

## INTRODUCTION

### Catalysts

The experimental work on the hydrocarbon synthesis with iron catalysts did not pursue a systematic catalyst study, but rather tests at random with catalysts which had been developed for other purposes and were available at the time. One was a fused-iron catalyst which had been developed for the hydrocarbon synthesis from CO + H<sub>2</sub> by Dr. Linckh. The influence of this catalyst upon the reaction temperature, the synthesis gas composition, the reaction velocity, and the nature and yields of synthesis products was determined. We also investigated a sintered iron catalyst which was developed by Dr. Michael and intended for the hydrocarbon synthesis. Finally, we worked with a Leuna ammonia catalyst. The catalysts were reduced with H<sub>2</sub> at atmospheric pressure and at various temperatures between 450° and 850°C. Depending upon the reduction temperature, the time of reduction lasted from 5 to 15 days.

It is interesting to observe that a certain amount of carbon mixed with approximately 15 to 20 percent Fe<sub>2</sub>O<sub>3</sub> was always found at the entrance to the catalyst bed. The carbon formation probably resulted from the methane and CO normally present in the hydrogen used.

### Description of Converters

The converters used for the synthesis were tube furnaces, the tubes of which were of 15 mm. diameter. A mixture of diphenyl and diphenyl-oxide was the heat transfer medium. The temperature distribution in these converters was not quite as good with oil as with water. With oil cooling, temperature differences up to 5°C. over the entire length of the tubes were unavoidable,

\*Explanation of symbols used in test will be found on page 40).

whereas when water was used, every section of the tube was at the same temperature.

### Composition of Synthesis Gas.

At first, a synthesis gas of composition  $\text{CO} + \text{H}_2 = 1:2.6$  was used. When the apparatus was operated at 20 atmospheres, a gas of composition  $\text{CO} + \text{H}_2 = 1.2:1$  was required. For this reason, we have endeavored to use a reasonably pure water-gas for our experiments, containing approximately 43 percent CO, 53 percent  $\text{H}_2$ , and 4 percent  $\text{CO}_2$ . If the yield of the reaction is calculated on the basis of an ideal gas, of composition  $\text{CO} + \text{H}_2 = 1:1$ , then synthesis gas and water-gas give approximately equal yields; however, the effective yields per cubic meter of synthesis gas and water-gas are in the ratio of 2:3. Under optimum working conditions, the yields obtained so far from the catalysts investigated, namely, WK17 ( $\text{NH}_3$  catalyst) and 997 (Duftschmied, Linckh) are between 90 and 100 grams per cubic meter.

### INFLUENCE OF MODE OF REDUCTION UPON CATALYST ACTIVITY

We shall first consider the influence of the mode of reduction of the catalyst upon the synthesis. Table 4 shows the influence of the reduction temperature upon the activity of the catalyst. The catalysts were later operated under similar conditions.

Table 4. - Influence of Reduction Temperature on Catalyst Activity

Reduction of WK17 at atmospheric pressure and hydrogen space velocity of 100

<u>Reduction temp., °C.</u>	<u>Time, days</u>	<u>Yield with water-gas (g./m<sup>3</sup> ideal gas)</u>
850	2/3	63
500	10	79
450	11	102
420	4	105
400	10	105

From the table it is evident that lower reduction temperatures produced more active catalysts. It appears that not much more is gained in catalyst activity by lowering the temperature below 500°C.\* The degree of reduction which

\*It appears from the data in Table 4, that this value should be 450°C. (ed. note)

may be estimated by the amount of water formed is obviously without significance as far as the activity of the catalyst for the synthesis is concerned. Of the catalysts mentioned in the table, only those were reduced entirely which were subjected to reduction for ten days or more; all the others were only partially reduced and retained considerable quantities of oxides. Under a pressure of 200 atmospheres complete reduction can be effected at a temperature as low as 300°C. in 40 to 60 hours. Reduction of catalyst WK17, under 100-150 atmospheres hydrogen and 300°C. for ten hours, produced no detectable water. Nevertheless, this catalyst produced 90 grams of hydrocarbons per cubic meter of water-gas, and reached its full activity. When we carried out the reduction for 24 hours at 200 atmospheres, 300°C., and a space velocity of 100, we observed approximately 50 percent reduction which, in most cases, was sufficient for all the necessary catalytic activity desired. The degree to which reduction took place could be recognized superficially by the changed appearance of the reduced catalyst. Fused-iron catalysts which were unreduced or only partially reduced had a black, glossy appearance ( $Fe_3O_4$ ). However, the reduced catalysts which were treated with  $H_2$  at 400°C. or higher appeared to be diffuse grey with a metallic sheen.

#### INFLUENCE OF VARIOUS CONDITIONS UPON THE NATURE OF THE SYNTHESIS PRODUCTS

The synthesis temperature, space velocity, and the catalyst itself exert a distinct influence upon the composition of the reaction product.

Higher space velocity and synthesis temperature have a tendency to increase the yield of the low-boiling constituents. A comparatively low synthesis temperature and a small gas rate cause a higher boiling point material to be formed, and, in general, the percentage of solid products formed increases. When two catalysts were used which had the same composition, but which were reduced at two different temperatures, the one which was reduced

at the lower temperature gave a lower boiling product. The catalyst which was reduced at the higher temperature yielded a product of higher boiling range.

#### Influence of the Catalyst

The results of tests in which the catalysts had been reduced at approximately 450°C. are given below in Table 5. The quantity of product formed boiling below 200°C. is used as a measure of the catalyst activity.

Table 5.- Influence of the Catalyst

Reduction temp., °C.	Catalyst	Benzine boiling below 200°C., percent
450	W. 17	55
450	997	60
450	Michael	73

#### Influence of Space Velocity

The influence which the space velocity has upon the boiling points of the synthesis products is shown in Table 6. The influence of the space velocity upon the boiling range of the products formed is graphically shown in Figure 9.

Table 6.- Influence of Space Velocity

Catalyst	Reduction temp., °C.	Space Velocity	Synthesis pressure, atms.	Benzine yield < 200°C., percent
997	450	200	20	51, synthesis gas
997	450	300	20	55, " "
997	450	400	20	57, " "
997	450	500	20	71, water gas
997	450	600	20	69, " "

From Figure 9, it is evident that at higher space velocities the products formed boil at lower temperatures. Particularly obvious is the increase in the benzine fraction when the gas velocity is greater than 400 liters of gas per liter of catalyst per hour. When a converter is used which has tubes of 15 mm. I.D., it is not possible to operate safely at space velocities greater than 400 for any length of time unless special precautions are observed. At space ve-

locities over 400 with comparatively minor temperature or gas rate irregularities, decomposition of the catalyst can occur with the deposition of considerable amounts of carbon, which has a tendency to clog up the passages through the reactor tube. Although with careful regulation of the temperature and the gas rate, it may be possible to work for several weeks at space velocities as high as 500 or 600, we have found that this is the upper limit if adequate removal of the heat of reaction from the catalyst is to be maintained.

#### Influence of Temperature

Overheating by 20 to 40 degrees at high space velocities is primarily the cause of the formation of lower-boiling constituents. The boiling point curves given in Figure 10 support these statements.

#### Influence of Pressure

Figure 11 gives a comparison between the products formed on cobalt catalysts at middle and atmospheric pressures, and those formed on iron catalysts. The Michael catalyst was operated at 20 atmospheres and a space velocity of 200; catalyst 17A862 was operated at atmospheric conditions and at 12 atmospheres at a space velocity of 100. The comparatively steep rise of the product curve (representing the activity of the Michael catalyst) between 80 and 200°C. indicates that this catalyst gives better benzine yields than does the cobalt catalyst.

### COMPOSITION OF THE SYNTHESIS PRODUCTS

#### Comparison Between Products from Cobalt and Those from Iron Catalysts

An essential feature in the synthesis with cobalt is the comparatively high yield of p raffins in the benzine fraction (86 percent paraffins, 14 percent olefins). The synthesis products obtained from the iron catalyst, however, contain considerably greater amounts of unsaturates (approximately 50 percent olefins and 45 percent paraffins).

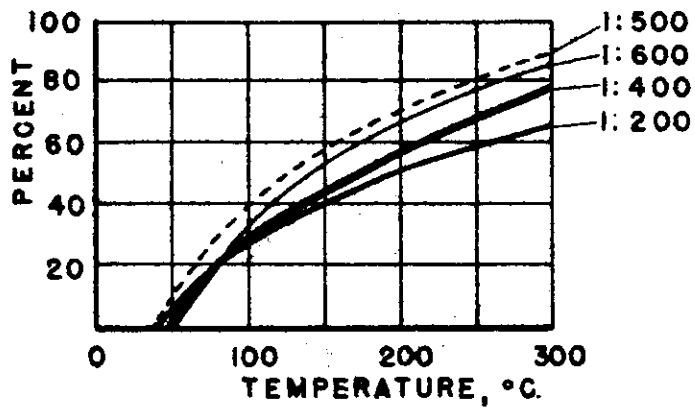


Figure 9.- Influence of space velocity upon the boiling range of the reaction products.

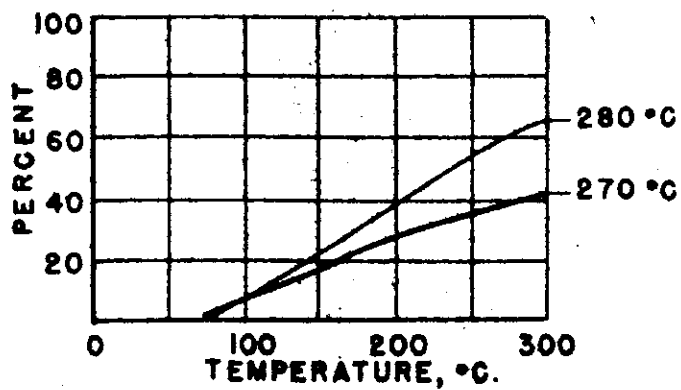


Figure 10.- Influence of temperature.

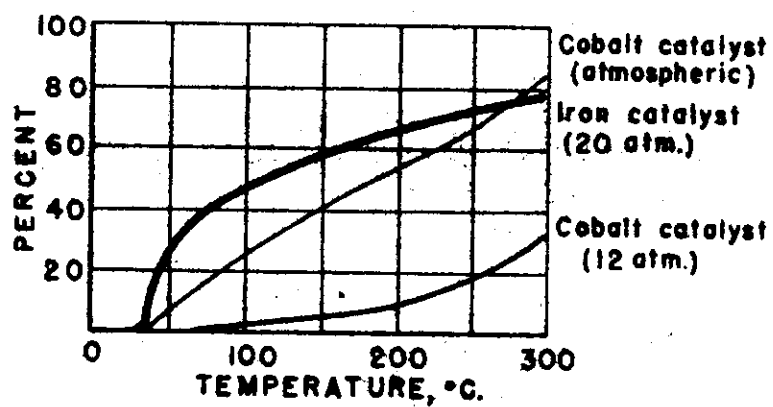


Figure 11.- Comparison between products from cobalt and iron catalysts.

### Effect of Olefin Content Upon Octane Number of Benzine Fraction

Table 7 demonstrates the effect of the olefin content upon the octane number of the benzine fraction. The olefin content has been tabulated for various catalysts with the corresponding octane number.

Table 7. – The Effect of the Olefin Content  
Upon the Octane Number of the  
Benzine Fraction

Olefin, percent	Catalyst	Octane number of the benzine fraction
15	R,CH <sup>a</sup>	25
48	56.5	57
57	997	56.5
72	997	63.5

a/ cobalt catalyst

It should be pointed out, however, that the degree of unsaturation of the benzine fraction is not the only factor which determines the octane number of the products (see page 36).

The operating temperature, space velocities, and characteristics of the catalysts influence the nature of the products of the reaction, and thereby also influence the octane number. In general, for the same olefin content of the benzine fraction, a high reaction temperature, a high space velocity, and an active catalyst, in other words, all factors which favor the formation of low-boiling constituents, will yield a product having the highest octane numbers.

### The Effect of Olefin Content Upon Boiling Point of Products

Figure 17 shows the relationship between the olefin content and the boiling point of the products. The olefin content as determined with phosphoric-sulfuric acid shows a slight decrease, the iodine numbers, a marked decrease with increasing boiling points. This indicates that the solubility in phosphoric-sulfuric acid corresponds very closely to the actual olefin content of the material.



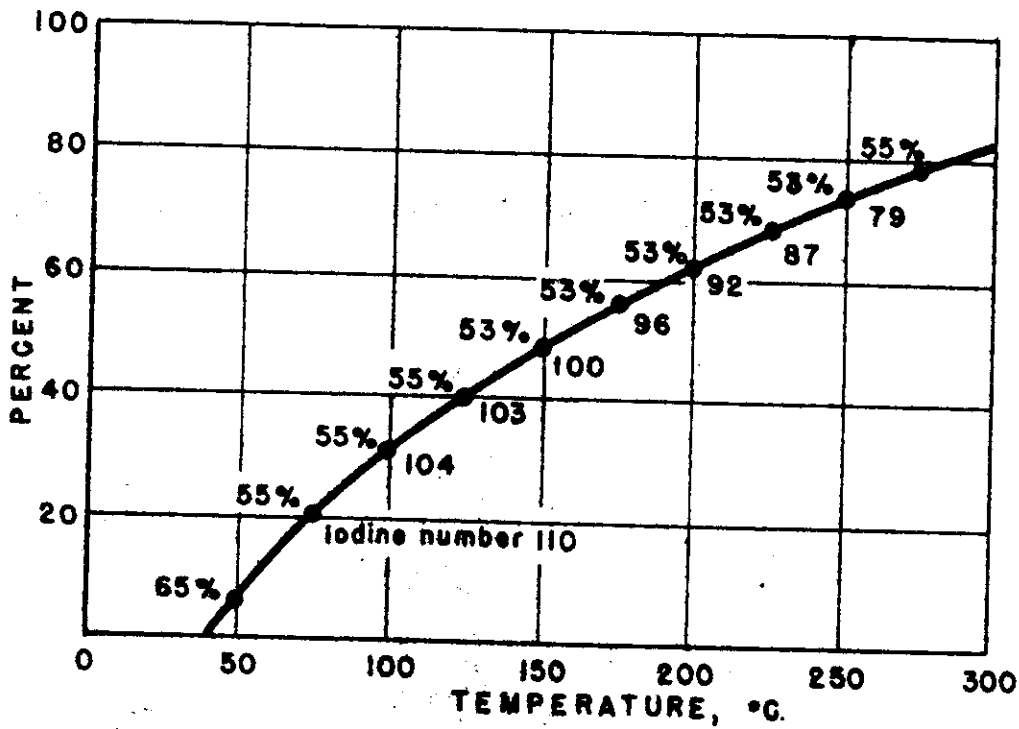


Figure 12.- Relationship between the olefin content, as determined by the iodine number, and boiling range.

Taking into consideration the high olefin content of the products, one would believe that rapid aging and polymerization should occur. If one performs the break-down test, in all cases a relatively high residue is obtained from the evaporation, but in no case is oxygen consumed. Consequently, storage under normal conditions should be possible for long periods of time. The addition of inhibitors is recommended (see Table 3).

Table 3.- Stability of the Benzines as Determined by the Bomb Test

Sample number	Time of induction, minutes	Pressure drop, atm.	Evaporating dish, residue mg/100 cc
245/39072	240	0.0	80.0
" 73	240	0.0	353.0
" 74	240	0.0	41.6
" 75	240	0.0	103.4
" 76	240	0.0	157.0
" 78	240	0.0	307.0
" 80	240	0.0	86.0
" 81	240	0.0	33.3

The question of whether the olefin content of the products is the only factor to be considered when the hydrocarbons are intended as motor fuel should be investigated in more detail. We are studying the improvement of the synthesis products by various methods such as the use of several other iron catalysts under pressure.

As to preliminary results, the following may be said: At a space velocity of 300 and 20 atmospheres pressure, possibly 80 grams of hydrocarbons per cubic meter of gas can be produced in one stage, and a total of 130 grams per cubic meter are expected for a considerable length of time (probably several months). Of this yield, approximately 60 percent consists of benzine having an octane number of about 60. Laboratory experiments indicate that better temperature control results when the gas is recirculated. By doing this, the same yields can be obtained; however, the space velocity can prob-

ably be increased to 600 and the synthesis carried out over a longer period of time.

## BEHAVIOR OF VARIOUS IRON CATALYSTS

### General Considerations

The object of the early systematic experiments was to investigate the influence of operating conditions upon the nature of the products of the reaction. We investigated primarily the influence of temperature, pressure, gas composition, and space velocity. The catalysts used were fused-iron preparations which had been recommended by Dr. Linckh as especially adapted for the hydrocarbon synthesis under pressure. Our first aim was to find the best catalyst for the following synthesis conditions: Pressure, 19 atmospheres; space velocity, 200; synthesis gas, water-gas. The space velocity was kept low so that the catalyst temperature in the converter could be controlled. The reduction temperature in every case was 450°C. In order to produce catalysts which had comparatively high activity at relatively low operating temperatures, like Fischer when he worked with cobalt catalysts, we were primarily interested in the solid and liquid hydrocarbons ( $>C_5$ ). For this reason, we did not pay too much attention to the analysis of the gaseous products. The main portion of the products was recovered every 24 hours from a receiver which was connected to the outlet of the converter. In some cases it was necessary to heat the contents before discharging them from the trap. Every 3 to 6 days, the low-boiling constituents and some benzene were removed from the activated charcoal trap immediately following the product receiver. The water formed during the reaction was tested for alcohol and ketone content. We calculated all yields on the basis of an ideal water-gas at 5°C. and 760 mm. Some important data are tabulated in Table 9. Correlations between the data given are not immediately obvious. The catalysts were operated in such a manner as to produce optimum yields.

Table 9. - Specific Yield and Product Composition for Some Iron Catalysts

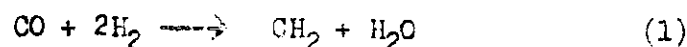
ite <sup>a</sup> /	Cat. No.	Gas	Pressure, atm.	Space velocity	Space time yield g./m <sup>3</sup> /hr.	Conversion yield, grams	Liquid fraction < 300°C. percent	Benzene, percent	Percent olefin in benzene	Oil: water
30.8	1388	Water	19	200	55.5	62	90	65	42	1:1.4
4.12	1200	"	19	200	43.3	62	87	72	40	1:1.2
2.11	1353	"	19	200	56.4	59	85	64	46	1:0.77
14.11	1350	"	19	200	80.7	83	50	37	60	1:0.5
14.11	1244	"	19	200	90.9	108	63	45	53	1:0.55
4.11	319	"	19	200	97.5	115	61	48	45	1:0.4
25.5	WK 17	"	19	200	102	116	80	55	48	1:0.4

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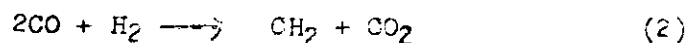
Product:Water Ratio

Catalysts No. 1388 and 1200 produced a high portion of low-boiling constituents, which contained an especially small quantity of olefins. Those catalysts gave a primary product containing approximately 90 percent of material boiling below 300°C., about 40 percent of which was unsaturated. The residue of the primary products obtained from catalyst 1200 was almost white and very similar to the corresponding products obtained from the hydrocarbon synthesis with cobalt catalysts. Further, it is interesting to note that the ratio of oil to water from these two catalysts was less than 1:1. This ratio approaches the figures usually obtained when operating with cobalt catalysts. With the cobalt catalysts, an oil-water ratio of approximately 1:1.7 and less is normally obtained; the iron catalysts when ordinarily operated with water-gas, show generally an oil-water ratio of 1:1 or greater.

For Co catalysts, the reaction proceeds primarily according to the equation:



For iron catalysts the reaction is primarily



With cobalt catalysts the reaction follows equation (1) very closely. However,

with iron catalysts, the reaction almost always proceeds according to equations (1) and (2) simultaneously. In the case of catalysts 1388 and 1200, the course of the reaction has a decided tendency to proceed according to the characteristic equation (1). This is evident from the oil:water ratio as well as from the low olefin content. The appearance of the primary products formed with catalyst 1200 is also very similar to that of the products obtained with cobalt catalysts.

#### Branched Chains and Octane Number

We believe that the chemical constitution of the benzine fraction is essentially the same for iron and cobalt catalysts as can be noted from the fact that the hydrogenated products of both catalysts behave very similarly when used as motor fuels, for example:

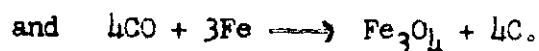
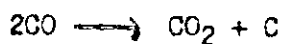
	<u>Olefin content, percent</u>	<u>Octane No.</u>	<u>Temp. range</u>
Product from iron catalyst, untreated	53	56.5	35°-200°C.
After hydrogenation	2	3.0	35°-200°C.
Product from cobalt catalyst, untreated	25	42	35°-200°C.
After hydrogenation	2	2.0	30°-200°C.

It appears therefore that branched chains which could influence the octane number are not present. This, however, does not exclude a small degree of branching, as has been pointed out by Dr. Leithe. Thus, for instance, using a cobalt catalyst and methanol gas ( $\text{CO} + \text{H}_2 = 1:2.5$ ) at atmospheric pressure, approximately 8 to 9 percent of the product was isomeric; whereas approximately 50 percent of a product manufactured by means of an iron catalyst from water-gas ( $\text{CO} + \text{H}_2 = 1:1$ ) was isomeric. (Compare communication of the ammonia laboratory, Oppau, December 28, 1939.)

#### X-Ray Investigations of Iron Catalysts.

In order to obtain some information concerning the nature of carbon deposition on the catalyst, we investigated some catalysts which were still active and others which had become inactive due to carbon deposition. X-ray analyses

performed on these catalysts (Dr. Britt, Dr. Roeber) showed that both samples contained Fe and  $\text{Fe}_3\text{O}_4$  simultaneously. The carbon could not be detected in the X-ray pictures, hence it was presented in an amorphous condition. We found that the ratio of Fe to  $\text{Fe}_3\text{O}_4$  had shifted towards the  $\text{Fe}_3\text{O}_4$  component in the catalyst which had suffered some carbon deposition. This led to the belief that the first cause of carbon deposition on the catalyst is the splitting of CO in a fashion shown by the equation:



Such a reaction may readily be observed with pure CO and Fe catalysts at ordinary operating temperatures. Newly formed  $\text{Fe}_3\text{O}_4$  is finely crystalline whereas the  $\text{Fe}_3\text{O}_4$  present in the reduced catalyst has a large crystalline structure from the very beginning. After carbon is deposited, the catalyst loses its mechanical strength and disintegrates. This may be explained by the formation of fresh  $\text{Fe}_3\text{O}_4$  from the iron present, and we are of the opinion that small particles of carbon deposit inside the catalyst between the newly formed  $\text{Fe}_3\text{O}_4$  crystals.

#### Yields from Semi-plant-scale Experiments

As an average specific yield with iron catalysts, we obtained approximately 80-85 grams of hydrocarbons per cubic meter of ideal water-gas when we operated in one stage at 19 atmospheres and a space velocity of 300 in a converter containing approximately 3 liters of catalyst. These conditions exclude the possibility of carbon deposition. The water contained between 4-10 percent of ethyl alcohol and acetone, so that the total yield was approximately 90 grams per cubic meter of water-gas. If the gasol is taken

into consideration also, the total yield under the conditions mentioned above rises to 105 grams. The conversion yield comes up to approximately 160 grams per cubic meter of converter ideal water-gas.

### Two-stage Operation

Since the converter end-gas has the composition  $\text{CO}:\text{H}_2 = 1:2$  or  $1:>2$  when operating under the conditions described above, in order to obtain a maximum yield of useful products, a second stage containing cobalt catalysts was added operating at atmospheric pressure.

The cobalt catalyst used up to 80 percent of the  $\text{CO} + \text{H}_2$  content of the end-gas. Since the first stage utilized approximately 50 percent of the  $\text{CO} + \text{H}_2$ , this means that approximately 90 percent of the total  $\text{CO} + \text{H}_2$  charged to the converter is used up when the first iron stage is followed by a second cobalt stage. The following experiment was carried out: First stage - 3 liters of catalyst; diameter of tubes, 15 mm.; fused-iron catalyst No. 997; standard water-gas; 19 atmospheres pressure; approximately  $270^\circ\text{C}$ . About 86 percent of the  $\text{CO} + \text{H}_2$  mixture was converted. The analysis of the starting gas was as follows:

	<u>Percent</u>
$\text{CO}_2$	4.92
$\text{O}_2$	0.0
$\text{H}_2$	51.8
$\text{CO}$	42.95
Paraffin hydrocarbons	0.19
$\text{N}_2$	0.86

After the gas has passed the first stage, a gas of the following composition leaves the converter:

	<u>Percent</u>
$\text{CO}_2$	19.60
$\text{O}_2$	0.0
$\text{H}_2$	50.8
$\text{CO}$	26.8
increase	0.20
Paraffin hydrocarbons	2.40
$\text{N}_2$	0.20

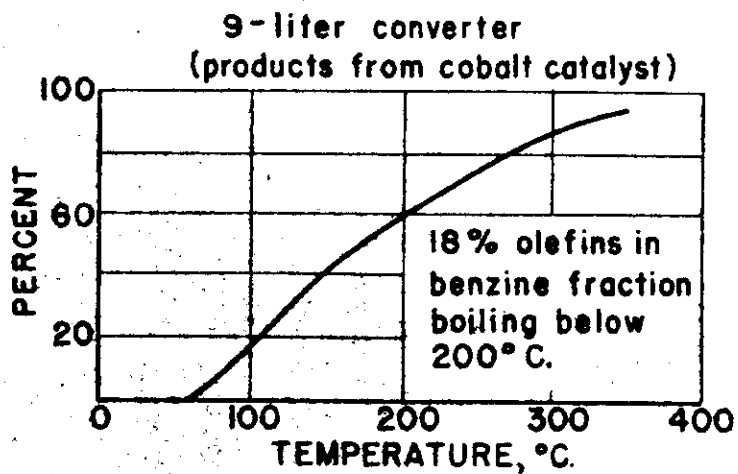
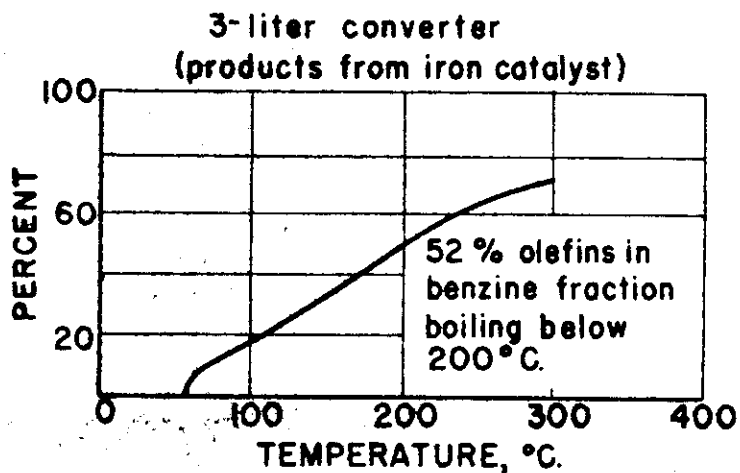
total volume of this end-gas was 34 cubic meters, that of the starting gas, 25 cubic meters. The contraction was approximately 40 percent, and in this stage about 90 to 100 grams of products per cubic meter of water were formed. At this point, the CO-H<sub>2</sub> ratio had the proper value so that it could be used over a cobalt catalyst. After releasing the pressure and removing the products of the reaction at approximately 10°C., the gas was led into the second stage in which cobalt catalyst filled the tubes of a 9-liter converter. Another 40 to 60 grams of product per cubic meter were formed. The final gas had the following composition:

	<u>Percent</u>
CO <sub>2</sub>	41.2
O <sub>2</sub>	0.0
H <sub>2</sub>	24.6
CO	18.0
increase	3.0
Paraffin hydrocarbons	12.20
N <sub>2</sub>	4.00

The total volume of this final gas was 16.5 cubic meters. About 86 percent of the CO + H<sub>2</sub> was converted.

The total yield obtained from both stages was between 135 and 150 grams per cubic meter of water-gas. The main reason for this efficient gas consumption is that the cobalt catalyst could be used with the gas which left the first stage of the apparatus. The two curves in Figure 13 indicate the boiling range of the products.





**Figure 13.-Boiling range of products from hydrocarbon synthesis.**

EXPLANATION OF SYMBOLS USED IN TEXT

1. Technically pure hydrogen.

Analysis =	CO <sub>2</sub>	O <sub>2</sub>	H <sub>2</sub>	CO	CH <sub>4</sub>	N <sub>2</sub>
	0.5		95.2	1.0	1.0	2.6
2. Water-gas	4.5		51.6	42.6	0.2	1.1
2a. Ideal water-gas			50	50		
3. Synthesis gas	1.6		71.0	26.6	0.4	0.4
3a. Ideal synthesis gas			66.7	33.3		

4. Specific yield = g. Pr./m<sup>3</sup> ideal  $\left\{ \begin{array}{l} \text{Water-gas} \\ \text{Synthesis gas} \end{array} \right.$

5. Conversion yield = g./Pr./m<sup>3</sup> converter ideal  $\left\{ \begin{array}{l} \text{Water-gas} \\ \text{Synthesis gas} \end{array} \right.$

6. Space time yield = kg. Pr./m<sup>3</sup>/catalyst per day.

7. Space Velocity = liter gas/liter catalyst/hour.

8. Liquid yield = C<sub>5</sub>+/m<sup>3</sup> ideal gas.

9. Gasol = C<sub>3</sub> + C<sub>4</sub>