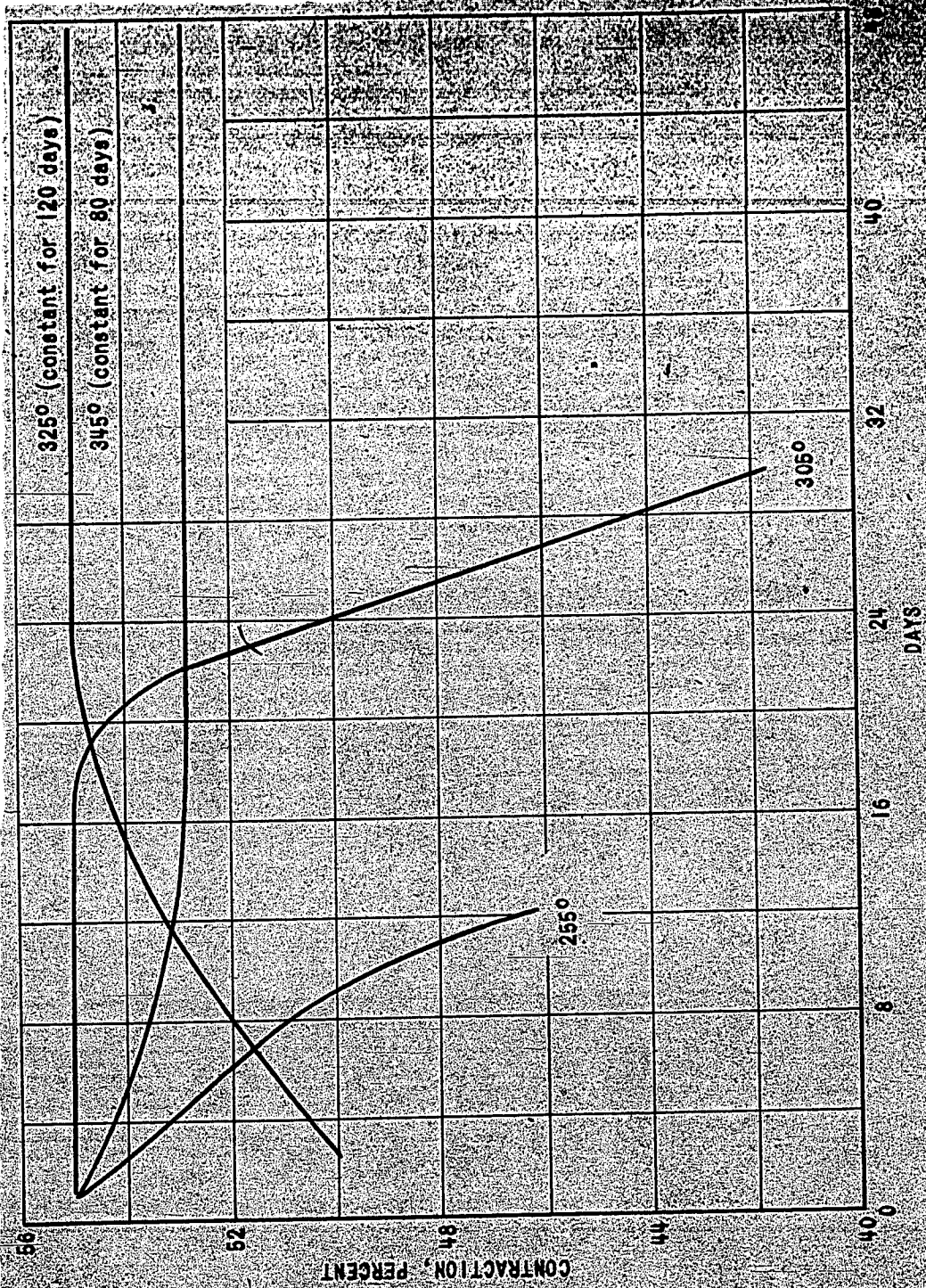


Figure 3. - Influence of the induction temperature upon the course of the synthesis after an induction with CO at 10 atmosphere.

During the first 20 days of the synthesis, the conversion gradually increased from 50 to 55 percent contraction. Up to the end of the fourth month and at 235°C., a constant conversion corresponding to a 55-percent contraction could be maintained. The catalyst, which was inducted at 345°C., caused a contraction of about 50 percent for 80 days. Lower induction temperatures, such as 255° and 305°C., and higher temperatures, such as 400°C., showed less favorable results.

A comparison of Figs. 2 and 3 shows that the catalyst which had been inducted with pure CO instead of CO and H<sub>2</sub> mixtures showed a longer lifetime. This can be said to hold for all temperatures. When the catalyst was pretreated with pure CO, the contraction decreased below 50 percent on the 12th day when the induction temperature was 255°C. When the catalyst was pretreated with synthesis gas at 305°C., the decrease in contraction below 50 percent occurred on the 12th day, as compared to pure CO, for which the drop below 50 percent took place after the 25th day. Similarly, for an induction temperature of 325°C., the decrease in contraction below 50 percent occurred on the 24th day when synthesis gas was used; and when pure CO was employed instead, under the same conditions, the same drop occurred at the end of 120 days. When the catalyst, inducted at 325°C. was used, the synthesis temperature had to be raised after 130 days of operation. When another catalyst inducted at 345°C. was employed, the temperature had to be increased after only 80 days. Some operating data of these experiments are presented in tables 1, 7, and 8.

Table 7.—Results of experiments with an iron catalyst inducted at 325°C. with CO

Induction: CO, 1/10 atmosphere, 4 liters per 10 grams of iron per hour, 25 hours. Synthesis: CO-rich gas, 15 atmospheres, 4 liters per 10 grams of iron; temperature, 235°C. and up

Operation, days	Temperature, °C.	Contraction, percent	Operation, days	Temperature, °C.	Contraction, percent
1	235	47	140	245	48
2	235	50	160	250	49
5	235	50	180	251	50
10	235	51	200	250	44
20	235	55	250	265	50
50	235	54	300	263	43
100	235	53	350	270	40
130	235	47			

	CO <sub>2</sub>	Olefins	O <sub>2</sub>	CO	H <sub>2</sub>	Hydrocarbons	Carbon No.	N <sub>2</sub>
<u>40th day</u>								
Initial gas	2.0	0.0	0.0	53.4	39.8	0.0	—	4.8
Final gas	57.0	2.6	.1	6.3	14.6	8.9	2.0	10.5
<u>70th day</u>								
Initial gas	2.5	.0	.2	54.7	37.9	.2	1.0	4.5
Final gas	64.0	2.9	.0	2.5	9.5	11.3	1.9	9.8
<u>100th day</u>								
Initial gas	3.5	.0	.0	54.4	37.1	.2	1.0	4.8
Final gas	61.2	3.3	.1	5.2	11.2	9.0	1.9	10.0
<u>300th day</u>								
Initial gas	2.0	.0	.2	56.6	34.8	.2	1.0	6.2
Final gas	48.9	2.9	.2	15.9	10.8	8.5	1.9	12.2

Yield per Nm<sup>3</sup> of ideal gas at the 40th day: 180 grams liquid and solid hydrocarbons, 44 grams of gasol hydrocarbons.

Yield per Nm<sup>3</sup> of ideal gas at the 70th day: 105 grams liquid and solid hydrocarbons, 45 grams of gasol hydrocarbons.

Yield per Nm<sup>3</sup> of ideal gas at the 100th day: 110 grams liquid and solid hydrocarbons, 47 grams of gasol hydrocarbons.

Yield per Nm<sup>3</sup> of ideal gas at the 300th day: 110 grams liquid and solid hydrocarbons, gasol hydrocarbons not determined.

**Table 8.—Results of experiments conducted with iron catalyst inducted with CO at 345°C.**

Induction: CO, 1/10 atmosphere, 4 liters per 10 grams of iron per hour, 24 hours. Synthesis: CO-rich gas, 15 atmospheres, 4 liters per 10 grams of iron per hour; temperature, 235°C.— up

Operation, days	Temperature, °C.	Contraction, percent
1	235	55
5	235	50
10	235	51
20	235	51
40	235	53
60	235	52
80	235	49
100	243	54
115	250	49

	CO <sub>2</sub>	Olefins	O <sub>2</sub>	CO	H <sub>2</sub>	Hydrocarbons	Carbon No.	N <sub>2</sub>
<u>50th day</u>								
Initial gas	2.2	0.0	0.0	53.4	39.6	0.0	—	4.8
Final gas	57.7	2.8	.2	6.1	13.8	8.9	1.9	10.5

The experiment with the iron catalysts inducted at 325°C. lasted through 1 year. This catalyst gave a constant conversion for 4 months at 235°C.; there-after, in order to maintain this conversion, the temperature had to be raised slowly up to 270°C. The yields remained approximately the same for the whole time of operation. They amounted to 105 to 110 grams of liquid and solid hydrocarbons and 44 to 47 grams of gasol hydrocarbons per normal cubic meter of gas.

Up to the second month of operation at 235°C., the catalyst which was inducted at 345°C. gave a yield of 110 grams of liquid and solid hydrocarbons and 41 grams of gasol hydrocarbons per normal cubic meter of ideal gas. Near the end of the fourth month, the temperature was 250°C., and the contraction was still approximately 50 percent.

The end-gas analyses in these experiments where a catalyst was used which was inducted with CO at 1/10 atmosphere and 325° to 245°C. showed no essential changes during many months of operation. This is in accord with the constant contractions observed.

Influence of induction pressure.—A series of pressure experiments was carried out with CO which was analogous to that run earlier with synthesis gas (see table 6). Table 9 shows contraction for various lengths of time of the synthesis. The induction pressures of the catalysts were 15 atmospheres, 1 atmosphere, and 1/10-atmosphere. The induction time again was 25 hours (4 liters per hour) and the induction temperature 325°C.

During the first days of operation, all three catalysts gave good conversions. The activity of the catalyst which was inducted at 15 atmospheres, however, decreased during the fourth week, whereas the catalyst inducted at 1/10 atmosphere remained intact through 3 months. (During the induction at high pressure, comparatively large quantities of carbon were deposited on the catalyst. Quantitative data on this are given elsewhere.)

Table 9.—Influence of induction pressure  
(at induction temperature of 325°C. and use of CO)  
upon course of synthesis at 235°C.

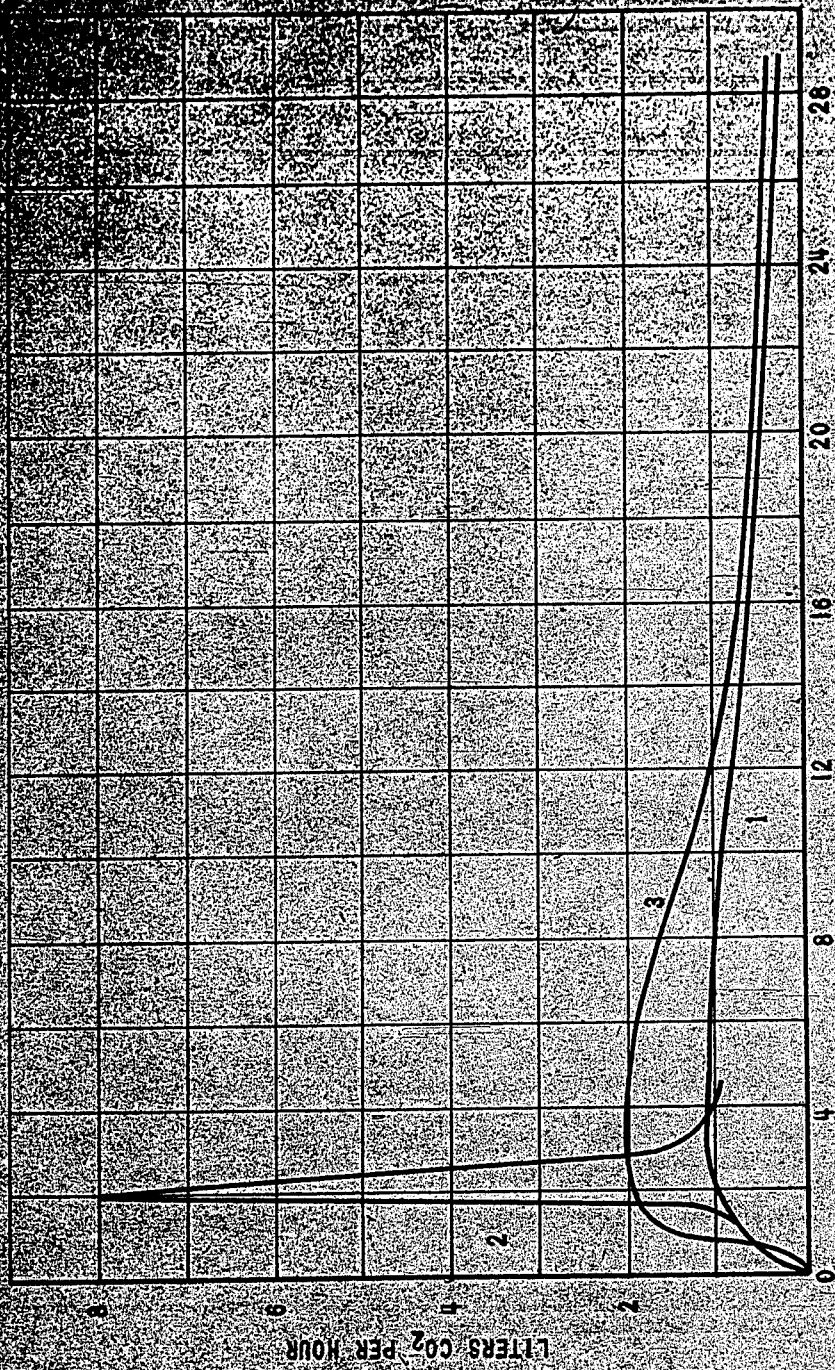
Pressure, atmospheres	Operation, days					
	1	10	20	25	30	60
	Contraction, percent					
15	58	52	48	40	—	—
1	58	57	53	—	—	—
0.1	—	51	55	54	56	54

A comparison of the results of this investigation with the results in table 6 showed that the catalyst acquired higher activity when it was activated at high pressures with CO instead of with CO-H<sub>2</sub> mixtures.

Induction time.—During induction at reduced pressure, approximately 100 liters of CO per 10 grams of iron were led over the catalyst. At the required rapid rates of gas feed, only a small part was used. The larger part of the unused gas could be used again for induction, after the CO<sub>2</sub> which had formed was removed.

The induction process may be followed closely by checking the CO<sub>2</sub> formation. Curves 1 and 2 in Fig. 4, represent the CO<sub>2</sub> quantities formed at 1/10 atmosphere and 325°C. per hour for every 10 grams of iron. In the case of curve 1, the temperature of 325°C. was reached after 2-1/2 hours. In curve 2 this same temperature was reached after 1-1/2 hours. During this starting period the flow velocity of the CO was 4 liters per hour in both cases. During the experiment represented by curve 1, this same flow velocity was maintained all through. The flow velocity of the experiment represented by curve 2 was 40 liters per hour. With 4 liters per hour of CO in the beginning, 1 liter of CO<sub>2</sub> was formed per hour. The CO<sub>2</sub> formation gradually decreased. After approximately 25 hours of operation and after a temperature of 325°C. was reached, the CO<sub>2</sub> formation approached a constant minimum value of 0.2 to 0.3 liter per hour. When 40 liters per hour of CO were used, the CO<sub>2</sub> maximum value amounted to 8 liters per hour, and after operating for 2-1/2 hours, the constant amount of approximately 1 liter per hour





DURATION OF CATALYST INDUCTION - HOURS

Figure 4. - CO<sub>2</sub> formation during the induction process.

was obtained. In both cases, it was necessary to pass approximately 100 liters of CO through the apparatus to obtain a constant minimum quantity of CO<sub>2</sub>. During experiment 1, altogether 16 liters of CO<sub>2</sub> were formed; during experiment 2, only 11 liters. The CO<sub>2</sub> is formed by the reduction of CO and the formation of combined and free carbon, according to the equation,  $2CO = C + CO_2$ .

For the flow velocity of experiment 1, more carbon was deposited than during experiment 2.

Four experiments are listed in table 10. Experiments 1a and 1b belong to the CO<sub>2</sub> curve 1 of Fig. 4; experiments 2a and 2b belong to curve 2. In the case of experiment 1a, formation lasted for 25 hours and was carried out with 4 liters per hour at 325°C. In the case of experiment 1b, the induction lasted 2-1/2 hours; for experiment 2a, 40 liters of CO per hour were used for 2-1/2 hours at 325°C. Experiment 2b lasted 20 minutes. The points at which the induction was terminated and the synthesis started are marked by crosses on Fig. 4. The following synthesis was carried out in all cases at 15 atmospheres and 235°C. As table 10 shows, after 100 liters of CO had been passed over the catalyst during experiments 1a and 2a, a good and lasting activity of the catalyst had been created. When the induction was interrupted before the CO<sub>2</sub> formation (experiments 1b and 2b) declined, catalysts were obtained which gave good initial conversion, but which lost their activity rapidly.

Table 10.—Influence of flow velocities of CO upon induction time and course of synthesis

Experiment	1a	1b	2a	2b
CO, liters per hour	4	4	40	40
Induction time, hours	25	2.5	2.5	0.3
Total quantity of CO used, liters	100	10	100	12
<u>Contraction for synthesis, percent</u>				
1st day	47	55	53	53
2d day	50	50	51	30
5th day	50	30	50	—
10th day	51	—	49	—
20th day	55	—	51	—
30th day	54	—	54	—

In all of the experiments (1a, 1b, 2a, and 2b) the flow velocities of the gases, at a pressure of 1/10 atmosphere, were sufficiently large to remove the CO<sub>2</sub> from the catalyst surface. The catalyst activity obtained through experiment 2a was equal to that of 1a, in spite of the fact that the contact time between the gases and the catalyst was greatly reduced and the CO<sub>2</sub> formation in the case of 2a was much lower than in the case of 1a (less carbon was deposited in the catalyst during experiment 2a). This constitutes an advantage.

For comparison, Fig. 4 also gives the corresponding CO<sub>2</sub> quantities for an induction at 1 atmosphere, curve 3 (see also the experimental results in table 9). A CO flow velocity of 4 liters per hour was used (analogous curve 1).

Curve 3 shows that during induction more CO<sub>2</sub> was formed at atmospheric pressure than at reduced pressure; this means that more carbon was also deposited.

Mixture of CO with other gases.—Mixtures of CO and H<sub>2</sub> have already been discussed. In general, they gave more unfavorable results at ordinary or high pressures than pure CO. This may be explained by assuming that synthesis products formed and blocked the catalyst surface.

The presence of CO<sub>2</sub> or water vapor impeded reduction and therefore should be avoided if possible.

The presence of small quantities of inert gases, especially of nitrogen, cannot be avoided if the induction is carried out on a technical scale. Large quantities of inert gases impede the process of induction. We have found that it is favorable to work at 1/10 atmosphere pressure, using CO. It is not permissible to use a gas mixture exhibiting 1/10 atmosphere partial pressure of CO and 9/10 atmosphere partial pressure of nitrogen. When induction was carried out under those conditions over a length of time of 25 hours with 40 liters of CO-nitrogen mixtures per hour (total flow 100 liters of CO), a catalyst was produced which gave only 37 percent contraction at 235°C. When we worked with a CO-nitrogen mixture of a ratio 1:3, an induction carried out for 10 hours with 40 liters per hour of gas yielded an iron catalyst which gave a contraction of 50 percent through 3 weeks of operation at 235°C. and 15 atmospheres.

#### Theory of Induction Process

It has been shown that to produce an active iron catalyst, pretreatment of the catalyst with CO or CO-rich gases is required at temperatures around 250°-350°C. Furthermore, we have recognized that this process which we call induction, should be carried out at lower pressures than the synthesis which is to follow.

We found that induction with CO and H<sub>2</sub> will give a lower activity than with CO alone. Our explanation for this phenomenon is that during induction with CO and H<sub>2</sub>, liquid and solid hydrocarbons form on the catalyst surface and prevent the activating gases from coming in contact with the catalyst.

Induction with H<sub>2</sub> has not been possible.

The action of CO upon the iron catalyst is fundamentally different from the action of H<sub>2</sub>. First of all, the reduction into iron oxides proceeds differently with CO than with H<sub>2</sub>; secondly, by using CO, the catalyst structure is loosened because carbon is deposited within the lattice; and thirdly, carbides are formed when CO is used.

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

The primary process during the reduction is the formation of ferromagnetic Fe<sub>3</sub>O<sub>4</sub>, which occurs during reduction with CO as well as with H<sub>2</sub>, and it may also be obtained by precipitating a mixture of ferric and ferrous salts with alkalis and following by dehydrogenation. However, it has no catalytic action in so far as the middle-pressure synthesis is concerned.

The equilibrium conditions for the system iron, carbon, and oxygen depend on temperature, gas pressure, and the ratio of CO to CO<sub>2</sub> contained in the gas. Figure 5a refers to atmospheric pressure. This corresponds to results of investigations by R. Schenck (12). The dotted curves were obtained by U. Hofmann and E. Groll (13) through calculations. Figure 5 shows the equilibrium conditions for 1/10 atmosphere. The Fe<sub>3</sub>O<sub>4</sub>-Fe<sub>3</sub>C curve was calculated by taking into consideration the pressure as a variable. The other curves were compiled through data by Schenck.

One can see from Fig. 5 that, at temperatures below 550° to 560°C., no FeO is stable (Schenck termed this "wüstite", because it always contains Fe<sub>3</sub>O<sub>4</sub>). At low temperatures, therefore, the reduction of Fe<sub>3</sub>O<sub>4</sub> may be accomplished without going through the FeO phase.

The metallic phase is only stable above temperatures of 550° to 600°C. (according to Schenck, it decomposes into oxoferrite containing oxygen and oxo-austenite containing oxygen and carbides). It is assumed, therefore, that at lower temperatures the carbide is formed by the direct action of CO upon Fe<sub>3</sub>O<sub>4</sub>. This is believed to take place over unstable oxygen deficient in the immediate compounds. Hofmann and Groll made X-ray analyses of the bodies which one obtains from CO and iron. Below 655°C., they were only able to detect small quantities of free iron. We have found that the reduction of the higher to the lower oxides of iron is independent of pressure. It depends only on the ratio of CO to CO<sub>2</sub> and the temperature. Raising the pressure favors the formation of carbides and carbon.

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

If it is desired to come to equilibrium for the interaction of pure CO upon metallic iron, carbide has to be formed first. At the same time, the CO<sub>2</sub> obtained exerts oxidizing influence upon the iron. It seems plausible that, for the induction of an iron catalyst, low pressures and high CO velocities are advantageous, since these factors lower the CO<sub>2</sub> partial pressure and effect a rapid removal of the CO<sub>2</sub> from the catalyst.

In both figures the cementite (Fe<sub>3</sub>C) has been recorded as carbides only, not, however, any higher carbides. Its existence was first assumed by Hilpert in 1915 (14). Fischer and his coworkers have repeatedly mentioned the formation of higher carbides as intermediate products during the benzine synthesis. Fischer and Bahr (15) also described such an iron carbide. Gluid and his coworkers (16) gave the formula Fe<sub>2</sub>C to this iron carbide. The X-ray analyses of Hofmann and Groll have ascertained that, at temperatures of over 400°C., this carbide becomes unstable because it splits off carbon. It is assumed that this decomposition occurs under the formation of cementite and free carbon.

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

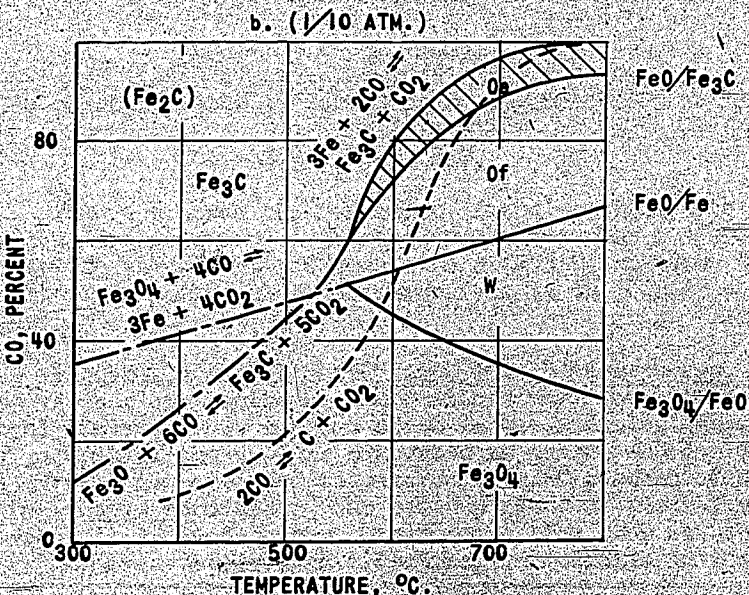
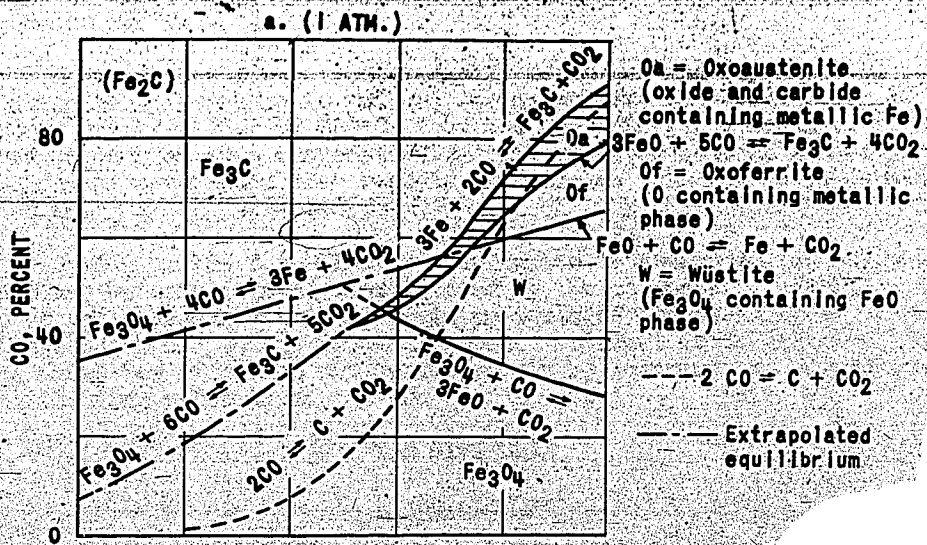


Figure 5. - Equilibrium conditions for the system Fe-C-O.

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

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

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

## THE SYNTHESIS

### Synthesis Gas

The optimum synthesis gas composition corresponds to the ratio in which the reaction components CO and H<sub>2</sub> are used up. The only limitation is that the catalyst used for such theoretical mixture possesses a sufficiently high lifetime. The conversion on iron proceeds according to the general equation:



As a side reaction water is formed according to:



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

Figures 7a and 7b show, for 0 and 15 atmospheres, the portion of CO-O which at various synthesis-gas compositions was converted to water and CO<sub>2</sub>. At an initial content of 30 percent of CO in the starting gas and at atmospheric pressure, 7 percent of the CO-O is converted to water, whereas at 15 atmospheres 25 percent of CO-O is converted to water. With 60 percent of CO in the starting gas under atmospheric conditions, the process proceeds virtually according to equation (1), whereas at 15 atmospheres, 4 percent of the CO-O is used up for water formation. In addition to elevated pressures, an increase in the H<sub>2</sub> content in the synthesis gas favors the water formation also.

Figures 8a and 8b show the influence of the synthesis-gas composition upon the yields of solid and liquid and gasol hydrocarbons. The dotted straight lines show the calculated yields by assuming the reaction to proceed according to equation (1) over CO<sub>2</sub> formation. The dotted pointed curves show the corresponding results according to equation (2) with concurrent water formation. The

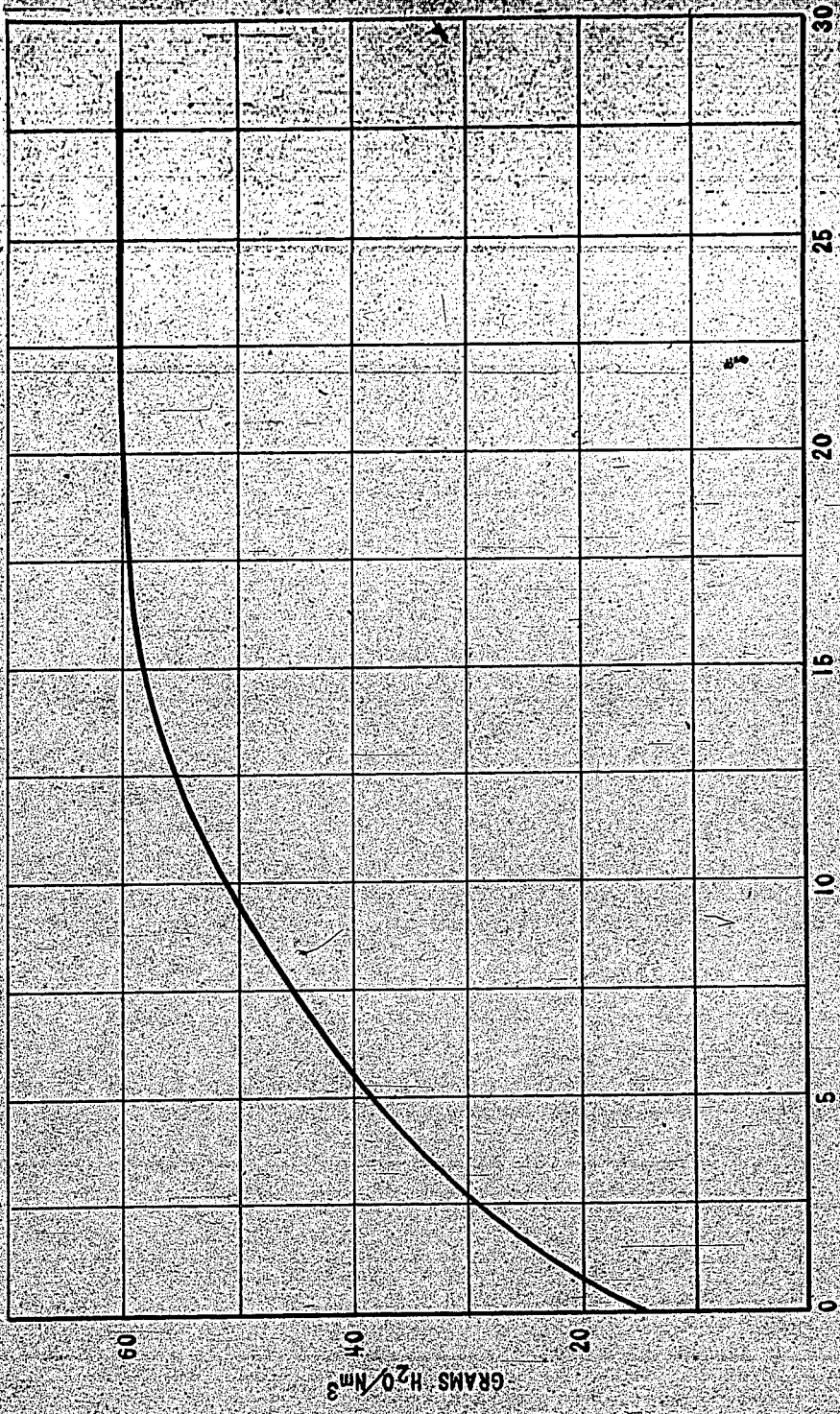


Figure 6. - Water formation at various pressures (synthesis gas composition CO:H<sub>2</sub> = 1).

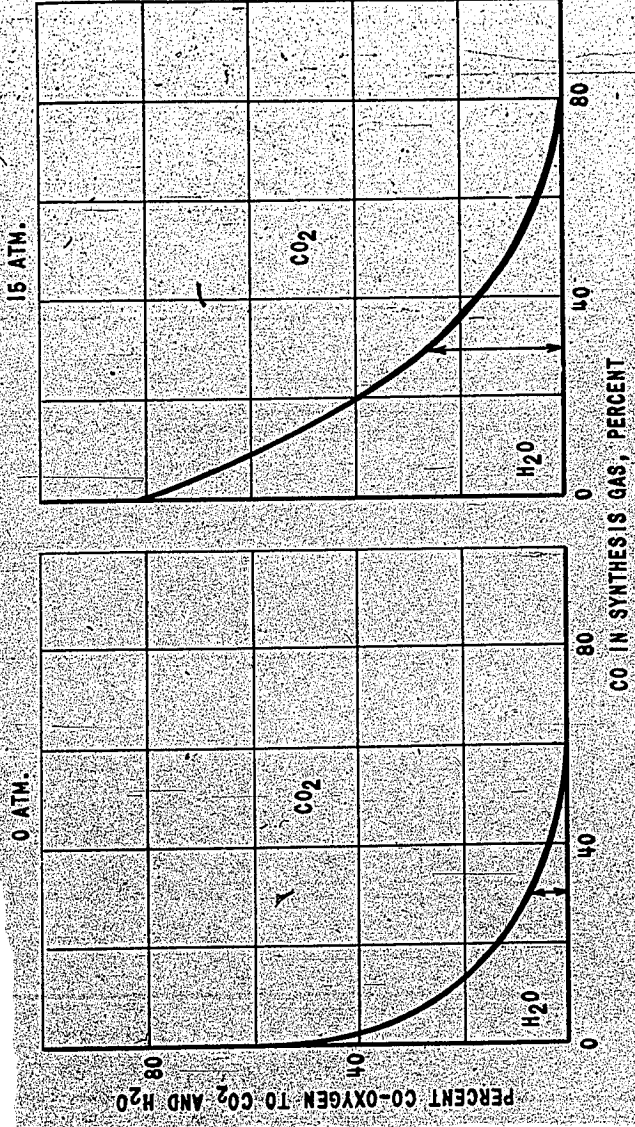


Figure 7. - Conversion of the CO-oxygen to CO<sub>2</sub> and H<sub>2</sub>O, respectively, for various synthesis gas compositions at 0 and 15 atmospheres pressure.



15 ATM.

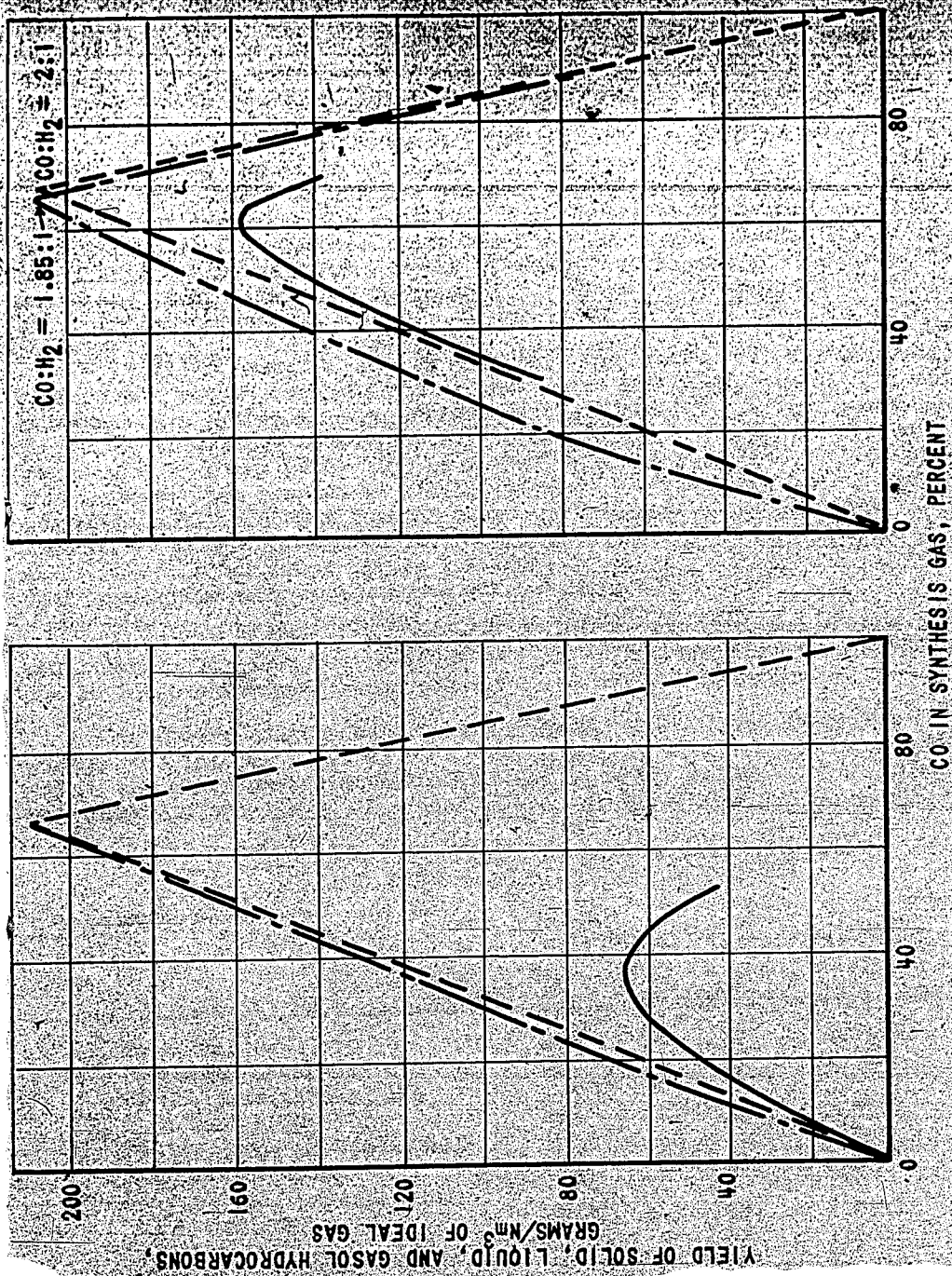


Figure 8. - Influence of synthesis gas composition upon the yields.

solid curves show an actually obtained yield (4 weeks average). Theoretically it should be possible to obtain 208 grams of hydrocarbons, with or without water formation, for every normal cubic meter of synthesis gas. At atmospheric pressure, taking into consideration only the formation of  $\text{CO}_2$ , the theoretical gas composition should be  $2\text{CO} + 1\text{H}_2$ ; at 15 atmospheres, it should be  $1.85\text{CO} + 1\text{H}_2$ .

Fundamental differences exist between the synthesis carried out at atmospheric pressure and at 15 atmospheres. One cannot work at atmospheric pressure with the theoretical  $\text{CO}$  mixture because, under these conditions, the activity of the catalyst decreases too rapidly. This is not the case for the middle-pressure synthesis. At 1 atmosphere synthesis pressure, a gas of composition  $1\text{CO} + 2\text{H}_2$  behaved best. For the first 4 weeks of operation it gave an average of 60 grams of solid and liquid and gasol hydrocarbons. These yields decreased rapidly during the fifth and sixth weeks.

It is possible to work well for many months with the theoretical gas mixture and obtain complete conversions. For the lower saturated homologs of methane, more hydrogen is required than equations (1) and (2) demand. Since the formation of methane is not entirely suppressed,  $\text{CO}$  and  $\text{H}_2$  are not consumed in the ratio of 1.85:1 but rather in the ratio of 1.6-1.8:1. Finally, it appears to be advantageous with respect to the lifetime of the catalyst, as the end-gas of the synthesis still contains a small excess of hydrogen, that the ideal synthesis gas contain 60 percent  $\text{CO}$  and 40 percent  $\text{H}_2$  ( $\text{CO}-\text{H}_2 = 1.5:1$ ). With such a gas mixture, it is possible to obtain 150 to 160 grams of solids, liquids, and gasol per normal cubic meter for many months, when iron catalysts are used.

Table 11 gives the ratio of  $\text{CO}$  and  $\text{H}_2$  for a series of various synthesis conditions. It gives the ratio of the two components for the initial gas and also the ratio in which both components are used up during the synthesis.

During all the experiments slightly more  $\text{CO}$  was used than would correspond to the initial ratio of  $\text{CO}$  and  $\text{H}_2$  in the starting gas. For experiments 1 and 2, the starting gas contained  $\text{CO}$  and  $\text{H}_2$  in the ratios of 1.4:1 and 1.5:1, respectively.  $\text{CO}$  and  $\text{H}_2$  were used up in the ratio, 1.54:1 and 1.58:1.

Table 11. - Ratio in which  $\text{CO}$  and  $\text{H}_2$  are used up during synthesis for various conditions

Experiment No.	Catalyst type	Pressure, atmospheres	Temperature, °C.	Operation, days	Conversion, percent	Ratio of $\text{CO}$ and $\text{H}_2$ initial gas	Ratio of $\text{CO}$ and $\text{H}_2$ used up
1	Fe-normal catalyst	15	235	30	56	1.41:1	1.54:1
2	Fe-normal catalyst	15	270	325	47	1.51:1	1.58:1
3	Fe- $\text{NH}_3$ precipitated, 1/4 percent $\text{K}_2\text{CO}_3$	15	255	24	51	1.5:1	1.7:1
4	Fe- $(\text{NH}_4)_2\text{CO}_3$ precipitated, 1 percent $\text{K}_2\text{CO}_3$	15	234	7	49	1.5:1	1.59:1
5	Fe- $(\text{NH}_4)_2\text{CO}_3$ precipitated, 1 percent $\text{K}_2\text{CO}_3$	15	237	14	50	1.64:1	1.78:1
6	Fe-normal catalyst	5	270	9	37	1.45:1	1.77:1
7	Fe-normal catalyst	60	254	6	52	1.46:1	1.67:1
8	Fe-normal catalyst	15	230	5	45	0.53:1	0.87:1
9	Fe-normal catalyst	15	240	4	50	1.76:1	1.96:1
10	Fe- $\text{Na}_2\text{CO}_3$ precipitated, 1 percent $\text{K}_2\text{CO}_3$	15	235	16	50	1.75:1	2.1:1
11	Fe- $\text{Na}_2\text{CO}_3$ precipitated, 5 percent $\text{K}_2\text{CO}_3$	15	238	7	49	1.76:1	2.08:1

In other experiments the difference was greater (experiments 3, 6, and 7). Experiments 4, 5, and 10 were carried out with a catalyst containing 1 percent  $K_2CO_3$ . For experiments 4 and 5, the  $CO:H_2$  ratio was 1.5 and 1.64:1, respectively, for the initial gas. For the same experiments, the end-gas contained 1.59 and 1.78 CO, respectively, to  $1H_2$ . For experiment 10, the initial gas contained too much CO and carbon formation is indicated. The catalyst of this experiment had only about half as long a lifetime as the catalysts of experiments 4 and 5. The situation is similar for experiments 9 and 11. Experiment 8 was carried out with mixed gas ( $CO:H_2$ , 0.53:1). Here, too, the ratio in which the components were used up was higher than the original and amounted to 0.87:1.

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

#### Synthesis Pressure

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

Following are a few series of experiments with catalysts inducted by different processes. The experiments are designed to show the influence of the synthesis pressure upon conversion.

First series of experiments.—The catalyst contained iron and copper in the ratio of 5:1. It was obtained from the solutions of ferrous chloride and copper chloride by precipitation with sodium carbonate and was alkalinized by adding 1/8 percent  $K_2CO_3$ . This catalyst was subjected to induction at atmospheric pressure for 4 days at a temperature of  $245^\circ C$ . (4 liters of mixed gas per 10 grams of iron per hour). After switching to 15 atmospheres pressure, we carried out the synthesis by using 4 liters of synthesis gas ( $CO + H_2 = 3:2$ ) per 10 grams of iron per hour. Table 12 gives the results of this series of experiments. Contractions are recorded for 5, 15, 30, and 80 atmospheres and the necessary working temperatures. (The temperatures of this series of experiments, in general, were high as compared to the induction of the catalyst.)

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

Table 12.--Reaction temperature and contraction at various pressures, Fe-Cu catalyst inducted with mixed gas at 245°C. and 1 atmosphere

Operation, days	5 atmospheres		15 atmospheres		30 atmospheres		80 atmospheres	
	Tem-perature, °C.	Con-traction, percent	Tem-perature, °C.	Con-traction, percent	Tem-perature, °C.	Con-traction, percent	Tem-perature, °C.	Con-traction, percent
10	257	44	257	42	263	50	270	38
20	265	45	265	50	275	50	286	49
30	270	42	270	53	280	48	300	48
40	272	45	274	53	287	52	302	50
50	275	45	275	55	289	52	-	-
60	285	48	272	52	290	49	-	-
90	278	50	281	51	-	-	-	-
120	-	-	285	49	-	-	-	-
150	-	-	290	47	-	-	-	-

Table 13 shows the end-gas analyses obtained for a contraction of 50 percent at 5, 15, 30, and 80 atmospheres. The corresponding initial gas analyses of the runs carried out at 5 and 15 atmospheres contained 56 percent CO and 36.1 percent H<sub>2</sub>; those carried out at 30 and 80 atmospheres, 55.5 CO and 39.5 H<sub>2</sub>.

Table 13.--Reaction gases at various pressures and constant contraction at 50 percent

Operation, days	Pressure, atmospheres	Tem-perature, °C.	Tem-perature, °C.						Hydro-carbons	Carbon No.	N <sub>2</sub>
			CO <sub>2</sub>	Olefins	O <sub>2</sub>	CO	H <sub>2</sub>				
6	5	257	53.8	3.4	0.2	12.3	13.3	7.0	1.9	10.0	
3	15	252	55.5	3.8	.2	11.5	11.6	8.0	1.8	9.4	
23	15	267	51.4	3.8(?)	.3	11.2	16.4	9.9	1.6	7.5	
10	30	263	51.1	2.3	.6	11.3	18.0	7.7	1.8	9.0	
23	80	297	51.1	1.4	.1	13.6	11.0	14.3	1.9	8.5	

The end-gas analyses show that, in spite of the various pressures and the correspondingly different temperatures, the course of the conversions does not change fundamentally. It had already been pointed out that, at high pressures, the formation of reaction water increases at the expense of the formation of CO<sub>2</sub>. Furthermore, it may be seen from the analyses that at higher pressures, the quantities of unsaturated hydrocarbons decrease and that the quantities of the saturated hydrocarbons increase correspondingly. The increased consumption of H<sub>2</sub> is well expressed in the ratio in which CO and H<sub>2</sub> are used up. This usage ratio for the various pressures is as follows: For 5 atmospheres, 1.7:1; 15 atmospheres, 1.66:1; 30 atmospheres, 1.6:1; 80 atmospheres, 1.44:1.

With respect to the lifetime of the catalyst at various working pressures, it should be pointed out that working temperatures above 290°C. should be avoided on account of the danger of carbon formation. The catalyst operated at 15 atmospheres had the longest lifetime. With the catalyst\* used for this series of experiments, a temperature of 290°C. was required for 5 months' operation and working at 15 atmospheres; the same temperature was required after 2 months when working under 30 atmospheres and during the first month when working under 60 atmospheres.

Second series of experiments.—For this series of experiments, a copper-free, so-called normal iron catalyst was used which had been inducted for 24 hours at 1/10 atmosphere and 325°C. with a CO-rich synthesis gas. Table 14 shows the results of experiments at various pressures, such as 1, 5, 10, 30, and 60 atmospheres. All the experiments were started at 235°C.

Table 14.—Reaction temperature and contraction at various pressures  
(normal iron catalyst inducted with CO-rich gas at 325°C. and 1/10 atmosphere)

Operation, days	5 atmospheres		10 atmospheres		30 atmospheres		60 atmospheres	
	Tem- pera- ture, °C.	Con- trac- tion, percent	Tem- pera- ture, °C.	Con- trac- tion, percent	Tem- pera- ture, °C.	Con- trac- tion, percent	Tem- pera- ture, °C.	Con- trac- tion, percent
1	235	30	233	42	235	53	235	50
2	-	-	234	42	235	56	238	42
3	235	25(?)	235	48	234	57	235	40
6	250	38	238	50	-	-	254	52
9	270	37	239	50	-	-	-	-
12	-	-	237	50	-	-	-	-

This catalyst did not give a conversion at atmospheric pressure and 235°C., nor did it give a conversion on the second day at 250°C. (When we switched to 15 atmospheres and 235°C., this catalyst immediately gave a contraction over 53 percent.) At 5 atmospheres the contractions lay between 30 and 40 percent; hence conversion was still incomplete. This did not improve even when the temperature was raised to 270°C. on the ninth day of operation. (When we went back to 15 atmospheres and 235°C., 50 percent conversion was obtained even then.) At 10 atmospheres and 235°C., a contraction of 50 percent was reached. This was the case also at pressures of 30 and 60 atmospheres. However, in the 30-atmosphere run, the conversion fell sharply on the third day, and for the 60-atmosphere run it decreased rapidly during the first day of operation. At 60 atmospheres a contraction of 52 percent could be reached only on the sixth day of operation when the temperature was raised to 254°C.

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

Here, too, we found that an optimum pressure of 10 to 30 atmospheres exists, giving the highest yields and longest catalyst life. (A comparison with experiments recorded in table 5 for the same catalyst at 15 atmospheres shows that the optimum pressure is above 10 atmospheres.)

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

Table 15.—Influence of synthesis pressure upon length of time of operation (length of time for which a contraction of 50 percent was possible at 235°C., when using an iron catalyst alkalinized with 1 percent K<sub>2</sub>CO<sub>3</sub>)

Operation, days	15 atmospheres		20 atmospheres		30 atmospheres		60 atmospheres	
	Tem- pera- ture, °C.	Con- trac- tion, percent	Tem- pera- ture, °C.	Con- trac- tion, percent	Tem- pera- ture, °C.	Con- trac- tion, percent	Tem- pera- ture, °C.	Con- trac- tion, percent
1	235	40	235	52	234	54	235	56
2	239	45	234	51	236	50	235	40
3	237	52	234	55	234	55	235	35
6	239	54	235	55	234	40	-	-
9	238	54	235	49	-	-	-	-
12	238	52	-	-	-	-	-	-
20	234	50	-	-	-	-	-	-
28	235	40	-	-	-	-	-	-

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

#### Reaction Temperature

The temperature of the following work refers to the temperature recorded in the aluminum block. (In the laboratory, we worked with pressure tubes embedded in a slanted position in the aluminum block furnace.) Since both ends of the reaction tube stick out of the aluminum block in spite of good insulation with asbestos rope, heat is conducted toward the outside. As a consequence, the temperature in the interior of the tube is somewhat lower. Calibrations have shown that the temperature in the interior is lower by approximately 5°. However, no temperature correction was taken into consideration, and the temperature of the block was taken as that of the synthesis.

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

### Influence of Induction

It has been pointed out previously that the induction temperature of the catalyst exerts an important influence upon the following synthesis. The curves in Fig. 9 supplement the material already presented. The abscissae give the length of operation in months, the ordinates, the operating temperatures and the steam pressure corresponding to these temperatures. All the experiments were carried out with a synthesis gas containing CO and H<sub>2</sub> in the ratio 3:2 (4 liters per 10 grams of iron per hour).

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

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

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

Table 16.--End-gas analyses of a time test at different temperatures during 16 months of operation

Operation, months	Temperature, °C.	Contraction, percent	End-gas composition, percent							
			CO <sub>2</sub>	Olefins	O <sub>2</sub>	CO	H <sub>2</sub>	Hydrocarbons	Carbon No.	H <sub>2</sub>
1	253	50	49.6	2.2	0.1	15.0	13.2	8.8	1.9	11.0
9	272	52	54.5	3.3	.0	8.1	7.4	11.2	1.8	15.5
14	254	50	50.1	2.8	.2	14.9	11.9	7.3	1.7	12.8
16	266	48	53.5	3.1	.1	8.2	10.6	11.9	1.9	12.6
16	259	48	51.2	3.2	.2	9.9	12.6	10.4	1.8	12.5

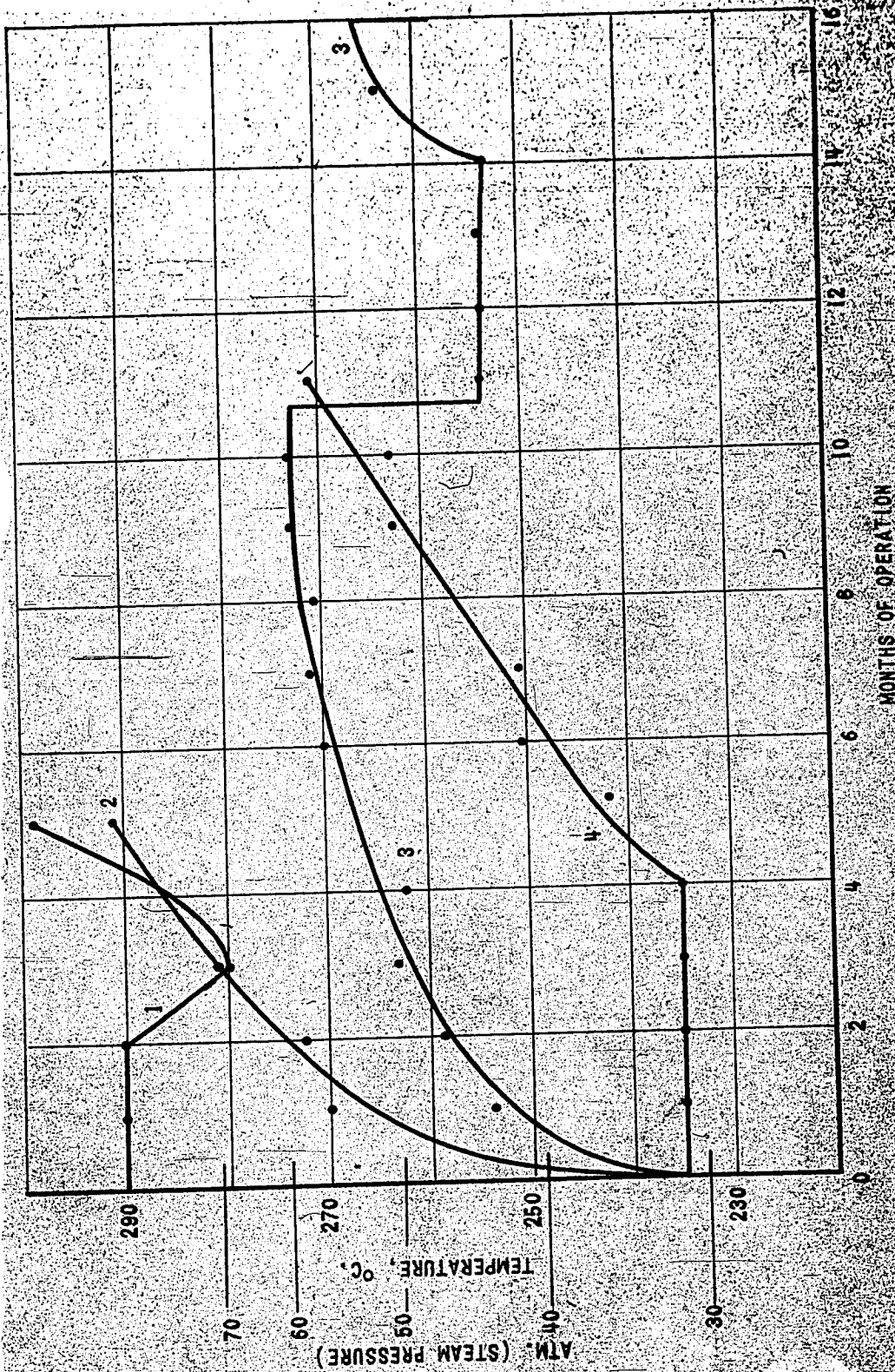


Figure 9. - Influence of Induction upon the synthesis temperature.



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

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

The curves of the figure show the effect of pretreatment of the iron catalyst on the synthesis temperature.

#### Influence of Gas Composition

In table 17, comparative results are given for conversions of CO-rich and H<sub>2</sub>-rich synthesis gases at a reaction temperature of 205°C. (synthesis pressure, 15 atmospheres).

Table 17.--Conversion of CO-rich and H<sub>2</sub>-rich synthesis gas at 205°C. and 15 atmospheres

	CO <sub>2</sub>	Olefins	O <sub>2</sub>	CO	H <sub>2</sub>	Hydro-carbons	Carbon No.	H <sub>2</sub>	Contraction, percent
CO-rich starting gas	2.2	0.0	0.2	58.9	33.9	0.2	1.0	4.6	20
end gas	10.3	.8	.2	52.9	28.4	1.6	1.3	5.8	
H <sub>2</sub> -rich starting gas	1.2	.0	.0	31.2	56.6	1.6	1.2	9.4	31
end gas	8.3	2.1	.2	19.5	52.3	3.9	2.0	13.7	

Table 18 shows the conversion of three different gases at 225°C.

Table 18.--Conversion of CO-rich gas, of water gas, and of H<sub>2</sub>-rich gas at 225°C. and at a pressure of 15 atmospheres

	CO <sub>2</sub>	Olefins	O <sub>2</sub>	CO	H <sub>2</sub>	Hydro-carbons	Carbon No.	H <sub>2</sub>	Contraction, percent
CO-rich starting gas	2.3	0.0	0.0	58.8	33.4	0.4	1.0	5.1	45
end gas	42.9	3.8	.2	4.5	15.1	4.3	1.5	9.2	
Water gas, starting	1.8	.0	.1	46.4	43.4	.8	1.0	7.5	52
end gas	40.6	4.0	.2	8.9	24.6	6.2	1.6	15.5	
H <sub>2</sub> -rich starting gas	.6	.0	.1	30.7	58.3	.2	1.0	10.1	46
end gas	22.6	1.6	.1	.0	43.8	13.1	1.7	18.8	

The analyses show that the reaction temperature can be lower if less CO is present in the synthesis gas, that is, less CO is converted. For the same temperature, an increase in H<sub>2</sub> content in the synthesis gas increases the percent contraction as long as the CO is not converted entirely, as shown by the last experiment of table 18. 0.66 and 0.71 liter, respectively, of CO is converted per hour at 205°C. (according to both experiments of table 17). According to table 18, 1.8, 1.7, and 1.23 liters per hour of CO were consumed at 225°C. In the last experiment of this table, all of the CO was converted. As long as CO and H<sub>2</sub> were present in the gas in sufficient quantity to react for the same temperatures and for the same length of time, the converted quantities of CO and CO:H<sub>2</sub> ratio remained independent.

#### Effect of Too Low Starting Temperature

In general, the experiments were started at 225° to 235°C., although good conversion could have been obtained at lower temperatures immediately after the induction. Thus, with an experiment conducted with H<sub>2</sub>-rich synthesis gas (CO:H<sub>2</sub> = 1:2), a contraction of 47 percent was still obtained at a temperature of 184°C. after the second day of operation. The ratio in which CO and H<sub>2</sub> were used up was 0.7:1, indicating a reaction proceeding according to the equation, CO + 2H<sub>2</sub> = CH<sub>4</sub> + H<sub>2</sub>O. At such low reaction temperatures, the conversion decreases after a few days, and the results are more unfavorable even after the temperature is raised again, than if operation had been begun at higher temperatures from the start (table 19). Table 19 contains the results of two comparative experiments using CO-rich synthesis gas and a normal iron catalyst. Experiment 1 was conducted at 235°C., experiment 2 started at 210°C.

Table 19:—Influence of too low a reaction temperature upon stability of catalyst

Operation, days	Experiment 1		Experiment 2	
	Tem- perature, °C.	Con- traction, percent	Tem- perature, °C.	Con- traction, percent
1	235	56	210	42
2	235	52	210	31
3	235	51	210	27
4	235	51	-	-
5	235	52	220	21
6	235	55	235	36
7	235	55	250	45
8	235	55		
9	235	55		
10	235	57		
15	235	55		

The catalyst taken into operation at 235°C. gave constant contractions of 50 to 55 percent. The catalyst started at 210°C. gave contraction of 42 percent after 1 day of operation; after 2 days it gave 31 percent and after 3 days only 27 percent. When the temperature was raised, the catalyst gave only 36-percent conversion at 235°C., and even at 250°C., 50-percent contraction could not be reached.

## Temperature and Reaction Products

It has been pointed out previously (for example, see table 16) that with high temperatures the formation of the gaseous products increases. Table 20 shows average yields obtained on an iron catalyst containing 1/4 percent potassium carbonate; temperatures were 235°, 270°, and 280°C. When the temperature was raised from 235° to 270°C., the yields of solid paraffin dropped from 39 to 4 grams per normal cubic meter. The quantity of liquid and especially of volatile liquid gasol hydrocarbons increased at the same time. At 280°C. the paraffin yields were still lower; however, at this temperature the yields of liquid and gasol hydrocarbons also decreased.

Table 20

Reaction temperature, °C.	Yields (grams/Nm <sup>3</sup> of ideal gas)		
	Solid paraffin	Liquid hydrocarbons	Gasol hydrocarbons
235	39	83	26
270	4	94	46
280	2	82	35

### Influence of Alkali Content of Iron Catalyst Upon Its Activity and Upon Nature of Reaction Products

The preparation of the catalysts and the nature of the addition of alkali have been discussed earlier. In the following, an analysis is presented to show the influence of the alkali upon the course of the synthesis. The alkali additions indicated in the tables refer to potassium carbonate expressed as percent potassium carbonate referred to metallic iron. In the case of the other alkali salts (permanganate, fluoride, etc.) the notation "1 percent  $KMnO_4$ " signifies that as much potassium was used in the formation of this salt as would correspond to 1 percent  $K_2CO_3$ . Table 21 describes an experiment, the catalyst of which was precipitated with ammonia and contained no alkali. The testing of this catalyst was carried out at constant temperature (235°C.) with a CO-rich synthesis gas ( $CO:H_2 = 3:2$ , containing 8 to 10 percent inert ingredients). The pressure was 15 atmospheres.

Table 21.—Activity of various alkalinized iron catalysts

Alkali addition	Operation, days								
	1	2	5	10	20	30	40	50	100
0	50	50	50	50	50	49	51	51	
0	53	50	48	49	50	45	54	54	53
1/4% $K_2CO_3$	47	50	50	51	55	56	54	54	53
1/2% $K_2CO_3$	54	—	54	47	—	45			
1% $K_2CO_3$	40	—	54	53	50				
1% $K_2CO_3$	45	45	45	52	48	48	47		
2% $K_2CO_3$	45	45	47	46	47	50			
5% $K_2CO_3$	—	—	45	50	50	51	50	40	
10% $K_2CO_3$	—	50	47	50	45	42			
1% $KMnO_4$	40	—	50	51	55	50			
1% $K_2F_2$	—	57	53	55	48				
1% $K_2SiO_3$	—	54	53	46	50				
1% $K_2HPO_4$	55	46	—	46	40				

The series of experiments shows that alkali addition to the catalyst is not required if one disregards the nature of the formed hydrocarbons. The catalyst which was precipitated with ammonia and was entirely free of alkali was tested for 50 days and gave contraction values which were similar to those obtained with a normal iron catalyst containing 1/4 percent  $K_2CO_3$ . We found that catalysts which contained up to 1 percent or more potassium carbonate showed a decrease in activity earlier than normal iron catalysts at 235°C.; the decrease occurred between the 30th and 50th days. When we used catalysts that had been alkalinized by salts other than potassium carbonate, no worthwhile variations in the course of the synthesis could be observed during the first few weeks. However, the catalyst containing potassium permanganate showed very good conversion, whereas the one containing potassium phosphate was less active.

Table 22 shows the quantity and the nature of the reaction products which were obtained with the various alkalinized catalysts at 235°C. and 15 atmospheres synthesis pressure. The yields, expressed in grams per normal cubic meter of ideal gas, vary to some extent through the first month of operation, corresponding to the changing contractions obtained. Thus, we obtained between 150 to 160 grams per normal cubic meter of ideal gas. The alkali content of the catalyst exerts a very essential influence upon the nature of the reaction products. When no alkali was present, only 12 percent of solid paraffin (referred to the total yields of solid, liquid, and gasol hydrocarbons) was obtained, according to the Butanone method. When 1/4 percent potassium carbonate was added to the catalyst, this increased to 26 percent; for 1 percent potassium carbonate, to 42 percent; for 2 percent, to 43 percent; and at 5 percent potassium carbonate, contents 45 to 46 percent of solid paraffin was obtained, referred to the total yields. The quantity of liquid and gasol hydrocarbons correspondingly fell as the alkali content increased.

Table 22 shows that the source of the alkali was unimportant, as far as the quantity and nature of the reaction products were concerned. The experiments with a catalyst containing 1 percent potassium carbonate and the corresponding quantities of potassium permanganate, potassium silicate, potassium fluoride, and potassium phosphate showed the same course of reaction within the limits of experimental error.

Table 22. — Yields with an iron catalyst containing various amounts of alkali additions

Precipitating agent	Alkali addition	Solid, liquid and gasol hydrocarbons, grams/Nm <sup>3</sup> of ideal gas	Liquid.		
			Paraffin, percent	hydrocarbons, percent	Gasol, percent
NH <sub>3</sub>	0	141	12	67	21
Na <sub>2</sub> CO <sub>3</sub>	1/4% K <sub>2</sub> CO <sub>3</sub>	148	26	56	18
	0	140	13	67	28
Na <sub>2</sub> CO <sub>3</sub>	1% K <sub>2</sub> CO <sub>3</sub>	157	42	47	11
	1% K <sub>2</sub> MnO <sub>4</sub>	155	41	45	14
	1% K <sub>2</sub> SiO <sub>3</sub>	158	43	41	16
	1% K <sub>2</sub> F <sub>2</sub>	163	46	42	12
	1% K <sub>2</sub> HPO <sub>4</sub>	154	38	52	10
	1% K <sub>2</sub> CO <sub>3</sub>	143	43	44	13
Na <sub>2</sub> CO <sub>3</sub>	2% K <sub>2</sub> CO <sub>3</sub>	161	45	43	12
	5% K <sub>2</sub> CO <sub>3</sub>	155	46	44	10

## Treatment with Hydrogen Before and After Synthesis

### Pretreatment with Hydrogen

The normal iron catalyst, instead of being treated with CO, was inducted with 6 liters per hour of H<sub>2</sub> at 1/10 atmosphere and 325°C. for 2-1/2 hours. When CO-rich synthesis gas was substituted and operation continued at 15 atmospheres and 235°C., an end-gas analysis made after 1-1/4 hours showed 2 to 3 percent contraction, and another gas analysis made after 3-1/4 hours disclosed 4 percent contraction. The catalyst behaved like a noninducted catalyst. Nevertheless, the catalyst, after removal from the reaction tube, was faintly pyrophoric and ferromagnetic. A comparative experiment with a catalyst inducted with CO instead of H<sub>2</sub> prior to the synthesis gave a contraction of 54 percent from the very beginning.

In a further experiment we used a catalyst of lower activity to determine whether a pretreatment with H<sub>2</sub> before induction would result in an improvement. For this purpose we passed 8 liters of H<sub>2</sub> per hour over the catalyst at 325°C. and 1/10 atmosphere for 6 hours. Then we passed 4 liters of CO per hour over the catalyst for 20 hours at 1/10 atmosphere and 325°C. Then we started operation with CO-rich synthesis gas at 15 atmospheres. The contraction was 42 percent on the second day at 234°C., 45 percent on the sixth day at 236°C., 47 percent on the eighth day at 238°C., and again 47 percent on the tenth day at 238°C. Comparing these data with the experiment conducted with a catalyst not pretreated with hydrogen, 42-percent contraction was obtained on the second day at 234°C. and 46 percent on the eighth day at 238°C. The hydrogen treatment before induction therefore was without influence upon the conversion.

### Hydrogen Treatment Between Induction and Synthesis

We passed 40 liters of CO for 2-1/2 hours at 325°C. and 1/10 atmosphere over the catalyst. Then we passed 6 liters of H<sub>2</sub> per hour over the catalyst at 325°C. We substituted CO-rich synthesis gas at 15 atmospheres, and the activity was tested at 210°C. The contraction went up to 42 percent immediately. After 1 day, it was 43 percent. For a comparative experiment in which the H<sub>2</sub> pretreatment was omitted, the contraction after 1 day was 42 percent. The intermittent H<sub>2</sub> treatment was therefore without influence upon the catalyst activity. (This result is surprising because one would expect that the H<sub>2</sub> would reduce the carbides formed during induction with CO.)

### Hydrogen Treatment During Synthesis

A catalyst that ordinarily should have been taken into operation at a somewhat higher temperature was tested at 235°C. and 15 atmospheres with 4 liters per hour of CO-rich gas. It gave 52-percent contraction on the first and second days (see Fig. 10), 50-percent contraction after 2 days, and 47-percent contraction after 3 days. The dotted curve shows that the contraction should have reached 40 percent if the experiment could have been continued for 1 week at 235°C. However, after 3 days an H<sub>2</sub> treatment was undertaken for 15 hours, using 8 liters per hour of H<sub>2</sub> at 1 atmosphere and 325°C. After this H<sub>2</sub> treatment, the contraction in the following synthesis amounted to 55 percent. It decreased slowly thereafter but remained at 51 percent for 12 days. Another H<sub>2</sub> treatment was undertaken under the same conditions as outlined earlier. The contraction rose again to 57 percent and decreased slowly to 50 percent on the 19th day. After the third H<sub>2</sub> treatment had been carried out, at first a contraction of 55 percent was obtained, after 3 days 51 percent, and after 4 days 52-percent contraction was measured. Then for 2 months of operation the contraction remained constant between 50 to 53 percent at 235°C.

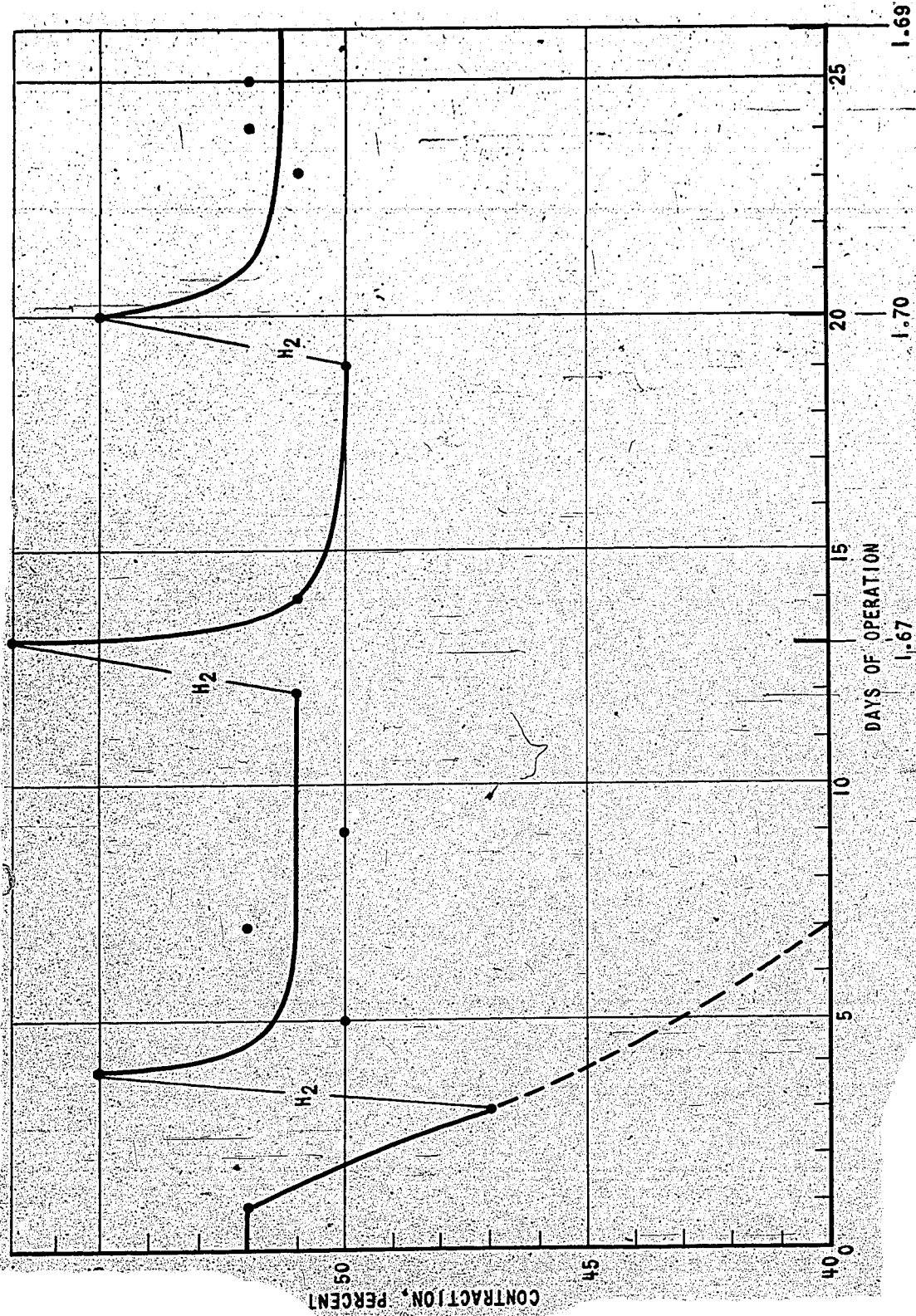


Figure 10. - Influence of a H<sub>2</sub> - pretreatment on the synthesis.

Figure 10 shows that the H<sub>2</sub> treatment undertaken between syntheses causes an increase in catalyst activity. This increase was especially pronounced during the first hours after the H<sub>2</sub> treatment, and it also resulted in a lasting improvement of the catalyst. When these peaks of activity were obtained immediately after the H<sub>2</sub> treatment, CO and H<sub>2</sub> were used up in the same ratio as during the course of the normal synthesis (at 50 to 52 percent contraction). In both cases, CO and H<sub>2</sub> were used in the ratio of 1.57 to 1.70:1.

Iron catalysts which had been in operation for a great length of time or had decreased in activity could not be improved by such H<sub>2</sub> treatment. As a matter of fact, an improvement will not even result if another induction is carried through with CO. If it is planned to give an H<sub>2</sub> treatment, it is important that this be done before the activity of the catalyst has decreased below 45 to 50 percent.

#### Catalysts Based on Ferrous Salts

In the initial description of the preparation of catalysts from ferrous salts, it was pointed out that these iron catalysts are obtained as voluminous brown powders. The catalysts from ferric salts are almost black and show glassy fracture. A fundamental distinction may therefore be made between the two catalysts from their appearance.

When the ferrous catalyst was employed without previous induction (CO-rich gas at 15 atmospheres) the results were as poor as those with the other catalysts. Thus, on the first day of operation at 244°C., 8-percent contraction was obtained and 45 percent on the ninth day at 265°C. The ferrous catalyst under these conditions could be brought to 50-percent contraction at 280° to 290°C.

After induction with mixed gas at 1 atmosphere and 254°C., and synthesis with CO-rich gas at 15 atmospheres and 245°C., 43-percent contraction was obtained at 245°C., 44-percent contraction at 255°C., and 47-percent contraction at 265°C. on the 10th day. When the catalysts prepared from ferrous chloride and ferrous nitrate and inducted with CO and 1/10 atmosphere and 235°C. were used in a synthesis at 15 atmospheres and a CO-rich synthesis gas, they showed an initial activity which, however, decreased rapidly after 1 to 2 days. Table 23 shows this for three experiments.

Table 23.—Experiment with ferrous catalysts

Operation, days	Catalyst preparation by					
	FeCl <sub>2</sub>		FeCl <sub>2</sub>		Fe(NO <sub>3</sub> ) <sub>2</sub>	
	Tem- pera- ture, °C.	Con- trac- tion, percent	Tem- pera- ture, °C.	Con- trac- tion, percent	Tem- pera- ture, °C.	Con- trac- tion, percent
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 contraction for the first experiment decreased from 57 to 34 percent on the third day when the operating temperature was 235°C. For the second experiment (after a contraction of 56 percent was obtained initially) the temperature was lowered on the first day to minimize any possible damage to the catalyst. At the lower temperature, however, the contraction decreased. A third experiment with a catalyst derived from ferrous nitrate behaved similarly.

Under the test conditions previously adhered to for the other normal catalysts (prepared from ferric salts), the ferrous catalysts were less active.

For the experiments in table 12, iron-copper catalysts built on ferrous chloride-copper chloride were employed. They were inducted with mixed gas at atmospheric pressure. The table shows that these ferrous catalysts gave full conversion for several months. However, it should be pointed out that the temperature has to be 260°C. and higher, corresponding to the induction conditions.

#### Effect of Adding Copper

The experiments of Fischer, Ackermann, and Meyer (17) have shown that the synthesis carried out at atmospheric pressure with copper-free catalysts is inferior to that carried out with copper-containing iron catalysts. The following table shows the best results with both catalysts at atmospheric pressure. The reaction temperature was 230° to 235°C. Four liters of mixed gas per 10 grams per hour of iron were used for the synthesis.

Table 24.—Effect of adding copper upon normal pressure synthesis

Catalyst:		Fe:Cu = 5:1		Fe (without Cu)	
Induction Time:		2 days		4 to 7 days	
Operation, days	Contraction, percent	Liquid products, grams/m <sup>3</sup>		Contraction, percent	Liquid products, grams/m <sup>3</sup>
1	30	56		32	55
5	30	56		31	50
10	30	55		30	48
20	30	56		27	38
30	29	50		26	34
40	27	46			

The copper-containing catalysts required a shorter induction time to reach the maximum contractions of approximately 30 percent. The maximum yields at the beginning of the synthesis in both cases were approximately the same; however, the copper-containing catalysts retained their activity somewhat longer than the copper-free catalysts.

When the catalysts were employed at 15 atmospheres pressure (without previous induction at lower pressures), the catalysts containing copper (5Fe + 1Cu) and the copper-free catalysts gave contractions of 40 to 44 percent after the reaction temperature had gone up to 260° to 270°C. Copper-free catalysts under these conditions and at 280° to 290°C. gave a contraction of 50 percent for several months. In comparison, the copper-containing catalysts deteriorated rapidly.

Table 25 shows two experiments in which the catalysts were produced from ferric salts and were inducted at 325°C. and 1/10 atmosphere with CO. Then the synthesis was carried out at 15 atmospheres with CO-rich gas. Results are compared for temperatures of 235° and 225°C. for catalysts containing copper and catalysts without copper.

The experiments show that the addition of copper to iron catalysts for use in the middle-pressure synthesis at 235°C. is of no advantage.



Table 25.—Effect of adding copper upon activity of iron catalysts

Operation, days	Synthesis temperature 235°C.		Synthesis temperature 225°C.	
	Fe without Cu	5Fe:1Cu	Fe without Cu	5Fe:1Cu
	1	55	54	52
2	53	56	—	54
3	53	—	50	50
4	55	50	—	—
5	55	50	45	50
10	54	52		

Effect of Adding Kieselguhr

In the synthesis of hydrocarbons with cobalt catalysts, kieselguhr plays an important part as a carrier used in the catalyst. Satisfactory yields of liquid and solid hydrocarbons may be obtained only with catalysts containing kieselguhr.

When iron catalysts were used in the normal-pressure synthesis, it was found that the catalysts that did not contain a carrier were more effective than with kieselguhr as carrier. In some cases yields of 50 to 55 grams of liquid hydrocarbons per cubic meter of gas were obtained, but the lifetime of such catalysts was only a few days. Recently, we have carried out experiments using iron catalysts containing kieselguhr for the middle-pressure synthesis. The purpose of this investigation was not so much to improve the yields of the synthesis as to operate with catalysts of lower density in vertical reaction tubes. Operation with catalysts containing no kieselguhr in vertical tubes results in much shorter life than when kieselguhr is present (see fourth part of this paper titled, "TOM REEL 101, DOCUMENT PG-21577-NID.").

The kieselguhr was added at various stages of the catalyst preparation. The following experiments were carried out: Experiment 1, 4 grams of kieselguhr per 10 grams of iron were added to the iron solution before precipitation; Experiment 2, 4 grams of kieselguhr per 10 grams of iron were added to the soda solution before precipitation; Experiment 3, 4 grams of kieselguhr per 10 grams of iron were added to the moist catalyst slurry after alkalization (see "THE CATALYST", page 2); Experiment 4, the possibility of adding dry kieselguhr to the finished catalyst must be dismissed if it is desired to produce a solid granular catalyst.

The results of experiments 1 to 3 are given in table 26. Experiment 3a refers to a synthesis temperature of 235°C.; 3b refers to 225°C. The various contractions obtained after various times of operations are recorded in the table. In all cases, the catalyst was inducted for 24 hours, using 4 liters per hour of CO per 10 grams of iron. The induction pressure was 1/10 atmosphere, and the temperature 325°C. After this the synthesis was carried out with a CO-rich gas ( $3CO + 2H_2$ ) at 15 atmospheres.

Table 26 shows that experiment 3a gives the best results. In this case, the kieselguhr was added to the catalyst after alkalization. The contraction remained above 50 percent for 2 months of operation (without regeneration). At 225°C. (experiment 3b), the contraction fell below 50 percent after 10 days of operation.

Table 26.—Effect of adding kieselguhr to catalyst

Operation, days	Experiment 1		Experiment 2		Experiment 3a		Experiment 3b	
	Tem- pera- ture, °C.	Con- trac- tion, percent	Tem- pera- ture, °C.	Con- trac- tion, percent	Tem- pera- ture, °C.	Con- trac- tion, percent	Tem- pera- ture, °C.	Con- trac- tion, percent
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 27 gives a composition of the product gas at contractions of 53 to 54 percent. Experiment 3a gives the maximum amounts of gaseous hydrocarbons. The catalysts in which the kieselguhr had an opportunity to be saturated with alkali during the process of precipitation (experiments 1 and 2), as well as experiment 3b carried out at 225°C., yielded essentially less saturated gaseous hydrocarbons for the same contraction. (A normal iron catalyst under analogous conditions gave a reaction gas containing 6 to 8 percent gaseous hydrocarbons.)

Table 27.—Analyses of product gases from the kieselguhr catalysts at a contraction of 53 to 54 percent

	CO <sub>2</sub>	Olefins	O <sub>2</sub>	CO	H <sub>2</sub>	Hydro- carbons	Carbon No.	N <sub>2</sub>
Experiment 1	59.1	3.5	0.2	6.3	12.9	4.7	1.8	13.3
Experiment 2	59.2	4.4	.1	5.4	11.1	6.1	1.7	12.7
Experiment 3a	64.8	3.0	.1	1.3	6.0	11.4	1.9	13.4
Experiment 3b	55.9	2.6	.2	8.8	9.9	7.7	2.1	14.2

A yield determination made for experiment 3a disclosed 87 grams of solid and liquid hydrocarbons and 36 grams of gasol hydrocarbons per normal cubic meter of ideal gas.

At the beginning, the liquid hydrocarbons contained 3 percent solid paraffin, 12 percent after 4 weeks, and 14 percent after 6 weeks. (This catalyst was alkalinized with 1 percent potassium carbonate; the formation of paraffin consequently is essentially smaller than in the case of the corresponding kieselguhr-free iron catalysts.)

The products were colorless; their composition will be discussed later.

A catalyst corresponding to that used in experiment 3b was charged into a vertical apparatus composed of 18 tubes (18 catalyst charges, 10 grams of iron per tube). After the catalyst was inducted with CO at 1/10 atmosphere and 325°C., CO-rich synthesis gas was substituted at 15 atmospheres and 225°C. Within 6 days, the contraction decreased from 54 to 50 percent. The catalyst was then treated with H<sub>2</sub> at the same temperature. On the eighth day, the contraction was 52 percent; on the tenth day, it was 47 percent. After a second H<sub>2</sub> treatment, the synthesis was carried out at 230°C. and then at 232°C. On the 17th day, the contraction had decreased to 48 percent again. After another H<sub>2</sub> treatment the experiment was conducted for another week at 236°C., etc. (see Fig. 11).

When the results of the experiments carried out in horizontal, slightly inclined tubes (experiment 3b, table 26) were compared with experiments carried out in vertical apparatus, it was observed that the latter showed a less uniform result. Nevertheless, it was possible to maintain a contraction of approximately 50 percent by treating several times with H<sub>2</sub>. (Details on the apparatus used in these experiments are contained in the section, "GENERAL PROBLEMS".)

#### THE REACTION PRODUCTS

In the middle-pressure synthesis with iron catalysts, paraffin and olefin hydrocarbons varying from methane and other gaseous hydrocarbons to high molecular solid paraffins are formed. In table 28 yields of solid paraffins, liquid products, and gasol hydrocarbons of some experiments carried out under different conditions are summarized.

Table 28.—Solid, liquid and gasol hydrocarbons at various reaction conditions

Catalyst	K <sub>2</sub> CO <sub>3</sub> , percent	Synthesis	Paraffin, percent	Liquid hydrocarbons, percent	Gasol, percent
		tem- pera- ture, °C.			
Fe(Na <sub>2</sub> CO <sub>3</sub> precipitated)	1/4	270	3	65	32
Fe-Cu	1/8	260	4	76	20
Fe-kieselguhr	1	235	8	63	29
Fe(NH <sub>3</sub> precipitated)	0	235	12	67	21
Fe-normal catalyst	1/4	235	26	56	18
Fe(Na <sub>2</sub> CO <sub>3</sub> precipitated)	1	235	42	47	11
Fe(Na <sub>2</sub> CO <sub>3</sub> precipitated)	5	235	46	44	10

As the table shows, the amount of paraffins formed varies between 3 to 46 percent (referred to total yield). If this is referred to liquid and solid products alone, it corresponds to 5 to 51 percent. The portion of liquid hydrocarbons produced varied between 44 and 76 percent of the total reaction products. Between 10 and 32 percent of gasol referred to total yield was obtained. The catalysts precipitated with soda and those precipitated with ammonia gave the best results. When the synthesis temperature was 235°C. it can generally be observed that lowering the reaction temperature and increasing the alkali content causes a high molecular weight hydrocarbon to be formed. The iron-kieselguhr catalyst forms an exception.

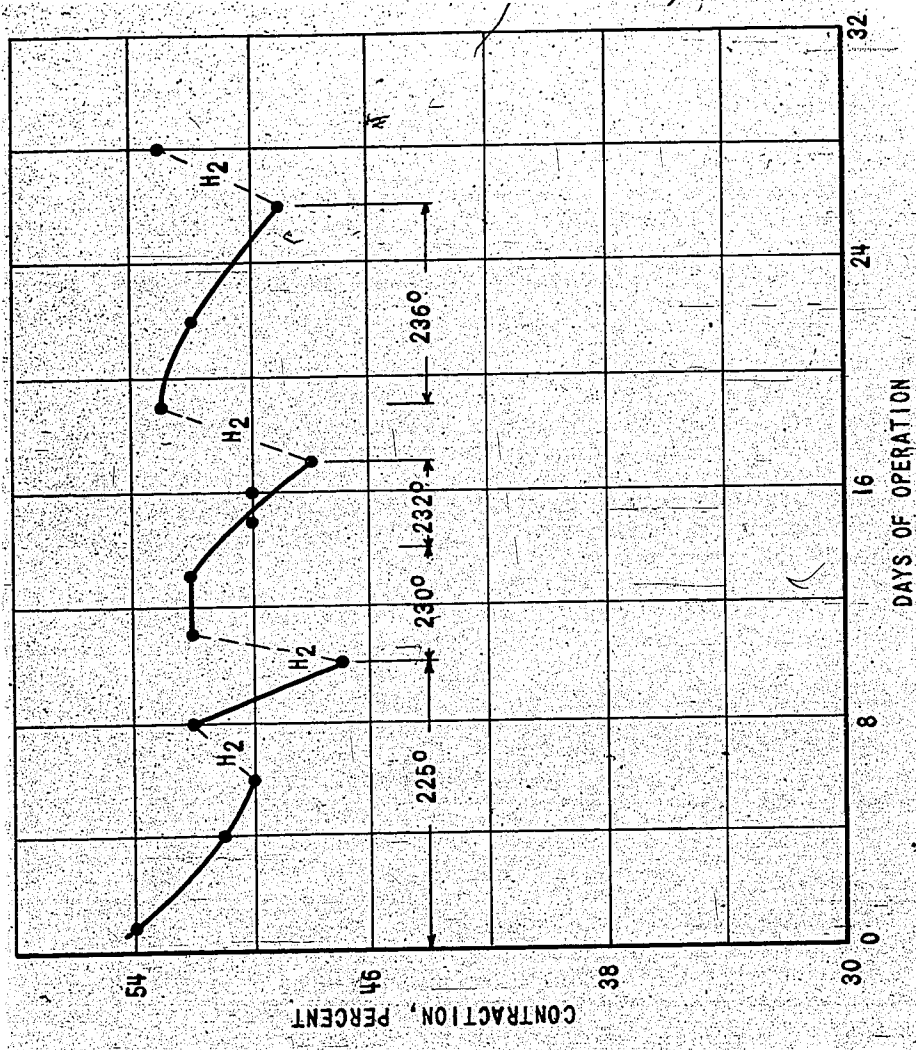


Figure 11. - Experiments with iron Kieselguhr catalysts in vertical units.

The liquid products obtained not only showed a different boiling range for the various reaction conditions but also contained a different percentage of unsaturated hydrocarbons.

As a by-product, the synthesis furnishes an exceedingly high-melting paraffin. Furthermore, oxygen-containing organic compounds similar to those of Fischer's Synthol (18) were formed.

Finally, the iron catalysts may be used under certain conditions for the production of city gas.

The middle-pressure synthesis with iron catalysts offers a possibility to control the formation of the products of reaction by imposing specific conditions upon the course of the reaction. In the discussion of the reaction products, only approximate limits concerning the formation of the various hydrocarbons can be set. This is on account of the many different variables which can occur in the synthesis.

#### Liquid Hydrocarbons

The crude liquid total product generally is not colorless, but somewhat yellowish. After distillation, one obtains water-clear colorless gasoline. The small quantities of yellow oil remain as a residue. The gasoline is stable and remains colorless after months of storage. The percentage of liquid hydrocarbons boiling below 180°C. is greatly dependent on the experimental conditions and can vary between wide limits. When a catalyst precipitated with ammonia and containing 1/4 percent  $\text{FeCO}_3$  was used at 250°C., 55 percent distilled below 180°C. When an iron-copper catalyst was used at a reaction temperature of 260°C., 80 percent came over below 180°C. When a catalyst was used at a reaction temperature of 235°C., 50 percent came over below 180°C.

Figure 12 shows a boiling-point curve of the products obtained with the normal iron catalyst at 235°C. Figure 13 shows an Engler-distillation curve for a gasoline synthesis at a reaction temperature of 250°C. and includes the fraction boiling up to 180°C. Fifty percent of this gasoline boiled below 88°C., 60 percent below 100°C. The boiling-point characteristics of the gasoline can be changed drastically by changing the working conditions during the synthesis. Thus, at 235°C. and using the normal iron catalyst, the gasoline was produced boiling up to 180°C. Of this, 50 percent boiled below 78°C. For another iron catalyst at a working temperature of 260°C. a gasoline boiling below 180°C. was produced, of which 50 percent could be distilled below 78°C. Table 29 shows the density, olefin contents, boiling-point characteristics, and octane number of some gasolines produced with the iron catalyst.

Table 29.—Properties of gasolines produced with iron catalysts

No.	Washed with NaOH	$d_{15}$	Olefin	Boiling-point analysis				P37.8°	Octane No.
				Starting	10%	50%	90%		
1	Yes	0.696	64	30°	46°	88°	145°	0.54	61
2	Yes	.678	65	30°	38°	73°	145°		62
3	No	.698	38					.48	63

Test 1 in table 29 refers to a catalyst precipitated with ammonia, test 2 refers to an iron-copper catalyst, and test 3 to an iron-kieselguhr catalyst. The density of the gasolines boiling below 180°C. was somewhat lower than 0.7. With phosphorus pentoxide-sulfuric acid, 64 and 65, respectively, 38 volume-percent of olefins could be taken out. The octane number of the 3 stabilized gasolines was found to be 61-63, according to the motor method. Possibilities of improving the antiknock properties of the gasoline are discussed in another section dealing with the development of the primary products.

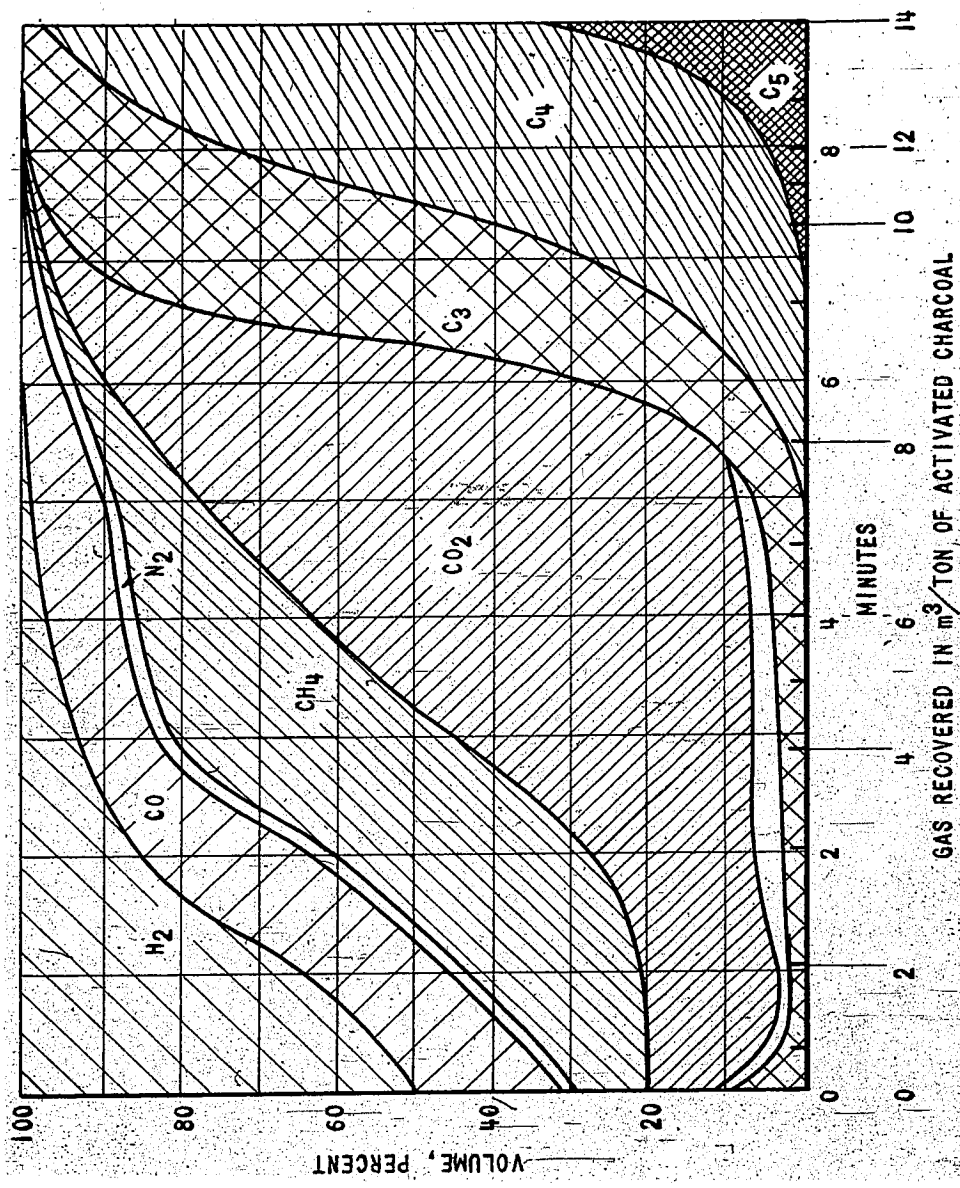


Figure 12. - Products recovered from active charcoal trap by steam distillation.

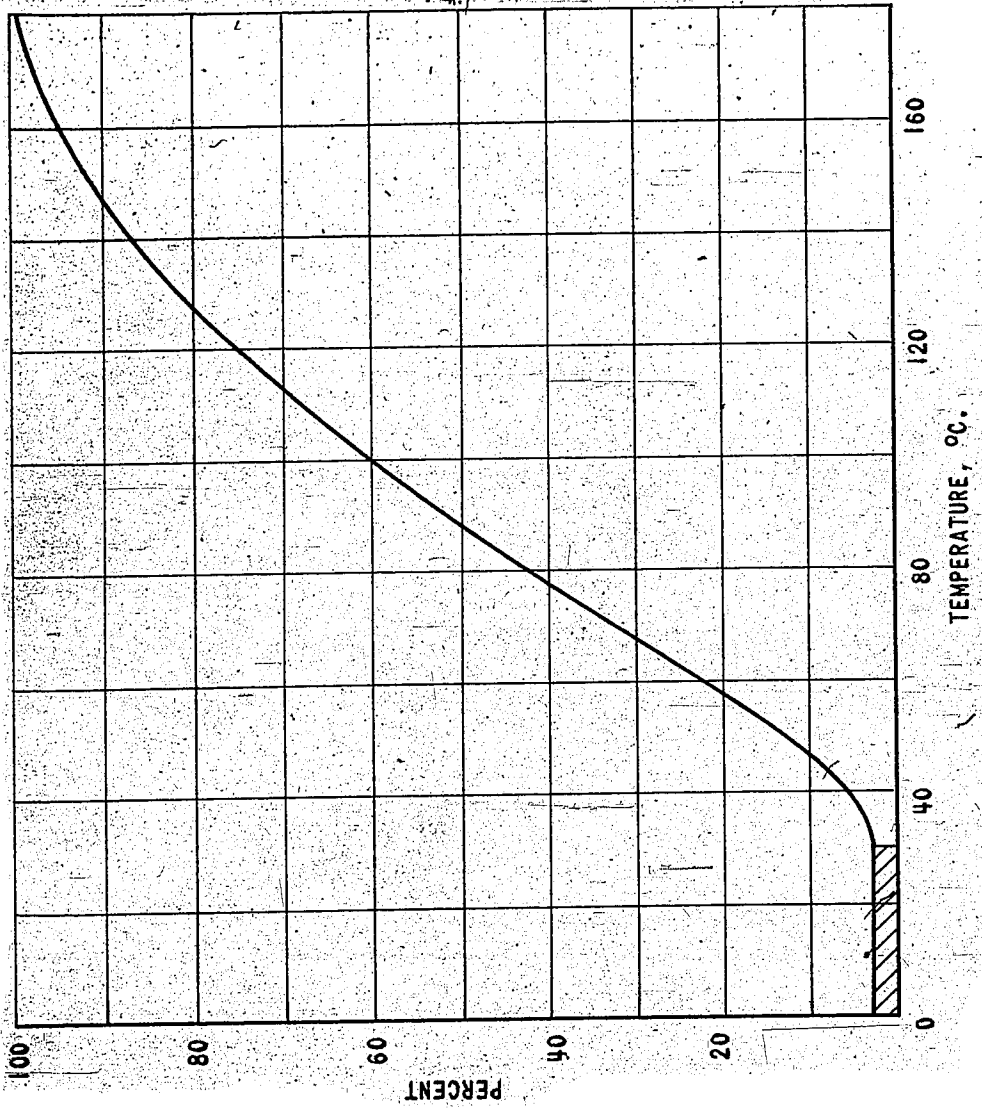


Figure 13. - Engler distillation of a benzene fraction.

If one compares the portions that have been removed from the gasoline by phosphorus pentoxide-sulfuric acid with the octane numbers, then one can observe that these do not depend exclusively on the olefin content.

The synthol products contained in the reaction products from the iron middle-pressure synthesis are important. The quantity and nature of the compounds obtained vary with the working conditions. Table 30 shows acid-ester saponification and hydroxyl numbers of some of the synthesis products.

Table 30.—Oxygen-containing constituents of liquid hydrocarbons

Catalyst	Boiling range, °C.	Acid No.	Ester No.	Saponification No.	Hydroxyl-group No.
Fe, 1/4% K <sub>2</sub> CO <sub>3</sub>	30-180				
Fe, 1/4% K <sub>2</sub> CO <sub>3</sub>	Under 180	0.2	0.2	0.5	2.3
Fe, 1% K <sub>2</sub> CO <sub>3</sub>	Under 180	1.8	8.1	9.9	7.0
Fe-kieselguhr, 1% K <sub>2</sub> CO <sub>3</sub>	30-180	1.4	15.0	16.4	
Fe-kieselguhr, 1% K <sub>2</sub> CO <sub>3</sub>	Under 180	.1	2.0	2.1	

The table shows that the synthesis produces esters and alcohols in addition to small quantities of acid. These compounds are not only lower-weight constituents, but they also contain higher-molecular-weight components (water and alcohols). The formation of these products is greatly favored by alkalization of the iron catalysts.

When the products obtained from the iron-kieselguhr catalyst were washed with a 30-percent calcium chloride solution, 2.5 percent was extracted. When another washing was carried out with sodium hydroxide, another 0.8 percent went into the aqueous fraction.

Table 31 shows results of an elementary analysis of the reaction products boiling below 180°C., obtained from the three different iron catalysts. The numbers refer to unwashed products. They show that the lowest-boiling gasolines have a higher oxygen content than the total products.

Table 31.—Elementary analysis of synthesis products

	Total product			Gasoline		
	C	H	O	C	H	O
Fe-normal catalyst						
Fe-Cu	84.60	15.16	0.24	83.94	14.97	1.09
Fe-kieselguhr						

#### Paraffin

The solid and liquid reaction products contain (according to the Butanone method) approximately 5 to 50 percent paraffins. When an H<sub>2</sub>-rich synthesis gas and an alkali-deficient catalyst are used, the paraffin obtained is white to



slightly yellowish. When a CO-rich gas is used and catalysts with 1 or more percent potassium carbonate, the paraffins are yellow to yellowish-brown. The color is believed due to iron in the form of iron salts. Generally, however, small quantities of higher-boiling oils are responsible for the discoloration. These oils may be extracted or may be made colorless by hydrogenation.

The melting points of the paraffins extend over the entire known melting-point range of the known paraffins. The total product contains high-melting constituents, so that it melts to a clear liquid at comparatively high temperatures. Meniscus formation was observed in the melting-point tubes at 80°C. for a paraffin freed of liquid hydrocarbons by the Butanone method produced through a catalyst with 1/4 percent  $K_2CO_3$ . When a catalyst containing 1 percent  $K_2CO_3$  was used, the meniscus formation was observed at 104°C. When an iron catalyst was used which contained 1 percent  $K_2CO_3$ , a paraffin was obtained which was 50 percent soluble in boiling ether (24 hours' extraction in Soxhlet apparatus). The product re-precipitated from the soluble fraction with methyl alcohol showed a final melting point of 66° to 70°C. Of the insoluble fraction, 41 percent was soluble in boiling hexane. The solid obtained from this solution had a final melting point between 90° and 104°C. The remaining 9 percent, insoluble both in ether and in hexane, produced a solid which had a melting point of 122°C.

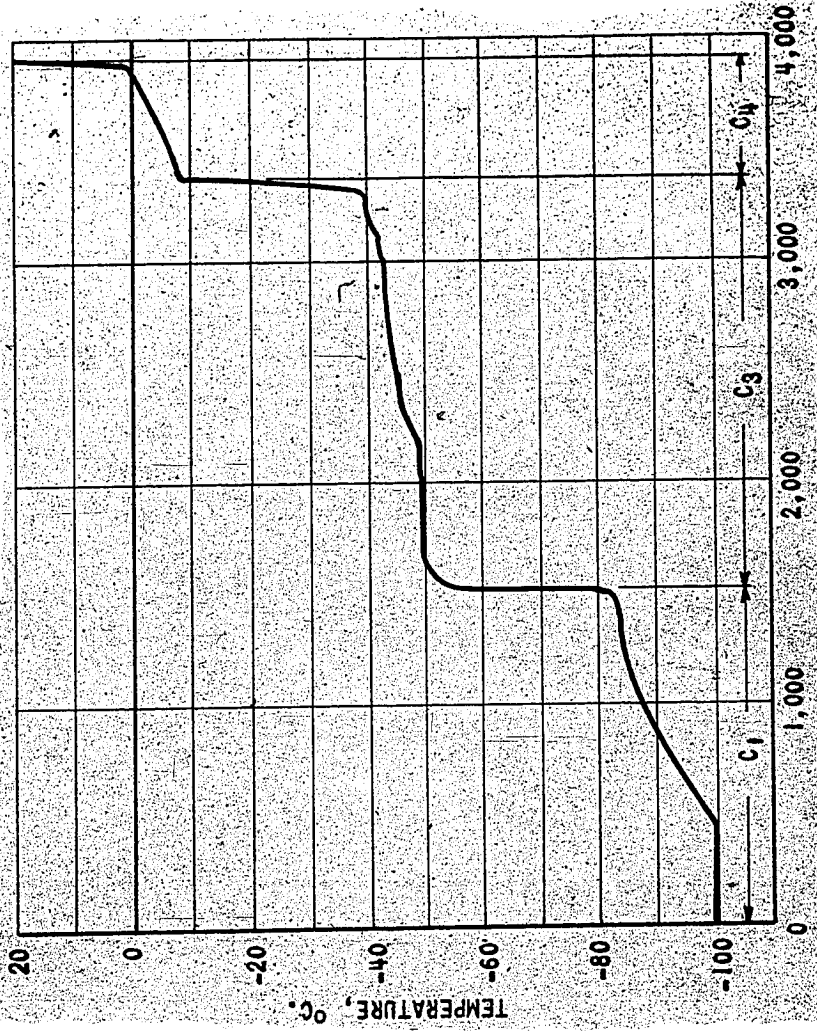
When the iron catalyst was extracted, a paraffin was obtained which, after fractional extraction, was insoluble in boiling benzol but soluble in boiling toluol. Constituents were isolated which melted at about 126°C.

#### Gasol

From table 28 it may be seen that 10 to 30 percent of the reaction products of the synthesis consists of gasol hydrocarbons ( $C_3+C_4$ ). In addition to that, the iron middle-pressure synthesis yields ethylene. Figures 14 and 15 show the results of some low-temperature distillations carried out at the Institute by F. Weinrotter. In order to obtain the gaseous reaction products, the whole end-gas of an experiment (Fe with 1 percent  $K_2CO_3$ ) was conducted through a cooler cooled with liquid air. All of the gaseous hydrocarbons and lower gasolines with the exception of the methane were retained in the receiver. The  $C_2$  to  $C_4$  fraction distilled over up to room temperature corresponds to Fig. 14 (distillation 1). The gasoline remaining in the receiver still contained considerable quantities of  $C_4$  hydrocarbons. They were removed by distillation. Figure 15 (distillation 2) refers to the  $C_4$  fraction. The presence of iso-butylene was not proved in both distillations.

Table 32 shows a summary of the results of the low-temperature distillations. The points in the second distillation curve include the points in the first distillation curve plus the gasol hydrocarbons. The portion of unsaturated hydrocarbons of the various fractions was determined with mercury nitrate.

The  $C_2$  fraction contained 55 percent by weight of ethylene; 74 percent of the total gasol fraction consisted of unsaturated hydrocarbons. For this experiment, 5.2 grams per normal cubic meter of ethylene, 11.1 of propylene, and 6.0 of butylene were obtained.



GAS, CUBIC CENTIMETERS

Figure 14. - Distillation of gaseous hydrocarbons.

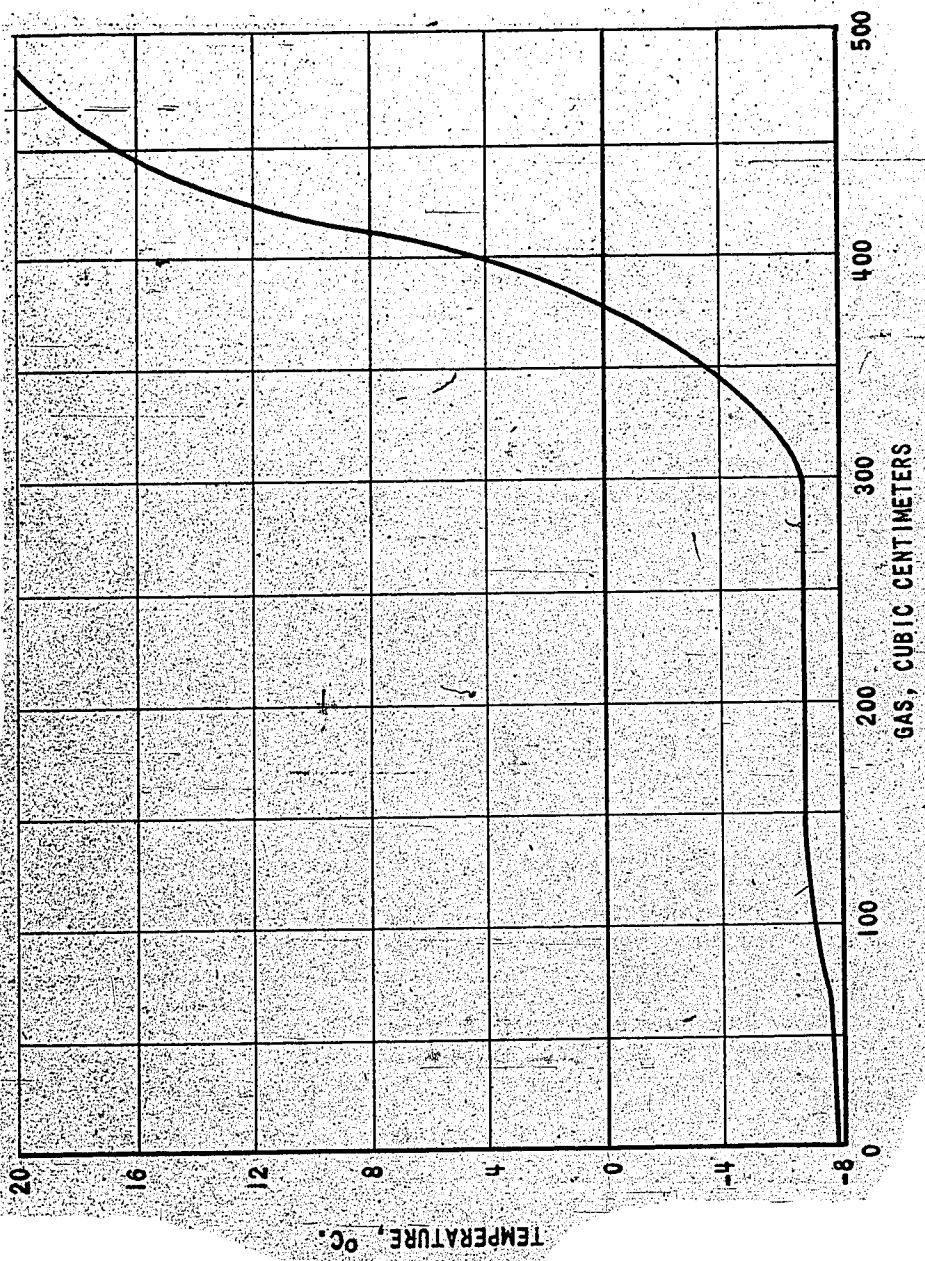


Figure 15. - Removal of C<sub>4</sub> - hydrocarbons from benzene.

Table 32.--C<sub>2</sub> to C<sub>4</sub> hydrocarbons formed during synthesis

	First distillation, cc.	Second distillation, cc.	Weight percent of C <sub>2</sub> + gasol-fraction
Ethylene	2360		15.8
Ethane	1830		13.1
Propylene	3480		34.9
Propane	1130		11.9
Butylene	1010	333	17.9
Butane	370	87	6.4

The quantity and composition of the gaseous hydrocarbons depend on the nature of the catalyst and the reaction temperature. Table 33 shows yields of gasol hydrocarbons with their respective content of unsaturated constituents for various synthesis conditions. All the experiments refer to a synthesis gas composed of 3CO + 2H<sub>2</sub> and synthesis pressure of 15 atmospheres.

Table 33.--Yields of gasol hydrocarbons with different catalysts<sup>a/</sup>

Catalyst	Temperature, °C.	Gasol per normal cubic meter of ideal gas, grams	Gasol unsaturated hydrocarbons, percent
Fe, NH <sub>3</sub> precipitated, 0% K <sub>2</sub> CO <sub>3</sub>	235	30	70
Fe, Na <sub>2</sub> CO <sub>3</sub> precipitated, 0% K <sub>2</sub> CO <sub>3</sub>	235	28	80
Fe, Na <sub>2</sub> CO <sub>3</sub> precipitated, 1/4% K <sub>2</sub> CO <sub>3</sub>	235	26	76
Fe, Na <sub>2</sub> CO <sub>3</sub> precipitated, 1% K <sub>2</sub> CO <sub>3</sub>	235	17	80
Fe, Na <sub>2</sub> CO <sub>3</sub> precipitated, 1/4% K <sub>2</sub> CO <sub>3</sub>	270	46	47
Fe-kieselguhr, 1% K <sub>2</sub> CO <sub>3</sub>	235	36	35

<sup>a/</sup> The quantity of gasol hydrocarbons produced during the synthesis may be increased. Research being conducted at present is concerned with that problem.

For the iron catalysts that were precipitated with ammonia or soda, and for a synthesis temperature of 235°C., 20 to 30 grams of gasol hydrocarbons per normal cubic meter of ideal gas were obtained, which were 70 to 80 percent unsaturated. At higher reaction temperature, the quantity of gasol hydrocarbons formed increased. The hydrogenation of the hydrocarbons increased at the higher reaction temperature also, with a result that at 270°C. reaction temperature approximately 20 grams of unsaturated hydrocarbons were formed. The gasol hydrocarbons produced with iron-kieselguhr catalysts vary considerably from those produced with the kieselguhr-free catalyst in so far as the amount is concerned. As in the case of the gasoline, here, too, the kieselguhr catalyst produces a gasol that contains less unsaturated hydrocarbons.

## Oxygen-Containing Products

### Reaction Water

With the iron-kieselguhr-catalyst and the reaction temperature 235°C. (CO-rich gas, 15 atmospheres), approximately 13 grams of aqueous products per normal cubic meter were formed. They contained acids, aldehydes, and esters, and alcohols. (Test for formic acid was negative, that for acetic acid, positive. Test with fuchsine for sulfuric acid was positive. The presence of ester was demonstrated by saponification. Little methyl alcohol was found; ethyl alcohol was recognized by its boiling point and the iodoform reaction.) The reaction water was subjected to a distillation through a micro column. Figure 16 shows the distillation analysis of the constituents boiling below 90°C. (28 percent of the total reaction water).

The boiling-point curve shows very distinctly the ethyl alcohol fraction. It corresponds to 7.5 percent of the total reaction water.

### Hydrocarbons

Table 30 has shown that the reaction products boiling above as well as those boiling below 180°C. contain more or less synthol, depending on the working conditions. In addition to organic acids, esters and alcohols were detected. Investigations are in progress to identify the higher alcohols and esters. The results of these investigations will be published separately.

In the following, a description is given of the products which can be extracted with a 30-percent calcium chloride solution from a gasoline boiling up to 180°C. (5.5 percent of the gasoline). Figure 17 gives the results of a distillation (corresponding to Fig. 16) of the aqueous solution distilled off up to 95°C.

### City Gas

The question has been asked repeatedly whether it is possible to use coke for the production of city gas. Since water gas has too low a heating value, it would be necessary to increase this heating value by partly converting the water gas into hydrocarbons. With the aid of nickel or cobalt catalysts, this is possible without any difficulty. The production of such a gas over the iron middle-pressure synthesis was investigated, as the normal pressure synthesis with iron catalysts did not produce a gas with the desired heating value.

A usable city gas should have the following properties:

#### 1. Combustion properties

- a. Heating value (higher heating value equals 4,200 to 4,600 kilogram-calories per normal cubic meter.
- b. Density equals 0.4 to 0.5 as referred to air = 1.
- c. Gas pressure, higher than 60 mm.
- d. Flash point, 60 to 100.

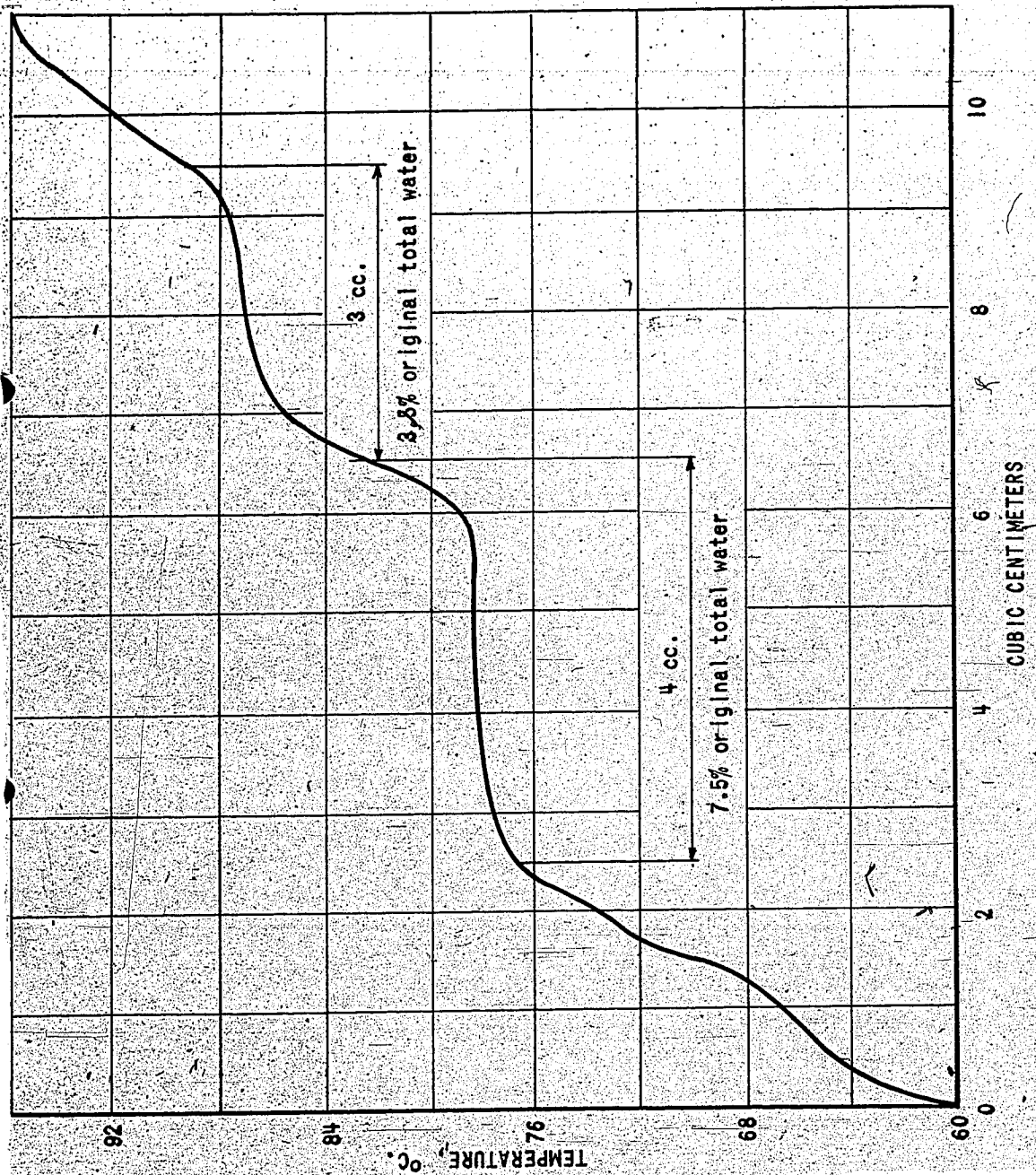


Figure 16. - Boiling point analyses of the reaction water boiling below 90° C. (charge 15 cc.).

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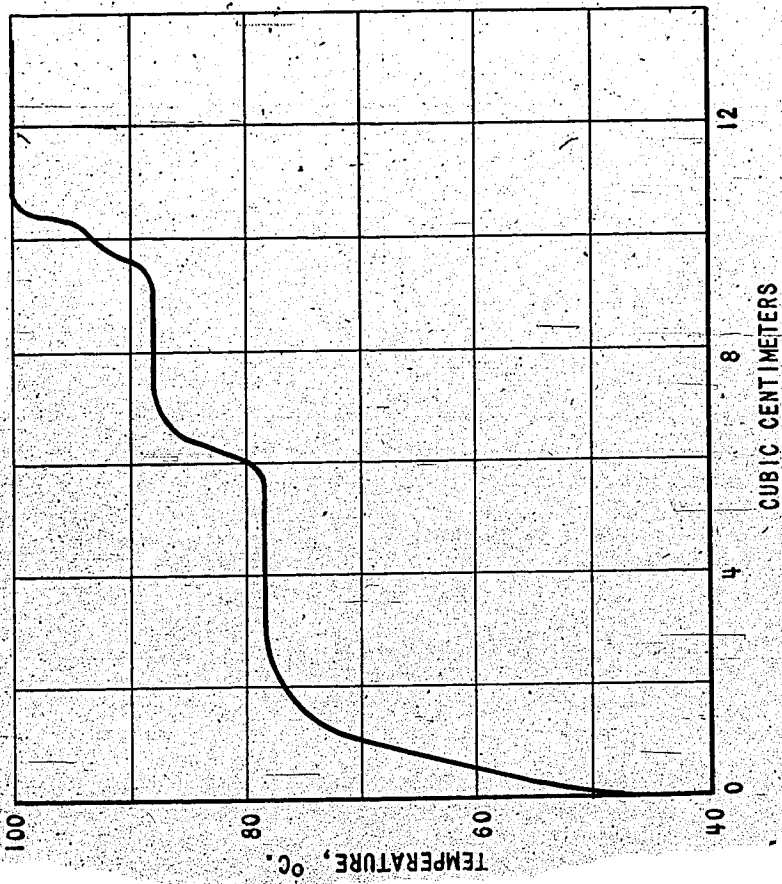


Figure 17. - Distillation of water soluble constituents of the liquid reaction products (charge 15 cc.).

## 2. Purity

- a. Oxygen, less than 0.5 percent.
- b. Hydrogen sulfide, less than 2 grams per 100 cubic meters.
- c. Ammonia, less than 0.3 grams per 100 cubic meters.
- d. Naphthalene,  $\frac{2 \text{ to } 10}{p}$  grams per 100 cubic meters.
- e. Organic sulfur, less than 25 grams per 100 cubic meters; hydrogen cyanide, less than 15 grams per 100 cubic meters; nitrogen oxides, 0.2 cc per cubic meter.
- f. Virtually free of tar.

## 3. Final purification

By keeping the hydrogen content low by a rigorous process of purification, the corrosive properties of the gas can be materially decreased.

Points 1 to 3 are no standard requirements. However, they are merely general requirements which should be fulfilled from the viewpoint of the public interest. These directions no longer contain the earlier limits of the contents of inert gases.

Brückner and Weisbach (20) have proposed to mix propane into the water gas. They have shown that propane-water gas mixtures with a propane content between 6 and 7-1/2 percent have the desired heating value of 4,200 to 4,500 kilogram-calories per normal cubic meter. Such a gas, however, has too high a density (0.61 to 0.63) and too low a flash point (40 to 46).

If one mixes all the tail-gas hydrocarbons, CO<sub>2</sub>-free, resulting from the Fischer synthesis, (the resulting gas consists chiefly of C<sub>1</sub> to C<sub>4</sub> hydrocarbons) with additional water gas, and a city gas may be produced which approximates the requirements for such a gas.

A city gas may also be produced from a CO-H<sub>2</sub> mixture (1:3) when one uses an iron catalyst at pressures of around 10 atmospheres.

To avoid the formation of higher hydrocarbons, an iron catalyst was used which was precipitated with ammonia and was alkali-free. Induction and gas rate corresponded to the usual conditions. The temperature at the beginning of the synthesis was 235°C., after 1 month it was 250°C., after 2 months 265°C., and after 3 months 270°C. For the whole time of operation, a gas of constant composition was obtained. Table 34 gives data on the initial and final gas of this synthesis.

This reaction gas has a heating value of 4,154 kilogram-calories per normal cubic meter (Junkers-Kalorimeter), a density of 0.4 to 0.5, and a flash point of 70 to 71. When a more H<sub>2</sub>-deficient gas is used, the heating value may be increased by 100 kilogram-calories. The gas therefore fulfills all requirements.

According to our experiences, the iron-kieselguhr catalyst is best suited for production of city gas.



Table 34.—Production of gas with properties required by a city gas

Catalyst: Alkali-free iron catalyst

Synthesis Gas: CO:H<sub>2</sub> = 1:3

Pressure: 10 atmospheres

Temperature: 235° to 270°C.

	CO <sub>2</sub>	Olafins	O <sub>2</sub>	CO	H <sub>2</sub>	Hydro-carbons	Carbon No.	H <sub>2</sub>
Initial gas	0.0	0.0	0.0	23.5	73.5	0.0	-	3.0
Final gas	10.9	.2	.1	1.0	69.8	13.1	1.8	4.9

### GENERAL PROBLEMS

#### Synthesis Gas Production

We found that a synthesis gas which contains CO and H<sub>2</sub> in the ratio 3:2 gives the best results during the middle-pressure synthesis on iron catalysts.

For our experiment, we generated such a gas in a normal water-gas generator (21) which we had at the Institute. We passed a mixture of steam and CO<sub>2</sub> over burning coke. Such a procedure we believe could also be recommended for the technical scale, since during the synthesis with the iron catalyst, much more CO<sub>2</sub> is formed than is required for the production of the synthesis gas. Use of synthesis gas of composition 3CO + 2H<sub>2</sub> gives approximately 250 liters of CO<sub>2</sub> at normal conversion. This occurs according to the equation,  $5C + 4H_2O + CO_2 = 6CO + 4H_2$ . According to this equation, only 100 liters of CO<sub>2</sub> are required per cubic meter of CO-rich gas. Therefore, it would only be necessary to wash part of the CO<sub>2</sub> out of the end gas and lead the end gas back into the gas generator.

The CO<sub>2</sub> may also be separated by activated charcoal. Herbert and Ruping (22) have recorded a procedure recently for the separation of CO<sub>2</sub> from gasol. When a cobalt catalyst is used in the Fischer synthesis, virtually no CO<sub>2</sub> is produced. However, if one uses a synthesis gas which was obtained from water gas by partial conversion, this synthesis gas is rich in CO<sub>2</sub>. In this case, one obtains approximately 35 to 45 percent CO<sub>2</sub>. If the activated charcoal is subjected to a steaming operation, the various gases are driven off separately, and it is possible to separate methane and CO<sub>2</sub> very well from the C<sub>3</sub> and C<sub>4</sub> hydrocarbons.

If one charged the whole end gas from the synthesis into the gas generator (CO<sub>2</sub>, methane, unreacted CO, and H<sub>2</sub>, etc.), one would approximate the theoretical yield of 208 grams of hydrocarbons per normal cubic meter of ideal gas.

In the following, the reactions which occur in the water-gas production, mixed-gas-production (CO:H<sub>2</sub> = 1:2), and CO-rich-gas (CO:H<sub>2</sub> = 3:2) production are compared with one another.

1. Water gas.  $C + H_2O = CO + H_2$ . For every cubic meter of water gas 267 grams of carbon and 500 liters of steam are used. Six hundred fifty kilogram-calories are required.

2. H<sub>2</sub>-rich mixed gas.  $3C + 4H_2O = 2CO + 4H_2 + CO_2$ . The equation represents the overall reaction for the primary production of water gas and partial conversion of this to CO<sub>2</sub> and H<sub>2</sub>. Theoretically, 269 grams of carbon per cubic meter of gas, 670 liters of steam, and 570 kilogram-calories are required.

3. CO-rich synthesis gas.  $5C + 4H_2O + CO_2 = 6CO + 4H_2$ . For producing 1 cubic meter of such a gas, 268 grams of carbon, 400 liters of steam, 100 liters of  $CO_2$ , and 690 kilogram-calories are required. For the production of all of these three gases, one requires the same amount of carbon per cubic meter of gas.

When a Dellwig-Fleischer generator is used, one requires 550 grams of coke per cubic meter of water gas, that is, twice as much as is theoretically necessary. The temperature and heat requirements for the production of the CO-rich gases are approximately the same as those for the water-gas production.

We were able to produce 100 cubic meters of CO-rich gas per hour in our water-gas generator for several years without interruption. The composition of the synthesis gas, for example, was as follows: 200% $CO_2$ , 550% $CO$ , 37% $H_2$ , and 6% $N_2$ . In several instances, in order to determine the expressed contraction more accurately, a little more nitrogen than given above was added to the synthesis gas.

The gases were purified in the same manner as was  $H_2$ -rich gas.

Another way to produce the desired synthesis gas is the gasification of coke or coal with addition of oxygen. It is not necessary to discuss this here.

#### Space-Time Yields and Apparatus Details

For most of the experiments in the laboratory, we used reaction tubes of 12 to 13 mm. I.D. The catalyst was distributed evenly over a length of 30 cm. within the tube. A normal catalyst charge contained 10 grams of iron. This corresponds to 15 to 16 cubic centimeters of freshly-prepared normal catalyst. The free space in the tube amounted to 35 cubic centimeters (in the reaction zone). Consequently, the catalyst filled approximately half of the reaction space. The upper half of the tube remained empty. Drawing 1 in Fig. 19 shows the relationships schematically.

If various synthesis-gas quantities are passed over the catalyst under the conditions of the synthesis, the reaction temperature has to be kept higher if it is desired to convert more gas per unit of time. According to Fig. 20, contractions of around 50 percent were obtained at an hourly gas rate of 1.7 liters (referred to 1 atmosphere pressure) at a temperature of 220°C. When 4.1 liters per hour of gas were used, the temperature was 233°C. At 8 liters per hour, it was 250°C., and for 16 liters, 275°C. In another experiment, 4 liters per hour of gas were passed over at 235°C., and a contraction of 15 percent was obtained; at 280°C. and 20 liters per hour, the same contraction was reached.

With respect to the life of the catalyst, the magnitude of the yields of higher hydrocarbons, and other technical reasons, it is advantageous to carry the synthesis through at as low a temperature as possible for as long a time as possible. With respect to the space-time yields, however, it appears more favorable to work at higher temperatures and higher gas rates. We found that at gas rates between 10 and 20 liters per hour per 10 grams of iron, serious difficulties arose when the reaction was carried out on a large scale, owing to the fact that the heat of reaction could not be carried away fast enough. The catalyst was overheated, and free carbon was formed which rapidly caused a decrease in catalyst activity. For this reason we chose to work at a flow velocity of 4 liters of synthesis gas per hour per 10 grams of iron. Drawing 1 in Fig. 19 shows the arrangement of the catalyst in the tubes, and it is to be observed that it was possible to operate for 1 to 2 years with the same catalyst without regeneration, and a satisfactory degree of conversion was always obtained.



1



2



3



4



5

Figure 19. - Schematic representation of positions of reaction tubes.

For the iron middle-pressure synthesis, we have discovered that with increased pressure the gas rate per unit weight of catalyst may not be increased. We have found that processes occurring on the surface of the catalyst which control the reaction velocity (transportation of the reaction products away from the catalyst, carrying the reactants to the catalyst surface) are not accelerated by increasing the pressure.

If the reaction tube is arranged in a vertical position (Fig. 19, schematic drawing 2), the catalyst layer length only amounts to 10 to 15 centimeters, instead of 30 centimeters, as compared to a horizontal arrangement. The contact time of the gases going through the catalyst is much shorter, therefore, when the tube is arranged in a vertical position. The empty space through which the gas flows is approximately four times as large in a horizontal tube as in a vertical tube. By taking into consideration the relationship between rate of gas flow and temperature (shown in Fig. 20), it may be understood that the same favorable results are not obtained when the work is carried out with an apparatus arranged according to drawing 2. In addition to that, we found that the catalyst takes up considerable quantities of the reaction products and large quantities of carbon are deposited on the catalyst. This causes the percentage voids in the catalyst to decrease with consequent shortening of the contact time between the gas and the catalyst.

Since on the large scale one would be chiefly interested in working with vertical reaction tubes, we have attempted to find a solution to the problem according to schematic drawings 3 and 4. The dotted lines represent perforated plates. In case 3, a perforated plate divides the reaction tube into two equal sections. In case 4, a perforated reaction tube is concentrically arranged within the larger reaction tube. The catalyst is distributed in the annulus between the two tubes. In both cases, the catalyst layer length and the percentage of free space correspond to the conditions of case 1. The results were similar for case 1 also. The perforated plates did not cause a noticeable decrease in conversions (the induction of the catalyst had been carried out in a separate apparatus, and the catalyst was transferred in an atmosphere of  $\text{CO}_2$ ). After several weeks of operation, the experiments carried out according to cases 3 and 4 showed a decline in the conversion as compared to the procedure of drawing 1. The reason for this, we believe, might be that the catalyst in case 1 had the possibility of expanding during the synthesis, whereas in cases 3 and 4 this expansion occurred mainly at the expense of the internal voids between the catalyst particles.

Schematic drawing 5 of Fig. 9 shows the arrangement when a catalyst was used the structure of which was loosened by the addition of kieselguhr. When the normal quantity of iron, namely 10 grams, is diluted with 4 grams of kieselguhr, this iron-kieselguhr catalyst fills a 12- to 13-mm. I.D. reaction tube up to a length of 30 centimeters. The percentage of free space is smaller than in case 1, in amount approximately equal to the quantities of kieselguhr used; on the other hand, loosening of the catalyst by the kieselguhr causes considerable improvement in its activity. A small percentage expansion of the iron on account of the deposition of carbon does not produce as unfavorable a result in case 5, as it has caused in cases 2 to 4. An experiment which has been under investigation for several weeks gives a satisfactory conversion (Fig. 11).

We want to mention here that the disturbing influence of the volume increase of the catalyst observed in experiments 2 to 4 was not observed in all cases. Thus, a catalyst precipitated by ammonia and inducted with mixed gas at 1 atmosphere yielded good conversions for 3 months in vertical position at temperatures between  $240^\circ$  and  $260^\circ\text{C}$ . Experiments to clarify the situation are still in progress.

TEMPERATURES FOR WHICH ABOUT 50 PERCENT CONTRACTION WAS OBTAINED

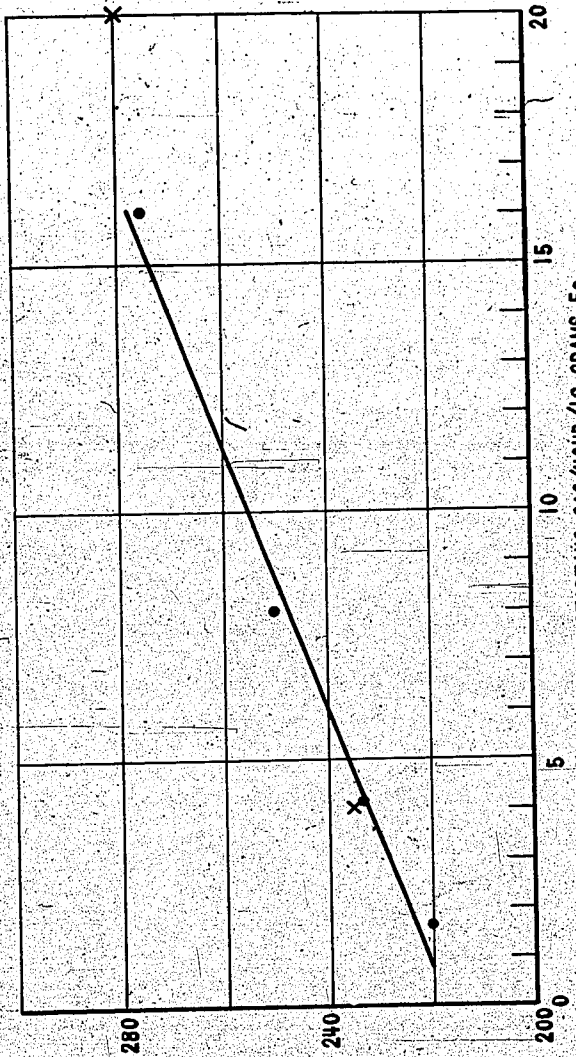


Figure 20. - Relationship between reaction temperature and gas throughput (for constant 50 percent conversion).

It can be mentioned here that the space-time yields observed with the iron-kieselguhr catalysts approximately correspond to those of the cobalt catalysts. If the iron-kieselguhr catalysts should be used on an industrial scale, similar pieces of apparatus as are used with cobalt catalysts should be satisfactory for the iron-kieselguhr catalysts. In the laboratory, we worked with water-cooled tubes. The steam pressures, of course, are higher, corresponding to the increased reaction temperatures. They vary between 30 to 50 atmospheres, all according to the duration of the test.

#### Pelleting of Catalyst

The catalyst described earlier, which was produced from ferric nitrate solutions with sodium carbonate, and the iron catalysts precipitated with ammonia (also ferric catalysts), were solid when dry; they broke with a glassy fracture. Their rigidity should be sufficient for industrial application.

Nevertheless, pelleting experiments were carried out. The blackish-brown color of the original granular catalyst becomes reddish-brown when it is ground. The pellets formed from the powder retain this brown color. We have discovered that the pellets do not always retain the original activity of the catalyst. It might be that the cause for this decrease in activity is related to the overheating which occurs when the catalyst is compressed into pellets.

We produced iron-catalyst pellets of very good activity and high lifetime when we mixed paraffin with the catalyst powder before pelleting. For this we used synthetic paraffin which had been made into fine scales.

Table 35, experiment 1, gives the results of an experiment with pellets which contained 25 percent paraffin as referred to the iron. Experiment 2 shows a comparative experiment in which no paraffin was added. The paraffin does influence the process of induction, and virtually all activity may be regained. The pellets retained their shape even after a long time of synthesis.

Table 35.—Experiments with pelleted catalyst

Operation, days	Experiment 1		Experiment 2	
	Temperature, °C.	Contraction, percent	Temperature, °C.	Contraction, percent
1	235	53	234	55
2	235	54	235	56
10	235	51	236	54
16	234	53	236	50
20	235	52	235	49
25	235	47	240	48
31	235	46	246	47
47	240	49		
60	240	45		

	CO <sub>2</sub>	Olefins	O <sub>2</sub>	CO	H <sub>2</sub>	Hydro- carbons	Carbon No.	N <sub>2</sub>
<u>Experiment 1</u>								
Initial gas	2.1	0.0	0.2	53.8	35.7	0.2	1.0	8.0
Final gas	59.7	3.9	.1	1.1	10.2	7.6	1.9	17.4
<u>Experiment 2</u>								
Initial gas	2.1	.0	.1	53.7	38.0	.4	1.0	5.7
Final gas	61.5	3.5	.0	1.8	13.2	7.2	1.8	13.0

At the beginning of the reaction period, the conversion obtained was virtually the same in both cases (this is also shown in the table with the corresponding gas analyses). After several weeks of operation, however, the temperature had to be raised more rapidly for case 2, where no paraffin had been used in preparing the catalyst. The activity of the catalyst of experiment 1 after 50 days of operation corresponds to the activity of the catalyst of experiment 2 after 25 days of operation.

Even with the addition of only 5 to 10 percent of paraffin, a favorable result upon the activity of the pelleted catalyst was observed.

#### Some Details on Further Processing of Primary Products

In the middle-pressure synthesis with iron catalysts, various types of reaction products are obtained, as will be shown in another chapter. They may be utilized like the products obtained from cobalt catalysts. It is superfluous here to mention the various usages of these products. In some respects, however, there are fundamental differences between the products from the iron synthesis and the cobalt synthesis. First, there are synthol-like by-products as, for instance, various alcohols, and secondly, there are also more unsaturated hydrocarbons. The oxygen-containing as well as the unsaturated compounds give the iron gasoline higher antiknock properties. These compounds have no tendency toward resin formation. The gasoline produced with iron catalysts remains entirely colorless and water-clear after months of storage.

The middle-pressure synthesis with the iron catalyst gives a greater amount of unsaturated gasol hydrocarbons. These may be polymerized to liquid hydrocarbons of high octane numbers. Therefore, the synthesis with iron catalysts seems to be especially adapted for the production of high-quality gasoline.

Catalytic polymerization of olefin hydrocarbons has been investigated by Ipatieff and coworkers (23) of the Universal Oil Products Company. We carried out some similar investigations in which the synthesis and polymerization took place concurrently.

The catalyst we used consisted of  $Cd_3(PO_4)_2 \cdot 4H_2PO_4$ . The carrier was cadmium phosphate,  $Cd_2(PO_4)_2$ , which was precipitated from cadmium nitrate solution and calculated quantities of  $Na_2HPO_4$  and  $NaOH$  at the boiling point. It was washed with hot water, mixed with 98 percent phosphoric acid, evaporated, dried, and pelleted.

When gasol containing 35 to 40 percent of unsaturated hydrocarbons was passed over this catalyst (1 liter of gaseous gasol per hour per 10 grams of catalyst) at a pressure of 7 atmospheres and  $140^\circ C.$ , 40 percent of the unsaturated hydrocarbons was converted; at  $160^\circ C.$ , 60 percent, and at  $180^\circ C.$ , 70-80 percent was converted. A polymerized gasoline was obtained from which was distilled 10 to 20 percent of the compounds boiling above  $180^\circ$  to  $200^\circ C.$  The residue was hydrogenated and had an octane number of 97 to 99. Next, we carried out a series of experiments in which we passed the total reaction gas from the iron middle-pressure synthesis at the synthesis pressure over the phosphoric acid catalyst (after precipitation of the products condensable at room temperature). Approximately the same catalyst volumes were used both in the synthesis and the polymerization. The synthesis was in progress for 2 months before we started polymerizing. We used an iron catalyst precipitated with ammonia, containing  $1/4$  percent  $K_2CO_3$ . It had

been inducted with mixed gas at atmospheric pressure. The yields of solid, liquid, and gasol hydrocarbons amounted to 140 grams per normal cubic meter of ideal gas. Table 36 shows some analyses of the reaction gases after the synthesis (a). Under (b) analyses of the reaction gases after the polymerization are given. The series of experiments was carried out at 15 atmospheres. The temperatures for the synthesis were near 250°C., and for the polymerization near 200° to 220°C.

Table 36.—Composition of reaction gases after synthesis and polymerization

	CO <sub>2</sub>	Olefins	O <sub>2</sub>	CO	H <sub>2</sub>	Hydro-carbons	Carbon No.	N <sub>2</sub>
a	58.3	3.7	0.2	8.7	12.8	6.7	1.6	9.6
b	59.8	1.1	.2	9.1	13.0	6.2	1.7	10.6
a	62.9	3.7	.2	7.0	10.1	7.7	1.8	8.4
b	64.8	1.2	.3	7.1	10.0	7.6	1.8	9.0
a	58.4	4.2	.0	10.9	5.1	6.4	1.7	15.0
b	60.6	1.2	.4	10.8	5.0	6.0	1.8	16.0

The analyses show that two-thirds to three-fourths of the volume of the hydrocarbons disappeared during the polymerization.

Table 37 shows the quantities expressed as grams per cubic meter of ideal gas of solid, liquid, and gasol hydrocarbons formed during the synthesis with, and during the synthesis without, polymerization. The first values correspond to approximately three weeks of operation. The latter correspond approximately to an additional week of operation, for which the polymerization step was omitted. The activated-carbon-gasoline was recovered only once at the end of the conversion (that is, between the synthesis and polymerization).

Table 37.—Coupling of synthesis and polymerization

Polymeri- zation	Yields, grams/normal m <sup>3</sup>		Weight percent of liquid hydrocarbons		
	Liquid hydrocarbons, including paraffin	Gasol	After synthesis	After polymerization	After activated- carbon-gasoline
With	125	14	70	20	10
Without	105	30	85	0	15

During the first period, 139 grams of liquid hydrocarbons (including paraffins) and gasol hydrocarbons were produced by the synthesis. During the second period (without polymerization) 135 grams per normal cubic meter were produced. The synthesis, therefore, furnished approximately 3 percent more products during the first period; the amount of liquid hydrocarbons formed, however, was 19 percent greater, mostly at the expense of the gasol converted by the polymerization. Seventy percent of the liquid products resulting from polymerization was collected in the room temperature traps behind the synthesis apparatus. Twenty percent of the products obtained therein originated from the polymerization apparatus and 10 percent consisted of activated-carbon-gasoline. Some of the activated-carbon-gasoline was not condensed in the first receiver and it was carried over the phosphoric acid catalyst. Consequently part of this activated-carbon-gasoline



polymerized and formed unsaturated benzene hydrocarbons. The gasol hydrocarbons during the polymerization decreased from 30 to 14 grams per normal cubic meter; the quantity of the activated-carbon-gasoline decreased only from 16 to 13 grams per normal cubic meter. This may be explained by the fact that the  $C_4$  hydrocarbons polymerize most readily, whereas molecules having either more or less carbon atoms polymerize more slowly. Therefore, over the phosphoric acid esters chiefly only the dimers of the olefins are obtained.

It is advantageous to remove the synthetic gasoline from the reaction gas before polymerization. Therefore, it is possible to further process the reaction gas obtained through the middle-pressure synthesis with iron catalysts and obtain polymer gasolines. This may be done in one step. Whether it is more economical to proceed in such a manner or to carry out a separate polymerization of the various constituents should be investigated in actual practice.

Experiments that have used acid iron phosphate instead of cadmium phosphate have shown similar results.

The gasolines reported in table 37 were stabilized and washed with sodium hydroxide and tested for the octane number in a motor. Approximately two-thirds of the total liquid products of this experiment boiled in a range of 30° to 180°C.

Table 38 shows the properties of a gasoline without following polymerization, of a gasoline boiling up to 180°C. which was produced by a synthesis and polymerization, and of a gasoline which boiled up to 150°C. with following polymerization. For all three products, table 38 shows the density, the olefin content, the boiling-point characteristics, and the vapor pressure at 37.8°C., as well as the octane number.

Table 38.--Influence of additional polymerization upon properties of gasoline obtained in middle-pressure synthesis with iron catalysts

No.	$d_{15}^4$	Olefin, percent	Boiling-point characteristics				$P_{37.8^\circ}$	Octane No.
			Beginning, °C.	10%, °C.	50%, °C.	90%, °C.		
1	0.696	64	30	46	88	145	0.54	61
2	.705	65	32	53	100	150	.48	67
3	.700	65	34	60	95	130	.55	71

With additional polymerization of the olefins (table 38, No. 1) an octane number of 61 was obtained; with polymerization the octane number was 67 (No. 2). With the gasoline fraction boiling to 150°C. (No. 3), an octane number of 71 was obtained.

When 0.7 cc. of tetraethyl lead was added to each liter of gasoline (No. 2), the octane number could be raised to 79; when the same amount of tetraethyl lead was added to the gasoline (No. 3), the octane number was 80.

## CONCLUSION

A survey was made of the work on the middle-pressure synthesis with iron catalysts. First we discussed the precipitation, alkalization, and induction of the catalyst. Secondly, we were concerned with determining the most favorable synthesis conditions (gas composition, pressure, temperature, additions, regeneration, etc.). Thirdly, we discussed the reaction products and lastly we discussed the general problem of synthesis-gas production, apparatus construction, pelleting of the catalyst, and further processing of the primary products.

The most important results of all the investigations are as follows:

1. Precipitation of iron catalyst. Generally, the catalysts were precipitated by treating ferric nitrate solutions with sodium carbonate or ammonia. The ferric nitrate solutions were obtained by dissolving technical iron in dilute nitric acid. The catalysts prepared from ferric solutions were superior to those prepared from ferrous solutions.

2. Alkalization of catalysts. The presence of alkali is not required for the synthesis and is of no importance to the yield. The addition of alkali, however, causes increased quantities of higher-molecular-weight hydrocarbons to form. In the production of paraffins, therefore, the addition of alkali is important. In general, we used potassium carbonate; however, other alkali salts produced the same effects.

3. Induction of catalyst. To produce an active catalyst it is necessary to carry out an induction with CO-rich gases or, better still, with pure CO. The induction is carried out at pressures which are below those of the synthesis as for example, atmospheric pressure. It was found, however, that reduced pressures are more favorable.

The gas used for the induction should be conducted over the catalyst surface at a high velocity and at temperatures of over 250°C., preferably between 300° and 350°C. This should be continued until the CO<sub>2</sub> formed reaches a more or less constant minimum value.

4. The synthesis. The optimum ratio of CO:H<sub>2</sub> in the synthesis gas was found to be 3:2. The optimum synthesis pressure was between 10 and 20 atmospheres. The optimum synthesis temperatures were between 230° and 240°C. The properly induced catalysts are able to convert the synthesis gas at very low temperatures from the beginning. However, this is unfavorable for the lifetime of the catalyst. Neither are temperatures above 280°C. recommended for the beginning (on account of carbon formation).

The addition of kieselguhr (after alkalization) causes a considerable increase in catalyst activity.

Hydrogen treatment of the catalyst before the synthesis shows no advantages; however, a hydrogen treatment given repeatedly between syntheses causes regeneration and reactivation of the iron catalyst.

5. Optimum yields. The best/solid, liquid, and gasol hydrocarbons were found to be somewhere near 150 grams per normal cubic meter of ideal gas. The longest lifetime was found with a catalyst which continued to produce 140 grams per normal cubic meter after 1-1/2 years of operation at a temperature of 260°C. without regeneration.

6. Reaction products. The nature of the reaction product can be varied within wide limits according to the operating conditions.

Five to fifty percent of the total solid and liquid hydrocarbons consisted of paraffins. Not only low-melting paraffins are obtained, but especially high-melting ones with a melting point above 125°C. were discovered.

The liquid reaction products differ from those of the cobalt catalysts in that they contain greater percentages of unsaturated hydrocarbons and synthol-like products. These, for example, contain alcohols and esters of various size molecular weight.

The octane number of the stabilized gasoline fraction boiling to 180°C. is 60 to 63. When the synthesis is followed by polymerization, the unsaturated gasol hydrocarbons may be polymerized, and the octane number raised by 10 points; by the addition of 0.7 cc. of tetraethyl lead per liter of gasoline, an additional increase of 10 points can be obtained.

Ten to thirty percent of the solid, liquid, and gasol hydrocarbons consists of gasol. Its content of olefins amounts to 80 percent. Increase in temperature or catalyst activity causes an increase in total gasol yield, and a lowering in olefin content.

Furthermore, we found that iron catalysts are capable of producing an acceptable city gas at 10 atmospheres pressure.

7. Synthesis-gas production. The production of a synthesis gas containing CO and H<sub>2</sub> in the ratio of 3:2 may be accomplished by interaction of CO<sub>2</sub> and steam in the water-gas generator. The necessary CO<sub>2</sub> is furnished by the synthesis itself. Furthermore, it is possible to produce a useful synthesis gas by gasification of coke or coal with oxygen.

8. Apparatus details. We discussed the relationship between apparatus details and the life and effectiveness of the catalyst. The best results are obtained in reaction tubes slightly inclined from the horizontal. If it is desired to cool the reaction vessels with water, they should be able to withstand a steam pressure of 30 to 50 atmospheres.