2. "3-Layer Experiment" With Iron-Kieselguhr Catalysts.

The previously mentioned experiments show that the CO contained in the mixed gas are comparatively incompletely converted when using kieselguhr catalysts. The degree of conversion depends on reaction conditions. The magnitude of conversion varied between 40 to 70 percent. This lower degree of conversion may be due to the fact that the kieselguhr catalysts were more dilute in iron, hence, for a certain catalyst quantity, smaller iron quantities were used than in the case of the metal catalysts. In a further series of experiments, we have attempted to increase the gas conversion in one single stage by simply using greater catalyst quantities. For this larger catalyst quantity, we employed longer catalyst layers (longer reaction tubes). The reaction tubes used were up to 80 cm. long. The catalyst tubes used so far, were only 30 cm. in length.

It is interesting to notice that with these experiments an increase in CO conversion in favor of the synthesis products was not obtained. It was found that the CO was used up to a greater extent; however, the extra CO converted went to CO_2 instead of synthesis products. At the same time, the water formation decreases sharply. These phenomena were observed universally irrespective whether the catalyst had the same composition over the entire catalyst layer length or whether the catalyst contained an increasing or decreasing amount of iron at various places in the reaction tube.

In the following an experiment is discussed for which 3 catalyst layers were used in series, each catalyst layer being richer in iron than the previous one. Table 31 gives information on the arrangement of the experiment. The total iron quantity was 14 grams. The first layer was composed of a catalyst having a composition of one metal to 3 kieselguhr, the second layer consisted of a catalyst of one metal to one kieselguhr, and the last layer contained no kieselguhr at all. It may be seen that the catalyst was arranged according to the countercurrent principle. The entering mixed gas thus was intended to first contact the iron-deficient catalyst and then proceed to the iron richer catalyst layers.

To start with, layer No. 1 was taken into operation at 235°C. up to such a time for which the contraction was 13 percent. Table 31 shows that at this point approximately 35 percent of the CO was converted, and the ratio of the CO which went to CO_2 and synthesis products respectively, was equal to 1:1.8. The CO to H_2 ratio shifted only moderately. It was 1:24 for the reaction gas. At this point, catalyst layer No. 2 was taken into operation. The second layer was contained in a glass tube of somewhat smaller diameter than the contact tube. The glass tube was open at both ends. After a total of 47 hours, the contraction then increased to 29 percent. A total of 75 percent of the CO was converted. The ratio of the CO which went to CO_2 to the CO which went to synthesis products had shifted to 1:1.3; hence it had become more unfavorable. The oxygen conversion also had shifted in the direction of an increased CO_2 formation. The H_2O to CO_2 ratio was now 1:6.4, and the CO to H_2 ratio in the reaction gas had increased to 1:5.1. When the temperature was lowered to 225°C., the CO conversion decreased to ? percent. The other conversion data shifted in the manner indicated in Table 31. When the temperature of 235°C., was

reached again, catalyst layer No. 3 was taken into operation. This caused a decrease of contraction to 25 percent, and conversion conditions prevailed which were similar to those when carrier-free catalysts were used. No more water was formed, only CO_2. The CO-H_2 ratio in the end-gas shifted sharply towards H_2 (1:7.2).

This experiment showed that it was not possible to use more CO for production of synthesis products by employing a longer catalyst layer length in connection with kieselguhr catalysts. The reason for this was that the water formed on the following catalyst layers entered into reaction with CO to form CO_2.

In order to re-use the CO when working with kieselguhr catalysts, we found that it was necessary to work in several stages. The water had to be removed between each stage of operation. In the following investigation, we carried out such an experiment using tonsil as a carrier. The experiment was not successful, however.

Table 31
Three-Layer Experiment

	35 cm.	25 cm.		20 cm.
	Fe-Cu-MnO 2:0.5:0.5 / kieselguhr 3 1	Fe-Cu-MnO 4:1:1 / kieselguhr 1	I	Fe-Cu-MnO 8:2:2 + 0.1% K_2CO_3
Temperature, °C.	235	235	225	235
Liters per hour	4.1	4.3	3.9	4.1
Contraction, percent	13.0	29.0	26.2	25.4
Hours of operation	23	47	53	73-3/4
CO conversion, percent to CO_2	12.3	32.4	22.7	40.2
Unchanged CO	65.2	25.1	42.2	19.4
Synthesis (difference)	22.5	42.5	35.1	40.9
CO_2:Synthesis	1 : 1.8	1 : 1.3	1 : 1.5	1 : 1
O_2 conversion, percent to CO_2	24.6	64.0	45.4	80.4
to H_2O (diff.)	10.2	10.1	12.4	0.2
H_2O:CO_2	1 : 2.4	1 : 6.4	1 : 3.7	1 : (400)
Reaction gas, vol. percent CO_2	5.5	14.8	10.3	17.2
sKW	0.9	0.7	0.8	0.6
O_2	0.0	0.1	0.1	0.0
CO	23.2	10.5	17.1	7.7
H_2	55.7	54.1	54.5	55.9
CH_4-KW	2.9	6.2	3.8	5.6
C-Zahl	1.59	1.86	2.01	1.98
N_2	11.8	13.6	14.4	13.0
CO:H_2	1 : 2.4	1 : 5.1	1 : 3.2	1 : 7.2
	Layer 1	Layer 1 and 2	Same at a 10° lower temperature	Layer 1,2, and 3

3. Experiments with Tonsil as Carrier.

It was interesting to study the influence of the addition of tonsil upon the activity of the iron catalysts and on the course of the reaction. The mode of adding the tonsil plays an important role. In Table 32, the results are described with a number of Fe-Cu catalysts containing different amounts of tonsil. They were precipitated by soda from ferrous chloride and copper chloride solutions. Experiments 1 and 2 show the effect of the tonsil when mixed in the dry state with an alkalized catalyst and with a non-alkalized catalyst. The catalyst contained 5Fe to 1Cu. To this, 4 grams of tonsil were added for every 10 grams of iron. The activity as compared to the tonsil-free catalysts is approximately 25 to 30 percent lower. Otherwise the course of the reaction is the same, that is to say, the reaction proceeds over CO_2 formation. When the tonsil is added prior to precipitation, an almost entirely inactive catalyst results (Experiments 3 and 4). The alkalized catalyst is still less active than the non-alkalized catalyst. A reduction with H_2 at $450°C.$, does not change the situation. When the same tonsil quantity is added after the iron copper precipitation has taken place, a decrease in activity results here too but it is by far not as serious as when the tonsil is added prior to precipitation. Both catalysts, with and without alkali, reach a maximum contraction of 16 percent, and in this condition furnish 26 respectively 22 grams of liquid products per cubic meter of mixed gas. Water is formed simultaneously. Up to 20 $g./m^3$ of mixed gas were obtained. A tonsil-free catalyst, under the same conditions of operation, yields no water at a contraction of 16 percent. It is evident, therefore, that for the tonsil-containing catalysts, the reaction proceeds partly over the formation of water just as in the case of the previously described kieselguhr catalysts. The CO_2 formation is suppressed and consequently more CO is available for the formation of hydrocarbons.

(Table 32, next page)

This is apparent by comparing the end-gas analyses for tonsil-containing and tonsil-free catalysts at approximately the same contraction (Table 33). The tonsil-containing catalysts for the same contraction form only approximately half the CO_2 quantity. Correspondingly, the CO contents in the end-gas is higher than in the case of the tonsil-free catalysts. Normally, using carrier-free iron catalysts, each mole of CO which is used up for the hydrocarbon synthesis should also form one mole of CO_2. In Experiment 5, we found that a total of 35 percent of CO was used up. Of this, 12 percent went to CO_2, and 23 percent to hydrocarbons. Consequently, for each mole of CO available for the synthesis, only 1/2 mole of CO went to CO_2 or in other works, for this experiment, the reaction proceded to 1/2 over the formation of water and the other half to the formation of CO_2.

Table 32

Influence of Tonsil Addition to 5Fe-1Cu Catalyst

Exp. No.	K_2CO_3 contents, percent	Tonsil quantity	Mode of addition	Reduction conditions	Max. contraction, percent	Maximum yield, percent	Remarks
1	1/4	4 grams	Mixed in dry after precipitation	Mixed gas immediately	24 235°	41	Decrease of activity by tonsil
(	without	4 grams	"	"	16 235°	17	
3	1/4	4 grams	Tonsil added prior to precipitation	Mixed gas immediately, H_2, 450°	3 235° 2 235°	– –	By adding tonsil prior to precipitation, the catalyst was almost entirely inactive.
4	without	4 grams	"	Mixed gas immediately, H_2, 450°	5 235° 7 235°	– –	
5	1/4	4 grams	Tonsil added after precipitation	Mixed gas immediately	16 4 l./hr. 32 1 l./hr.	26 36	After 6 days, still 16 percent contraction. Water formation 7 days, later contraction still 27 percent.
6	without	4 grams	"	Mixed gas immediately	16 4 l./hr. 29 1 l./hr.	22 35	Still 13 percent contraction after 6 days. Water formation 7 days, Later still 26 percent contraction
7	without	4 grams	"	H_2 450°	16 235°	–	Behaved like catalyst in Exp. 6.
8	1/4	10 grams	"	Mixed gas immediately	14 250	–	Increase of tonsil quantity causes more rapid activity decrease
9	without	10 grams	"	"	11 250°	–	

Table 33
Influence of the Tonsil Upon the End-Gas Composition.

Catalyst 5Fe-1Cu	Contraction, percent	End-gas Composition							
		CO_2	sKW	O_2	CO	H_2	KW	C-Zahl	N_2
Contains tonsil + 1/4% K_2CO_3	15.5	4.9	0.4	0.2	24.8	57.8	2.1	1.76	9.8
"	16.0	5.4	0.6	0.1	23.0	58.9	2.1	2.0	9.9
Contains tonsil without K_2CO_3	16.0	5.2	0.6	0.1	23.3	58.9	2.6	1.85	9.9
Without tonsil, 1/4% K_2CO_3	15.5	9.9	0.9	0.1	17.1	59.6	1.7	1.4	10.7
"	15.0	9.0	0.4	0.1	17.6	60.6	1.5	1.67	10.8

Next we tried to obtain a better degree of conversion by raising the reaction temperature. We regret to state that increasing the temperature by 15°C. (from 235 to 250°C.), the contraction only increased to 20 percent. The CO_2 contents, however, went up from 4.9 to 8.6 percent, and the water formation ceased almost entirely. We are forced, therefore, to assume that at higher temperatures, the primary water reacts with the secondary CO under CO_2 formation. By decreasing the flow velocity from 4 to 1 liter per hour (Experiments 5 and 6, Table 32), a significantly higher conversion was obtained. We observed that the contraction increased from 16 to 32 percent respectively 29 percent. The water formation, however, decreased very considerably; whereas the CO_2 contents increased to 17 percent. The course of the reaction, therefore, was the same as for the normal iron catalysts. The decrease of flow velocity caused a higher formation of gaseous hydrocarbons so that the yield of liquid products amounted only to 36 respectively 35 grams although 85 percent of the CO was converted.

Therefore, it is apparent that neither by raising the temperature nor by decreasing the flow velocity are we in a position to cause a reaction to take place in the desire manner. We tried one further arrangement which was generally recognized as favoring water formation, namely multi-stage operation in series. The experiment temperature was 235°C., and the flow velocity, 4 liters per hour. The end-gas of the first stage after removing the liquid reaction products was recirculated. In this manner, 90 percent of the CO was worked up in 4 stages. The total contraction amounted to 40 percent (See Table 34), and the total of all the liquid hydrocarbons formed in all stages was 48 grams. One can see, therefore, that in comparison to a one-stage operation for the same CO conversion, the formation of gaseous hydrocarbons is favored. This is also evident from the comparatively high contents of gaseous hydrocarbons in the end-gas. It has to be taken into consideration that part of the gas is removed by the activated charcoal behind the individual stages. A CO balance gives the following picture: Of the total CO converted (90 percent) 40 percent went to CO_2 and 60

percent was converted to hydrocarbons. The ratio of CO_2 to hydrocarbons is, therefore, 2:3. From the CO quantity which was used up for the synthesis, theoretically 100 grams of liquid products could be obtained. Since in reality only 48 grams of liquid products were obtained, the portion of the CO which went to gaseous hydrocarbons amounted to 50 percent.

Table 34.
Four-Stage Experiment with Tonsil-Containing Catalyst

Stage	Contraction, percent	Grams of liquid products per m^3 of mixed gas	Gas composition							
			CO_2	sKW	O_2	CO	H_2	KW	C-Zahl	N_2
1	13.5	22	5.1	0.4	0.3	23.4	58.8	1.8	2.3	11.0
2	10.5	14	10.5	0.3	0.3	17.1	56.0	4.0	1.88	11.8
3	10.0	8	15.6	0.0	0.0	9.8	55.4	5.8	1.76	13.4
4	6.3	4	19.5	0.1	0.3	5.2	54.9	6.0	1.83	14.0
1 - 4	40.3	48								

In conclusion, we should like to give some of our speculations on why we believe that carrier catalysts are capable of forming water and why metal catalysts are incapable of doing so. Obviously with iron catalysts, the formation of water is the primary reaction just as it is with cobalt and nickel catalysts. With the carrier-free iron-metal catalysts, this phenomena of primary water formation is not noticeable because the water formed reacts with part of the CO according to the water-gas equation. The CO_2 once formed is, however, as pointed out in Section XIV, not reduced on the iron catalyst at the temperature range in question. With the carrier catalysts, however, according to observations from the experiments, this subsequent CO conversion by the reaction water takes part only to some extent. It may be that the reason for this behavior is in the dilution of the catalyst and in the fact that the temperatures at the various active centers are not quite as high as they are in the case of metal catalysts. The metal catalysts, on account of their concentrated form, develop more heat per unit volume, whereas the carrier catalysts develop less heat for the same volume on account of the carrier dilution.

IX. Best Catalyst Obtained.

Of the iron catalysts described in Sections III and IV, the best catalyst found, especially with respect to stability, was a 5Fe-1Cu containing 1/8 percent K_2CO_3. Its method of preparation is as follows: 130 grams of $FeCl_2 + 4H_2O$ (50 g. of Fe) and 26 grams of $CuCl_2 + 2H_2O$ (10 g. of copper) are dissolved in one liter of water. The chloride solution is heated to the boiling point and precipitated with a solution containing 160 grams of soda in 1-1/2 liters of water (time for precipitation, 1/12 to one minute). The precipitate is filtered and washed 6 times with one liter of hot water each. After drying at 105°C., the catalyst mass is powdered and impregnated with 67-1/2 mg. of K_2CO_3 (1/8 percent referred to iron). The K_2CO_3 was dissolved in 100 cc. of water. The impregnated mass is heated

with a small flame on the sand bath. It is also permissible to mix the K_2CO_3 solution immediately after the washing operation of the precipitate into the still moist and not previously dried catalyst mass.

A catalyst mass which contained 10 grams of iron was taken into operation immediately and without any previous pretreatment. The gas used was mixed gas (29CO - 58 H_2), and the flow velocity was 4 liters per hour at a temperature of 235°C. The maximum contraction was 31 percent, and was already reached after 2 days of operation. After lowering the temperature to 228°C, a yield of 56 grams o.f liquid products (uncorrected) per cubic meter of mixed gas was found. The average yield for 6 weeks of operation amounted to 52 g./m³ of ixed gas. For 7 weeks of operation, it was 50 g./m³ of mixed gas, and for 8 weeks, it was still 47 g./m³ of mixed gas.

From Table 35 ((see also curve __?__) the behavior of such a catalyst may be observed for 8 weeks of uninterrupted operation. The experiment temperature was raised by approximately 10 degrees for a time of operation of 7 weeks. From the gradually decreasing ratio of yield:contraction, one recognizes that the formation of gaseous hydrocarbons increases at the expense of the liquid hydrocarbons. After 7 weeks of operation, the experiment temperature was lowered from 237 to 230°C. By doing this, the contraction decreased from 25 to 15 percent. The yield amounted to only 25 grams. The ratio yield: contraction had increased from 1.52 to 1.66.

Table 35
Efficiency of a 5Fe-1Cu Catalyst + 1/8 percent K_2CO_3
Prepared by Precipitating $FeCl_2$ and $CuCl_2$ with Soda

	Time of Operation, days							
	7	14	21	28	35	42	49	56
Experiment Temperature,°C.	230	228	229	230	233	233	237	230
Contraction, percent	30	30	30	30	28	26	25	15
Yield in g./m³ of mixed gas	56	55	56	52	47	45	38	25
Average yield in g./m³ of mixed gas	56	56	56	55	53	52	50	47
$\dfrac{\text{Yield}}{\text{contraction}}$	1.87	1.84	1.87	1.73	1.68	1.72	1.52	1.66

In some cases catalysts were obtained with the above mentioned method of preparation which gave a maximum yield of 60 grams of liquid products per cubic meter of mixed gas. For the above described experiment with a maximum yield of 56 grams of liquid products, a catalyst was used the activity of which may be surpassed in some instances.

X. Regeneration of the Iron Catalysts.

With regard to the possibility of regeneration, the iron catalysts are much easier to handle than the cobalt and nickel catalysts. Whereas, for the cobalt catalyst, a complete reworking of the catalyst is necessary in order to obtain the original

activity (dissolving the catalyst in nitric acid and reprecipitation), iron catalysts may be regenerated simply by treating them with air at the synthesis temperature. A preceding extraction with benzene is recommended in order to recover the high boiling accumulated paraffin hydrocarbons which are always present in the catalyst.

A. Regeneration of Fe-Cu Catalysts.

Table 36

5Fe - 1Cu Catalyst + 1/4 Percent K_2CO_3

Regeneration Under Various Conditions

Mode of regeneration	Extracted paraffin in grams	Yields in $g./m^3$ after days				
		6	17	24	32	39
1. H₂ treatment at 235°C., benzene extraction, then treatment with air at 235°C.	7.2	55	53	50	43	37
2. Benzene extraction, then air treatment at 235°C.	9.0	53	50	48 after28	44 36	35 43 days
3. Air treatment at 235°C. only.	-	55	52	49	48	43

Table 36 shows the course of the second operation period, when using a 5Fe-1Cu catalyst containing 1/4 percent K_2CO_3 which was regenerated under various conditions. These catalysts furnished, during the first operation period, a maximum yield of 56 grams, and after 6 weeks, they still produced 39 g./m³ of mixed gas (average yield for 6 weeks operation, 49 grams uncorrected.). Catalyst 1 was, at first, treated with H₂ at 235°C., then extracted with synthetic benzene (boiling point 80 to 100°C.), and finally oxidized with air. Catalyst 2 was extracted with benzene and then oxidized with air; whereas catalyst 3 was merely oxidized with air.

For all three catalysts, after the regeneration under varying conditions, practically the original maximum yields could be obtained again. Catalyst 3 is even superior to both the other catalysts in so far as stability is concerned. Whereas for catalysts 1 and 2, after removal of the paraffin, a 24-hour oxidation with air was sufficient, the unextracted catalyst 3 still consumed part of the oxygen so that it was treated with air for another 48 hours. The reason for the better stability of catalyst 3 seems to be therefore the complete removal of the last traces of the high molecular paraffins, respectively acids.

It should be mentioned here that a 5Fe-1Cu catalyst containing 1/4 percent K_2CO_3 and formed with starch reached its original activity after a paraffin extraction with benzene and a subsequent oxidation with air had been performed. The shape of the catalyst had not suffered any during the reactivation. Even after a second oxidation, the shape of the catalyst was still the same. We want to mention here that no reactivation is possible by merely conducting H₂ respectively H₂-NH₃ mixtures over the iron catalysts. When the catalyst was treated with H₂-NH₃ mixtures, a small degree of reactivation is obtained; it is, however, of short duration only.

The 5Fe-1Cu catalysts which contained only 1/8 percent K_2CO_3 could be extracted with benzene and could subsequently be oxidized in a stream of air, so as to regain their activity completely. When the catalysts contained only 1/16 percent K_2CO_3, by regeneration, an initial yield of 51 grams was obtained also; however, the stability was somewhat impaired and was not quite as good as during the first period (53 grams during first period). Similar observations could also be made with a catalyst which was activated with Na_2CO_3. However, it seemed that the time of induction for these catalysts, after regeneration, was somewhat longer than for the first period of operation. For this reason too, an activation of Fe-Cu catalysts with Na_2CO_3 instead of K_2CO_3 is not recommended. It should be mentioned here that an extraction alone without subsequent oxidation only causes an incomplete regeneration. Other processes of regeneration such as treatment with steam or heating in a stream of N_2 at $250°C$, were without effect.

β. Regeneration of Cu-free Catalysts.

A regeneration by simple air treatment did not prove successful with the Cu-free catalysts.

The catalysts which were prepared by dissolving iron shavings in dilute nitric acid and subsequent precipitation with Na_2CO_3, containing 1/4 respectively 1/2 percent K_2CO_3 alkali (they gave a maximum yield of 45 grams respectively 47 grams of liquid products) after being treated with air after 8 days of operation gave only a contraction of 13 respectively 3.6 percent. During the first two days of operation, these catalysts had already given a contraction of 20 respectively 23 percent.

Meyer) XI. Regeneration of the Exit Gases.

In Section VII, we have mentioned a disadvantage which occurs when the benzene synthesis is carried out on iron catalysts by using mixed gas of composition $1CO + 2H_2$. The disadvantage cited is that an approximately equal quantity of CO is used up for the formation of hydrocarbons and for the formation of CO_2. This conversion to CO_2 is responsible to a great degree for the comparatively small yield of approximately 60 grams of liquid products per cubic meter of mixed gas. The degree of liquefaction by which we understand the percentage of liquid hydrocarbons formed during the synthesis for a certain quantity of CO reacted, is just as good as in the case of the cobalt catalysts, namely 60 to 65 grams per cubic meter. A further increase of the degree of liquefaction at the expense of the already small quantities of gaseous products formed appears therefore barely possible, since we do not succeed well to direct the reaction over the course of water formation when iron is used instead of cobalt. In some cases, it appears purposeful to reconvert the exit gas obtained during the benzene synthesis into synthesis gas. This is to be recommended especially since by using iron catalysts, approximately 700 liters of end-gas are obtained from each cubic meter of synthesis gas. The average contraction is approximately 30 percent. For this reason we carried out a few experiments on the recovery and regeneration of the exit gases.

    A. α. Use of Coke at High Temperature.
    B. b. Use of Coke at High Temperature, and in Presence of Illuminating Gas.
    C. c. Use of Coke at High Temperatures in Presence of Broken Clay.

A. Use of coke at high temperature.

(a) The exit gas was conducted over a layer of coke 10 cm. in length. The coke was granular in shape and was approximately of pea-size. It was contained in a porcelain tube cf 16 mm. I.D., and the temperature under which the gas was conducted over the coke was 1000°C. In order to protect the reaction gas from later changes which might occur when the reaction gas comes in contact with regions of lower temperature, it was conducted away from the hot zone as rapidly as possible by using a 2 mm. wide porcelain capillary. The heating of the porcelain tube was accomplished in a Mars furnace.

In Table 37, the composition of the reaction gases is tabulated for various regeneration temperatures.

Table 37.

Conversion of the Reaction Gas on Coke at High Temperatures.

Temperature, °C.	CO_2	sKW	O_2	CO	H_2	KW	C-Zahl number	N_2	Expansion, percent
Final gas from the benzene synthesis.	20.5	0.5	0.0	4.0	60.5	3.2	1.2	11.7	-
At 1030°	2.7	0.2	0.0	31.0	53.7	2.0	1.0	10.0	10
At 1100°	1.8	0.2	0.0	33.4	53.9	0.7	1.0	10.0	19
At 1150°	0.6	0.1	0.0	34.8	54.7	0.5	1.0	9.3	23

A synthesis gas is obtained which contains more CO than corresponds to the composition $1CO-2H_2$.

Proof that the carbon has participated in the reaction furnishes the gas expansion experienced during the conversion. This expansion amounted to 23 percent at 1150°C. From 700 liters of exit gas, therefore, 870 liters of new synthesis gas were regenerated. The carbon used up during the reaction could be accounted for by differences in weight.

B. Use of coke at high temperature, in the Presence of Illuminating Gas.

(b) In order to arrive at a CO-leaner respectively H_2-richer synthesis gas, various quantities of city gas were mixed to the exit gas obtained from the benzene synthesis. The mixture thus obtained was conducted over coke at 1100°C. Table 38 shows experimental results of this regeneration.

Table 38.

Conversion of the Reaction Gas on Coke in the Presence of City Gas at 1100°C.

Added quantity of illuminating gas, percent	CO_2	sKW	O_2	CO	H_2	KW	C-Zahl number	N_2
15.5	1.2	0.0	0.1	32.4	55.9	1.6	1.0	8.8
18.0	1.0	0.0	0.0	31.6	57.1	1.6	1.0	8.7
20.5	0.7	0.0	0.0	31.4	57.6	1.3	1.0	9.0
23.0	0.5	0.1	0.2	30.8	57.6	1.2	1.0	9.6
26.0	0.9	0.0	0.1	29.3	58.3	1.6	1.0	9.8
28.5	0.8	0.0	0.2	28.6	59.1	1.6	1.0	9.7
Composition of the exit gas from the benzene synthesis	21.8	0.1	0.0	4.4	58.6	3.2	1.13	11.9

With an addition of 26 respectively 28.5 percent illuminating gas to the exit gas obtained from the benzene synthesis (the composition of the exit gas as obtained from the synthesis is given in the last column) a synthesis gas is obtained which contains CO and H_2 in the ratio of 1:2. This, however, is not to indicate that for all exit gases obtained from iron catalysts, the situation is as described for the synthesis. So, for example, we found that for a CO_2-leaner end-gas containing only 19 percent CO_2 and 61.8 percent H_2, the addition of 18 percent illuminating gas was sufficient to arrive at a synthesis gas containing 28.3 percent CO and 58.4 percent H_2. The gas expansion experienced in this conversion (the conversion of end-gas to synthesis gas) amounted to 17-20 percent.

C. Use of Coke at High Temperature, in the Presence of Broken Clay.

{x} A third possibility to regenerate the exit gas obtained from the benzene synthesis consists in heating the gas to very high temperatures in the presence of ceramic material. Table 39 summarizes the reaction gas analysis after the end-gas was conducted over broken clay at various temperatures.

Table 39.

Conversion of the Reaction Gas on Broken Clay.

Temperature, °C.	CO_2	sKW	O_2	CO	H_2	K	Number C-Zahl	N_2
Composition of the exit gas from the benzene synthesis	17.8	1.0	0.1	5.2	62.3	2.6	1.31	11.0
1000°	9.6	0.0	0.0	18.1	57.9	3.0	1.0	11.2
1100°	4.7	0.0	0.3	23.9	56.6	2.9	1.0	11.7
1200°	2.5	0.0	0.1	26.6	57.3	2.2	1.0	11.3
1230°	1.8	0.0	0.3	27.2	57.6	1.9	1.0	11.5
1300°	1.6	0.0	0.0	28.1	58.4	0.8	1.0	11.1

As is noticeable from the table, a reaction temperature of 1200°C. is required if it is desired to produce a synthesis gas containing 2.5 percent CO_2, 26.6 percent CO, and 57.3 percent H_2. In accordance with the equation $CO_2 + H_2 = CO + H_2O$, the conversion is associated with a contraction, which to a certain extent is compensated by expansion reactions of the hydrocarbons. In the best instance, a maximum contraction of 8 percent was ascertained.

This mode of regeneration of the exit gas has the advantage that no new sulfur compounds are introduced into the synthesis gas and consequently no additional sulfur purification is necessary.

(Meyer) XII. Two-stage Experiments with Water Gas and Mixed Gas on Iron-Copper Catalysts.

a. Water-Gas Experiment.

As has already been pointed out in Section IX, a catalyst composed of 5Fe-1Cu containing 1/4 percent K_2CO_3 (precipitated from $FeCl_2$ and $CuCl_2$ and by using Na_2CO_3 as precipitant) will give 50 grams of liquid products per cubic meter of mixed gas when permitted to act on mixed gas of composition 29 percent CO and 58 percent H_2. This was found to hold for 6 weeks of operation during which time no regeneration of the catalyst was required. Since during this experiment the synthesis gas is

depleted in CO quite considerably and since only moderate quantities of gaseous hydrocarbons are formed, we felt that no considerable increase in yield could be expected in a one-stage operation by merely changing the experimental conditions. We therefore tried to employ water gas instead of mixed gas. We worked in two stages using iron catalysts of the same composition in both stages. The object was to increase the yield per cubic meter of synthesis gas. To start with, we attempted to find the highest possible yield and the stability of the iron catalyst. The result of this investigation is given in Table 40.

Table 40

Maximum Yields and Stability of the Fe-1Cu Catalyst
Containing 1/4 Percent K₂CO₃ When Water Gas Is Used

Days of operation	Experiment Temperature, °C.	Contraction, percent	Yield in grams of liquid products/m³ of water gas
6	255	40	75
10	237	35	67
14	237	29	53

With an initial maximum yield of 75 grams per cubic meter, the effectiveness of the catalysts decreases rapidly as compared to the operation for which mixed gas was used. After 14 days of operation, the quantity of liquid hydrocarbons formed had already decreased to 53 g./m³. Aside from the actual decrease in yield, the deterioration of the catalyst in this case is already noticeable from the early appearance of yellow-colored reaction products. As compared to the water gas experiment, the yellow-colored products appear much later when mixed gas is employed. With mixed gas, we could operate for 4 to 5 weeks before the colored product was noticeable. Here again, we had the old experience, namely, that a catalyst loses its activity approximately at the same rate at which the yellow products are formed which we believe to be paraffin decomposition products. It should be plausible to assume that the iron catalyst should exhibit a longer lifetime when only part of the CO in the water gas was converted. For this reason we worked in two stages. Two tubes, each containing 10 grams of iron, were operated in series and charged with water gas at a flow rate of 4 liters per hour. The temperature was chosen so that the contraction after the first stage was 28 to 30 percent. After the gases had passed the first stage, the liquid reaction products were removed and the end-gas was passed on over the second catalyst without removal of the CO₂. The results of this experiment are summarized in Table 41. The sum of the hydrocarbons formed in the first and second stages amounted to a maximum of 85 grams, after 12 days of operation, this was 80 grams, and after 18 days, only 70 grams of total liquid products were obtained. In spite of the higher yields, the decrease in activity is not quite as pronounced as when water gas was used in a one-stage operation. One should keep in mind, however, that during the two-stage experiment, twice the catalyst quantity was used.

Table 41.

Two-Stage Experiment with Water Gas on a 5Fe-1Cu Catalyst Containing 1/4% K_2CO_3

Days of operation	Temp., °C.	First stage		Second stage		Sum of liquid products collected in 1st. and 2nd. stages
		Contraction, percent	Liquid products, g/m^3	Contraction, percent	Liquid products, g/m^3	
7	230	30	55	20	30	85
12	232	27	52	18	28	80
18	230	20	42	18	27	70

It is our belief that if we should increase the flow velocity from 4 to 8 liters per hour, corresponding to twice the catalyst quantity, the results obtained with the two-stage experiment should be less favorable. However, we have not carried out this experiment. The reason for not having investigated this was that even with a flow velocity of 4 liters per hour, the yield had already decreased from 55 grams to 42 grams in the first stage after only 18 days of operation. Since the load on the catalyst for the first stage of the operation was no larger than that of a one-stage operation operating with mixed gas (because here also for the same contraction of 30 percent, the same yield was observed, and in addition, for a considerably longer time of operation) the faster decrease of the activity in the first stage when using water-gas should be blamed on the higher CO concentration which the water-gas has. If the flow velocity should be doubled, this disadvantage would become even more pronounced than with a corresponding increase in flow velocity when mixed gas is used. In the later case, the maximum yield is 51 grams with a flow velocity of 8 liters per hour (60 grams at 4 liters per hour), and after 10 days of operation, it has already decreased to 46 grams.

With respect to the stability of the Fe catalysts, we consider it unfavorable for the reasons mentioned above to employ them with water gas.

B. Mixed Gas Experiments:

1.

k. ~~Two-stage experiment with mixed gas~~ Without regeneration of the end-gas after the first stage.

Two-stage experiments with mixed gas in which the end-gas was passed over a second iron catalyst after the benzene had been removed appeared not very promising to us. The reason for this is that the CO is already converted rather completely after one single stage. It is to be noted that gaseous products appear only in small quantities. In fact, when we did carry out a two-stage experiment for which we worked with twice the flow velocity, namely 8 liters per hour, corresponding to twice the catalyst quantity, no improvement in the yield of liquid hydrocarbons was observed.

2.

~~Two-stage experiment with Mixed Gas~~ With Regeneration of the End-gas after the First Stage.

We were interested in finding out what kind of yields per cubic meter of mixed gas could be obtained when the end-gas was scrubbed of the benzene, and then passed over pieces of clay at 1200°C. This operation regenerated the gas and made it over to synthesis gas. It was carried over an iron catalyst again. The arrangement of the experiment was as follows: The first stage was charged with 3(Fe-Cu catalyst) containing 1/8 percent K_2CO_3. The flow velocity was 3 x 4 liters per hour, in other words, 12 liters of mixed gas per hour. The reaction gas was depleted of liquid reaction products and continuously regenerated on

pieces of clay by passing it through a Mars furnace at 1200°C. The synehtsis gas thus formed was immediately conducted into the second stage. In accord with the contraction in the first stage and the gas volume reduction resulting from passing through the Mars furnace (from 12 to 8 liters per hour), the second stage was only charged with 2 parts of iron catalysts. Table 42 contains the results of this experiment.

Table 42

Two-stage Experiment with Mixed-Gas
Regeneration of the End-Gas from the First Stage

	Temp., °C.	Contraction, percent	Grams of liquid products per cubic meter of mixed gas
1st Stage	230	30	56
2nd Stage	230	26	37
1st and 2nd Stage	-	approximately 50% referred to starting gas.	93

Table 43

Composition of the Starting Gas and Reaction Gas for Both Stages

	CO_2	sKW	O_2	CO	H_2	KW	C-Zahl *Number*	N_2	Residual gas quantities still present from 1000 liters
Starting gas, first stage	1.0	0.0	0.0	29.6	59.5	1.8	1.0	8.1	1000
End-gas, first stage	19.9	0.1	0.3	3.9	59.9	5.6	1.21	11.2	700
Regenerated end-gas	2.4	0.0	0.2	26.3	56.9	3.0	1.0	11.2	680
End-gas, second stage	19.8	0.9	0.2	2.5	58.6	4.9	1.5	14.9	500

It is possible therefore to obtain 93 grams of liquid products from one cubic meter of mixed gas. 56 grams of the 93 grams were obtained in the first stage, and the residual 37 grams from the second stage. However, it was required that the gas was regenerated after the first stage before it was admitted into the second stage. Referring the yield to normal conditions, the number increases from 93 to 102 grams per cubic meter of mixed gas. From the last column of Table 43, it is seen that from originally 1000 liters of mixed gas employed, 500 liters were still present leaving the second stage. After another regeneration of this end-gas, 25 grams additional liquid hydrocarbons could be obtained; so with a 3-stage operation, a yield of 127 grams per cubic meter of mixed gas should be anticipated.

Nothing definite can be said about the economic feasibility of such a process.
Perhaps it is to be recommended to pass the synthesis end-gas through the gen-
erator during the gas production period. A two-stage operation with water-gas
for which the end-gas is regenerated after having passed the first stage, gives
a higher yield for the first days of operation as compared to mixed gas. The
yield with water gas amounted to 70 grams for the first stage, and 33 grams for
the second, a total therefore of 103 grams (uncorrected). The activity of the
iron catalyst, however, decreases more rapidly with the use of water-gas. This
holds especially for the second stage. The reason is that the end-gas contains
more CO than H_2 after it has gone through the broken clay and was regenerated
at 1200°C. For example, its CO content was 44 percent and H_2 content only 32
percent.

C. d. Two-stage experiment with water-gas.

     1st Stage: Fe catalyst.
     2nd Stage: Co catalyst.

Finally we want to give the results of a two-stage experiment for which the
first stage was operated with an iron catalyst, and the second stage with a
cobalt catalyst. As a starting gas, we used water-gas. It was our intention
to convert sufficient CO during the first stage containing the iron catalyst,
so that the end-gas from the first stage had approximately the composition,
$1CO + 2H_2$. A gas of such a composition is most favorable for the execution
of the benzene synthesis on cobalt catalysts. In this manner, benzene may be
easily obtained in places where the local conditions provide sufficiently
cheap water-gas. The results of such an experiment are summarized in Table 44.
Benzene and oil were removed after the first stage. The CO_2 formed was not
scrubbed out.

Table 44.

Two-Stage Experiment With Water-Gas

(1st Stage Fe catalyst) 10 g. Fe
(2nd Stage Co + 18% ThO₂) 4 g. Co

Stage	Temp., °C.	Con-traction, percent	Liquid products g./m³
1st Stage (Fe)	224	21	35
2nd Stage (Co)	180	64	68
1st and 2nd Stage			103
1st Stage (Fe)	228	27	47
2nd Stage (Co)	180	57	68
1st and 2nd Stage			115

Table 45

Composition of the Reaction Gas Behind the Various Stages

	CO_2	sKW	O_2	CO	H_2	KW	C-Zahl number	N_2
End gas 1st Stage	14.7	0.5	0.0	28.5	46.6	1.2	1.75	8.5
End gas 2nd Stage	35.7	1.7	0.1	25.6	13.9	6.0	1.74	17.0
End gas 1st Stage	20.1	1.1	0.1	23.3	44.2	2.2	1.77	8.9
End gas 2nd Stage	46.4	1.5	0.3	8.9	15.2	10.3	1.82	17.4

The first row shows that the first stage gives 35 grams of liquid products at a contraction of 21 percent (iron catalyst). The end-gas analysis (Table 45) shows however, that the gas composition 1CO + 2H_2 has not been reached yet, instead CO is still present in excess. With this end-gas, a yield of 68 grams was obtained in the second stage using a cobalt catalyst. The CO_2 was not previously removed, and the contraction was 64 percent (Table 45, row 2). In both stages together, therefore, 103 grams per cubic meter of water-gas (uncorrected) were formed. The end-gas analysis of the second stage indicates plainly that an excess CO was present as far as the cobalt catalyst was concerned. During a second experiment, therefore, we charged the Fe catalyst stage somewhat more heavily. One can see that with a contraction of 27 percent (row 3), the yield amounts to 47 grams, and that the end-gas approximately corresponds to a 1CO + 2H_2. This end-gas furnished 68 grams of liquid products per cubic meter of water gas when going through the cobalt stage (row 4). Consequently a total of 115 grams per cubic meter of water-gas were formed. The end-gas leaving the second stage still contains CO and H_2 in approximately the ratio of 1:2 which is proof of the fact that the gas used for charging the second stage corresponded nearly to the usage ratio of CO and H_2. If one expresses the residual CO and H_2 in percent, taking into consideration the contraction which had occurred, one finds that only 5.7 percent CO and 9 percent H_2 did not enter into the reaction. 14.5 percent CO was utilized to form gaseous hydrocarbons. A certain quantity of CO_2 (corresponding to the quantity of hydrocarbons formed) appeared at the end of the first stage. During the second stage, no additional CO_2 was observed to have formed. The CO_2 which was obtained in the first stage and which entered the second stage was apparently not attacked while going through the second stage. We believe this to be true because it appeared that the CO_2 quantity after the second stage was equal to that after the first stage. Furthermore, if the CO_2 would have been partly hydrogenated, the H_2 balance should have given an indication of that, the gaseous hydrocarbons formed should be composed of molecules incorporating fewer carbon numbers. The question of CO reduction with iron catalysts will be discussed in detail in Section XIV. It is apparent from the experiments that with mixed gas advantages result in a multi-stage operation only then when the end-gas, after each stage, is regenerated by thermal treatment.

The execution of such an experiment with water-gas is not recommended on account of the rapid decrease of activity of the iron catalysts, especially after the second stage.

Water-gas, however, can be used successfully in a two-stage operation without regeneration if the first stage is charged with an iron catalyst, and the second stage with a cobalt catalyst. A more frequent regeneration of the iron catalysts becomes necessary however.

Meyer)

XIII. Significance of the Iron Catalysts for the Simultaneous Production of CO-deficient City-Gas and Benzine in Connection with Gas Works.

Considering the byproduct coke which is obtained from the illuminating gas industry, it would be desirable for many gas works to use part of the coke for production of a standard city gas, and simultaneously benzene. For this purpose, the water-gas produced has to be processed first to a greater or lesser extent and the CO_2 formed has to be removed.

From the H_2-rich synthesis gas thus produced, containing for example, 20 parts of CO and 70 parts of H_2, by means of cobalt catalysts under proper reaction conditions, approximately 50 g./m^3 of liquid products may be obtained, and the end-gas from the synthesis, which is lean in CO, conforms closely to the specifications of a standard city gas.

The further possibility for the production of a standard city gas, practically free of CO, and the simultaneous production of benzine on cobalt catalysts will not be discussed any further here. We only want to discuss the possibility of perhaps producing a standard city gas when iron catalysts are used during the synthesis.

Table 46.

End-Gas with Fe Catalysts for Gases of Various CO Contents

Temp., °C.	Days of operation	Con- traction, percent	Grams of liquid products per cubic meter of gas	End-gas composition							
				CO_2	sKw	O_2	CO	H_2	Kw	C-zahl number	N_2
			1a Synthesis Gas: 20CO-75H_2								
226 — After removal of CO_2		27	47	10.2 --	0.5 0.6	0.0 0.0	1.8 2.0	80.5 90.4	2.1 2.3	1.67 1.67	4.2 4.7
			1b Synthesis Gas: 29CO-58H_2								
230 20 After removal of CO_2		30	52	19.3 --	1.4 1.7	0.0 0.0	4.0 5.0	60.1 74.4	4.4 5.5	1.68 1.68	10.8 13.4
230 15 After removal of CO_2		31	56	19.7 --	0.9 1.1	0.0 0.0	3.5 4.4	61.3 76.6	4.3 5.4	1.63 1.63	10.3 12.5

Table 46 gives some end-gas analyses which were obtained when various starting gases were used with Fe-1Cu catalysts containing 1/4 percent K_2CO_3 (precipitated from $FeCl_2$, $CuCl_2$, and soda). The experimental conditions were such that optimum yield of liquid hydrocarbons were produced. By using an H_2-rich synthesis gas of composition 20 percent CO and 75 percent H_2 which is also especially suitable for the production of a proper city gas when cobalt catalysts are used, iron catalysts produce an end-gas which after removal of the CO_2 contains approximately 90 percent H_2 and only small quantities of hydrocarbons (Experiment 1a). With mixed gas (29CO-58H₂) and under conditions favorable for the benzine synthesis, an exit gas is obtained during Experiment 1b, of the indicated composition. By raising the experiment temperature from 230 to 245°C temporarily, twice the quantity of gaseous hydrocarbons may be obtained (as may be seen by comparing experiment 1 with 2 in Table 47.

Table 47
End-Gases with Fe Catalysts and Mixed-Gas at Elevated Temperatures

Starting gas	Temp., °C.	Days of operation	Contraction, percent	Grams of liquid products, m³. gas	CO_2	sK.	O_2	CO	H_2	K.	C-	N_2
1. 29 CO - 58 H₂	230	6	30	53	19.3	0.5	0.2	3.4	61.8	3.3	1.5	11.5
After removal of CO_2					--	0.6	0.3	4.2	76.5	4.1	1.5	14.3
2. 29 CO - 58 H₂	245	7	33	-	20.0	1.5	0.3	1.7	57.5	6.4	1.5	12.6
After removal of CO_2					--	1.9	0.4	2.1	71.9	8.0	1.5	15.7
3. 29 CO - 58 H₂	245	11	28	-	19.2	1.2	0.3	4.0	59.1	4.4	1.4	11.0
After removal of CO_2					--	1.5	0.4	5.0	73.1	5.4	1.4	14.3
4. 29 CO - 58 H₂	270	12	34	-	20.2	1.9	0.4	1.8	56.0	7.0	1.27	12.4
After removal of CO_2					--	2.4	0.5	2.3	70.0	8.3	1.27	16.0
5. 29 CO - 58 H₂	270	14	26	-	17.2	1.4	0.2	4.8	60.0	5.1	1.25	11.3
After removal of CO_2					--	1.7	0.2	5.8	72.5	6.2	1.23	13.6
6. 29 CO - 58 H₂	300	14	34	-	19.2	2.3	0.0	3.5	54.5	8.1	1.26	12.4
After removal of CO_2					--	2.8	0.0	4.3	67.5	10.0	1.26	15.4
7. 29 CO - 58 H₂	300	15	11.5	-	9.7	0.9	0.2	17.4	59.1	3.1	1.07	9.6
After removal of CO_2					--	1.0	0.2	17.3	65.5	3.4	1.07	10.6

On account of the higher experiment temperatures, the activity of the catalyst decreases rapidly with a simultaneous formation of yellowish-colored products. After 4 days of operation, starting from the moment when the temperature was raised to 245°C., the contraction decreased from 33 to 28 percent. The end-gas has a composition as given in row 3. The quantity of the gaseous hydrocarbons formed, therefore, has decreased and is approximately of the same order of magnitude as that of an iron catalyst operated at 230°C. A further increase in the reaction temperature to 270°C. causes the contraction to go up again as well as the formation of the gaseous hydrocarbons (column 4). It is apparent from the low carbon numbers that primarily CH_4 was formed. After 2 further days of opera-

tion, the contraction had decreased from 34 to 26 percent. Correspondingly, the quantity of gaseous hydrocarbons decreased (column 5). We also ~~maxexamxexperimx~~ ~~mextxferxxhixixxxexxxxx~~ at 300°C. Referred to CO_2-free gas initially 10 percent of gaseous hydrocarbons were formed. ~~Already~~ After 24 hours, the contraction had decreased to 11.5 percent, and only 3.4 percent of saturated gaseous hydrocarbons were observed.

Table 48

End-Gases with Fe Catalysts and Water-Gas

Starting gas	Temp., °C.	Days of operation	Contraction, percent	Grams of liquid products, ㎥ gas	End-Gas Composition						C-Number	N2
					CO2	akm	O2	CO	H2	KH		
1. Water gas 44 CO-47 H2	236	6	40	75	36.1	2.3	0.2	6.1	41.5	4.2	1.88	9.6
After removal of CO2		.			—	3.6	0.3	9.5	65.0	6.6	1.88	15.0
2. Water gas 44 CO-47 H2	236	10	36	67	30.5	2.8	0.3	11.0	40.8	4.8	1.6	9.8
After removal of CO2					—	4.0	0.4	15.8	58.3	6.9	1.6	14.1

Table 48 reports the composition of two end-gases which were obtained with water-gas acting on an iron catalyst. An essential increase of the gaseous hydrocarbons as compared to the mixed-gas experiments had not taken place. experiments at elevated temperatures were not carried out. The reason for not investigating higher temperatures was that iron catalysts lose their activity considerably faster when water-gas is employed than when mixed-gas is used. This even holds for low temperature regions for which chiefly liquid products are formed. An increase in temperature therefore and/the use of water-gas with iron catalysts would certainly have a tendency to decrease the lifetime of the iron catalysts still more than in the case of mixed gas.

Summarily, we can say that the reaction gases obtained from the benzene synthesis when using iron catalysts do not possess the proper requirements of a good city gas. The contents of gaseous hydrocarbons in the exit gas are too low, and the required heating value thus is not assured. The different composition of the end-gases obtained with iron catalysts as compared to the composition of endgases obtained with cobalt catalysts may be explained by the different course of the reaction which takes place respectively on iron or cobalt. Since, on account of the CO_2 formation, only approximately half of the CO in the synthesis gas is converted into hydrocarbons when iron is used, the amount of gaseous hydrocarbons left in the exit gas is considerably lower than when cobalt is used. Furthermore with cobalt catalysts, a considerable increase in gaseous hydrocarbon contents occurs due to the high contraction which is caused by the water formation. This is not the case with iron catalysts because chiefly CO_2 is formed which does not reduce the contraction as much as the condensable water. By scrubbing out the CO_2, this disadvantage can be overcome to a certain extent. The H_2 usage with iron catalysts is small. Consequently, after the CO_2 has been scrubbed out of the end-gas, the remaining gas contains approximately 60 to 65 percent H_2 when water gas was used originally. When mixed gas was used to start with, a final end-gas containing 70 to 75 percent of H_2 is obtained after the CO_2 has been scrubbed out and when a starting gas of composition 20 percent CO

and 75 percent H_2 is (was) employed, an end-gas results (resulted) containing 90 percent H_2. For this reason, the end-gas has too small a density and does not correspond to the city gas requirements.

An increase in experiment temperature is not to be recommended in connection with iron catalysts since the yield increase in gaseous hydrocarbons does not reach the desired degree and the lifetime of the iron catalyst is considerably impaired. With the decrease in lifetime of the catalyst the amount of gaseous hydrocarbons formed decreases as well.

It is thinkable (was thought) that a small addition of nickel respectively (or) cobalt to the iron catalyst should favor the formation of gaseous hydrocarbons, and thereby increase the heating value of the end-gas.

For this reason we added one and five percent nickel respectively (and) cobalt to a 5Fe-1Cu catalyst. The preparation of the catalyst was carried out by simultaneous precipitation of the three metals. The catalysts were taken into operation with mixed gas at 235°C., in one case directly, and in another case, after a previous H_2 treatment had been given the catalyst. All catalysts furnished a final gas which did not differ appreciably from the end-gas obtained directly with a 5Fe-1Cu catalyst without nickel or cobalt as far as the contents of gaseous hydrocarbons was concerned.

With a content of 5 percent nickel, the activity of the catalyst is somewhat inferior to the nickel-free catalyst, whereas with a content of 5 percent cobalt, the activity does not seem to have been impaired as yet.

(Bahr) XIV. Reduction of the CO_2 on Iron Catalysts.

In the previous chapters, we have referred repeatedly to the fact that the end-gas obtained from carrier-free iron catalysts has a high content of CO_2. We have had end-gases containing as much as 20 percent or more of CO_2 in addition to a high H_2 content (60 percent). Since it is known that the CO_2 may be reduced at a lower temperature than the CO, this simultaneous appearance of CO_2 and H_2 in the same gas in the presence of the iron catalysts seems astonishing. Especially is this true since CO_2 is reduced with noticeable speed already at 150°C., when cobalt or nickel catalysts are present. The explanation may be that the iron catalyst in the presence of cobalt and nickel is not in a position to reduce CO_2 at low temperatures. As has been investigated by Kuester[5]

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[5] Kuester, H., Brennstoff-Chemie 17, 203, (1936).

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no noticeable reduction of CO_2 to methane occurs if the temperature is below 300°C., and only at elevated temperatures in the range of 350-400°C. will iron catalysts reduce CO_2 to methane. However, at temperatures of around 200°C., a reduction of CO_2 to CO will occur.

The kieselguhr catalysts which are in a position to form some reaction water, do not behave differently as far as the CO_2 reduction is concerned. Of the experiments mentioned, let us consider the following in greater detail: A Fe-Cu-MnO (4:1:1) (kieselguhr)(1:1) catalyst was used, and the temperature in the be-