

We have endeavored to activate such an inactive 1:1 catalyst, for example, by boiling it with water in order to remove the possible unfavorable excess of alkali. No improvement of the catalyst resulted through this measure. It has to be mentioned here, however, that we did not succeed in removing any residual precipitating salts out of a kieselguhr catalyst which was dried at 105°C. This may be seen from the following experiment.

A 1:1 kieselguhr catalyst precipitated with Na_2CO_3 was dried in the filter funnel, and then subjected to drying in an oven at 105°C. The moist precipitate still reacted stronger alkaline when tested with litmus. After the drying, the catalyst was boiled for some time with water in order to remove the residual alkali. Neither the aqueous filtrate nor the catalyst reacted alkaline when tested with litmus after the boiling operation had been carried out. This was an indication that the residual alkali was held firmly by the catalyst (the kieselguhr) after the drying operation.

Considering that such an ineffective 1:1 kieselguhr catalyst could contain too little alkali, we have taken already dried catalysts and added some additional alkali to them. Thus, we added 0.1 percent K_2CO_3 referred to the total weight of the catalyst. When the dried catalyst was treated with alkali, we found that the alkalization had no effect on the activity, neither was the activity effected when 0.1 percent K_2CO_3 was added to the still moist precipitate.

A decrease of the kieselguhr quantities did not improve the iron-kieselguhr catalyst any further.

2. 1(4 Fe-1 Cu-1 MnO): 0.5 kieselguhr catalyst.

A 1(4Fe-1Cu-1MnO):0.5 kieselguhr catalyst was only little active. It only gave 11 percent contraction at 235°C. Strangely enough, no water formation was observed with this catalyst. This peculiarity of the carrier-catalyst was not yet pronounced with the small quantity of kieselguhr used.

3. 1(4Fe-1Cu-1MnO): 2 kieselguhr catalyst.

Better yields than with a 1:1 kieselguhr catalyst were obtained with a 1(4Fe-1Cu-1MnO):2 kieselguhr catalyst. With the application of only 4 grams of iron in the catalyst quantity and 4 liters per hour of gas at 235°C., the maximum contraction after 16 hours was 32 percent. At this point, the catalyst gave 47 grams of liquid products per cubic meter in addition to 30 grams of water (inclusive water vapor). Although this yield is smaller than that obtained with the carrier-free precipitated catalysts, the result may be looked upon as favorable anyhow, because it was obtained with the application of only 4/10 of the otherwise customary quantity of iron, and also at a considerably smaller CO consumption. In the present case, approximately 55 percent altogether of the furnished CO were used up. At a complete CO usage, a yield of 85 grams per cubic meter would result. In comparison with this, a carrier-free catalyst gave a yield of 55 grams per cubic meter. The total CO consumption was approximately 90 percent of the furnished CO. Here a yield of 61 grams would result for a complete conversion of the CO.

At 225°C., and with a 1:2 catalyst, a contraction of 20 percent was still obtained for 4 liters per hour of gas, and 26 percent contraction for 2 liters per hour. The corresponding yields were 27 respectively 36 grams per cubic meter.

By using a larger catalyst quantity corresponding to 16 grams of iron, we succeeded with a 1:2 catalyst to increase the yield some more, and at the same time, we were able to suppress the reaction temperature somewhat. The following results were obtained:

Temp., °C.	gas rate liters/hour	Contraction, percent	Liquid products, g./m ³
215	4.3	28	35
225	4.1	33	55

These results may be looked upon as favorable from the point of view of CO usage, and the water formed during the reaction.

In most cases, the 1:2 kieselguhr catalyst was reproducible. The lifetime of the catalyst so far cannot be regarded as satisfactory up to now. With a catalyst quantity corresponding to 4 grams of iron at an hourly gas rate of 4 liters after already 120 hours at 235°C., a decrease in the contraction was observed. Apparently, a reaction temperature of 235°C. is too high a temperature to employ when working with kieselguhr catalysts. More favorable results were obtained at 225°C., working temperature, although a smaller conversion was observed when the same quantity of iron, namely 4 grams, was used.

No experiments have been conducted on the regeneration of the 1:2 catalyst.

4.1 (4Fe-1Cu-1VnO):3 kieselguhr catalyst.

When we used this catalyst, we could only charge the tube with a catalyst quantity corresponding to 3.3 grams of iron, extending over a length of 30 cm.; the hourly gas rate was correspondingly decreased to 3 liters. The 1:3 catalyst at 225°C., gave, under the most favorable conditions, a contraction of 28 percent and correspondingly a yield of 45 grams of liquid products per cubic meter. Along with the liquid products, 40 grams of water per cubic meter were formed, so that water and oil were produced in the ratio of 1:1.1. We investigated this catalyst at 235°C., and found more unfavorable results, namely only 30 grams of liquid products per cubic meter, were obtained. This was attributed to the shorter lifetime of the catalyst. The contraction decreased from 30 to 26 percent within 70 hours of operation.

5.1 (4Fe-1Cu-1VnO):4 kieselguhr catalysts.

A further dilution of the catalyst to 1:4 proved to be unfavorable. By doing this, the time of induction of the catalyst was considerably prolonged. For example, such a catalyst when using an equivalent quantity of iron of 2 grams, and 4 liters per hour of gas, and 235°C., gave 3 percent contraction after 46 hours, 9 percent after 118 hours, and after 142 hours, only 12 percent. At 245°C., such a catalyst containing 4 parts of kieselguhr, gave 20 percent maximum contraction. We did not make any yield determination for the experiments with the 1:4 catalysts on account of the low degree of conversion. Superficially judged, the catalyst behaved similarly as did the previously described catalysts, namely it had the ability to form water during the reaction from the very beginning.

With kieselguhr catalysts of composition 1:5 and 1:8, using the same normal catalyst layer length, only one respectively 0.5 gram of iron could be used. With an hourly gas rate of 2 liters, these catalysts were tested at 250°C., and did not give a contraction surpassing 6 percent. Nevertheless even these catalysts formed oil and water.

F. General Considerations on the Kieselguhr Precipitated Catalysts.

As has been mentioned in previous paragraphs, the kieselguhr catalysts offer the possibility (even if only theoretical) to increase the yields of liquid products. This is due to the fact that they convert less CO to CO₂ than do the carrier-free catalysts. In order to use the experiences made with the kieselguhr catalysts on the technical scale, 2 hindering properties of the catalysts have to be overcome, namely, the unsatisfactory activity and the comparatively short lifetime.

We have tried by several means to increase the activity of the kieselguhr catalysts. First of all, we studied the influence of subsequent alkalization. The catalysts as previously mentioned gave contractions up to 30 percent even without alkalization, or in other words, contractions of the same order of magnitude as corresponded to the carrier-free catalysts. The CO conversion was, however, much lower on account of the prevalent water formation. A series of experiments showed that the activity of such a carrier catalyst could not be improved by subsequent addition of alkali. It gave a maximum contraction of around 30 percent. When the alkali (K₂CO₃) was added in larger quantities (one percent) to the already dried catalyst (at 105°C.) in some cases, we observed that the alkali addition had even a damaging effect, and it led to catalysts of lesser activity. Smaller additions remained without influence. If the alkali was added to the still moist catalyst immediately after precipitation, additions amounting to 0.1 to 0.2 percent did not cause any noticeable effect. With additions amounting to 0.5 to one percent, we observed that the reaction showed a tendency to take the course over the CO₂ formation again.

These facts were especially outstanding with catalysts which were precipitated with ammonia. The simultaneous or separately precipitated ammonium carbonate kieselguhr catalysts of composition 1:1 to 1:2 were only mildly active in the absence of alkali. At 235°C. and 4 liters of gas per hour, they gave a contraction of 15 to 20 percent. When alkali was added to this catalyst, we could observe that the water formation decreased as the alkali added to the catalyst was increased. With approximately 0.5 to one percent K₂CO₃, the visible water formation stopped entirely.

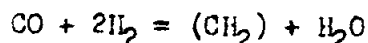
We have furthermore tried to utilize the mixed gas to a greater extent when using iron-kieselguhr catalysts (in one stage), by using correspondingly wide and longer catalyst tubes and larger catalyst quantities. On the other hand, we tried to increase the conversion by reducing the gas rates and keeping the catalyst layer length at its normal value. A noticeable increase in contraction was observed in any case. The maximum contraction with kieselguhr catalysts which was reached in this manner amounted to 37 percent. A more thorough investigation showed why a further increase in contraction is no longer possible. We found that the CO under the given conditions is converted to a large degree

however, not under increased water formation, but rather increased CO₂ formation. It is, therefore, apparent that the carrier catalyst approaches more and more the behavior of the carrier-free metal catalyst when the conversion of the CO increases. In Section VIII, page 114 of the original manuscript, the conversion conditions for a kieselguhr catalyst are described when the catalyst layer length varied. The experiment discussed there, indicated that the water formed in the first section of the catalyst is decomposed again in the following sections, and enters into a reaction with the CO according to the water-gas reaction.

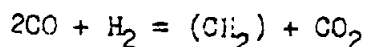
In spite of the difficulties mentioned, we are of the opinion that by continuing the experiments with the iron catalysts containing kieselguhr, we may eventually obtain yields which are higher on the average than 55 grams of liquid products per cubic meter.

(Bahr) VII. Course of the Reaction with the Iron Catalyst.

Between the carrier-free iron catalysts and the cobalt catalysts used for the benzene synthesis, a remarkable difference exists, namely, the oxygen contained in the CO is chiefly converted into CO₂ when iron catalysts are used, whereas with cobalt catalysts (as well as nickel catalysts) practically only water is formed. The course of the reaction with cobalt catalysts follows the following equation:



whereas for iron, the reaction chiefly proceeds according to:



This equation states that with iron catalysts for every molecule of hydrocarbons one molecule of CO₂ is produced, that is, in presence of iron catalysts only 1/2 of the CO goes to synthetic products of some nature. As already pointed out, the reaction with iron catalysts does not proceed exclusively according to the equation given above, but here also, varying with experimental conditions, water is formed to a greater or lesser extent. In general, one can say that an iron catalyst converts larger quantities of the CO-oxygen to water when:

1. The reaction temperature is high;
2. The exit gas is rich in hydrogen;
3. The catalyst layer length is longer for a certain flow velocity; in other words, the smaller the gas rate is for a given catalyst layer length.

In order to bring out the differences between iron and cobalt catalysts more closely, Table 18 shows experiments with an Fe-Cu-MnO catalyst as well as with a cobalt-manganese and cobalt-thorium catalyst. The conversion of the various gas constituents was calculated in the following manner: The corresponding CO conversion into CO₂ is found from the analysis of the reaction gases under consideration of the contraction. In this way, the percentage of the converted CO is found also. The difference of both quantities referred to 100 parts gives the percentage of CO used up. This comprises the total synthetic products, including the paraffin which remains in the catalyst. It also takes into consideration the carbon deposited on the catalyst as elementary carbide carbon and originating from the CO. In order to ascertain how much oxy-

gen (from the CO) went to water, we calculated at first how much CO-oxygen went into CO₂. The difference between this value as compared to 100 parts gives the percent of oxygen converted into water, (including the perhaps formed oxygen containing synthetic products). Although the calculations outlined here incorporate some inherent errors (for instance, the measurement of contraction in gas analysis), we have found it sufficient to obtain a general picture on the course of the conversion.

Table 18.

Comparison of Gas Conversion (Mixed Gas) With an Fe-Cu-MnO₂ and Cobalt-Manganese (15%) and Cobalt-Thorium (18%) Cat.^{1/}

	Fe-Cu-MnO + 1% K ₂ CO ₃	Fe-Cu-MnO + 1% K ₂ CO ₃	Cobalt- Manganese	Cobalt- Thorium
Temperature, °C.	220	220	195	190
Liters per hour.	4.4	2.2	4	4
Contraction, percent	30	36	70	70
CO conversion, percent to CO ₂	43.4	40.5	1.1	1.6
Unchanged CO Synthese (difference)	7.2 49.4	6.5 53.0	15.6 84.4	12.3 87.7
O ₂ conversion, percent to H ₂ O.	6.0	12.5	83.3	86.1
Liquid products, g./m ³	50.0	49.0	98.7	94.5
Reaction water, ccm/m ³ ^{2/}	16	28	--	--

^{1/} Fe-Cu-MnO (4:1:1) + 1% K₂CO₃ was precipitated with NaOH from the nitrates. The cobalt catalysts were precipitated with soda, and the nitrates, and the details are described in the experimental description of Dr. Koch (1932).

^{2/} Including the water of humidification of the not-dried starting gas. The water contents amounted 8 to 12 cc/m³.

The comparison of both contact species in Table 18 shows that the cobalt catalysts practically do not form any CO₂. Hence, they convert almost all the CO-oxygen into water. In contrast to the cobalt catalysts, the iron catalysts form a considerable part of CO₂. With them, only approximately half of the CO is used for the synthesis as such. Only approximately 16-12 percent of the CO-oxygen is converted into water when iron catalysts are used. By comparing column one with column 2, it may be observed that by reducing the gas rate down to 1/2, the water formation doubles approximately. The water formation increases from 16 to 28 cc. of water per m³ of gas. On account of the prevalent CO₂ formation, the yields with iron catalysts are only approximately half those of the cobalt catalysts. This different reaction mechanism which forms CO₂ rather than H₂O is the chief reason why iron catalysts give lower yields than cobalt catalysts. The following example will point this out: Referring to

Table 18, the mentioned cobalt-manganese catalyst acted on a mixed gas and gave 70 percent contraction. The reaction gas had the composition:

	CO ₂	SKW	O ₂	CO	H ₂	CH ₄ -KW	<i>Number</i> C-Zahl	N ₂
Percent	10.8	3.2	0.0	13.6	32.8	16.2	1.56	23.4

It is evident that the catalyst uses CO and H₂ approximately in the ratio of 1:2 that is, very close to the original ratio of the two gases in the mixed gas. The CO-H₂ ratio in the reaction gas is still 1:2.4. Theoretically, the possibility exists to remove the hydrocarbons from the reaction gas and obtain a more complete conversion by recycling the unreacted components once more. An essentially different picture is obtained from the reaction gas analyses of the iron catalysts. The catalyst mentioned in Table 18 gave 30 percent contraction at 220°C., and a reaction gas of the following composition:

	CO ₂	SKW	O ₂	CO	H ₂	CH ₄ -KW	<i>Number</i> C-Zahl	N ₂
Percent	21.8	0.7	0.3	3.2	58.8	5.4	1.72	9.8

Here, 93 percent of the CO converted (3.2 percent CO in the end-gas). The CO:H₂ ratio used up was, however, not in the ratio of 1:2. On account of the greater CO₂ quantity formed, more CO was used up with respect to hydrogen than would correspond to 1CO:2H₂. Consequently, the final gas has a CO:H₂ ratio of 1:18.

Another experiment is discussed during which (on account of the low reaction temperature of 210°C.) a somewhat larger part of the CO was not converted. For this experiment (Table 19, No. 2), the following end-gas analysis was obtained with 26 percent contraction:

	CO ₂	SKW	O ₂	CO	H ₂	CH ₄ -KW	<i>Number</i> C-Zahl	N ₂
Percent	13.2	0.3	0.2	9.0	59.8	2.5	2.75	10.0

The analysis shows that the shifting of the ratio of CO to H₂ in the end-gas is very considerable for this catalyst (approximately 78 percent of the CO was converted). The ratio is only still 1:6.6 in the final gas.

The following experiment finally shows that the shifting of the ratio of CO to H₂ was already noticeable in the first stages of the reaction. An Fe-Cu-MnO catalyst was tested at 220°C., and it gave 10 percent contraction at a certain gas rate. The reaction gas had the following composition:

	CO ₂	SKW	O ₂	CO	H ₂	CH ₄ -KW	<i>Number</i> C-Zahl	N ₂
Percent	8.1	0.0	0.4	21.4	60.1	2.8	1.43	7.2

Although only 26.5 percent of the CO was converted, the CO₂ to H₂ ratio in the reaction gas had shifted already from 1:2 (mixed gas) to 1:2.8.

In contrast to the cobalt catalyst which uses CO and H₂ approximately in the ratio of 1:2, the gas composition changes very rapidly all along the course of the reaction tube when iron catalysts are used. This is true even for very small contractions, and becomes more pronounced as the conversion increases. With an iron catalyst, therefore, only the first zones of the catalyst receive a gas of the original composition of CO to H₂. The following zones receive gases which are more and more enriched in H₂ and are leaner in CO. To convert such a gas to liquid products, obviously different reaction conditions are necessary than were required for the original gas.

Considering the comparatively high CO usage in connection with iron catalysts, it is obvious that a gas richer in CO than ordinary mixed gas should be used. This is evident from the equation, $2CO + H_2 = CO_2 + CH_4$. We have, however, found that the activity of the iron catalyst decreases extremely fast when such a gas is used. The activity cannot be maintained even when the gas rate is reduced. Already when water-gas is employed, this rapid decrease of activity with the iron catalysts is noticeable. The mentioned shifting of the CO to H₂ ratio in the gas in connection with iron catalysts is the reason for not resorting to recycling in order to obtain a higher yield of liquid products and a more complete conversion.

In the following, a summary of the reaction gas analyses is given as it is obtained with an iron-copper-manganese catalyst at a temperature of 190 to 230°C. In order to facilitate working at a temperature of 190°C., a larger catalyst quantity was used for this experiment. The catalyst used corresponded to 120 grams of Fe-Cu-MnO. The analyses show how comparatively independent of the reaction temperatures the final gases become richer in H₂ and CO.

Temp. °C.	Gas rate, liters/hr.	Contr., percent	CO ₂	SKW	O ₂	CO	H ₂	CH ₄ -KW	<i>Number</i> C-Zahl	N ₂
190	1.5	20	14.8	0.5	0.2	12.8	61.5	1.5	2.33	8.8
200	2.7	24	19.8	0.2	0.2	6.8	61.1	2.5	2.20	9.4
220	3.9	32	22.4	0.3	0.1	1.7	60.0	6.6	2.55	8.9
230	4.6	33	21.6	0.6	0.2	1.9	55.4	10.5	1.46	9.3

(Bahr) VIII. Experiments on Water Formation.

As is mentioned already in Section VII, the smaller yields obtained with iron catalysts as compared to cobalt catalysts are caused chiefly because the reaction yields considerable CO₂ and not water. It has already been pointed out that with iron catalysts under certain conditions the formation of water may be observed. We investigated this some more and in the following series of experiments, we have attempted to prevent the CO₂ formation on the catalyst in order to obtain a higher yield of liquid products. We investigated the following:

1. The influence of gas composition (of CO to H₂ ratio) upon the CO₂ and water formation.
2. The influence of alkali contents upon the CO₂ formation on the iron catalysts.

3. The CO₂ formation on the iron catalysts by using a CO₂ containing initial gas.

4. The CO₂-water formation on iron catalysts containing carriers.

1. A The Influence of Gas Composition (CO to H₂ ratio) Upon the CO₂ and Water Formation.

During the following experiments, Fe-Cu-K₂O (4:1:1 containing one percent K₂CO₃) catalysts were used. They were prepared by precipitation from the nitrates with sodium hydroxide. According to our experiences at that time, we have found this to be the most favorable way of preparation. The comparatively high alkali content of one percent had an advantageous effect on NaOH precipitated catalysts. Later on, however, we used catalysts which were precipitated with soda, and we found that these catalysts are still more favorable. These catalysts should only be weakly alkalized containing no more than 0.1 to 0.2 percent K₂CO₃.

1. Experiments with Mixed Gas.

The mixed gas used had the following composition:

	CO ₂	SKW	O ₂	CO	H ₂	CH ₄ -KW	<i>Number</i> C-Zahl	N ₂
Percent	2.2	0.0	0.0	30.6	58.1	1.5	--	7.6

The ratio of CO to H₂ was equal to 1:1.9. To start with, we investigated the influence of the experiment temperature on the course of the CO conversion in the mixed gas. In order to extend the experiments and to be able to vary the temperature and gas velocity in wide ranges, a comparatively large contact quantity (120 grams to 80 grams of iron) was used. The results of the experiments are given in Table 19. They are arranged in increasing reaction temperatures. The table shows, in the first place, that at low temperatures of 200-210°C., a comparatively large quantity of the CO remains unconverted. This is mainly caused by the fact that the iron catalysts in this range of temperature show only little activity. In addition to that, we want to point out that one cannot succeed according to our present experiences to get an iron catalyst started at 200 or 210°C. over a period of time of 30 to 60 hours. We found that the time of induction is longer than that. The catalysts are first allowed to act at 220-230°C., up to such a time that they give a contraction of 20 to 25 percent. Thereafter, the temperature is lowered. The table then shows how, with increasing reaction temperature, the quantity of CO converted to CO₂ decreases when compared to the CO required for the synthesis. At 200-210°C., approximately the same amount of CO is converted to CO₂ as is converted to hydrocarbons. At these temperatures, no water was formed yet. Practically all of the oxygen went to CO₂. At 220°C., 6 percent more of the CO was used for the synthesis proper, at 230°C., 10 percent, and at 240°C., 21 percent more CO was used for the synthesis than was used for CO formation. In accordance with all that, an ever increasing quantity of water formed with the oil. The horizontal row indicates what part of the CO-oxygen was converted into water at the various temperatures. Experiments 6 and 7 bring out the influence of the flow velocity.

At 9.8 liters of gas per hour and 240°C., approximately 40 percent of CO went to CO₂, whereas 54 percent was used for the synthesis. At 1.6 liters of gas per hour, approximately 1/3 of the CO went to CO₂ and 60 percent went into the synthesis. From the table, it is not apparent that the yield of liquid products was increased, however. This is apparent by comparing experiments 3 and 5. For experiment 3, 49 percent and for experiment 5, 59 percent of the CO was used for the synthesis. In spite of that, the yield of liquid products for both experiments was 50 respectively 49.5 g./m³ of gas.

Table 19.
Influence of Temperature Upon CO Conversion (Mixed Gas) With
Fe-Cu-2/nO Catalysts Containing One Percent K₂CO₃

	1	2	3	4	5	6	7
Temperature, °C.	200	210	220	230	240	240	240
Hours of operation	263	191	436	602	741	864	858
Liters per hour	2.7	4.0	4.4	4.6	3.4	9.8	1.6
Contraction, percent	24	26	30	32	36	30	38
CO conversion, percent to CO ₂	41.8	38.6	43.4	41.8	37.7	39.4	35.5
Unchanged CO	17.0	22.1	7.2	6.5	3.8	6.5	4.5
Synthesis (difference)	41.2	39.3	49.4	51.7	58.5	54.1	60.2
O ₂ conversion percent to H ₂ O	0.6	0.7	6.0	9.9	20.8	14.7	24.7
Reaction water, cc/m ³ ^{1/}	12.3	10.7	16.4	26.5	42.9	26.7	n.b.*
Liquid products, g./m ³	22.7	29.6	50.0	49.7	49.5	n.b.	n.b.
Calculated theoretical yield grams of hydrocarbons/m ³	73.5	69.4	87.5	92	99.8	92.2	102.7
Reaction gas							
CH ₄ contents, percent	2.6	2.5	5.4	10.5	10.9	8.1	14.3
Carbon number	2.20	2.75	1.72	1.46	1.37	1.34	1.46

^{1/} Including humidification water.

If the "theoretical yield" of gaseous, liquid, and solid hydrocarbons is calculated for the synthesis on the basis of the CO contents (expressed in grams of hydrocarbons per cubic meter of gas); then on comparing these calculated yields with the liquid products obtained, the difference between the total yield and the liquid product yield should account for the gaseous hydrocarbons and other compounds formed. The table shows that for experiment temperatures of 200 to 210°C., comparatively larger quantities of products other than liquid are formed. At 200°C., they amount to approximately 51 grams and at 210°C., they amount to 40 g./m³. Since the reaction gas from these experiments contains a comparatively small amount of methane hydrocarbons, one is justified to assume that during the reaction larger paraffin quantities remained in the catalyst when the working temperature was lower. For the following experiments which were con-

*n.b. = not observed

ducted between 220-240°C., we observed increasing amounts of methane hydrocarbons in the reaction gas. The carbon number of the hydrocarbons decreases with increasing temperature. The difference between the calculated yield and the experimental yield of liquid ~~of-liquid~~ product yield obviously is caused here chiefly by the increased formation of gaseous hydrocarbons. The gaseous hydrocarbons may be gasol or methane. If experiments 3 and 5 are compared one with another, one observes that during experiment 3, 37 grams of products other than liquid were formed, and for experiment 5, 50 grams of synthesis products were formed which were not liquid. The analyses of the reaction gases show that during experiment 5, approximately twice as many methane hydrocarbons were formed as were during experiment 3. By raising the temperature, the conversion of the CO during the synthesis appears more complete. Obviously however, this larger conversion did not cause an increase in yield of liquid products, but only increased the portion of gaseous hydrocarbons formed.

In particular, we want to refer back to experiments 6 and 7 which are listed in the table. From them, the influence of the flow velocity upon the nature of the conversion at 240°C., may be observed. One recognizes that by reducing the hourly throughput from 9.8 to 1.6 liters, the contraction increases from 30 to 38 percent; and 60 percent of the CO is consumed during the synthesis. From this data, a theoretical yield of 103 grams of hydrocarbons per cubic meter of gas can be calculated. No yield determination was made. However, it is already apparent from the gas analysis that for this slow gas throughput, a large amount of gaseous hydrocarbons had formed (14.3 percent methane hydrocarbons).

From a further series of experiments, one can observe that for still lower experiment temperatures, the benzene formation on the iron catalyst proceeds predominantly over CO₂ formation. The results of the experiments are tabulated in Table 20. In order to be able to lower the experiment temperature considerably, we used for this experiment a Fe-Cu-MnO catalyst which contained 5 percent K₂CO₃ (90 grams, 60 grams of iron). We initiated the catalyst at 220°C., whereafter the temperature was lowered gradually-the lowest experiment temperature was 170°C. For this temperature and a gas rate of approximately one liter per hour, still a contraction of 11 percent was observed. On account of the low throughput, we decided not to make a yield determination, and we merely checked up on the nature of the end-gas.

Table 20
CO Conversion (Mixed Gas) on Fe-Cu-MnO + 5% K₂CO₃ at Low Temperatures

	1	2	3	4
Temperature, °C.	220	200	190	170
Hours of operation	41	48	140	185
Liters per hour	4.0	4.1	1.2	1.1
Contraction, percent	31	22.1	22.8	10.8
CO conversion, percent to CO ₂	44.5	37.6	44.0	19.3
Unchanged CO	6.2	23.8	10.6	61.0
Synthesis (difference)	49.3	38.6	45.4	19.7
O ₂ conversion, percent to H ₂ O	4.8	1.0	1.4	0.4
percent to CO ₂	89.0	75.2	88.0	38.6

Table 20 shows (as is apparent from earlier experiments already) that in the range of the low reaction temperatures, the reaction practically only proceeds over CO₂ formation. For instance, at 170°C., the CO quantity converted to CO₂ was approximately the same as the CO₂ quantity converted to hydrocarbons. This condition does not change appreciably at 190 to 200°C., but at 220°C., we could observe that the quantity of CO converted to hydrocarbons was larger than the quantity of CO converted to CO₂. At this temperature too, we could observe the formation of small water quantities. Originally, we were inclined to believe that the differences in the reaction mechanism between iron as compared to cobalt catalysts was mainly due to the higher reaction temperatures which the iron demands. The above described experiments point out, however, that the iron catalyst under investigation did not form increasing quantities of water when it was permitted to work in the reaction temperature range of the cobalt catalysts. In fact, we observed just the opposite, namely, that in this temperature range CO₂ was formed exclusively. The lower, the reaction temperature, the more CO₂ was formed.

2. Experiments with H₂-rich Gas.

For the following experiments, instead of using mixed gas, a H₂-rich gas was employed. We intended to find out whether the CO₂ formation could be suppressed by using a larger excess of H₂. The gas employed had a CO to H₂ ratio of 1:4.2. The theoretical yield of liquid products may be calculated to be 108 grams of hydrocarbons per cubic meter. The composition of the gas was as follows:

	CO ₂	SKW	O ₂	CO	H ₂	CH ₄ -KW	^{Number} C-Zahl	N ₂
Percent	0.0	0.0	0.0	18.6	79.2	--	--	2.2

The catalyst quantity used was 60 grams which was equivalent to 40 grams of iron. The experimental results are arranged according to reaction temperatures in Table 21.

Table 21
CO Conversion When Using H₂-rich Gas (CO-H₂ = 1:4.2) on Fe-Cu-MnO Catalysts Containing One Percent K₂CO₃

	1	2	3	4	5
Temperature, °C.	200	210	220	230	240
Hours of operation	593	473	353	113	287
Liters per hour	4.0	4.1	3.9	3.7	7.9
Contraction, percent	19.7	20.6	23.1	25.0	22.7
CO conversion, percent to CO ₂	32.8	45.1	41.4	42.5	41.4
Unchanged CO	28.0	3.8	6.5	7.5	7.0
Synthesis (difference)	39.2	51.1	52.1	50.0	51.6
O ₂ conversion, percent to H ₂ O	6.4	6.0	10.7	7.5	10.2
Reaction water, cc/m ³ ^{1/}	16.6	24.1	28.3	25.4	23.8
Liquid products, g./m ³	16.2	35.1	35.9	29.9	29.3
Reported theoretical yield, g. CH ₂ /m ³	42.6	55.5	56.5	54.0	56.0
Reaction gas: CH ₄ contents, percent	3.5	2.2	1.3	2.6	1.9
Carbon number	1.0	2.27	2.08	1.65	1.89

^{1/} Including humidity.

In general, Table 21 shows that an H_2 -rich gas does not give any more favorable results as far as the suppression of the CO_2 is concerned. By using an H_2 -rich gas, the water formation seems to set in somewhat earlier. We could observe water already at 210 and 200°C. However, at higher temperatures, as for instance, 230 and 240°C., the reaction water predominantly proceeds the CO_2 formation. The comparison with Table 19 (mixed gas experiments) shows that an H_2 -rich gas does not give any better results than does a mixed gas as far as water formation is concerned at higher temperatures. Some additional interesting information may be obtained by studying Table 21. It appears that a H_2 -rich gas has a tendency to produce comparatively large quantities of gaseous hydrocarbons in addition to the usual liquid products. This may be seen by comparing the calculated theoretical yields with the observed yields of liquid products. It is remarkable also that for low temperatures, 200°C., considerable difference exists between both values. In general, the experiments may be summarized as follows: When using a H_2 -rich gas, the degree of conversion of CO to liquid products is not essentially larger than the degree of conversion with mixed gas. With a mixed gas containing 30 percent of CO (compare Table 19) on the average, 50 grams of liquid products per cubic meter are obtained. If this figure is referred to CO_2 , it corresponds to a degree of liquefaction of 57 percent. For the H_2 -rich gas (18.6 percent CO), the yields amounted to 35 to 36 grams per cubic meter, which corresponds to a degree of liquefaction of 65 to 66 percent when referred to CO_2 .

In general, we want to bring attention to the percent contractions obtained by using the H_2 -rich gas. On the average, we observed 20 to 23 percent, that is, numerically it was approximately 2 to 5 percent above the CO contents of the initial gas. The situation was similar for the mixed gas. With mixed gas, the average maximum contraction was 30 to 35 percent with an initial CO content of 28 to 30 percent in the synthesis gas.

It should be mentioned here that the iron catalyst required a longer time of induction when used with H_2 -rich gases as compared to the time of induction for mixed gas.

The experiments with H_2 -rich gas were repeated with another Fe-Cu-MnO catalyst containing one percent K_2CO_3 (8 grams of iron). We wanted to investigate how the gas composition shifts at elevated temperatures (up to 260°C.). We obtained the following picture, (Table 22). With increased temperature, the CO_2 contents diminished and for the maximum case (260°C.), it decreased down to 35 percent of the originally employed CO. At this point, 57 percent of the CO was used for the synthesis. Such and similar results were observed earlier with mixed gas at 240°C., when larger catalyst quantities were employed, (compare Table 19, Experiment 5).

Table 22. - CO Conversion with H_2 -rich Gases (CO to $H_2 = 1:4.2$)
On Fe-Cu-MnO Catalysts Containing 1% K_2CO_3 , for a Temperature Range of 230-260°C.

	1	2	3	4
Temperature, °C.	230	240	250	260
Liters per hour	3.7	4.0	4.2	4.0
Contraction, percent	21.3	19.8	24.4	25.8
CO conversion, percent to CO_2	41.3	44.0	39.7	34.9
Unchanged CO	9.0	6.4	7.4	7.9
Synthesis (difference)	49.7	49.6	52.9	57.2
O_2 conversion, percent to H_2O	8.4	12.8	13.2	22.3

3. Experiments with CO-Deficient Gas.

The conditions for conversion were investigated again with a starting gas containing CO and H₂ in the ratio of 1:8.5. The gas had the following composition:

	CO ₂	SKW	O ₂	CO	H ₂	CH ₄ -KW	C-Zahl	N ₂
Percent	0.0	0.0	0.3	10.4	88.3	--	--	1.0

The theoretically possible yield for this gas was 61 grams of hydrocarbons per cubic meter.

The experiments carried out in this connection followed those described in Table 21, without timely interruption. The same catalyst was used without a previous regeneration. The catalyst (60 grams = 40 grams of iron) at this time had been in operation already for 980 hours. A decrease of its activity had not been observed up to this time.

By using the CO-deficient gas, the experimental results of Table 23 were obtained.

Table 23.
CO Conversion for a CO-deficient Gas (CO-H₂ = 1:8.5)
on Fe-Cu-MnO Catalysts Containing 1% K₂CO₃

	1	2
Temperature, °C.	220	220
Liters per hour	4.3	5.3
Contraction, percent	13.9	18.2
CO conversion, percent to CO ₂	34.6	27.0
Unchanged CO	8.6	9.6
Synthesis (difference)	56.7	53.4
O ₂ conversion, percent to H ₂ O	22.1	36.4
Liquid products, g./m ³	n.b.*	19.7
Reaction water, cc/m ³	--	23.2

Table 23 shows that it was possible to decrease the conversion of CO to CO₂ to a value of 27 percent when using a large excess of H₂. For the same experiments, 63 percent of the CO went to synthesis hydrocarbons. Roughly, 36 percent of the available oxygen in the CO was converted into water. A conversion of 63 percent of the CO to synthesis products would correspond to a yield of 39 grams of hydrocarbons per cubic meter. The determination showed, however, that only 20 grams of liquid products per cubic meter would form; hence, an approximately equal quantity of other synthesis products was produced. The reaction gas contained 2.3 volume percent of methane hydrocarbons with a carbon number of 1.78. The obtained yield of approximately 20 grams of liquid products would correspond to a degree of liquefaction of 65 percent as referred to half of the CO quantity in the original gas. As already pointed out, 65-60 percent of the liquefaction was reached with the previously described H₂-rich gas. One can see, therefore, that even by using a large H₂ excess, it was not possible to exceed this degree of liquefaction.

*n.b. = not determined.

The result of the series of experiments showing "the influence of gas composition (CO-H₂ ratio) upon the CO₂ formation" may be summarized as follows: By using larger catalyst quantities (respectively smaller gas throughputs) and working at higher reaction temperatures or using a H₂-richer original gas, one succeeds in directing the reduction of CO partly over water formation (for a Fe-Cu-MnO catalyst). In the most favorable case, 20 to 36 percent of the oxygen contained in the CO could be converted into water. The ratio of the CO which was converted into CO₂ and the CO which was converted into synthesis products was 1:2.3 for the most favorable case (Table 23, Experiment 2). An essential increase in the yield of liquid products was however not connected with the water formation. The degree of liquefaction obtained was 57 percent when mixed gas was used; and for an H₂-rich gas (up to a CO-H₂ ratio of 1:8.5), 65 to 66 percent liquefaction was obtained referred to CO₂.

From the experiments reported here, one may conclude that the water formation obviously proceeds in a different manner than it does with cobalt catalysts. It does not show up before a certain dilution of the CO in the reaction gas has been reached. When H₂-rich gases are used, this condition is already met in the range of low contractions - for mixed gas, the formation of reaction water (visible separation of water in the receiver) is generally observed when a contraction of 25 percent is reached. Obviously, the CO was converted in the first sections of the apparatus to such a degree that the following sections of the unit were practically charged with a H₂-rich gas. Such a gas, however, furnishes predominantly gaseous hydrocarbons for the temperatures in question. Therefore, the yield of liquid products does not increase essentially any longer with the water formation.

2.G. Influence of Alkali Contents Upon CO₂ Formation Using Iron Catalysts.

In order to acquire full activity, the carrier-free Fe-Cu-MnO catalysts need an activation with fixed alkali. This is contrary to experience with cobalt catalysts. It could be assumed that the different course of the reaction with the precipitated iron catalysts may be due to the alkali contents of the catalyst. (By different course of the reaction, CO₂ formation is meant). This may refer to the alkali (K₂CO₃) which was added subsequently to the catalyst or it may refer to the alkali residual alkali contents of the precipitated catalysts (such as Na₂CO₃). Even if the iron catalysts are washed thoroughly, considerably quantities of Na₂CO₃ remain in them.

In order to investigate this point, a number of Fe-Cu-MnO catalysts were prepared for which ammonium carbonate was used as a precipitant. The method of preparation and the general behavior of these little-active catalysts has been described in Section III. In the following, we only want to discuss whether such catalysts which are free of fixed alkali favor the formation of water. In Table 24, the nature of the gas conversion for two such ammonium carbonate catalysts is described. Two Fe-Cu-MnO (4:1:1) catalysts were subjected to investigation.

Table 24
CO Conversion (Mixed Gas) With Fe-Cu-MnO Catalysts
Precipitated with Ammonium Carbonate

	1	2
	Fe - Cu - MnO 10 : 2.5 : 2.5	Fe - Cu - MnO 40 : 10 : 10
Temperature, °C.	235	235
Throughput, liters per hour	4.1	2.0
Contraction, percent	17.4	32
CO conversion, percent to CO ₂	13.8	44.4
Unchanged CO	61.5	8.0
Synthesis (difference)	24.7	47.6
O ₂ Conversion, percent to CO ₂	27.6	29.8
percent to H ₂ O (diff.)	10.9	3.2
Reaction gas, volume percent		
CO ₂	6.2	20.3
CO	22.0	3.5
H ₂	57.3	53.9
CH ₄	4.5	10.2
carbon number	1.51	2.34

The experiments listed in Table 24 seem to point out that an immediate relationship between the alkali contents of the catalyst and the CO₂ formation during the synthesis does not exist. This seems to be obvious because the catalysts which were precipitated with ammonium carbonate and were free of alkali, produced predominantly CO₂. The catalyst used in the first column was an exception. This catalyst produced water already at a time when the contraction was only 12 percent. Eleven percent of the CO converted went to water, whereas 28 percent went to CO₂. Next we tried to increase a conversion of the CO by using larger catalyst quantities and by decreasing the gas throughputs (Experiment 2). However, here also we observed the characteristic feature already met before with iron catalysts, namely, CO₂ formed almost exclusively. For Experiment 1, the H₂O-H₂ ratio was 1:2.5. For Experiment 2, it had increased to 1:2.8. For Experiment 1, the end-gas showed a ratio of CO-H₂ of 1:2.6. For Experiment 2, however, this same ratio was 1:15.4.

7C. Experiments on the CO₂ Formation on Iron Catalysts When Using a CO₂-Containing CO₂-rich Starting Gas.

In the following, we attempted to suppress the formation of CO₂ on iron catalysts by adding a certain percentage of CO₂ to the starting gas. Thus, the possibility might exist to use CO for the synthesis proper. For these experiments, we employed Fe-Cu-MnO catalysts (10:2.5:2.5) which were precipitated with soda and which contained 0.1 percent K₂CO₃. The original analysis is given in Table 25, and the CO-H₂ ratio amounted to 1:1.8. This was somewhat too low. Of several experiments, which on the whole gave substantiating results, only two are discussed here.

Table 25.- Reaction Gas Analyses by Using a CO₂-rich Starting Gas

Exp.	Temp. °C.	Throughput l. per hr.	Contraction percent	Composition of the Reaction Gases, Percent							
				CO ₂	alk	O ₂	CO	H ₂	CH ₄	C-2sil	N ₂
			Initial gas:	10.3	0.0	0.0	30.8	55.1	—	—	3.8
1	235	4.1	26.4	28.9	1.5	0.1	7.8	56.4	1.6	1.63	3.7
2	240	4.0	32.8	28.7	1.2	0.2	8.0	54.4	3.9	1.38	3.6

By comparing the two reaction gas analyses with the initial gas, one can say already qualitatively that the addition of CO₂ to the starting gas does not impede the CO₂ formation. In both cases, the enrichment in H₂ has occurred in the end-gas which we are already familiar with from using mixed gas as initial gas. The ratio of the residual CO and H₂ has shifted to 1:7.2 for Experiment 1, and for Experiment 2, to 1:6.8. It shows that for Experiment 1, at least, the CO₂ formation was not influenced by the CO₂ addition to the starting gas. Neither was more CO-oxygen converted to water than when working with mixed gas. No reduction of CO₂ formation from CO was observed. Experiment 2 shows somewhat more favorable results. The ratio of water to CO₂ was 1:2.4. No increase in the yield of liquid products was obtained during this experiment. 44.5 g./m³ were found. This corresponds to a degree of liquefaction of 55 percent by taking into consideration the somewhat low H₂ contents of the starting gas. The degree of liquefaction just mentioned was referred to 1/2 of the usable CO of the starting gas.

Table 26.- Course of the CO Conversion By Using a CO₂ Containing Starting Gas

	Experiment 1 (235°)	Experiment 2 (240°)
CO conversion, percent to CO ₂	35.7	29.2
Unchanged CO	18.5	17.5
Synthesis (difference)	45.8	53.3
O ₂ conversion, percent to CO ₂	71.4	58.4
to H ₂ O (diff.)	10.1	24.1
H ₂ O:CO ₂	1:7.2	1:2.4

4.9. The CO₂ and Water Formation on Iron ^{carrier} Catalysts.

An essentially different result with respect to CO₂ and water formation is observed when the previously described carrier catalysts are used instead of the so-far investigated metal catalysts. We investigated carrier catalysts for which the kieselguhr was added immediately and which were precipitated with soda. We also investigated precipitated catalysts for which the carrier material (tonsil*) was added after the precipitation.

* The term "tonsil" refers to a silica clay which is used as a catalyst carrier.

Fe-Cu-MnO-kieselguhr catalysts.

A description of the method of the preparation and the behavior of the kieselguhr precipitated catalysts containing various quantities of kieselguhr has been presented in Section VI. In general, we limited ourselves to investigate the influence of the kieselguhr addition upon the CO₂ and H₂O formation. When a precipitated catalyst (Fe-Cu-MnO, 4:1:1) was taken into operation, precipitated with soda, and contained 6 grams of kieselguhr, the water formation set in simultaneously with the oil formation from the very beginning. The temperature was 235°C., and the gas throughput was 4 liters of mixed gas per hour. For the earlier metal catalysts as already described, the formation of water could only be detected after higher percentages of contractions were observed. The catalyst gave 30 percent contraction after 22 hours; in other words, just as much as the carrier-free catalysts gave in the same time. The reaction gas had the following composition.

	CO ₂	skt.	O ₂	CO	H ₂	CH ₄	C-H ₆	N ₂
Kieselguhr catalyst, 30% contraction	11.5	1.1	0.2	13.9	59.4	2.7	3.37	11.2
Metal catalyst, 32% contraction	17.9	1.3	0.1	5.0	59.5	4.8	1.32	11.4

For comparison, the kieselguhr catalyst was compared with a carrier-free precipitated metal catalyst (precipitated with soda). The comparison showed that the kieselguhr catalysts, at approximately the same contraction, gave essentially smaller quantities of CO₂. Furthermore, it appears that with the kieselguhr catalysts, a larger proportion of the CO remained unconverted. The final gas did not show such a pronounced shifting of the ratio of CO to H₂. As was experienced with metal catalysts, the ratio was 1:4.3 for the kieselguhr catalyst as compared to 1:11.9 for the metal catalyst.

A better insight in the various gas conversions for the two mentioned catalysts may be obtained from Table 27.

Table 27.- Gas Conversion (Mixed Gas) With an Fe-Cu-MnO (4:1:1) Catalyst
Precipitated with Na₂CO₃ and Gas Conversion for Kieselguhr Catalysts

	Metal Catalyst	Kieselguhr catalyst
Temperature, °C.	235	235
Liters per hour	4	4
Contraction, percent	32.4	30.0
CO conversion, percent to CO ₂	38.2	26.1
Unchanged CO	11.7	33.8
Synthesis (difference)	50.1	40.1
O ₂ conversion, percent to CO ₂	76.4	52.2
to H ₂ O (diff.)	11.9	14.0
H ₂ O:CO ₂	1 : 6.4	1 : 3.7

A comparison between the two series of experiments brings out that the reaction on the kieselguhr catalyst has a tendency to proceed more over water formation. For a total of 56 percent conversion of the CO, the ratio of H₂O to CO₂ formed was 1:3.7. Whereas the metal catalyst, at 88 percent conversion of the CO, gave a ratio of 1:6.4, that is approximately 6 times as much oxygen went to CO₂ than did to H₂O.

We did not make a yield determination of liquid products for the experiments described above. From calculations, we could observe already that in spite of the increased water formation on the kieselguhr catalysts (on account of the lower gas conversion) an increase in yield did not occur when compared to metal catalysts.

Further experiments confirm the observation of increased water formation on the kieselguhr catalysts. These experiments, to some extent also, gave better results on the conversion relationships of CO.

Table 28 shows the results of two further experiments. One of the tests was conducted with a catalyst which was somewhat leaner in copper.

Table 28.
Gas Conversion (Mixed Gas) on Kieselguhr Precipitated Catalysts

	1	2
	Fe-Cu-PnO 4 : 1 : 1 kieselguhr	Fe-Cu-PnO 4 : 0.2 : 1 kieselguhr
Temperature, °C.	235	235
Liters per hour	4	4
Contraction, percent	32.4	29.2
Reaction gas, volume percent		
CO ₂	14.4	7.6
SKV	0.8	0.0
O ₂	0.2	0.0
CO	11.2	18.5
H ₂	54.2	57.1
CH ₄ -KV	5.9	2.8
C-Zahl	1.73	2.25
N ₂	13.3	14.0
CO conversion, percent to CO ₂	28.1	15.5
Unchanged CO	24.5	44.3
Synthesis (difference)	47.4	40.2
O ₂ conversion, percent to CO ₂	56.2	31.0
to H ₂ O (difference)	24.5	24.7
H ₂ O:CO ₂	1 : 2.3	1 : 1.3

With catalyst No. 1, a conversion of 76 percent of the CO was obtained, and only 2.3 times as much CO₂ was formed than water. With catalyst No. 2, only 1.3 times as much CO₂ was formed as water, however, at a total CO conversion of 56 percent.

equivalent catalyst of composition 1(Fe-Cu-MnO) + 1 kieselguhr. The catalyst was precipitated with soda, taken into operation at 235°C., then gradually the temperature was lowered to 200°C., step by step. Thus, we obtained the conditions reported in Table 30.

Table 30

Gas Conversion (Mixed Gas) on 1Fe-Cu-MnO (16:4:4) + 1 Kieselguhr at 215 - 200°C.

	1	2	3
Temperature, °C.	215	205	200
Liters per hour	4.2	4.3	2.2
Contraction, percent	29	25.4	27
CO conversion, percent to CO ₂	17.8	10.8	14.5
Unchanged CO	47.7	61.0	50.7
Synthesis (difference)	34.5	28.2	34.8
O ₂ Conversion, percent to CO ₂	35.6	21.6	29.0
to H ₂ O (diff.)	16.7	17.4	20.3
H ₂ O:CO ₂	1 : 2.1	1 : 1.2	1 : 1.4
Reaction gas, volume percent CO ₂	8.0	5.0	7.0
SKW	0.9	0.6	0.8
O ₂	0.0	0.0	0.0
CO	19.3	23.4	20.6
H ₂	58.9	58.8	58.8
CH ₄ -KW	1.8	1.0	n.b.*
C-Zahl Number	3.3	2.3	n.b.*
N ₂	11.1	11.2	n.b.*
CO:H ₂	1 : 3.2	1 : 2.5	1 : 2.3

Table 30 shows that for the temperatures in question (215-205°C.) comparatively favorable results were obtained in so far as the CO-oxygen conversion was concerned. For Experiment 1, approximately twice as much CO went to synthesis products than did to CO₂. For Experiment 2, almost 3 times as much was used up for synthesis products than was converted into CO₂. The ratio of H₂O-oxygen to the CO₂-oxygen lies somewhere between 1:2 and 1:1.2. It has to be mentioned, however, that at these low temperatures, only 40 to 50 percent of the total CO entered the reaction. However, the possibility exists to re-use the end-gas once more and lead it back over the catalyst. This can be done because the CO to H₂ ratio in the reaction gas has not changed considerably. For the experiments discussed, this ratio lies between 1:3 and 1:2.5.

The kieselguhr catalysts differ essentially from the metal catalysts in that they can form water at low reaction temperatures and are capable of converting a greater portion of the CO to synthesis products. For the metal catalysts (see Tables 19 and 20), we found that the water formation decreases as the reaction temperatures increases. As the reaction temperature drops, the water formation finally comes to an end. For lower temperatures, therefore, the CO₂ value became more and more pronounced when compared to the synthesis value,

* n.b. = not determined.