

FIAT FINAL REPORT NO. 426

PB 7745

INTERROGATION OF DR. PIER AND
STAFF

I. G. FARBENINDUSTRIE, A. G.

LUDWIGSHAFEN/ OPPAU

JOINT INTELLIGENCE OBJECTIVES AGENCY
WASHINGTON, D. C.

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OFFICE OF MILITARY GOVERNMENT FOR GERMANY (U.S.)
Office of the Director of Intelligence

FIAT FINAL REPORT NO. 426

14 November 1945

INTERROGATION OF DR. PIER AND STAFF
I. G. FARBENINDUSTRIE, A.G.
LUDWIGSHAFEN/OPPAU

BY

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Joint Intelligence Objectives Agency

FIELD INFORMATION AGENCY, TECHNICAL

29 p. diagrs.

TABLE OF CONTENTS.

<u>SUBJECT.</u>	<u>PAGE No.</u>
I. INTRODUCTION	1.
II. SYNTHESIS OF HYDROCARBONS FROM WATER GAS	1.
A. Fixed Bed Gas Recycle Process-Michael	
B. Foam Process-Michael	
C. Iron Catalyst in Tubular Reactors-Michael.	
D. Fixed Bed, Oil Circulation Process-Duftschild	
III. TOLUENE PRODUCTION	8
A. Double DHD Process - Donath	
B. DHD Extraction - Donath	
IV. OXIDATION PROCESSES	9
A. Fatty Acid Production - Schiller and Kürzinger	
B. Methane-Oxygen Process - Schiller, Koch and Bartholome.	
C. Hydrogen Peroxide from Propane - Bartholome	
D. Acetylene from Ethane - Sachsse	
V. POLYMERIZATION AND CONDENSATION PROCESSES	15
A. Oppanol Production - Gäterbock and Schwarz	
B. Isobutylene Polymerization - Kuhn	
C. Lupolen H. - Hopff and Schwarz	
D. Paraflow - Christmann	
E. Bunol - Steinhöfer	
F. Buna D. - Herbeck	
G. Koresin - Christ	
VI. CHLORINATION PROCESSES	19
A. Preparation of Alkyl Dichloride - Leutner	
B. Butadiene from Butylene - Leutner	
C. Butadiene from Butane - Weldmann	
VII. MISCELLANEOUS PROCESSES AND PRODUCTS	21
A. Hydrogenation of Butadiene to Butylene - Conrad	
B. Kybol - Waldmann	
C. Tannol - Kuhn	
D. Vanol HS - Lorenz	
E. Diolefins from Olefins and Formaldehyde - Bueren	
F. Preparation of Alkyl Alcohol - Klein	
G. Methacryl nitrile - Lorenz.	
VIII. SPECTROGRAPHIC STUDIES	27
A. Research - Fromherz	
B. Equipment - Luft	

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I. INTRODUCTION

Previous interrogation of German scientific personnel by numerous investigators and the examination of evacuated documents indicated that further information was desirable on a miscellany of products and processes of interest to the Petroleum Industry. Accordingly, Dr. Pier and a large number of other men of the I.G. Farbenindustrie, A.G. plant at Ludwigshafen/Oppau were further interrogated in July 1945.

The information contained in this report supplements that previously reported in the CIOS report of 16 August, 1945: "Report on Investigations by Fuels and Lubricants Teams at the I.G. Farbenindustrie A.G. works at Ludwigshafen and Oppau", edited by Lt. Col. R. Holroyd (MFP).

II. SYNTHESIS OF HYDROCARBONS FROM WATER GAS MICHAEL PROCESS.

The following information concerning the synthesis of hydrocarbons from water gas was obtained by the interrogation of Dr. Wilhelm Michael who was conducting the research and development on the so-called "Michael Process". Two methods of operation had been studied that were outlined briefly in the earlier report on Ludwigshafen.

Both methods employed an iron catalyst which was stated to have the following advantages over the cobalt catalyst:

- a. The gasoline is better.
- b. A higher concentration of gasoline is formed.
- c. The process is cheaper.

Dr. Michael had also investigated the use of iron catalyst in a tubular reactor at reduced temperatures.

Special precautions are required with the iron catalyst, which more than the cobalt catalyst, is subject to "run-away" reaction and the formation of carbon on the catalyst. The methods investigated were designed to prevent the conditions which lead to carbon formation.

A. Fixed-Bed Circulating-Gas Process

In this process gas is recirculated over the catalyst and through a cooler at such a rate that the temperature rise in the catalyst bed is limited to a maximum of 10°C. The reaction is

carried out at a pressure 20 atmospheres. At lower pressures the reaction velocity is too small. The gas recycle ratio is 100 volumes of recycle to one volume of fresh gas. Contact time in the catalyst bed is approximately one half to one second per pass, with a gas velocity of about 1 m. per second. The flow sketch (Fig. 1) illustrates the process. An important limitation is that the gas must flow through the catalyst bed without turbulence, otherwise static zones form and lead to a dangerous temperature rise resulting in the formation of methane and carbon. This necessary flow condition has been obtained in small-scale experiments (as shown in Fig 1), using a 5 liter catalyst bed which were conducted successfully for as long as 10 months. Experiments of shorter duration have been successful in the same type of system with a 400 liter catalyst bed. Dr. Michael believes this single-bed design could be built to still greater diameter; channeling is the limitation.

With larger scale experiments (4-cubic meter catalyst bed), space restriction required the bed construction shown in Fig. 2. The operation of this unit was unsuccessful, because the gas undergoes a change of direction simultaneously with a velocity change (owing to change in diameter), which results in turbulent flow and stagnant spots develop in the catalyst bed. This unit was shut down after 2 months of operation because of the formation of carbon pockets. A further large-scale experiment utilizing cylindrical construction was proposed but the equipment was not built, due to the war. This unit was to have alternating sections of catalyst and condensers, in one container, as shown in Fig. 3.

Reaction Data.

Gas	CO: H ₂ about 1:1 or 4:5
Pressure	20 atm.
Gas purity	Sulphur - under 2 mg. per cu.m., CO ₂ free.
Gas recirculation	100 times.
Temperature change of gas	10° C.
Working temperature	300-325°C. (mainly 325°C.)
Catalyst	Sintered iron catalyst. Pellets about 1 cm.
CO ₂ in exit gas	40-45%
Output per cu.m. of catalyst:	700-800 kg./day.

Catalyst

The best gasoline is obtained with iron catalysts when the synthesis is conducted above 300°C. Therefore it is necessary that the catalyst be insensitive to such temperatures and a good conductor

of heat. This type of catalyst is obtained by high-temperature sintering of iron powder pasted with about 1% of alkali during the reduction with hydrogen. An example of the catalyst preparation is as follows: Fine iron powder prepared by thermal decomposition of iron carbonyl is pasted with a concentrated solution of borax (1 gram of borax per 100 grams of iron) and formed into approximately 1 cm. cubes. In order to insure loose packing, the cubes are made with slightly irregular edge lengths. The cubes are sintered and reduced with hydrogen at 800-850°C. for 4 hours. The catalyst is cooled in a hydrogen atmosphere, which is replaced by carbon dioxide before charging to the reactor. In place of iron powder, Fe_2O_3 may be used in the preparation but it yields a catalyst which is very porous and of relatively low stability.

Reaction:

In contrast to the cobalt catalyst which yields, besides hydrocarbons, mainly water, the iron catalyst forms predominantly carbon dioxide. Under the conditions given above, 80-85% gas conversion is obtained with 40-45% of carbon dioxide in the exit gas. If a two-stage process is employed, this carbon dioxide must be removed. Condensation takes place in 3 cooling stages as follows:

- 1) Cooling to 120°C to condense the paraffin and some of the water;
- 2) Cooling to 20°C to condense the gas oil, heavy naphtha and additional water;
- 3) Cooling to minus 40°C to condense light gasoline and part of the liquefiable hydrocarbon gases. Prior to this stage the gas must be intensively dried with calcium chloride or silica gel.

The exit gas from this third cooling stage is washed free from carbon dioxide with water or alkaline solution and is further converted in a smaller second system, whereby an overall conversion of 92 to 95% is obtained. The products from this second system are separated in a manner similar to that described above.

Composition of Product.

When operating with a hydrogen to carbon monoxide ratio in the charge gas of 5:4, the exit gas from the first stage is as follows:

CO_2	40-45%
H_2	25-30%
CH_4	5-10%
CO	15-20%

The so-called "useful" products are as follows:

C ₂ - C ₄ (excluding ethane)	30%
Ethylene	8%
Propylene	9%
Propane	3%
Butylene	8%
Butane	2%
} 3/4 of iso-structure	
Gasoline (to 200°C.)	48% (7% alcohol content)
Gas oil	14% (4% " " ")
Paraffin	1%
Alcohol (in aqueous layer)	7% (mainly C ₂)

Only straight-chain and alpha methyl primary alcohols are produced. For every 100 kg. of these useful products, 25 kg. of methane and ethane are formed. From the liquefied hydrocarbon gases, additional gasoline can be prepared by polymerization and alkylation.

The crude gasoline product has an octane number of 68 to 70 (research method). By passing this crude product over alumina at 400-450°C, for the removal of oxygen and then refining over fuller's earth at 180-200°C, the octane number is increased to 84 (research method) and to 75-78 by motor method. The refining loss is about 5%. The gasoline, which has an olefin content of about 70%, must be inhibited for storage. The gas oil has a cetane number of 45 to 50.

Oxygenated Products in the Water.

Acetaldehyde	5%
Acetone	10%
Ethenol	55%
Propanol	20%
Butanol and over	10%

B. The Foam Process.

If the object of the operation is not to produce a gasoline, but rather chemical products, olefins of greater chain length, such as occur in the gas-oil fraction, are the more desirable compounds. To increase the gas-oil yield, the operating temperature must be lowered (250° or below). Therefore, to obtain a reaction, a more active catalyst than the sintered catalyst is required. The following process was developed to work with the highly active catalyst in a liquid phase in which the reaction gases are only slightly soluble and in which the catalyst is suspended in a finely divided state. Fig. 4 shows the flows.

Apparatus.

The gas distribution is best effected by ceramic plates (0.15 mm. pore size). The finely divided catalyst is kept in suspension in the

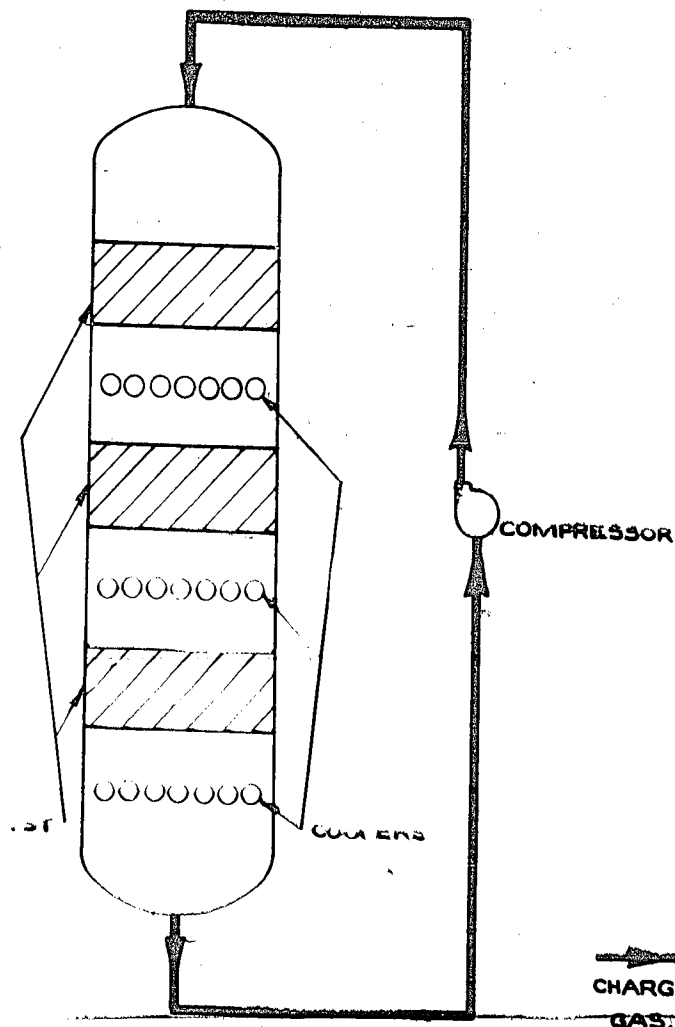
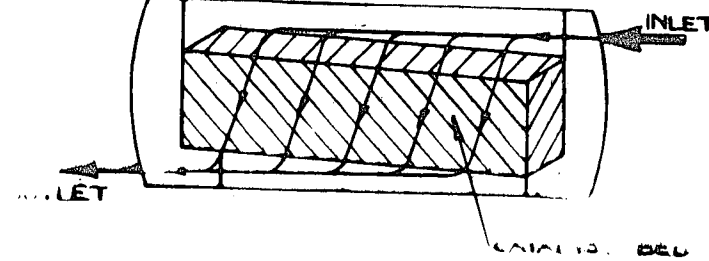
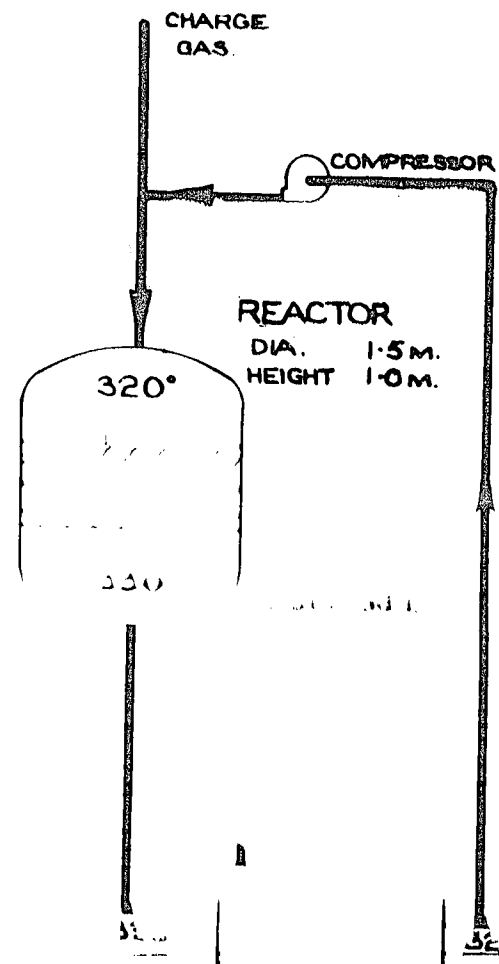


FIG. 3.

FIG. 4.

SKETCHES FROM Dr. MICHAEL

IG. LUDWIGSHAFEN / OPPAU.

31ST. JULY. 1945.

oil in the reactor by the ascending gas stream. The high-boiling part of the reaction product serves as the suspending medium (250-300 kg. of iron per cu.m. of oil). The gas passes out overhead through a separator. The liquid is slowly carried upward and flows overhead into the separator. The spent gas and the admixed vaporized product pass to the condensers. From the separator, only the excess liquid is removed. The recycle suspension passes into a cooler, and thence to a pump, which returns it to the reactor. At a circulation temperature of 250°C, the suspension temperature increases 10°C over the period of 3 minutes in the reactor.

After the separation of the product as described in section A. further conversion of the gas is possible by recirculation (after removal of CO₂). Several stages are preferred, since in a second stage 85% conversion is reached and in a third, 90%.

Reaction Data.

Gas	-	CO:H ₂ about 1:1 or 4:5
Pressure	-	20 atm.
Temperature	-	about 250°C
Reaction duration	-	about 3 minutes/cycle
Temperature rise	-	10°C.
Conversion	-	70%
CO ₂ in exit gas	-	40-45%
Yield	-	1 cu.m. reaction volume yields 350-450 kg./day.

Catalyst.

In contrast to the sintered catalyst, the reduction of the catalyst for the "Feam" process is effected at lower temperature (350-450°C) with a very high hydrogen throughput. Iron oxide is obtained in the finely divided state either by precipitation or by the decomposition of iron carbonyl. The oxide is stirred into a paste with Alkali solution (K₂CO₃ or potassium borate) and formed into small granules which are dried, reduced and ground fine in a ball mill in admixture with gas oil.

The iron carbonyl can also be decomposed in the suspension oil, in which case, a smaller amount of iron suffices.

Product

Liquefiable gas (C ₃ and C ₄)	10%
Gasoline <200°C	40-50% with 70% olefins.
Gas oil <350°C.	30% with 40-50% olefins.
Paraffin.	20-25%, of which 2/3 boil over 450°C.

For 100 Kg. of utilisable product, there are 5-10 kg. of CH_4 .

Utilization of Product.

The olefins are readily polymerised to lubricating oil or converted to sulphonates (detergents) with sulphuric acid. By reaction with CO-H_2 , the olefins may be converted into higher alcohols, aldehydes or acids.

Large-Scale Experiment.

The largest unit, tried out was a $1\frac{1}{2}$ cu.m. system (including the separator). It produced 450-500 kg. of product per day. After two months a catalyst deposit was observed in the upper portion of the reactor. A stirrer was added to prevent this occurrence, but so much deposit formed around the stirrer and then fell off that the foam-plate was covered.

The final solution of these problems was prevented by the war.

C. Iron Catalyst in Tubular Reactors.

Dr. Michael also gave the following information on iron Fischer-Tropsch catalysts.

Synthesis iron catalysts produced by precipitation in the same manner as the cobalt catalyst, is unsatisfactory because a "run-away" reaction develops: a sudden temperature rise occurs, in which the formation of methane and carbon predominates. The catalyst preparation was changed, therefore, in order to obtain a solid catalyst with good heat conductivity and high activity. In this method the sintering was carried out before the reduction and the reduction itself performed at as low a temperature as possible while maintaining a high hydrogen velocity.

In order to attain high activity, 5-25% of alkali-earth metal in the form of oxide or carbonate, (MgO or MgCO_3 preferably) is incorporated into the catalyst. The iron oxide or hydroxide is mixed with the alkali earth and 1-2% of K_2CO_3 or $\text{K}_2\text{B}_4\text{O}_7$, pressed into pellets, heated to 850°C , and then reduced with hydrogen after cooling to $350-450^\circ\text{C}$. The catalyst has a very high activity at 240°C and lower temperatures, and excellent thermal stability in the tube reactor. The catalyst was used in a 20-liter tube reactor for several months under the following conditions:

Pressure, atm.	20
Temperature, $^\circ\text{C}$	230-250
Charge-gas composition CO:H_2	4:5 to 5:4
Conversion	70-80%

Under the above conditions the yield was 0.35 - 0.45 kg. per liter of catalyst per day of the following products:

Liquefiable gas (C ₃ , C ₄)	10%	with 70% olefins
gasoline (<200°C:)	35-50%	" 70% "
gas oil (<350°C:)	25-35%	" 40-50% "
Paraffin wax:	15-25%,	(60% boiling above 450°C.)

The oxygen content of the gasoline was 4-6%

The oxygen content of the gas oil was 3-5%

The methane yield was about 10 kg. per 100 kg. of the above products.

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 H₂ is required, for example, CO:H₂ = 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 H₂ in the synthesis gas is about 150 gms. of product of the following composition:

16% C ₃ plus C ₄ 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 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 re-treating 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.

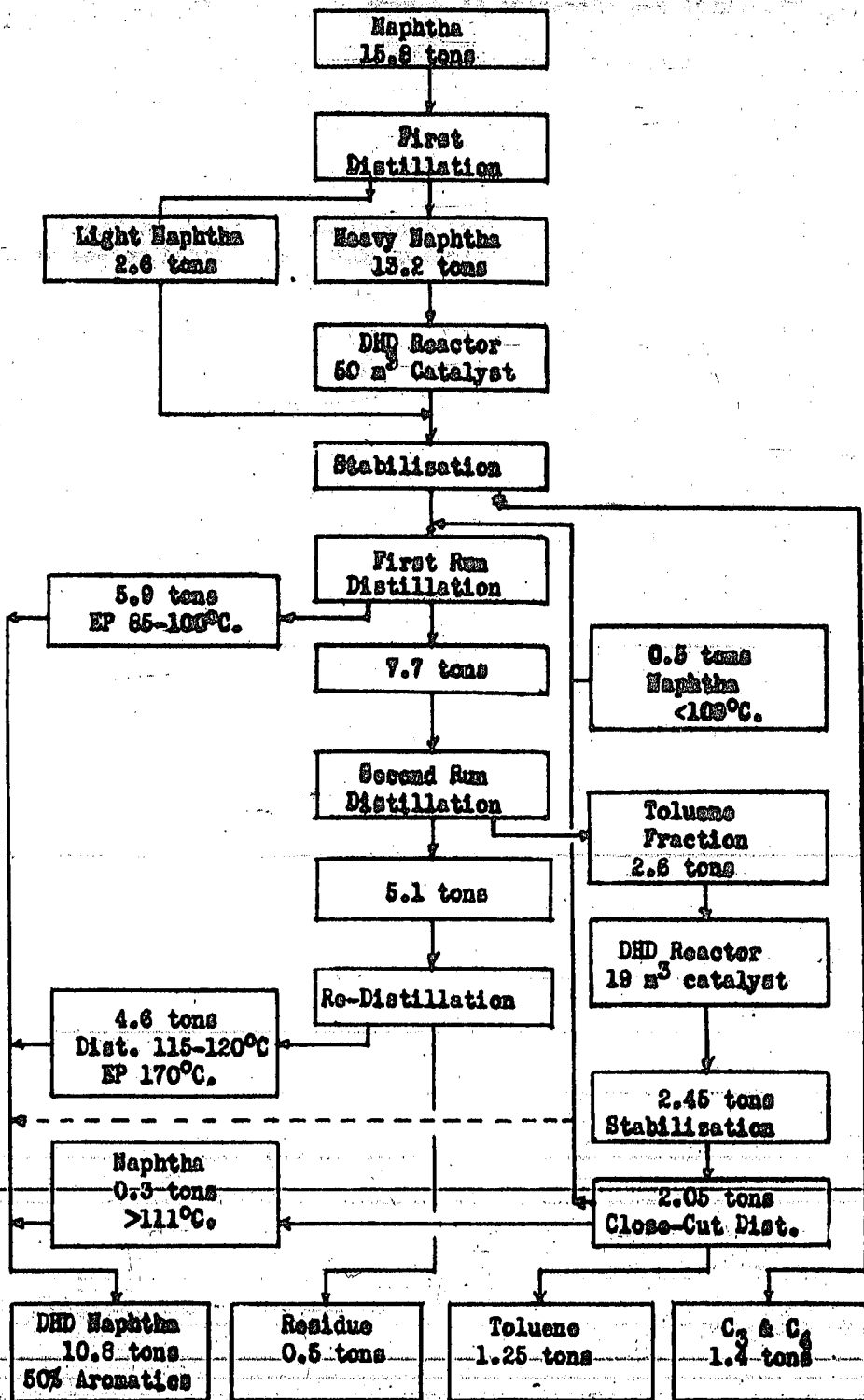
This process gives a good yield of toluene, and at the same time, aviation gasoline of excellent quality.

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 Bräx, as well as at a Brabag plant.

B. Sulfur Dioxide - Propane Extraction of DHD Naphtha.

~~In 1939 a project was worked up for Pöhlitz for the production of about 15,000 tons per year of toluene by extraction of DHD naphtha with SO₂ - propane. A similar project was also discussed for Scholven. Neither plant was built.~~

The DHD naphtha was fractionated to yield an aromatic cut



-8a-

Fig. I TOLUENE BY DOUBLE-DEHYDROGENATION (DHD)

(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 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.

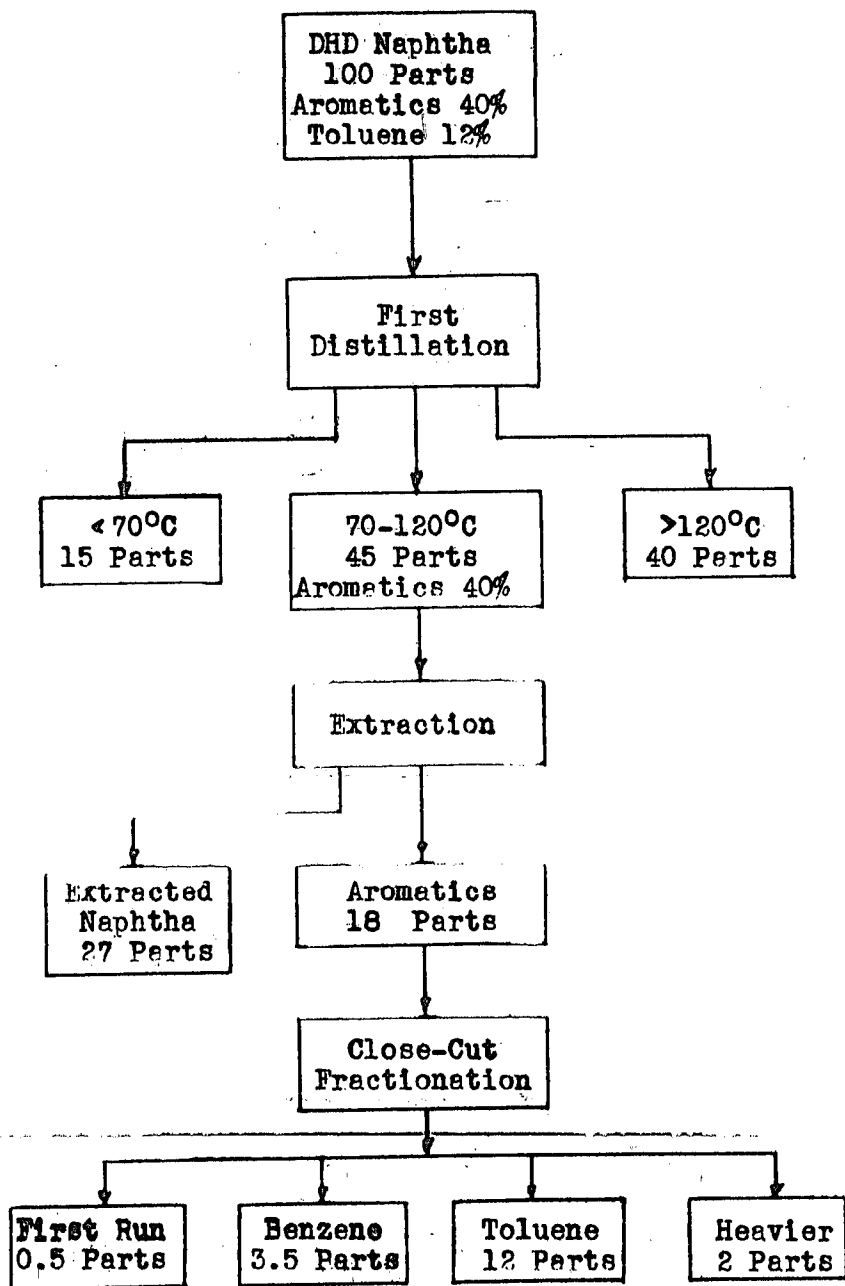
The following information was obtained from Dr. Schiller and Dr. Kürzinger.

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) Aniline point 100°C.

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



**Fig. II TOLUENE EXTRACTION FROM DHD-NAPHTHA
USING PROPANE-SO₂**

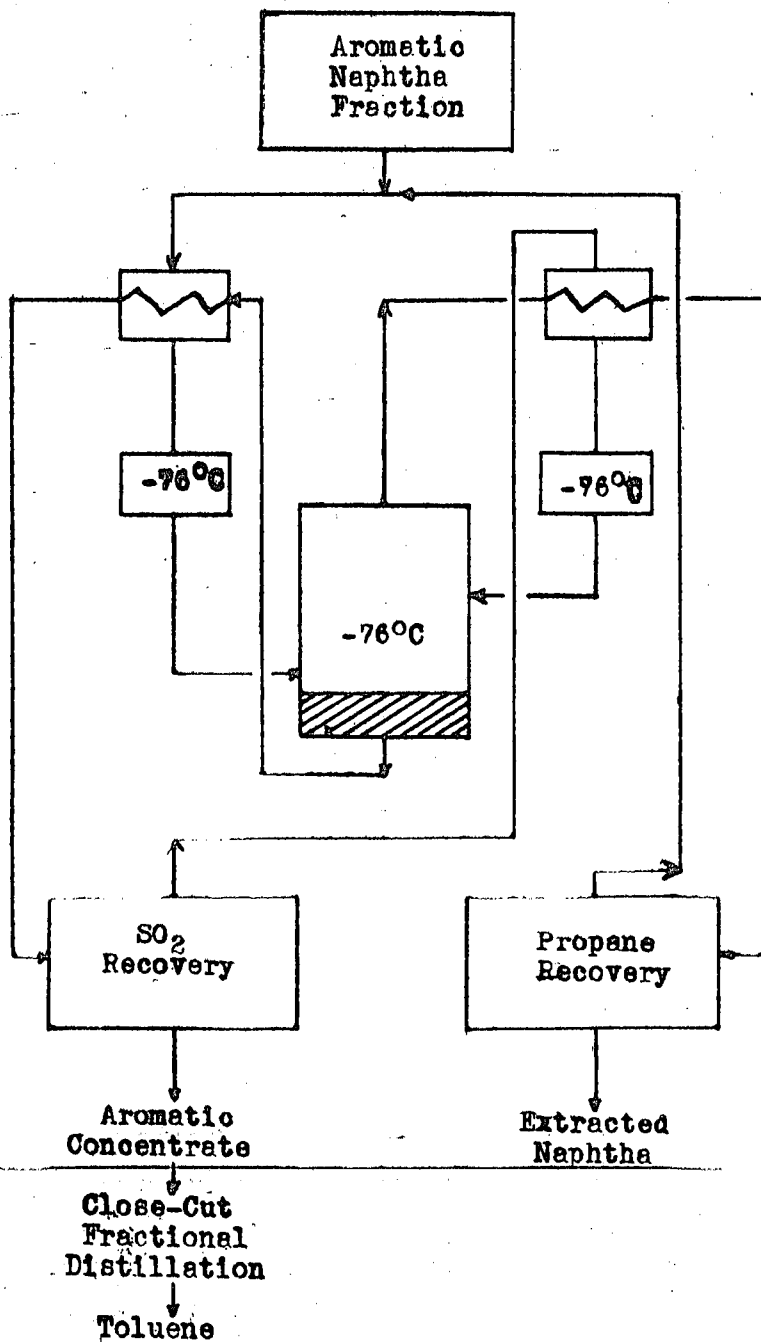


Fig. III FLOW SHEET FOR TOLUENE EXTRACTION PLANT

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 0.03 - 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 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:

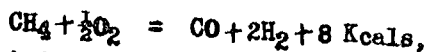
1. Acids, C_3 to C_{10} , boiling point to 150°C . at 3 mm. 7-15%.
2. Soap acids, C_{10} - C_{18} , boiling point 150°C . to 240°C . at 3 mm, 45-55%.
3. Higher acids, C_{18} - C_{25} boiling point 240 - 300°C , at 3 mm, 2-5%.
4. Residue - 5-20%.

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. Bartholomé. The information on materials of construction was obtained from Dr. Koch.

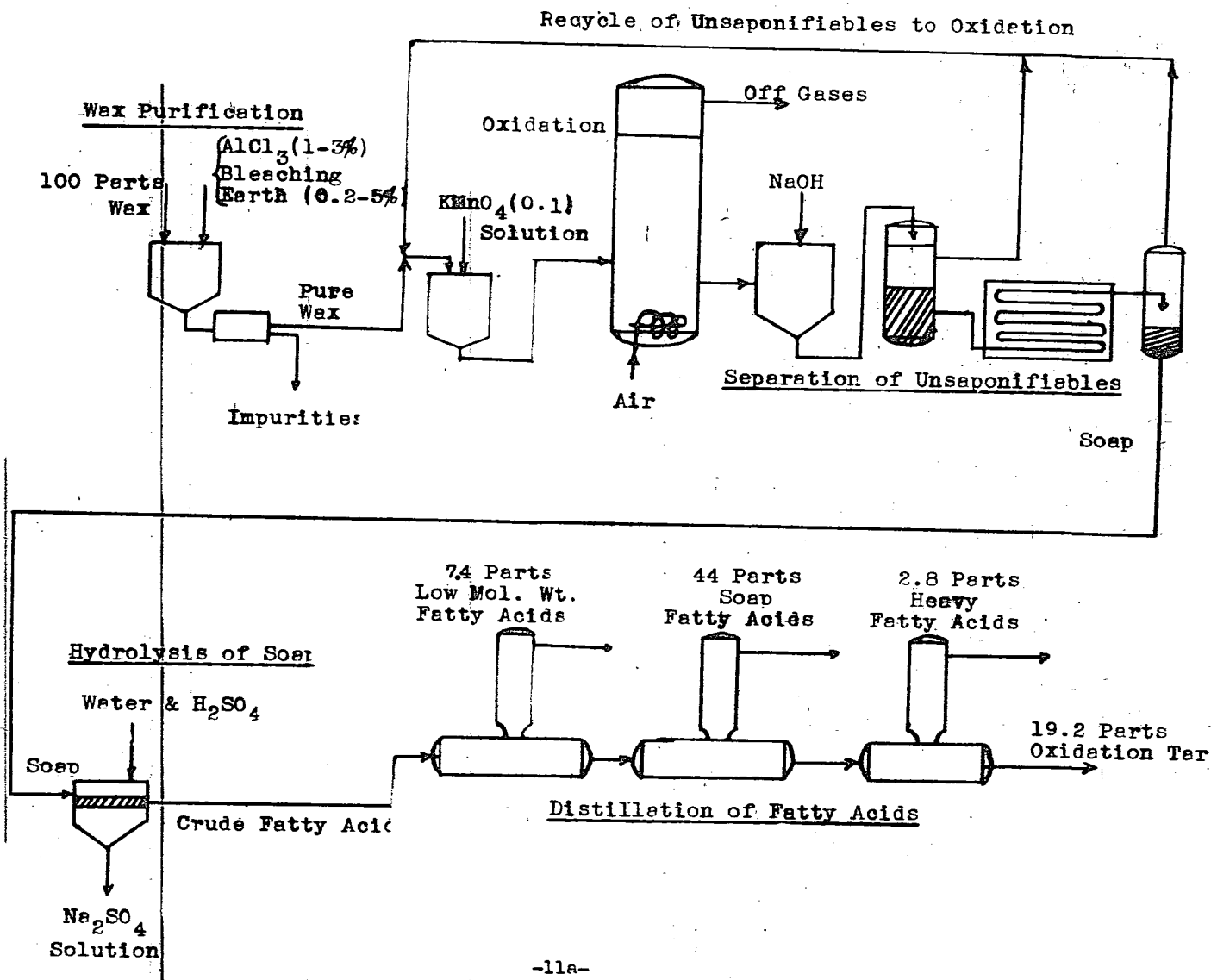
The conversion of methane with oxygen according to the equation:



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 Lins, 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^3 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



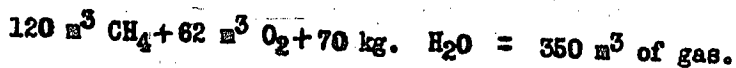
-11a-

Fig. IV FLOW SHEET FOR OXIDATION OF WAX

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.

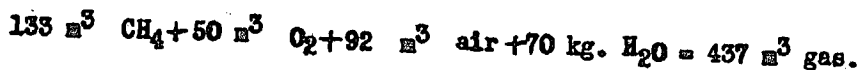
The following examples illustrate the conversion of methane:

1) Conversion with oxygen and steam:



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

2) Conversion with air, oxygen and steam:



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

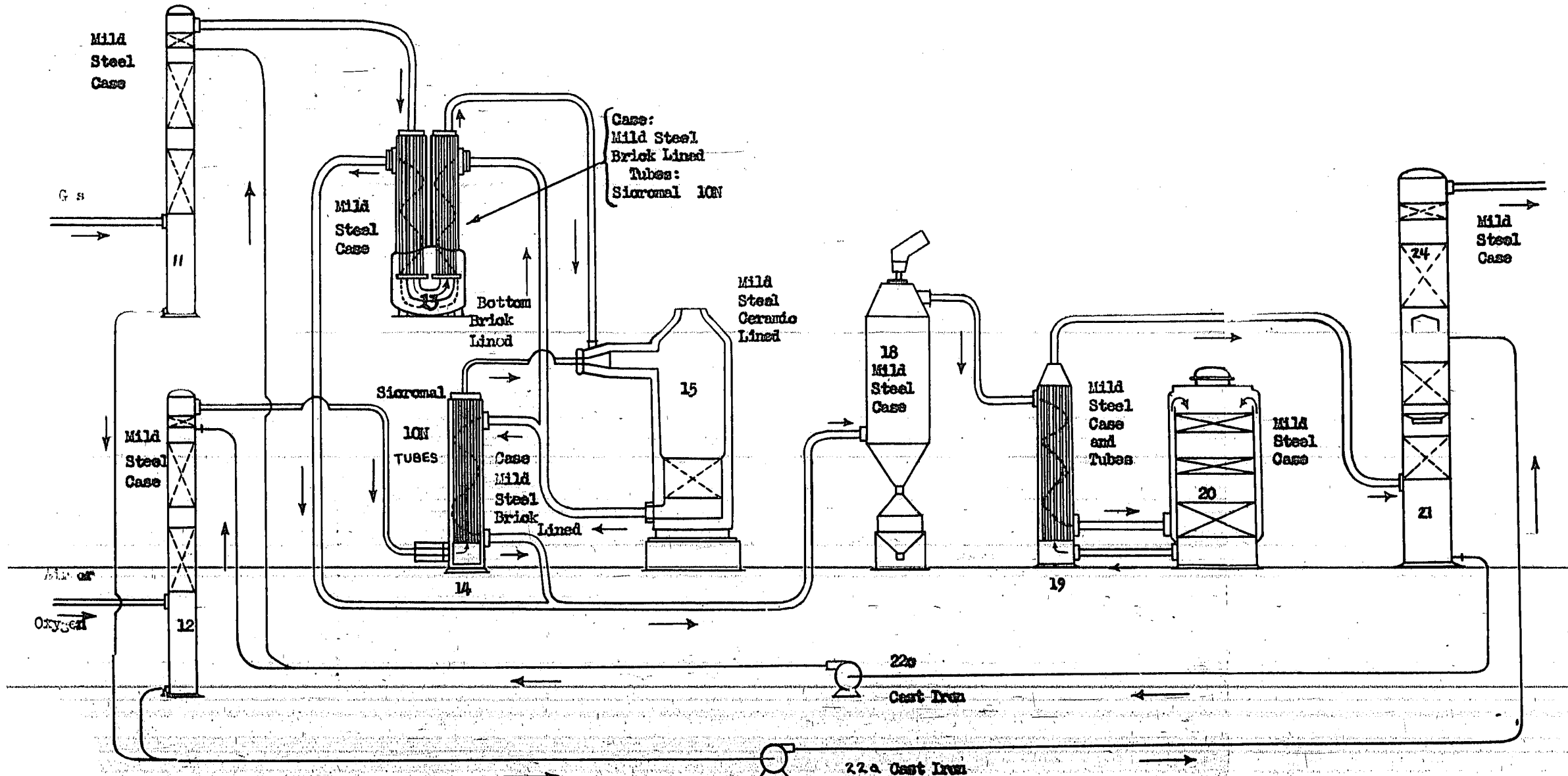
In the first example, the methane was preheated to 200°C. and in the second to 300°C.

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,

FLOW SCHEME FOR METHANE CONVERSION

- | | |
|-----|------------------------|
| 11 | Gas Saturator |
| 12 | Air Saturator |
| 13 | Gas Heat Exchanger |
| 14 | Air Heat Exchanger |
| 15 | Methane Converter |
| 18 | Filter |
| 19 | CO Heat Exchanger |
| 20 | CO Converter |
| 21 | Recycle Cooler |
| 24 | Final Cooler |
| 22a | Pump for Recycle water |
| 22b | " " " " |



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^3 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_2 and hydrogen, and is then cooled to air temperature in a spray tower.

At full production, the Oppau plant charges 8300 m^3 of coke oven gas with 4100 m^3 of oxygen to produce $18,300 \text{ m}^3$ of synthesis gas of the following composition:

CO_2	16%
CO	3%
H_2	60.4%
CH_4	0.5%
H_2	20.3%

For 8300 m^3 per hour of gas, the following utilities are required:-

Electricity, high voltage,	150 KW
low voltage,	35 KW
River Water	70 tons
Steam, low pressure	0.5 ton

The catalyst has a life of more than three years.

Three men per shift are required to operate the plant.

The same plant can operate on other gases containing up to 50% hydrocarbons, figured as CH_4 . If the feed gas contains more hydrocarbons, part of the synthesis gas is recycled as a diluent.

This process has the advantage that it can be carried out with gases containing sulfur, since the conversion temperature can be raised easily so high that the nickel catalysts are not poisoned.

The formation of carbon is troublesome, but this difficulty can be overcome, probably by changing the design of the combustion chamber.

When gas is manufactured for the methanol synthesis, only oxygen is used and the feed gas must be low in nitrogen.

C. Production of Hydrogen Peroxide by Propane Oxidation.

The following brief description of this process was obtained from Dr. Bartholome.

Propane is preheated to a temperature of 350 to 450°C. and admixed with 5 to 10% by volume of oxygen. This mixture flows into an empty reaction chamber where it remains for about 10 seconds, 90% of the oxygen reacting in this interval. The reaction gases are cooled to give an aqueous product containing 30-37% of peroxides. Approximately 50% of these peroxides are organic and the remainder is hydrogen peroxide, which is equivalent to a conversion of about 25% of the oxygen. The dry gas analyzes about 90% propane and 10% propylene.

The reaction vessel consists of apparatus glass "Duran" or of quartz.

These experiments were carried out on a scale of 300 liters of propane per hour.

D. Production of Acetylene by Oxidation of Ethane.

The following information was obtained from Dr. Sachsse. Additional details were not obtained due to the similarity of these experiments to the process of converting methane to acetylene. (See Ludwigshafen CIOS Report of 16 August 1945).

Ethane and oxygen are preheated separately and mixed, whereby an incomplete combustion occurs, resulting in a flame. No catalyst is used. The reaction takes place at 1-2 m. of water pressure and a reaction temperature of 1300-1600°C. The exit gas contains about 9% of acetylene besides carbon oxides, hydrogen and unconverted hydrocarbon. The yield of acetylene is about 0.33 kg. per kg. of ethane.

V. POLYMERIZATION AND CONDENSATION PROCESSES.

A. Oppanol.B.

The following information on the preparation and properties of Oppanol was given by Dr.Güterbock and on applications, by Dr.Schwarz.

Oppanol is polyisobutylene, prepared by polymerizing isobutylene in the presence of ethylene to control the temperature at -100°C . and of about 0.05% of boron fluoride as catalyst. The isobutylene and ethylene (liquid ratio 1:2) with the boron fluoride are charged in liquid phase onto a concave endless belt. The ethylene evaporates as the polymerization progresses, maintaining the temperature at -100°C . The belt is inclosed in a case from which the vaporized ethylene is recovered for recycling. The boron trifluoride (prepared from CaF_2 , B_2O_3 and H_2SO_4) leaves the reactor with the ethylene and is removed from it by contacting with CaO . The polymerized product is scraped from the belt into a heated kneader, where the last traces of ethylene are evaporated.

The belt is made of V2A steel; the case and other equipment, of iron.

The ethylene and isobutylene must be of the highest purity obtainable (99.5 %). The isobutylene is prepared by the dehydration of isobutanol at 400°C under atmospheric pressure with an aluminagel catalyst.

Products of various molecular weights are obtained by adding a polymerization "poison"; the best results were obtained with diisobutylene. The commercial grades were as follows:-

B3	3,000 mol. wt.
B15	15,000 "
B50	50,000 "
B100	100,000 "
B200	200,000 "

Properties of B-15 are:

Sp.gr.	0.9
Ignition Point	Very high
M.P.	Not definite, thermoplastic.
Neutralization No.	Neutral.

The applications of these products were as follows:

a) Oppanol B3

Cable oil, lubricating oil, softeners for resins and waxes, etc.

b) Oppanol B15

Viscosity improver for lube oil and cable oil. Additive to bitumens, waxes, paraffin, etc. Softener for polyethylene, gutta percha, and similar resins.

c) Oppanol B50, B100 and B200.

Foils for electrical insulation and protection against corrosion. Gaskets for chemical containers and grooved-can joints. Combination with polystyrene and polyethylene for electrical insulation for high-frequency cable casing and packing. Combination with polyethylene for submarine cable. Adhesive plasters and adhesive tape. Combination with wax, paraffin etc. for doubled steam-impermeable paper. Covering materials of all kinds in liquid form, with special stability against aging and chemicals. Blending with bitumens to increase viscosity and "dripping point". Mixed with natural and synthetic rubber for special applications.

B. Isobutylene Dimerization.

The following information was obtained from Dr. Kuhn:

Isobutylene is passed in the liquid phase at a space velocity of 3 to 5 liters per liter catalyst per hour over phosphoric acid on activated charcoal as catalyst. Conditions: 180-200°C., 25 atm. gage pressure. Thirty to fifty percent of this isobutylene polymerizes per pass, the remainder, after distillation, is recycled. Diisobutylene is the desired product but triisobutylene cannot be avoided. One liter of catalyst can produce one to two cubic meters of product. Isobutylene as pure as possible is used to avoid losses in (pressure ?) vent-release in the recycle system. Construction material is iron. The yield is practically 100 percent if the equipment is gas tight. There are no byproducts, excepting 0.1-0.5 percent of tetraisobutylene which is separated by distillation. The product is a mixture of diisobutylene and triisobutylene, which is hydrogenated to "Tannol". The product is tested for octane number and distillation range.

C. Lupolen H.

The following information on the preparation of Lupolen was obtained from Dr. Heinrich Hopff, and on the properties, from Dr. Schwarz.

The process is carried out at a pressure at 1500-2000 atm., using 0.05-0.10 percent of oxygen as catalyst. The reaction starts at 220°C. and temperature is controlled between 180 and 220°C. by cooling. The

apparatus, as shown in Fig. VI, consists of (a) a first-stage compressor to 300 atm., (b) a high pressure compressor to 1500-2000 atm., (c) a pipe coil 24 mm. diameter and 80 m. long, 40-50 l. volume, (d) a separator, and (e) a caustic washer. Heating and cooling are done by water under pressure at 200-220°C. in the first section of the coil, and 100-120°C. in the second section. The conversion to polymerization products is 8 to 10 percent per pass. Monthly production is 5 tons.

The ethylene feed is 98-99% ethylene, about 1% ethane, about 0.5% nitrogen and a trace of acetylene.

The viscous Lupolen H is drained into a tub and after cooling it becomes a snow-white mass. The product contains 0.2 to 0.3 percent of oxygen. Testing is done by milling a thin sheet on heated rolls and determining the stress, crease number (Knitterzahl) and dielectric-loss angle. In addition, the molecular weight which should be between 15,000 and 25,000 is determined in boiling tetralin by the method of Staudinger.

Lupolen H is a horny, tough material of paraffin-like character, tasteless and odorless, waterproof, heat-proof up to about 100°C., stable against chemicals, and with good dielectric properties. It is used alone or with Oppanol B as electrical insulating material, including use in submarine cable, as a low-loss insulation in high-frequency work, also as a cable-covering material.

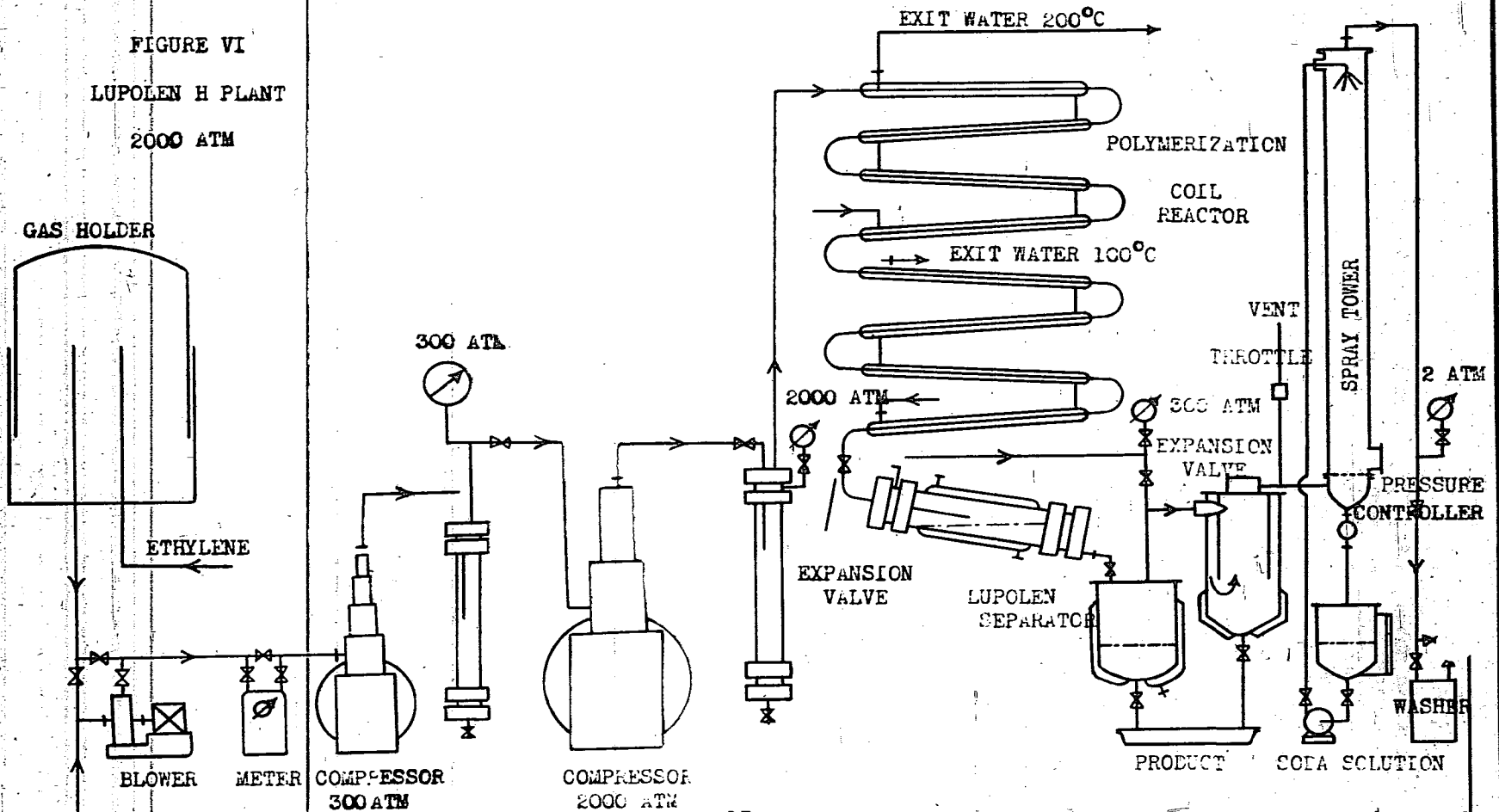
It is also used alone or with Oppanol B. for acid-proof covers, packing etc., and for taste- and odor-free wrappings of all kinds.

D. Parafflow.

The following information concerning the preparation of Parafflow was obtained from Dr. Fritz Christmann.

Hard paraffin, 1000 kg., 50-52°C M.P., is chlorinated to 12-14 percent chlorine by the addition of gaseous chlorine at a temperature of 80°C. It is then diluted in a stirred vessel with about 1000 kg. of ethylene chloride. After cooling to 20°C., 150 kg. of naphthalene, 10 kg. of polystyrene and 35 kg. of zinc oxide are added. Gradually, over 12 hours, 70 kg. of $AlCl_3$ is added, with stirring. In this period, the reaction temperature rises slowly to 30 to 35°C. After an additional 24 hours, the reaction temperature reaches 60°C., after which the

FIGURE VI
LUPOLEN H PLANT
2000 ATM



reaction product is centrifuged to remove insoluble salts.

The centrifuged product is then treated with 30 kg. of fuller's earth (Terrana) in a gas-heated agitator, during which time (12 hours) the temperature is raised to 240-270°C. The ethylene chloride is distilled off in the process and is replaced with kerosene. The product is cooled to 100°C. and filtered. The filter cake is twice extracted with kerosene. The filtrates are combined and vacuum-steam distilled in a pipe still, where kerosene and a paraffin-containing spindle oil are recovered as overhead products. The residue of 650 kg. (65% of original paraffin) is Paraflow fluid with a viscosity of 50-80°E. at 100°C, which is mixed with other oils (motor oils, spindle oils) in a ratio of 10:90 and sold as Paraflow.

The Ludwigshafen Paraflow plant has a capacity of about 20 T/Month Paraflow Fluid (= 200 T/Mo commercial Paraflow). The plant is practically intact and can reach this capacity in a few months.

E. Bunol.

The following information was obtained from Dr. Steinhofer on the preparation of Bunol, which is a butadiene polymer, claimed to be a suitable substitute for drying oil, such as linseed oil.

Butadiene is introduced with stirring into a suspension of two parts of potassium sodium alloy in 400 parts of toluene at 90°C. The reaction takes place violently, the temperature rising to 170°C. so that the toluene boils under reflux. After 8 to 10 hours, the reaction subsides. About 8000 parts of oil are formed; half is taken off and filtered. The other half, remaining in the kettle, is mixed anew with 200 parts of toluene and can be used again for the reaction without the addition of catalyst.

Details could not be furnished since the process was carried out at Schkopau, and due to lack of communications, the information was not available.

F. Buna D.

The following statement concerning Buna D was obtained from Dr. Herbeck.

~~Buna D is a co-polymer of butadiene and Dimol. Dimol is ethylene dimethylvinylcarbonol, and is made by the addition of vinyl acetylene to acetone.~~

The product is polymerized in emulsion by customary methods and its qualities are about the same as those of Buna S.

G. Production of Koresin.

The following brief information was obtained from Dr. Christ on Koresin preparation:

Koresin is prepared by treating a mixture of p-tert butylphenol (distilled product) and 8% zinc naphthenate ("Solingenzink") in a stirred autoclave with a mixture of acetylene and nitrogen until 1.3 to 1.5 mols of acetylene have reacted with 1 mol of the butylphenol. Operating conditions are 200-240°C, 20 atm. total pressure, 3 atm. partial pressure of nitrogen. The reaction product is forced by pressure to another agitator at 200°C., and from this vessel is emptied at 180-200°C. into wooden barrels or paper bags. It sets to a brittle brown resin of 120-130°C. melting point, corresponding to a dripping point of 130-140°C. by the method of Kramer and Sarnow.

Report No. 241, Dr. Hecht, May 25, 1940, "Koresin" is available through CIOS, CAFT III.

VI. CHLORINATION PROCESSES.

A. Preparation of Alkyl Dichlorides.

The following information was obtained from Dr. Leutner:

The chlorination of propane to dichlorides is carried out by mixing liquid propane and liquid chlorine in equimolar amounts in the presence of propylchloride, ten times the equivalent of the chlorine. This mixture is precooled and exposed to a mercury-arc lamp, in several stages. Intermediate cooling takes place between the stages so that the temperature does not exceed 70°C. The pressure has to be sufficient to maintain the liquid phase and insure solution of the hydrogen chloride formed. The process may be carried out batchwise or continuously by recycling the products through the coolers and exposure stages, removing product equivalent to the fresh feed.

The products are separated, by distillation, into hydrogen chloride, propane, propyl chloride, propyl dichloride (50% of 1,3 dichloropropane) and a small residue of higher chlorinated products. The propane is mixed with fresh propane and returns to the process with the propyl chloride. The yield of propane dichloride is about 99% of theory.

~~Butane dichloride can be produced in a similar manner. In this process, the temperature must not exceed 40-50°C. A pressure of 15 atm. is required. A yield of almost 100% is realized, including some trichlorobutane.~~

B. Preparation of Butadiene from Butylene.

This information on the production of butadiene from butylene was obtained from Dr. Leutner:

The chlorination of butylene is carried out in a high-speed centrifugal pump by introducing gaseous chlorine into a mixture of liquid butylene and an excess of dichlorobutane. In order to obtain an immediate reaction with the butylene, the chlorine is introduced axially into the pump through a nozzle. At a pressure of 4-6 atm. the circulating mixture is maintained in the liquid phase at 40-60°C. In order to be certain that the chlorine enters in the vapor phase, the supply line is steam jacketed. The liquid is circulated through a cooler and product corresponding to the feed is removed continuously. Distillation yields the dichlorobutane, the unreacted butylene being returned to the system.

The production of butadiene by splitting off of hydrogen chloride is carried out in empty tubes heated to 600-610°C. The best results are obtained with a 1:1 mixture of dichlorobutane to monochlorobutane, the monochlorobutane being obtained by splitting hydrogen chloride from dichlorobutane. The mixture is vaporized and passes into the reaction tubes; almost quantitative yields of butadiene are obtained.

The monochlorobutane and unreacted dichlorobutane are recycled to the decomposer.

In principle, the chlorination of propylene can be carried out in the same manner, but due to the higher boiling point, lower temperatures and higher pressures are required to maintain the liquid state.

C. Preparation of Butadiene from Butane.

The following information on the vapor-phase chlorination of butane was obtained from Dr. Waldmann.

With reference to Figure VII, butane and chlorine are mixed at atmospheric pressure in the proportion of 1 to 1 and brought to a temperature of 300-350°C. The reaction takes place very rapidly in the absence of a catalyst and produces more heat than is necessary to maintain the temperature. The products are cooled to condense the chlorides and are washed with dilute hydrochloric acid to wash out the HCl. The chlorinated butanes are caustic washed and distilled to separate the higher chlorides ("Poly"). The monochloride and dichlorides are decomposed without a catalyst at 550-600°C., and the products are worked up in the same system and together with the chlorination product.

The gaseous product, Butane, butylene and butadiene, passes to an absorber where it is contacted with a copper solution. The butane-butylene stream is conducted back to the chlorinator. The butadiene is liberated from the rich absorber solution by decomposition with heat and the lean copper solution recycled.

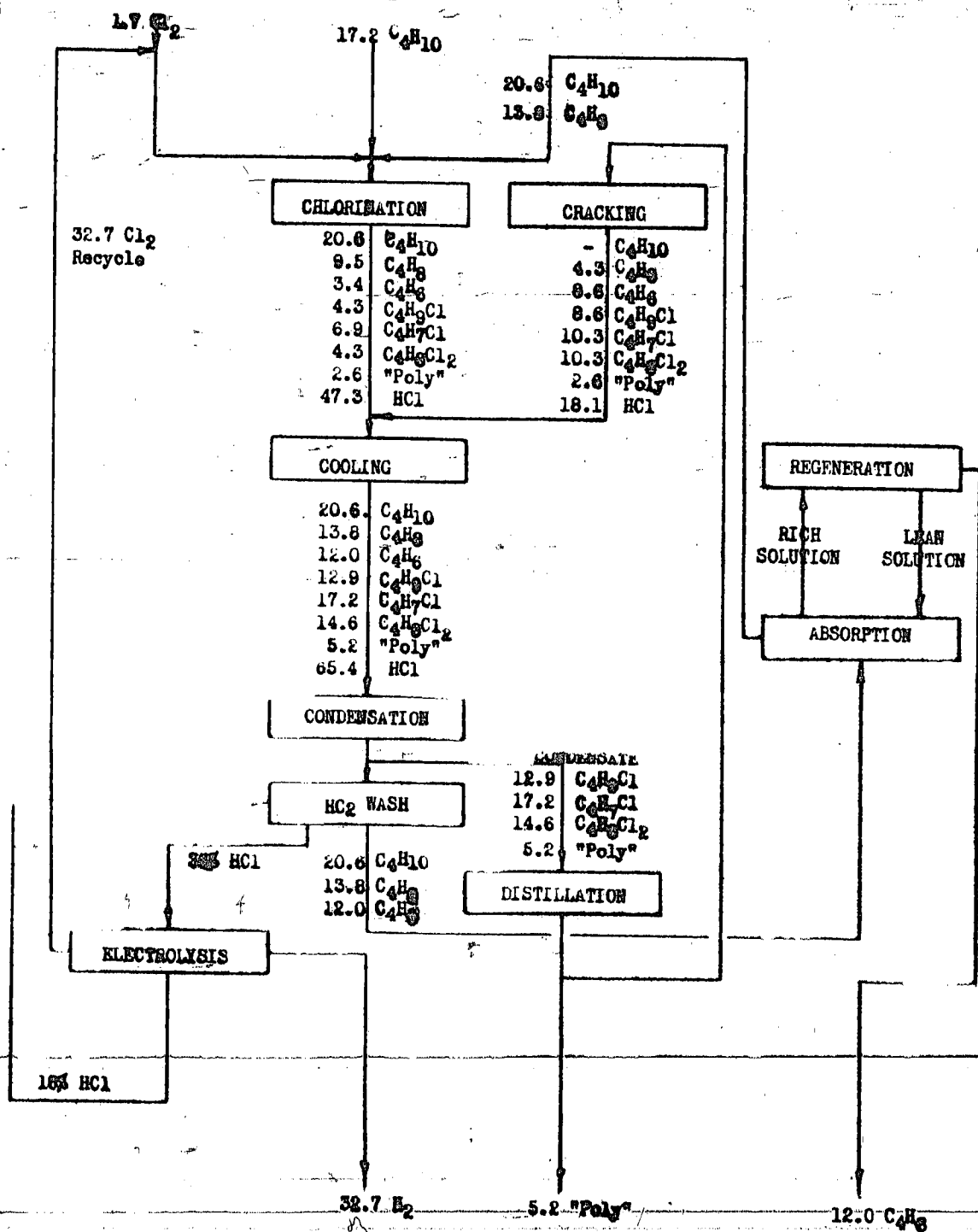


Fig. VII FLOW SCHEME FOR BUTADIENE PRODUCTION.

The concentrated hydrochloric acid is electrolyzed, yielding chlorine, which is recycled, and hydrogen. The chlorine is recovered to the extent of about 90%; the remaining 10% being present in the polychlorobutane produced.

From 1000 kg. of butane and 120 kg. of chlorine, the following yields are obtained:

C_4H_6	650 kg.
H_2	65 kg.
Polychlorobutane (25-30% Cl)	400 kg.

The process has thus far been carried out only on a small scale (10 kg. per hour). It is believed it can be successfully applied to the production of butylene or to butylene and butadiene, as well as for the production of propylene from propane.

VII. MISCELLANEOUS PROCESSES AND PRODUCTS.

A. Hydrogenation of Butadiene to Butylene.

The following information on the investigation of catalysts for the hydrogenation of butadiene to butylene was obtained from Dr. Conrad.

In the catalytic dehydrogenation of normal butane, a certain percentage of the butylene is dehydrogenated to butadiene. A small percentage of butadiene is detrimental in the alkylation of butylene to iso-octane, since the consumption of sulfuric acid is greatly increased.

In the experimental plant, Op.339, in which normal butane is dehydrogenated on a semicommercial scale by a multistage process, experiments were made to hydrogenate the butadiene with the hydrogen contained in the gas. A hydrogenating catalyst was tried which had been developed for the removal of small quantities of acetylene in the gas stream of an ethane cracking plant. It was possible to reduce the butadiene content from about 1-1.5% to 0.1% without changing the total olefin content of the gas. Since the dehydrogenation of butane as well as alkylation was interrupted by changed requirements, the investigation could not be pursued further on a commercial scale, especially the determination of the sulfuric acid consumption in the alkylation step. Further laboratory experiments, however, were made with a series of catalysts, the preliminary results of which follow:

The method of experimentation was as follows. The gas produced in a butane dehydrogenation plant was collected in a gas holder and the butadiene content brought to 1-2% by the addition of butadiene.

The mixed gas had, on the average, the following composition:-

Olefins	20-25%
Butadiene	1-2%
Hydrogen	23-28%
Butane	remainder

The gas was drawn from the gas holder at the rate of 25 liters per hour through a gas meter and a drying section, then into the catalyst chamber, which was a vertical tube of 30 mm. diameter, heated electrically. The different space velocities were obtained by altering the quantity of catalyst. The freedom of the gas from butadiene was determined by the failure of a portion of the stream to discolor 87% sulfuric acid. The butylene content was determined in the usual way by absorption in 87% sulfuric acid. The following observations were made in the series of experiments.

If the temperature of the catalyst is raised at a given space velocity of the charge gas, hydrogenation of butadiene to butylene begins at a definite minimum temperature, and with further increase of temperature, all the butadiene disappears without any hydrogenation of butylene, that is, the olefins remain unchanged. This result holds over a definite limited temperature range which is different for each catalyst. Further increase of temperature generally causes a decrease in the olefin content of the gas, since butylene is then hydrogenated to butane. The temperature range of selective hydrogenation is different for each catalyst and can change for a given catalyst in the course of continued use, an effect which can, of course, be ascribed to a change of catalyst activity. All catalysts investigated showed this behavior, with the exception of copper chromite on silica gel. With this catalyst only, selective hydrogenation was observed over a wide temperature range. Further increase of temperature resulted only in the reappearance of butadiene and no butylene was hydrogenated. A further investigation of this catalyst and other chromite catalysts is planned.

In the course of the experiments it was found necessary to remove from the gas stream the polymerization products which are always present in such dehydrogenated gases as vapor or entrained as mist. The removal is necessary to protect the catalyst from fouling. The removal was easily effected by a mist filter and an activated carbon filter. The lack of such purification was the reason that the butadiene content was not completely reduced to zero in the commercial experiment.

The principal results are summarized in the following table.

The second column shows the space velocity employed, stated in liters per hour per liter of catalyst. The third column gives the

temperature range within which the catalyst hydrogenates selectively at the space velocity shown.

Catalyst	Space Velocity	Temperature range °C
Cr ₂ O ₃ +NiO (Dr. H. Huber)	1000 2000	85-130° 80-138°
8376/High Pressure expts Sulfide catalyst, clay support	250 1000 4000	110-260° 130-240° 160-270°
CuO Cr ₂ O ₃ on silica gel	1000 2000 4000	140-320° 220° and higher 260° and higher
Cu On clay	1800 4500	105-150° 130-200°
Ni on clay	500	225-300°

These experiments show that the selective hydrogenation of butadiene in the presence of butylene is possible with each catalyst tried, and it is only necessary to find by experiment the particular conditions that a given catalyst requires.

In order to determine accurately the hydrogenation product, pure butadiene was hydrogenated over copper supported on clay. In this experiment, the catalyst was fully active at 75°C. The products were removed as solids by carbon dioxide. The Raman analysis gave the following results:

Trans-butene - 2	80%
Cis-butene-2	15%
Butene-1	5%

No butane and no butadiene were present. These results show that the addition of hydrogen is principally 1,4-addition.

B. Kybol.

The following information concerning the manufacture of Kybol was obtained from Dr. Waldman.

Kybol (diethyl benzene) is manufactured from benzene by alkylation with ethylene, using aluminum chloride as catalyst. Ethylene and benzene (mol ratio 2:1) are reacted in a tower containing aluminum chloride at the boiling point of benzene at atmospheric pressure, vaporization removing the exothermic heat of reaction. The ethylene is nearly completely absorbed in one pass. The product is washed and distilled.

The first fraction containing benzene, as well as the third fraction containing triethyl benzene, is recycled to the alkylation towers. The middle fraction (about 30% of the mixture) represents the final product, "Kybol". There is also a residue of the higher alkylated benzenes.

From 1000 kg. of benzene and 720 kg. of ethylene, 1450 kg. of Kybol are produced with a consumption of 5-7% of aluminum chloride (based on the benzene).

Kybol was chiefly obtained as a by-product of the manufacture of ethyl benzene for styrene.

In the same manner, isopropyl benzene can be prepared from benzene and propylene.

C. Tannol.

The following brief statement on Tannol was obtained from Dr. Kuhn.

Diisobutylene and triisobutylene from polymerization are hydro-genated in the liquid phase at 200 atm. pressure and 250°C. over a tungsten-sulfide catalyst. A space velocity of 3 liters of liquid charge per liter of catalyst per hour was employed. Yield is practically 100% of Tannol (isooctane and isododecane), which is used for a gasoline blending agent.

At first, nickel on a carrier such as pumice or kieselguhr was used, but was later replaced by tungsten-sulfide pellets.

D. Vanol H.S.

The following description of the preparation of Vanol was obtained from Dr. Lorenz.

A mixture of 1 mol of formaldehyde and 2 mols of methanol with 2% H_2SO_4 as catalyst is introduced into a distillation

column (see Fig. VIII). Methylal (dimethoxymethane) in an azeotrope with 8% of methanol is taken overhead. The azeotrope is mixed with 0.1% cobalt acetate (dissolved in methanol) and reacted with CO:H_2 in the ratio of 1:2 at 170°C . and 300 atm. The product is stabilized to remove dimethyl ether and methane. Methylal is taken overhead in distillation I, methanol in distillation II, and both are recycled. After adding sufficient water to form the 82% water azeotrope of vanol acetal (1,1,2 trimethoxyethane), the mixture is distilled off at 92°C . and hydrolyzed in the presence of H_2 at 300 atm. and 250°C . The products, methanol, water, and methyl glycol are charged to distillation II.

The main product, methyl glycol (2 methoxyethanol) is obtained by distillation IV, and finally in a vacuum distillation, Vanol HS is recovered, leaving a viscous residue. The vanol HS is a mixture of polyoxy compounds, partly ethers, containing acetal groups which can be hydrolyzed by hydrogenation over nickel.

The technical experimental plant for this investigation was working only partly. It was built for 50 tons per month of methyl glycol in continuous operation. The methyl glycol was to be hydrolyzed to glycol but this stage had not been satisfactorily developed.

From 100 parts of reactor product, the following materials are obtained:

Dimethyl ether	5 parts
Methylal	45
Methane	14
Vanol acetal	12
Methyl glycol	13
Vanol HS	9
Residue	2

E. Diolefins from Olefins and Formaldehyde.

The following brief information on the preparation of isoprene was obtained from Dr. Bueren.

The preparation of diolefins is carried out by first reacting the olefin with formaldehyde in the liquid phase at ordinary temperature in the presence of hydrogen chloride, to form a 1,3 dioxane. The dioxane is then decomposed to the diolefin by contacting with phosphoric acid catalyst at about 220°C .

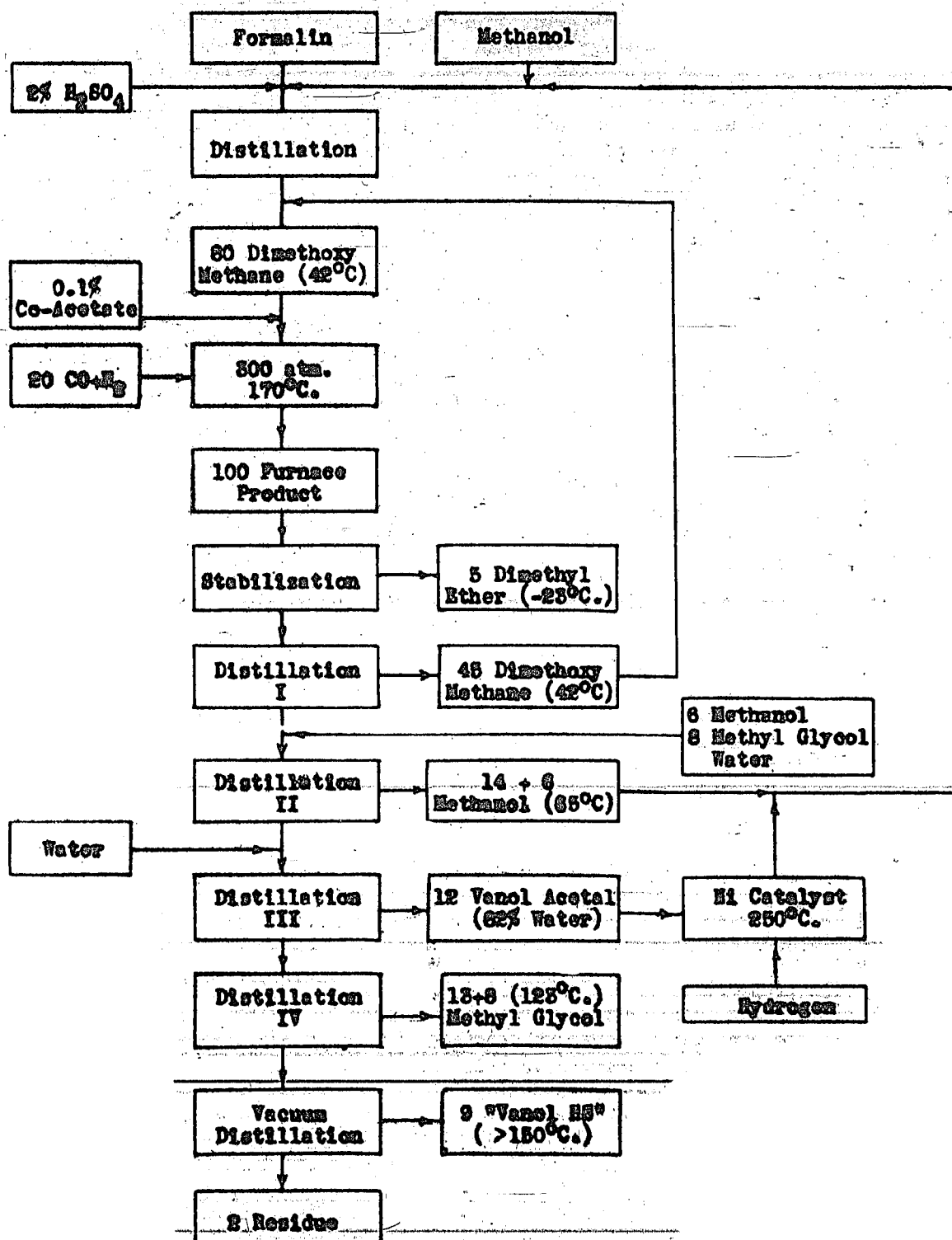
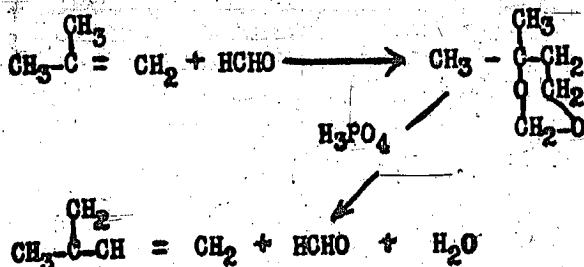


Fig. VIII FLOW SHEET FOR PRODUCTION OF VANOL

This is illustrated in the following reaction:



When trimethyl ethylene is used, besides dimethyl butadiene, pinacolin is obtained.

Further details may be obtained in DRP. IG. No.663/43 and DRP. 610,371

F. Preparation of Allyl Alcohol.

The following information on the preparation of allyl alcohol from allyl chloride was obtained from Dr.Klein.

Soda solution (1.25 m³/h. of 2.5 normal) is preheated to 130-140° C. and mixed with 250 liters per hour of allyl chloride. The allyl chloride contains 3-4% of isomers of lower molecular weight.

The mixture passes into a steam-jacketed reactor (see Fig.(IX) where it is maintained at 150°C, afterwards flowing into a secondary reactor. As it is unknown in which stage of the reactor the major portion of the CO₂ is liberated, the contact time cannot be calculated exactly, but it is estimated to be 20-30 minutes. Pressure in the reactor is maintained at 10-11 atm.

The reaction mixture is expanded to 8 atm. into a spray tower, in which the liquid phase separates from the CO₂. The gases pass through a cooler to a separator and are then vented.

The liquid phase from the spray tower is charged to a distillation column heated by direct injection of steam where an azeotrope (250 liters per hour) containing 30% water and 70% allyl alcohol is taken overhead. The allyl alcohol frequently contains small quantities (0.5-1.5%) of diallyl ether. The salt solution leaving the column should have a slightly alkaline reaction and contain no traces of allyl alcohol (by bromine test).

G. Methacryl Nitrile.

The following information on the preparation of methacryl nitrile was obtained from Dr.Lorenz.

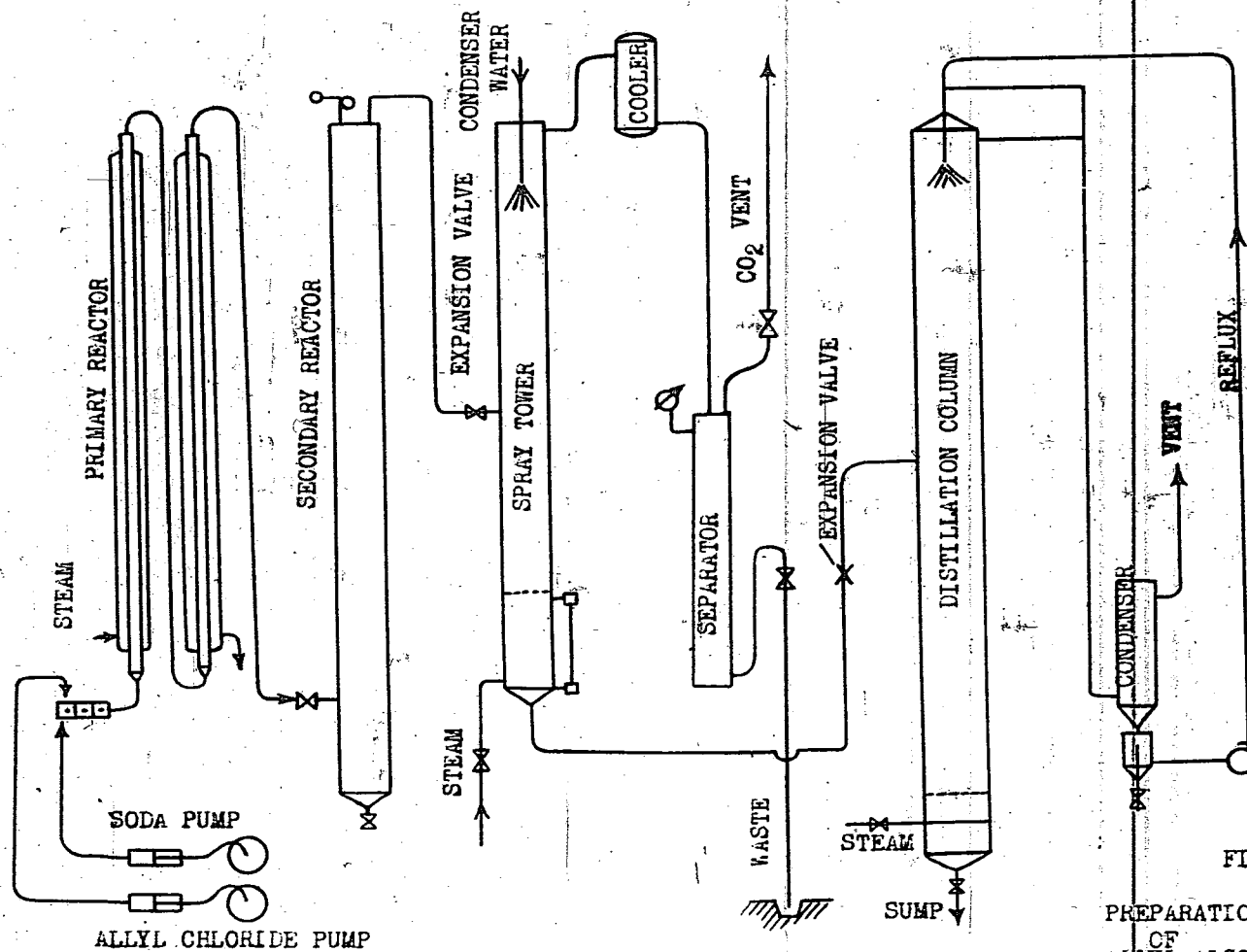


FIGURE IX
PREPARATION
OF
ALLYL ALCOHOL.

Isobutyl alcohol is oxidized, through the aldehyde, to isobutyric acid. This acid with ammonia is contacted over bauxite at 500°C. to obtain isobutyronitrile in 95% yield. The isobutyronitrile is chlorinated at 65-70°C. in a quartz tube by exposure to a mercury vapor lamp, the chlorine being added in such amounts that the chlorination does not exceed 40%. The product is distilled, and the first fraction containing unconverted isobutyronitrile and so-called "alpha-chloroisobutyronitrile" (BP 119°C) is recycled to the chlorinator. A second fraction (160-170°C), containing the so-called "beta-chloroisobutyronitrile" and an unknown "dichloroisobutyronitrile", is treated with 10% KOH. Approximately 5% of an unsaponifiable, highly chlorinated product is obtained as a residue.

By the KOH hydrolysis, the beta-chloroisobutyronitrile splits off HCl yielding methacrylonitrile I which is separated by distillation. The dichloride residue is passed over TiO_2 at 420°C., yielding methacrylonitrile II, which is less pure. The yield of methacrylonitrile is about 75% based on the butyric acid.

This investigation had not proceeded beyond the experimental stage, and the preparation for pilot-plant construction.

VIII. SPECTROGRAPHIC STUDIES.

A. Research.

The following information was obtained from Dr. Fromherz. As other investigators were covering this subject thoroughly, only a brief summary of the conclusions was obtained.

Experiments were performed by Dr. Fromherz together with Dr. Luft (of Oppau Manufacturing Control Dept.) on the use of the infrared spectrum of hydrocarbons for qualitative and quantitative analysis of hydrocarbon mixtures, and to prove the advantages and disadvantages of infrared analysis as compared with Raman analysis. The studies led to the following conclusions:

1. The infrared fundamental oscillations between 3 μ and 12 μ are very characteristic for the individual hydrocarbons; they give sufficiently intensive absorption bands and permit a good qualitative analysis of mixtures with not more than three components, and a quantitative analysis with a precision up to 0.5 per cent.

2. A comparison of infrared analysis with the Raman analysis shows that the Raman analysis is in general preferable for qualitative investigations, because the characteristic Raman lines of different

hydrocarbons can be observed lying adjacent to each other, while infrared absorption bands for different hydrocarbons are overlapping. Therefore, the individual hydrocarbon in a mixture can be identified more easily by the Raman spectrum, and mixtures of more than three components can be qualitatively analyzed satisfactorily.

3. For quantitative analysis, the infrared method is generally better, because the intensity of absorbed light can be measured easily with great accuracy. In quantitative Raman analysis, it is necessary to measure photometrically the blackness of photographic places, which is difficult, not too accurate and subject to many errors. If special precautions are not taken, the accuracy may not exceed 5%. Further, the results are not expressed in absolute concentration, but only in relative ratios.

4. The latter fact leads to a further advantage of infrared analysis. If, in Raman analysis, one component is missed because of its very weak Raman line, the remaining components (by ratios) will still add up to give a total of 100 per cent for the analysis. If the same mixture is analyzed by infrared rays, it can be determined if the sum is actually 100 per cent, or if it is less than 100 per cent (beyond the limits of errors). If the latter condition is found, some component has escaped Raman analysis, and the infrared analysis will give the quantity of this component by difference from 100%, and possibly from some disagreement in the infrared spectra, a clue to the identity of the missing component may be gained.

B. Equipment.

The information given below was obtained from Dr. Luft.

In Oppau, two infrared spectrographs were developed; one registers the course of the energy, the other gives directly the spectral course of the absorption relation (ratio ?) of the substance being examined. The spectral range of the first apparatus extends from 1 to 8; that of the second from 1 to 14. Both instruments have rock-salt prisms. In the last few years, these apparatus have been used to investigate the infrared absorption of a number of substances (including paraffinic and aromatic hydrocarbons).

Both of these apparatus were described in the "Zeitschrift für technische Physik". In addition, a recording apparatus was developed for plant analysis using a summing up (integrating) method of infrared absorption. This apparatus serves to record continually the analysis of CO, methane, etc. (Infrared absorption recorder).

Both spectrographs are in the Lenard Institute at Heidelberg. Spectra, calibrating curves, etc. are partly in the Lenard Institute and partly in the salt mine at Heilbronn. Both places are under control of the American authorities.

The standard samples had mostly remained in Oppau, Building Op. 567, where they were partly destroyed in the air raid in December, 1944. The others were stored in the basement of building Op. 567. A few samples were stored in the Lenard Institute in Heidelberg. Infrared absorption recorders are in place in various parts of the Oppau and Ludwigshafen plants.