

slowly decreased thereafter but remained at 51 percent for 12 days. Here again, another H<sub>2</sub> treatment was undertaken at the same conditions as outlined earlier. The contraction held up again to 57 percent and slowly decreased down to 50 percent at the 19th. day. After the third H<sub>2</sub> treatment had been carried out, at first a contraction of 55 percent was obtained, after 3 days the value of 51 percent, and after 4 days, 52 percent contraction was measured. Then for 2 months of operation the contraction remained constant between 50 to 53 percent at 235°C.

Figure 10 shows that the H<sub>2</sub> treatment undertaken between syntheses causes an increase in catalyst activity. This increase was especially pronounced during the first hours after the H<sub>2</sub> treatment, and it also resulted in a lasting improvement of the catalyst. When these peaks of activity were obtained immediately after the H<sub>2</sub> treatment, the ratio CO-H<sub>2</sub> were used up (at 50 to 52 percent contraction) and was the same as under normal circumstances. In both cases, CO and H<sub>2</sub> were used in the ratio of 1.67 to 1.70:1.

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

#### F. Catalysts Based on Ferrous Salts.

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

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

After an induction with mixed gas at one atmosphere and 254°C., a synthesis was undertaken with CO-rich gas at 15 atmospheres and 245°C. 43 percent contraction was obtained at 245°C., 44 percent contraction at 255°C., and 47 percent contraction at 265°C. on the 10th day. When the catalysts prepared from ferro chloride and ferro nitrate and inducted with CO at 1/10 atmosphere and 235°C. were used in a synthesis at 15 atmospheres and a CO-rich synthesis gas, they showed an initial activity which, however, decreased rapidly already after one to two days. Table XXIII shows this for 3 experiments.

Table XXIII  
Experiment With Ferro Catalysts

Catalyst preparation by	FeCl <sub>2</sub>		FeCl <sub>2</sub>		Fe(NO <sub>3</sub> ) <sub>2</sub>	
	Temp., °C.	Contraction percent	Temp., °C.	Contraction percent	Temp., °C.	Contraction percent
1	235	57	235	56	235	56
2	235	57	225	56	235	57
3	235	34	225	49	235	40
4	235	30	215	38		
5			225	35		
6			225	29		

The contraction for the first experiment decreased from 57 to 34 percent on the third day when the operating temperature was 235°C. For the second experiment (after a contraction of 56 percent was obtained initially) the temperature was lowered on the first day, in order to minimize any possible damage to the catalyst activity which could have occurred due to the high temperature. At the lower temperature, however, the contraction decreased as well. A third experiment carried out with a catalyst derived from ferro nitrate behaved similarly.

Under the previously adhered to test conditions for the other normal catalysts (prepared from ferri salts), the ferro catalysts showed essentially more unfavorable behavior.

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

G. The Influence of the Addition of Copper.

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

Table XXIV. The Influence of the Addition of Copper Upon the Normal Pressure Synthesis

Catalyst: Induction time:	Fe:Cu = 5:1 2 days		Fe (without Cu) 4 - 7 days	
	Days of operation	Contraction percent	Liquid products grams per cu. m.	Contraction percent
1	30	56	32	55
5	30	56	31	50
10	30	55	30	43
20	30	56	27	38
30	29	50	26	34
40	27	46		

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

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

Table XIV shows 2 experiments the catalysts of which were produced from ferri salts and were inducted at 325°C. and 1/10 atmosphere by using CO. Then the synthesis was carried out at 15 atmospheres with CO-rich gas. Results are compared for temperatures of 235 and 225°C. for catalysts containing copper and copper-free catalysts.

Table XIV

The effect of the Addition of Copper Upon the Activity of Iron Catalysts

<u>Synthesis temperature</u> <u>Days of operation</u>	235°		225°	
	Fe without Cu	5Fe:1Cu	Fe without Cu	5Fe:1Cu
1	55	54	52	55
2	53	56	-	54
3	53	-	50	50
4	55	50	-	-
5	55	50	45	50
10	54	52		

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

#### H. The Effect of the Addition of Kieselguhr.

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

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

The kieselguhr was added at various stages of the catalyst preparation. The following experiments were carried out: Experiment 1, 4 g. of kieselguhr per 10 grams of iron were added to the iron solution prior to precipitation; Experiment 2, 4 grams of kieselguhr per 10 grams of iron were added to the soda solution prior to precipitation; Experiment 3, 4 grams of kieselguhr per 10 grams of iron were added to the moist catalyst slurry after alkalization (see Part I, "Catalyst Preparation"); Experiment 4, the possibility of adding dry kieselguhr to the finished catalyst has to be dismissed if one desires to produce a solid granular catalyst.

The results of experiments 1 to 3 are given in Table XXVI. Experiment 3a refers to a synthesis temperature of 235°C., 3b refers to 225°C. The various contractions obtained after various times of operations are recorded in the table. In all cases, the catalyst was induced for 24 hours using 1 liter per hour of CO per 10 g. of iron. The induction pressure was 1/10 atmosphere, and the temperature, 325°C. After this, the synthesis was carried out with a CO-rich gas (3CO + 2H<sub>2</sub>) at 15 atmospheres.

Table XXVI  
The Effect of the Addition of Kieselguhr to the Catalyst

Days of operation	Experiment 1		Experiment 2		Experiment 3a		Experiment 3b	
	Temp. °C.	Contraction percent	Temp. °C.	Contraction percent	Temp. °C.	Contraction percent	Temp. °C.	Contraction percent
1	235	53	234	55	235	54		
2	235	50	234	53	235	54	225	50
3			234	51			225	56
4			234	50			225	56
5			235	49	235	54	225	54
6	234	45	236	50	235	54	225	54
8			235	49	235	56	225	54
9			234	40	235	55	225	50
10					235	54	225	56
20					235	54		
30					235	52		
40					235	52		
50					235	50		
60					235	50		

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

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

Table XXVII  
Analyses of the Reaction Gases  
From the Kieselguhr Catalysts at a Contraction of 53-54 Percent

	CO <sub>2</sub>	sKW	O <sub>2</sub>	CO	H <sub>2</sub>	KW	CZ	N <sub>2</sub>
Experiment 1	59.1	3.5	0.2	6.3	12.9	4.7	1.9	13.3
Experiment 2	59.2	4.4	0.1	5.4	11.1	6.1	1.7	12.7
Experiment 3a	54.8	3.0	0.1	1.3	6.0	11.4	1.9	13.4
Experiment 3b	55.9	2.6	0.2	8.8	9.9	7.7	2.1	14.2

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

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

The products were colorless. The composition will be disclosed at another place.

A catalyst corresponding to that used in experiment 3b was charged into a vertical apparatus composed of 18 tubes (18 catalyst charges, 10 g. of iron per tube). After the catalyst was inducted with CO at 1/10 atmosphere and 325°C., it was switched over to the synthesis at 15 atmospheres and 225°C. using a CO-rich gas. Within 6 days, the contraction decreased from 54 to 50 percent. After this, the catalyst was treated with H<sub>2</sub> at the same temperature. On the eighth day, the contraction was 52 percent, on the tenth day, it was 47 percent. After a second H<sub>2</sub> treatment, the synthesis was carried out at 230°C. and then at 232°C. On the 17th day, the contraction had decreased to 43 percent again. After another H<sub>2</sub> treatment, the experiment was conducted for another week at 236°C., etc. (see Figure 11).

When the results of the experiments carried out in horizontal respectively slightly inclined tubes (experiment 3b, Table XXVI) were compared with experiments carried out in a vertical apparatus, it was observed that the latter showed a less uniform course. Anyhow, it was possible to maintain a contraction of approximately 50 percent by treating several time with H<sub>2</sub>. (Details on the apparatus used in those experiments are contained in Part IV).

### Part III The Reaction Products

In the middle-pressure synthesis with iron catalysts, paraffin and olefin hydrocarbons are formed showing great variation in molecular size. They vary from methane and low gaseous hydrocarbons up to high molecular solid paraffins. In Table XXVIII the yields of solid paraffins, liquid products, and gasol hydrocarbons of some experiments carried out under different conditions are summarized.

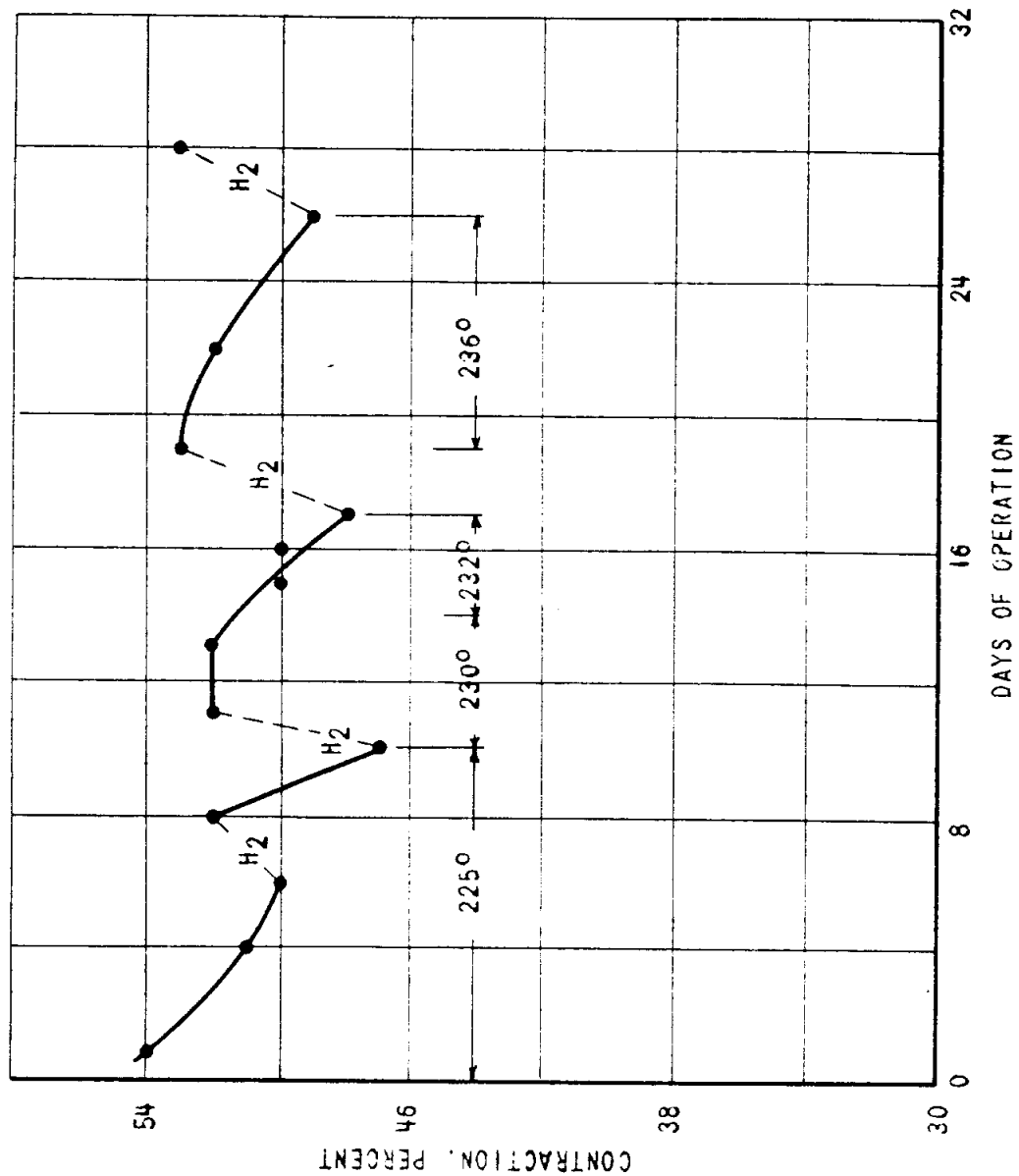


Figure 11. - Experiments with iron Kieselguhr catalysts in vertical units.

Table XVIII  
Solid, Liquid, and Gasol Hydrocarbons at Various Reaction Conditions

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

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

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

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

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

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

#### A. Liquid Hydrocarbons.

The crude liquid total product generally is not colorless but is somewhat yellowish. After distillation, one obtains water-clear colorless benzine. The small quantities of yellow oil remain as a residue. The benzine is stable, it remains colorless after months of storage. The percentage of liquid hydrocarbons boiling off below 180°C. is greatly dependent in the experimental conditions

and can vary between wide limits. Thus, ? percent boiled off below 130°C. from liquid hydrocarbons produced with a normal catalyst containing 1/4 percent  $K_2CO_3$  and a reaction temperature of 235°C. When a catalyst containing one percent  $K_2CO_3$  was used (at 235°C.), ? percent boiled off below 130°C. When a catalyst was used which was precipitated with ammonia, and contained 1/4 percent  $K_2CO_3$  at 250°C., 55 percent distilled over below 130°C. When an iron-copper catalyst was used at a reaction temperature of 260°C., 80 percent came over below 180°C.

Figure 12, shows a boiling point curve of the products obtained with the normal iron catalyst at 235°C.

Figure 13, shows an Engler-Distillation curve for a benzene synthesis at a reaction temperature of 250°C. and boiling up to 180°C. 50 percent of this benzene boiled below 80°C.; 60 percent below 100°C. The boiling point characteristics of the benzene can be changed drastically by changing the working conditions during the synthesis. Thus, at 235°C., and used the normal iron catalyst, the benzene was produced boiling up to 180°C. Of this 50 percent boiled below ? °C. For another iron catalyst and a working temperature of 260°C., a benzene boiling below 100°C. was produced of which 50 percent could be driven over below 73°C. Table XXIX shows the density, olefin contents, boiling point characteristics, and octane number of some benzenes produced with the iron catalyst.

Table XXIX  
Properties of Benzenes Produced with Iron Catalysts

No.	Washed with NaOH	$d_{15}^4$	Olefin	Boiling Point Analyses				P37.8°	Octane No
				Starting	10%	50%	90%		
1	Yes	0.696	64	30°	46°	85°	145°	0.54	61
2	Yes	0.678	65	30°	38°	75°	145°		62
3	No	0.698	38					0.48	63

Test No. 1, in Table XXIX, refers to a catalyst precipitated with ammonia, that of test No. 2, refers to an iron-copper catalyst, and test No. 3, to an iron-kieselguhr catalyst.

The density of the benzenes boiling below 130°C. was somewhat lower than 0.7. With phosphorous pentoxide-sulphuric acid, 64 respectively 65 respectively 38 volume percent of olefins could be taken out. The octane number of the 3 stabilized benzenes was found to be (1-63 according to the motor method. Possibilities of improving the anti-knock properties of the benzene are discussed in another section dealing with the development of the primary products.

If one compares the portions which have been removed from the benzene by phosphorous pentoxide-sulphuric acid with the octane numbers, then one can observe that these do not depend exclusively on the olefin contents.

The synthol products contained in the reaction products from the iron middle-pressure synthesis are of importance. The quantity and nature of these compounds obtained varies considerably with the working conditions also. Table XXX shows acid-ester-saponification-and hydroxyl numbers of some of the synthesis products.

? German illegible



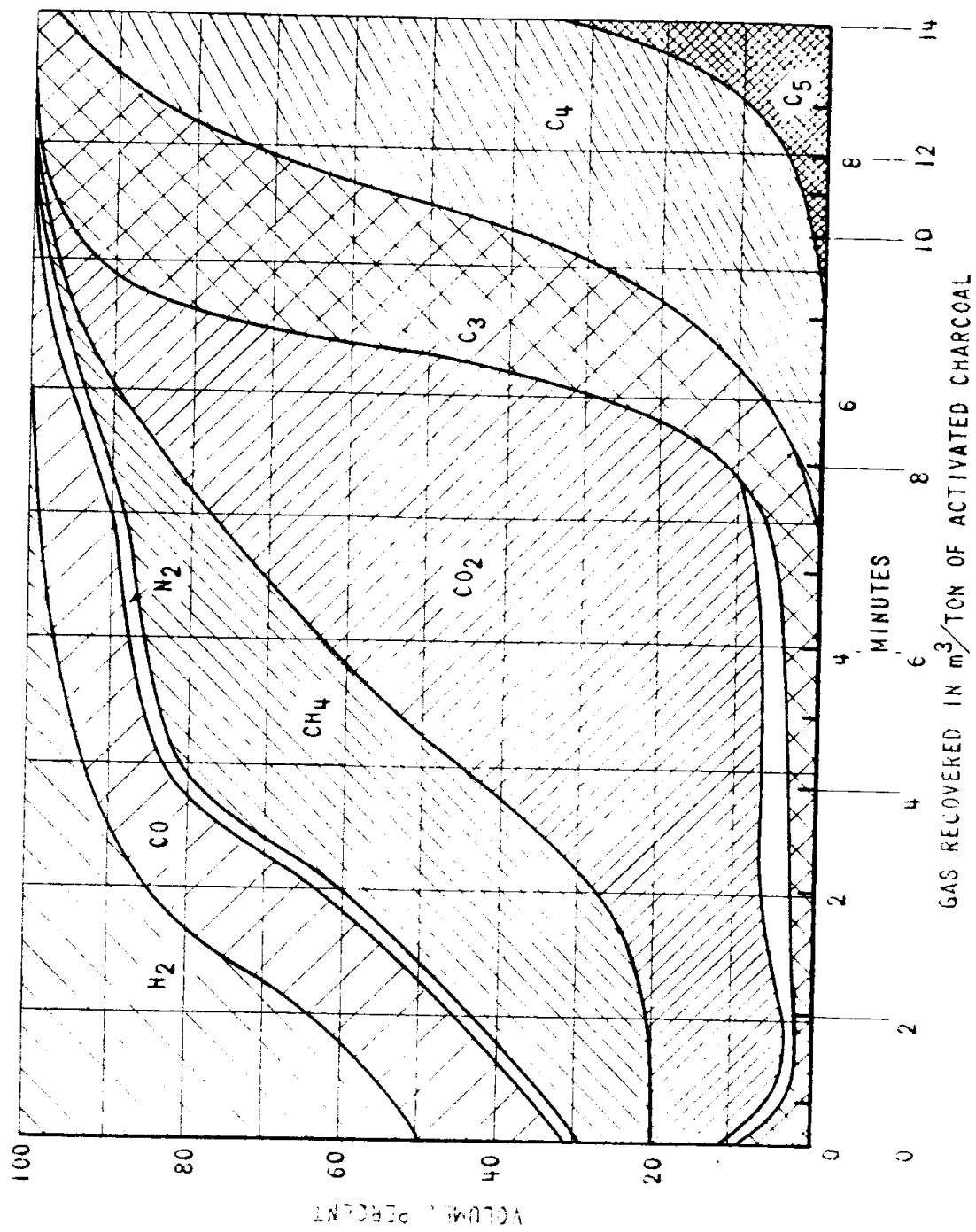


Figure 12. - Products recovered from active charcoal trap by steam distillation.

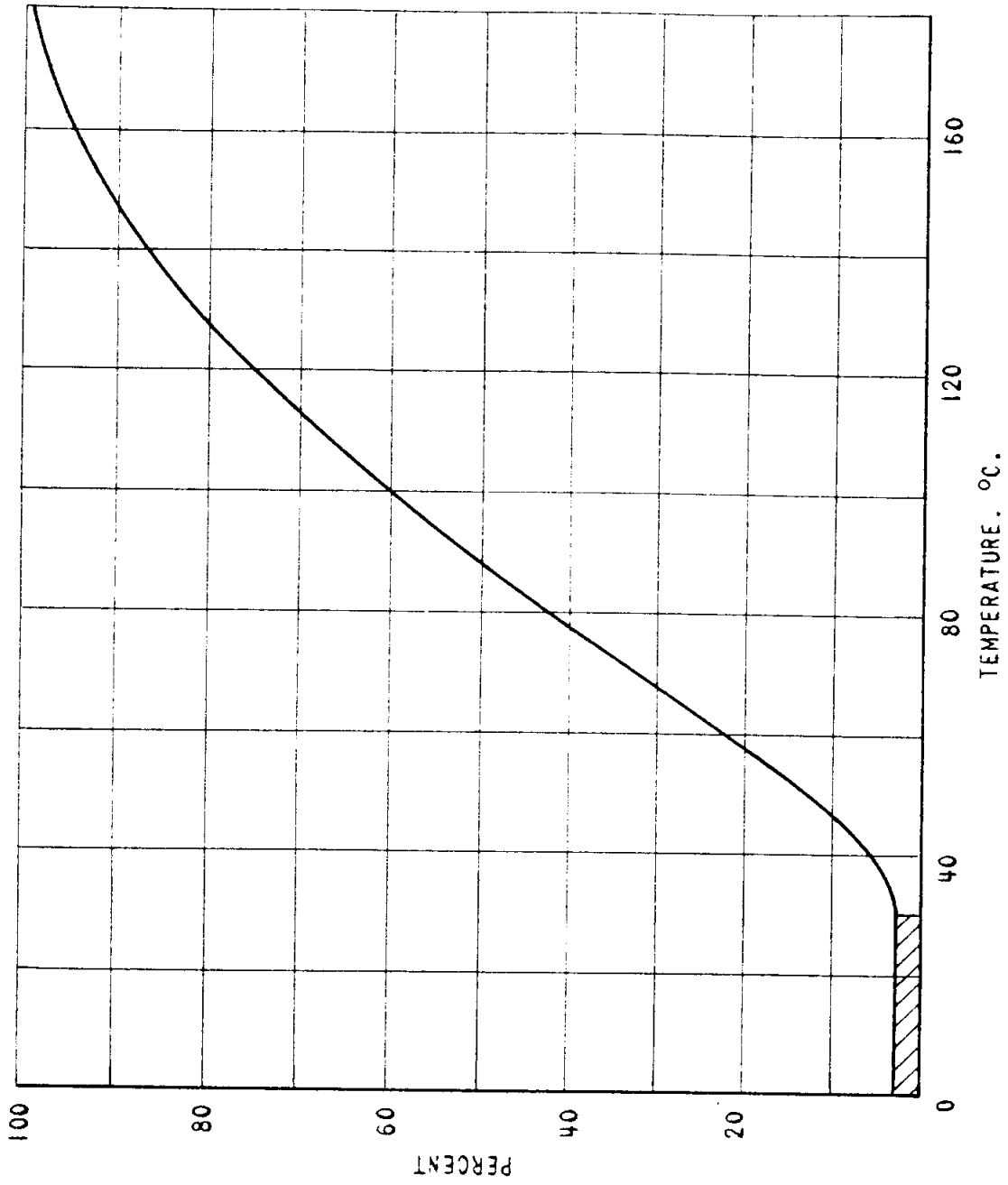


Figure 13. - Engler distillation of a benzene fraction.

Table XXX  
Oxygen-Containing Constituents of the Liquid Hydrocarbons

Catalyst	Boiling range °C.	Acid number	Ester number	Saponification number	Hydroxyl group number
Fe 1/4% K <sub>2</sub> CO <sub>3</sub>	30 - 130				
Fe " "	under 180	0.2	0.2	0.5	2.3
Fe 1% K <sub>2</sub> CO <sub>3</sub>	under 180	1.3	5.1	9.9	7.0
Fe-Kieselguhr 1% K <sub>2</sub> CO <sub>3</sub>	30 - 180	1.4	15.0	16.4	
Fe-Kieselguhr 1% K <sub>2</sub> CO <sub>3</sub>	under 180	0.1	2.0	2.1	

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

When the products obtained from the iron-kieselguhr catalyst were washed with a 30 percent calcium chloride solution, 2.5 percent was extracted. When another washing was carried out with sodium hydroxide, another .3 percent went into the aqueous solution.

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

Table XXXI  
Elementary Analysis of the Synthesis Products

	Total product			Benzene		
	C	H	O	C	H	O
Fe-Normal Catalyst						
Fe - Cu	84.60	15.16	0.24	83.94	14.97	1.09
Fe-Kieselguhr						

#### B. Paraffin

The solid and liquid reaction products contain (according to the Butanon method) approximately 5 to 50 percent paraffins. When a H<sub>2</sub>-rich synthesis gas and an alkali-deficient catalyst is used, the paraffin obtained is white to slightly yellowish. When a CO-rich gas is used and catalysts with one or more percent potassium carbonate, the paraffins are yellow to yellowish-brown. The coloring substances are believed due to iron respectively iron salts. Generally however, small quantities of higher boiling oils are responsible for the discoloration. These oils may be extracted or may be made colorless by hydrogenation.

The melting points of the paraffins extend over the entire known melting point region of the known paraffins. The total product especially contains high melting constituents, so that it melts to a clear liquid at comparatively high temperatures. Meniscus formation was observed in the melting point tubes at 80°C. for a paraffin freed of liquid hydrocarbons by the Eutanon method produced through a catalyst with 1/4 percent  $K_2CO_3$ . When a catalyst containing one percent  $K_2CO_3$  was used, the meniscus formation was observed at 104°C. When an iron catalyst was used, which contained one percent  $K_2CO_3$ , a paraffin was obtained which was 50 percent soluble in boiling ether. The product reprecipitated from this solution with methyl alcohol showed a final melting point of 66 to 70 percent. 41 percent was insoluble in ether (24 hours extraction in the soxhlet). It was, however, soluble in boiling hexane. They had a final melting point between 90 to 104°C. The rest (9 percent) which was insoluble in hexane had a melting point of 122°C.

When the iron catalyst was extracted, a so-called paraffin was obtained which after fractional extraction was insoluble in boiling benzol, but soluble in boiling toluol. It contained constituents melting at about 126°C.

### C. Gasol.

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

Table XXXII brings a summary of the results of the low temperature distillations. The figures referring to the first distillation are calculated on the basis of the gasol quantities referring to the second distillation. The portion of unsaturated hydrocarbons of the various fractions was determined with mercury nitrate.

Table XXXII  
 $C_2$  to  $C_4$  Hydrocarbons Formed During the Synthesis

	First distillation ccm	Second distillation ccm	Weight percent of $C_2 +$ gasol fraction
Ethylene	2360		15.3
Ethane	1830		12.2
Propylene	3480		24.9
Propane	1130		11.9
Butylene	1010	233	17.9
Butane	370	87	6.4

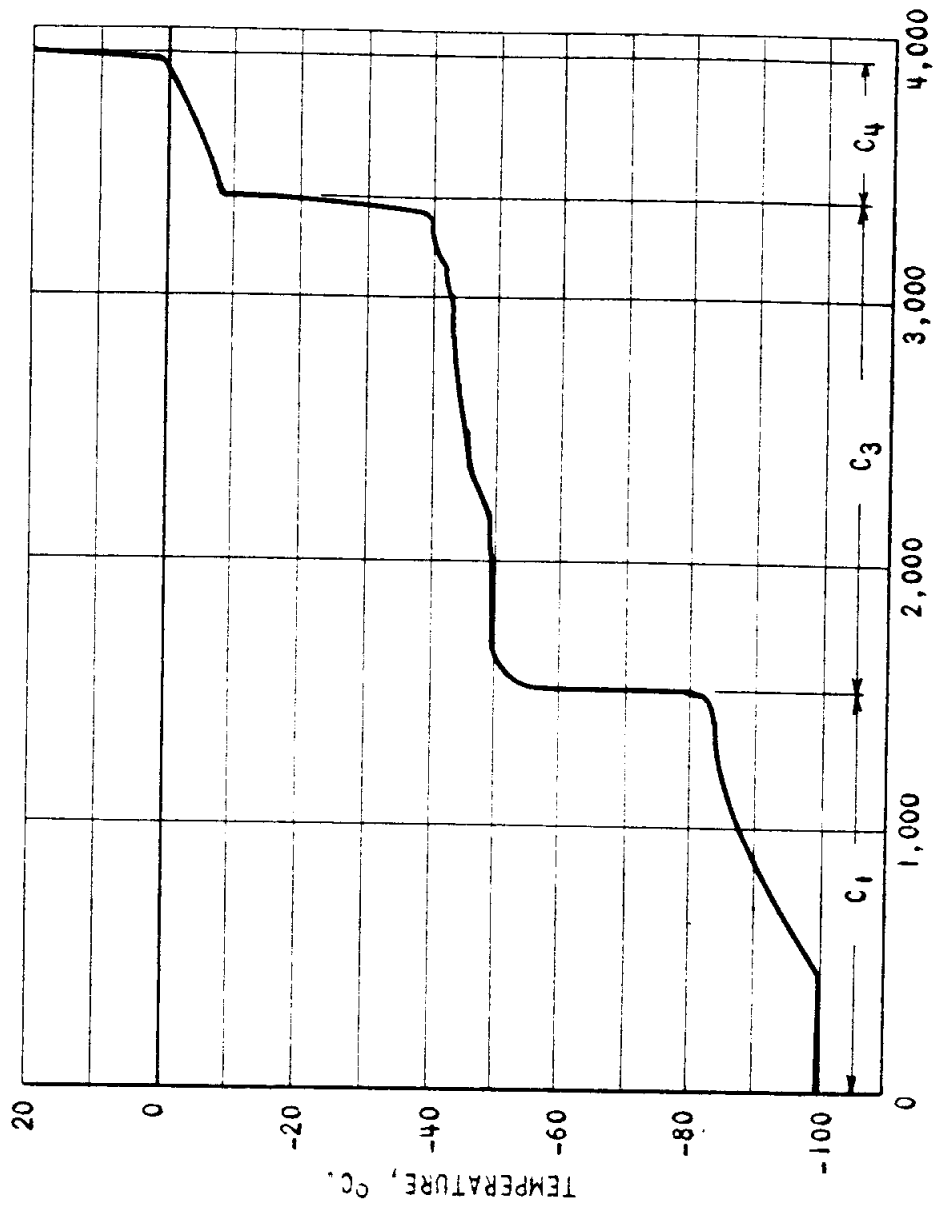


Figure 14. - Distillation of gaseous hydrocarbons.

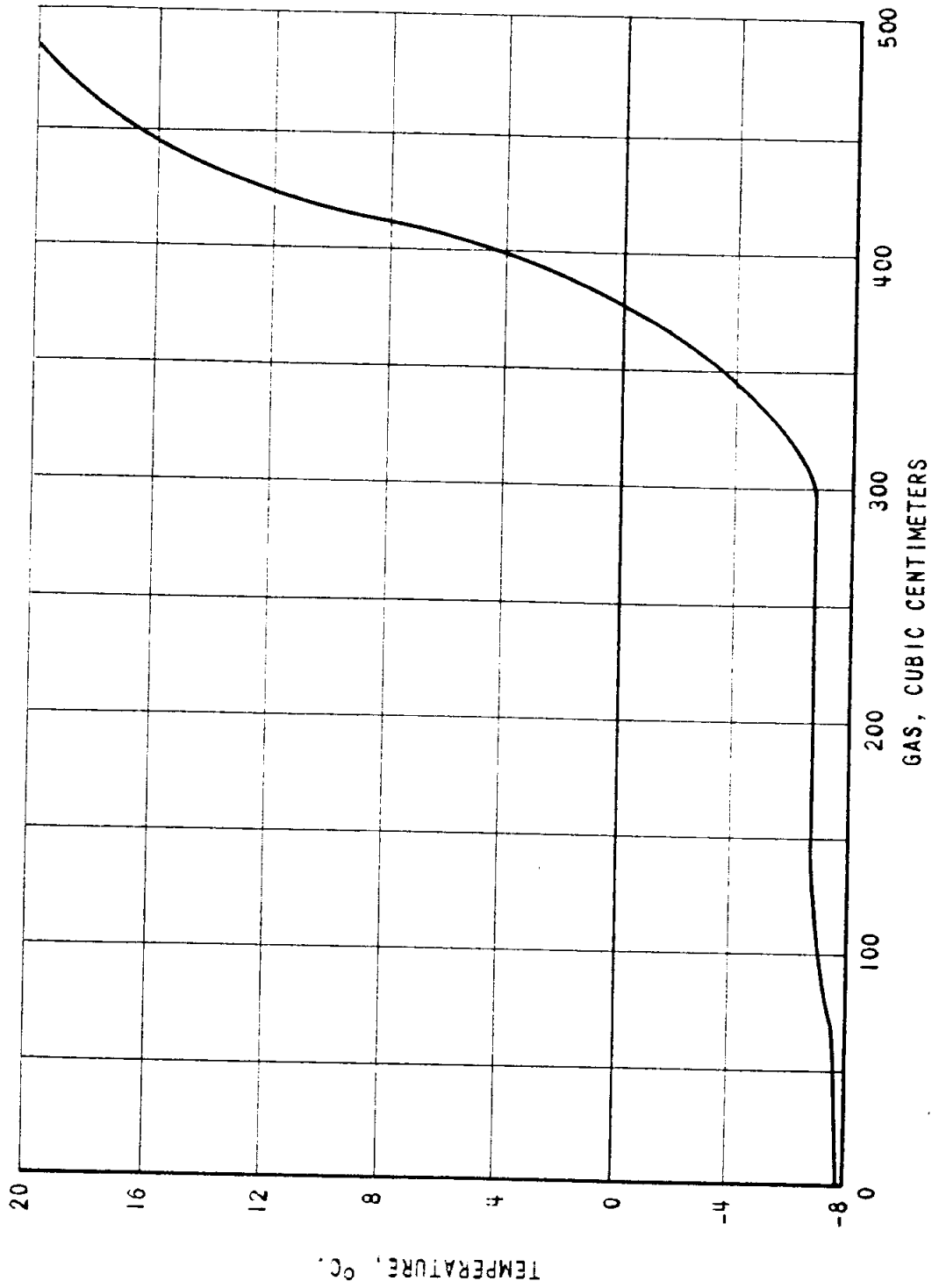


Figure 15. - Removal of C<sub>4</sub> - hydrocarbons from benzene.

The C<sub>2</sub> fraction contained 55 weight percent of ethylene, 74 percent of the total gasol fraction consisted of unsaturated hydrocarbons. For this experiment, 5.2 grams per normal cubic meter of ethylene, 11.1 of propylene, and 6.0 g. per normal cubic meter of butylene were obtained.

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

Table XXXIII  
Yields of Gasol Hydrocarbons With Different Catalysts\*

Catalyst	Temp., °C.	Grams of gasol per normal cubic meter of ideal gas	Percent of gasol unsaturated hydrocarbons
Fe, NH <sub>3</sub> precipitated, 0% K <sub>2</sub> CO <sub>3</sub>	235	30	70
Fe, Na <sub>2</sub> CO <sub>3</sub> precipitated 0% K <sub>2</sub> CO <sub>3</sub>	235	28	80
Fe, " " 1/4% "	235	26	75
Fe, " " 1% "	235	17	80
Fe, " " 1/4% "	270	46	47
Fe-Kieselguhr 1% K <sub>2</sub> CO <sub>3</sub>	235	36	35

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

#### D. Oxygen-containing Products.

##### 1. The Reaction Water.

With the iron-kieselguhr catalyst and the reaction temperature 235°C. (CO-rich gas, 15 atm.), approximately 13 g. per normal cubic meter of aqueous products were formed. They contained acids, aldehydes, and esters as well as alcohols. (Test for formic acid was negative, that for acetic acid, positive. Test with fuchsine sulphurous acid, positive. The presence of ester was demonstrated by saponification. Little methyl alcohol was found, ethyl alcohol was recognized but its boiling points, and the iodoform reaction.) The reaction water was subjected to a distillation through a micro column. Figure 16 shows the boiling point analysis of the constituents boiling below 90°C. (23 percent of the total reaction water).

\*The quantity of the gasol hydrocarbons produced during the synthesis may be increased. Research being conducted at present is concerned with this problem.

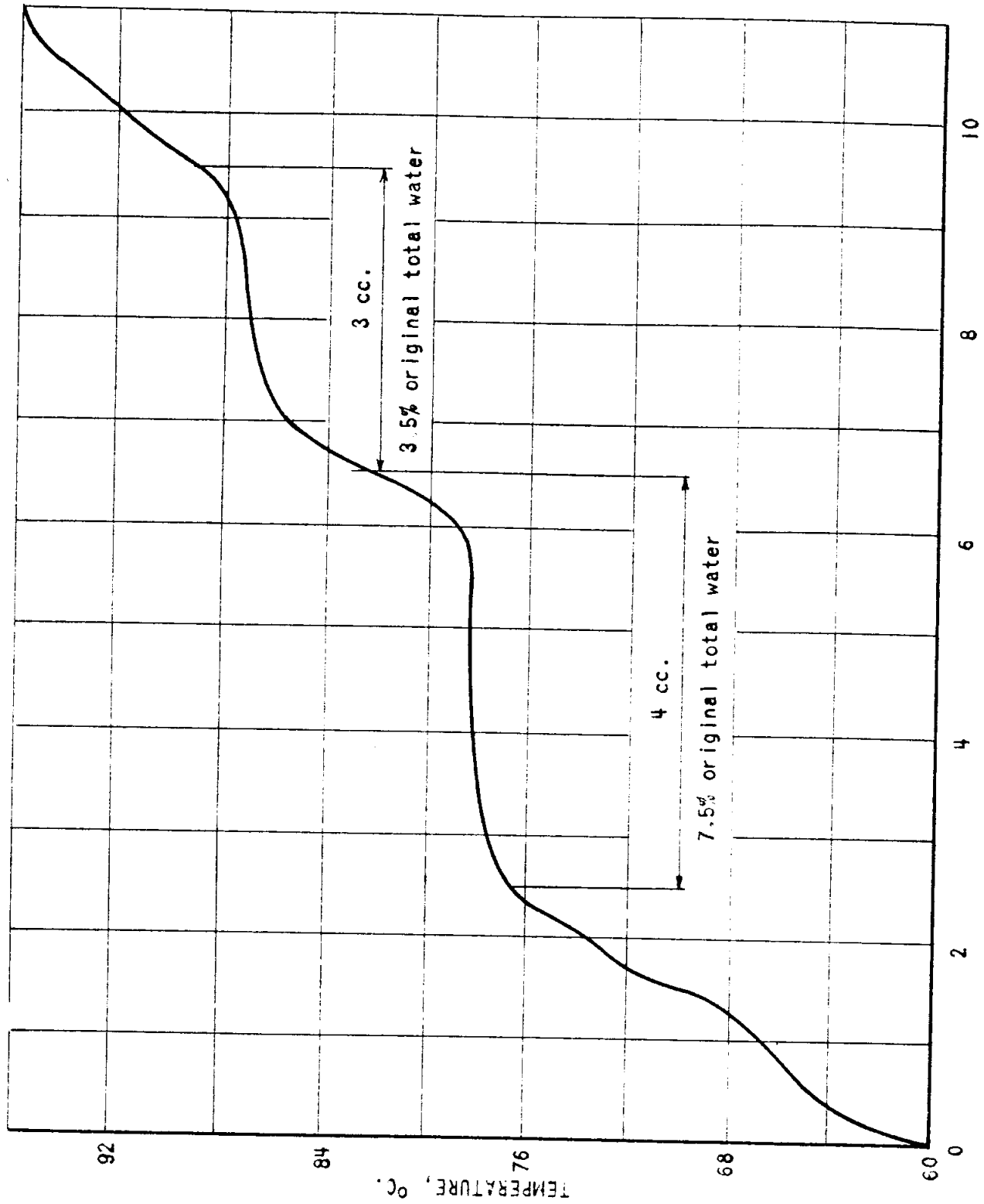


Figure 16 -- Boiling point analyses of the reaction water boiling below 90°C. (charge 15 cc.).



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

## 2. The Hydrocarbons.

Table AIA has shown that the reaction products boiling above as well as those boiling below 130°C. contain more or less synthol, depending on the working conditions. In addition to organic acids, esters and alcohols were detected. Investigations are in progress designed to disclose the nature of the higher alcohols and esters. The results of these investigations will be published separately.

In the following, a description is given of the products which can be extracted with a 30 percent calcium chloride solution from a benzene boiling up to 130°C. (5.5 percent of the benzene). Figure 17 gives the results of a distillation (corresponding to Figure 16) of the aqueous solution distilled off up to 95°C.

## 3. City Gas.

The question has been asked repeatedly whether it is possible to use coke for the production of city gas. Since water-gas has too low a heating value, it would be necessary to increase this heating value by partially converting the water-gas into hydrocarbons. With the aid of nickel or cobalt catalysts, this is possible without any difficulties. It was investigated whether the production of such a gas could also be accomplished over the iron middle-pressure synthesis. With a normal pressure synthesis and using iron catalysts, the gas which was produced did not possess the desired heating value.

A usable city gas should fulfill the following requirements and possess the following properties:

### I. Combustion properties.

1. Heating value (higher heating value) is equal to 4,200 to 4,600 kilogram calories per normal cubic meter.
2. Density is equal to 0.4 to 0.5 as referred to air = 1.
3. Gas pressure, higher than 60 mm.
4. Flash-point, 60 to 100.

### II. Purity.

1. Oxygen less than 0.5 percent.
2. Hydrogen-sulfide less than 2 g. per 100 m<sup>3</sup>
3. Ammonia, less than 0.3 g. per 100 m<sup>3</sup>
4. Naphthalene  $\frac{5 \text{ to } 10}{5}$  g. per 100 m<sup>3</sup>
5. Organic sulfur, less than 25 g. per 100 m<sup>3</sup>, hydrogen cyanide less than 15 g. per 100 m<sup>3</sup>, nitrogen oxides, 0.2 cc. per m<sup>3</sup>.
6. Practically free of tar.

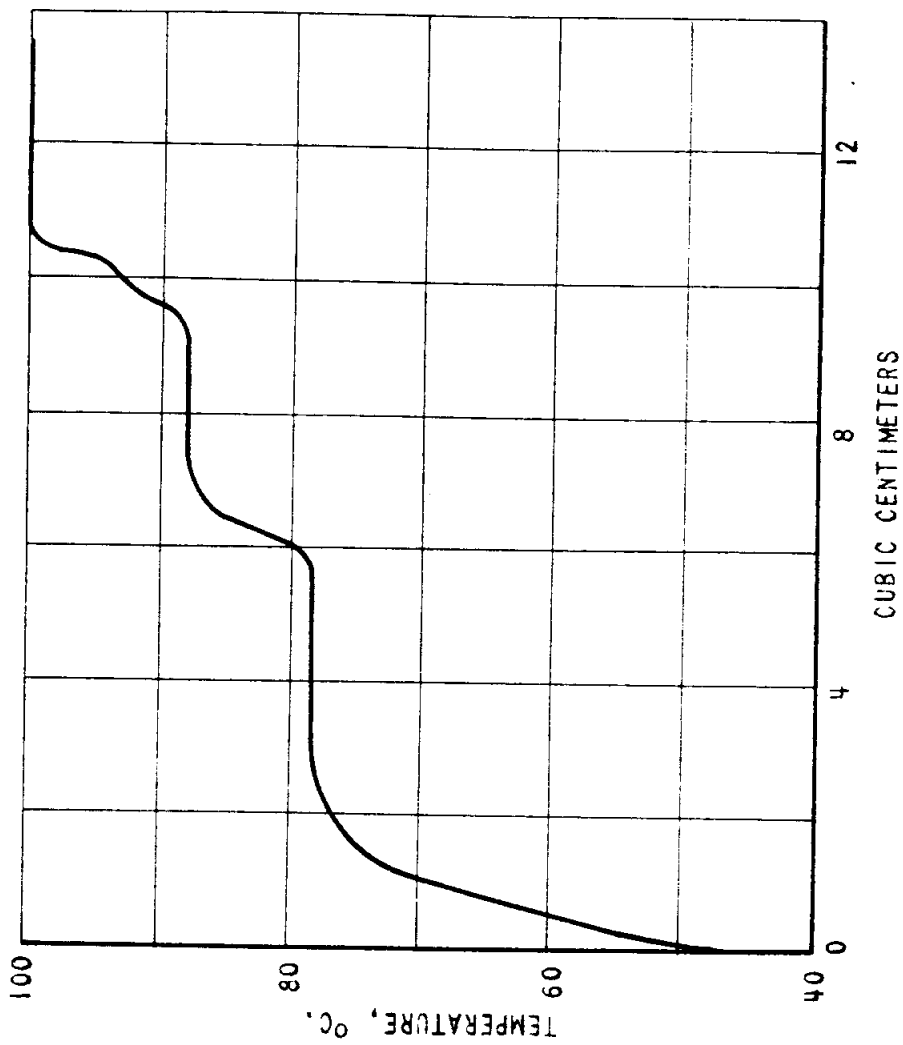


Figure 17. - Distillation of water soluble constituents of the liquid reaction products (charge 15 cc.).

### III. Final purification.

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

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

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

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

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

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

Table XXXIV

Production of a Gas With the Properties Required by a City Gas

Catalyst: Alkali-free iron catalyst.  
Synthesis Gas: CO to H<sub>2</sub> is equal to 1:3  
Pressure: 10 atmospheres  
Temperature: 235 to 270°C.

	CO <sub>2</sub>	SKW	O <sub>2</sub>	CO	H <sub>2</sub>	KW	<i>Mo.</i> %	N <sub>2</sub>
Initial gas	0.0	0.0	0.0	23.5	73.5	0.0	-	3.0
Final gas	10.9	0.2	0.1	1.0	69.8	13.1	1.8	4.9

This reaction gas has a heating value of 4154 kilogram calories per normal cubic meter (Junkers-Kalorimeter), a density of 0.4 to 5, and a flashpoint of 70 to 71. When a more N<sub>2</sub>-deficient gas is used, the heating value may be increased by 100 kilogram calories.

The gas, therefore, corresponds to all requirements.

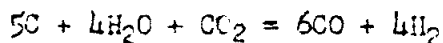
According to our experiences, the iron-kieselguhr catalyst is best suited for the production of a city gas.

Part IV  
General Problems

A. Synthesis Gas Production.

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

For our experiment, we generated such a gas in a normal water-gas generator (21) which we had here at the Institute. We passed a mixture of steam and CO<sub>2</sub> over burning coke. Such a procedure we believe could also be recommended for the technical scale, since during the synthesis with the iron catalyst, much more CO<sub>2</sub> is formed than is required for the production of the synthesis gas. Use of one m<sup>3</sup> of synthesis gas of composition 3CO + 2H<sub>2</sub>, gives approximately 250 liters of CO<sub>2</sub> at normal conversion. This occurs according to the equation:



According to this equation, only 100 liters of CO<sub>2</sub> are required per cubic meter of CO-rich gas. Therefore, it would only be necessary to wash the CO<sub>2</sub> out of the end-gas partially, and lead the end-gas back into the gas generator.

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

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

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

1. Water gas.  $C + H_2O = CO + H_2$  for every cubic meter of water-gas; 267 g. of carbon, and 500 liters of steam are used. 650 kilogram calories are required.

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

3. CO-rich synthesis gas.  $5C + 4H_2O + CO_2 = 6CO + 4H_2$ . For producing one cubic meter of such a gas, 268 g. of carbon, 400 liters of steam, 100 liters of CO<sub>2</sub>, and 690 kilogram calories are required. For the production of all of these three gases, one requires the same amount of carbon per cubic meter of gas.