

#### IV. GERMAN OIL DEVELOPMENTS

Hubmann expressed some views on the German oil position during the war. Since 1942 all efforts have been made to increase the output of low temperature tar from brown coal. The biggest effort had been made in the Sudeten area where the brown coal had a high tar content.

The Bräx plant, which was a Herman Goering project, was capable of producing a million tons of low temperature tar a year. He believed that the actual output prior to the damage from bombing was at the rate of about 600,000 tons per year. The carbonisation ovens were designed for a through-put of 250 tons per day, but actually operated at 350 tons.

The production programme for finished products had to be changed to meet altered circumstances. When the plant started operating the primary product was gasoline. The programme was then altered to provide for a maximum output of diesel oil and then a further change was made to convert the plant to the output of high octane aviation fuel. Just before the war ended, plans were being made to make Bräx the principal producer of jet fuel.

No attempt was made to bring in any feedstocks, either tar or crude oil, from other areas. The low temperature tar from the Leipzig area was unsuitable for Bräx as the tar contained a proportion of arsenic which poisoned the catalyst.

Hubmann expressed the opinion that the petroleum crude oil produced in the latter stages of the war had been extremely expensive, the producing operations being very uneconomical in comparison with pre-war standards.

#### V. FISCHER-TROPSCH

Small scale research on the Fischer-Tropsch process has been conducted at the Lurgi laboratory east of Frankfurt, and pilot plant research has been carried out in the plants of customers, particularly Hoesch Benzin at Dortmund. This research was concentrated on the development of middle pressure recycle operation, particularly with iron catalysts. This type of operation was claimed to have the following attractive characteristics:

1. Use of charge-gas having a ratio of hydrogen to carbon monoxide little if any above 1:1, which is essentially water gas.
2. Easier temperature control due to high gas velocities through catalyst bed.
3. More olefinic product.
4. Formation of less carbon on the catalyst and less methane.

In working along these lines Lurgi appears to have been ahead of Ruhrchemie or more aggressive (or both) and developed a patent position which led to a contract with Ruhrchemie giving Lurgi the exclusive right to build Fischer-Tropsch plants under Ruhrchemie patent licenses in all countries except the United States and Japan. Lurgi's favorable position in the field of high pressure gasification was also a factor in reaching this agreement. Up to the end of the war Lurgi had exercised the rights thus acquired only in the building of city gas conversion units under the Geilenberg plan as discussed later in this report. The pilot plant work at Hoesch Benzin had demonstrated the merits of middle pressure recycle operation so that both Hoesch and Schaffgotsch had given orders for the conversion of their commercial plants to this type of operation. However these conversions had not been accomplished because of bombings of the plants in question and scarcity of necessary materials and equipment.

The Lurgi laboratory had done considerable work on the development of iron catalysts. It was stated that Ruhrchemie, Brabag, Rheinpreussen, and I.G. were also known to have worked on iron catalysts. At the request of some government bureau comparative tests on iron catalysts from different sources were conducted by Ruhland, but the results were inconclusive since different criteria of catalyst quality were used by different companies depending on the products which they desired to make. Details of these Ruhland tests were not available at Frankfurt. The catalyst submitted by I.G. for these tests was believed to be their fused ammonia synthesis catalyst containing some alkali and uranium and was inferior to some others tested. No commercial synthesis plants using an iron catalyst have been built in Germany, but one such plant was designed by Ruhrchemie and Lurgi for erection in Italy. It was stated that Lurgi could produce with the iron catalyst liquid products containing at least 60% wax.

Lurgi has been particularly interested in recycle operation of the Fischer-Tropsch process using a conventional externally cooled middle pressure reactor and a relatively low recycle ratio. This is to be distinguished from the I.G. process developed by Michael, which involves a very high recycle ratio, so that the heat of reaction is carried away by the circulating gas. Dr. Herbert stated that this I.G. process has been operated only on a pilot plant scale and in his opinion the cost of such recycling on a commercial scale would be prohibitive.

The Lurgi low recycle operation was developed in a pilot unit installed at Hoesch Benzin at Dortmund in 1938. This unit consisted of a single tube of the standard middle pressure reactor as built by Gutehoffnungshutte. (See Fig. 7, page 15). The annular layer of catalyst had an inside diam. of 24 mm. and an outside diam. of 44 mm. with an overall length of 5 meters. The tube was water-jacketed with a vapour chamber connected to the top by means of which the steam

pressure could be controlled to give the desired synthesis temperature. The unit was operated under varied conditions with a Ruhrchemie cobalt catalyst for about two years. Single pass operation with this catalyst gave a yield of 155-162 grams of liquid plus "gasol" per cubic meter and the liquid product had the following composition:-

Benzin boiling below 200°C	...	45%
Oil boiling 200/300°C	...	25%
Wax boiling above 320°C	...	30%
(Wax boiling above 460°C	...	12%

The octane number of the benzin was 40 and the cetane number of the fraction boiling from 120° to 280°C was above 100. With a recycle ratio of about 3:1 it was possible to increase the throughput by 30% without sacrifice of yield in grams per cubic meter or to obtain a yield of 170 grams per cubic meter at the same throughput. With recycle operation charging water gas instead of ideal gas the olefin content of the liquid was 50-60% instead of 20% as normally. The general characteristics of the preferred recycle operation with a cobalt catalyst are shown by Figures 1 and 2, pages 9 and 10. Figures 3, 4, 5, and 6, pages 11, 12, 13 and 14 show the characteristics of recycle operation with two different iron catalysts.

Figure 7, page 15, illustrates the conventional middle pressure reactor preferred for such operations. It was stated that six different engineering firms had collaborated in developing this reactor. Its upper limit of operating temperature is 230 C. and it is doubtful if it can stand much more than the commonly used synthesis pressure of 20 atmos.

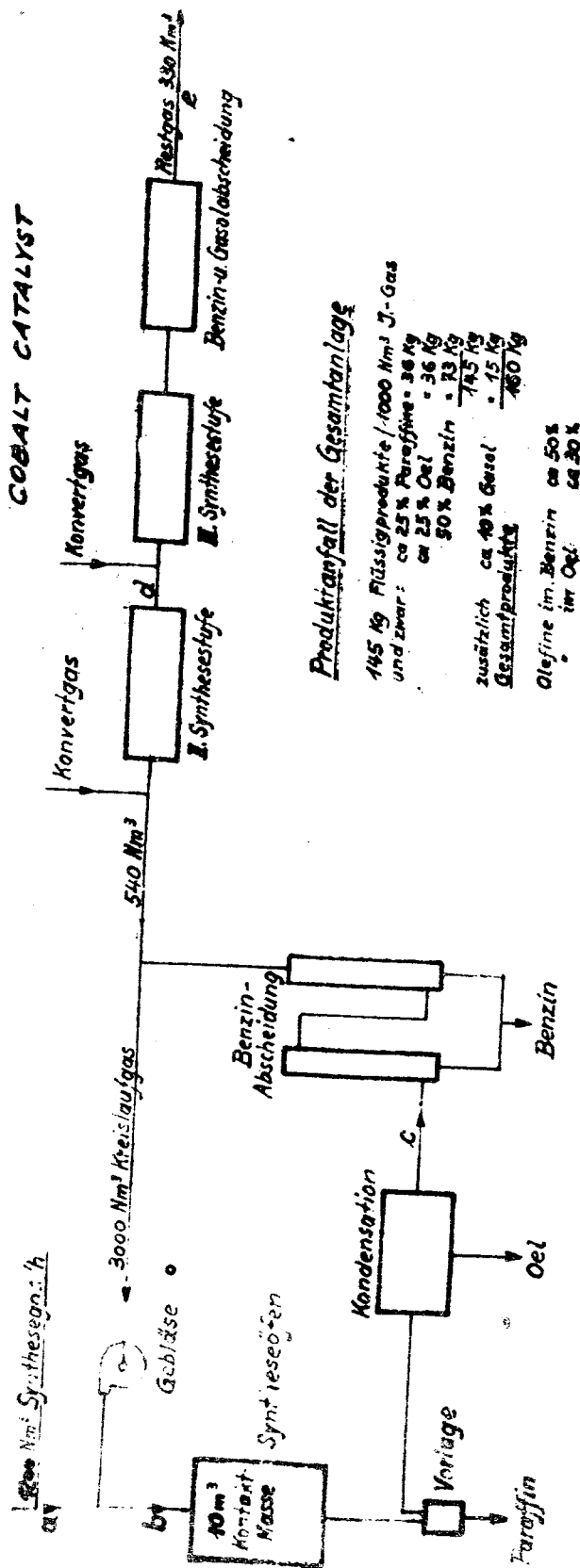
Dr. Herbert stated that the best iron catalyst developed by his laboratory has the following composition:

100 Fe, 25 Cu, 9 Al<sub>2</sub>O<sub>3</sub>, 2 K<sub>2</sub>O 30 SiO<sub>2</sub>

To make this Catalyst, copper nitrate and aluminum nitrate are dissolved in a 10% solution of ferric nitrate in such quantities as will give the specified ratio of metals. The solution is heated nearly to boiling and a 10% solution of sodium carbonate is added rapidly at about 70°C. in the quantity required to precipitate the metals as hydroxides. The kieselguhr is then added rapidly and stirred for about one minute. Lurgi has used kieselguhr No. 120 from the Deutsche Kieselguhr Co. The exact nature of this kieselguhr is unknown and no information is available about the suitability of other grades. The kieselguhr-hydroxide mixture is washed with hot water to a p H of 8.0 after which it is washed with a potassium carbonate solution to incorporate the specified quantity of K<sub>2</sub>O. Herbert told Capt. Chaffee that it is important to remove nitrates completely in order to make subsequent reduction temperature control easy and positive.

FIGURE 1

RECYCLE SYNTHESIS  
WITH  
COBALT CATALYST



Produktionsfall der Gesamtanlage

145 kg Flüssigprodukte / 1000 Nm³ J-Gas  
und zwar: ca 25% Paraffine - 36 kg  
ca 25% Öl - 36 kg  
50% Benzin - 73 kg  
zusätzlich ca 40% Gasöl - 145 kg  
Gesamtprodukte - 155 kg  
Olefine im Benzin ca 50%  
im Öl ca 30%

REACTION CONDITIONS

PRESSURE 7-10 atm  
TEMPERATURE 170-225°C  
CATALYST 1000 STNO, 8MPO 200 SiO<sub>2</sub>

# Reaktionsbedingungen:

Druck 7+10 atü  
Temperatur 190+225°8  
Katalysator 100 Co : 5 TiO<sub>2</sub> : 8 MgO : 200 Kgr

## Gasanalysen

### Frischgas a

CO<sub>2</sub> : 10,5  
CO : 31,8  
H<sub>2</sub> : 51,4  
CH<sub>4</sub> : 0,4  
N<sub>2</sub> : 5,9

### Konaktogeneintrittsgas b

CO<sub>2</sub> : 19,7  
CO : 28,3  
H<sub>2</sub> : 35,4  
CH<sub>4</sub> : 5,2  
N<sub>2</sub> : 10,4

### Endgas hinter I. Stufe c

CO<sub>2</sub> : 23,5  
CO : 26,9  
H<sub>2</sub> : 28,9  
CH<sub>4</sub> : 8,0  
N<sub>2</sub> : 12,7

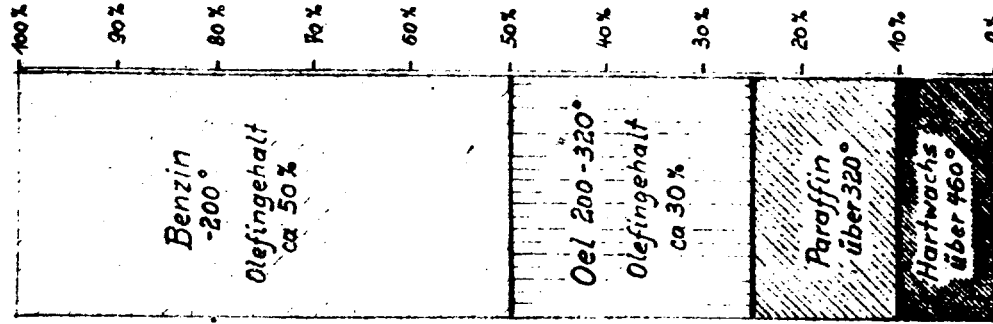
### Endgas hinter II. Stufe d

CO<sub>2</sub> : 37,1  
CO : 46,9  
H<sub>2</sub> : 12,4  
CH<sub>4</sub> : 13,1  
N<sub>2</sub> : 19,1

### Restgas hinter II. Stufe e

CO<sub>2</sub> : 44,8  
CO : 9,5  
H<sub>2</sub> : 6,4  
CH<sub>4</sub> : 4,3  
N<sub>2</sub> : 22,5

## Zusammensetzung der flüssigen Produkte



## Kohlenwasserstoffbilanz bez. auf 1 Nm<sup>3</sup> umgesetztes CO + H<sub>2</sub>

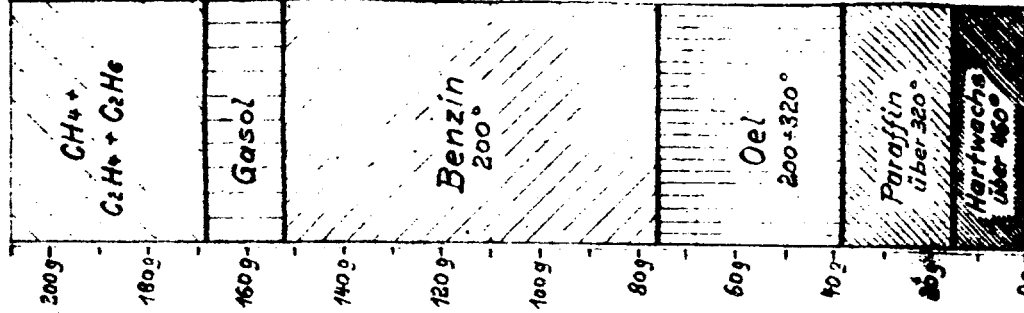
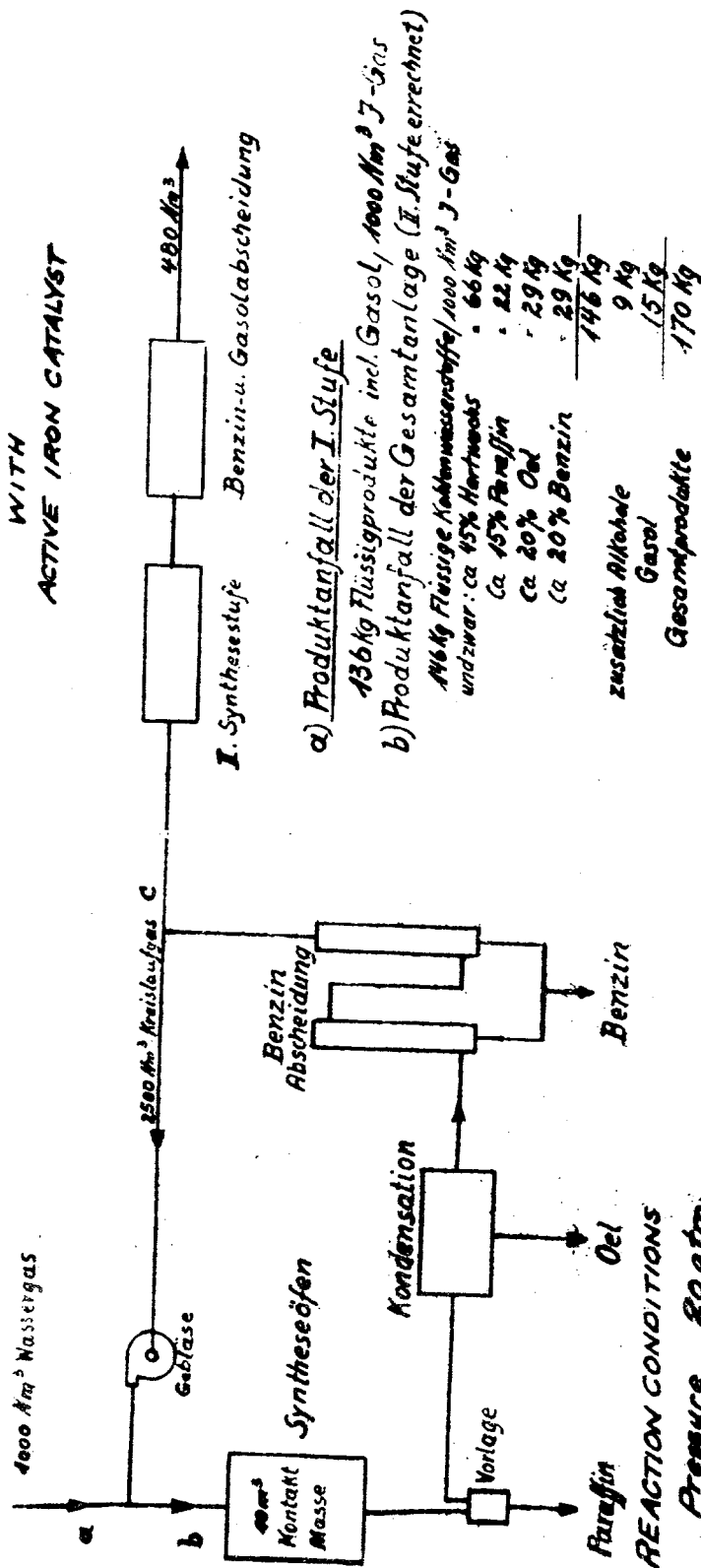


FIGURE 2  
CHARGE AND PRODUCT  
DATA  
PERTAINING TO FIG. 1

FIGURE 3  
RECYCLE SYNTHESIS

WITH  
ACTIVE IRON CATALYST



# Reaktionsbedingungen:

Druck: 20 atü

Temperatur: 230°

Katalysator: MoFe: 25Cu: 9Al<sub>2</sub>O<sub>3</sub>

2K<sub>2</sub>O 30SiO<sub>2</sub>

# Gasanalyse:

## Fruchtgas a

CO<sub>2</sub> = 5.8

CO = 37.6

H<sub>2</sub> = 48.1

CH<sub>4</sub> = 0.4

N<sub>2</sub> = 8.4

## Offeneintrittsgas b

CO<sub>2</sub> = 22.9

CnHm = 1.4

CO = 26.9

H<sub>2</sub> = 31.8

CH<sub>4</sub> = 2.0

N<sub>2</sub> = 15.0

## Restgas I c

CO<sub>2</sub> = 28.2

CnHm = 1.9

CO = 22.6

H<sub>2</sub> = 27.0

CH<sub>4</sub> = 2.7

N<sub>2</sub> = 17.6

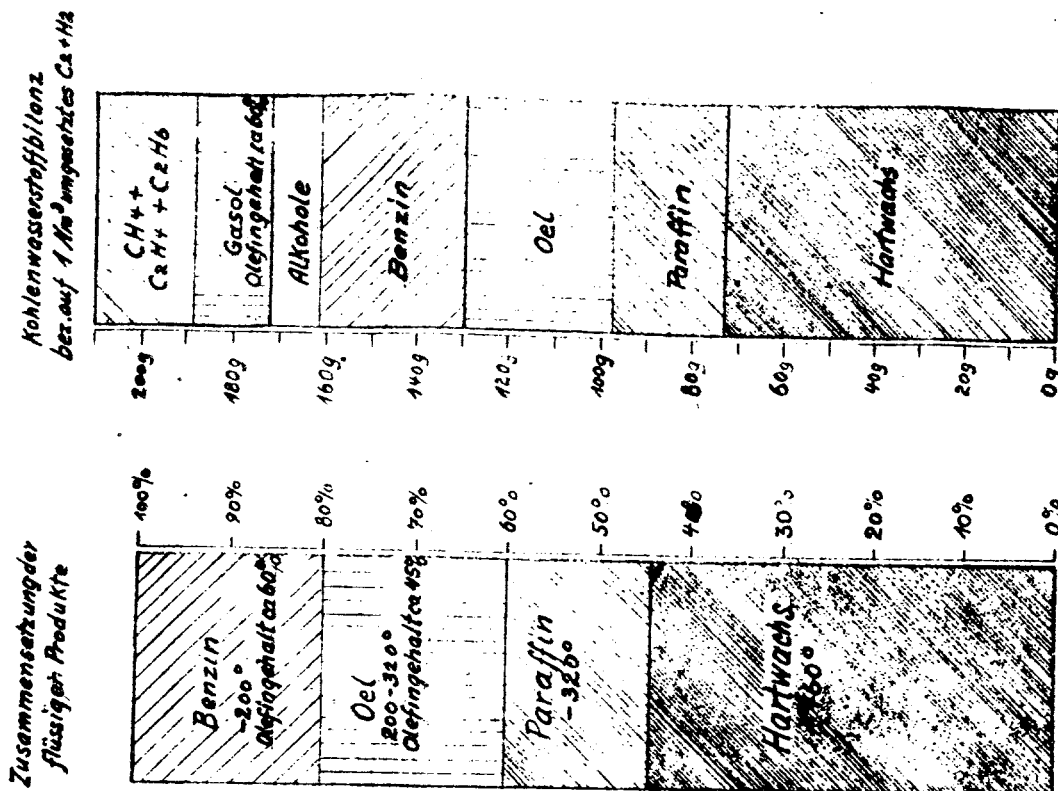
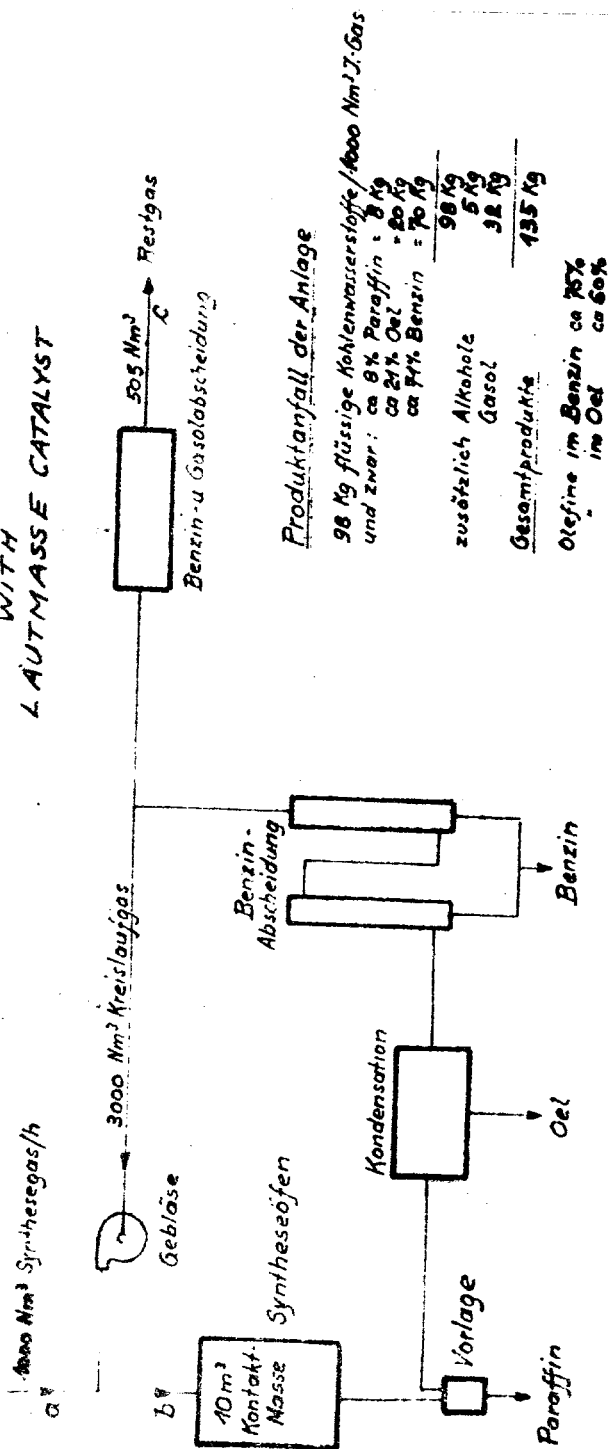


FIGURE 4  
CHARGE AND PRODUCT  
DATA  
PERTAINING TO FIG 3

FIGURE 5  
RECYCLE SYNTHESIS  
WITH  
LAUTMASS CATALYST



Reaction Conditions  
Pressure 20 atm.  
Temperature 275°C  
Catalyst Lautmass impregnated  
with 3% Copper.



# Reaktionsbedingungen

Druck: 20 atü  
Temperatur: 275°C  
Katalysator: Lautamasse imprägn  
mit 3% Cu

## Gasanalysen

### Frischgas a

CO<sub>2</sub> : 2,8  
CO : 53,2  
H<sub>2</sub> : 35,6  
CH<sub>4</sub> : 0,1  
N<sub>2</sub> : 8,3

### Kontaktfolgeneintrittsgas b

CO<sub>2</sub> : 48,0  
C<sub>2</sub>H<sub>4</sub> : 2,2  
CO : 46,7  
H<sub>2</sub> : 11,3  
CH<sub>4</sub> : 5,3  
N<sub>2</sub> : 16,5

### Restgas c

CO<sub>2</sub> : 31,6  
C<sub>2</sub>H<sub>4</sub> : 1,3  
CO : 29,8  
H<sub>2</sub> : 19,8  
CH<sub>4</sub> : 3,5  
N<sub>2</sub> : 14,0

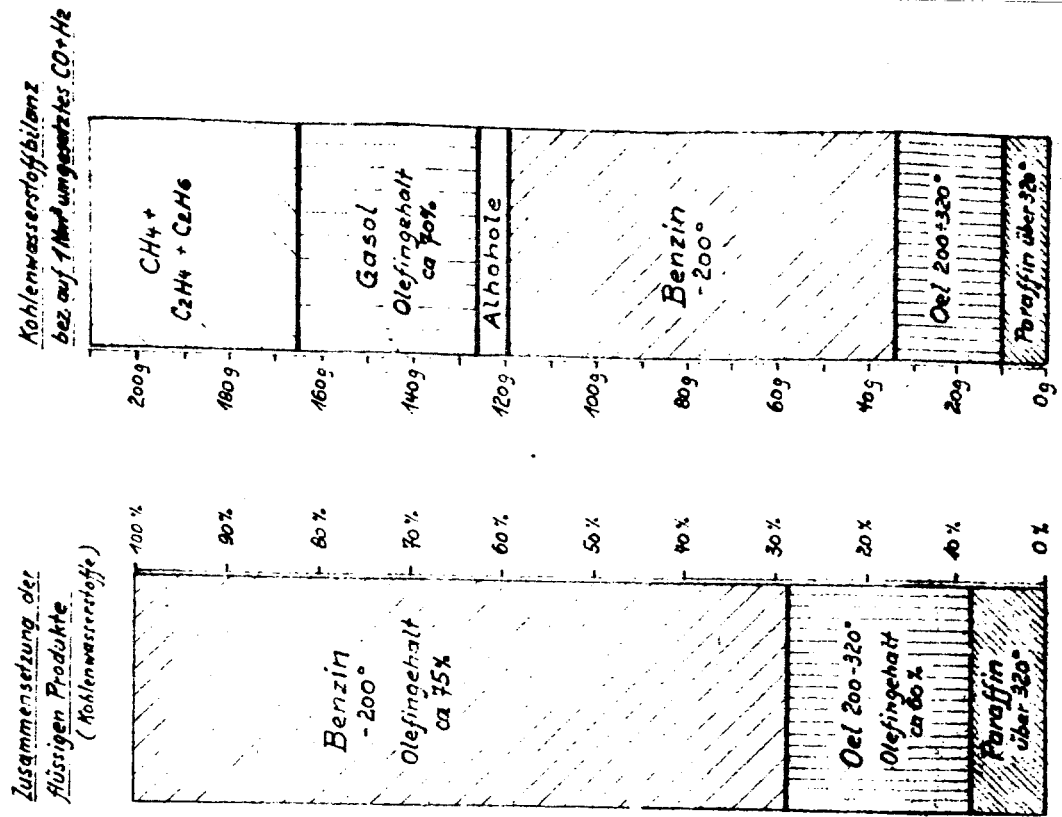
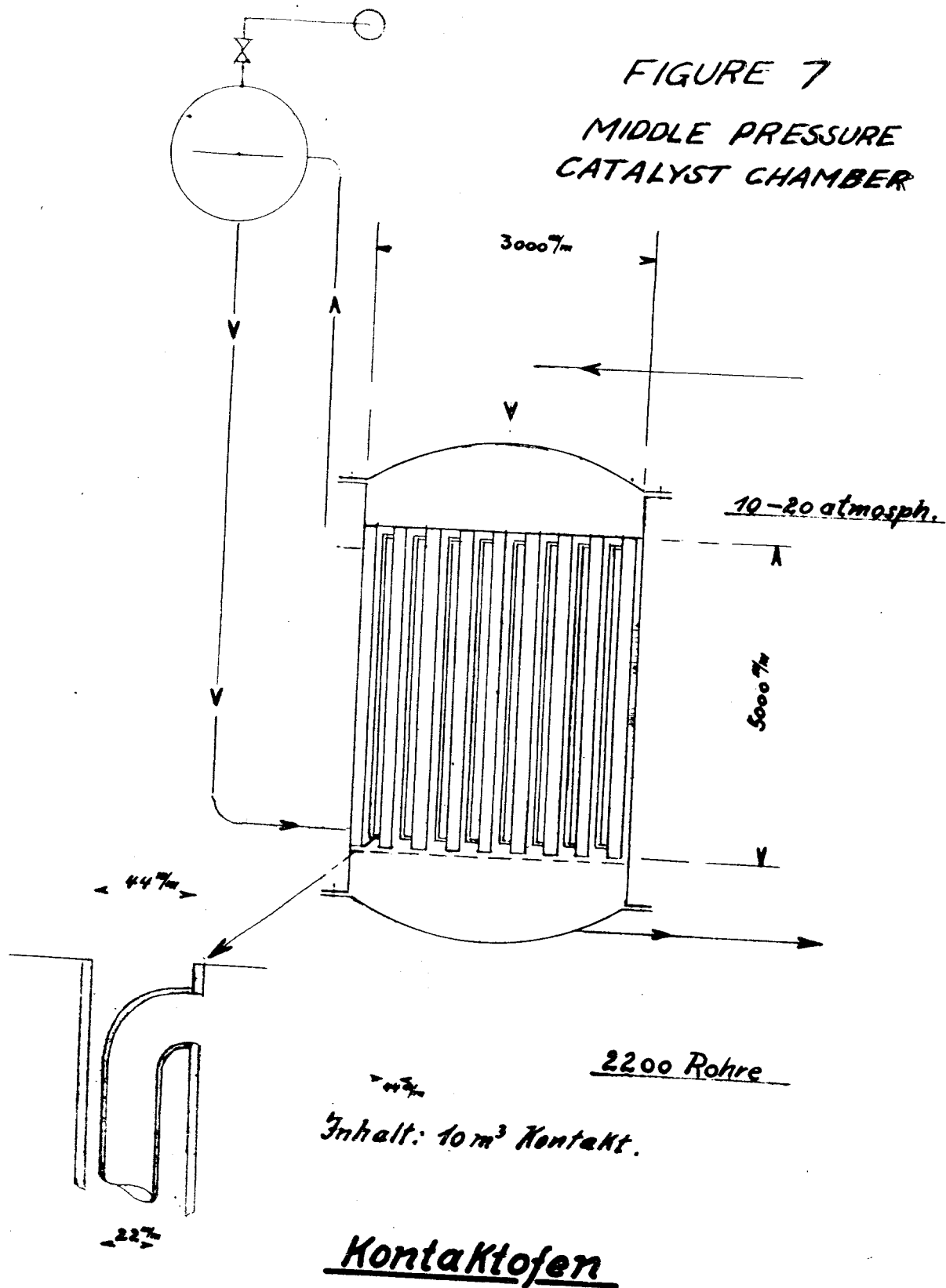


FIGURE 6  
CHARGE AND PRODUCT  
DATA  
PERTAINING TO FIG. 5

FIGURE 7  
MIDDLE PRESSURE  
CATALYST CHAMBER



The product is dried in a centrifuge sufficiently to permit its extrusion and is further dried on a conveyor belt by a blast of hot air to facilitate cutting up the spaghetti into desired lengths. Final drying is carried out at 100°C.

This catalyst is preferably reduced in the synthesis unit with hydrogen at 250 to 350°C for 1 to 4 hours. The rate of hydrogen flow is one cubic meter per kilogram of catalyst per hour. (The lower the rate of hydrogen the higher the reduction temperature required). Reduction with synthesis gas is possible. Synthesis is started at about 180°C and the temperature is raised to 220°C in two days. Over an operating period of three months the temperature should be raised from 220°C to 230°C. Such a catalyst has not been run to exhaustion by Lurgi but it is believed that its life would be about one year.

The catalyst used for high benzin production as illustrated by Fig. 3 is made by impregnating Luxmasse (as used for rough purification of synthesis gas) with 3% metallic copper. The Luxmasse is wet with a solution of copper ammonium nitrate in suitable proportions to give this final copper content. The resulting catalyst is not highly active and requires a high operating temperature, but at this temperature gives a relatively low boiling product with less catalyst deterioration due to CO cracking than would occur with a more active catalyst. In a somewhat similar manner a more volatile product can be obtained by high temperature operation with a cobalt catalyst containing more than the normal proportion of kieselguhr.

It was stated that the most favorable financial position was achieved by working for the maximum yield of hard wax, which was valued at 45 pf. per kilo. The capital cost for a new plant was stated to be 800-900 Marks per ton of liquid product per year, although a figure of 600 Marks per ton per year had been quoted recently for one new plant. The following typical operating costs were cited for a plant using coke for making synthesis gas:

		Pf. per Kg. Product	
Coke per ton	24 Mk.	Gas	14.
Steam " "	2½ Mk.	Cap. & repairs	6
Power per Kw.Hr.	2 pf.	Labor	2
Labor per hr.	1 Mk	Steam	2
		<hr/>	
		24	

Lurgi had the contract for the decentralization of Fischer-Tropsch units under the Geilenberg plan, which called for the operation of a few synthesis ovens in conjunction with each of several scattered city gas plants. It was stated that Lurgi officials protested against this plan but could not dissuade Geilenberg. The plan called for 12 ovens at Leipzig, and 2 or 3 each at Dresden (Heidenau), Goerlitz,

Gottbus, Plauen, Wurtz burg, Fuerth, Erfurt and Chemnitz. All of these plants were to be built for atmospheric pressure operation with a cobalt catalyst and most of the ovens were to be moved from the Rheinpreussen or Wintershall plants. The Leipzig, Dresden, and Wurtzburg installations were 80-90% complete and the others were less than 50% complete at the end of the war.

Lurgi has developed a process for de-poisoning city gas, comprising removing the bulk of the carbon monoxide by passage over an iron catalyst to make chiefly methane with some incidental hydrocarbons. This process would normally be used with Lurgi high pressure coal gasification units. The catalyst for this de-poisoning treatment would have the following composition:

100 Fe, 5-10 Cu,  $9Al_2O_3$ , 120 Kieselguhr.  
Single stage treatment with this catalyst at 20 atmospheres pressure and 250-280°C. is stated to leave only 5% of CO in the gas. A second stage would reduce the CO content to 1% but would probably not be economical. The liquid production amounts to 30-40 grams per cubic meter, of which about half is high melting paraffin. The diesel fuel fraction has a cetane number of 65 which could be raised to 90-100 by hydrogenation. The gasoline fraction contains 50-60% olefins and has an octane number of about 70 which can be raised to about 80 by the Ruhrchemie isomerization process using a non-metallic catalyst at 320°C. An experimental plant of this type located between Boehlen and Pulgar and treating between 1000 and 1500 cubic meters of gas per day from an adjoining Lurgi high pressure generator was inspected by CAFT No.3 on 28 April, 1945.

Lurgi has built the charcoal absorption units for nearly all of the Fischer-Tropsch plants in Germany. They believe that charcoal absorption is definitely more economical than oil absorption up to 10 atmos. pressure and that oil absorption is preferable above 15 atmos. pressure, with the choice between 10 and 15 atmospheres depending on local conditions. The Lurgi built plants used I.G.charcoal which was made from peat at Leverkusen, and is believed to be a little more active than American charcoal. It was stated that there have been no new developments in charcoal manufacture in Germany during the war. The I.G.experts in this field are Drs. Neimann and Doeptke.

A recent advance in charcoal absorption technique has been the design of a plant to work at -50°C, the objective being the separation of methane. Reference was made to similar work by the British Magnesium Corp. at Swansea designed to keep the CO percentage in the gas below 5 per cent. Carbon for the purpose should be highly reactive (S Kohle or nut shell charcoal). Studies made in conjunction with the Linde Co., indicated costs to be slightly less than for refrigeration. Reference was made to a plant in the gas works at Nuremberg to produce 3000 cubic meters of methane per day (purity 85%),