D. Oxygen-Containing Products

1. The Reaction Water

About 13 g of aqueous products were obtained/ncbm gas at 235°C, CO - rich gas, 15 atm, with an iron-kieselguhr catalyst. They contained acids (the test for formic acid was negative, for acetic acid was positive), aldehydes (positive test with Schiff's reagent), esters (determined by saponification, 5.2 g calculated to ethyl acetate/li of the reaction water), also alcohols (small amount of methyl alcohol, ethyl alcohol determined by boiling point and the iodoform reaction). The reaction water was distilled in a microcolumn and a rotating band. Figure 16 shows the boiling point analysis of a fraction boiling below 90°C (28 percent of the total reaction water).

The boiling point curve shows distinctly the ethyl alcohol fraction. It represented 7.5 percent of the total water of reaction.

2. Hydrocarbons

Table 30 shows that the reaction products boiling below 180°C as well as those boiling above 180°C contained varying amounts of synthol - like products, depending on the operating conditions. The presence of organic acids, esters and alcohols has been proven. Investigations of the composition of the higher alcohols and esters are at present in process, and will be published separately.
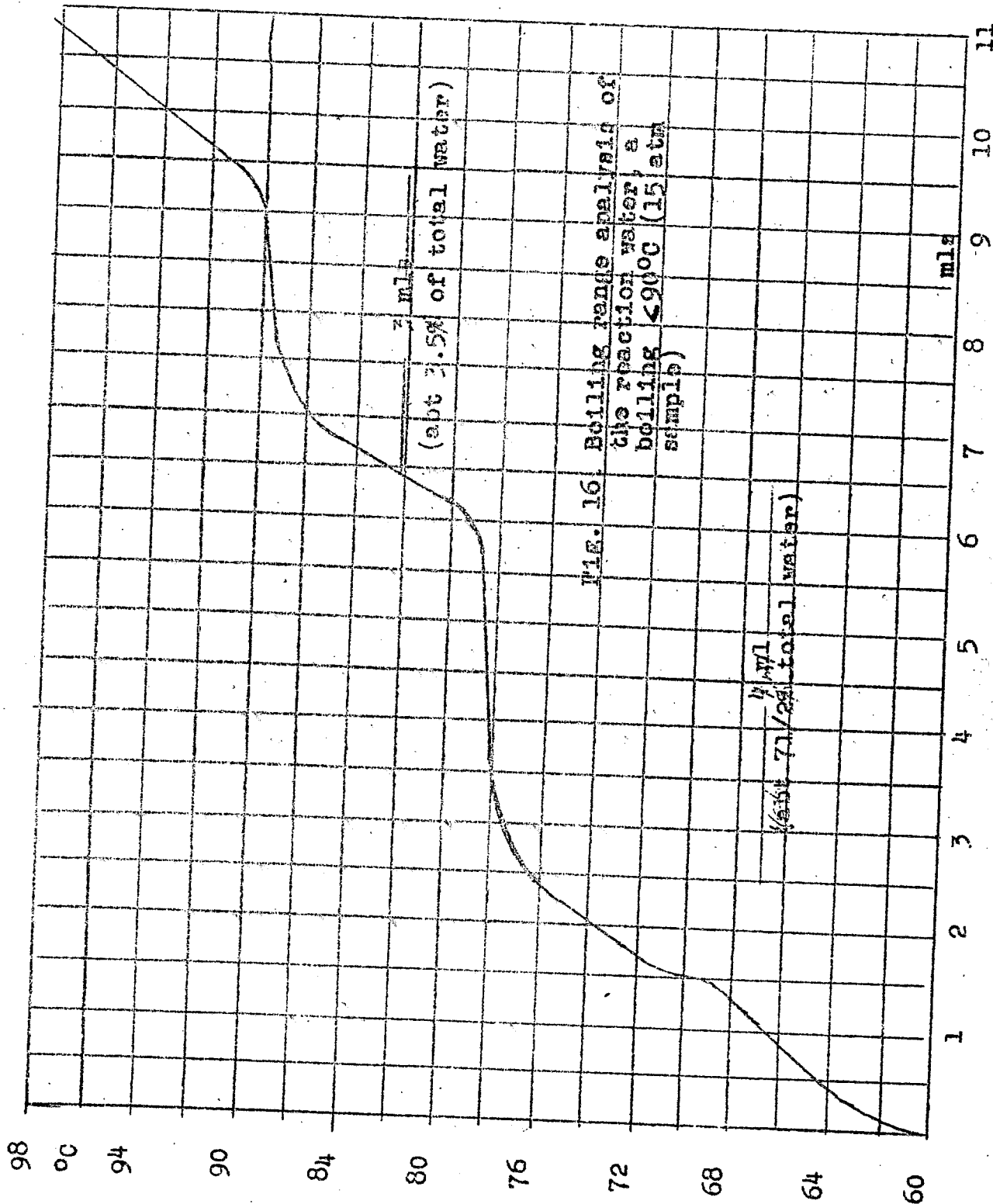
Fig. 16 Boiling range analysis of the reaction water, a boiling <90°C (15 atm sample)

We will discuss briefly the products obtained by extraction of a 180°C b.p. gasoline obtained with an iron-catalyst (total 5.5 percent of the gasoline) with a 30 percent calcium chloride solution of the products. Figure 17 shows the distillation(similar to figure 16) of a water solution distilled to 95°C.

E. City(Illuminating)Gas

As a result of the present shortage of coke oven gas, the question is frequently asked about the possibility of preparing a suitable city gas from coke. The heating value of water gas is too low and to obtain the required heating value hydrocarbons would have to be made by synthesis. This is readily possible with nickel or cobalt catalysts. It was necessary to find out whether the production of such a gas was also possible by way of the iron middle pressure synthesis. Under normal pressure iron catalysts did not produce a gas with a sufficiently high heating value.

According to specifications 19/ for the properties of this gas, the following properties had to be met:

I. Combustion properties

    1. Heat of combustion (upper heating value) 4,200 to 4,600 kcal/ncbm.

    2. Density (Air = 1) = 0.4 - 0.5

    3. Gas pressure over 60 mm

    4. Flash point (Ottzahl) 60 - 100

II. Purity

    1. Oxygen less than 0.5 percent

    2. Hydrogen sulfide less than 2 g/100 cbm.

    3. Ammonia less than 0.3 g/100 cbm.

    4. 5 to 10 g/100 cbm at atmospheric pressure

    5. Organic sulfur less than 25 g/100 cbm, Hydrogen cyanide less than 15 g/cbm, nitric oxide 0.2 ml/cbm.
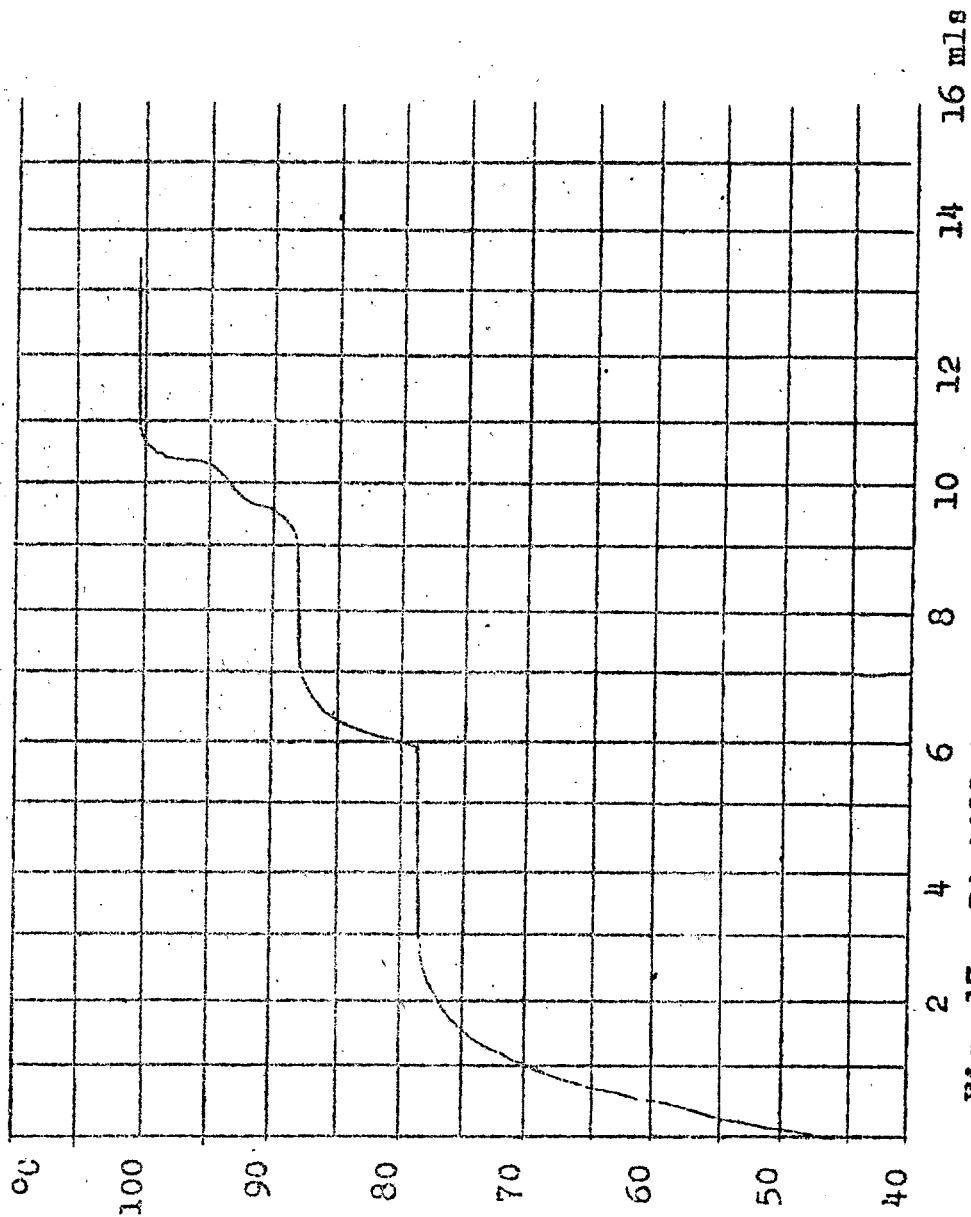
Fig. 17, Distillation of the water fraction of
the liquid reaction products (14 mls sample)

6. Practically tar-free

III. Final Purification

1. Any possible corrosion is considerably reduced by lowering the values under II, using final purification methods. Points I - III are not specifications but only directions for having a gas operating perfectly in the gas equipment. These specifications do not contain the formerly common limits of content of inert constituents.

Bruckner and Weissbach [20] have suggested the addition of propane, formed during synthesis, to water gas. They have shown that mixtures of propane and water gas containing 6 - 7 1/2 percent of propane had heating values of 4,200 - 4,500 kcal/ncbm. Such gas would have however, too high density (0.61 - 0.63) and too low flash point (40 - 46).

A gas satisfying the specifications can be readily obtained by mixing water gases or hydrogen-carbon monoxide mixtures with the total hydrocarbons of the synthesis gas obtained by removal of the liquid reaction products and the major part of the carbon dioxide, and containing the hydrocarbons $C_1 - C_4$.

City gas can also be obtained in the gasoline production by converting a carbon monoxide - hydrogen mixture 1 : 3 with iron-catalyst at about 10 atm pressure.

The formation of the higher hydrocarbons is greatly reduced by using an ammonia precipitated iron-catalyst, free from alkalies. Forming and thruputs were the same as usual. The initial temperature was $235^\circ C$, $250^\circ C$ after one month of operation, $265^\circ C$ after two months and $270^\circ C$ after three months. A gas of constant composition was obtained through the whole operation period. Table 34 shows the initial and end gas composition of this synthesis.

Table 34

Preparation of Gas Conforming to the Specifications

Catalysts: alkali free iron-catalysts
Synthesis gas: $CO : H_2 = 1 : 3$
Pressure 10 atm
Temperature 235 - 270°C

	CO_2	Heavy hydro- carbons	O_2	CO	H_2	Hydro carbons	Carbon number	N_2
Starting gas:	0.0	0.0	0.0	23.5	73.5	0.0	-	3.0
End gas:	10.9	0.2	0.1	1.0	69.8	13.1	1.8	4.9

The gas produced has a heating value of 4,154 kcal/ncbm (Junkers calorimeter), density of 0.425 (effusion method), Flash number of 70 - 71. When somewhat lower nitrogen gas is used the heating value can be raised by about 100 kcal without affecting the other constituents.

The gas thus meets the specification requirements, and is moreover sufficiently pure because of the final purification necessary for synthesis.

According to our more recent experience, the iron-kieselguhr catalysts is particularly well suited as a catalyst for the preparation of city gas because of its specific tendency to form gaseous hydrocarbons.

IV. General Problems

A. Manufacture of Synthesis Gas.

The best results in synthesis with iron catalysts are obtained with a gas in which carbon monoxide and hydrogen are in the proportion of 3 : 2, as has already been shown. This gaseous mixture was manufactured in our experimental installation at the institute using the usual water gas producer 21/ by passing steam and carbon dioxide over glowing coke. This method of preparation might also be suitable occasionally to a large scale industrial production, because much more carbon dioxide is formed during the synthesis with iron-catalysts than is required for the manufacture of synthesis gas. With normal conversion, 250 ll of carbon dioxide is formed/cbm of synthesis gas with $CO : H_2$ ratio of 3 : 2, while only 100 ll of
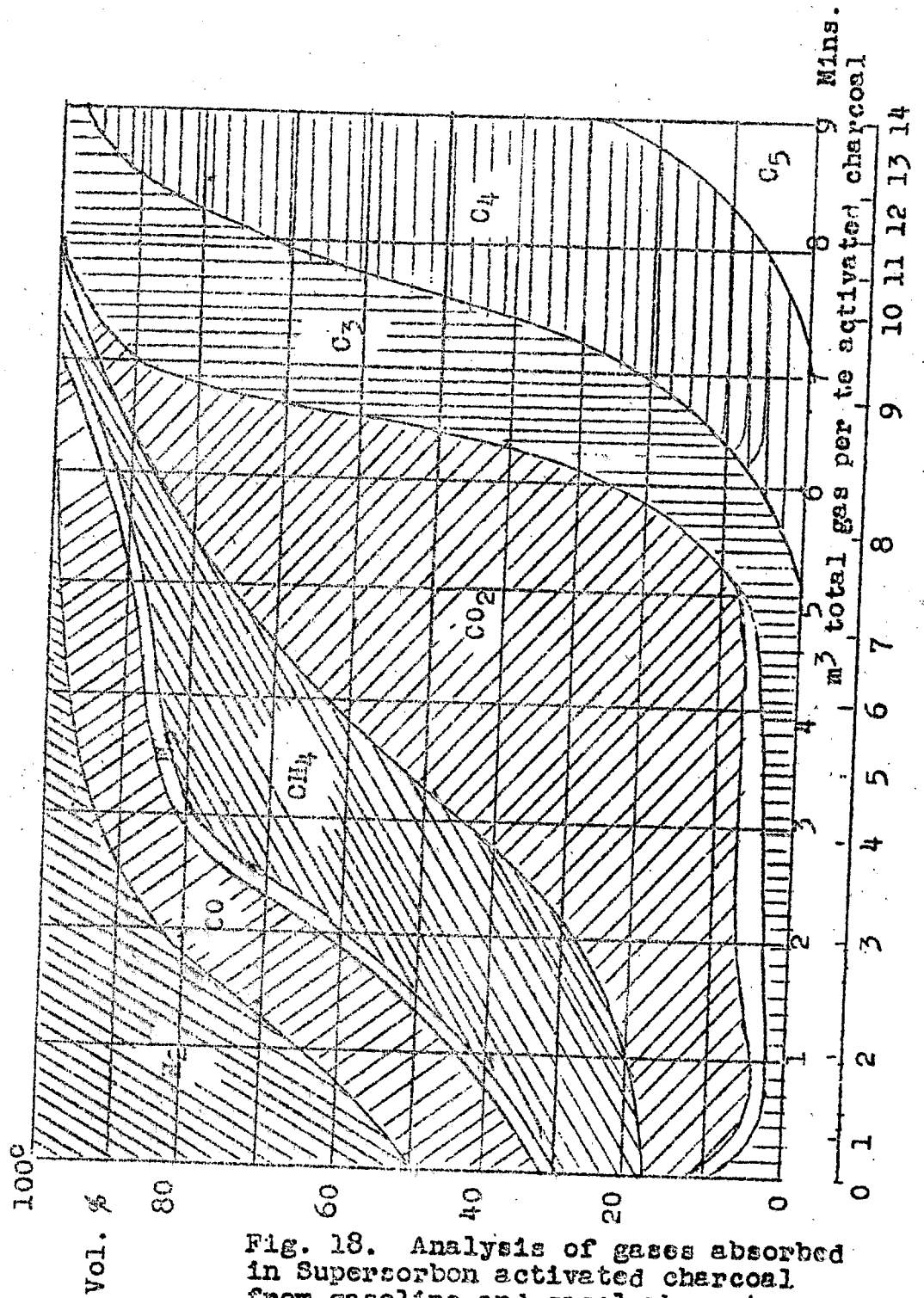
Fig. 18. Analysis of gases absorbed
in Supersorbon activated charcoal
from gasoline and gasol when steam-
ing it out (Instantaneous values
after 1,2, mins) (Herbert and Ruping)

carbon dioxide are necessary/cbm of carbon monoxide - rich gas according to the equation $5C + 4H_2O + CO_2 = 6CO + 4H_2$. Even a partial scrubbing out of the carbon dioxide from the end gas, and its return into the gas producer would cover the increased requirements of carbon dioxide against normal water gas.

The separation of carbon dioxide may be done with activated charcoal. Herbert and Ruping [22] reported briefly on such a method of operations for the separation of carbon dioxide from gasol in the Fischer-Tropsch synthesis. In this synthesis (with cobalt catalysts) almost no carbon dioxide is formed, but if a synthesis gas be used, obtained by a partial conversion of water gas and containing CO_2, a reaction gas with 35 - 40 percent carbon dioxide is formed resulting from the contraction of the gas during synthesis. If activated charcoal saturated with this reaction gas is steamed out in the reverse direction to the direction to charging it, the different gases are set free one after the other (as shown in figure 18), and methane and carbon dioxide can to a great extent be separated from the $C_3 - C_4$ hydrocarbons.

If the methane present together with carbon dioxide in the reaction gas (5 to 10 percent) and the unconverted carbon monoxide and hydrogen (10 - 15 percent combined) or passed with steam through the gas producer, the additional conversion would increase the synthesis yield to a value approaching more nearly to the theoretical (208 g/hydrocarbons/ncbm ideal gas).

We will compare below the theoretical conversions during the production of water gas, mischgas (CO : H_2 = 1 : 2) and carbon monoxide - rich gas (CO : $H_2 = 3 : 2$) used in the middle pressure synthesis with iron catalysts.

1. Water Gas

$$C + H_2O = CO + H_2$$

267 g carbon, 500 li steam and 650 kcal of heat are used up per cbm of water gas (without regard to the efficiency of the gas producer).

2. Hydrogen-rich Mischgas

$$3C + 4H_2O = 2CO + 4H_2 + CO_2$$
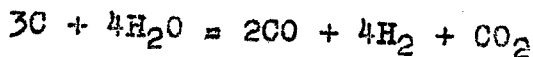
The formula represents the primary formation of water gas and its partial conversion into carbon dioxide and hydrogen. Theoretically 269 g carbon, 670 H_2O and 570 kcal of heat are consumed per cbm of the gas.

3. Carbon monoxide-rich synthesis gas.

$$5C + 4H_2O + CO_2 = 6CO + 4H_2$$
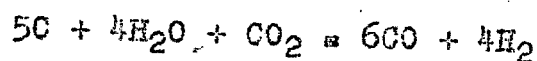
268 g carbon, 400 li steam, 100 li CO_2 (from synthesis) and 690 kcal of heat are consumed in the preparation of 1 cbm of this gas.

The same amount of carbon is therefore necessary per cbm of any of the three gases.

With a Dellwik-Fleischer gas producer, about 550 g coke were used per cbm of water gas, or about double the amount calculated theoretically without taking into account the heat of the reaction. The temperature and the heat requirements are about the same in the preparation of the carbon monoxide-rich gas as in the preparation of the water gas, and the coke requirements per cbm of the gas to be produced are also approximately the same.

The manufacture of carbon monoxide-rich gas in a water gas producer of 100 cbm per hour capacity was accomplished for several years at the Institute without any trouble. The composition of the synthesis gas was, for instance:

$$2\% \ CO_2$$
$$55\% \ CO$$
$$37\% \ H_2$$
$$6\% \ N_2$$

In several experiments with an accurate determination of the contraction (increase in the proportion of the nitrogen content during synthesis) some nitrogen was added.

The gas was purified in the same way as the hydrogen-rich gas.

Another method for the preparation of synthesis gas is the gasification of coke or coal with the addition of oxygen. It will not be discussed here any closer.