

The oxygen-containing products are mainly alcohols, with aldehydes, ketones and esters, as well as a small quantity of free acids, as the other compounds.

#### D. Iron Catalysts in the Fixed Bed. Oil Circulation Process.

The following information was given by Dr. Duftschmid on the fixed-bed, oil-circulation process which he had developed for iron catalysts.

The object of this development was to remove the heat of reaction by circulating product-oil of fixed boiling range over the catalyst. The heat is removed by raising the temperature of the oil as well as by partial evaporation. This procedure eliminates local overheating and prevents the formation of excess methane and carbon.

Dr. Duftschmid believes that the capacity of a reactor would be limited only by the economics of construction. The process has been tested for a long time in a pilot unit of 8-10 tons per month capacity.

The process operates at a pressure of 20-25 atm. and at temperatures of 260-300°C in the first stage and 280-330°C. in the second stage. Synthesis gas with a high ratio of CO to H<sub>2</sub> is required, for example, CO:H<sub>2</sub> = 55:45. The throughput is controlled to yield 20-25 gms. of total product per liter of catalyst per hour. The catalyst employed is the same as that used by Dr. Michael in his fixed-bed process.

The yield from 1 cu.m. of CO plus H<sub>2</sub> in the synthesis gas is about 150 gms. of product of the following composition:

16% C <sub>3</sub> plus C <sub>4</sub> hydrocarbons,	85%	unsaturated
40% gasoline (<200°C)	50%	"
20% gas oil	25%	"
20% paraffin wax.		
4% alcohols. (largely methanol and ethanol)		

The gasoline contains about 1% of oxygen and the gas oil, about 0.5%.

The crude gasoline has a research-octane number of 62-65, and must be further refined. The gas oil has a cetane number above 70.

Further details of this process may be found in English Patents Nos. 468, 434 and 465,668.

### III. TOLUENE PRODUCTION

Nearly all the toluene produced in Germany was a by-product of the coke ovens. At the beginning of the war, production amounted to about 7,000 tons per month; and during the course of the war, the quantity was increased to about 12,000 tons per month by the building of precision-fractionation

plants. In 1944 the synthetic plant at Waldenburg came into production, adding 4,000 tons per month. (This synthesis of toluene from benzene and methanol by means of a phosphoric-acid catalyst is described in the Leuna report.)

Two other processes were considered for the production of toluene but neither had been carried out commercially.

A. Double DHD Process.

One of the most important research projects at Ludwigshafen was the development of the double DHD process. This process consists in treating heavy naphtha by the DHD process, fractionating the product to remove a toluene concentrate (100-115°C Boiling range), and retreating this fraction in the DHD unit. Close fractionation of this product yields nitration grade toluene (99%) without further treatment. The flow scheme for this process is shown in Figure I.

This process gives a good yield of toluene, and at the same time, aviation gasoline of excellent quality.

In 1943 an expansion of the DHD plant at Ludwigshafen was begun for the production of 10,000 tons per year of toluene by this process. Also, projects were discussed for units at Leuna and Brux, as well as at a Brabag plant.

B. Sulfur Dioxide - Propane Extraction of DHD Naphtha.

In 1939 a project was worked up for Politz for the production of about 15,000 tons per year of toluene by extraction of DHD naphtha with SO<sub>2</sub> - propane. A similar project was also discussed for Scholven. Neither plant was built.

The DHD naphtha was fractionated to yield an aromatic cut (70-120°C) which was extracted at -76°C.

The quantities used were as follows:

100	volumes	of	naphtha
100	"	"	Propane
100-150	"	"	sulfur dioxide.

The aromatic extract was then fractionated closely to yield nitration-grade toluene in practically 100% yield (based on the toluene in the naphtha charge).

The flow is illustrated in Figures II and III. The fractions other than toluene are blended back to produce gasoline, which is of inferior

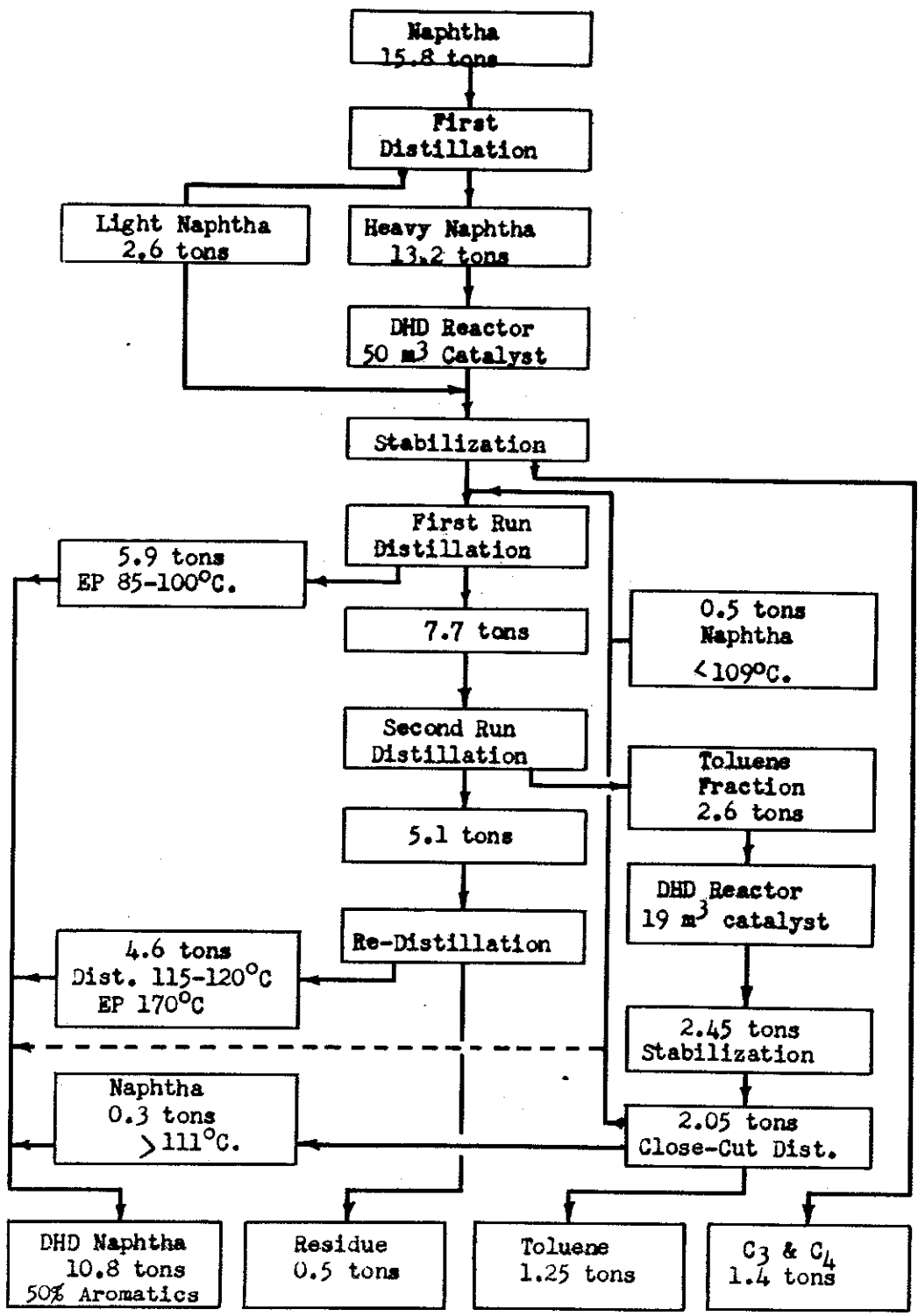


Fig. I TOLUENE BY DOUBLE-DEHYDROGENATION (DHD)

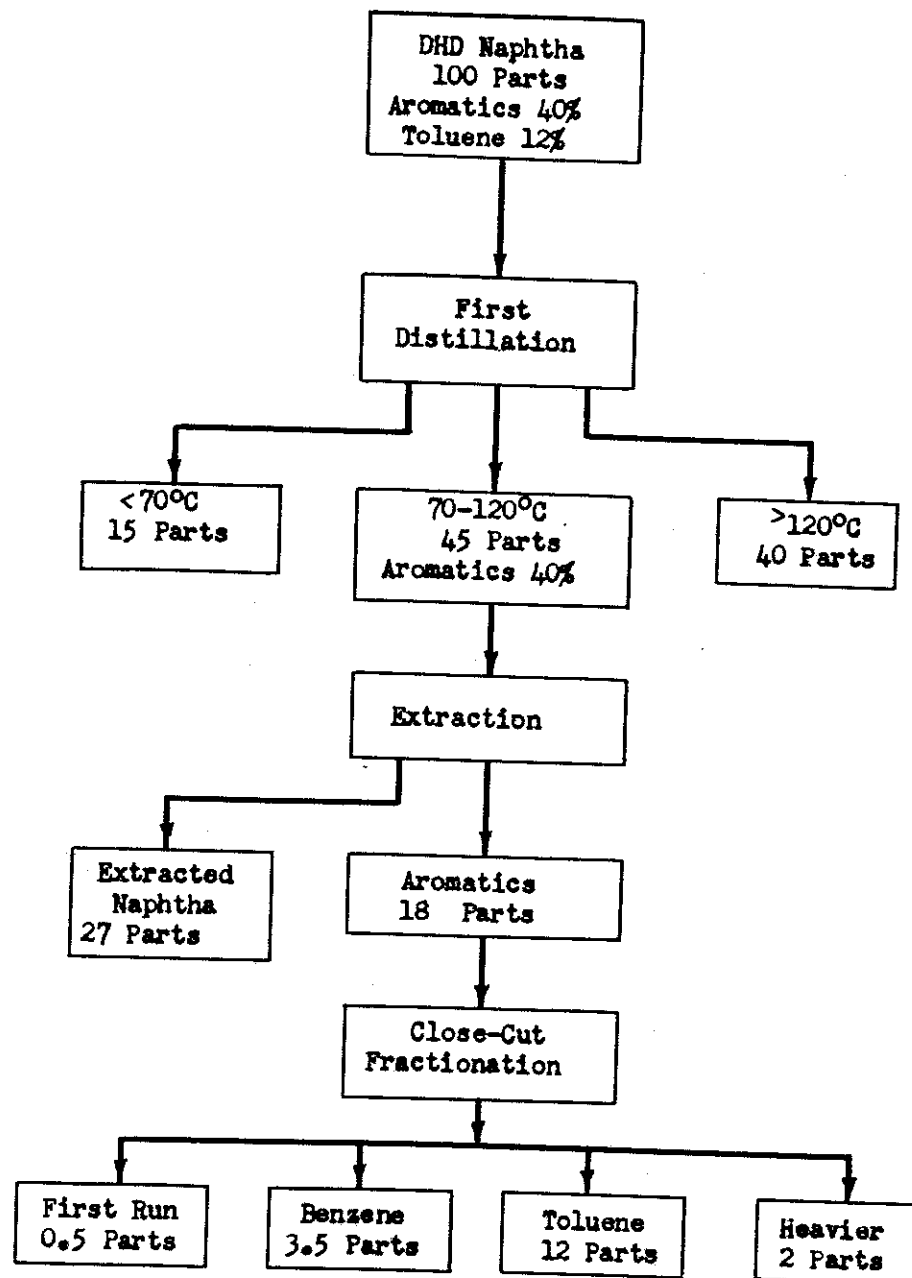


Fig. II TOLUENE EXTRACTION FROM DHD-NAPHTHA  
USING PROPANE-SO<sub>2</sub>

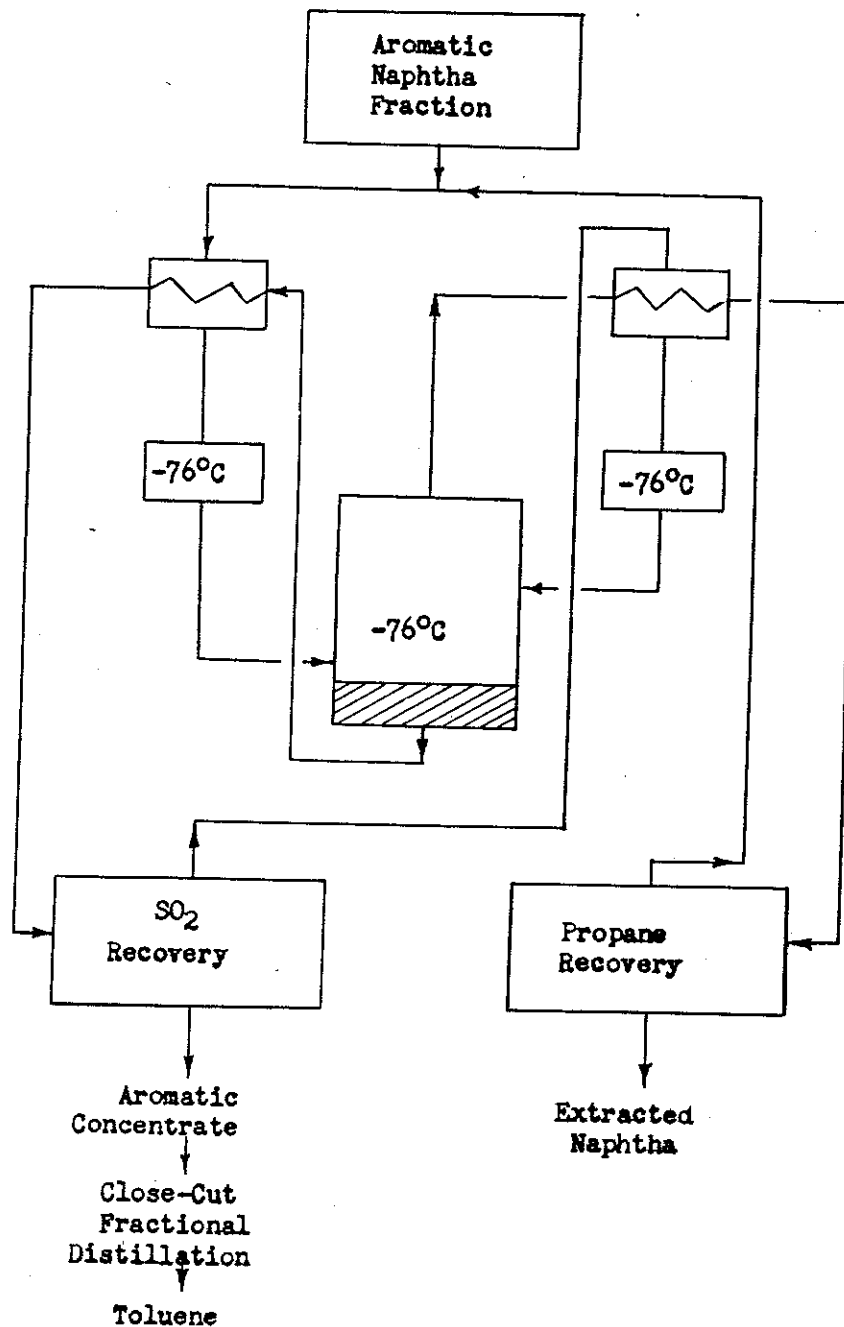


Fig. III FLOW SHEET FOR TOLUENE EXTRACTION PLANT

quality. The process costs are about the same as for the double-DHD process.

This information was obtained from Dr. Donath.

#### IV. OXIDATION PROCESS

##### A. Fatty-Acid Production.

The following information was obtained from Dr. Schiller and Dr. Kürzinger.

The paraffin wax used for the production of fatty acids by oxidation with air should consist of straight-chain hydrocarbons as largely as possible; that is, it should not contain large amounts of branched chain or cyclic hydrocarbons. The preferred chain length is between 16 and 30 carbon atoms. Sulfur compounds and phenols should not be present because they inhibit oxidation. The density of the paraffin wax should not be appreciably higher than that of the corresponding pure paraffin hydrocarbon. The specifications for the paraffin wax are as follows:

##### Paraffin for Oxidation.

- |    |               |           |            |       |
|----|---------------|-----------|------------|-------|
| 1) | Sulfur        | <0,1%     |            |       |
| 2) | Melting point | 40°C      | Sp.gr./70° | 0.765 |
|    |               | 50°C      | " " /70°   | 0.770 |
|    |               | 55°C      | " " /70°   | 0.775 |
| 3) | Boiling Range | @ 15 mm   | 180-350°C. |       |
|    |               | 760 mm    | 320°C.     |       |
| 4) | Melting Point | 35-60°C.* |            |       |
| 5) | Anilins point | 100°C.    |            |       |

\* If the melting point is above 60°C, the wax can be cracked until it meets the specification.

A trial run will determine if the purity of the paraffin wax is sufficient. Paraffins that can be oxidized only with difficulty must be purified: for example, by heating with 1-3% of aluminum chloride, by hydrogenating, or by prior oxidation with air until a small amount of fatty acid is formed which is then removed as soap.

Paraffin wax produced by the hydrogenation (TTH) of brown coal, from crude petroleum oils and from the Fischer Tropsch synthesis, have been oxidized successfully to fatty acids.

##### Oxidation

The molten paraffin wax is blown with air in pure aluminum towers in the presence of manganese compounds, such as 0.1 - 0.2% of potassium permanganate or manganese soaps. There is also added 0.08 - 0.15% of sodium, or

potassium carbonate which greatly improves the quality of the oxidation products. The temperature is maintained at 130 to 160°C. until oxidation begins and is then lowered to 100 to 120°C. The lower the oxidation temperature, the smaller is the formation of peroxides, but the longer the time of reaction. The air flow is continued until approximately 30% of the paraffin is converted to acid (10-30 hours). The product from the oxidizer has an acid number of 75 and a saponification number of 130-150.

#### Saponification.

The oxidation product is saponified with aqueous sodium hydroxide (20-25% at 80°C.) The mixture is then pumped into an autoclave where it is heated to 130-150°C under pressure, the greater part of the unsaponifiable product separating in an upper layer (paraffins, alcohols, ketones.) This upper layer is recycled to the oxidation tower. The lower layer (soap solution) is heated (in a pipestill) to 280-350°C at a pressure of 80-100 atmospheres. On release of the pressure, water vapor and the remaining unsaponifiable material are flash. The unsaponifiable material is recycled to the oxidation stage.

#### Hydrolysis, and Distillation.

The molten soap obtained as a residue from the flash tower, is dissolved in water and hydrolyzed with sulfuric acid. The raw fatty acid is washed with water and distilled under a vacuum of 3-5 mm. The distillation yields three overhead fractions. The properties of the fractions depend on the molecular size and quality of the paraffin.

Based on 100 parts of paraffin. The following quantities are obtained:

1. Acids,  $C_3$  to  $C_{10}$ , boiling point to 150°C. at 3 mm. 7-15%.
2. Soap acids,  $C_{10}$ - $C_{18}$ , boiling point 150°C. to 240°C. at 3 mm, 45-55%.
3. Higher acids,  $C_{16}$ - $C_{25}$  boiling point 240-300°C, at 3 mm, 2-5%.
4. Residue - 5-20%.

The quantities shown on the drawing (Figure IV) are for a typical plant run at Oppau with TTH paraffin. The plant at Oppau has a capacity of 20,000 tons of paraffin wax per year.

#### B. Methane-Oxygen Process.

The following information on the methane-oxygen process was obtained from Dr. Schiller and Dr. Bartholome. The information on materials of construction was obtained from Dr. Koch.

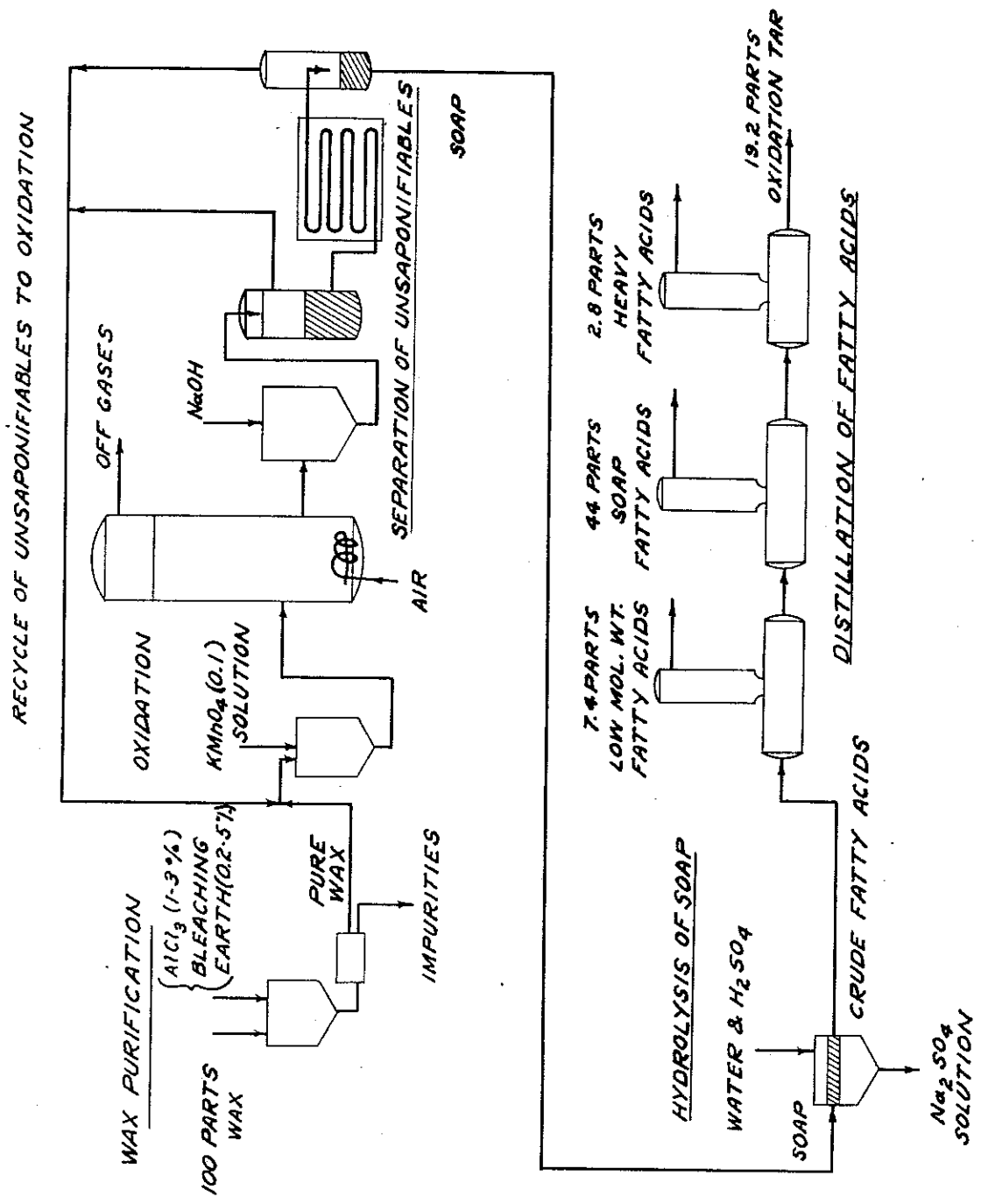
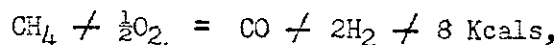


FIG. IV FLOW SHEET FOR OXIDATION OF WAX



The conversion of methane with oxygen according to the equation:



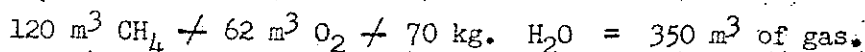
has been carried out during the last several years for the production of hydrogen for the ammonia and methanol synthesis. In most cases, coke-oven gas has been used as the raw material. Plants were operating at Linz, Waldenburg and Oppau, and a plant was under construction at Auschwitz.

The conversion does not take place exactly according to the equation above, part of the methane remaining unconverted, and part being oxidized to carbon dioxide and water. Besides, some carbon black is formed from methane cracking. Most of the methane and some of the carbon can be eliminated by conversion with water at elevated temperatures. Therefore, there are two stages in the conversion. The first stage, the combustion with oxygen, is carried out without a catalyst, and the second stage, the conversion of the hydrocarbons with steam is carried out over one of the standard nickel catalysts.

This process was investigated in 1927/30 in experimental plants at Oppau and Leuna for about 100 m<sup>3</sup> of gas per hour. Raw materials were pure methane, coke-oven gas or waste gases from coal hydrogenation containing higher hydrocarbons. The gas was mixed with oxygen as rapidly as possible in several burners and passed over a layer of active nickel catalyst (20% nickel). It was found suitable to add steam and to use a temperature of about 1200°C. in the first stage. The gas produced was practically free from carbon black and contained about 1% of methane.

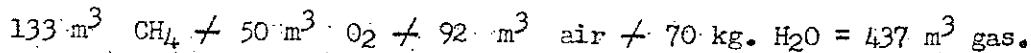
The following examples illustrate the conversion of methane:

- 1) Conversion with oxygen and steam:



	<u>Charge</u> Gas. %	<u>Product</u> Gas. %
CH <sub>4</sub>	91.6	0.7
CO <sub>2</sub>	1.0	8.5
H <sub>2</sub>	1.0	64.1
N <sub>2</sub>	6.4	5.3
CO	-	21.0
O <sub>2</sub>	-	0.4

- 2) Conversion with air, oxygen and steam:



	<u>Charge</u> <u>Gas. %</u>	<u>Product</u> <u>Gas. %</u>
CH <sub>4</sub>	91.6	0.9
CO <sub>2</sub>	1.0	6.5
H <sub>2</sub>	1.0	51.7
N <sub>2</sub>	6.4	22.3
CO	-	18.4
O <sub>2</sub>	-	0.2

In the first example, the methane was preheated to 200°C. and in the second to 300°C.

The reaction vessel contained 400 liters of catalyst in each experiment.

At first, no technical application resulted from this work, but the process was taken up again. It was tried to lower the quantity of oxygen by using less steam and allowing more carbon black to form. For separating the carbon black, special filters were designed, consisting of towers filled with coke or pumice. These filters were constructed to allow continuous removal of part of the packing for regeneration.

The operation of the commercial plants is as follows (see Fig. V).

The coke-oven gas and an air-oxygen mixture are saturated with water vapor in separate towers and preheated separately in the heat exchangers. These exchangers are subjected to very high temperatures and the slightest permeability of the tubes will lead to combustion and melting of the metals. The actual alloy used for the tubes is Sicromal 10 (13% Cr, 1% Si, 1% Al). This alloy is not the final answer but was a war necessity. Seamless tubes of higher alloying metal content would probably be more satisfactory. Due to the high temperature differences in the exchangers, the alloy must have a high tensile strength. The gases are mixed and burn in the upper portion of the converter. As considerable carbon is formed in the conversion, a small quantity of nickel nitrate solution is injected into the combustion space to decrease the carbon formation. The gases then pass through a catalyst bed of 5% nickel on refractory (such as MgO). The throughput of the oven is 2000 m<sup>3</sup> of gas per sq. m. of reactor cross-section per hour.

The converted gas heats the fresh gas and air and is then cooled to the dew point by the injection of water. The soot is removed in the shaft filters filled with coke. In the second part of the plant, the gas passes through a heat exchanger, a reactor to convert the CO and steam into CO<sub>2</sub> and hydrogen, and is then cooled to air temperature in a spray tower.

At full production, the Oppau plant charges 8300 m<sup>3</sup> of coke oven gas with 4100 m<sup>3</sup> of oxygen to produce 18,300 m<sup>3</sup> of synthesis gas of the following composition:

