

ITEM No. 30  
FILE No XXX-103

*copy 1*  
~~COPY No 118~~

RESTRICTED

I.G. FARBENINDUSTRIE  
A.G. WORKS  
LUDWIGSHAFEN AND OPPAU.

*Hilroyd, R.*

REC'D. FEB 14 1946  
TIIC I.F. & L. S-C.

RESTRICTED

COMBINED INTELLIGENCE OBJECTIVES  
SUB-COMMITTEE

RESTRICTED

REPORT ON INVESTIGATIONS BY FUELS & LUBRICANTS TEAMS  
at the  
I.G.FARBENINDUSTRIE A.G. WORKS AT LUDWIGSHAFEN AND OPPAU

Edited by

Lt.Col. R. HOLROYD  
Min. of F. & P.

on behalf of  
Min. of F. & P. and T.L.I.C.

CIOS Target No. 30/4.03  
Fuels and Lubricants

16th August 1945

Combined Intelligence Objectives Sub-Committee  
G-2 Division SHAEP (Rear) APO 413

RESTRICTED

70p. illus.

CONTENTS

	<u>Page</u>
I <u>Introduction</u>	1
II <u>Synthesis Gas Production</u>	
A. General	2
B. Pressure Operation of the Water Gas Shift Reaction. (J.F.Ellis)	2
C. Methane-oxygen process for Synthesis Gas. (E.B.Peck & L.P.Evans)	6
D. Methane-oxygen process for Acetylene and Synthesis Gas. (E.B.Peck & L.P.Evans)	9
III <u>Synthesis of Ammonia</u> (R.Holroyd)	13
IV <u>Synthesis of Methanol &amp; Higher Alcohols</u> (V.Haensel)	14
V <u>Hydrogenation &amp; Related Processes</u> (R.Holroyd & W.F.Faragher)	
A. Production of Synthetic Fuels at Ludwigshafen and Oppau.	16
B. General Review of German Wartime Operations and Developments.	16
(a) Bituminous Coal Hydrogenation	16
(b) Brown Coal Hydrogenation	18
(c) Brown Coal Tar Hydrogenation (T.T.H. & M.T.H. Processes)	18
(d) Bituminous Coal Tar Hydrogenation	19
(e) Hydrogenation of Petroleum Oil Residues.	19
(f) 300 ats Vapour Phase Hydrogenation	20
(g) 700 ats Vapour Phase Hydrogenation	21
(h) D.H.D. Process	21
(i) Iso-octane and Alkylate Production	24
(j) Fuel for Jet Planes	25
(k) Summary Table of German Hydrogenation Activities	26
C. Costs of Hydrogenation Processes	26
D. Research	27
E. Methods of Manufacture of Catalysts (W.F.Faragher & W.A.Horne)	30
VI <u>Lubricating Oil</u> (B.Cotton)	35
VII. <u>Fischer-Tropsch Synthesis</u> (R.Holroyd & W.F.Faragher)	35
"Michael" Synthesis. (W.A.Horne)	35
VIII <u>Miscellaneous Chemical Processes</u> (V.Haensel)	37

		<u>Page</u>
IX	<u>Information on other German Factories</u> (R.Holroyd & W.F.Faragher)	44
	A. Heydebreck	44
	B. Auschwitz	47
	C. Politz-Stettin	48
X	<u>I.G/Japanese Army Negotiations</u> (R.Holroyd & W.F.Faragher)	50
XI	<u>Development of Wickel Pressure Vessels</u> (J.F.Ellis)	53
XII	<u>Development of High Pressure Vessels</u> (J.F.Ellis)	57
XIII	<u>Hydrogen-Resistant Steels, etc.</u> (J.F.Ellis)	60

Appendices:

A.	Personnel of C.I.O.S. Team visiting Target 30/4.03	62
B(1)	Heat Exchangers Used in KW Plants at Oppau and Heydebreck	63
(2)	Calculations on K.W. Plant, Heydebreck	64
C.	Large-scale Production of Synthetic Fertilizers.	66



## I. INTRODUCTION

1.

The Ludwigshafen and Oppau plants are largely independent I.G. factories situated some 2 - 3 miles apart on the west bank of the Rhine facing Mannheim. The former factory is a general organic chemical works specialising in dyes, dye intermediates, plastics and synthetic rubber, while the latter is a heavy organic chemical factory producing ammonia, methanol, higher alcohols and their derivatives. Before the war much of the I.G. research and development work was carried out at Ludwigshafen; in particular the high pressure research section directed by Dr. Mathias Pier played a very active part in all hydrogenation developments.

Apart from the possibility that a full scale hydrogenation or Fischer Tropsch plant had been erected at Ludwigshafen/Oppau during the war, the main objectives of an oil team investigation were:-

- (a) To obtain from Dr. Pier and his staff an advance general picture of German fuel production processes.
- (b) To study the fuel developments still in the research and pilot plant stage.
- (c) To examine any new developments in hydrogen or synthesis gas manufacture.
- (d) To look for new processes for production of high anti-knock fuel constituents and for new fuel additives.
- (e) To investigate new chemical syntheses based on raw materials obtainable from oil.

The Ludwigshafen and Oppau factories were first visited by the large team listed in Appendix A during the period 25-31st March. The investigation revealed that no large plant for synthetic fuels or lubricants had been operated at this target. All the important members of the Fuel Research Section staff had been evacuated to Heidelberg and information on the work of this department was therefore limited to that contained in seized documents, the greater part of which have still to be examined in detail. Valuable information on synthesis gas production from hydrocarbon gases was obtained as well as interesting data on a number of chemical syntheses.

Two members of the above team - Holroyd and Faragher - accompanied by Major Tilley (interrogator) went on to Heidelberg, contacted Dr. Pier and the chief members of his staff on April 1st and obtained from them the hydrogenation information given later in the body of the report.

Later, after visiting Leuna, Holroyd, Faragher and Ellis paid a second visit to Heidelberg and to Ludwigshafen/Oppau on 27th-30th May to check a number of details, particularly with respect to hydrogenation costs, and to obtain information on the pressure conversion of water gas to hydrogen and on the manufacture of Wickel pressure vessels.

The following report presents, under subject headings, the information obtained in the course of these various visits.

SCHIERENBECK - SYSTEM - BLECHHAMMER OHW

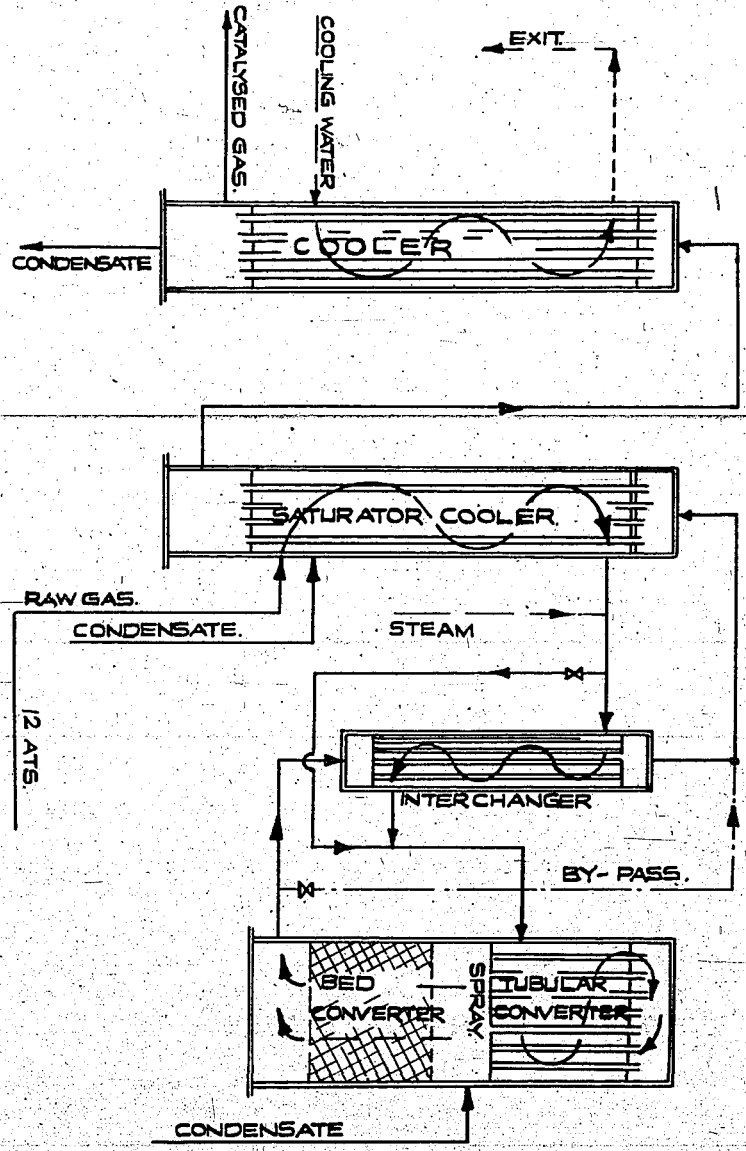


FIG. 1

(A) General

Oppau had a maximum capacity for production of 180,000 M<sup>3</sup>/hour of synthesis gas plus 40-50,000 M<sup>3</sup>/hour of producer gas. Synthesis gas was made mainly from water gas produced from coke in 31 generators of conventional design, the novel feature being that three of the water gas to hydrogen shift units operated a 25-30 ats. pressure process.

The remaining synthesis gas was obtained by Linde fractionation of Saar and Ruhr coke oven gas to give hydrogen, and by a modified methane-steam process (the Methane-Oxygen or K.W. process) from coke oven gas or hydrocarbons recovered by Linde fractionation of coke oven gas. The latter process was operated in two large scale pilot units at Oppau and these had a total capacity of 20,000 M<sup>3</sup>/hour synthesis gas. The units had also been run experimentally using a modified process which gives rise to acetylene as a by-product.

Both the pressure shift and the methane-oxygen processes are of particular interest because they have been adopted extensively in the new eastern plants built during the war. They were therefore investigated in considerable detail and are described fully in the following sections.

(B) Pressure Operation of the Water Gas "shift" reaction.(i) Objectives behind the Development.

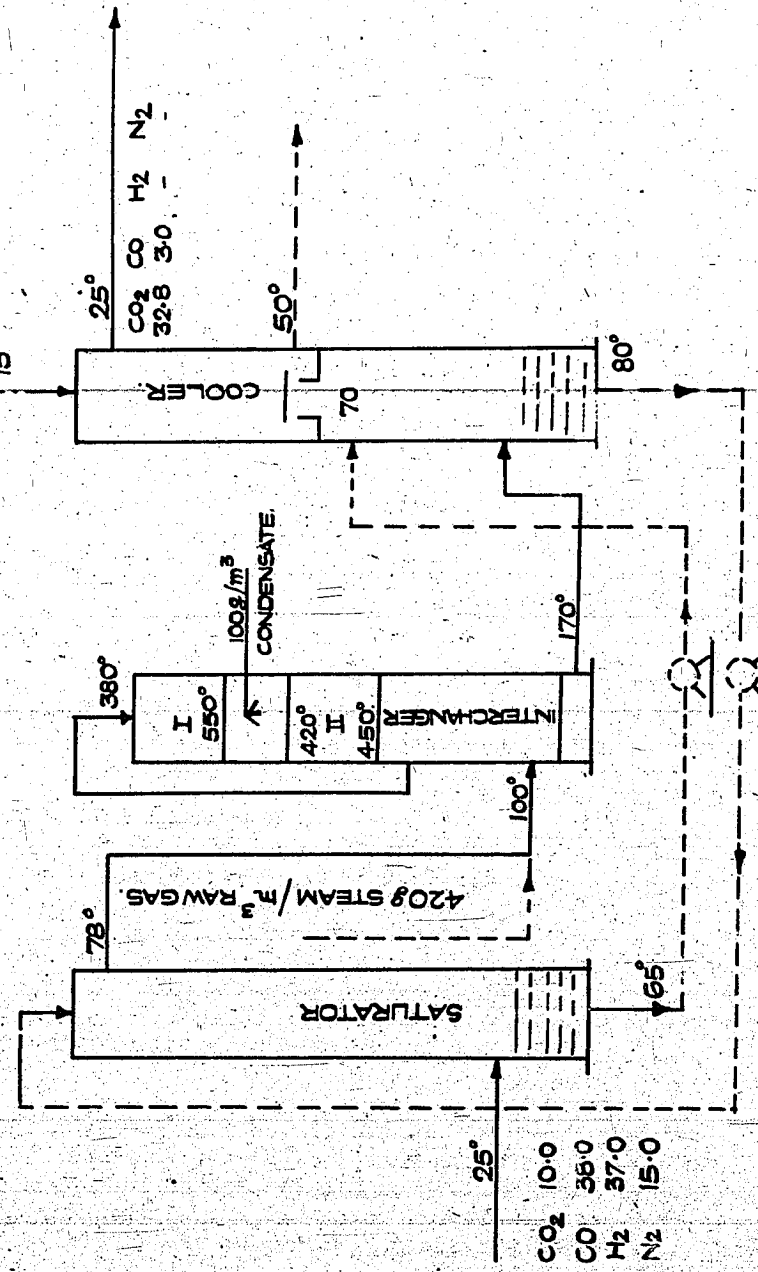
Information on this process was obtained from Dr. Schierenbeck, Ing. Lampe, Ing. Funk during the second visit to Oppau. Dr. Schierenbeck had directed the I.G. development work in this field and Ing. Funk had been in charge of a large scale installation at Blechhammer.

Theoretically, there are sound reasons for the use of a pressure process. The final products have in any case to be compressed for the removal of carbon dioxide and, since the reaction  $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$  gives a 100% increase in volume of permanent gases, operation under pressure eliminates compression charges in respect of the newly-formed carbon dioxide. As far as compression is concerned there is clearly no advantage to be gained by use of pressure higher than that to be employed for carbon dioxide removal.

Secondly, the equilibrium of the reaction is unaffected by pressure. Pressure operation therefore simply increases the volume of gas (measured at NTP) which can be treated in a plant of given size and catalyst capacity. No change in reaction temperature and no special catalyst is necessary. The I.G. use a catalyst consisting of 91% Fe<sub>2</sub>O<sub>3</sub> and 7% chrome oxide for both pressure and atmospheric units.

LOW PRESSURE CO CONVERSION - LELUNA

COOLING WATER - APPROX. 5 l/m<sup>3</sup>  
CAT. GAS.



RECYCLE APPROX. 16 l/m<sup>3</sup> RAW GAS.

CATALYST/GAS  
12 m<sup>3</sup>/3000 m<sup>3</sup>

FIG. II

The increase in unit capacity was particularly attractive for Germany during the war because of the resulting economy in steel, but as will be seen later, the advantage has been offset by the necessity to use special steels for the pressure process. 3.

The third potential advantage of pressure operation is economy in steam. Under normal atmospheric pressure conditions one of the chief heat losses from the system results from the comparatively large quantity of water vapour carried away by the exit gases from the water heater and condensed in the final cooler, see figure II. Provided that use of increased pressure is not accompanied by an increase in exit temperature of the final gases, it will reduce this loss of water vapour, and therefore the heat loss, because of the reduction in volume of exit gas. In addition, the general heat losses from the system (per  $M^3$  of gas product) should be reduced by the increase in unit capacity.

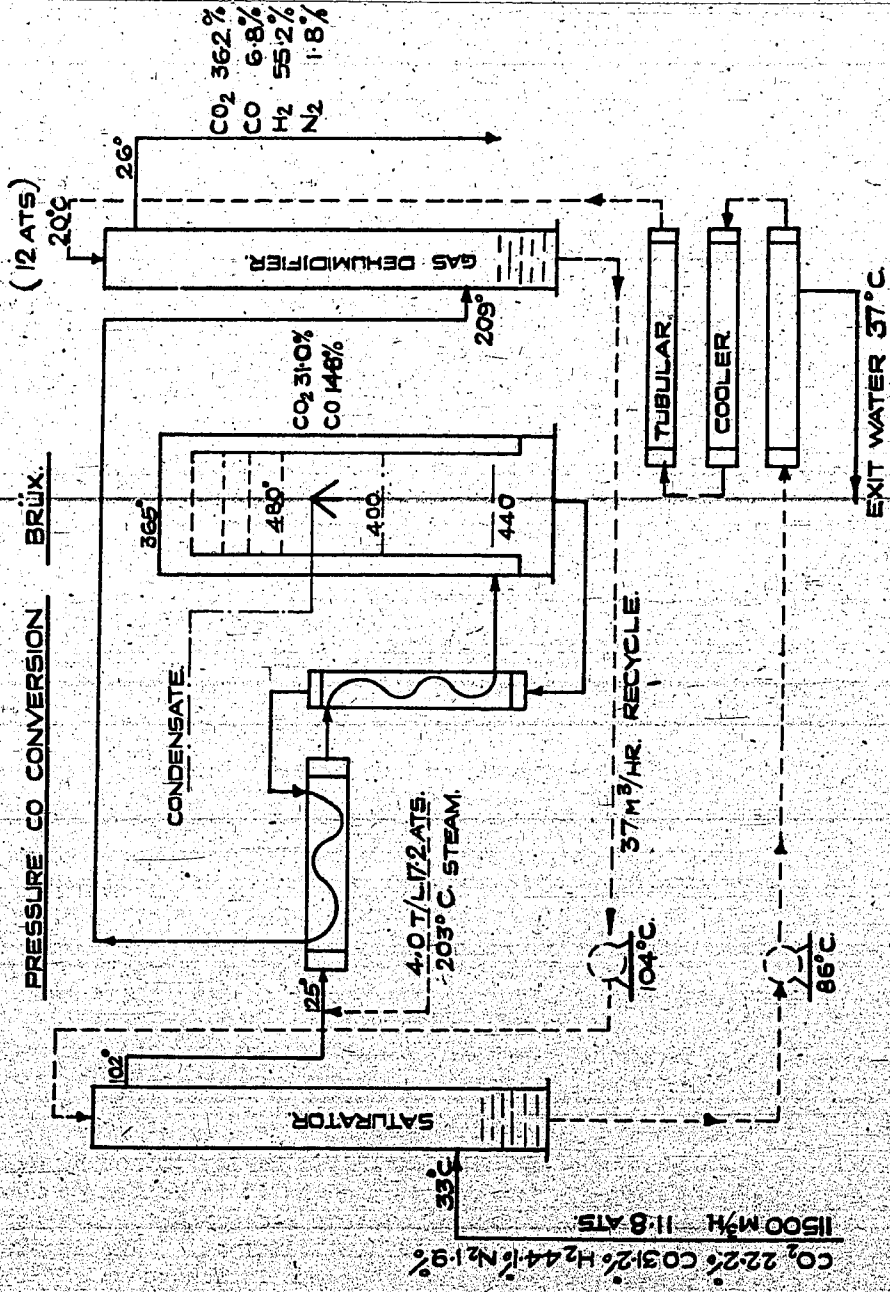
The potential disadvantage of the pressure process is corrosion due to an increased concentration of dissolved carbon dioxide, oxygen and sulphur gases in the water.

#### (ii) Description of Plant

The pressure plant developed by the I.G. attempts to secure all three of the above advantages. A flow diagram of the plant is shown in figure I and, for comparison, figure II illustrates a typical low pressure unit.

The feed gas under a pressure of 12-30 atmospheres together with condensate water is introduced to the shell of a tube interchanger (40 mm tube diam.) where it absorbs heat from the exit gas from the process and becomes saturated with water vapour. This heat exchanger takes the place of the direct water heater and the saturator vessel used in atmospheric pressure plants. The efficiency of the interchanger is controlled by varying the level of water held in the shell, thereby varying the amount of tube surface available for interchange. The latest I.G. design for this saturator/heater employs flattened tubes of 4 mm/60 mm cross section, it being claimed that tubes of this shape result in a saving of steel and in equal heat transfer coefficients on both sides of the tubes. Individual tubes are separated by a space of about 4 mm.

The partially preheated saturated gas is joined by make-up steam and passes to the main interchanger where it is heated to about 300°C. It then passes to the upper reaction zone of the converter which consists of a bank of tubes containing catalyst. The ingoing gas first travels upwards outside the tubes and is heated to 450°C after which it passes downwards through the catalyst tubes. Heat is generated during reaction, but is simultaneously absorbed by interchange with the inlet gas. The result is that the temperature of the reactant gases in the tubes first rises to about 500°C and then falls gradually to about 400°C at the exit of the upper reaction zone.



**FIG. III**

Before passing to the second part of the reaction vessel, which consists of a normal catalyst bed, additional water condensate is introduced as a spray. The final gas product leaves the bottom of the reactor at about 440°C and travels through the tubes of the two interchangers to a final indirect water cooler.

An alternative design of pressure plant developed by Bamag is shown in figure III: The separate water heater and inlet gas saturator employed in atmospheric pressure units are retained. The main change is that the final indirect water cooler is used to cool the water condensate recycled from the saturator to the water heater. In this way the water heater becomes the final cooler for the exit gas.

It was stated that, in some Bamag designs, the second interchanger (shown in figure III in use for preliminary preheat of saturated inlet gas) is used to preheat water passing from the water heater to the saturator.

In order to combat the corrosion problem, the parts of a pressure plant with which liquid water is likely to come into contact should be made of special steel. The I.G. at Oppau prefer to use 17% chrome steel, but have used V<sub>2</sub>A and occasionally FFN 6% chrome steel. For the new flat tube saturator/heater it is proposed to use Sicromal 8 (5% chrome 1% silica).

Pressure conversion units are reported to have been erected at the following factories:-

Oppau	I.G.	Design	25 ats.
Blechhammer	"	"	12.5 ats.
Heydebreck	"	"	30 ats.
Anschwitz	"	"	21 ats.
Brux	Bamag	"	12.5 ats.
Iins	I.G.	"	30 ats.
Lutzkendorf	Bamag	"	8 ats.

(iii) Comparison of the Pressure and Atmospheric Processes.

With a catalyst volume of 10 M<sup>3</sup>, a 25-30 atmosphere pressure plant has a capacity for 25,000 M<sup>3</sup>/hour inlet gas. An atmospheric pressure unit of the same catalyst volume will treat only 3,000 M<sup>3</sup>/hour. Dr. Schierenbeck was of the opinion that it would not be practicable to build an atmospheric unit with a capacity of more than 10,000 M<sup>3</sup>/hour inlet gas.

It is unlikely that this increase in unit capacity results in any appreciable reduction in capital cost per M<sup>3</sup> of synthesis gas product, (a.) because of the necessity for special steels and (b.) because, generally, the use of high capacity units means that a bigger percentage spare capacity has to be installed. For regular production of 100,000 M<sup>3</sup>/hour synthesis gas, five pressure units with a total capacity of 125,000 M<sup>3</sup>/hour would have to be installed compared with

5.  
say 11 atmospheric units with a total capacity of 110,000 M<sup>3</sup>/hour.

On the operating side there should be a saving in labour and repairs, but the former will be small because labour requirements for any type of water gas shift plant are extremely low, and the latter can easily be offset by increased cost of replacement materials in the event that any appreciable corrosion takes place.

Oppau claim that the requirement of make-up steam when using the 25-30 ats. process is only 250 grams per M<sup>3</sup> of inlet gas compared with 400 grams for the atmospheric pressure process. The I.G. seem to set great store by this steam saving, and this is rather surprising in view of its relatively small influence on cost particularly when the process is operated at a factory where H.P. steam has a premium value.

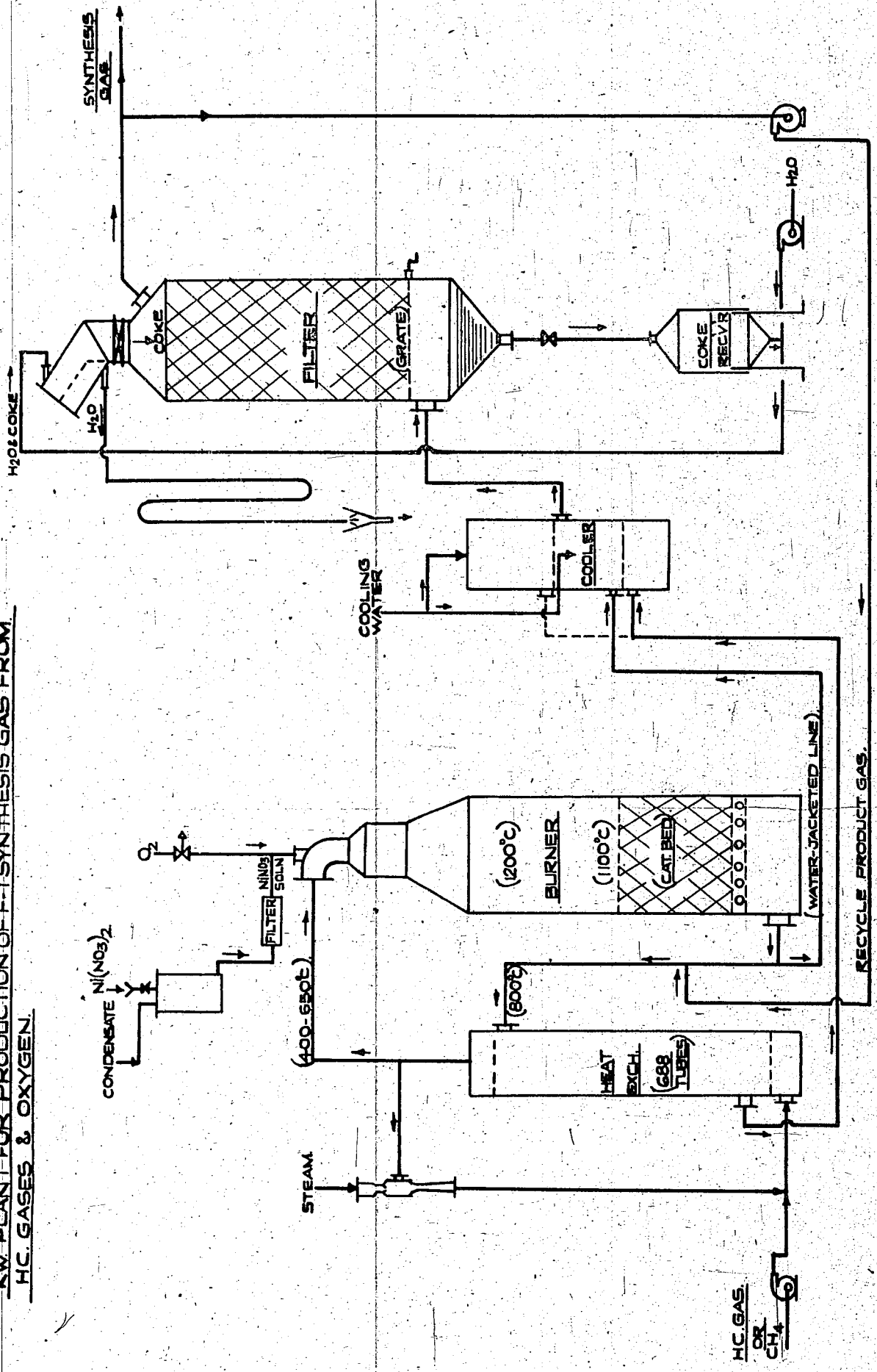
The main saving effected by the pressure process appears to be the reduction in compression charges, which, of course, is considerably greater when hydrogen or ammonia synthesis gas is the required product than is the case when synthesis gas for Methanol or Fischer-Tropsch is being made.

The I.G. at Oppau continue to be enthusiastic about the merits of the pressure process and claim that its operation at Oppau has saved the capital cost of the new plant in 3 to 4 years. The managements of the new plants in Eastern Germany, on the other hand, are dissatisfied with the process and the Brux and Blechhammer staff feel that troubles experienced with the pressure shift plants have limited the output of the main plant. Corrosion troubles have been frequent and severe on all these plants, but they have certainly been aggravated by attempts to use inferior materials because of the shortage of special steels. Trouble has also been experienced with short catalyst life, but this again has probably been largely a secondary effect of corrosion, scale from the plant being deposited on the catalyst. Bombing may also have contributed to this trouble in a number of cases; for example, gas lines have been damaged and dust introduced into the plant.

A good deal of the trouble experienced at Blechhammer was caused by a definite mistake in design. All the preliminary design work was carried out on the assumption that the plant would operate at 30 atmospheres, and it was only in the late manufacturing stages that it was realised that the plant was to operate at 12½ atmospheres. In order to reduce the pressure drop across the unit, various interchanger tube bundles and the catalyst beds were cut in two and arranged for operation in parallel. This apparently led to a reduction in heat efficiency of the unit.



**FIGURE IV**  
**KW PLANT FOR PRODUCTION OF F-T SYNTHESIS GAS FROM**  
**HC. GASES & OXYGEN.**



(SCHEMA B14)

(c) The Methane-Oxygen Process for Synthesis Gas Production 6.

(i) General Process Description

The following information was obtained (a) by interrogation of Dr. Kosbahn (assistant to Dr. Sachse who was mainly responsible for the development of the process) and (b) from an incomplete examination of documents removed from Dr. Sachse's Oppau office.

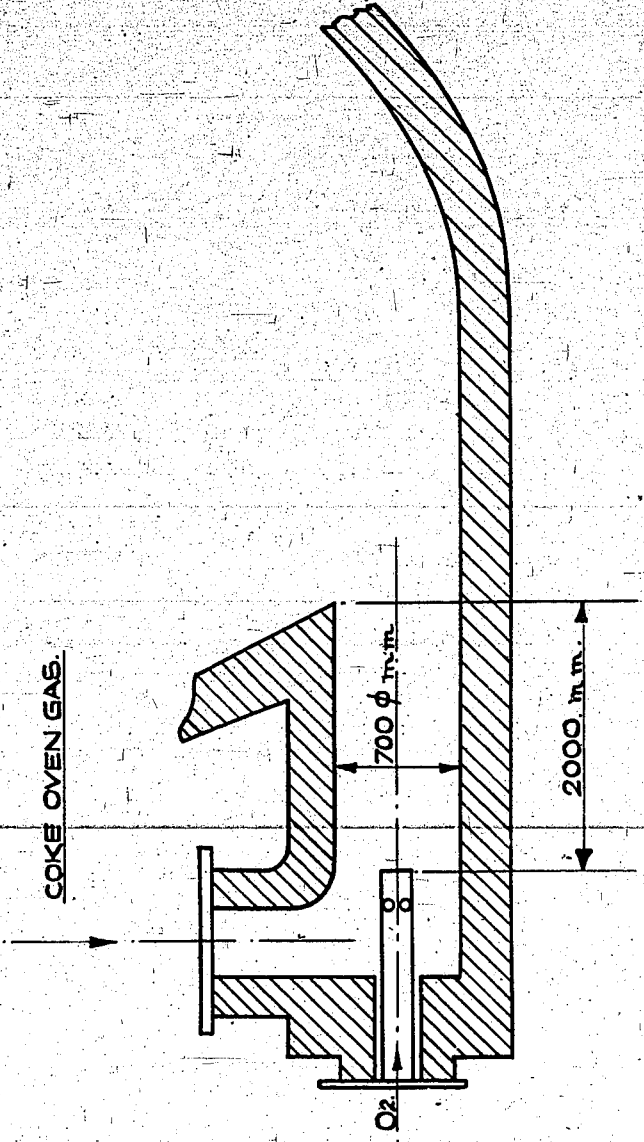
The process provides an autothermic method for the production of synthesis gas ( $\text{CO} + \text{H}_2$  or  $\text{CO} + \text{H}_2 + \text{N}_2$ ) from gaseous hydrocarbons. The first step consists of burning the preheated hydrocarbon ( $650^\circ\text{C}$ ) with oxygen or oxygen-enriched air, the amount of oxygen used being substantially the theoretical requirement for the reaction  $\text{CH}_4 + \frac{1}{2} \text{O}_2 = \text{CO} + 2 \text{H}_2$ . Actually the reactions occurring in the burning zone are considerably more complex; some  $\text{CH}_4$  is burnt completely to  $\text{CO}$  and  $\text{H}_2\text{O}$  while some remains unchanged. Mainly as a result of the above side reactions, the temperature of the gases in the burning zone is raised to at least  $1200^\circ\text{C}$ . The products from this stage thus have sufficient sensible heat for the next step of the process, which consists of the conversion of residual methane by the methane-steam reaction and the attainment of the water gas equilibrium. These secondary reactions are brought about by passing the reactant gases through a bed of nickel-on-magnesite catalyst. The final product leaves this catalyst bed at  $800-900^\circ\text{C}$  and is interchanged with the incoming hydrocarbon gas.

With a 50% efficiency of heat exchange and when using pure methane and 98% oxygen, the overall result of this process, both chemically and thermally, is the same as would be obtained if only the following three reactions were involved:-

- (1) 98% of the methane feed reacting according to the equation  
$$\text{CH}_4 + \frac{1}{2} \text{O}_2 = \text{CO} + 2 \text{H}_2$$
  
Heat of reaction at  $650^\circ\text{C} = +269 \text{ WE/M}^3 \text{ of CH}_4$
- (2) 2% of methane feed reacting according to the reaction  
$$\text{CH}_4 + \text{H}_2\text{O} = \text{CO} + 3 \text{H}_2$$
  
Heat of reaction at  $650^\circ\text{C} = -2689 \text{ WE/M}^3 \text{ of CH}_4$
- (3) The reaction  $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$  proceeding to equilibrium at  $850^\circ\text{C}$ .

The composition of the final gas is  $\text{CO}_2$  7%,  $\text{CO}$  23.8%,  $\text{H}_2$  69% and  $\text{CH}_4$  .2%. The consumptions per  $\text{M}^3$  of  $\text{CH}_4$  fed are oxygen .487  $\text{M}^3$ , steam .107 kg., cooling water at  $15^\circ\text{C}$ . 9.6 kg. The above figures are taken from the preliminary design data for a plant to be erected at Heydebreck which are given in more detail in Appendix B(2).

FIGURE V.  
KW PLANT MIXING ZONE.



The process requires a hydrocarbon feed which is very low in sulphur. It was stated that the presence of 15 mg of sulphur/M<sup>3</sup> of methane feed necessitates an increase in reaction temperature of about 200°C. 7.

It is unnecessary to use pure hydrocarbons as feed. Coke oven gas or purge gas from methanol synthesis is also suitable. It is also possible to work with oxygen-enriched air instead of pure oxygen when ammonia synthesis gas is the required product. No satisfactory flowsheet figures are available, however, on these applications. It would appear from the data for pure methane given above that, unless much improved heat exchange efficiency is obtained, considerably more oxygen than corresponds to reaction (1) above would be required. It is hoped that further information will be forthcoming either from a closer examination of documents or from further contacts with the I.G. staff.

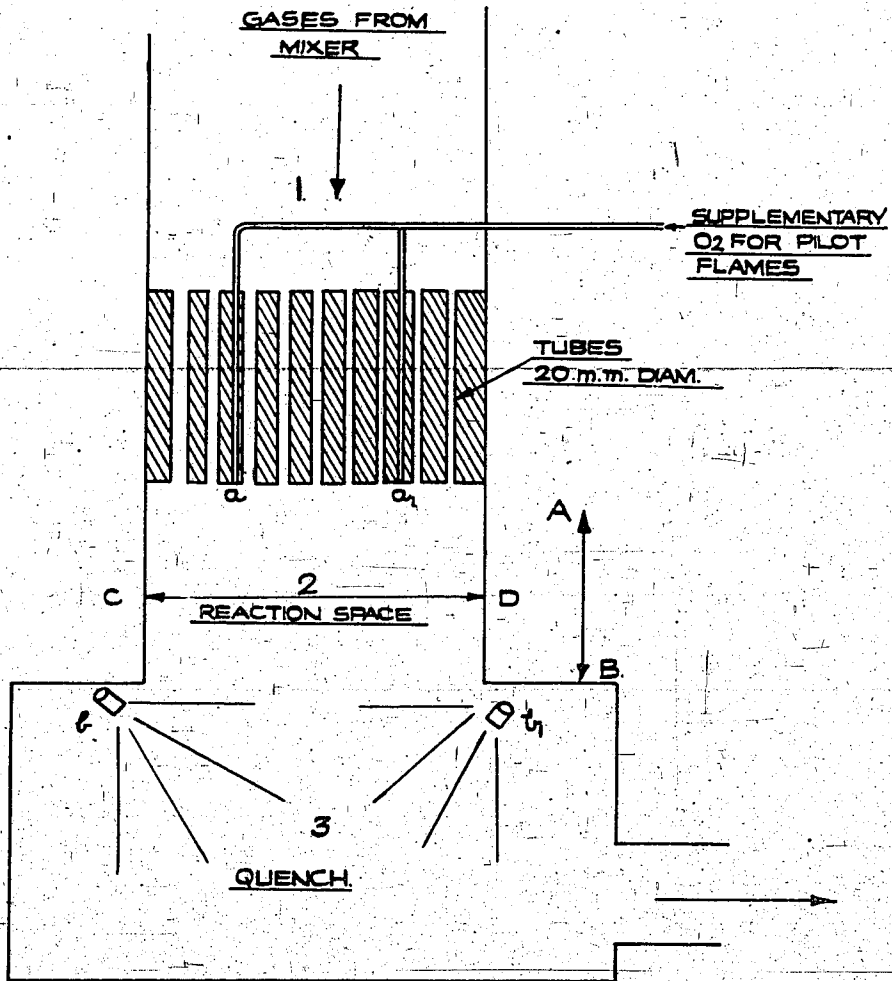
It is interesting to note that the methane-oxygen process has been adopted at Heydebreck, Waldenburg, Auschwitz and Linz in preference to the methane-steam process, and when rather fuller data are available, it will be of considerable interest to compare these two methods. Using pure methane, the methane-oxygen process gives little more than 75% of the yield of synthesis gas which can be obtained by the methane-steam method and requires substantial quantities of oxygen. On the other hand, no external fuel gas is required and the use of a tube reactor is avoided. The methane-oxygen process also has the advantage that it produces directly a high CO content gas suitable for synthesis of methanol, higher alcohol or Fischer Tropsch product.

#### (ii) Plant Operation and Details of Equipment

The following description relates to a plant treating 6-7,000 M<sup>3</sup>/hr of coke oven gas. A line diagram of the process is shown in Fig. IV.

Coke oven gas is introduced by means of a low pressure blower. It first enters the tubes of a tube and shell heat exchanger which, in the case of the Oppau plant, has 688 tubes, the upper portions of which are made of special heat-resisting alloy to contend with temperatures of the order of 800°C. The exchanger shell is fitted with baffles (9) in order to improve heat transfer. Further details of the Oppau and Heydebreck heat exchangers are given in Appendix B(1). Part of the preheated gas is recycled and the incoming steam (roughly 1 mole of steam/mole hydrocarbon in reactant gas) is injected into this recycle system. The object is to avoid condensation of water which would occur if the steam were injected into the cold gas. The preheated gas and steam mixture, at a temperature of about 850°C, is next mixed with the oxygen or oxygen-enriched air in a mixer of the type shown in Fig.V. This is situated at the top of the main reaction vessel. Efficient mixing of the reactants is essential for satisfactory reaction and is achieved by introducing the preheated hydrocarbon at a pressure of .25 - .30 ats tangentially to the stream of oxygen which enters through

**FIGURE VI.**  
**K.W. PLANT - ACETYLENE BURNER (SCHEMATIC)**



REACTION SPACE, CROSS SECTION CD IS 2 x HEIGHT AB, TO PREVENT  
CARBON DEPOSIT. α & α₁ ARE O₂ LEADS TO MAINTAIN  
A CONSTANT FLAME TO START REACTION.  
r & s, WATER JETS TO QUENCH REACTION.  
IF AB IS LONGER CARBON BLACK IS FORMED AND  
C<sub>2</sub>H<sub>2</sub> 7-8% IF OVERCOME WITH HIGHER THROUGHPUT  
THE FLAME BECOMES UNSTEADY  
OUTLETS FROM 1 TO 2 NOT OVER 20 m.m.

8.  
a vertical central tube at a pressure of .5 - .6 ats. It is claimed that mixing is complete within a length of mixing tube 1.5 times its diameter.

The mixed gases have a composition within the explosive limits and must be protected from back fire from the combustion zone. They are therefore separated from this zone by a bank of 20 mm. tubes in which the gas velocity is greater than the critical extinction velocity of the reaction, see Fig.VI.

In order to obtain uniform and complete reaction the burner chamber which comprises the upper portion of the main reaction vessel has to be free of dead spaces where eddies can build up, and must be of such a size that the gas velocity is less than the flame extinction velocity. Pilot flames must also be provided at the entrance to the combustion chamber. These pilot flames are maintained by introducing pure oxygen through small jets uniformly placed at the exit of the flame trap tube bank. This arrangement is shown in Fig. VI. The burner section of the reactor, which is 11½ ft. external diameter, is lined with 15" of refractory material in order to withstand the temperature of 1200-1500°C which is reached in this stage.

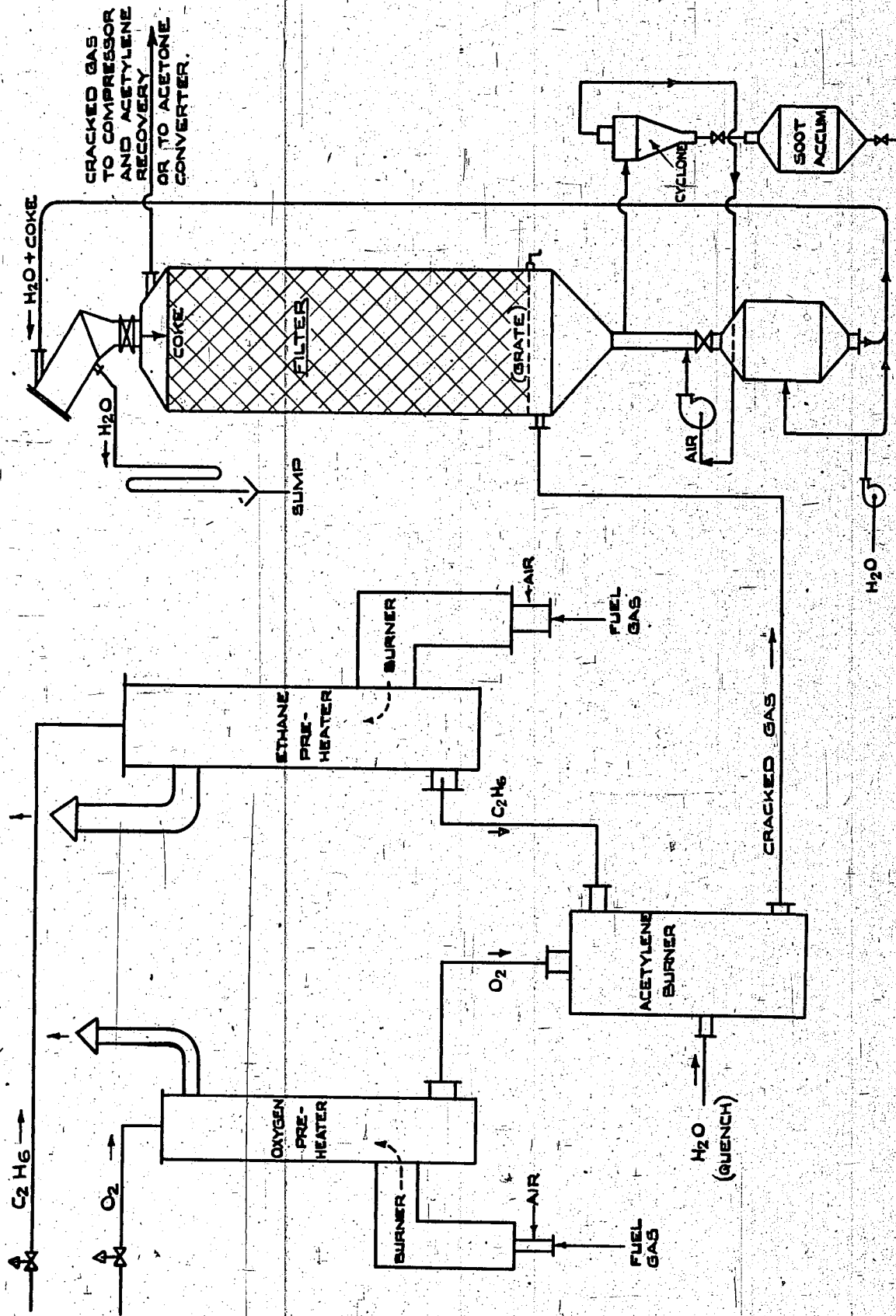
The products of the combustion zone pass downwards through a catalyst bed approximately 6 ft. deep and 9 ft. in diameter. Loss of nickel as nickel carbonyl is replaced by introducing a solution of nickel nitrate into the combustion zone. The overall height of the complete reaction vessel is about 40 ft.

The gas leaves the catalyst bed at 800-900°C and the greater part passes to the shell of the heat exchanger. Exit gas from the exchanger at a temperature of 350°C. is cooled in spray coolers. Facilities are provided for passing a part of the exit gas from the reactor direct to the coolers as a means of control on the preheat of the hydrocarbon feed. Further control is provided by recycling, if necessary, a small quantity of cooled and clean synthesis gas to the interchanger.

Gas from the cooler finally passes through filter beds of ¼" coke for removal of soot and tarry residues. These filters are cylindrical shells about 20 ft. high and 12 ft. diameter with conical ends. The bed of coke is supported on a movable grate situated just above the bottom cone. The grate is manipulated to permit a slow discharge of coke. Discharged coke falls through a column of water maintained in the bottom cone and this washes off the deposited soot. The clean coke is returned to the top of the filter by means of a water lift, the water is removed by a screen and the coke admitted intermittently to the filter through a slide valve. The rate of coke recycle corresponds to a coke travel through the filter of about 3"/minute.

FIGURE VII

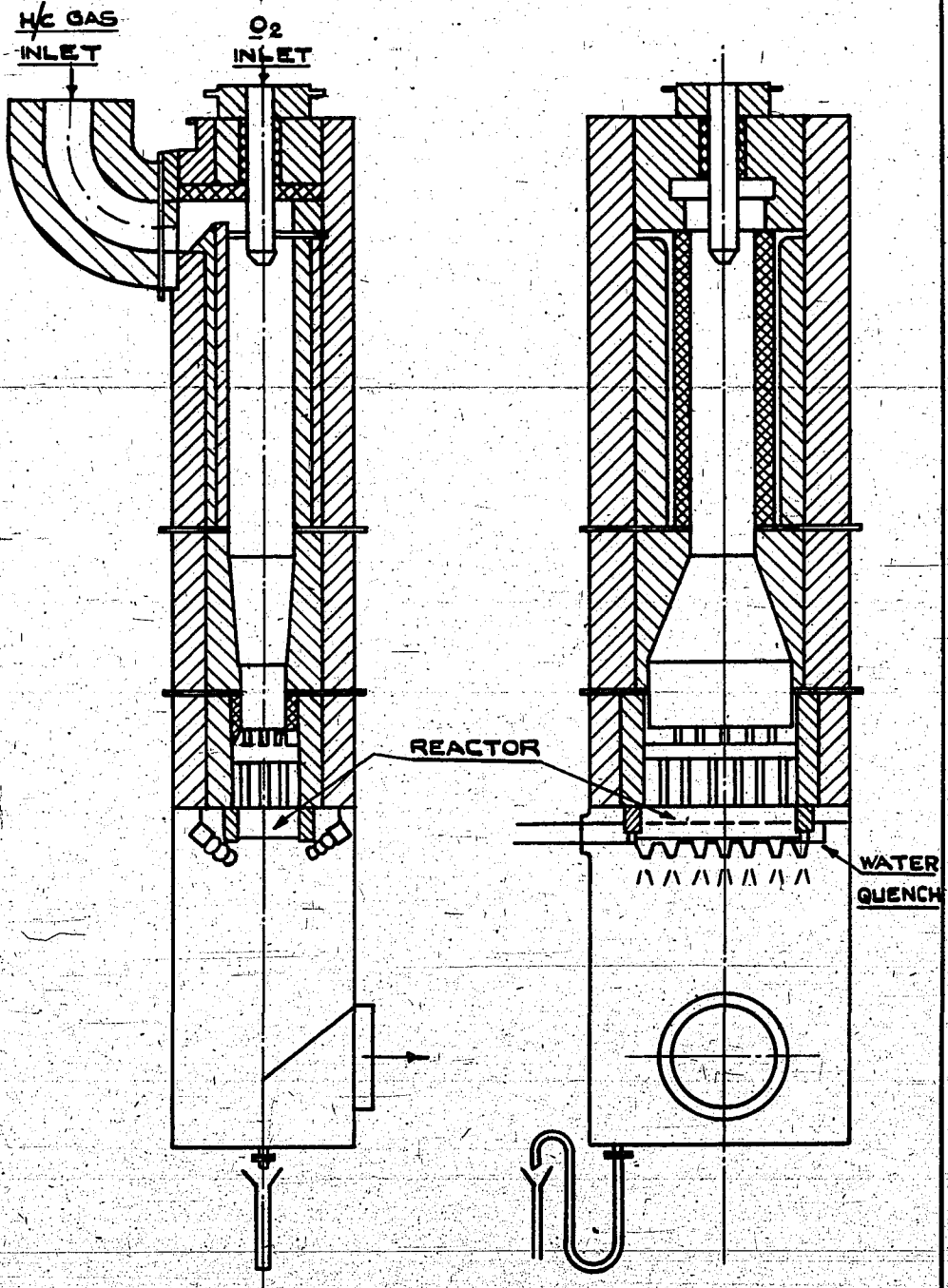
KW. PLANT FOR PRODUCTION OF ACETYLENE FROM ETHANE AND OXYGEN



REF. SCHEMA B1-1

**FIGURE VIII**

**KW PLANT - ACETYLENE BURNER (DETAIL)**





No German cost data were obtained. In view of the interest in comparing this process with the methane-steam method, a special effort should be made to acquire fuller details of utilities consumption and labour requirements as well as more complete general technical information on the application of the process to a feed such as coke oven gas.

(D) Methane-Oxygen Process for Production of Acetylene and Synthesis Gas

(i) Process Details

Substantially 100% hydrocarbon gas and pure oxygen are necessary for this process. It consists essentially of the burning stage of the normal synthesis gas process with the addition that the products of combustion are cooled very rapidly by water quenching. The reaction chamber has to be small enough and the mixing of the reactants sufficiently efficient to ensure that the duration of the burning reaction does not exceed one-hundredth of a second.

A line diagram of the process is shown in Fig. VII. Both the hydrocarbon gas and the oxygen have to be preheated to 400°C in gas-fired heaters. When using methane as the feed, the ratio of hydrocarbon to oxygen is 2:1. No steam is introduced with the reactant gases.

The reaction vessel consists of a mixer, a combustion section and a water quenching arrangement. The very efficient mixing which is necessary is obtained by adding a second bank of flame trap tubes. The two tube banks are separated by a very small space and are arranged so that the orifices are staggered, see Fig. VIII. The burning zone has generally a diameter of 700 mm. and a length of 350 mm. and the gas velocity through this zone is 8.5 M/second. A temperature of around 1500° is reached.

The water sprays cool the reacted gases to 80-90°C, after which they are passed to a coke filter for removal of soot and tarry matter. This part of the apparatus is identical to that used for synthesis gas production except that soot is removed from the spent coke by air blowing instead of by water treatment. Soot is recovered from the circulating air by means of a cyclone.

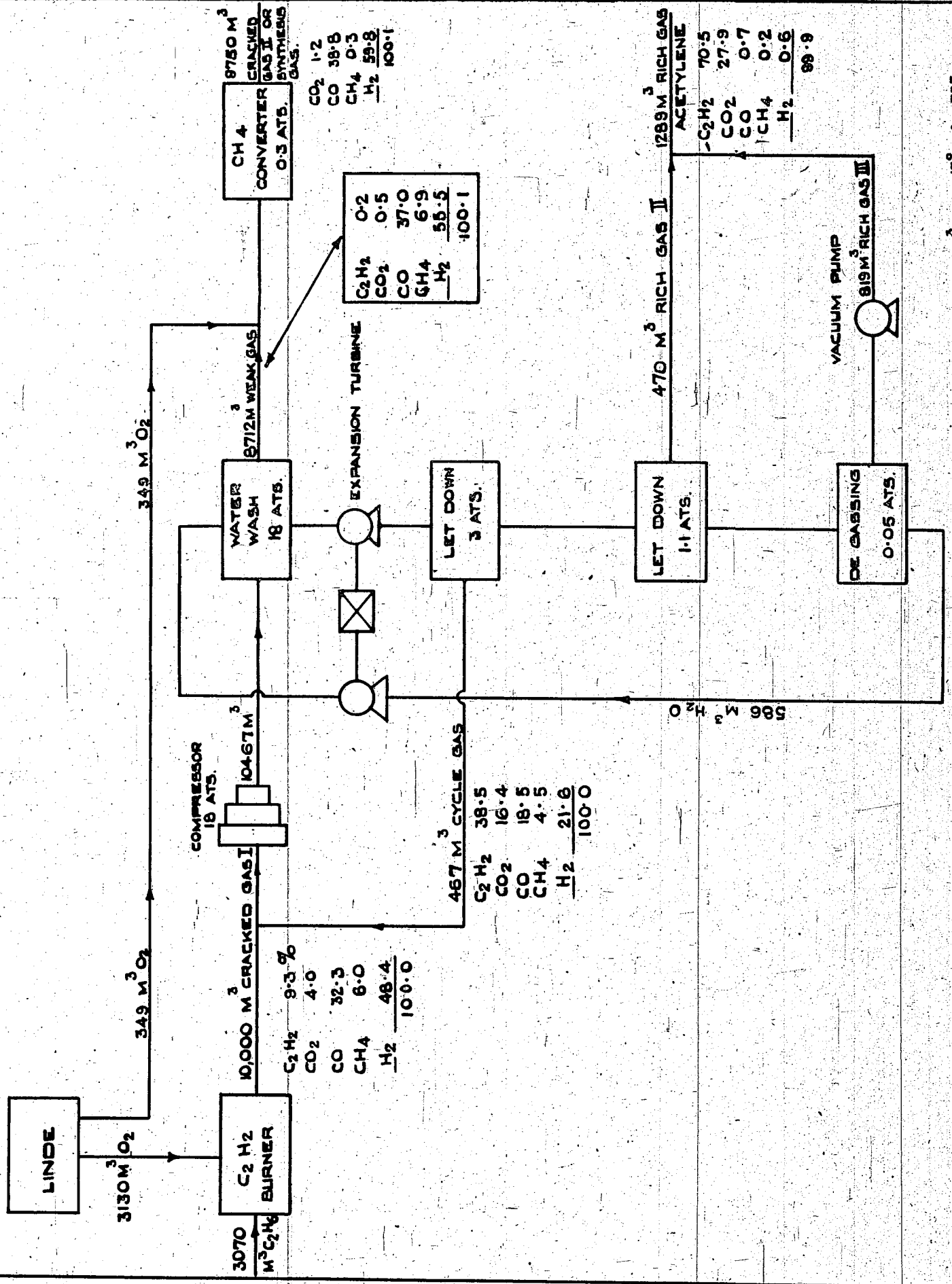
When using methane as a raw material, the gas leaving the scrubber contains 8-9% acetylene, 3-4% CO<sub>2</sub>, 6-7% methane, 24-26% CO and 56% H<sub>2</sub>.

(ii) Acetylene Concentration

When concentrated acetylene is required, this exit gas is compressed to 18 ats. and washed with water. The solution of gases in water is let down in two stages - (a) to 3 ats., the gas evolved being recycled to the compressor, and (b) to 1.1 ats. Before recycle the wash water is degassed under a vacuum of .05 ats. Gas

FIGURE IX

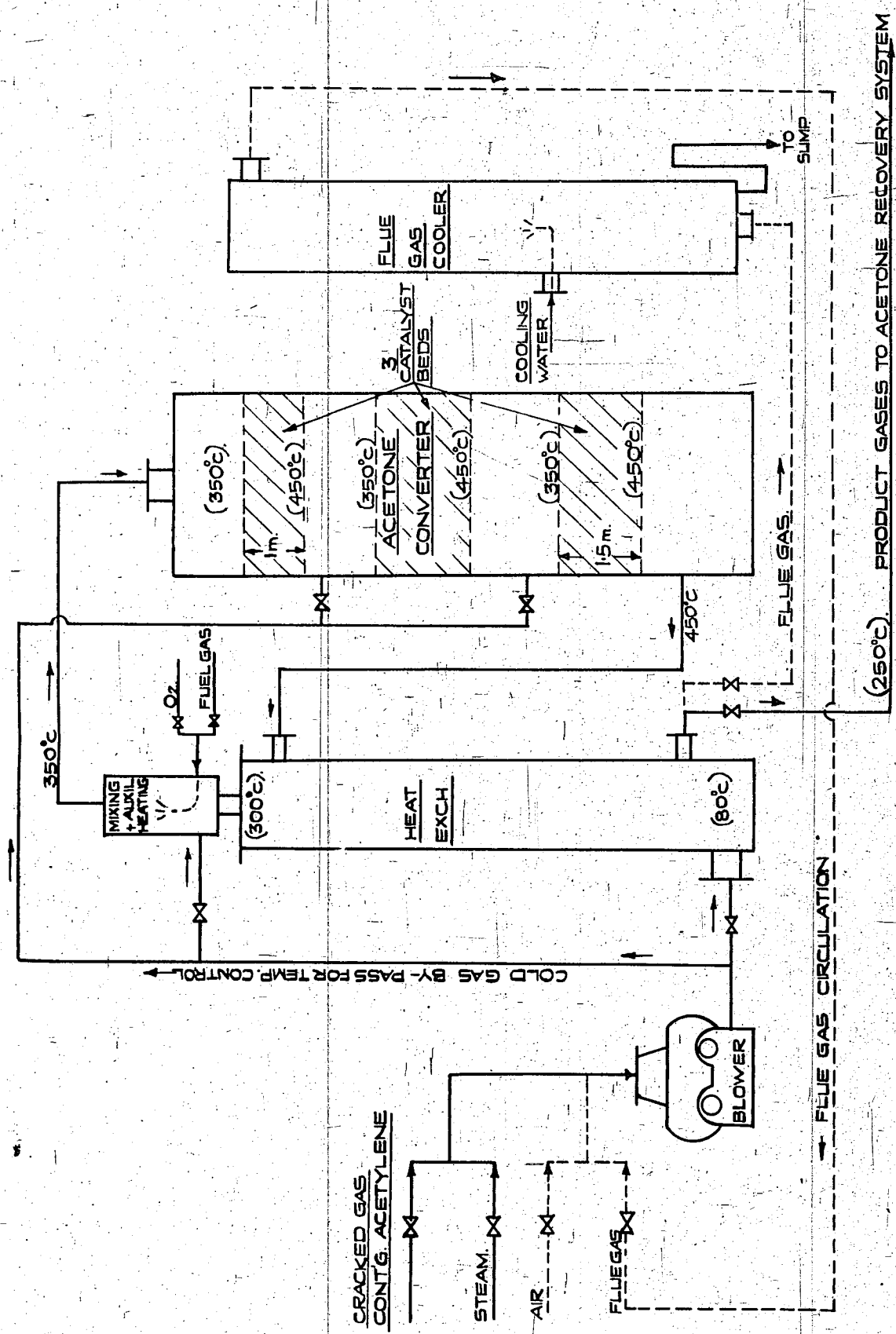
PROPOSED FLOW PLAN OF HEYDEBRECK ACETYLENE OPERATION



M<sup>3</sup> IS AT 15°C & 735 MIN.

FIGURE X

KW PLANT - CONVERSION OF ACETYLENE TO ACETONE



obtained in the second let down and in the degassing operation 10.  
are mixed and this final product contains roughly 70% acetylene and  
28%  $\text{CO}_2$ .

Gas leaving the water washer at 18 ats. contains  
50-60%  $\text{H}_2$ , 35-40%  $\text{CO}$  and 6-8%  $\text{CH}_4$ . If this gas has too great a  
methane content for synthesis purposes, it is given a second oxygen  
burning treatment. This is apparently carried out without steam  
and in a unit containing no catalyst bed. There are also indications  
that this second stage burning may be carried out under pressure of  
18-30 ats. More detailed information is desirable.

A flow diagram for the acetylene concentration method is  
shown in Fig. IX. This is a summary flowsheet of the proposed  
Heydebreck operation using ethane as raw material, and in addition  
to the acetylene concentration steps it provides data on the ethane  
burning and on the secondary combustion of the synthesis gas.

#### (iii) Use of Dilute Acetylene for Acetone Synthesis

Another way of dealing with the dilute acetylene adopted  
by the I.G. is its use for acetone synthesis. Fig X gives a line  
diagram of this process.

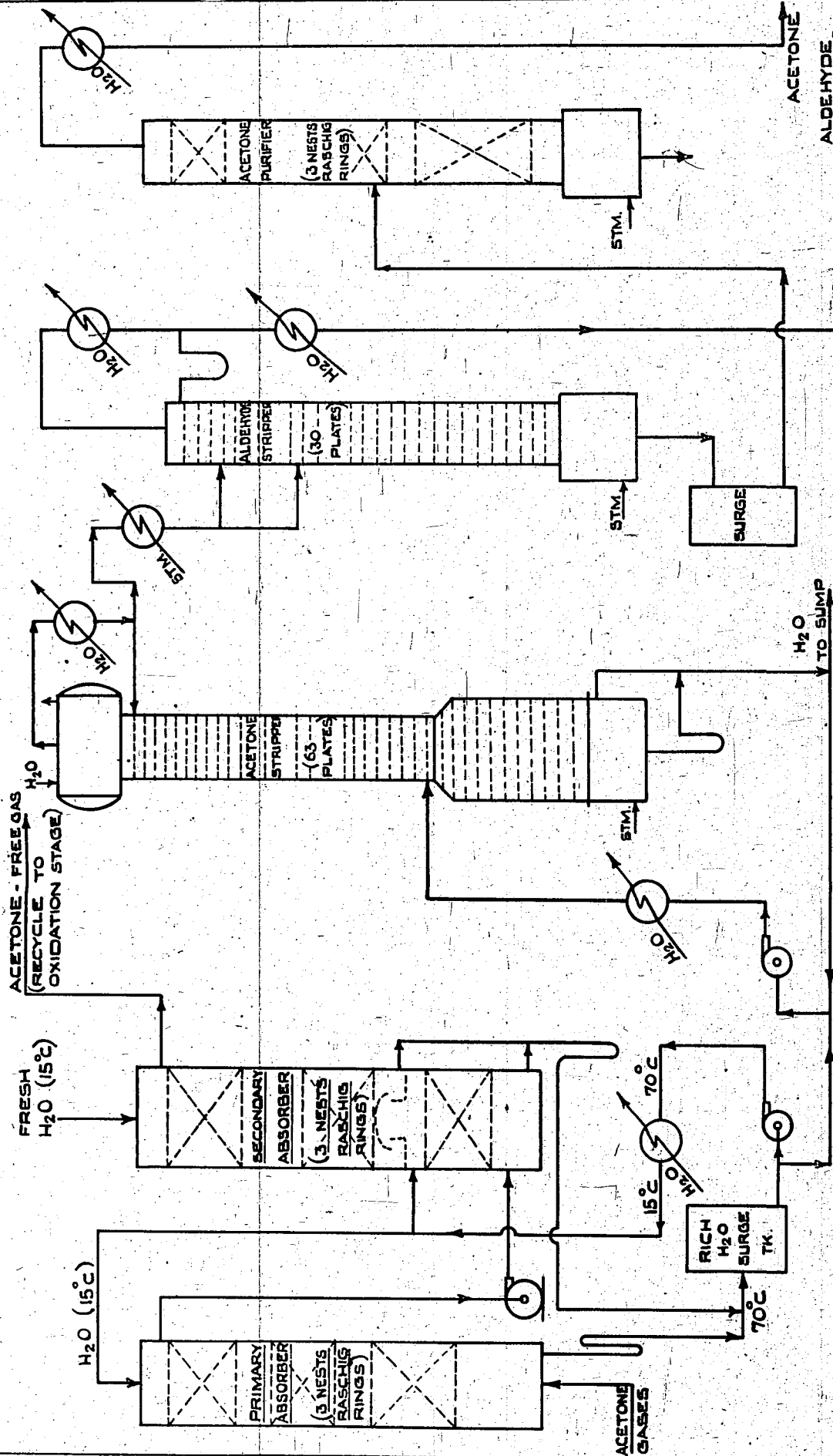
The acetylene-containing gas is mixed with the  
required amount of water (steam) and passes through a blower  
operating at a discharge pressure of 0.2-0.4 ats. The gas mixture  
is split into three main streams, which are introduced at separate  
points in the reactor system in order to provide the proper temperature  
control for the exothermic reaction. The stream charged to the top  
of the reactor first passes through a heat exchanger and an auxiliary  
heater where, by means of a fuel/oxygen mixture, the final temperature  
of this stream is adjusted to  $350^\circ\text{C}$ .

This stream then passes through a top bed of catalyst,  
emerging at  $450^\circ\text{C}$ , and is mixed with the second stream (cold gas)  
with a resulting drop in gas temperature to  $350^\circ\text{C}$ . The latter  
mixture passes through the second catalyst bed, blends with the  
third stream (cold gas) and flows through the final bed, emerging  
at  $450^\circ\text{C}$ . The hot effluent gas ( $\text{C}_2\text{H}_2$  content less than 0.2%), after  
passing through the heat exchanger, proceeds to the acetone scrubbing  
system, described below.

The catalyst used in this synthesis is zinc oxide in  
cylindrical pellets 15 mm long x 8 mm diameter. Temperature control  
is extremely important in preserving the activity of this catalyst,  
and is complicated by the fact that the reaction rate is also highly  
sensitive to temperature, e.g. a  $2^\circ\text{C}$  rise in inlet gas temperature is  
claimed to cause a ten-fold, or  $20^\circ\text{C}$  rise in catalyst bed temperature.  
The safe maximum catalyst temperature is about  $350^\circ\text{C}$  and the optimum  
depth of the various catalyst beds is 1 meter in top and middle beds,  
and 1.5 meters in bottom bed.

FIGURE VI

KW PLANT ACETONE RECOVERY SYSTEM



NOTE: - ENTIRE SYSTEM OPERATES AT ATMOSPHERIC PRESSURE

Due to formation of some free carbon, etc. in the synthesis, the catalyst bed gradually becomes fouled, with consequent increase in pressure drop, and requires cleaning every 8-10 days. This is effected by recirculating a mixture of flue gas and air through the converter, maintaining catalyst temperature at 300°C. The flue gas is circulated through a spray cooler. Despite the careful temperature control exercised in this process, however, the catalyst does gradually lose activity, as evidenced by decrease in acetone yield, and requires ultimate replacement about every three months.

The portion of this system dealing with the recovery of the acetone from the product gases is illustrated in Fig. XI. It comprises two pairs of Raschig ring columns in which water is used as the scrubbing agent, a 63-plate stripper column for concentrating acetone, a 30-plate stripper column for fractionating out aldehyde, and a Raschig ring column for redistilling the acetone to final purity. The entire system operates at atmospheric pressure and is of conventional design. The only innovation found in this part of the plant is a new type of absorber recently being tested as a possible improvement over the original Raschig ring column. The experimental tower contains a number of trough-like trays which are mounted on a central rotating shaft, extending the full height of the column. The rotating trays have serrated edges which disperse the falling liquid and provide intimate vapour-liquid contact. Details of this equipment were not obtained.

#### (iv) Costs

An estimate of the costs of acetylene production from ethane was made by the I.G. in connection with the proposed Heydebreck plant.

The capital cost for a plant to produce 1 ton/hour of acetylene, together with 10,000 M<sup>3</sup>/hour of synthesis gas was calculated to be 2 million RM, made up as follows :-

Acetylene Generators (5 units)	700,000 RM
Compressors for acetylene concentration	600,000 RM
Acetylene scrubbing plant	400,000 RM
Secondary treatment of synthesis gas with oxygen	300,000 RM

The estimated operating costs are shown below:-

Ethane 3070 M<sup>3</sup>/hr. @ 0.71 pfz/1000 WE 307.00 RM/hr.

#### Acetylene Synthesis costs

Oxygen 3130 M <sup>3</sup> /hr. @ 2.2 Pfz/M <sup>3</sup>	68.20 RM/hr.
Fuel Gas 1.67 x 10 <sup>6</sup> WE @ 0.45 Pfz/1000 WE	7.55
Electric Power 120 KWH @ 0.014 RM	1.68
Cooling Water 160 M <sup>3</sup> @ 0.02 RM/M <sup>3</sup>	3.20
Wages 5 Man hours @ 2.40 RM	12.00
<u>including 50% oncost.</u>	

Repairs )		
Amortisation )	18% on capital value	14.50 RM/hr.
Taxes etc. )		

TOTAL

414.13

Acetylene Concentration

Electric Power 1900 KWH @ 1.4 PfG/KWH	26.60
Cooling & Wash Water 300 M <sup>3</sup> /hr. @ 2.0 PfG/M <sup>3</sup>	6.00
Lube Oil 1 kg/hour @ 50 PfG/kg.	0.50
Wages etc. 3 Man/hours @ 2.40 RM including 50% oncost.	7.20

Repairs )		
Amortisation )	18% on capital value	20.70
Taxes etc. )		

TOTAL

61.00

Secondary Treatment of Synthesis Gas.

Oxygen 349 M <sup>3</sup> /hr. @ 2.2 PfG/M <sup>3</sup>	7.70
Cooling Water 30 M <sup>3</sup> /hr. @ 0.02 RM/M <sup>3</sup>	0.60
Wages 2 Man/hours @ 2.40 RM including 50% oncost.	4.80

Repairs )		
Amortisation )	18% on capital value	6.20
Taxes etc. )		

TOTAL

19.30

Grand Total

494.43

Credits 9750 M<sup>3</sup>/hr. Synthesis gas at 2.7 PfG/M<sup>3</sup> 264.00

Cost of 0.975 Tonnes Acetylene. 230.43

Cost RM/Tonne Acetylene 236.00

\* Oppau cost at end of 1939.

The above data should be sufficient for the process to be costed under British or American conditions.

(v) Fundamental Data for Design of Burner.

The I.G. have clearly carried out a great deal of fundamental research on flame speeds, flame extinction velocities etc. for various gas mixtures. Some of this work is covered by the documents brought back from Germany but a much closer study of these papers, and possibly further contact with the authors, is necessary in order to prepare an intelligible summary of this research.

III.  
AMMONIA SYNTHESIS

A very casual inspection of the plant and interrogation of Dr. Gogel (head of the Oppau high pressure department) revealed no major developments in this field. The maximum capacity of the Oppau plant was 800 T/day nitrogen as ammonia and a considerable part of this was exported as liquid ammonia to Höchst, Wolfen and Mittelfeld.

There is a plant at Oppau for the synthesis of 60 T/day of Urea. It operates at a pressure of 150 atmospheres without a catalyst. Formerly, the plant was lined with Monel metal but, during the war, lead linings have had to be used. The compressor units attached to this plant have been badly damaged by air attack.

A note prepared by Dr. Wurster (Managing director of Oppau and Ludwigshafen) for the Ludwigshafen Military Government, giving the latest estimates of the potential production capacity of the Oppau plant for ammonia and fertilisers, is reproduced in Appendix.C.



Two methanol units were normally on line at Oppau. Each had a single 800 mm x 12 M converter with a capacity of 70 T/day of methanol. Reaction pressure was 230 atmospheres, reaction temperature 360°C and the catalyst a mixture of zinc and chromium oxides.

Eight similar units were normally in operation for synthesis of higher alcohols. Pressure and reaction temperature is the same as for methanol but the throughput is lower and the catalyst is alkalisied. The average catalyst life is three months. Each unit produced 40-50 T/day crude product of the following average weight composition:-

Methanol	55%
Dimethyl Ether	1.5-- 2.0%
Olefins (C <sub>2</sub> -C <sub>7</sub> )	0.7%
n-Propyl Alcohol	1-1.3%
Iso Butyl Alcohol	11-13%
Higher Alcohols	6-7%
Ketones	0.6-0.7%
Water	20.3-24.2%

The crude product is separated into two layers, the upper layer going to a stabilizer operating at 3 atms. pressure. In this stabilizer the overhead material consists of dimethylether and a part of the olefins. The bottoms pass to column II, operating at atmospheric pressure, where methanol is taken overhead. The bottoms from this column are blended with benzene in the ratio of 2 to 1 and pass to column III where water, benzene and normal propyl alcohol are taken overhead; isobutyl, some n-propyl alcohol and some of the higher alcohols are taken off as a side stream, while the remainder of the higher alcohols and ketones is removed as bottoms. The sidestream from column III is fed to column IV where normal propyl alcohol is removed overhead, and the bottoms are fed to column V which separates isobutyl alcohol from higher alcohols. The isobutyl alcohol coming overhead in column V has a purity of 97-98%.

The overhead from the azeotropic distillation carried out in column III, using benzene, is separated into two layers, and the upper layer, consisting of benzene and normal propyl alcohol, is redistilled in column VI to give benzene (for recycle) as the overhead fraction, and normal propyl alcohol which is sent to storage. Another auxiliary column separates higher ketones which are removed as a sidestream in column II.

An interesting point in the isobutanol synthesis is the fact that all the methanol produced in the process is returned as recycle to the reaction system. The main reason given for this is that the methanol from this process is difficult to refine up to market specifications.

The higher alcohols produced in the isobutanol synthesis have been hydrogenated to the corresponding hydrocarbons which are used as aviation fuel components. The higher ketones, consisting primarily of di-isopropylketone, have been used as solvents and have also been hydrogenated to hydrocarbons.

(A) Production of Synthetic Fuels at Ludwigshafen/Oppau.

Production of synthetic fuels at Ludwigshafen/Oppau has been limited to the emergency use of the high pressure Research Department pilot plants consisting of 6 - 500 mm. diam. and 4 - 800 mm. dia. hydrogenation converters. The chief production use to which this equipment was put was the improvement of gasoline quality by dehydrogenation (See D.H.D. process).

The feed material was partly imported from Wesseling and partly derived from Bruxhal crude petroleum during the course of its refining to give lubricating oil at Oppau. The maximum output of "D.H.D. gasoline" was at the rate of 25,000 tons/year. It was planned to extend D.H.D. activities and a plant on the Oppau site for production of roughly 100,000 tons/year had been practically completed. At the time of the Allied occupation this plant was being dismantled and removed for re-erection, probably at Bitterfeld.

Distillation connected with the emergency production of D.H.D. gasoline in the research equipment was carried out in new stills built on the Oppau site adjacent to the new D.H.D. plant.

There was also a small production of finished liquid fuel products from the operation of the pilot plant converters principally on tar and petroleum oil residues. This was probably incidental to research work on these raw materials. The total hydrogen delivered to the hydrogenation Research Department was not more than 1,500 - 2,000 M<sup>3</sup> per hour and it is therefore unlikely that the production of finished products could have exceeded 5,000 tons per year.

(B) General Review of German War-Time Operations and Developments.

Although there was no large-scale hydrogenation at Ludwigshafen/Oppau, the Research and Technical Department directed by Dr. Pier was known to have played a great part in the planning of the new hydrogenation projects in Germany. All the more important members of the staff of this Department, including Dr. Pier himself, were located in Heidelberg on 1.4.45 and interrogation revealed the following general picture of German war-time hydrogenation development :

a) Bituminous Coal Hydrogenation

The plant at Scholven, put into operation in 1936, employs a pressure of 300 ats. for the coal liquefaction stage. Acid catalyst conditions are employed, i.e. tin oxalate catalyst (.06% on coal) is added to the feed paste and ammonium chloride (.7-1% on the coal) is injected to the first converter. Corrosion is avoided by the injection of sodium carbonate at the end of the last converter.

The number of coal stalls at Scholven has been increased to 6 during the war and the capacity of the plant brought up to 200,000 tons/year of finished product, mainly aviation base gasoline.

Because of the difficulty in obtaining tin oxalate, other tin compounds, and occasionally lead salts, have been substituted. The latter were found to give higher yields of "unconverted" coal. Apart from minor changes of this type, there has been no modification of the process and no marked improvement in efficiency during the war. The yield of aviation gasoline obtained is just over 50% on the a.m.f. coal.

The new bituminous coal hydrogenation plants, namely, Gelsenberg, Stettin, and Blechhammer, employ a pressure of 700 ats. in the liquid phase stalls. Alkaline catalyst conditions are employed. 1.2 - 1.7% of iron sulphate (including water of crystallization) is added to the coal before drying. 1.5 - 2.5% of Bayermasse (an iron rich residue from aluminium manufacture) is then added and finally, at the pasting stage, .3% of sodium sulphide is introduced. The above quantities are % by weight on the dried coal treated. It should be noted that acid reaction conditions cannot be used at 700 ats. because the iron/HCl/H<sub>2</sub>S equilibrium is such that corrosion occurs in the converter and hot catchpot. At 300 ats, corrosion does not occur above about 350°C and addition of alkali before the products are cooled in the interchangers is sufficient to avoid corrosion trouble.

The use of the higher pressure permits the use of a higher average reaction temperature, 480°C as compared with about 460°C for the 300 ats process. As a result of the increased temperature and pressure, the throughput of coal for a given reaction volume is some 60% greater in these new plants than at Scholven. On the other hand, standard 700 ats converters have only 75% of the reaction volume of those operating at 300 ats so that the throughput of coal per converter is only some 20% higher at the higher pressure.

From the standpoint of yield, the main advantage of 700 ats operation is a reduction in the amount of "unconverted" coal residue. This is usually 3-4% on the ash and moisture-free coal at 700 ats compared with 7-8% for 300 ats operation. This has the secondary effect that, since less solid material has to be purged from the system, the loss of oil in the sludge recovery section is lower. Under 700 ats operating condition the asphalt destruction is also improved. This leads to much easier handling of the intermediate products and also to an improved efficiency of oil recovery in the carbonisation of the final sludge residue. 700 ats operation gives no reduction of hydrocarbon gas make in the coal liquefaction stage. This is presumably because the alkaline catalyst conditions are, other things being equal, less favourable from a standpoint of gas production than tin and chlorine.

MAKE UP GAS  
(96% H<sub>2</sub>)

RAW COAL (8% WATER)

ALL QUANTITIES IN TONNES/HOUR

72900 M<sup>3</sup>/HR.  
(15° 735 MM. HG.)

COAL DRYING

DRY COAL AND CATALYST  
44.6 T<sub>2</sub>

PASTE PREPARATION

COAL PASTE  
92.5 T<sub>2</sub>

COMPOSITION OF THE COAL PASTE

A.M.F. COAL	40.7	} 48.0 = 52%
ASH	1.7	
CATALYST	1.3	
RECYCLE SOLIDS	4.3	
WATER	0.9	
<b>COAL PASTE</b>	<b>92.5 T<sub>2</sub></b>	

OIL	43.6 T <sub>2</sub>
SOLIDS	4.3 T <sub>2</sub>
<b>TOTAL</b>	<b>47.9 T<sub>2</sub></b>

52300 M<sup>3</sup>/HR.  
(15° 735 MM. HG.)

COAL STALLS  
3 WITH TOTAL OF 105 M<sup>3</sup>  
REACTION VOLUME

WASH OIL 4.1 T<sub>2</sub>

50.4 T<sub>2</sub>

HEAVY OIL LET DOWN

OIL	26.7 T <sub>2</sub>
SOLIDS	8.9 T <sub>2</sub>
<b>TOTAL</b>	<b>35.6 T<sub>2</sub></b>

FUGAL DILUENT

20.2 T<sub>2</sub>

OIL	= 46.9 T <sub>2</sub>
SOLIDS	= 8.9 T <sub>2</sub>
<b>TOTAL</b>	<b>= 55.8 T<sub>2</sub></b>

LOSS  
0.3 T<sub>2</sub>

LIQUID PHASE  
STILL

27.2 T<sub>2</sub>  
MIDDLE OIL  
+ PETROL

LOSS  
0.3 T<sub>2</sub>

FUGALS

FILTRATE	
OIL	= 39.0 T <sub>2</sub>
SOLIDS	= 4.3 T <sub>2</sub>
<b>TOTAL</b>	<b>= 43.3 T<sub>2</sub></b>

14,800  
M<sup>3</sup>/HR.

SATURATION STALL  
WITH  
34 M<sup>3</sup> REACTION VOL

SATURATED  
PRODUCT STILL

16.1 T<sub>2</sub>

24.2 T<sub>2</sub>

5800 M<sup>3</sup>/HR.  
10.0 T<sub>2</sub>

6434 STALL  
25 M<sup>3</sup> REACTION  
VOLUME.

22.0 T<sub>2</sub>

6434  
VAPOUR PHASE  
STILL

15.0 T<sub>2</sub>

25.0 T<sub>2</sub>

WASHING AND  
STABILISATION

25 T<sub>2</sub> MOTOR GASOLINE

8.1 T<sub>2</sub>

23.5 T<sub>2</sub>

51.0 T<sub>2</sub>

LOSS  
0.3 T<sub>2</sub>

CONCENTRATE

OIL	= 7.6 T <sub>2</sub>
SOLIDS	= 4.6 T <sub>2</sub>
<b>TOTAL</b>	<b>= 12.2 T<sub>2</sub></b>

KILNS

LOSS  
0.3

COKE  
5.8 T<sub>2</sub>

RECOVERED HEAVY OIL  
5.4 T<sub>2</sub>

RECOVERED LIGHT OIL  
0.6 T<sub>2</sub>

14.7 T<sub>2</sub>

4.7 T<sub>2</sub>

4.1 T<sub>2</sub>

FLWSHEET FOR BITUMINOUS COAL HYDROGENATION (RUHR COAL) TO 200,000 T<sub>2</sub>/YR MOTOR GASOLINE

FIGURE XII

TABLE IHydrocarbon Gas Production when making Motor  
Gasoline from Different Raw Materials

200,000 t/year = 25 t/hour Motor Spirit

<u>Raw Material</u>		<u>Bituminous Coal</u>	<u>Bituminous Coal High Temperature Tar</u>	<u>Natural Oil Residuum</u>
<u>Liquid Phase</u>				
Methane	t/hr	2.3	1.3	0.96
Ethane	"	2.0	1.2	0.63
Propane	"	2.6	1.5	1.16
n-Butane	"	1.3	0.76	0.95
i-Butane	"	<u>0.16</u>	<u>0.09</u>	<u>0.02</u>
<u>Total</u>	t/hr	8.36	4.85	3.72
<u>Saturation</u>				
Methane	t/hr	0.13	0.13	0.08
Ethane	"	0.10	0.10	0.06
Propane	"	0.27	0.27	0.17
n-Butane	"	0.16	0.16	0.10
i-Butane	"	<u>0.16</u>	<u>0.16</u>	<u>0.10</u>
<u>Total</u>	t/hr	0.82	0.82	0.51
<u>Splitting</u>				
Methane	t/hr	0.028	0.037	0.035
Ethane	"	0.014	0.018	0.016
Propane	"	0.28	0.37	0.35
n-Butane	"	0.24	0.32	0.30
i-Butane	"	<u>0.71</u>	<u>0.94</u>	<u>0.90</u>
<u>Total</u>	t/hr	1.272	1.685	1.601
<u>Overall</u>				
Methane	t/hr	2.46	1.47	1.08
Ethane	"	2.11	1.32	0.71
Propane	"	3.15	2.14	1.68
n-Butane	"	1.70	1.24	1.35
i-Butane	"	<u>1.03</u>	<u>1.19</u>	<u>1.02</u>
<u>Total</u>	t/hr	10.45	7.36	5.84

improvement in gasoline + middle oil  
 coal when using 700 ats is roughly  
 equivalent to 7-8% improvement on the

Table I summarise the results which Dr. Pier  
 could be achieved under steady operating  
 using a Ruhr coal of 83% carbon content (ash -  
 motor gasoline (max. FHP 200°C, minimum  
 100 ats alkaline catalyst process is assumed  
 stage, vapour phase treatment of the  
 carried out at 300 ats. This flowsheet  
 shows the achieved results at Gelsenberg and  
 obtained at Scholven for 300 ats acid

tion.

It was forced to turnover to brown coal tar  
 of air raid damage in 1944, but prior to this  
 this factory continued to be brown coal.  
 had been considerably increased to more than  
 brown coal per year. Beyermasse was used as  
 it suffered from the disadvantage that the  
 (ats). There have been no major modifications  
 made.

Coal is hydrogenated at Wesseling to give  
 finished product. This particular brown  
 middle German coals, and the coal liquefaction  
 plants.

Hydrogenation, L.T.H. and M.T.H. Processes.

Three bag plants, Bohlen, Magdeburg and Zeitz,  
 produce brown coal tar and one of the newer  
 plants, Factory at Brux, also operates on this  
 type of finished products from the three Brabag  
 plants of 250,000 tons a year each, while the  
 Zeitz plant of 400,000 tons/year. At Bohlen, Magdeburg  
 plants in all major respects identical to that operated  
 with the exception that iron on active coke had  
 been used as liquid phase catalyst. This was  
 due to the scarcity of molybdenum.

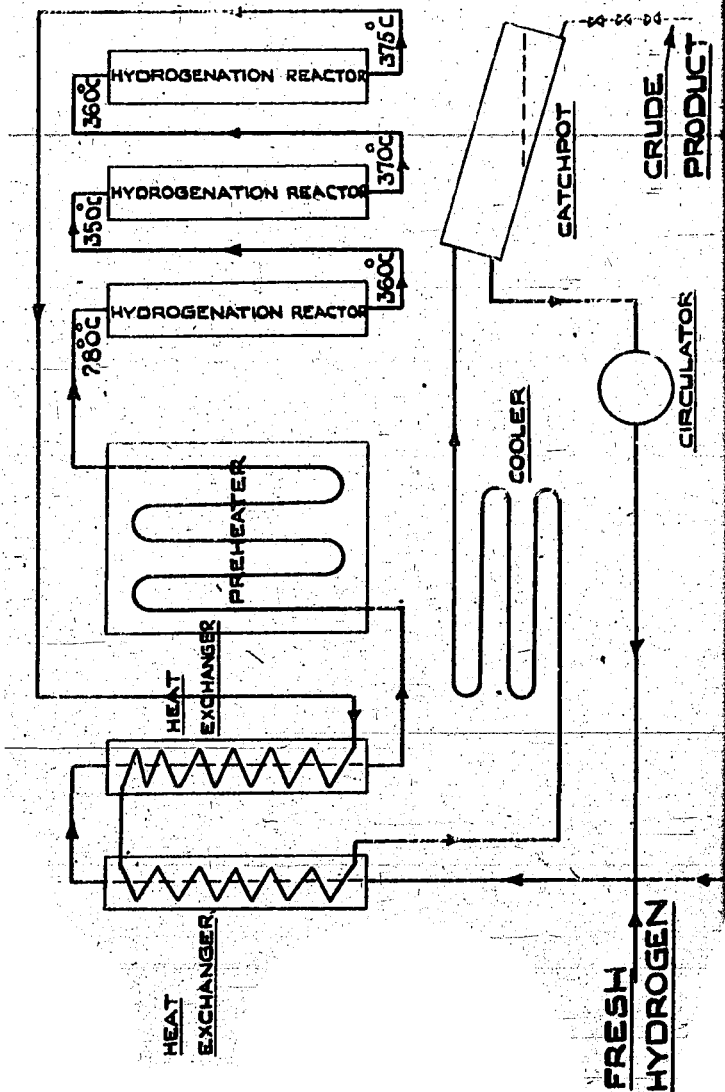
Zeitz brown coal tar plants produced motor and aviation  
 grade in amount of diesel oil. Latterly, they  
 produce quantities of jet fuel. (See Jet Fuel).

The plant at Zeitz operated under entirely different  
 conditions developed by the Ludwigshafen Research  
 Institute. The L.T.H. process, consists of single pass treatment  
 of coal tar over an active hydrogenation catalyst under

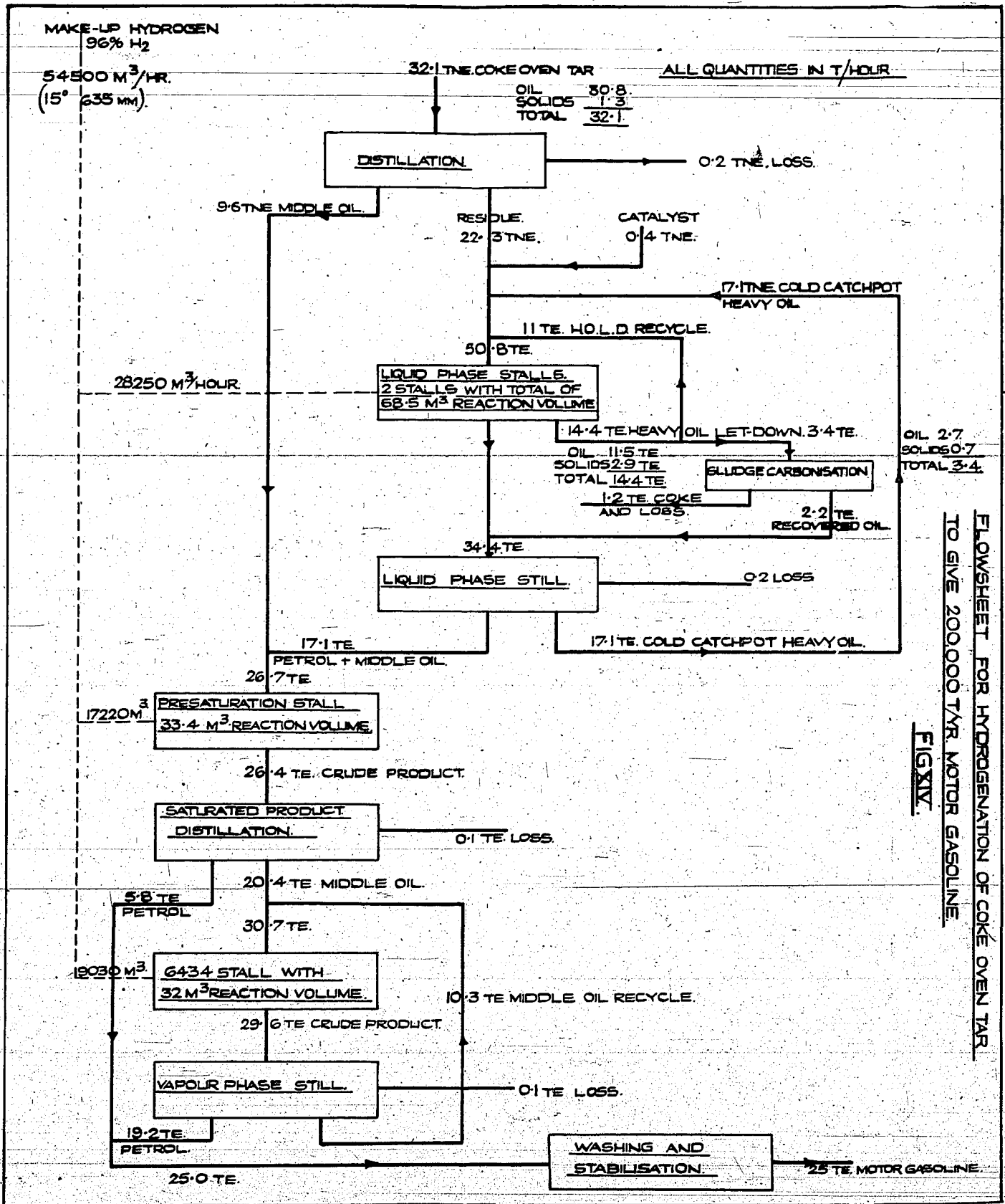
FIG. XIII

FLOW DIAGRAM

T. T. H. PROC







FLOWSHEET FOR HYDROGENATION OF COKE OVEN TAR  
 TO GIVE 200,000 TYR MOTOR GASOLINE  
 FIG. XIV.

low temperature conditions. The refined tar product, is fractionated to give low quality petrol, a moderately good diesel oil, a refined wax and lubricating oil. The main features of the process are shown in Fig. XIII. In order to reduce its solids to less than .1%, the tar is first fuggalled and filtered. The fuggalled tar is then preheated with hydrogen (2,300 m<sup>3</sup> hydrogen per ton of oil) and fed to reactors operating at 300 ats and an average temperature of 360°C. The catalyst employed is tungsten sulphide (5053) or a new saturation catalyst (8376) which will be described later under vapour phase hydrogenation. The throughput is 1 kilo per litre of catalyst per hour. Catalyst life is of the order of 6 months. The hydrocarbon gas make is 1-2% of the fresh feed and the hydrogen absorption 500-550 m<sup>3</sup> per ton of tar.

The crude product is worked up to give 25% by weight of gasoline with an octane number of only 55-60 motor method, 50% diesel oil with 50-55% cetane number, 10-15% refined wax and 10-15% lubricating oil which had a good viscosity index but a low absolute viscosity. The refined wax obtained by this process is particularly suitable, because of low sulphur content, for oxidation to carboxylic acids or for cracking to olefines for synthetic lubricating oil manufacture. Dr. Pier stated that latterly most of the wax product had gone to Stettin for lubricating oil manufacture.

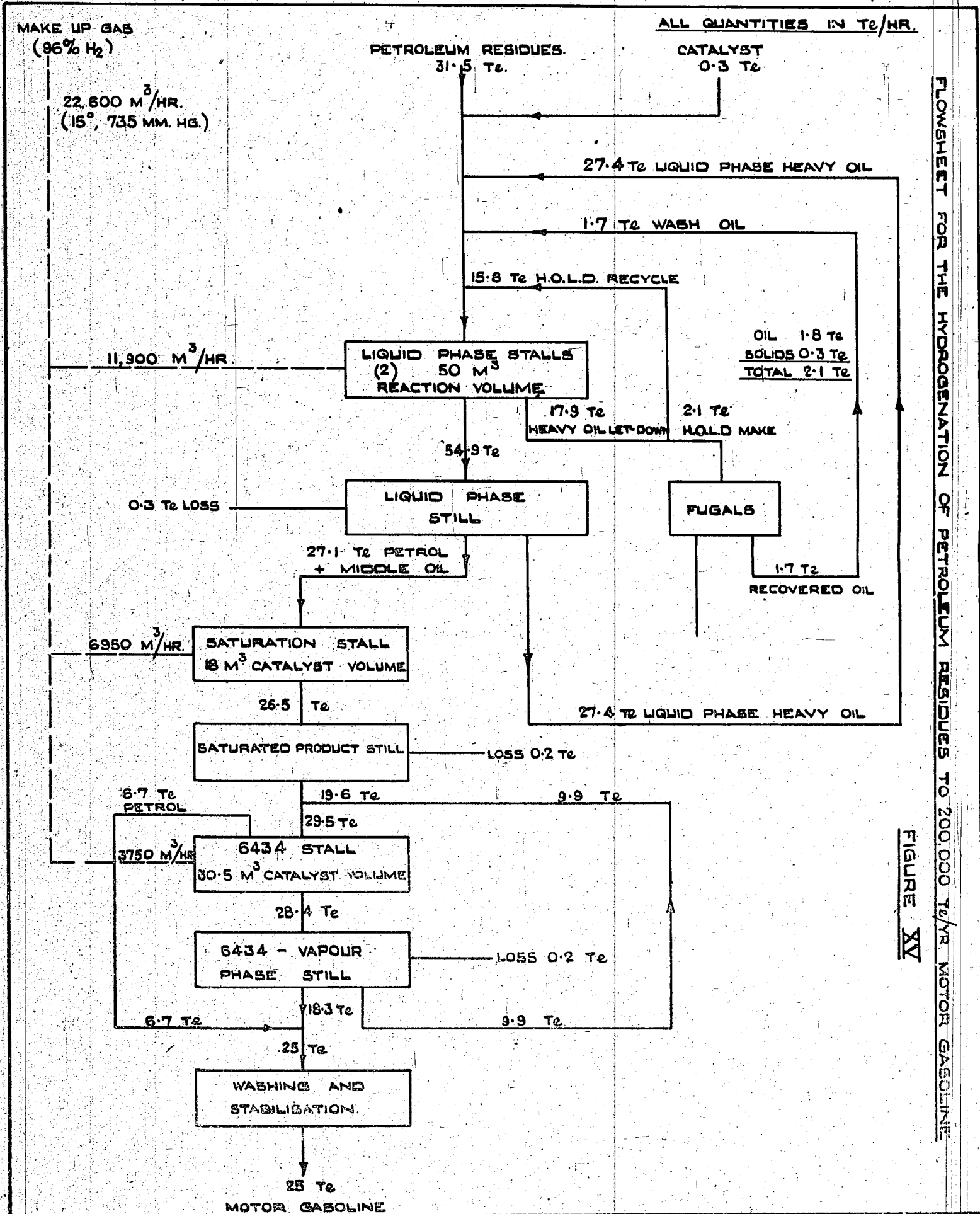
ZeitZ also operated a modified version of the above process, known as M.T.H. process. The conditions are substantially the same as for T.T.H. except that throughput is lower and the temperature higher (390°). The crude product consists of 35% gasoline, 60% diesel oil and 5% heavy bottoms which were probably sent to Bohlen for liquid phase hydrogenation. The hydrocarbon gas make is roughly 6% and the hydrogen absorption 650-700 m<sup>3</sup> per ton of tar.

#### d) Bituminous Coal Tar Hydrogenation.

Bituminous coal tar is hydrogenated at PölitZ and at Lutzkendorf. Bituminous coal tar pitch is used as raw material at Welheim. When treating crude tar, it is usually distilled to give middle oil which goes direct to the vapour phase stages and a light pitch which is hydrogenated at 700 ats. using the same catalyst conditions as are employed for hydrogenation of heavy fractions of brown coal tar. The attached flowsheet, Fig. XIV, was prepared by Dr. Pier's staff and shows the yields, etc, which they feel should be obtainable under steady operating conditions in a plant working entirely on bituminous coal tar.

#### e) Petroleum Oil Residues.

Residues from the distillation of crude petroleum and heavy residues from cracking operations are hydrogenated in the liquid phase at PölitZ. A pressure of 700 ats is employed. At Lutzkendorf, asphaltic residues obtained from the lubricating oil plant are also hydrogenated at 700 ats. The catalyst is the normal liquid phase catalyst, iron on activated coke.



FLWSHEET FOR THE HYDROGENATION OF PETROLEUM RESIDUES TO 200,000 T<sub>2</sub>/YR MOTOR GASOLINE

FIGURE XV

The following flowsheet, Fig. XV, is typical of operation on heavy oil residue obtained by straight distillation of German crude petroleum. The figures for gas make and gasoline yield are unlikely to vary greatly with different types of crude oil, but it should be borne in mind that the hydrogen absorption will vary appreciably according to the nature of the crude.

f) Normal 300 ats. Vapour Phase Hydrogenation.

Vapour phase hydrogenation of the gasoline + middle oil product obtained from the liquid phase operations described above or from straight distillation of tars or crude petroleum is usually carried out in two stages. The first stage consists of saturation hydrogenation, the main object of which is the removal of nitrogen compounds which reduce the reactivity of the oil in the second vapour phase splitting hydrogenation step. It is usual to fractionate the crude saturation product from the first stage into gasoline and middle oil, only the latter going forward to splitting hydrogenation. The main reason for this is to segregate the comparatively poor quality saturation stage gasoline from the main splitting hydrogenation product. The saturation stage gasoline is frequently used as feed for the D.H.D. process which is described later.

The saturation stage consists of once-through treatment at 300 ats pressure and temperature of 400-410°C over an active catalyst. Formerly, the catalyst used was tungsten sulphide (5058) but this has now been largely substituted by a new catalyst developed by Ludwigshafen which consists of 20-25% tungsten sulphide and 3% nickel sulphide supported on activated alumina, (8376). It is claimed that this catalyst has as good an activity for the purification of oils from nitrogen, oxygen, etc, as 5058 but it causes less splitting to lighter products. This is advantageous because it reduces the amount of comparatively poor quality petrol made in the saturation stage. Actually, the impression was gained that the main reason for employment of the new catalyst was the necessity to conserve tungsten and that the new catalyst was in certain respects, e.g. life, inferior to 5058. Dr. Hier also stated that Bohlen and Magdeburg had used 6434 (see below) as a saturation catalyst. Hydrocarbon gas make in the saturation stage is small; of the order of 1% on the oil treated.

As will be seen from the flowsheets in Figs. XII, XIV and XV, the throughput through the saturation stage, expressed in kgms. per litre of catalyst per hour, varies with the nature of the feed. The determining factor is the temperature control of the converter, which is achieved by arranging the catalyst in beds with intermediate introduction of cold hydrogen. Aromatic feed stocks requiring a higher hydrogen absorption give rise to a greater heat of reaction and have to be fed at a lower rate.

In the splitting hydrogenation stage saturated middle oil is reacted over tungsten sulphide on activated Terrana catalyst (6434) at a temperature of 410-420°C and pressure of 300 ats. The pass conversion to gasoline is of the order of 60%. Hydrocarbon gas make depends on the end-point and volatility of the petrol product. When making a motor

gasoline of end-point about 180, it is about 12% by weight on the middle oil hydrogenated and this rises to 18-20% when aviation gasoline of 150 end-point or 65-70% volatility at 100°C is the required product. 21.

No catalyst other than 6434 has been used for large scale splitting hydrogenation at 300 ats. Other catalysts have been tried in the laboratory, particularly an iron on activated Terrana catalyst which was suggested by A.N.I.C. (Italy). None of these alternative catalysts have been found to be superior to 6434.

g) 700 ats. Vapour Phase Hydrogenation.

An interesting development at the Welheim and Lutzkendorf plants has been the elimination of the saturation stage and the direct splitting hydrogenation of liquid phase gasoline and middle oil at 700 ats. In the case of Welheim, a new splitting catalyst is being used, probably consisting of 3% chrome oxide and 1% molybdc oxide supported on Florida earth. The I.G. Research Department at Lutzkendorf have been working on parallel lines and have found this to be the optimum catalyst. The reaction temperature is 450°C, i.e. some 30° higher than that employed in the normal 300 ats process, but in spite of this, because of the lower reactivity of the feed oil, the amount of gasoline obtainable from a given reaction volume is little more than half that obtained in the normal process. For a petrol product of the same volatility, the gas make in the 700 ats process is some 5-6% greater than that obtained by the normal method. The chief advantage is the elimination of the saturation step and the production of a much more aromatic gasoline and therefore one having a higher octane number. The aromatic content of the final gasoline is very dependent on the nature of the feed stock. Middle oil obtained by the liquid phase hydrogenation of pitch or bituminous coal or from the fractionation of bituminous coal tar gives rise to a gasoline containing around 45% aromatics and having an octane number of at least 78 without lead. Middle oils from brown coal or from petroleum oil give rise to gasolines of much lower aromatic content.

At Lutzkendorf, the use of 700 ats pressure in the vapour phase plant was mainly for the purpose of eliminating the saturation step. The normal 6434 catalyst was employed. (See Leun and Lutzkendorf Reports).

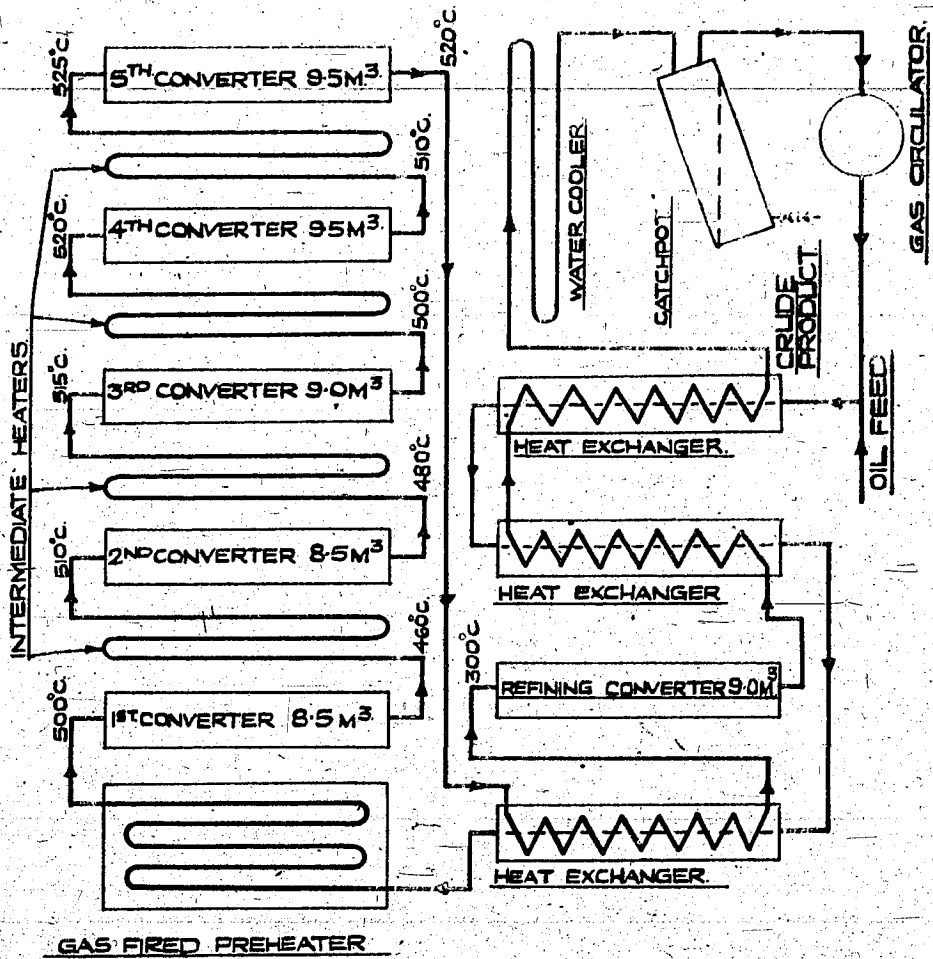
h) D.H.D. Process.

For the highest quality aviation gasoline, the Luftwaffe insisted on a high aromatic content. The 700 ats hydrogenation method described above met this requirement, but only as far as very high aromatic middle oil feed stocks were concerned. Another method was therefore adopted for the main production of first quality aviation gasoline which consisted of the dehydrogenation of the 80 - 185% cut of gasolines obtained from petroleum distillation or by 300 ats splitting hydrogenation of coal and tar products. In particular, this process was applied to the comparatively low quality gasoline distilled from the crude saturation stage product. Usually, the naphtha cut was 80-85% by weight of the original petrol. The process is discontinuous, reaction periods of rather more than 100-150 hours for bituminous coal naphthas and about 60-80 hours

FIG. XVI.

FLOW DIAGRAM.

D.H.D. PROCESS.



for brown coal and petroleum feeds alternating with 20-24 hour catalyst reactivation periods. The usual reaction conditions were -

Pressure: 25 ats for brown coal tar and petroleum oil feeds. 50 - 70 ats for feeds derived from coal hydrogenation and from bituminous coal tar.

Average Reaction Temp: 510 - 520°C.

Throughput: .4 Kgs. of fresh feed per litre of catalyst per hour.

Circulating hydrogen to oil feed ratio: Approx. 1,000 m<sup>3</sup> per ton.

Yield data were given as follows:-

	% by wt. of feeds derived from Bituminous coal hydrogenation and bituminous coal tar.	% by wt. of feeds derived from brown coal tar and petroleum oil.
Stabilised crude D.H.D.		
Product:	82-84	76-77
Hydrocarbon gas make:	16	22-23
Carbon:	.1-.2	.5-1
Hydrogen made in reaction:	1	.5

The hydrocarbon gas made in the reaction is roughly made up of equal proportions of C<sub>1</sub>, C<sub>2</sub>, C<sub>3</sub> and C<sub>4</sub> hydrocarbons. Heavy polymer is formed during the reaction and re-distillation of the crude product to an end point of 130°C left a residue of approximately 4% by weight.

The method of operation during the reaction cycle can be seen from the following diagram, Fig.XVI.

Fresh feed and recycle gas (containing 50-65% by volume of hydrogen) is heated by interchange with the out-going product and with a gas-fired preheater to a temperature of 500°C. It then enters the first of a series of converters, usually four or five in number. The reaction volume of each converter is 9-10 m<sup>3</sup>. Each converter contains a single bed of catalyst, which is active alumina on which has been deposited 10% of molybdc oxide. The reaction being strongly endothermic, it is necessary to re-heat reactants before passing them from one converter to the next. This intermediate heating is done in the same furnace as the main preheating step. On leaving the last reaction converter, the products are interchanged with incoming feed and the temperature reduced to 300°C, after which they pass to a final refining converter for removal of unsaturated products by hydrogenation. The catalyst in this refining stage is usually the same as is used in the D.H.D. reaction, but it is possible to work with 80% D.H.D.

~~catalyst and 20% activated Terrana with no metal addition.~~  
 The product is finally cooled by further interchange with the feed and by water coolers, let down to atmospheric pressure, stabilised and redistilled. The final distillate is blended back with the light 0 - 85°C fraction of original gasoline.

Gaseous products produced in the process are purged, (a) as dissolved gas released on letting down the crude product and (b) as a purge from the recycle gas system.

For the catalyst regeneration cycle the whole apparatus is let down and purged with inert gas obtained from a previous regeneration cycle. Carbon is then burnt off the catalyst by introducing air to each oven, the concentration of oxygen at the inlet to each oven being 3-4% by volume of the ingoing gas. A pressure of about 40 ats is maintained, and inert gases are circulated continuously using the same circulator as used during the reaction period. Cold inert gas can be introduced between the converters in order to control temperatures, which must not exceed 530°C. With properly controlled reactivation, the life of a batch of catalyst is about 12 months.

The final D.H.D. naphtha contains 65-68% aromatics, and when blended back with the corresponding light gasoline fraction gives a finished D.H.D. gasoline with an aromatic content of 40-55% and a minimum octane number of 78 unleaded and 87 with .09 vol.-% of lead tetraethyl. The octane number of D.H.D. gasoline made from coal hydrogenation and bituminous coal tar products is at least 2 units higher.

The important feature in the manufacture of D.H.D. catalyst is the use of carefully prepared activated alumina. The I.G. make this themselves, either by precipitation from aluminium sulphate or sodium aluminate. The active alumina is impregnated with ammonium molybdate solution. The product is dried and finally calcined to remove ammonia at about 400°C.

It has already been pointed out that, when aromatic middle oils are available, direct 700 ats gas phase splitting hydrogenation can produce a gasoline of practically the same quality as that obtainable by the 3-stage saturation/300 ats splitting/D.H.D. method. It is therefore interesting to compare the yield efficiencies of these two processes. The single-stage process gives a yield of about 83% of final gasoline. The first two steps of the multi-stage process produce from the same raw material 89% by weight of the normal hydro gasoline. This, on distillation, gives 73.5% of naphtha and 15.5% of light gasoline, both expressed as-% by weight on the original feed stock. Treatment of the naphtha by D.H.D. process gives 60% by weight on the original middle oil of redistilled naphtha which, when blended back with the light gasoline, gives a total of 75.5% by weight of final aromatic petrol. Thus, in addition to the multi-stage process being much more complicated to operate, it would appear to give 9% less final product than the direct



24.

700 ats hydrogenation process. It is also interesting to note that the yield of finished D.H.D. gasoline from brown coal tar or petroleum middle oil calculated in the same way as above, is only 71-72%. This compares with an 89-90% yield of ordinary 6434 hydro-gasoline, showing that the Luftwaffe were prepared to sacrifice up to 20% output in order to obtain a highly aromatic fuel. In assessing this cost of the improvement in aromatic content, it must, of course, be borne in mind that the hydrocarbon gases, particularly the butane produced in the D.H.D. process, could be used for increasing the output of other aviation components, such as iso-octane or alkylate.

The D.H.D. process was first tested out on a large scale on a modified vapour phase hydrogenation stall at Pölitz. This plant also had the first properly designed commercial unit which started up at the beginning of 1942. D.H.D. plants have also been in operation at Scholven and Leuna and are in course of erection at Blechhammer, Bohlen, Brux and Ludwigshafen.

Naphtha dehydrogenation is also carried out on a scale of about 60,000 tons/year at Moosbierbaum. The D.H.D. process is not employed. A slightly modified version of the normal American "hydroforming" method is used.

#### i) Iso-Octane and Alkylate Production.

The first method adopted in Germany for the production of iso-octane consisted of the dehydration of iso-butanol (made by the higher alcohol synthesis from carbon monoxide and hydrogen) to give iso-butylene, the polymerisation of this iso-butylene to di and tri iso-butylene, and the hydrogenation of the dimer and trimer. This process was operated at Ludwigshafen/Oppau and at Leuna in the early days of the war and is still the process employed at the new plants, Heydebrech and Auschwitz.

Iso-butanol of 97-98% purity is dehydrated over an alumina catalyst at a temperature of 330-360°C. The yield is 95% theory and the catalyst life from 3-4 months. Polymerisation is carried out over a catalyst consisting of active carbon containing 10% phosphoric acid. Temperature is approximately 150°C and pressure of the order of 20 ats, this being adjusted to ensure liquid phase conditions at the reaction temperature employed. The polymer is redistilled, usually to remove as bottoms only the polymers of greater molecular weight than trimer, and the distillate is hydrogenated at 250-300 ats pressure over nickel molybdenum sulphide catalyst (5615).

By 1940, the I.G. had developed a process for dehydrogenation of butane available from the hydrogenation plants and this opened up the second phase of branch/paraffin production in Germany. Butane from the hydrogenation plants was fractionated into iso and normal isomers, the normal butane was used for liquid gas and the iso-butane dehydrogenated. The resulting iso-butylene was worked up to iso-octane as before. The butane

dehydrogenation process, which was developed at Leuna, is a continuous process operating at 550-570°C and at substantially atmospheric pressure with a chromium on alumina catalyst (10-15% chromium). The process was made continuous by adopting the moving catalyst bed principle. The catalyst, which was made in the form of spheres, passed downward through externally heated reactor tubes concurrently with the butane feed. The residence time of catalyst in the tubes is approximately 4 hours, after which it is removed to an external reactivation vessel. Reactivation is carried out by burning off deposited carbon with diluted air. The rate of butane feed is about 700 m<sup>3</sup> per m<sup>3</sup> of catalyst per hour and 20-25% of the inlet butane is converted per pass. About 85% of the butane converted goes to butylene. Carbon content of catalyst leaving the converter is 4% and this is reduced to about 1.5% in the reactivation step. No attempt is made to burn off all the carbon in the inner core of the catalyst and there is a theory that the presence of a certain amount of carbon in regenerated catalyst helps to keep down carbon formation. The process was first operated on a large scale at Leuna, Pölitz and Scholven.

Early in 1943 there was a further change which resulted in a greatly increased potential output of branched paraffins. Normal butane was dehydrogenated instead of iso-butane. The resulting normal butylene was used to alkylate the iso-butane fraction giving a blending alkylate of about 92 octane number. The alkylation process was carried out with sulphuric acid in stirred vessels. The method was developed at Leuna and the Indwigham staff could not provide any detailed information.

#### j) Fuel for Jet Planes

This was known as T.L. fuel in Germany. It was made by saturating a specially cut middle oil fraction of brown coal tar. A fuel was required which would have the highest possible calorific value per unit volume. At the same time it was essential for the pour point to be less than -25°C and for the viscosity to be less than 1.2° Engler at 20-25°C and not more than 3° Engler at -20°C. The fuel had also to be substantially free from phenols in order to avoid acid corrosion.

In order to meet the above requirements, the brown coal tar middle oil had to be cut to a lower end point than usual, namely, 280-300°C. The crude saturation product was stabilised and despatched without distilling out the gasoline component. The synthetic fuel was normally blended with petroleum oil fractions. Leuna and the Brabag plants have produced commercial quantities of the fuel, for which the first demand was in July 1944. It was planned to produce up to 20,000 tons/month of this material in the German hydrogenation plants but only a fraction of this output was reached.

TABLE II

Plant	Main Raw Material(s)	Type of Hydrogenation Process	D.H.D. Plant installed or working	Iso-octane or Alkylate Plant working or installed	Ann. Prodn. Capacity of Finished Fuels T/Yr.
SCHOLVEN		300 ats Liquid	2 units of 100,000 T/Yr. Wkg.	Alkylate Plant working	200,000
GELSENERG	Bituminous Coal	700 ats Liquid & Vapour Phase.	None	late. Plt operating	350,000
ALECHHAMMER	Bituminous Coal	300 ats Vapour Phase.	2 units in course of erection.	None	400,000
POLLITZ	Bituminous Coal	700 ats L. Phase	4 units working.	Alkylate. Plant operating.	600,000
	Bituminous Coal Tar	500 ats V. Phase	None	60-70,000 T/Yr.	
	Petroleum Residues			Alkylate. 20,000 T/Yr. Plant in course of erection	200,000
WESSELING	Brown Coal			Alkylate. Plant operating 60,000T/yr	600,000
LEUNA	Brown Coal	250 ats Liquid & Vapour Phase	4 units. 1 working.	None	150,000
VELHEIM	Bituminous Coal Tar Fractions and Pitch	700 ats Liquid & Vapour Phase	None	None	250-300,000
BOHLEN		250-300 ats L. & V. Phase	2 units not ready	Alkylate. Plant in course of erection	250-300,000
MAGDEBURG		300 ats T.T. H. process	None	None	250-300,000
ZELTZ		Normal 300 ats L. & V. Phase	2 units not finished.	None	250-300,000
FRUX		700 ats Liquid & Vapour Phase	2 units not finished.	Alkylate. Plant in course of erection	400,000
LUTHERENDORF	Petroleum Residues		None	None	50,000
	Bituminous Coal Tar Fractions				
HEIDENRECH	Higher Alcohol a.				?
ANSCHLITZ	Higher Alcohol a.				?

TABLE III

## COST CALCULATION FOR THE PRODUCTION OF 200,000 T/YEAR

Raw Material	Bituminous Coal	RM/te Motor Gasoline
Raw Materials	1.84 te. Bit. Coal (1) at 21.50 RM/te	39.50
Hydrogen (100%)	2800 cbm at, 4.5 Pfg/m <sup>3</sup>	126.00
Catalysts and Chemicals		5.00
<u>Credits:</u>		
<u>Liquefied Gases</u>	230 kg at 220.65 RM/te (3)	<u>50.80</u>
<u>Fuel Gases (2)</u>	$3.4 \times 10^6$ WE at 6 RM	<u>20.40</u>
Running Costs		121.35
Production Cost		220.65
Export Cost		3.00
General Costs and Licence	5% of Production Cost	11.05
<u>Total Cost (Loaded)</u>		<u>234.70</u>

(1) Bituminous Coal with 8% Water and 4% ash.

(2) If Ethane is recovered the credit is increased by RM 2.-/te.

(3) Valued at the production cost of Motor Gasoline.

MOTOR GASOLINE BY THE HYDROGENATION OF VARIOUS RAW MATERIALS

Bituminous Coal High Temperature Tar		Natural Oil Residuum			
	RM/te Motor Gasoline		RM/te Motor Gasoline		RM/te Motor Gasoline
1.29 te. H.T. Tar at 40 RM/te	51.50	1.26 te. Residuum at 40 RM/te	50.50	1.26 te. Residuum at 60 RM/te	75.50
2090 cbm at 4.5 Pfg/m <sup>3</sup>	94.90	870 cbm at 4.5 Pfg/m <sup>3</sup>	39.20	870 cbm at 4.5 Pfg/m <sup>3</sup>	39.20
	7.20		3.00		3.00
186 kg at 193 RM/te	<u>35.80</u>	143 kg at 148 RM/te	<u>21.20</u>	143 kg at 170 RM/te	<u>24.80</u>
2.0 x 10 <sup>6</sup> WE at 6 RM	<u>12.00</u>	1.44 x 10 <sup>6</sup> WE at 6 RM	<u>8.60</u>	1.44 x 10 <sup>6</sup> WE at 6 RM	<u>8.60</u>
	87.20		85.10		85.10
	193.00		148.00		170.00
	3.00		3.00		3.00
	9.65		7.40		8.50
	205.65		158.40		181.50

Residues at 80 RM/te give Total Cost of 204.60

TABLE IV.

ANALYSIS OF RUNNING COSTS PER TONNE OF MOTOR GASOLINE

	Bituminous Coal		Total
	Liquid Phase	Vapour Phase	
<u>Capital Cost in Mill. RM</u>			
Hydrogenation Proper.	46	17	63
Associated Bldgs. 25%(1)			<u>16</u>
			79
<u>Running Costs</u>			
Wages, Man-days	525	220	745
Man-hrs/Te gasoline	7.75	3.2	10.95
	<u>RM/Te Motor Spirit</u>		
Wages at 1.30 RM/hr.	10.---	4.15	14.15(2)
Salaries 20% of Wages	2.---	0.85	2.85
<u>Energy Costs</u>			
Water at 0.01 RM/cbm	(110m <sup>3</sup> ) 1.10	(80m <sup>3</sup> ) 0.80	1.90
H.P. Steam at 3.-/Te	(0.43Te) 1.30	(0.2Te) 0.60	1.90
L.P. Steam at 2.25/Te	(1.64Te) 3.70	(0.59Te) 1.30	5.---
Electricity Energy at 0.015/KWH	(800KW) 12.---	(146KW) 2.10	14.10
Fuel Gas at 6.-/10 <sup>6</sup> WE	(2x10 <sup>6</sup> WE) 12.---	(0.7) 4.20	16.20
<u>Maintenance Costs</u>			
6% of the plant	13.90	5.10	19.---
2% of the associated buildings	1.15	0.45	1.60
<u>Working Materials</u>			
10% of wages	1.00	0.40	1.40
<u>Amortisation</u>			
10% of the plant	23.---	8.50	31.50
5% of the associated buildings	2.85	1.05	3.90
<u>Taxes, Fire Protection, etc.</u>			
2% of the Capl. cost	5.75	2.10	7.85
	89.75	31.60	121.35

(1) The "Associated Buildings" include:- Main Offices, Main Workshop, Gas Protection, Laboratories, Change-rooms, Construction equipment, Garages, Railway sidings, Roads, Stores, Pipe Bridges, Drains, Culverts, etc.

In this cost are generally included the costs for:- initial design work, Construction management, Equipping of stores, Spare catalyst, Personnel training, Interest on capital during construction, Working Capital, Land Costs, Railway connections and housing. These vary greatly according to the location of the plant and are not included.

(2) Because of the necessity of using untrained and unqualified staff the personnel requirement is 1/3 higher than necessary.

(Plant capacity: 200,000 Te/year Motor Gasoline)

Bituminous Coal High Temperature Tar			Natural Oil Residues				
Liquid Phase	V.Phase	Total	Liquid Phase	V.Phase	Total		
31.5	17	48.5	30	17	47		
		12			12		
		60.5			59		
285	220	505	260	220	480		
4.2	3.2	7.4	3.8	3.2	7.0		
<u>RM/Te Motor Spirit</u>			<u>RM/Te Motor Spirit</u>				
5.45	4.15	9.60	4.95	4.15	9.10		
1.10	0.85	1.95	1.—	0.85	1.85		
(80 m <sup>3</sup> )	0.80	0.80	1.60	(80 m <sup>3</sup> )	0.80	0.80	1.60
(0.33 Te)	1.00	0.60	1.60	(0.23 Te)	0.70	0.60	1.30
(0.76 Te)	1.70	1.30	3.—	(0.69 Te)	1.55	1.30	2.85
(400 KW)	6.—	2.10	8.10	(420 KW)	6.30	2.10	8.40
(1.2x10 <sup>6</sup> WE)	7.20	4.20	11.40	(1.2x10 <sup>6</sup> WE)	7.20	4.20	11.40
	9.40	5.10	14.50		9.—	5.10	14.10
	0.80	0.40	1.20		0.80	0.40	1.20
	0.55	0.40	0.95		0.50	0.40	0.90
	15.75	8.50	24.25		15.—	8.50	23.50
	1.95	1.05	3.—		1.95	1.05	3.—
	3.95	2.10	6.05		3.80	2.10	5.90
	55.65	31.55	87.20		53.55	31.55	85.10

If the capacity of the plant is doubled the Running Costs will be reduced by RM 10.—/Te Motor Gasoline.

Table II lists the hydrogenation plants in Germany and summarises the information obtained at Heidelberg concerning their mode of operation and capacity for finished fuels.

(C) Comparative Cost Data on the Hydrogenation of Bituminous Coal, Bituminous Coal Tar and Heavy Petroleum Residues.

Fraulein Dr. HBring and Dr. Donath provided the following cost estimates for hydrogenation of bituminous coal, bituminous coal tar and heavy petroleum residues.

These estimates are based on the flowsheets shown in Figs. XII, XIV and XV and the hydrocarbon gas yields given in Table I. They should be compared with any data on achieved costs obtained at Gelsenberg or from Pöblitz documents.

Table III shows the build up of the works cost of petrol in terms of raw material cost (coal tar or heavy oil, hydrogen, catalyst or chemicals and operating cost and overhead charges).

Credits for liquid gas and for fuel gas are taken into account.

Table IV shows the build up of the operating costs in terms of wages, utilities, etc. It will be noted that this operating cost includes amortisation.

The data on utilities consumptions, labour requirements, etc. are sufficiently complete for the costs to be re-calculated for British or American conditions. This has not been attempted in the present report.

A number of general conclusions can, however, be drawn from a very brief consideration of the figures. For example, the relative value of the three feed stocks is as follows:-

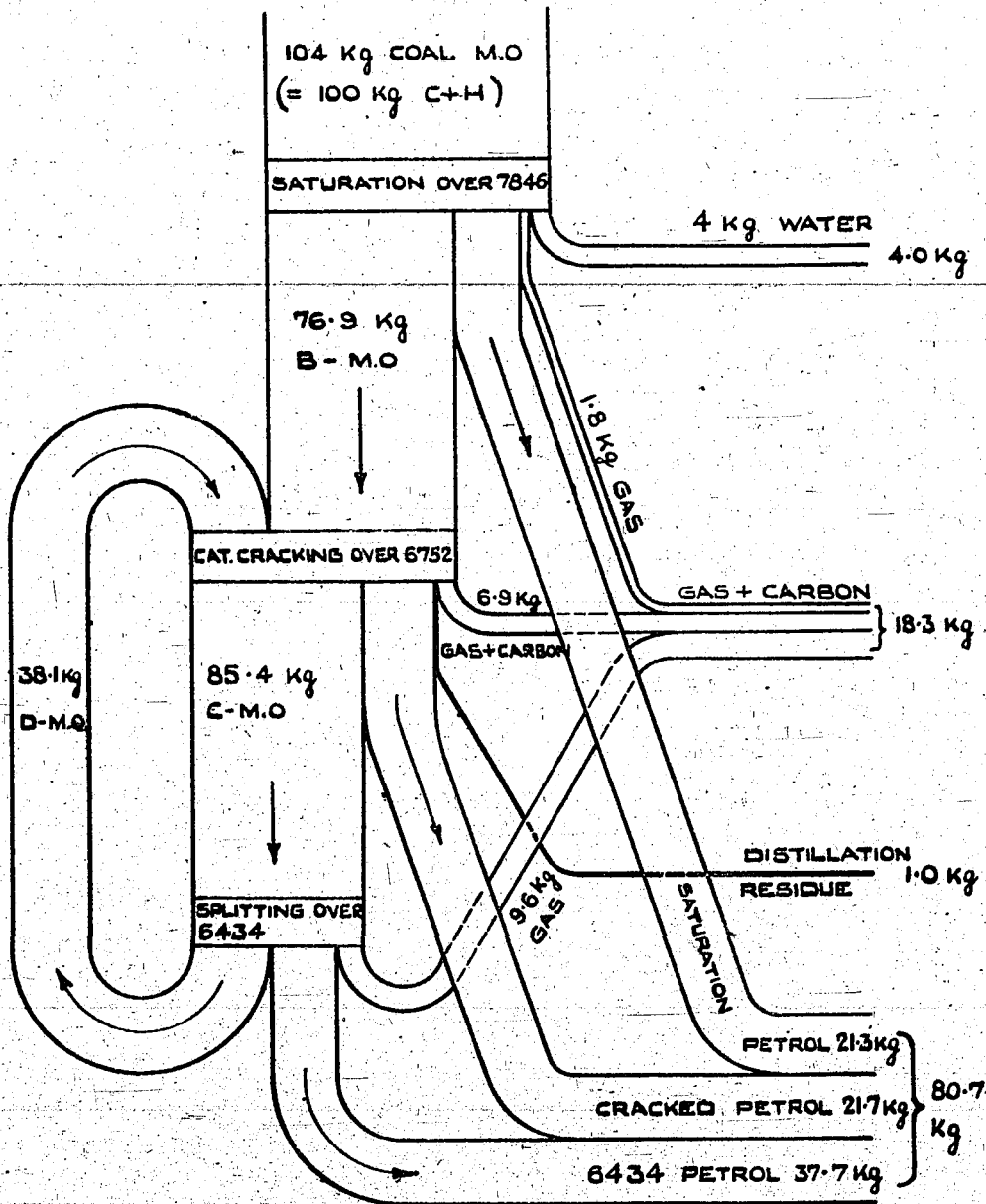
Bituminous Coal	21.5 RM per ton.
High Temperature Tar	62.5 RM " "
Petroleum Heavy Residues.	100 RM " "

It is also clear that the use of 700 atms pressure does not alter the position that the liquid phase stage is the really expensive part of the synthesis of petrol from high molecular weight raw materials. It may be calculated from the figures supplied at Heidelberg that, starting with bituminous coal at 21.5 RM per ton, the cost of production of 1 ton of crude liquid phase product is 155 RM. Similarly, starting with H.T. tar at 40 RM a ton, it costs 124 RM for each ton of crude liquid phase product. Compared with the above, the total cost of producing



FIG. XVII

COMBINATION OF HYDROGENATION & CAT. CRACKING



a ton of petrol from liquid phase product, including hydrogen but excluding the cost of the oil feed, is not more than 75 RM per ton. Expressed in another way, the value of liquid phase product from bituminous coal or bituminous coal tar hydrogenation compared with bituminous coal at 21.5 RM per ton is roughly 150 RM per ton. The comparative value, on the same basis of liquid phase product from petroleum residue (which requires less hydrogen in the gas phase treatment than does bituminous coal product) is as high as 170 RM a ton.

(D) Research

A large proportion of the effort and equipment of the Ludwigshafen Oil Research Section has been devoted during the war to the development of the D.H.D, T.T.H and the 700 atms vapour phase splitting hydrogenation processes and to routine evaluation of raw materials and catalysts. A mass of reports and documents relating to this work has been evacuated and awaits detailed study. In the writer's opinion it is questionable whether the effort entailed can be justified and it is suggested that the easiest way to obtain a full account of these researches would be to bring a selected team of German workers to this country and have them write up summary reports of their work using the captured documents for reference.

In addition to work on processes which are now in use on the large scale, considerable research was carried out on catalytic cracking, isomerisation, synthesis of branched chain hydrocarbons, etc. The following brief notes give an idea of the type of work in hand on these subjects.

Catalytic cracking.

The main idea behind this work was to improve petrol quality and, at the same time, to reduce the number of high pressure vapour phase hydrogenation stalls by complete or partial substitution of splitting hydrogenation by catalytic cracking. Fig. XVII shows a typical scheme which, at one time, was considered for application to the Gelsenberg plant. The feed is middle oil from coal hydrogenation which is first saturated by high pressure vapour phase hydrogenation in the ordinary way. The middle oil component of the saturated product is then subjected to straight-through catalytic cracking and the product is distilled to remove petrol. The residual middle oil is hydrogenated over 6434 and the product fractionated to give petrol and middle oil bottoms which are recycled to the catalytic cracking process. The final petrol consisting of a mixture of saturation stage, catalytic cracking and splitting hydrogenation petrol is obtained in at least as good a yield as is given by the normal hydrogenation process and has an unleaded octane number of 75-76 and 87 with 0.09% tetraethyl lead or 89-90 with 0.12%.

Other schemes cut out splitting hydrogenation completely and the middle oil component of the crude catalytically cracked product is recycled to the saturation hydrogenation stage. In this case the final petrol product tends to be too unsaturated and petrol from catalytic cracking has to be subjected either to a hydrogenation saturation process or to acid treatment.

### Isomerisation

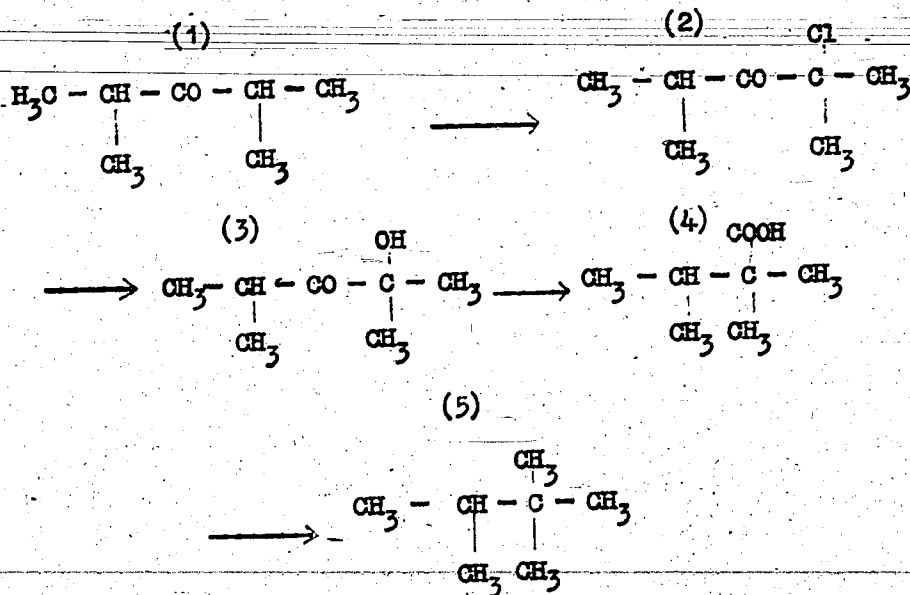
A considerable amount of work has been devoted to an attempt to develop a technique for isomerisation of straight chain paraffins (from n-butane to Kogasin) over a solid catalyst. Fairly satisfactory laboratory results were obtained with n-butane using tungsten sulphide as catalyst but compared with the Aluminium Chloride method there was excessive breakdown to lighter products. This tendency towards splitting increased with increasing molecular weight of the fuel and further, it was concluded that the solid catalyst method shewed very little promise as regards the production of multi - branched hydrocarbons, e.g. dimethylbutanes from normal hexane.

### Synthesis of branched chain hydrocarbons.

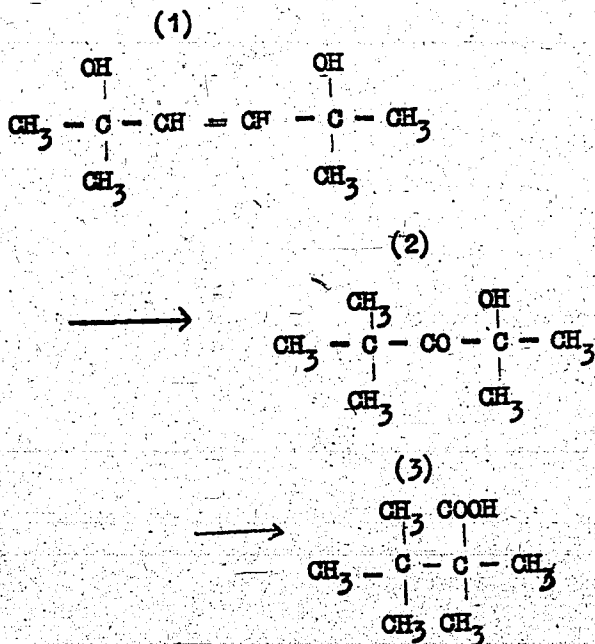
This was done mainly for evaluation of the effect on knock rating of different types of hydrocarbon structures but, in view of the lengths which the Germans were prepared to go to secure high anti-knock constituents, e.g. isooctane from higher alcohols, the possibility that they were exploring methods for large scale manufacture cannot be ruled out.

The condensation of isobutane with ethylene in the presence of  $AlCl_3$  was studied at Ludwigshafen. The product was mainly 2:3-dimethylbutane. This hydrocarbon was also made by reacting isobutylene with hydrogen and carbon monoxide over a cobalt oxide catalyst (120-150°C and 200 ats) to give iso-valeric aldehyde, condensing this with formaldehyde to produce isopropyl acrolein and finally, hydrogenating this product to 2:3-dimethylbutane. 2:2.3-trimethylbutane (Triptane) was prepared by acetylating Pinacoline alcohol with Ketene, splitting out acetic acid, coupling the product with formaldehyde and finally hydrogenating to the hydrocarbon.

Triptane had also been made from diisopropylketone which is a by-product obtained in the synthesis of isobutyl alcohol from carbon monoxide and hydrogen. This ketone was chlorinated and the chlorine atom replaced by an OH group. This product was isomerised to the acid shown in Formula 4 below and this was hydrogenated to Triptane.



Hexamethylethane or 2.2.3.3. tetramethylbutane was synthesised from 2.5. dimethylhexenediol obtained by condensing acetylene and acetone under alkaline conditions and hydrogenating the product. The 2.5. dimethylhexenediol was subjected to the isomerisation reactions shown below to give the acid depicted in Formula 3 which was hydrogenated to 2.2.3.3. tetramethylbutane.



(E) Methods of Manufacture of Catalysts for Hydrogenation and related processes.

1. Molybdenum-Grude catalyst (for liquid phase hydrogenation of heavy oils).

Composition:	Grude	98%
	MoO <sub>3</sub>	2%

Grude containing 40-50% ash (obtained by carbonisation of brown coal in a Winkler generator) is treated with sulphuric acid to effect 90% neutralisation of its alkalinity. The neutralisation is made necessary by the fact that alkali poisons the molybdenum catalyst. The Grude is impregnated with an ammonia molybdate solution to give 2% MoO<sub>3</sub> in the finished catalyst. It is then dried at 140°C and ground to a fine powder (60% through 10,000 mesh). The catalyst is used as a 40% paste in asphalt-free oil.

2. Iron-Grude Catalyst (for liquid phase hydrogenation of heavy oils).

Composition:	Grude	90%
	FeSO <sub>4</sub> .7H <sub>2</sub> O	10%

For this catalyst the Grude is not neutralised. The impregnation with hot concentrated iron solution is carried out in a screw conveyor. An amount of NaOH solution equivalent to the iron is then added. The catalyst is dried to an 18% water content and then pasted with oil.

3. 5058 : Vapour Phase Saturation Catalyst (also used in T.T.H. process and formerly used in a combined saturation splitting process).

Composition:	WS <sub>2</sub>	100%
--------------	-----------------	------

500 kg. H<sub>2</sub>WO<sub>4</sub>, alkali and chlorine free, is dissolved in 1200 litres mother liquor in an agitator. The mother liquor, from an earlier operation, contains 9 - 10% NH<sub>3</sub>, 10 - 12% H<sub>2</sub>S and 2 - 3% WO<sub>3</sub> as (NH<sub>4</sub>)<sub>2</sub>WS<sub>4</sub> in solution. Before adding the H<sub>2</sub>WO<sub>4</sub>, however, the NH<sub>3</sub> content of the mother liquor is brought up to 12 - 13% by addition of liquid ammonia. Solution requires ca 1½ hrs. at 150 mm Hg pressure and 60-70°C, and gives a solution containing the equivalent of 27% WO<sub>3</sub>. 3 - 4% WO<sub>3</sub> remains undissolved and is filtered off as a sludge; the sludge contains some silica and is returned to the H<sub>2</sub>WO<sub>4</sub> plant. The filtered solution is introduced at 50°C to either of two saturators where it is gassed with H<sub>2</sub>S under 200 mm. Hg pressure while stirred. During the first half-hour the temperature is raised to 60°C and then maintained at 60°C for 3½-5 hrs. After a further 2 hrs. at 50°C the solution is cooled to 20°C over 2½ hrs, being stirred under

~~H<sub>2</sub>S all the time. Yellow crystals of (NH<sub>4</sub>)<sub>2</sub> WS<sub>4</sub> separate and the filtered solution shows only 4 g WO<sub>3</sub>/100 ccs.~~

The yellow crystals are filtered off under 0.5 atm. nitrogen pressure and after running off the filtrate a current of nitrogen at 60°C is drawn through the cake. The yellow salt is finally dried at 100-120°C in nitrogen in a rotating or stirred drier and then has the following composition: 9-10% NH<sub>3</sub>, 54% W, 36.8 - 37.0% S.

The decomposition of the yellow salt to WS<sub>2</sub> is carried out in a scroll-type furnace which has two passes, each 8 M long. The first pass is electrically heated along the whole of its length, the second pass along only half its length, the second half of the second pass serving as an atmospheric cooler. The maximum temperature of the hot section of the furnace is maintained at 420-450°C and the residence time is ca 1 hr. A hydrogen rate of up to 100% in excess of the theoretical requirement is maintained through the furnace. The black powder has the following analysis: 73-74% W, 25-26% S, ca 0.1% H<sub>2</sub>O, 0.1-0.2% H<sub>2</sub>SO<sub>4</sub>.

The powder is milled in a hammer-type ("schlagkreuz") mill to the following grading:

70 - 80% through 10,000 mesh  
100% " 7,000 "

and is then pelleted. The last two operations also are carried out in an N<sub>2</sub> or CO<sub>2</sub> atmosphere and, after breaking off their edges in a rotary sieve, the pellets are stored under N<sub>2</sub> in gas-tight drums, since oxidation by air results in a loss of activity which cannot be restored.

The life of the catalyst depends on the nature of the middle oil but normally extends to two years. When used in the T.T.H. process, the life depends on the ash content of the charge. Although the activity can sometimes be restored by grinding and re-pelleting, it is eventually necessary to regenerate by roasting pellets to WO<sub>3</sub> in air and repeating the whole preparation via the yellow salt.

4. 6434 : Vapour Phase Splitting Catalyst (has occasionally been used directly on petroleum (120-325°C) and brown coal tar middle oils).

Composition: Terrana (Fuller's earth) 90%  
WS<sub>2</sub> 10%

Not all Fuller's earths are catalytically active and it is necessary to test each particular sample for activity. 200 kg. earth, 200 l. of 10% HF and sufficient tungsten solution to give 10% WS<sub>2</sub>, in the finished catalyst are introduced into an Birich mixer and the mixture kneaded for half an hour. The tungsten solution is prepared by dissolving yellow salt in mother liquor to give a solution containing 75 - 80 g. WO<sub>3</sub>/l. The slurry from the mixer

is dried in an L.P. steam-heated stirred pan at 120°C. After cooling, the product is coarsely milled and then sulphided in the 5058 scroll-type furnace - temp. 425°C, residence time 1 hr, atmosphere H<sub>2</sub>+H<sub>2</sub>S. The sulphided powder is cooled in a nitrogen stream, kneaded with 30% of water in a small Eirich mixer and then pelleted damp. The pellets are first allowed to dry in the air for 3-4 hours and then dried at 120-130°C in an inert atmosphere. Finally, the pellets are heated in H<sub>2</sub> to 80°C for a day, to 120°C for 2 days, to 450°C for 12 hours and then cooled off in a stream of N<sub>2</sub>. Packaging and storage are on the same lines as for 5058.

5. 3510 : Vapour Phase Aromatising Catalyst - now superseded by D.H.D. Process. (has been used as a saturation catalyst and as catalyst in the T.T.H. Process.)

Composition:	MoO <sub>3</sub>	53.5%
	ZnO	30%
	MgO	16.5%

21.6 kg. of MoO<sub>3</sub>, 12.15 kg. of ZnO and 6.75 kg. of MgO are mixed dry in a mixer for 5 minutes; 15 - 17 l. of water are added and further mixed for about 20 minutes. The paste is spread on trays, allowed to stand for 2 - 4 hours, cut into pieces and further dried for about 12 hours at 120 - 140°C. After drying, the catalyst breaks up into separate pieces which, after sieving, are used as catalyst. The sieving is carried out on an 8 mm. mesh screen and gives 7 - 10% fines, which are added to the raw materials for the next batch.

If required in the pelleted form, dry cake is ground in a hammer mill. 8.8 kg. of the powder is mixed with 1.2 kg. of raw materials which have been previously mixed in the correct ratio and then 8 - 10% water added in an Eirich mixer. The moist material is then suitable for pelleting. As freshly prepared, the catalyst is not sensitive to oxygen.

6. 7846 : Vapour Phase Saturation Catalyst. (first substituted for 5058, later superseded by 8376).

Composition:	Al <sub>2</sub> O <sub>3</sub>	87%
	MoO <sub>3</sub>	10%
	Ni <sub>2</sub> O <sub>3</sub>	3%

The carrier is an alumina that is prepared from technical alumina containing 60% Al<sub>2</sub>O<sub>3</sub> and 40% water. This alumina is dissolved in NaOH, and reprecipitated with nitric acid, the acid additions being made as quickly as possible at a pH of 5.5 - 6.5 at a temperature not exceeding 50°C. The precipitate is filtered through a filter press and washed with water for a short time. After re-slurrying with water, the alumina is

again filtered and washed with water until alkali-free. The filter cake is dried at 200°C and then powdered. After peptizing with about 2% HNO<sub>3</sub>, the paste is spread on aluminium trays, partially dried, cut into cubes of 1 - 2 cm. sides, slowly dried and then calcined at 400 - 500°C. The cubes are washed with 5% ammonia solution and again ignited. They are then soaked with an ammoniacal molybdic acid solution, dried, soaked with a solution of nickel carbonate in acetic acid, and finally ignited at 500 - 600°C. If sulphuric acid is used in place of nitric acid, NiSO<sub>4</sub> is converted to NiS in the presence of H<sub>2</sub> at 400°C.

7. 8376 : Vapour Phase Saturation Catalyst (has also been used for the T.T.H. Process, for reduction of higher alcohols and for hydrogenation of di-isobutylene. Sometimes known as 7846 w 250).

Composition:	Al <sub>2</sub> O <sub>3</sub>	70%
	WS <sub>2</sub>	27%
	NiS	3%

The alumina used as carrier is prepared from technical aluminium sulphate containing 18% Al<sub>2</sub>O<sub>3</sub>. The raw Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> is dissolved in water at 50-70°C. to give a solution containing 10 - 12% Al<sub>2</sub>O<sub>3</sub> and is then precipitated with a 20% ammonia solution. A slight excess of ammonia is used, the quantity being such that 20 cc of filtrate is equivalent to 10 cc of N/10 sulphuric acid. The precipitate is washed with a 0.1% ammonia solution until free from sulphate. The filter cake is dried to an ignition loss of 15 - 20%. After addition of 1% graphite, the mixture is pelleted and the pellets calcined at 450°C.

The pellets are saturated with an ammoniacal solution of WO<sub>3</sub> and NiSO<sub>4</sub>, dried in an air stream at 140°C and then converted to the sulphide in an H<sub>2</sub>S stream at 400 - 450°C. The pellets are then powdered, the powder repelleted and the pellets again treated with H<sub>2</sub>S.

8. 5615 : Vapour Phase Saturation Catalyst. (specially applicable to hydrogenation of di-isobutylene. Has also been used for reduction of higher alcohols and improvement of lubricating oil.)

Composition:	WS <sub>2</sub>	85%
	NiS	15%

100 parts by weight of H<sub>2</sub>WO<sub>4</sub> is mixed dry with 24 parts of nickel carbonate in a ball mill for one hour and then pasted in a stirred vessel with 100 parts water. The paste is dried for about 6 hours and the dried mass pulverized. The powder is sulphided to a 28 - 30% sulphur content in the scroll-type furnace used for 5058. The



The sulphided powder is pelleted in the same way as 5058. An alternative method of manufacture, giving a catalyst referred to as 6718, involves the mixing of the corresponding amounts of ammonium sulpho-tungstate and nickel carbonate in a ball mill. The mixture is then converted into the sulphide at 450°C, and pelleted as described in the preparation of catalyst 5058.

9. 7360 : D.H.D. Catalyst. (also referred to as 5436)

Composition:  $\text{Al}_2\text{O}_3$  90%  
 $\text{MoO}_3$  10-12%

An alumina carrier prepared from commercial alumina containing 60%  $\text{Al}_2\text{O}_3$  and 40% water, is used. Cubes of alumina are prepared and ignited as described under Catalyst 7846. The cubes are soaked with an ammoniacal  $\text{MoO}_3$  solution (20%  $\text{NH}_3$ ) so that the finished catalyst contains 10-12%  $\text{MoO}_3$ . After impregnation, they are dried at 140°C and ignited at 400°C to remove ammonia. The catalyst is then screened and packed.

10. 7935 : Improved D.H.D. Catalyst. (gives slightly better yield than 7360, but requires shorter cycle times).

Composition:  $\text{Al}_2\text{O}_3$  85%  
 $\text{MoO}_3$  15%

The carrier is an alumina prepared from technical aluminium sulphate containing 18%  $\text{Al}_2\text{O}_3$ . This raw material is brought into a concentrated solution at 50-70°C. and precipitated with 20% ammonia solution at 92-95°, filtered hot and washed. The filter cake is dried to a content of 80%  $\text{Al}_2\text{O}_3$ , pelleted and the pellets calcined at 450°C. The pellets are then soaked with an ammoniacal  $\text{MoO}_3$  solution, so that the final catalyst contains 15%  $\text{MoO}_3$ . After impregnation, the pellets are dried at 140°C and calcined at 400° until the ammonia is removed.

11. 7019 : Aromatisation Catalyst.

Composition: Activated charcoal 80%  
Chromic Oxide 15%  
Vanadium pentoxide 5%

Anthracite coal, peat and bituminous coal tar pitch are finely ground, mixed in the ratio of 100:10:40, dried with stirring 2 hours at 110°, ground and pelleted. The pellets are lightly sintered in a drying chamber at 100-120°C., then carbonised in a rotating kiln at 500°C, and finally activated in a vertical-pipe furnace with steam at 800-900°C. The activated pellets are soaked first with a saturated (6%) aqueous solution of ammonium vandate, and then

with a 40-50% aqueous solution of chromic acid, the pellets being dried after each impregnation. The amounts of the solutions are so controlled that the finished catalyst contains 15%  $\text{Cr}_2\text{O}_3$  and 5%  $\text{V}_2\text{O}_5$ . The catalyst has good mechanical strength and cannot be broken by hand.

#### 12. Methane Steam Catalyst.

Composition:	$\text{Ni}_2\text{O}_3$	25%
	$\text{MgO}$	14%
	Cement	28%
	Kaolin	33%

Metallic nickel is dissolved in 40° Be nitric acid. The resulting solution, which is somewhat alkaline from the ammonia formed, is precipitated at 60°C with sodium carbonate and the filtered nickel carbonate is washed free from sodium nitrate. The nickel carbonate is mixed with sulphur-free MgO and kaolin and heated on aluminium trays in an electric oven at 400°C. It is then ground to 0.4 mm. size and mixed with sulphur-free alumina cement. After the addition of 15% water, the material is rapidly pelleted in a small Kilian press. The pellets are broken without delay into 1-2 mm. granules and the granules formed into Raschig rings in a Wilkinson press.

#### 13. Water Gas Shift Catalyst - Brown Oxide.

Composition:	$\text{Fe}_2\text{O}_3$	about 85%
	$\text{Cr}_2\text{O}_3$	" 15%

Details of preparation not obtained.

#### 14. 6448 : Butane Dehydrogenation Catalyst.

Composition:	$\text{Al}_2\text{O}_3$	90%
	$\text{K}_2\text{O}$	2%
	$\text{Cr}_2\text{O}_3$	8%

22.5 kg. finely powdered activated alumina, 2 kg. water-soluble alumina, 1.5 kg. KOH, 1.6 kg.  $\text{Cr}_2\text{O}_3$ , and 2.7 l. 62% nitric acid are kneaded for about 40 minutes in a kneader lined with stainless steel. During the process, 7-9 l. of water are added. The plastic mass is extruded and then formed into spheres on a special stainless steel machine. The spheres are dried at 150°C for 16 hours and then ignited at 450°C until nitrate-free.  $\text{K}_2\text{O}$  has proved to be the most suitable alkali for inclusion in this catalyst.

15. Polymerisation Catalyst.

Composition:	SiO <sub>2</sub>	6.45%
	Al <sub>2</sub> O <sub>3</sub>	0.30%
	Fe <sub>2</sub> O <sub>3</sub>	0.28%
	CaO	0.71%
	MgO	11.09%
	SO <sub>3</sub>	0.1%
	Na <sub>2</sub> O	0.09%
	Total	P <sub>2</sub> O <sub>5</sub> 65.73%
	Free	H <sub>3</sub> PO <sub>4</sub> 26.75%
		H <sub>2</sub> O 1.23%

46 kg. of phosphoric acid (1.698 gravity, 84% analysis 62.44% P<sub>2</sub>O<sub>5</sub> + 2% H<sub>3</sub>PO<sub>4</sub>) is poured into a 150 l. steel (V4A) pot, and a suspension of 5.55 kg. magnesia<sup>‡</sup> in 10 l. H<sub>2</sub>O is slowly added to the phosphoric acid. This is followed by rapid addition at 80°C of 3.32 kg. of kieselgu (13% volatile matter content) suspended in 13 l. H<sub>2</sub>O. To this is further added 9 kg. of catalyst powder from a previous preparation which is wetted with 9 l. H<sub>2</sub>O. The total water content is 36 l., 4 l. having been used to wash out the charging vessels. The mass is stirred and kept at 84-112°C for 22-27 hours. The viscous mass is then poured on aluminium trays and dried at 120°C under a low vacuum (40-70 mm.). The catalyst is then cut into cubes and dried for an additional 46 hours at about 120°C. The total weight of the recovered material is about 52 kg. The cubes have a crushing strength of 7-13 kg/cm<sup>2</sup> and an apparent density of 0.8.

16. 6752 : Catalytic Cracking Catalyst.

Composition:	Al <sub>2</sub> O <sub>3</sub>	33%
	SiO <sub>2</sub>	67%

Commercial waterglass solution (26% SiO<sub>2</sub>) is treated with an excess of concentrated (76%) hydrochloric acid to form a sol without gel precipitation. To this

<sup>‡</sup> Obtained from "Zillertaler Magnesitwerke", the magnesia had the following composition:

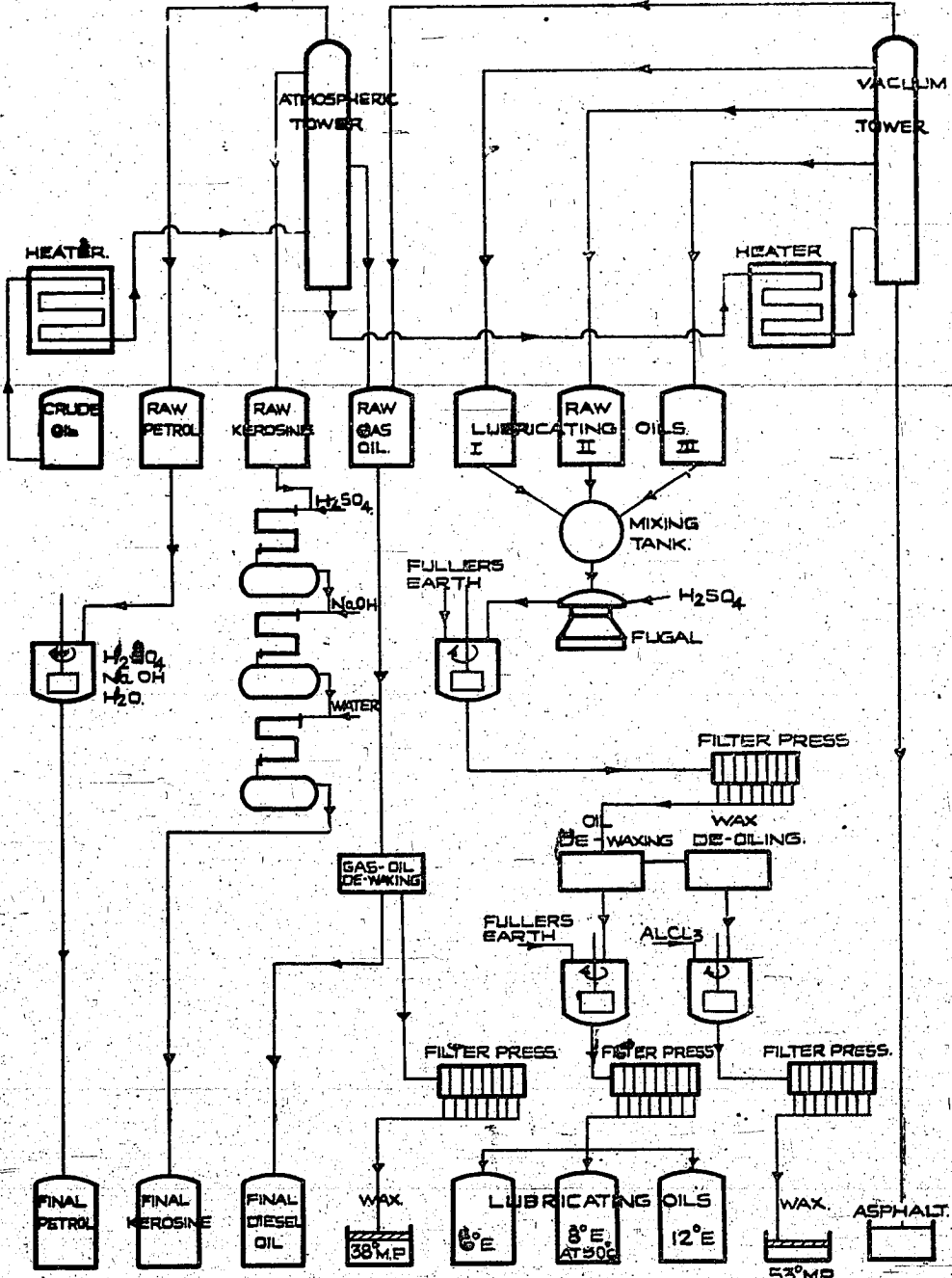
CaO	2.7%
Al <sub>2</sub> O <sub>3</sub> + Fe <sub>2</sub> O <sub>3</sub>	1%
K <sub>2</sub> O	0.15%
Na <sub>2</sub> O	traces
Cl	0.036%
SO <sub>3</sub>	1.9%
MgO	87.6%
H <sub>2</sub> O	6.21%
SO <sub>2</sub>	0.7%

~~SiO<sub>2</sub>-sol~~ aluminium nitrate solution is added in proportion to the desired final composition of catalyst. The acidic SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> solution is precipitated at 90°C and a pH of 5.5-6.0 (antimony electrode) by continuously adding small amounts of ammonia solution. The precipitate is filtered and washed with hot water until free from alkali and chloride. The filter cake is then dried at 110°C, powdered, pelleted, and activated in the presence of air by heating at 450° (2 hours to 450°, 6 hours at 450°).

This catalyst is less sensitive to steam and temperature than are catalysts based on Fuller's earth.

The catalyst can be used at temperatures up to 650°C; but loses all activity on heating to 800°C. Catalyst based on Fuller's earth can be used only up to 550°C.

**FIGURE XVII.**  
**OIL REFINERY - GPPAU.**



There was no commercial production of synthetic lubricating oil at Ludwigshafen, but 30-50 tons/day of crude oil was brought in from Brücksel, near Karlsruhe, and was subjected to conventional refining to products including lube oils. The plant capacity is 500 barrels of crude oil per day. A flow diagram of the plant is attached as Fig. XVIII.

The crude oil is distilled in a two column atmospheric-vacuum tube still provided with two side stream draw-offs on the atmospheric tower and three draw-offs on the vacuum tower.

Straight-run gasoline is taken overhead on the atmospheric tower, treated with sulphuric acid, neutralized with caustic soda and water-washed. Kerosene is taken off the upper draw-off on the atmospheric tower, treated with sulphuric acid, neutralized and water-washed. Light gas oil is taken off the lower draw-off on the atmospheric tower. The reduced crude from the bottom of the atmospheric tower passes through a second fired heater to the vacuum tower.

Heavy gas oil is taken overhead in the vacuum tower. The light and heavy gas oil is mixed and then dewaxed to produce diesel oil.

Lubricating oil cuts are taken off the three side stream draw-offs on the vacuum tower. Asphalt is made as a bottoms product.

The yields were as follows:

Straight Run Gasoline	4.0% by vol.
Kerosene	21.0%
Atmos. Gas Oil	12.6%
Vacuum Gas Oil	8.4%
Light Lube Oil	21.0%
Med. Lube Oil	21.0%
Heavy Lube Oil	3.0%
Asphalt	9.0%

Proper proportions of the three lube cuts are mixed to produce three grades of lubricating oils. The oil, after mixing for the proper viscosity, is first treated with sulphuric acid, using a centrifuge to separate the sludge, and then with clay. The clay is filtered out in a filter press and the oil passed to a solvent dewaxing plant.

The dewaxing plant is a "Barisol" type plant employing centrifuges for the separation of the wax. Ethylene dichloride is used as the solvent, but it was reported that butyl alcohol was to be used.

34.

Following the dewaxing step, the oil is again treated with clay, the clay being removed in a filter press.

The wax from the dewaxing plant is treated with aluminium chloride in an agitator, filtered and moulded into cakes.

Three grades of lubricating oil were produced. The viscosities of the three oils were 6°E, 8°E, and 16°E.

The I.C. have continued research on this process during the war, partly in the hope of achieving some important improvement which might give them an entry into this side of the synthetic fuel business and partly because of the interest in certain Fischer products as chemical raw materials, e.g. Kogasin fractions for carboxylic acids and synthetic soaps.

At Ludwigshafen one senior man - Dr. Michael and two or three juniors were engaged on this work. Up to 1940 the main objective was an improved quality of petrol, using medium pressure and high space velocity of reactants over an iron catalyst. Carbon formation on the catalyst was the chief trouble. Periodic revivification with air was not entirely satisfactory because this had no effect on carbon combined with the catalyst as iron carbide. Revivification with oxygen introduced the danger of melting the iron. The best catalyst life achieved in a 500 mm. diam. pilot converter was 2 months. In these pilot plant experiments the catalyst was removed from the converter for revivification and it was intended that any large scale plant would work on some sort of moving catalyst bed principle. The best quality petrol product obtained with this process had an octane number of 75-78 motor method.

Michael failed to have his ideas accepted for any large scale project and, after 1940, shifted his attention to higher molecular weight products particularly olefines. Liquid phase reaction conditions were employed using a finely divided iron catalyst in suspension in the reactants. The catalyst was made by suspending finely ground iron oxide in recycle Fischer Tropsch product and reducing it with hydrogen. Potash was also added to the suspension to the extent of 1-2% on the iron. The catalyst input was said to be 250 mgs. Iron/M<sup>3</sup> of oil product leaving the reaction. A 500 mm. diameter hydrogenation converter was converted for trial of this process at Ludwigshafen. With a reaction volume of 1½ M<sup>3</sup>, 520 Kgs/day of crude product were made. Reaction temperature was kept as low as possible but it was not found feasible to get below 450°C. The crude product consisted of:

- 10% C<sub>2</sub>-C<sub>4</sub> hydrocarbons
- 30 - 40% gasoline.
- 30 - 45% Diesel oil.
- 15 - 20% wax.

Two thirds of the wax boiled above 450°C under a high vacuum, and one third of it had a melting point above 100°C. The wax contained 2-4% O<sub>2</sub>. It was suitable for shoe polish etc., but for most purposes it had to be hydrogenated before it was of satisfactory quality.



The Diesel oil contained 30-35% unsats and had a Cetane number of 70.

The above sketchy information was obtained hurriedly from Dr. Pier and Dr. Donath. Dr. Michael himself was interrogated by the U.S. Navy team (Messrs. Spaight and Reichl) who may have a much more complete story.

Additional information was obtained at Heidelberg during a later visit by W.A. Horne, in early July. According to the information then received, the process differs in several essentials from that described above. No attempt has therefore been made to reconcile the two versions and the information obtained on the later visit is given in its entirety below:-

#### Michael Process.

This process involves the conversion of carbon monoxide and hydrogen to a mixture of hydrocarbons and alcohols. It has been carried out in two types of equipment: fixed bed catalyst and suspended catalyst.

The first method is similar to that used in the Synol process at Leuna. The catalyst bed in the largest reactor studied, was 2 metres in diam. and 1 metre high, containing a solid bed (no internal cooling tubes) of fused-iron ammonia catalyst in the form of 1 cm. cubes or lumps. The temperature was controlled to a 2-3°C rise by extremely high gas recycle rates and low conversions per pass.

The temperature of operation is 280 to 320°C, with a gas recycle of approximately 100 volumes per vol. of fresh carbon monoxide and hydrogen. The linear velocity of the gas through the reactor should be at least 1 metre per second for proper operation. The fresh charge gas ratio is 4 CO to 5 H<sub>2</sub>. The ratio of hydrogen to carbon monoxide in the recycle gas is quite high, and this provision accounts for the low carbonyl formation. The gas composition corresponds to approximately 10 to 12 atmospheres partial pressure of hydrogen, 2 to 3 atmospheres partial pressure of carbon monoxide, and 5 to 7 atmospheres partial pressure of residual gas, consisting of carbon dioxide, nitrogen, methane and uncondensed higher hydrocarbons.

The process is operated in two stages, each with recycle, and with intermediate condensation and a carbon dioxide scrubbing tower between the stages. The conversion cited in an example of the operation was 91.5%, based on the pure gas. The yield of products based on one N cubic metre of 4CO : 5H<sub>2</sub> was as follows:

35 gms. of methane and ethane  
160 gms. of useful product.

The useful product consists of the following:

14 gms. of alcohols  
105 gms. of oil  
41 gms. of ethylene, propane-propene and butane-butens.

On distillation the oil yielded:

2 gms. of wax  
21 gms. of Diesel oil  
82 gms. of gasoline.

The gasoline fraction was stabilised and cut to 195°C end-point to yield 77 gms. of refined gasolines of 84 to 88 research-octane number, 50 - 60% boiling up to 100°C and 70 - 80% of unsaturated substances.

The second method of operation, the so-called "Schaum" or foam process, was carried out with the same catalyst suspended in a liquid phase with the gas blown through the suspension.

Very few data were available on this type of operation because experiments had not been satisfactory. The principal difficulty was the formation of high molecular weight products on the catalyst particles, which caused them to agglomerate and to settle from the reaction zone. Also the concentration of catalyst when suspended in the liquid medium was considerably less than for a corresponding fixed-bed gas phase operation.

In a comparison of the two methods of operation, the conversion per weight of catalyst was the same. Thus, the increased surface of the powdered catalyst was apparently balanced by the slower diffusion through the liquid phase and did not compensate for the higher concentration of catalyst in the large pieces which were used in the fixed-bed gas phase operation.

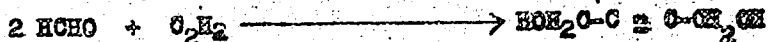
Introduction

Incidental to the study of processes related directly to the synthetic fuels, some information was obtained at Ludwigshafen on a number of miscellaneous chemical processes which may be of interest to the oil industry. These processes are listed and described below. No attempt was made, in view of the very limited amount of time and the secondary interest of these processes, to get complete details.

- (1) Condensation of acetylene with formaldehyde.
- (2) Hydrogenation of 2,3-butanediol-1,4 to 1,4-butane-diol.
- (3) Dehydration of 1,4-butanediol to tetrahydrofuran and butadiene.
- (4) Ethylbenzene and styrene.
- (5) Polyisobutylene (Oppanol).
- (6) Polyethylene.
- (7) Nitroparaffins.
- (8) Nylon and Koresin.
- (9) Catalyst preparations for miscellaneous processes.

(1) Condensation of Acetylene with Formaldehyde.

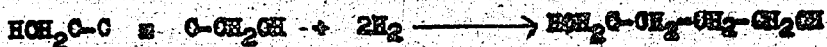
The reaction is that of adding formaldehyde to acetylene to produce 2,3-butanediol-1,4 according to the equation:



The reaction is the first step of the so-called Reppe process, and is carried out in the presence of one of two catalysts. According to the first operation, the catalyst is copper acetylide in water suspension. Approximately 1% of copper acetylide is present. The reaction takes place at 100-120°C. and 4-5 atm. pressure. The total catalyst volume is 30 cu.m. and 30 tons of butanediol is produced per day. The catalyst is prepared by passing acetylene over copper oxide in aqueous suspension at 70°C. According to the second method of operation, the catalyst employed consists of 1-3% bismuth and 10% copper on silica gel. The bismuth and copper are impregnated on the silica gel in the form of nitrates followed by drying and decomposition.

(2) Hydrogenation of 2,3-butanediol-1,4 to 1,4-butanediol.

This reaction is the second step of the Reppe process:

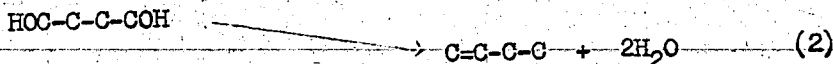
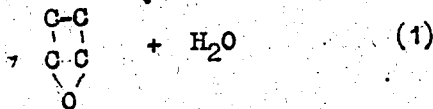


and is carried <sup>out</sup> at 200 atm. pressure and "low" temperatures, in the presence of a catalyst which is prepared as follows:

Silica gel, 4 mm. granules, is impregnated twice with a nickel-copper-manganese nitrates solution. The total concentration of the nitrates in the impregnating solution is 12-14% based on the metals. The ratio of the various nitrates is such as to give, in the final catalyst, 15% Ni, 5% Cu and 1% Mn. After each impregnation the catalyst is dried at 100°C. Finally, the catalyst is dried in a muffle furnace at 450°C until there is no further evolution of nitrogen oxides.

(3) Dehydration of 1,4-butanediol to tetrahydrofuran and butadiene.

The dehydration of 1,4-butanediol can be carried out according to the following equations:



To effect reaction (1), the diol in 30% water solution is treated at 300°C and 100 atms. pressure with a liquid phosphoric acid catalyst. To make butadiene, according to reaction (2), the diol is passed over a sodium acid phosphate catalyst at 280°C, and atmospheric pressure (vapour phase reaction). The catalyst is actually a mixture of sodium acid phosphates, the major constituent being  $\text{NaH}_2\text{PO}_4$ . This is deposited on carbon, so that the sodium acid phosphate concentration on the catalyst is 40%. The catalyst life is approximately 4 weeks, the changeover requiring 1-2 days. The yield of butadiene is 94% of the theoretical. In some cases, tetrahydrofuran has been added to the diol and the mixture then dehydrated to butadiene. It is said that tetrahydrofuran, being a heat-stable compound, can be used as a heat carrying medium for the less stable diol.

(4) Production of ethylbenzene and styrene.

Ethylbenzene is manufactured from ethylene and benzene using aluminium chloride as a catalyst. There are two reactors, their dimensions are 1 metre ID and 6 metres high. The production of ethylbenzene is 500 tons per month. The reaction is carried out at 80°C, fresh aluminium chloride, recycle sludge and benzene being introduced at the top of the reactor while ethylene is pumped in at the base of the reactor. The product is removed from the bottom, the sludge is separated from the hydrocarbon layer and the latter is fractionated. The reaction product contains 60% unreacted benzene and 40% alkylbenzenes. The ratio of ethylbenzene to higher ethylbenzenes in the converted material is 4 to 1. The higher ethylbenzenes fraction is recirculated together with fresh benzene to produce more ethylbenzene by the disproportionation reaction. The conversion efficiency to ethylbenzene is 90%. The consumption of aluminium chloride is 5-10% by wt. of the ethylbenzene produced.

The ethylbenzene produced is dehydrogenated to styrene at 600°C. and atmospheric pressure in the presence of steam. The weight ratio of ethylbenzene to steam is 5 to 1. Each reactor contains 20 tubes. The catalyst is prepared as follows:

The following components -

- (1) 204 kg. of ZnO
- (2) 12.5 kg. of CaO
- (3) 24.6 kg. of Al(OH)<sub>3</sub>
- (4) 7.5 kg. of K<sub>2</sub>CrO<sub>4</sub>
- (5) 7.5 kg. of K<sub>2</sub>SO<sub>4</sub>
- (6) 64 kg. of H<sub>2</sub>O

are mixed together in the form of a homogeneous paste and extruded. The extruded material is dried at 100°C. for 12-24 hours followed by heating to 450°C. in air for 8 hours. The finished catalyst is screened to 4-5 mm. particle size. The zinc oxide used in the preparation is made from zinc sulphate and sodium carbonate, the precipitate is washed free of electrolytes and calcined at 450°C. The aluminum hydroxide is prepared from sodium aluminate solution (8-10% Al<sub>2</sub>O<sub>3</sub> in solution) to which is added nitric acid (30-40%), followed by washing of the precipitate free of electrolytes. The catalyst is regenerated every few months.

#### (5) Production of polyisobutylene (Oppanol) and isooctane.

The source of isobutylene at Ludwigshafen was the dehydration of isobutyl alcohol. This was done by passing isobutyl alcohol over alumina at 330-350°C. and atmospheric pressure. The yield of isobutylene was 95% of theoretical; the catalyst life was 3-4 months. The dehydration was apparently carried out in two stages; the first stage, where the reaction conditions were less severe, produced purer isobutylene than the second stage. The polyisobutylene process required very pure isobutylene and, therefore, the first stage was used for the polyisobutylene production. The total production of isobutylene was 35 tons per day.

The Oppanol process is carried out using boron trifluoride as a catalyst. The reaction takes place at low temperatures using ethylene as the temperature controlling medium. The ethylene is mixed with the isobutylene, but the former does not enter into the reaction. By maintaining a constant pressure in the reactor, the ethylene is refluxed at a constant temperature. The molecular weight of the Oppanol is 100,000-200,000 and it is used for insulating equipment etc. The cost of the finished oppanol is 3-5 RM. per kilogram. No further details of the process have been obtained.

The manufacture of isooctane, which was then converted to isooctane, was formerly carried out on a minor scale at Ludwigshafen, but has been completely suspended during the last 12 months. The process is described in section VB(i).

### (6) Production of polyethylene.

Two types of polyethylene were made at Ludwigshafen: Lupolen A, having a molecular weight of 2,000-3,000 and a melting point of 110°C, and Lupolen H with a molecular weight of 15-20,000. Lupolen A is a hard wax and has been made to the extent of 20 tons per month, while the production of Lupolen H was 5-7 tons/month. The process for the manufacture of Lupolen A has been developed at Ludwigshafen and later used on a larger scale at Zweckel. The following is the method of manufacture of Lupolen A:

The apparatus consists of a preheater, reaction coils immersed in an oil bath, a separator, a distilling column and a silica gel tower. A mixture of methanol and benzoyl peroxide goes through the preheater and is mixed with a stream of ethylene before it reaches the reaction coils. The weight ratio of methanol to ethylene is 4 to 1, the benzoyl peroxide concentration being 3-5% based on the total mixture. The entire mixture passes through the oil-heated coils at 120-150°C and 200 atms. pressure using a residence time in the coils of 30 minutes. The conversion to wax in the coils is 20% per pass. The product from the coils enters a separator where the methanol-insoluble wax is removed as a lower layer and the methanol/benzoic acid layer goes to a distilling column where methanol is flashed off and then pumped back to the preheater. The ethylene which flashes off in the separator is purified by silica gel, then recompressed and recycled to the reaction coils. As indicated above, an operating pressure of 200 atms. is employed; however, it has been stated that it is possible to use 60 atms.

The use of other solvents, such as benzol, produces polyethylene of a different molecular weight. With benzol, the molecular weight of the product is 3000, as compared to 15-20,000 with methanol. Lupolen A is used in combination with Oppanol for preventing cold flow of insulators and also finds applications as a wax and floor polish.

Lupolen H is made at 1500-2000 atms. pressure in the presence of oxygen.

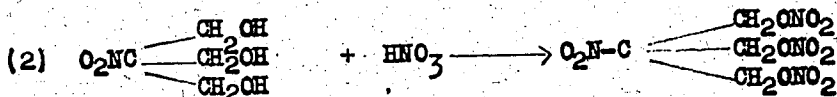
### (7) Production of Nitroparaffins.

The production of nitroparaffins at Ludwigshafen was directed toward their utilization as starting materials for explosives. Thus, nitromethane, nitroethane and nitropropane were condensed with formaldehyde in the presence of lime to give the corresponding polyalcohols. These were in turn esterified with nitric acid and the resulting nitrocompounds were used in anti-aircraft ammunition.

The nitration is carried out as follows:

A mixture of ethane and propane enters through a nozzle into a stainless steel mixing chamber. 60% conc. nitric acid is also supplied

through a nozzle into the mixer, the latter being maintained at 200°C. From the mixer the gases enter a stainless steel coil which is maintained at a temperature of 400°C. The coil contains no catalyst and the reaction time in the coil is 2 minutes. After leaving the coil, the reaction products are cooled and pass to a separator. The unconverted gas is recycled to the mixer. The conversion to nitro-paraffins per pass is 20-25% and a 20-25% loss is incurred by oxidation. The nitroparaffins produced are distilled in glass columns. The products obtained were then reacted according to the following equations:



### (8) Production of Nylon and Koresin.

The production of "Igamid A" (hexamethylene adipate polycondensation product-nylon) at Ludwigshafen amounted to 50 tons a month; Igamid B (aminocaproic acid) was produced to the extent of 200 tons per month. Both Igamids A and B are insoluble in alcohol, while a mixture of 60% A and 40% B is soluble.

Igamid B is produced by hydrogenation of phenol to cyclohexanol using a nickel-on-kieselguhr catalyst at 200°C. The cyclohexanol is dehydrogenated to cyclohexanone over copper spirals at 250°C. Cyclohexanone is converted by the use of hydroxylamine to cyclohexanone oxime, the latter upon treatment with sulfuric acid undergoes a Beckmann rearrangement to the lactam. The latter, in 70% water solution, is heated to 270°C. in a large autoclave under 16 atms. pressure until all the water is evaporated. It is important to maintain an atmosphere of pure nitrogen (0.003% impurities) above the melt during the heating, otherwise the product darkens in colour. The heating is done by steam at 100 atms. for 5 hours, the charge in the autoclave being 2 tons. The melt is then extruded under water and the solid is ground in the wet state to chips (5 mm. size) and then dried.

Igamid A is prepared by hydrogenating phenol to cyclohexanol followed by oxidation of the latter to adipic acid. The oxidation is carried out by means of 65-70% nitric acid using a water-cooled reactor. The yield of adipic acid is 60-70% of the theoretical. The adipic acid separates out on cooling and is crystallized from water. Adipic acid is then reacted with ammonia at 300°C, using a boron phosphate catalyst, to give pure adiponitrile in a 70% yield of the theoretical. The adiponitrile is then hydrogenated to hexamethylene diamine at 120-150°C., 200 atms. pressure in the presence of Raney cobalt catalyst. A three ton charge was hydrogenated within 5 hours in the presence of 3% Raney cobalt catalyst and 10-12% NH<sub>3</sub>. The yield of hexamethylene diamine is 85% of the theoretical. Finally, adipic acid in methanol

solution is added to a 20% hexamethylene diamine solution in methanol.

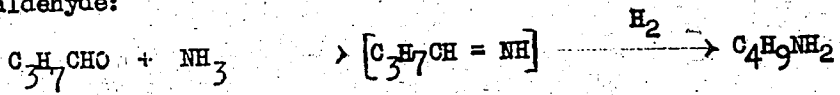
Koresin, a condensation product of para tertiary butyl phenol and acetylene was manufactured at Ludwigshafen to the extent of 100 tons/month. The reaction is carried out at 15-20 atms. pressure and 150-180°C. in the presence of zinc salt of a naphthenic acid. No further particulars on the catalyst or other details have been obtained.

(9) Miscellaneous chemicals and catalyst preparations.

(a) Ethylene oxide preparation at Ludwigshafen was carried out along conventional lines using hypochlorous acid etc.; the newer method using a silver catalyst for direct oxidation was studied in the laboratory. However, a large scale unit for the production of 500 tons of ethylene oxide per month was to be built at Zweckau. This plant was to employ the direct catalytic oxidation method.

(b) Catalyst preparations:

(1) Catalyst for the production of butylamine from butyrylaldehyde:



The catalyst is prepared as follows:

825 kg. of finely powdered Italian pumice is suspended in 3660 kg. of app. 8% solution of sodium carbonate. This suspension is mixed with a solution of 1275 kg. of nickel sulphate (cryst.) in 2500 litres of water. The mixing is done in a vessel which is previously filled with approximately 7 cu.m. of water at 50°C. The precipitation is carried out at 60°C. The addition requires about 12 hours and this is followed by stirring for 24 hours at the same temperature. The precipitate is then washed by decantation until the wash water is free of electrolytes. This is followed by filtration, using a filter press. The cake thus obtained weighs 3100-3200 kg. and contains 75% water. (This amount of water appears to be somewhat high considering the original input of pumice and the amount of basic nickel carbonate produced on precipitation). 100 kg. of the paste are used to incorporate the desired amount of chromia by treating it in a rotating drum with a solution made up as follows: 1 kg. of water, 1 kg. of chromium trioxide and 1 kg. of 25% ammonium hydroxide. The impregnated mass is dried at 100°C. and ground to dust on a mill.

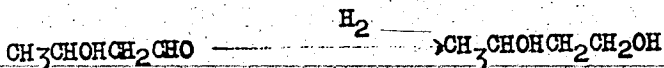
(2) Catalyst PH-86 for the preparation of fatty alcohols from fats.

Preparation: -



5200 kg. of a copper nitrate solution containing about 12% copper is added at room temperature, to about 2000 kg. of a 6% sodium carbonate. After the precipitation has been completed, the precipitate is washed by decantation until the wash water is free of electrolytes. This requires about 10-15 washings with 15 cu.m. of water per each washing. This is followed by the addition of 44 kg. of barium nitrate, 42 kg. of zinc nitrate and 62 kg. of chromium nitrate to the suspended basic copper carbonate. The precipitation is carried out using a solution of 176 kg. of sodium carbonate in 1760 litres of water. Upon the completion of the precipitation, the precipitate is washed by decantation until the wash water is free of electrolytes. This requires about the same number of washes as the washing of the basic copper carbonate. The precipitate then goes to a filter press and the cake is dried at 100°C. The dried catalyst is powdered.

(3) Catalyst 4711 for the hydrogenation of aldol to 1,3-butylene glycol.



The catalyst is prepared by impregnating silica gel, 3-6 mm. particle size, with a copper nitrate-chromic acid solution. The impregnation is carried out twice and after each impregnation the catalyst is dried at about 100°C. The impregnating solution contains about 35% copper nitrate and a correspondingly smaller amount of chromic acid, so that the final catalyst contains 20% copper and approximately 1% Cr. After the second impregnation and drying, the catalyst is heated in a muffle furnace at 450°C. until there is no further evolution of nitrogen oxides. The resulting catalyst is screened to 1.5-3 mm. size.

It should be noted that this is one of a number of catalysts used for hydrogenation of acetaldo. In another preparation, silica gel is impregnated twice with a solution containing the calculated amount of nickel-copper-nitrate-chromic acid solution, the concentration of nitrates in the solution being about 35%. After each impregnation, the granules are dried at 100°C. and finally heated at 450°C. in a muffle furnace until there is no further evolution of nitrogen oxides. The resultant catalyst is screened to 1.5-3 mm. size. The final catalyst composition is 15% Ni, 5% Cu and 1% Cr, the rest being silica gel.

A. HEYDEBRECK

Heydebreck, referred to in black target lists as Blechhammer South, is a tremendously large new factory built and operated by the I.G. It commenced operations early in 1944 but full outputs were never achieved because of air raids, and erection of many parts of the plant was never completed. The following general information was obtained at Oppau from Dr. Saanksen (General Manager at Heydebreck), Dr. Muller Conradi and Dr. Schierenbeck.

The fundamental raw material for processes operated at Heydebreck was synthesis gas, (carbon monoxide and hydrogen), the greater part of which was to have been obtained from coke oven gas from the Upper Silesian grid system. As previously mentioned, the methane-oxygen process was used. Actually, a considerable amount of equipment for production of synthesis gas from coke was also installed and was used extensively for the early stages of operation of the Heydebreck plant.

(a) Higher Alcohols Synthesis - Iso-octane

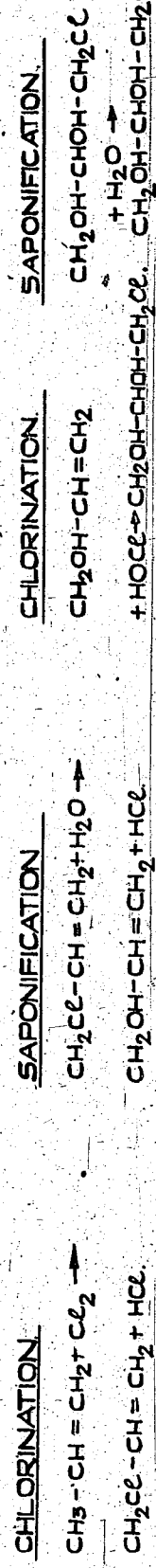
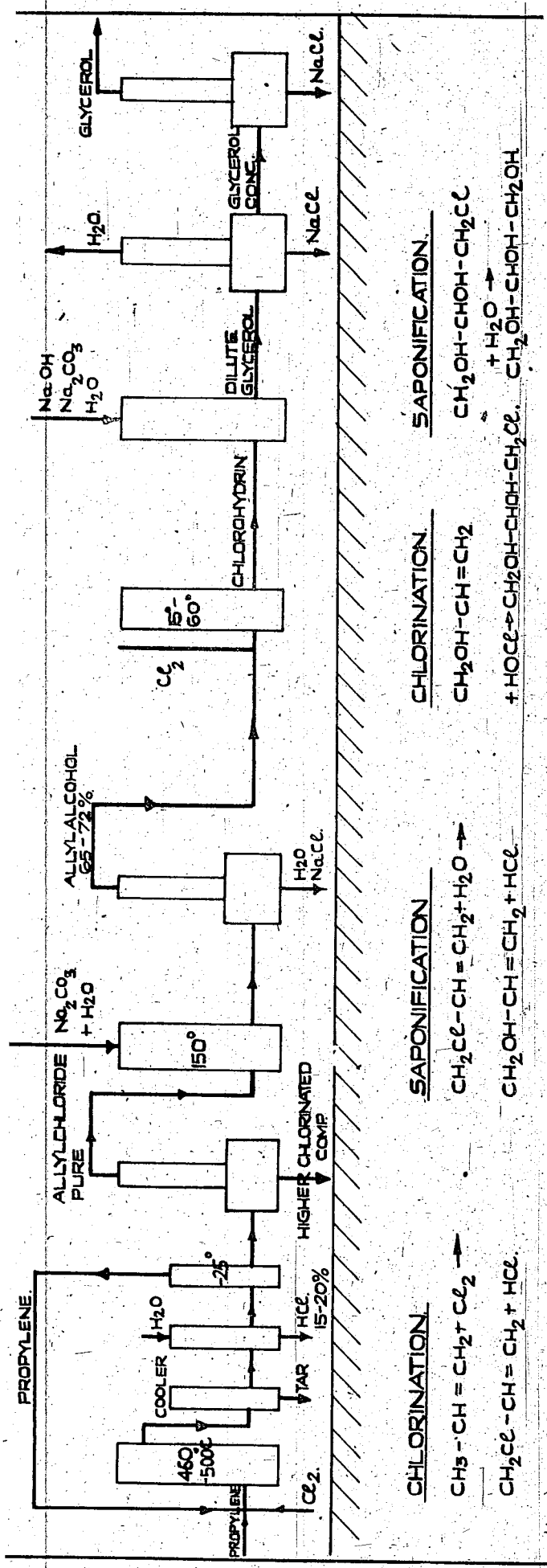
From the standpoint of synthetic fuels, the most important activity at Heydebreck was the higher alcohols synthesis. Thirteen units were planned, each unit having one converter 1,200 mm. dia. and 18 M long. Each unit had a capacity of 150 tons/day crude product of the average composition - methanol 57%, propyl alcohol 1-1.5%, isobutyl alcohol 12%, and higher alcohols 10%, the remainder being water. Methanol was recycled and the remaining products worked up as at Oppau. The catalyst employed was exactly the same as at Oppau. Only six of the units were put into operation.

The isobutanol from the higher alcohols synthesis was converted into iso-octane by dehydration, polymerisation of the resultant butylenes and hydrogenation of the final polymer, the operating conditions for these steps being as follows :-

1. Dehydration Catalyst-alumina, reaction temperature-330-360°C, pressure-atmospheric.
2. Polymerisation Catalyst-10% phosphoric acid on coke. (Note: This does not check on the other information which indicates that the polymerisation catalyst is a magnesium silico phosphate). Temperature 120-160°C, adjusted to catalyst activity; pressure-around 20 ats, adjusted to maintain liquid phase conditions.
3. Polymer Hydrogenation 300 ats. pressure, nickel tungsten sulphide catalyst (5615).

The full capacity for iso-octane was to have been about 50,000 tons/year but the maximum achieved was only half this figure.

FIG. XIX.  
PRODUCTION OF GLYCEROL.



45.

Alcohols of higher molecular weight than isobutyl alcohol, were hydrogenated over the same catalyst as was used for polymer hydrogenation in order to produce branched chain paraffin for use as aviation fuel components. The pressure employed was 300 atg., the reaction temperature 30-400°C. and the throughput was 2 M<sup>3</sup>/M<sup>3</sup> of catalyst per hour. The crude product was distilled before it was suitable for use as a fuel component. When cut to an end point of 160-170°C the distillate product had a C.F.R. motor octane No. of 64 clear or 82 when leaded with 0.12% by weight of tetra ethyl lead. Cut to an end point of 110°C the product had a clear octane No. of 78-79, rising to 99-100 leaded. The planned capacity for this product was 30-40,000 tons/yr. dependent on the end point. Again, actual output was only 50% of this figure.

The cost of isobutyl or other higher alcohols fractions was said to be of the order of 80 pfg/kg including capital charges. It would therefore appear that the cost of iso-octane or 110° end point paraffin from higher alcohols hydrogenation must have been about 1,200 marks/ton.

The propyl alcohol from the higher alcohols synthesis was used for synthesis of glycerine by the process shown diagrammatically in Fig. XIX. No complete yield data were obtained for this process but it was stated that 1 ton of propylene gives approximately 1 ton of glycerol. The planned output of the glycerol plant was 6,000 tons/yr. but actual production never exceeded a 2,000 tons/year rate.

(b) Methanol

Heydebreck has three methanol stalls each with a single converter 800 mm. dia., 12 m. long and with a catalyst capacity of slightly under 3 M<sup>3</sup>. The catalyst used was the same as at Oppau, and it had a six months life at Heydebreck. The methanol output per unit, averaged over a six months period, was 140-150 tons/day, compared with 70-80 tons/day obtained in Oppau or Leuna units with the same catalyst volume. The improvement in output is due to the use at Heydebreck of

1. 300 atg. pressure.
2. A CO content of 18-20% in circulating gas.
3. Converters containing beds of catalyst with intermediate mixing and cooling chambers.
4. Higher efficiency interchangers.

Shortly after the start up of the plant in 1944, the methanol output was at least 80,000 tons/year. The impression was gained that by July 1944 an output corresponding to 120,000 tons/year was being obtained.

Dr. Muller Conradi stated that the total methanol production in Germany in 1944 was approximately 450,000 tons made up as follows :-

Leuna	200,000
Heydebreck	80,000

Waldenburg  
Oppau  
Anschwits

80,000  
50,000  
60,000

46.

In established plants the cost of methanol averaged 15 pf./kg., this cost being made up of 9 pf. for synthesis gas, 2 pf. plant costs and 4 pf. capital charges. In the case of the newer plants the cost was of the order of 20 pf./kg., this allowing for a high rate of obsolescence. The capital cost per ten year of methanol in the newer plants was about 400 marks.

Practically all the methanol produced in Germany was converted into formaldehyde. Most of this was used for the manufacture of the explosive "Hexagon" although considerable quantities were condensed with acetylene to make 1,4-butene-diol for buna rubber.

(c) Ammonia

The capacity planned for Heydebreck was 200,000 tons/year. Only two stalls were actually operated, the total output being at the rate of 50-60 tons/day. These two stalls were of the old design and consisted of a single converter 800 mm. dia. and 12 M. long. It was intended that the later ammonia stalls should have a 1,200 mm. x 18 M. reaction vessel with catalyst beds and intermediate mixing and cooling chambers.

(d) Chlorine<sup>by</sup> Electrolysis

A plant for the electrolysis of 17,000 tons/year of salt was in operation. The chlorine was used in the glycerine process.

(e) Fatty Acids

These were being made at the rate of 20,000 tons/year by oxidation of paraffin wax. The paraffin wax was melted in aluminium vessels, catalyst in the form of a manganese soap was dissolved in the mass and air was blown in at a temperature of 80-90°C. The temperature was controlled by water coils and oxidation of each batch required 8-10 hours. The product was treated with soda solution, the resultant two layers were separated and the aqueous layer was subjected to steam distillation to remove hydrocarbons. The fatty acids were used in the form of sodium salts for soap.

(f) Kaurit

This is a urea formaldehyde resin which was sold as an adhesive for plywood. It was produced at Heydebreck at the rate of 20,000 tons/year using urea imported from Oppau. It was intended that Heydebreck should eventually have its own urea plant.

(g) Other Projected Activities

It was intended to build the following additional plants at Heydebreck :-

- 47.
- (i) Oppanol 7,000 tons/year (no building or plant erection commenced).
  - (ii) Hydrogen peroxide 24,000 tons/year (buildings erected but no plant).
  - (iii) S.S.lub.oil. This is made by polymerisation of pure ethylene (see Leuna report). A plant for the production of 22,000 tons/year was complete but was never operated. The ethylene was to be made partly by oxygen cracking of ethane pipelined from Blechhammer North, the remainder being separated from coke oven gas by Linde treatment.
  - (iv) Tetra Ethyl Lead. It was proposed to make 2,400 tons/year and the necessary buildings had been erected.
  - (v) Sodium Sulphide. It was intended to make 1,800 tons/year sodium sulphide which was required as a catalyst in coal hydrogenation plants. (No building or plant erection had commenced).
  - (vi) Formamide and Formaldehyde. A production of 1,500 tons/month of formamide and 3,000 tons/month of formaldehyde was intended but no work had started on the plant.
  - (vii) Concentrated Nitric Acid. A plant for 20,000 tons/month was projected.
  - (viii) Calcium Ammonium Nitrate. Designs were being prepared for a plant for 130,000 tons/year.

(h) Bomb Damage at Heydebreck

The first raid on Heydebreck was in June 1944 when the synthetic glycerine plant was the only one to be damaged. There was another attack in July 1944 when the isobutyl<sup>alcohol</sup> distillation plant, the synthesis gas production plant including gasholders, the boiler house and the salt electrolysis plant were fairly badly damaged. The entire plant was shut down for four weeks. The isobutyl alcohol, the iso-octane and the methanol plants had just been restarted at full capacity and the glycerine and synthetic lubricating oil units put on line at a considerably reduced output when they were again badly damaged by air attack. After July 1944, raids followed at regular intervals of approximately one month and no appreciable production was possible.

B. AUSCHWITZ

This factory like Heydebreck is owned and operated by the I.G. The following very limited information on the products and production capacities of the various Auschwitz plants was obtained from Dr. Miller Conradi and Dr. Schierenbeck during the second visit to Oppau. More detailed information could be obtained

from Dr. Durfeld (the managing director of Auschwitz), who, it is understood, is now at Leuna. 48.

Buna rubber	3,000 tons/yr. ex acetylene from carbide.
Polystyrene	Capacity not stated.
Iso-octane	25,000 tons/yr. ex iso-butyl alcohol.
Branch-chain paraffin hydrocarbons.	12,000 tons/yr. ex hydrogenation of alcohols higher than C <sub>4</sub> .
Methanol	125,000 tons/yr.
Chlorine	12,000 tons/yr.
Glycol	7,000 tons/yr.
Gasoline and motor benzol.	11,000 tons/yr. made from coal carbonisation gases and by distillation of tar.
Pitch	15,000 tons/yr. ex tar distillation.
Propyl alcohol	5,000 tons/yr. ex higher alcohol synthesis.
Ester lub. oil	4,000 tons/yr.

This is iso-butyl alcohol esterified with adipic acid. It is used as a cold starting lube oil, and has a pour point of about -70°C.

### C. PÖLITZ-STETTIN

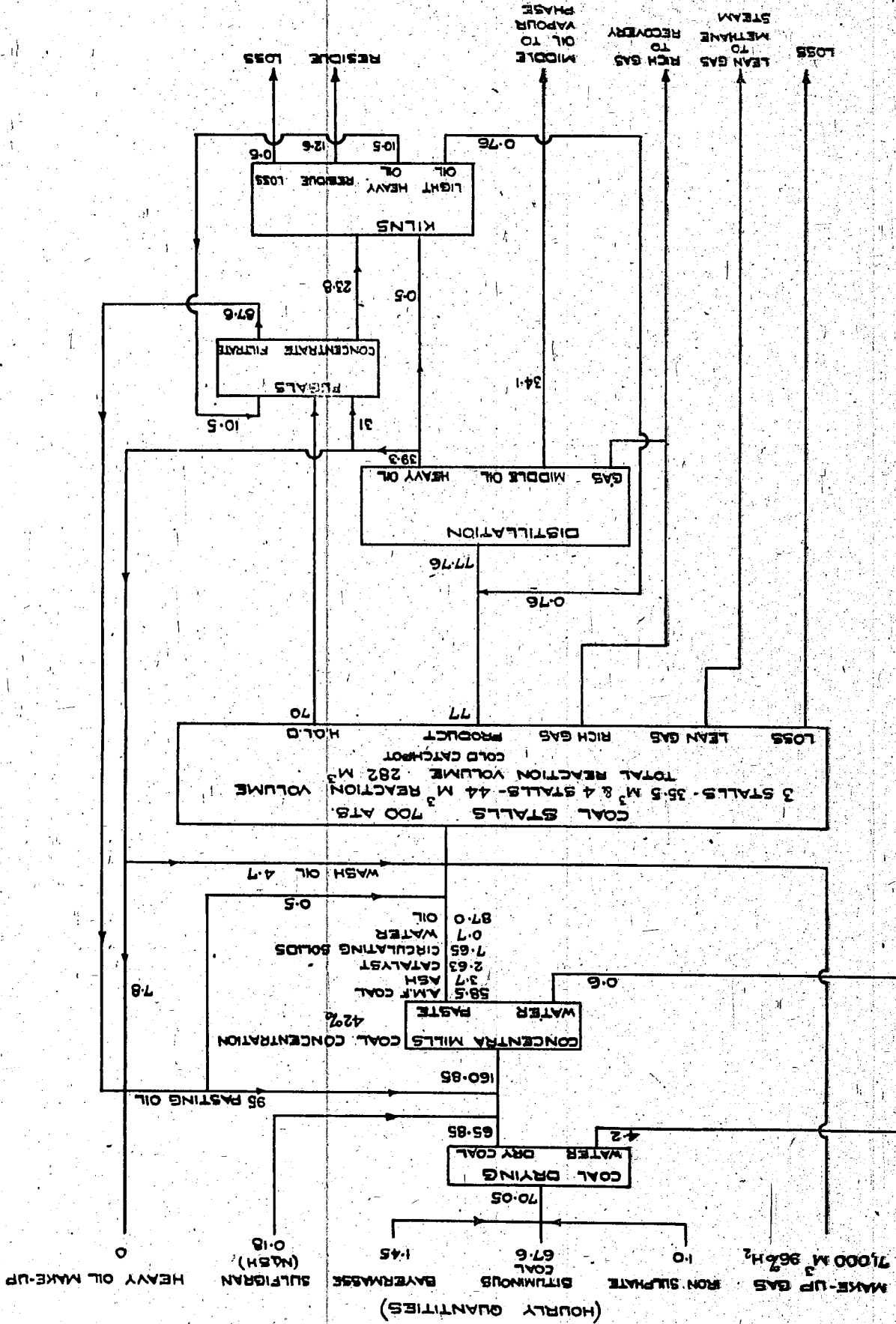
The following preliminary information was obtained by interrogation of Dr. Pier and Dr. Müller Conradi at Ludwigshafen/Oppau. A considerably more detailed account of Pölitz activities will be presented in another C.I.O.S. report following the interrogation of Dr. Wissel (chief chemist of the Hydrogenation Plant) by a U.S. team and the seizure of a very complete collection of plant documents.

The hydrogenation plant at Pölitz was originally planned to make 250,000 tons/yr. of motor gasoline from Upper Silesian coal, and a further 200,000 tons/yr. from cracked petroleum residues imported from Venezuela. It was planned to install six 700 atmospheres liquid phase hydrogenation stalls, two being designed purely as coal stalls, two as liquid phase stalls for petroleum cracked residue or tar and finally two capable of operation on either coal, tar or petroleum residues.

A tube and tank petroleum oil cracking plant has been built at Pölitz during the war, but its capacity is only 250,000 tons/yr. of crude oil. The original plan for Pölitz operation therefore had to be modified, and during the war, 4-5 stalls were normally in service for hydrogenation of Upper Silesian bituminous coal, one treated heavy petroleum residues (mainly uncracked) and another operated on bituminous coal tar or pitch. Pre-saturation of middle oils in the vapour phase has been carried out in three to four 300 ats. stalls, and the vapour phase splitting

FIGURE XX

POLITZ COAL HYDROGENATION LIQUID PHASE





# FIGURE XXI

## POLITZ

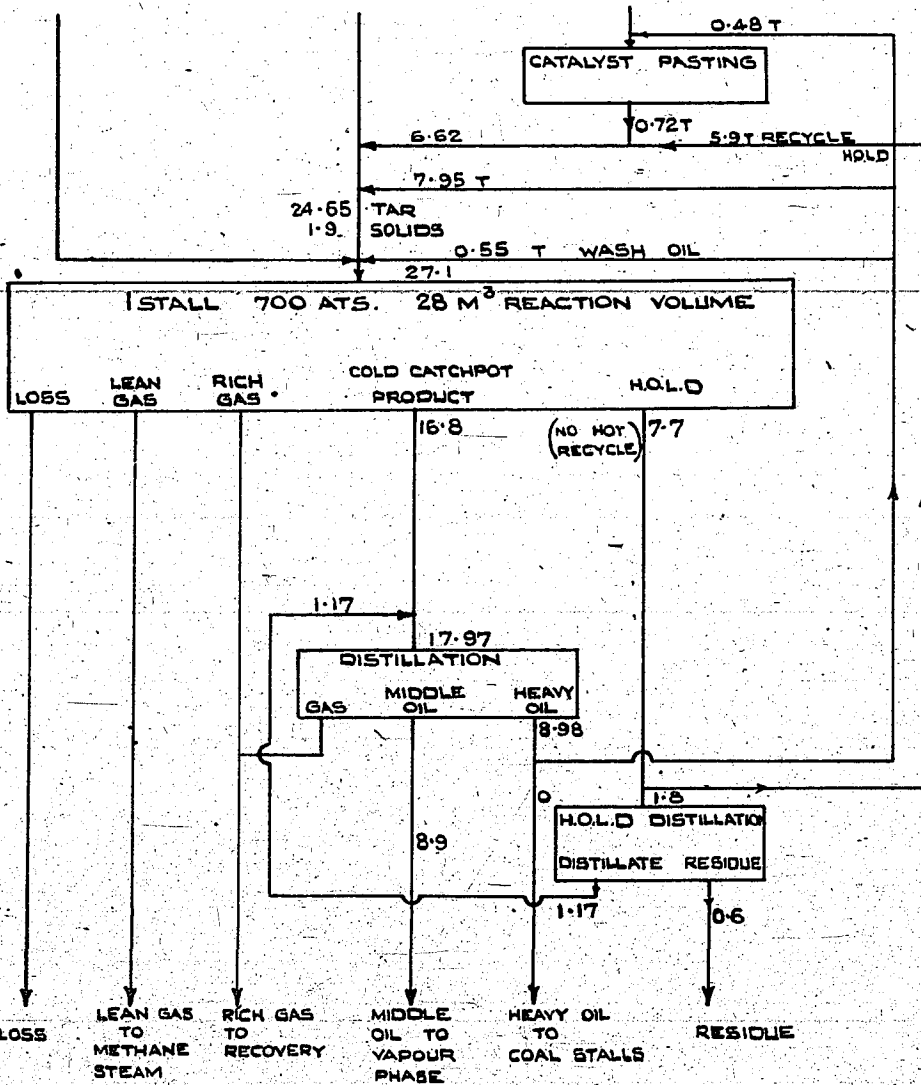
### LIQUID PHASE STALL ON PITCH

(HOURLY QUANTITIES)

MAKE-UP GAS  
14,000 M<sup>3</sup> 96% H<sub>2</sub>

PITCH  
12.0 T

CATALYST 10927  
0.24 TNE.



**FIGURE XXII**  
**PÖLITZ**

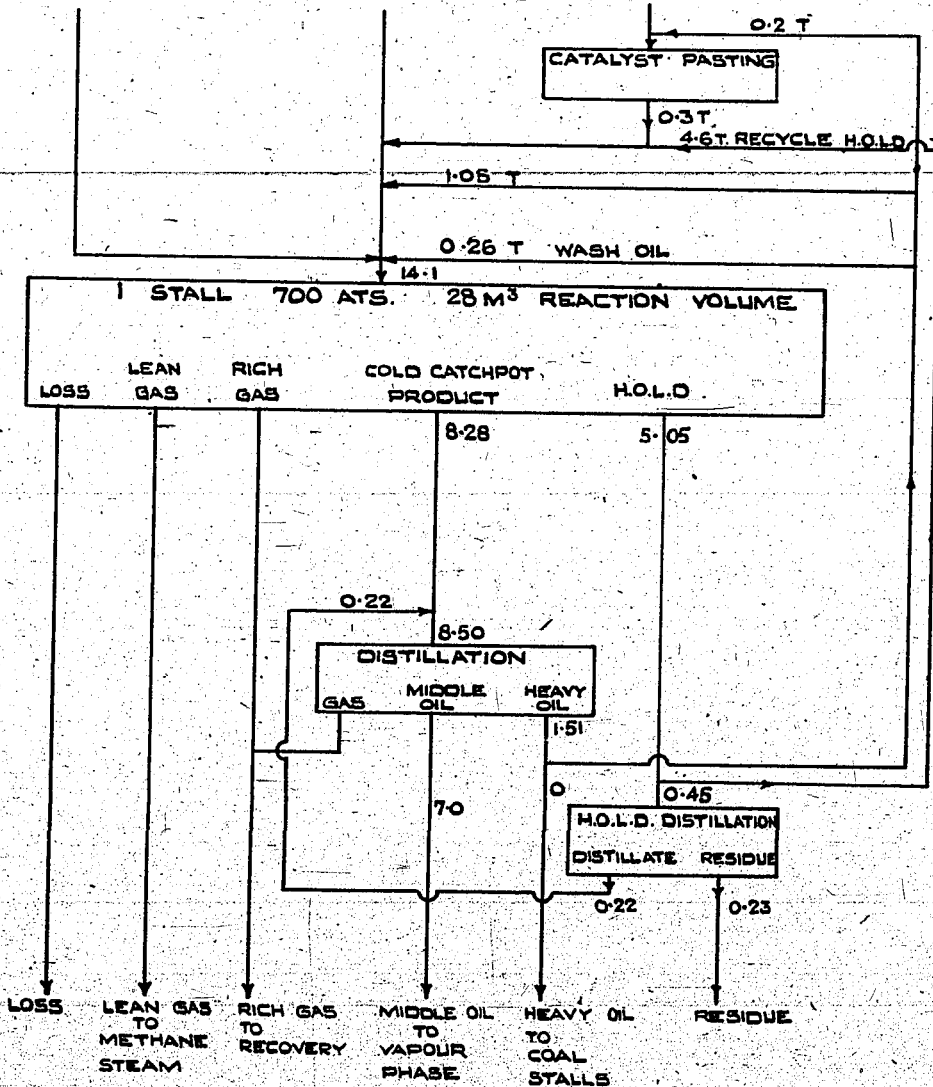
**LIQUID PHASE STALL ON NATURAL OIL RESIDUES.**

(HOURLY QUANTITIES)

MAKE-UP GAS  
4900 M<sup>3</sup> 96% H<sub>2</sub>

NATURAL OIL RESIDUES  
7.9 TNE

CATALYST K927  
0.1 TNE.



PÖLITZ

VAPOUR PHASE HYDROGENATION

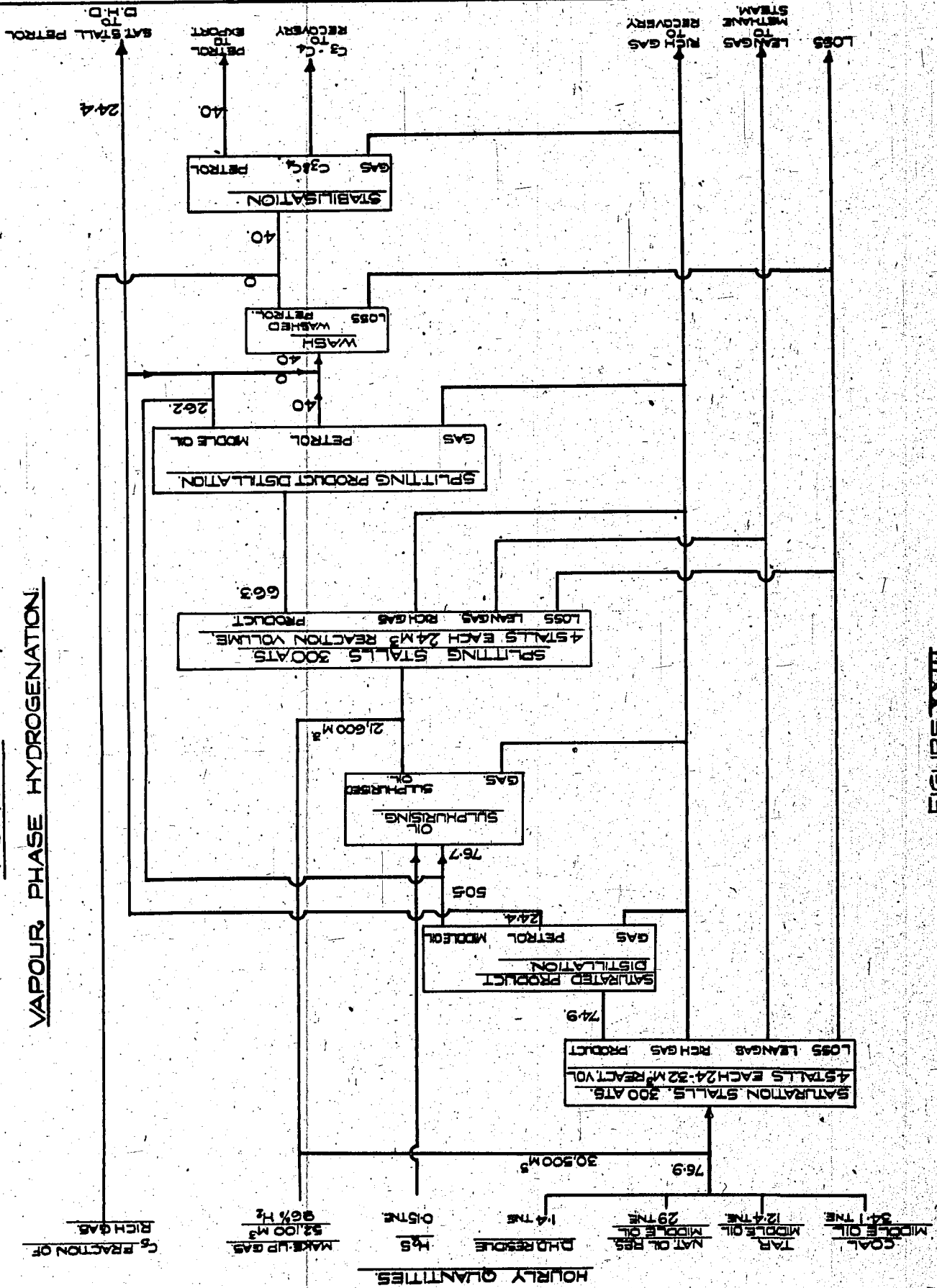


FIGURE XXII

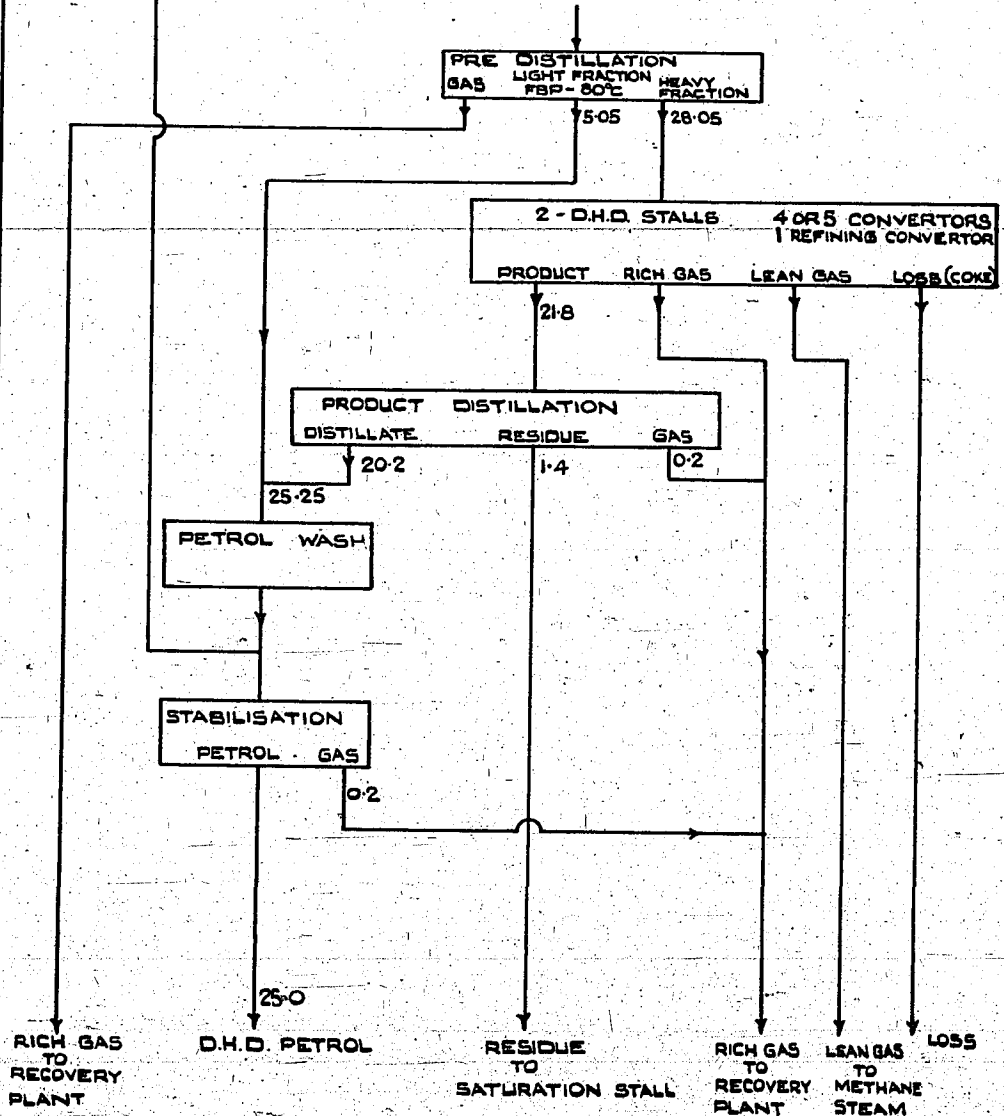
# FIGURE XXIV

## FOLITZ

### D.H.D. FLOWSHEET

C5 - FRACTION  
(FROM RICH GASES)

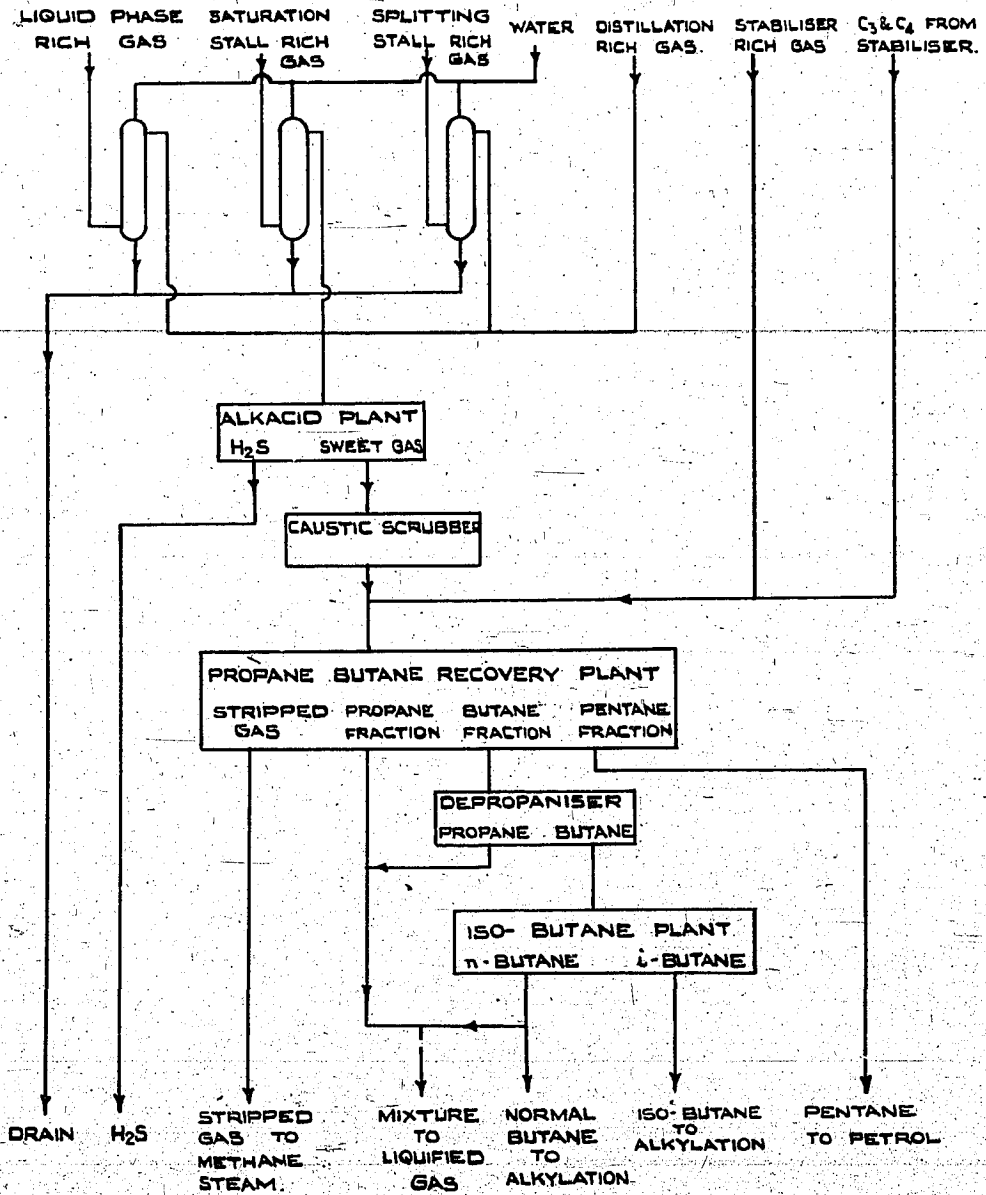
HYDROGENATION STALL PETROL 185°C FBP  
AND RUMANIAN AND HUNGARIAN PETROL 185°C FBP  
AN. PT. 47-49 NAT. OIL :: COAL OIL :: 1:2



# FIGURE XXV

## POLITZ

### RICH GAS FLOWSHEET



hydrogenation of saturated middle oils has been conducted in 4-5 stalls also operating at 300 atmospheres pressure.

The peak gasoline output reached at Pölitz during the war was roughly 600,000 tons/yr, the greater part of this being aviation base stock. This output included some 250,000 tons/yr. of D.H.D. gasoline made mainly from naphthas distilled from the crude vapour phase saturation product and from imported petroleum oil (Rumanian and Hungarian). The flowsheets (figures XX to XXV) prepared by Dr. Pier's staff illustrate the operation of the Pölitz plant. It should be borne in mind, however, that under war conditions there were considerable variations in the relative amounts of the various raw materials treated.

The interesting statement was made in connection with the 700 atmospheres liquid phase hydrogenation of pitch that it is beneficial to saturate the feed oil with  $H_2S$  (.3 to .4 by weight on the feed oil).

Hydrogen was made at Pölitz partly from coke water gas and partly from hydrogenation plant lean gases using the methane steam process. This process was substantially the same as that operated at Baton Rouge and at Billingham and appears to be the only large scale methane steam plant which has been installed in Germany. Pölitz did not employ the pressure water gas shift process.

Plant for dehydrogenation of butane and for production of Alkylate was installed at Pölitz and Alkylate production was stated to be about 5,000 tons/month.

Refined wax was cracked to olefines of  $C_5-C_{10}$  molecular weight range and these were polymerised to lubricating oil using Aluminium chloride as catalyst. The output of these synthetic lube oils at Pölitz was approximately 20,000 t/year.

Pölitz had a catalyst factory making 5058, 6434, 8376 and D.H.D. catalyst. This particular plant was very badly damaged by air raids.

The first raid on Pölitz was in August 1940 when the  $CO_2$  removal plant was hit and the whole factory put out of action for  $2\frac{1}{2}$  days. There was a second raid in October 1940 in which 30 tanks were destroyed and production was stopped for  $2\frac{1}{2}$  weeks. No more raids occurred until May 1944 after which it rapidly became impossible to operate the hydrogen plant with any appreciable output. In the early months of 1945 the only production of gasoline at Pölitz resulted from operation of the cracking plant and the use of the, D.H.D. units and the coal hydrogenation sludge ovens as improvised cracking units for crude petroleum.

FIG XXVI

LOCATION OF PLANT AT KINSEI.

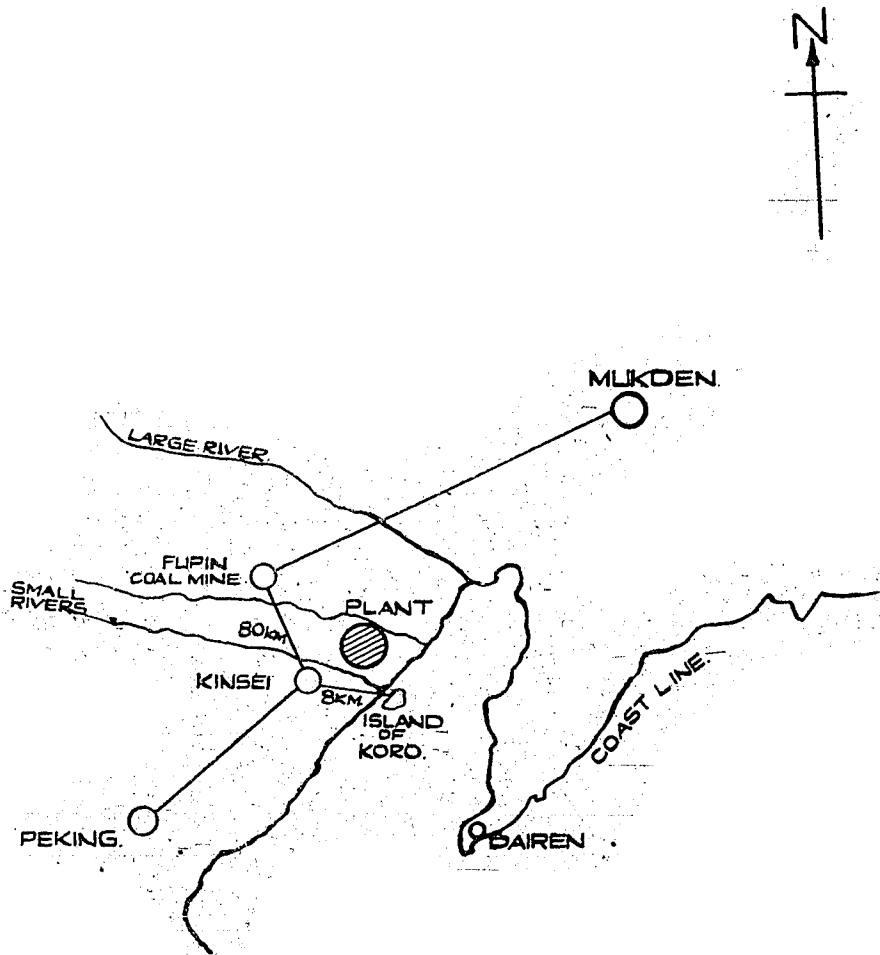


TABLE V  
HYDROGENATION OF UTIBUTI COAL

	1	2	2a	3
	100,000 M <sup>3</sup> = 73,000 t. Av. Petrol by direct Coal Hydrog.	100,000 M <sup>3</sup> = 73,000 t. Av. Petrol by combined coal & tar hydrogenation	128,000 M <sup>3</sup> = 93,000 t. Av. Petrol from coal and tar.	100,000 M <sup>3</sup> = 73,000 t. Av. Petrol from tar only.
<u>Raw Materials T/yr.</u>				
Coal (5% Ash, 2% wtr)	165,000	85,000	110,000	0
L.T. Coal Tar	0	54,000	68,000	107,000
Coal or coke for gas manufacture. (H <sub>2</sub> M <sup>3</sup> /hr)	180,000 (28,000)	120,000 (22,000)	160,000 (28,000)	85,000 (15,500)
<u>Energy requirements</u>				
Electricity KW.	28,000	21,000	28,000	16,000
Steam T/hr.	50	42	53	31
Water M <sup>3</sup> /hr.	10,500	9,000	11,500	6,500
Of which fresh water is M <sup>3</sup> /hr	1,600	1,300	1,600	1,000
Approx. coal or coke for energy prodn.	155,000	120,000	155,000	90,000
<u>Converters</u>				
Liquid Phase	5(1,200 mm)	4(1,200 mm)	5(1,200 mm)	2.5(1,000 mm)
Vapour Phase	4(1,000 mm)	4(1,000 mm)	6(1,000 mm)	4(1,000 mm)
<u>Carbonisation. (L.T)</u>				
Coal t/yr.	0	390,000	500,000	780,000
Tar t/yr.	0	54,000	68,000	107,000
Coke t/yr.	0	250,000	320,000	500,000
Coke in excess of that for comb. L.T. carbonation and hydrogenation. t/yr.	0	ca 0	ca 0	ca 325,000
<u>Total Coal. T/yr</u>	500,000	475,000	610,000	780,000



TABLE VI

List of Drawings handed to the Japanese Army.

A. LIQUID PHASE

1. Coal stall line diagram	N 3194-2
2. Arrangement of Liquid Phase converter. 1200 mm dia. x 18 M long.	N 954-1
3. Converter body. 1000mm dia. x 18 M long.	N 892-1
4. Converter body. 1200mm dia. x 18 M long.	N 890b-1
5. Arrangement of Interchanger.	N 1834-1
6. Interchanger Body. 600mm dia. x 18 M long.	N 2112c-2
7. Arrangement of Hot Catchpot.	N 939-1
8. Hot Catchpot and Neutralisation vessel Body. 1200 mm dia. x 9 M long.	N 1572d-1
9. Arrangement of Oil Washer.	N 1520-2
10. Washer Body. 1300mm dia. x 15 M long.	N 1036-2
11. Cold Catchpot without fittings. 1000mm dia. x 6 M long.	N 2105-2
12. Cold Catchpot with fittings. 1000mm dia. x 6 M long.	N 2241-2
13. Various vessels.	N 4759a-2 N 4760d-2
14. Gas Cooler	N 2368-2
15. Gas-fired Preheater.	L 2714-1
16. Paste Injector.	N 1013-1
17. Let-Down Engine.	N 598-1

B. VAPOUR PHASE

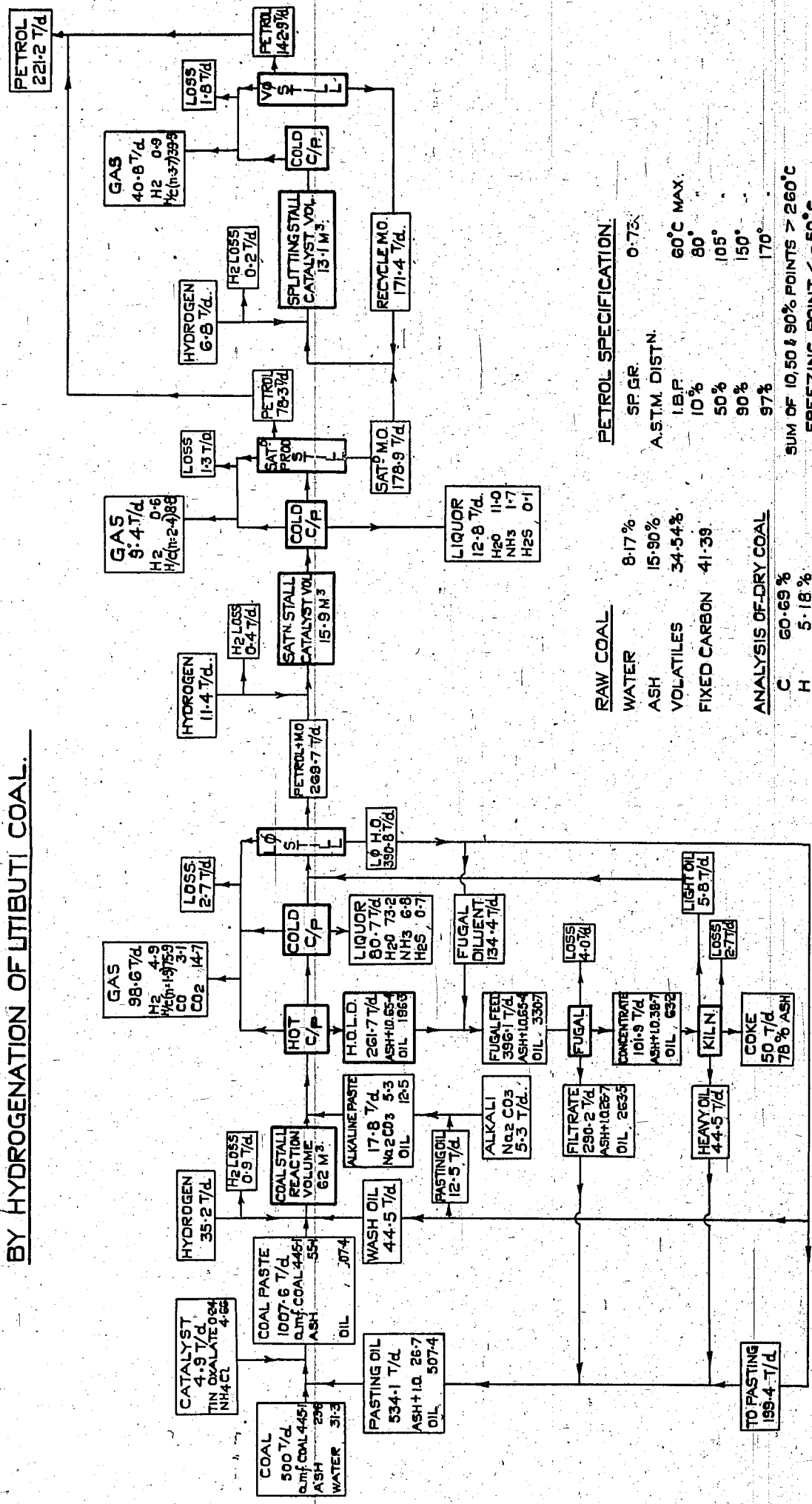
18. 6434 Stall line diagram.	N 5416a-2
19. 5058 Stall line diagram.	N 3108b-2
20. Arrangement of Vapour Phase Converter. 1000mm dia. x 18 M long.	N 972-1
21. Converter body. (Identical with item No.3)	N 892-1
22. Arrangement of Interchanger. (Identical with item 5)	N 1834-1
23. Interchanger body. (Identical with item no.6)	N 2112c-2
24. Cold Catchpot body without fittings. (Identical with item no.11)	N 2105-2
25. Cold Catchpot with fittings (Identical with item no.12)	N 2241-2
26. Various vessels. (Identical with item no.13)	N 4579e-2 N 4760d-2
27. Gas-fired Preheater. (Identical with item no.15)	L 2714-1
28. Electric Preheater.	N 2341-2
29. Injector line diagram.	N 1546-16

C. CO PURIFICATION.

30. Scrubber Body. 800 mm dia. x 15 M long.	N 2117-2
---	----------

FIGURE XXVII

FLWSHEET FOR PRODUCTION OF 73,000 T/YEAR AVIATION PETROL BY HYDROGENATION OF UTIBUTI COAL.



**MATERIALS & SERVICES.**  
 COAL FOR HYDROGENATION 165,000 T/YEAR  
 HYDROGEN; 28,000 M<sup>3</sup>/HR. REQUIRING COKE FROM 180,000  
 ELECTRIC POWER. 28,000 KW.  
 STEAM. 50 T/HR.  
 WATER. 10,500 M<sup>3</sup>/HR.  
 TOTAL COAL REQUIREMENT, 500,000 T/YEAR  
 INCLUDES 1600 M<sup>3</sup>/HR FRESH WATER.

**RAW COAL**

WATER	8.17%
ASH	15.90%
VOLATILES	34.54%
FIXED CARBON	41.39%

**ANALYSIS OF DRY COAL**

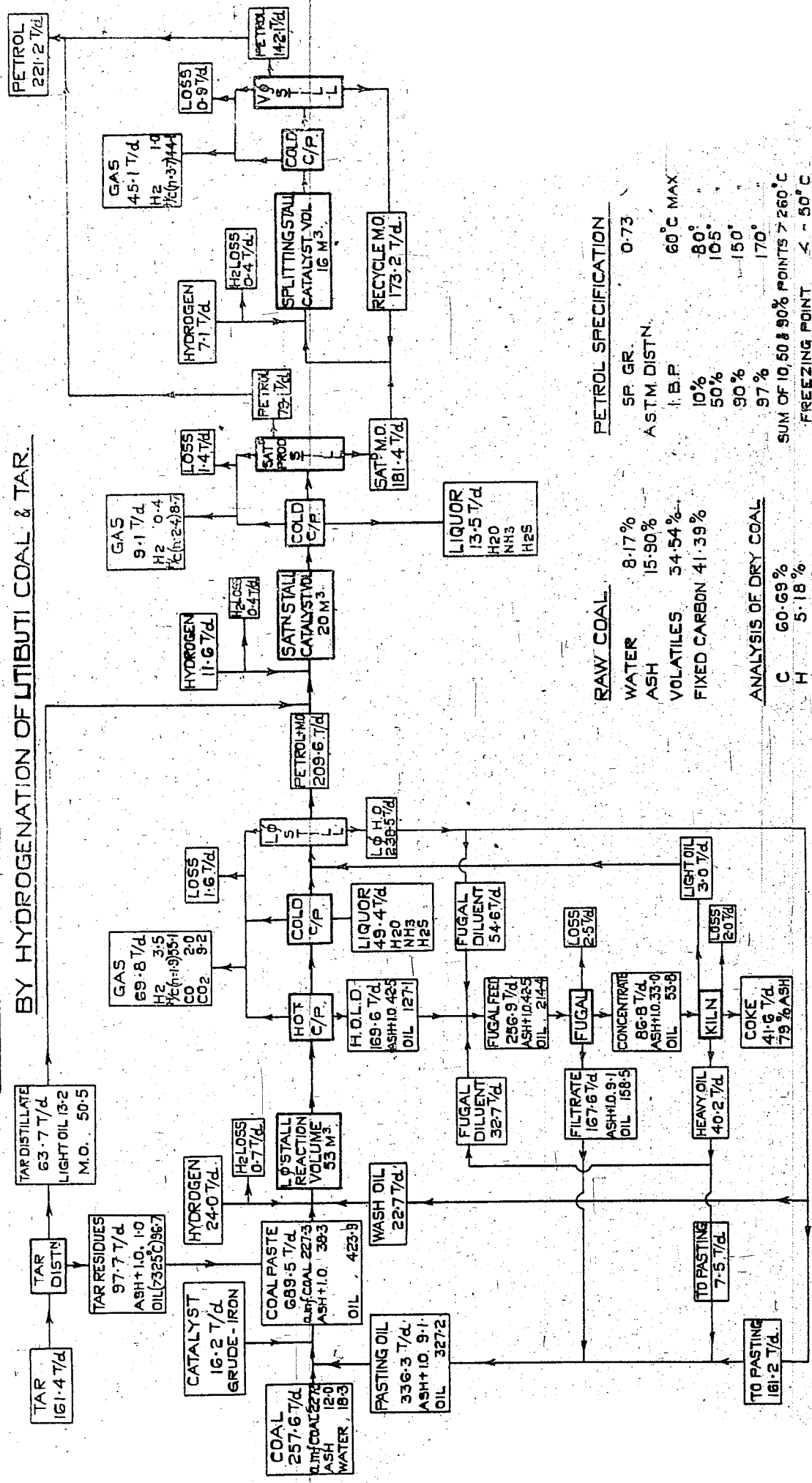
C	60.69%
H	5.18%
O	16.78%
N	1.32%
S	0.14% (COMBUSTIBLE)

**PETROL SPECIFICATION.**

SP GR.	0.73
A. STM. DISTN.	60°C MAX.
I.B.P.	80°
50%	105°
90%	150°
97%	170°
SUM OF 10, 50 & 90% POINTS	> 260°C
FREEZING POINT	< -50°C
R.V.P.	8.9 LB/IN <sup>2</sup> MAX.
GUM CONTENT	5 mg/100 ml
S CONTENT	0.1%
C.F.R. (M.M.) ON	70-72 CLEAR
	91 ATTAINABLE WITH
	4-5 ml TEL./IMP. GALL.

FIG. XXVIII

FLWSHEET FOR THE PRODUCTION OF 73,000 T/YEAR AVIATION PETROL BY HYDROGENATION OF LITUBUTI COAL & TAR.



PETROL SPECIFICATION

WATER	8.17%	SP GR.	0.73
ASH	15.90%	ASTM DISTN.	60°C MAX
VOLATILES	34.54%	I.B.P.	10°
FIXED CARBON	41.39%	50°	105°
		90°	150°
		97°	170°
SUM OF 10, 50 & 90° POINTS > 260°C			
FREEZING POINT < - 50°C			
R.V.P.	8.9 LBS/IN <sup>2</sup> MAX		
GUM CONTENT	5 mg/100 ml		
S. CONTENT	0.1%		
C.F.R. (M.M) O.N.	70-72 CLEAR		
	91 ATTAINABLE WITH		
	4.5 mL TEL/IMP GALL		

RAW COAL

WATER	8.17%
ASH	15.90%
VOLATILES	34.54%
FIXED CARBON	41.39%

ANALYSIS OF DRY COAL

C	60.69%
H	5.18%
O	16.78%
N	1.32%
CL	
S	0.14% (COMBUSTIBLE)

MATERIALS & SERVICES

COAL	85,000 T/YEAR
TAR FOR HYDROGENATION	54,000 T/YEAR REQUIRING 390,000 "
HYDROGEN	22,000 M <sup>3</sup> /HR
ELECTRIC POWER	21,000 KW
STEAM	42 T/HR
WATER	9,000 M <sup>3</sup> /HR
	INCLUDES 1300 M <sup>3</sup> /HR FRESH WATER

NB THE 250,000 T/YEAR OF COKE BALANCES ALMOST EXACTLY THE REQUIREMENT (240,000 T/YR) FOR HYDROGEN AND ENERGY PRODUCTION.

Before the war the Japanese had several preliminary discussions with International Hydrogenation Patents on the question of acquiring rights of the hydrogenation process. Similar discussions have apparently taken place from time to time with the I.G. during the war years, but it was not until late in 1944 that the I.G. were instructed by the German Government that it was essential that they should conclude an agreement with the Japanese Army.

Serious discussions began in November 1944, centring round the erection of a plant at Kinsei in Manchukuo for the production of 70-100,000 tons/year of aviation gasoline from Fupin coal. A document was found which gave an extremely rough sketch showing the proposed site for this plant. This is reproduced as Fig. XXVI. The same document mentioned, incidentally, that a new port which can be used by 10,000-ton ships has been built on the island of Koro.

The Fupin coal after washing contains 6% of water and 3% of ash and the a.m.f. coal has a carbon content of 79%.

In mid-January 1945 the Japanese changed their plan regarding the location of the first hydrogenation plant and decided on a site in South Sakhalin using Utibuti coal. This coal has a lower carbon content, 72-73% on the a.m.f. coal. The I.G. provided detailed flow-sheets for the production of 73,000 tons/year aviation petrol by (a) direct coal hydrogenation, (b) by combined coal and tar hydrogenation and (c) by hydrogenation of tar alone. It was assumed that the tar would be obtained by low temperature carbonization of the Utibuti coal. (Yield 17-18% by wt. on coal carbonized).

Information supplied by the I.G. was limited to 300 atms. coal hydrogenation technique and no data were supplied concerning naphtha dehydrogenation or alkylate synthesis processes. Details of the flow-sheet information supplied by the I.G. are given in Figures XXVII & XXVIII and in Table V. The drawings shown in the attached list (Table VI) were also handed to the Japanese.

A general hydrogenation licence agreement between the I.G. and the Japanese Army was signed on the 11th January 1945. This agreement provided for the use of the hydrogenation process in Japan, Manchukuo and China for the production of gasoline of all types, hydrocarbon gases, burning oil, gas oil, fuel oil, lubricating oil and paraffin wax from crude petroleum, bituminous coal, brown coal, peat, wood, shale or from products derived from these raw materials. The I.G. agreed to hand over their knowhow and patent rights as far as they were able to do so in view of the I.H.P. agreement. There is a special clause in the agreement to the effect that the Japanese were solely responsible for the legality of any compulsory licensing of I.H.P. patents. The Japanese Army agreed to pay the I.G. a lump sum of 18,000,000 marks, there being no additional running royalty. 20% of this lump sum was to be paid on signing the agreement, 30% within 6 weeks after the supply of all the

necessary information for erection of the first industrial size Japanese plant and 50% spread over the next five years. The I.G. agreed to send specialised technical personnel to Japan for the erection and start up of the new plant and to afford facilities for training of Japanese technicians in German plants. It was agreed that the Japanese and the I.G. should continue to exchange technical information. The agreement was for a period of 10 years after which time the Japanese should continue to have free use of patents, irrespective of whether the agreement was renewed or not.

It was intended that there should be separate building agreements for each plant. A draft building agreement for the first hydrogenation plant is amongst the evacuated documents and this provides for a lump sum of 800,000 marks to be paid to the I.G. to compensate them for their costs in designing the plant. It is uncertain whether this building agreement was ever signed, although a special Design Department was actually set up by the I.G. and this operated for a time in Heidelberg and was later transferred to Unterlockwitz.

From the start of the discussions the Japanese were anxious to obtain a full description of the German hydrogenation plants and processes in advance of flowsheet and design data on the new Japanese project. They were also anxious to get the German technicians out to Japan immediately. From letters written at the end of February and beginning of March 1945, it seems doubtful whether the Japanese seriously intended building a new plant and that the main object in concluding a general hydrogenation agreement with the I.G. was to secure the necessary information to operate existing Japanese plants.

Extremely little information concerning these Japanese plants was available either from documents or from interrogation of the I.G. staff. It is understood that there are three plants for the hydrogenation of tar. These are located in Kinsei, Mukden and Hokkaido.

There is some confusion as to whether these plants have a rated capacity for gasoline production of 50,000 tons/year each or whether their combined capacity is this figure. The plants are built for 300 atms. pressure operation and comprise liquid phase and vapour phase stalls. The converters are 10 m. long and 600 mm. internal diameter. Chlorine is used as a catalyst in both liquid and vapour phase and considerable difficulty has been experienced due to corrosion. There is also a hint that other substances were used as catalyst in one or both of the hydrogenation steps and that difficulty was experienced in maintaining their activity.

In a cable from the I.G. agent in Japan (Herr Ruhl) there is an indication that the achieved production of these plants was of the order of 10,000 tons/year of gasoline each.

The I.G. asked for more specific details of the operation of the Japanese plants and of the difficulties which were being experienced, but the Japanese representatives appeared to be out of touch with the plants and were unable to produce the information.

A questionnaire was sent to Japan, but there is no evidence in the captured documents that any reply was received.

Interrogation of Dr Pier and Dr Donath at Heidelberg produced only vague information on Japan's general fuel production position. It was stated that the Japanese had a licence for the Fischer process some years before the war and that they have a plant somewhere in Manchuria. The Japanese have also a carbonisation plant of their own construction for Fushun shale and it is thought that they have a cracking plant, probably of U.O.P. design, which has been very much enlarged during the war. At least 300,000 tons of shale oil is treated.

The Japanese have several carbonisation plants using Lurgi ovens and it was suggested that the members of the Lurgi organisation in Germany might be able to give more information on the Japanese oil position.

Dr Donath stated that he had heard that the Japanese made aviation petrol from rubber, but he did not know any details of the process, location or the extent of this activity. Dr Donath had also heard that the Japanese had some production of iso-octane or alkylate.



A. INTRODUCTION & GENERAL DESCRIPTION OF PROCESS

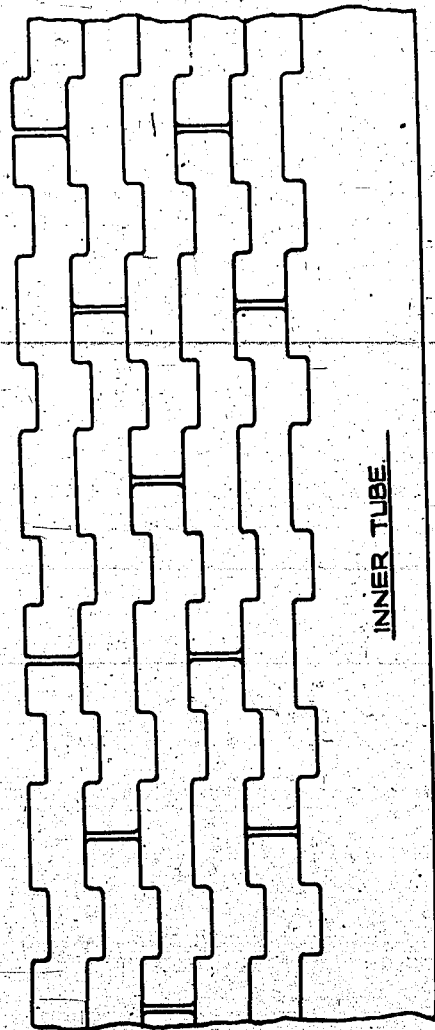
The following account of this development was obtained from Dr. Schierenbeck, the inventor of the process for producing high pressure vessels by winding tape on to a thin walled tube. The need for a large number of vessels for the Four Year Plan was first felt in 1937 and the I.G. were not satisfied that the Forgemasters could deal with the demand in the time set by the State. They therefore set out to see whether they could produce vessels suitable for use at high temperatures and pressures using the old process for wire-winding of guns or some modification of this method. The initial intention was to speed up the delivery of vessels rather than make any great technical advance in vessel design such as saving weight.

At first the experiments were made with small vessels of 100 to 300mm bore and 1-2 M long, the winding being done on a small hand-controlled machine. These vessels were tested to destruction, measurements being taken of the extension of vessels in several directions. On the basis of the tests, the I.G. set up at Oppau a plant for the production of wound vessels up to 1200 mm bore and 18 M long and, from the beginning of 1938, were able to make vessels on a production basis.

The process requires a lathe capable of taking the finished vessel and a large travelling bed to carry the tape spool and the other equipment for handling the tape. A length of tape sufficiently long to wind one length of the vessel is first wound on the tape spool which is roughly 7 ft. in diameter. (These long lengths of tape are made by welding together a number of lengths as delivered to the plant by the tape makers). The free end is then welded on to the end of the vessel and winding begins. The tape, on its passage from the drum, passes between two rollers which act as one connection to a source of low voltage electric current. When the tape reaches the vessel it is pressed on to it by another roller which acts as the other electric connection. The current passing through the tape is about 4-6,000 amps. at 30-40 volts. Immediately before winding the tape is thus heated to about 850°C. Immediately after the tape has been wound it is cooled fairly rapidly by means of high velocity air jets and some distance later, about 5-6 turns of the tape, a series of water jets play on the tape to ensure that the vessel does not heat up. The intensity of this cooling depends on the rate of winding and the thickness of the tube. On completion of the winding of each layer of tape, the tape end is welded to the inner vessel or to the previous tape layer. The speed of winding can be as high as 15 ft./min.

In 1939, under I.G. licence and under I.G. patents, Krupps and Deutsche-Röhren Werke at Mülheim Ruhr, started to make these vessels. Since this date they have made 50 vessels for testing purposes and about 200 for service in plants. It is estimated that at least 75% of these vessels have been in service. They have been built for production





ARRANGEMENT OF LAYERS OF WICKEL WOUND VESSEL

FIGURE: XXIX.

plants for pressures up to 700 ats. and small ones for research laboratories up to 4,000 ats.

The first vessel to go into service (1938) was a 500 mm 200 ats. CO scrubber on the Oppau plant. The first converter to be used in a production plant was a 800 mm ammonia converter at Oppau in 1939. The largest vessel so far built is a Tanol converter of 1,200 mm bore and 18 M long, and this was put into operation at Oppau in 1940.

The I.G. feel that they made a mistake when they gave a licence to Krupps instead of to a competitor. They have been charged the same price for the Wickel bodies as for solid wall forgings, while their own experience has shown them that a Wickel body is cheaper than a solid wall forging by about 20%.

## B. DETAILED DESCRIPTION OF PRESSURE VESSEL MANUFACTURE

### Production of the Wound Body

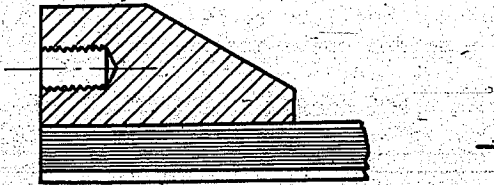
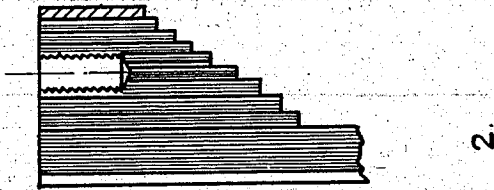
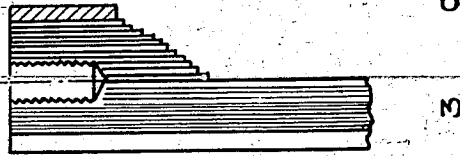
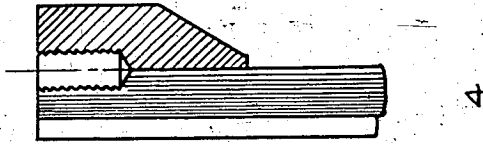
The inner tube on which the tape is wound is made from the material most suited to the service for which the vessel is intended, i.e. material which is corrosion resistant, hydrogen resistant etc. So far, the thickness of this inner tube has been 20 mm. Up to 800 mm bore the tube is built up of seamless tubes welded together to get the necessary length. For greater diameters the tube is built up of rolled plate welded both circumferentially and longitudinally. Recently, in order to save costs where the tube has to be made of high alloy material or where the alloys required are in short supply, tests have been made with thin walled tubes of 5-6 mm thickness. In order to obtain the necessary stiffness of the tube for winding purposes, the thin walled tube is filled with concrete. This means that internal water cooling cannot be used as in the case of the 20 mm thick tubes and resort has been made to more intensive external water cooling. The inner tubes themselves need not be truly round as far as the winding process is concerned as the tape is continuously pressed on to the tube by the roller. The degree of roundness depends on the service for which the vessel is intended, i.e. whether or not any internal parts have to be inserted.

The Wickel tape used for large high-pressure vessels is 80 mm wide and 8 mm thick. Its cross-sectional shape is shown in figure XXIX. The surface of the inner tube is machined with a spiral groove so that the tape sits closely and longitudinal movement is prevented. Tape of smaller dimensions (5 x 50 mms) is used for smaller vessels, it being essential that, in any vessel, the number of layers of tape should exceed a certain minimum.

The material of the tape was as follows:-

FIG. XXX.

DEVELOPMENT OF WICKEL OFEN END WINDINGS.



NOT TO SCALE.

For cold vessels F.T.2 52. A normal carbon steel of 0.20% Carbon having an elastic limit of 23 Tons/sq.in.

For hot vessels F.K.15, an alloy steel of 1% Cr., 0.5% Mn., 0.15% C, and having a creep limit at 350°C of 22 Tons/sq.in. The temperature of 350°C instead of 300°C (normal for solid wall vessels) is specified because windings have a lower conductivity than solid metal and therefore the wound vessel wall is hotter than that of a solid vessel under the same conditions.

By special heat treatment of the tape either before winding or during winding, the elastic limit of the metal is raised to 44 Tons/sq.in. For cold vessels, it should therefore be possible to reduce the first weight below that of a corresponding forging. Also when designing a normal solid wall vessel one has to take into account the fact that the metal, because of its thickness, is not homogeneous. With a wound vessel, one can be certain that the material is homogeneous and it should therefore be possible to reduce the design factor of safety. So far, however, the I.G. have made Wickel vessels of the same dimensions as forgings.

As previously mentioned, the tape is electrically heated on its way to the tube to 800-900°C. As it passes under the roller, which is grooved to the same profile as the tape, and has a diameter of 150 mm, it is pressed on to the tube with a load of one Tonne. This small load ensures that the tapes sit against one another closely and that the lands on one tape are thoroughly pressed into the grooves of the underlying tape. Each successive tape is laid on so that the gaps between successive turns are staggered by a distance of one third the length of the tape, the tape having three grooves and three lands. This ensures that the successive turns are interlocked and that there is not a straight passage from inside to outside of the tube. Variations in the proportions of the grooves and lands were being experimented with, to try to produce a vessel which has a smaller longitudinal extension than the normal wound vessel.

In order to ensure that the tube does not distort during winding, owing to the pressure of the contact roller, a supporting roller is fitted diametrically opposite.

When the main parallel wall body has been completed, the ends have to be stiffened to take the cover. This is achieved either by screwing heavy solid stiffening rings on the ends of the vessel or by building up the end with more windings of tape and finally screwing on a thin ring to secure the windings. In both cases, the ends of the original wound tube where the windings are welded together and to the inner vessel are finally cut off, leaving only the interlocking grip of the tape to hold the turns together. The studs for the cover are screwed into the tape or into heavy solid stiffening rings. (Fig. XXX).

Dr. Schierenbeck felt that the Wickel method should enable much lighter vessels to be used for processes requiring very high pressures, for example 700 ats. and above. He pointed out that with solid wall vessels the stress distribution in the wall of the vessel was such that the maximum stress was at the inner face and that, as the working pressure was increased, the wall thickness went up much faster than the pressure. With the wound vessels the stress throughout the wall thickness was even, so that an increase in pressure of 50% meant an increase in wall thickness of 50%.

During the winding of Gun-barrels, Dr. Schierenbeck said that great care was taken to ensure that the tape was wound on with the correct tension, so that the final stress distribution was the one desired. No special precautions of this nature had been taken in the case of pressure vessels. No tests had been made to prove that the desired stress distribution in the vessel wall had actually been obtained, apart from a number of tests made to compare the strength of the vessel in the condition it left the winding machine and also after the vessel had been annealed at 700°C for one day to relieve all shrinkage stresses. Photographs of the test curves were seen for these vessels and they showed that a normal wound vessel was 1.4 times as strong as the same dimensioned solid wall vessel and that after annealing the vessel was still 1.2 times as strong.

### C. OTHER USES OF THE WICKEL METHOD.

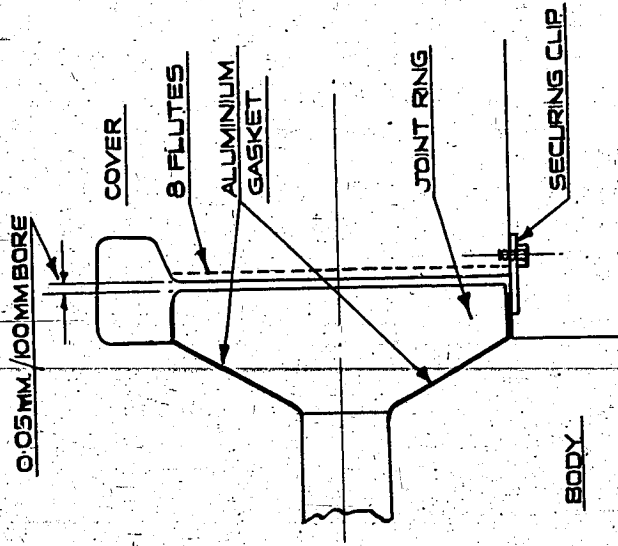
The method of producing tubes which are resistant to high pressure by winding on a grooved tape has been tried for the production of GUN-BARRELS, where it was said that the better stress distribution resulted in a lighter barrel.

The I.G. have also experimented with the manufacture of covers for the ends of high pressure vessels, using the same tape as for the manufacture of bodies. They had done tests but had not tried any in service.

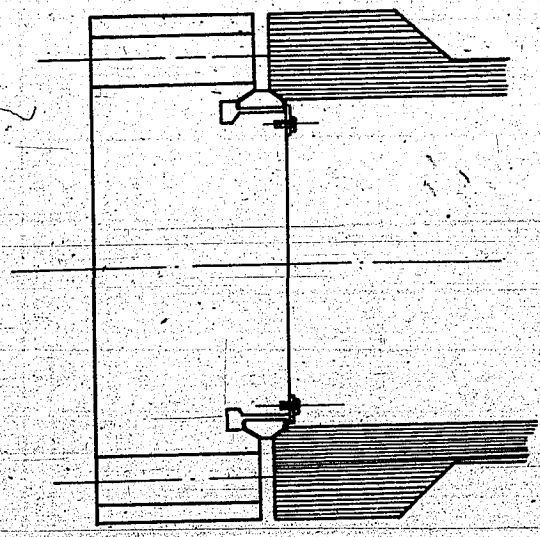
Because of troubles with the parts of feed pumps of 700 ats. plants, they had tried the manufacture of pump cylinders and stuffing boxes for their own design of paste injectors and although they had made and tested the parts they had not had any in service. The flanges of the stuffing box were wound direct on to the body and drilled to suit the studs in the body of the cylinder.

FIGURE XXXI

1G. DOUBLE CONE JOINT



DETAIL OF JOINT RING.



ASSEMBLY

TABLE VII

WEIGHT SAVINGS EFFECTED BY THE VARIOUS DESIGN CHANGES.

Based on the original 1,000 mm. Bore vessel, and weights for the complete vessel with covers, etc.

Type of Vessel	325 ats Pressure		700 ats Pressure		Plant using this type
	Weight, Tonnes	%	Weight, Tonnes	%	
Single Cone Joints Both Ends Equal Diameter	79.14	100			
Single Cone Joints One End 600 mm.	67.87	85.7			
Large Double Cone Joints One End 600 mm.	66.8	84	151.6	100	Gelsenberg, Pöhlitz, Wesseling
Small Double Cone Joints One End 600 mm.	60.8	77	141.5	93.5	Bleehammer
Small Double Cone Joint One End 600 mm. Studs in Body Threads.	58.7	74	131.4	87	Bleehammer

XII. DEVELOPMENT OF HIGH PRESSURE VESSELS.

Since 1937, I.G. have made a number of developments in the construction of high pressure vessels with the object of reducing their weight. Altogether, a 26% reduction in the weight of a 1000 mm. bore vessel has been achieved in two steps. The first improvement, which accounted for a 16% saving, was the introduction of double-cone joints in place of single-cone joints and a reduction in the size of the bottom joint and cover; the remaining 10% saving resulted from the redesign of the end covers and stiffening rings.

Originally, I.G. vessels were parallel throughout their length to facilitate lining with a thin tube whose function was to protect the wall of the vessel from corrosion and hydrogen attack. Experience showed, however, that the lining was unnecessary and the design of the 1000 mm. bore vessels for Böhlen and Scholven was modified so that the bottom joint was only 600 mm. in diameter and the end plate correspondingly smaller. In this way, the weight of the vessel was reduced by 14.3%.

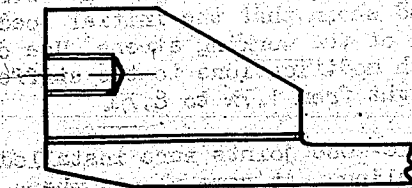
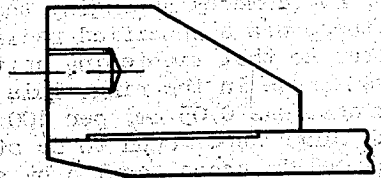
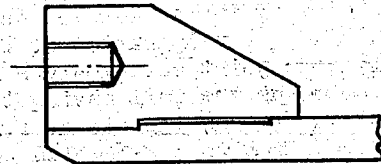
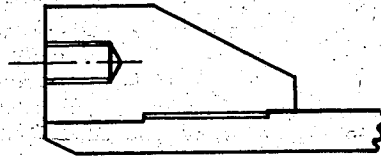
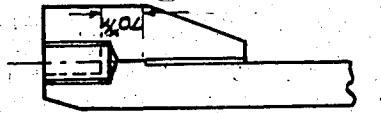
The double-cone joint was developed not only to save weight but also to increase ease of handling in the case of the larger vessels, particularly those designed for operation at the higher pressures. The original double-cone joint saved only a further 1.7% but this represented by no means the full saving that could be derived from the change to the double-cone joint. At first some trouble was experienced with the joint when assembled according to a procedure similar to that used for single-cone joints, i.e. merely limiting the initial load in the end-cover studs. Thus, in a number of cases the ring was distorted as a result of excessive compressive stresses. This difficulty was overcome by arranging that when the ring was fitted to the cover there was a specified radial clearance between ring and cover so that tightening up the studs could not lead to an excessive stress in the ring. This clearance, according to a number of drawings, was 0.05 mm. per 100 mm. diameter of vessel. The original rings were found to be stiffer than was required and were reduced in cross section by some 25%; a greater reduction was inadvisable if distortion due to lack of rigidity during machining was to be avoided. A smaller ring would also have suffered from too high a compressive stress on its faces; experimental work had shown that the initial load required in the cover studs was 120% of the working stress. Use of the more flexible ring, together with modifications to the stiffening rings, increased the saving in weight from 1.7% to 8.7%.

Converters with double-cone joints were installed at Gelsenberg, Pöhlitz and Wesseling. At some plants where the original heavy double-cone joint had been installed, the lighter joint-rings were being used by merely fitting filler rings to the end covers so that the correct radial clearances between joint rings and covers were being maintained. It was claimed that the



FIG. XXXII.

DEVELOPMENT OF END COVER OF SOLID WALL FORGING.



1942

NOT TO SCALE.

LARGE DIAMETER

VESSEL

1935.

SMALL DIAMETER

VESSEL

1935.

double-cone joint was self-tightening. Trials had been carried out on another type of joint variously referred to as the Bretttschneider or Uhde joint. As at Leuna, the opinion was expressed that for hydrogenation plant vessels the joint was not as suitable as the cone joint.

It was soon realised that use of a double-cone joint avoided the very large outward radial forces at the vessel ends which arose from single-cone joints. As mentioned above, modifications were made to the stiffening rings in order to take advantage of the reduced stresses. These modifications, as always, were principally directed towards reduction of diameter of the stud circle and at first took the form of a reduction in thickness of the vessel wall where the stiffening rings screwed on. In the final design, however, there is no reduction in wall thickness of the vessel, but the stiffening rings are much thinner radially. The studs are screwed into both ring and vessel wall, the pitch circle diameter of the studs being the external diameter of the vessel before threading to receive the stiffening rings. In order that the studs should always be evenly loaded both in the vessel wall and in the stiffening ring it was decided to give the ring an initial load such that movement relative to the vessel wall could not be brought about by any test or working load. Steps were therefore machined on the nose of the vessel and on the ring and the ring screwed up against the shoulder while heated to 200-250°C. On cooling, a tensile stress is developed in the ring between the shoulder and the first thread, which is spaced 70 mm. away from the shoulder. Tests were first carried out on a small 160 mm. bore vessel. At 1.7 x design working pressure the vessel body showed signs of permanent set. At 2.6 x design working pressure the stiffening ring showed signs of permanent set. On two occasions at 3 x design working pressure, the aluminium gaskets on the joint ring blew out and on another occasion the nuts on the cover studs were found to have become slack after the vessel had been up to this pressure. Finally, the vessel itself split at 4 x design working pressure. A number of vessels of this last design had been in service and no failures had occurred.

No doubt experience with "Wickel" vessels, where the studs for the covers had to be screwed into the wound layers, provided the background for the last development in stiffening rings for solid-wall vessels.

To comply with German legal requirements the Test pressure for all vessels is 1.3 x the maximum working pressure. Cold vessels are designed with a working stress of at least  $\frac{1}{1.6}$  x the elastic limit. In the case of hot-walled vessels, the working stress is set at  $\frac{1}{1.6}$  x the creep limit for the steel at 300°C for solid walls and at  $\frac{1}{1.6}$  x the creep limit at 350°C for "Wickel" vessels. For both types of vessel, allowances are made for the process in which the vessel is to be used, e.g. for well-established processes the factor of  $\frac{1}{1.6}$  is adhered to, but for processes still undergoing development a ratio of  $\frac{1}{1.7}$  to  $\frac{1}{2.0}$  may be used.

The maximum ingot which can be cast by Krupps or other Forgemasters has a weight of 270 Tonnes and the largest forge is rated at 15,000 Tonnes. The largest solid wall vessel obtainable from this equipment is the 1000 mm. bore, 18 M long, 700 ats. converter, which weighs 110 Tonnes. Very few vessels had been lost on account of casting and forging faults; faults were ground out locally and extra metal left on the outside of the vessel or, if necessary, stiffening rings shrunk on.

The practice of grinding out local faults had been applied to the removal of marks on forgings caused by bomb splinters.

XIII. HYDROGEN-RESISTANT STEELS, ETC.

Ob. Ing. Koch and Dr. Class were interrogated on the 28th May regarding the development of hydrogen-resistant steels and their experience with them during the war. The steel in most widespread use was known as N.10, and its analysis given as 3.0 - 3.6% Cr, < 0.5% Mo, < 0.3% W, < 0.75% V, 0.18 - 0.22%C; this is identical with the analysis quoted at Leuna. 520°C was given as the maximum metal temperature, and when this steel was used in preheaters at 700 ats, flue gas temperatures were restricted to 560°C maximum. N.10 tubing had an O.D./I.D. ratio of 1.7 to 1.8, which at 700 ats, gives a stress of 11.3 tons/sq.in. or 8.2 tons/sq.in. according as to whether the stress calculation is based on the elastic or plastic theory.

On account of failures of N.10 in service, the method of testing steels for hydrogen resistance had been changed during the war. The original testing period of 200 hrs. had been found too short and tensile testing of test pieces had not given satisfactory results. It was considered that the normal methods were not satisfactory for the testing of material to be used so near its limits and that test conditions should approach more nearly the actual plant conditions. The life-testing of tubes under working pressure and temperature had therefore been developed, the tubes themselves being scaled-down versions of plant tubes. In this way it was hoped to obtain results which would be of more direct applicability.

N.10 tubing was delivered in lengths of 3-4 m. when in the rolled form and 4-5 m. lengths when in the form of bored-out bars. The latter type had been favoured because with such thick-walled tubes the cost was very little greater than that for rolled tubes and there was no risk of trouble from the small faults that were always present in the bores of rolled tubes. The tubing was heat-treated according to a method developed at Leuna. After heating to 1050°C the steel has a Brinell hardness of at least 350, which falls to 250-280 on annealing.

Great difficulty had been experienced in heat-treating forged pieces of the alloy and the use of N.10 for forgings had been abandoned.

It was disclosed that V2A was in use at Welheim for 700 ats preheaters and that no running difficulties had been experienced. It was stated that I.G. would have used V2A for 700 ats. preheaters if nickel had been available, since the creep strength of V2A was superior to that of N.10 at high temperatures.

Formerly, V2A sheets had been used for lining catalyst baskets in order to guard against H<sub>2</sub> attack and sulphur attack.

When supplies became difficult, 15 mm. thick ordinary steel shells were used with an internal plating of V2A only 1 mm. thick; at the same time, this gave a stronger basket which was not so likely to fail during a rapid blow-down.

Because of the shortage of chromium and molybdenum, manganese had been used instead in the case of flange steels, and there had been considerable difficulty in achieving the required tensile properties without getting a steel which was too brittle and susceptible to cracking. Because of its reduced ductility, the substitute steel was used only up to 350°C. The steel had the following analysis:- 1.1%-1.4% Mn., 1.1-1.4% Si., and 0.4% C; after water quenching, the tensile strength was 50-60 tons/sq.in.

In connection with the failure of injector pump blocks, it was considered that the trouble was due to the presence of occluded hydrogen and other impurities left in the steel during casting which did not manifest themselves at pressures of 300 ats. but which became important at 700 ats. The reason for the more numerous failures on the three-throw pumps arose from the fact that they underwent much more frequent stress reversals than the I.G. paste pumps.

APPENDIX A.G.I.O.S. OIL TEAM VISITING LUDWIGSHAFEN/OPPAU 25-31/3/45

Leader: Mr. P. K. Kuhne U.S. Petroleum Administration  
for War.

Deputy Leader: Lt. Col. R. Holroyd British Ministry of Fuel  
and Power.

Dr. E. L. Baldeschwieler

Mr. E. Cotton

Mr. L. P. Evans

Dr. W. F. Faragher

Dr. V. Haensel

U.S. Petroleum Administration  
for War

Dr. L. L. Hirst

Dr. G. Von Elbe

U.S. Department of the  
Interior, Bureau of Mines.

Dr. E. B. Peck

U.S. Foreign Economic  
Administration.

Lt. Col. D. Morton

Lt. Col. H. C. Tett

Major C. Cookram

Major F. A. Williams

Capt. C. M. Cawley

Capt. T. A. G. Plant

British Ministry of Fuel  
and Power.

Later Visit (July)

Dr. W. A. Horne

U.S. Petroleum Administration  
for War.

APPENDIX B(1)

HEAT EXCHANGERS USED IN KW PLANTS AT OPPAU & HEIDENRUCK

	<u>OPPAU</u>		<u>HEIDENRUCK</u>
No. Tubes	688		400
Tube Material	<u>Upper Portion</u> Fireclit 10		FR-18
Tube Length, mm.	2625		4850
" O.D. mm.	24		22
" I.D. mm.	21		18
<u>SHELL</u>		<u>Lower Portion</u> ST-00	
Material	Fireclit 8		Sticromal 3
Length (overall) mm.	7400		5900
I.D. mm.	1184		1300
Thickness mm.	8		8
No. Baffles	9		12
REF. DRAWING No.	F. 10268-1		4760

⊞ Photograph of tube bundle during shutdown in March 1941 also available, in documents.

APPENDIX B(2)Calculations on KW Plant, Heydebreck 9.3.42

For 3,500 m<sup>3</sup>/hour of CH<sub>4</sub>; for preheat of gases to 650°C and reactor outlet of 850°C

Analysis

	Input		After Reaction	Water Gas Equilib.(1)	Cracked Gas	
					Parts	%
CO <sub>2</sub>	-	-	-	+ 0.225	0.225	7.0
		0.487 O <sub>2</sub>	-	-		
CO	-	-	0.994	- 0.225	0.769	23.8
H <sub>2</sub>	-	-	2.008	+ 0.225	2.233	67.0
CH <sub>4</sub>	1.000	-	0.006	-	0.006	0.2
Dry Gas	1.000	-	-	-	3.233	100.0
m <sup>3</sup> H <sub>2</sub> O	1.000	-0.020	0.980	- 0.225	0.755	
gms H <sub>2</sub> O	735				556	

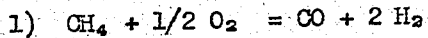
(1) Water gas equilibrium constant at 850°C, K = 1.16

For the above conditions the heat balance in the reactor is estimated as follows.

(a) Oxygen requirements per cu.m. CH<sub>4</sub> are 0.487 cu.m.

(b) Heat balance

Heat generated



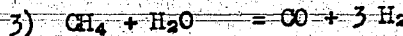
$$\Delta H \text{ at } 650^\circ = 269 \text{ WE/} \text{m}^3 \\ 269 \times 0.974 = 262$$



$$\Delta H \text{ at } 650^\circ = 337 \text{ WE/} \text{m}^3 \\ 337 \times 0.225 = 76$$

338

Heat consumed



$$\Delta H \text{ at } 650^\circ = -2689 \text{ WE/} \text{m}^3 \\ 2689 \times 0.02 = 54$$

4) Heat the cracked gases from 650-850°

$$\Delta T \times C_p = 200 \times 1.322 = 264$$

5) Heat losses (WE/m<sup>3</sup> CH<sub>4</sub>)

20

338



Heat ExchangerInput

Sensible heat of cracked gas 0-850° in WE/l<sup>3</sup> CH<sub>4</sub>  
 $850 \times 1.257$  (2)  
 Latent heat of water in gas  $0.556 \times 595$

1,068

331

1,399 WE/  
l<sup>3</sup> CH<sub>4</sub>Output

Sensible heat of feed gases (0-650°) (3)  
 $650 \times 1.098$   
 Latent heat of water in gas  
 $0.735 \times 595$  } 1150

Less heat in O<sub>2</sub> at 15°C  
 $-0.487 \times 15 \times 0.917 \times 0.311$  -2

Less heat in steam added  
 206 gms H<sub>2</sub>O from saturator 156 WE  
 -156

529 gms steam at 1.5 ats (111°)  
 $.529 \times 643.8$  340 WE  
 -340

652

652 WE/l<sup>3</sup> CH<sub>4</sub>

Heat left in cracked gas after heat exchanger

$$1399 - 652 = 747 \text{ WE/l}^3 \text{ CH}_4$$

and the indicated outlet temperature is

$$(747 - 331) : 1.322 = \frac{416}{1.32} = 315^\circ$$

AVERAGE SPECIFIC HEATS

(2) Cracked Gases	mols	Sp. heat (0-850)	
CO <sub>2</sub>	0.225	$\times 0.503$	= 0.114
CH <sub>4</sub>	0.006	$\times 0.746$	= 0.005
H <sub>2</sub> O	0.755	$\times 0.390$	= 0.294
Diatomic gases	3.002	$\times 0.319$	= 0.958
			<u>1.371</u>

$$1.371 \times 0.917 = 1.257$$

Note (3)

Feed Gases

CH <sub>4</sub>	1.000	$\times 0.661$	= 0.661
H <sub>2</sub> O	1.000	$\times 0.382$	= 0.382
O <sub>2</sub>	0.487	$\times 0.316$	= 0.154
			<u>1.197</u>

$$1.197 \times 0.917 = 1.098$$

LARGE SCALE PRODUCTION OF SYNTHETIC FERTILIZERS.

In our letter to Military Government, dated April 15th, we gave a survey of the minimum production capacities for synthetic fertilizers at our Oppau plant and described in particular the requirements of coke and coal for this limited production volume. On special request we have now made an investigation of conditions for maximum output of final products, and we give the results of this investigation in the table attached to this report.

The output of fertilizers depends on the repair-work at those installations that have suffered most damage by bombing. While the gas and ammonia plants are in good working conditions, there is some damage at the coal transport system for the boiler houses, and this repair will require about 6 months. Although the production of the ammonia plant might be as large as 500 tons/day per September 1st, it is limited to 170 tons/day for this decreased efficiency of the coal conveyance. After December 1st, the state of the different manufacturing plants governs the real output of final products as given in the columns 9-16 of the table. From column 16 and the note to it results a maximum capacity of about 500 tons/day of nitrogen or a production of about 180,000 tons/year of nitrogen, out of which more than 900,000 tons of marketable fertilizers can be manufactured.

As we had already occasion to point out we always had a surplus production of ammonia which we despatched for manufacturing into fertilizers to our plants at Hoechst, Wolfen and Bitterfeld. The quantity available for despatch is given in column 17 of the table. The manufacturing capacity at Hoechst being of the order of 200 tons/day, there will be no demands for transportation to the plants at Wolfen and Bitterfeld before January 1946, the only condition being a regular communication between Ludwigshafen and Frankfurt/M - Hoechst.

The requirements for coke and Ferngas for the synthesis, and coal and lignite for the power plants are given in the column 5-8. We are prepared to receive Ferngas up to 400,000 cbm/day with a corresponding decrease in the demand of coke.

In column 3 we have mentioned a production of 50 tons/day of methanol as it was suggested to Military Government at Ludwigshafen in our memorandum dated April 20th, 1945. This production of methanol and an additional one of butyl may be raised with the progress of repair-work at the coal conveyance of our plant; the output of nitrogen is not afflicted by the simultaneous production of these chemicals.

The maximum capacity of the primary plants for the four main products will be :-

nitrogen	-	750 tons/day
methanol	-	120 " "
Butyl	-	400 " "
hydrogen	-	192,000 cbm/day

and will be obtained during the first months of 1946.

Beyond the demand for coke, Ferngas, coal and lignite, we shall require limestones for the production of Kalkammonsalpeter and gypsum for the production of ammonium sulphate. A lime of good qualities for our purposes can be got at Gundersheim/Neckar. Gypsum was supplied till now from Niedersachswerfen/Harz; as long as there are transport difficulties we might use a gypsum that can be taken from a quarry at Obrigheim/Neckar and belongs to the Portland Zementwerke at Heidelberg. The quarries at Gundersheim and Obrigheim are not far from each other and the distance from Ludwigshafen is approximately 50 miles.

The total transport volume for these auxiliary raw materials will be :-

per	gypsum tons/day	lime tons/day	total tons/day
1.6.45	-	80	80
1.9.45	90	130	220
1.12.45	250	310	560
1.5.46	420	325	745
1.5.47	420	325	745

There is an ample stock of lime available at Oppau to run production of Kalkammonsalpeter for at least 2 months before new supply from Gundersheim will be necessary.

TIME-TABLE FOR RE-ESTABLISHMENT OF NITROGEN PLANT AT

Date	Production capacities of primary plants			Fuel requirements			
	nitrogen	methanol	hydrogen	coke	Ferngas	coal	lignite briquettes
1	2	3	4	5	6	7	8
	tons/day	tons/day	cbm/day	tons/ day	cbm/ day	tons/ day	tons/day
at once	50	50	48,000	200	100,000	400	-
1.6.45.	170 <sup>(1)</sup>	50	120,000	500	100,000	800	100
1.9.45.	170	50	120,000	500	100,000	800	100
1.12.45.	500	50	192,000	1,100	100,000	1,500	200
1.5.46.	750	50	192,000	1,600	100,000	1,800	200
1.5.47.	750	50	192,000	1,600	100,000	1,800	200

(1) output limited by damage at internal coal transport system.  
Repair work requires 5-6 months.

I.G. LUDWIGSHAFEN-OPPAU.

Real output of marketable products								Spare nitrogen for dispatch
ammonium sulphate	ammonium chloride	ammonium bicarb.	urea	Kalkammonsalpeter	sodium nitrate	calcium nitrate	total	
9	10	11	12	13	14	15	16	17
tons/day N	tons/day N	tons/day N	tons/day N	tons/day N	tons/day N	tons/day N	tons/day N	tons/day N
-	-	5	-	45	-	-	50	-
-	4	5	19	45	-	-	73	97
33	4	7	31	68	3	-	146	24
50	4	9	32	168	7	-	270 <sup>(2)</sup>	230
84	10	15	46	180	12	29	376	374
84	10	15	46	180	16	76	427 <sup>(3)</sup>	323

(2) after repair of coal transport system bottle-neck at the final production plants.

(3) after full repair of all damage and further completion of Kalkammonsalpeter plant the whole capacity may be raised to 500 tons/day N.