

that very little fundamental improvement was made in the process itself.

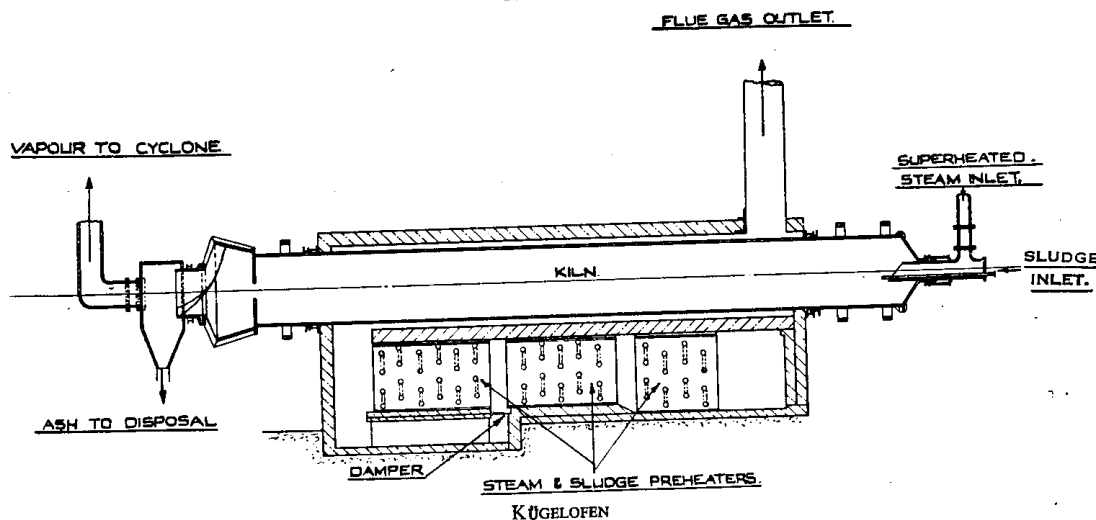
The greatest achievement in the hydrogenation field in Germany during the past 6 years lies in the practical demonstration in large-scale plants that there is no technical difficulty in converting complex organic material to vaporisable middle oil in a liquid phase process operated at 700ats. It is clear, however, from the German costs that operation at 700ats does not materially improve the economics of hydrogenation of such complex materials which, under existing conditions, is completely out of the question in this country.

The demonstration in the Blechhammer plant that coal can be converted at 700ats into a product consisting mainly of asphalt-free heavy oil is of considerable interest in that it opens up the possibility of a two-stage liquid phase process for coal treatment, which would

by the Luftwaffe and by aero-engine manufacturers. The latter, in particular, required a very high rich mixture rating which was most easily obtainable by increasing the aromatic content of the base petrol. IG were the original inventors of the hydroforming process, and the Germans turned to this type of treatment as their main method for improving the quality of petrol from both hydrogenation and natural petroleum sources.

The original process (HF process) employing twin reaction units, one of which is on stream and the other under reactivation treatment, was in use on a large scale at only one German plant, namely, Moosbierbaum. All the new plants, either operating or under construction, were based on a modified process (DHD process) which employs only one reactor system and in which the time on stream is very much longer than the catalyst reactivation period.

FIGURE 43



be expected to give about a 5% higher yield of petrol than processes used at present. Such improvement is not nearly sufficient, however, to alter the economic picture of coal hydrogenation at the existing level of coal and petrol prices. A second point of interest in the German work which, if followed up, might considerably improve the yields of petrol obtainable from such raw materials as low-temperature tar and certain types of petroleum heavy oil, is the successful hydrogenation of brown coal tar over fixed 5058 catalyst.

In connection with hydrogenation of vaporisable middle oils to petrol which appears to be the only application of the hydrogenation process in which there is likely to be any immediate UK interest, the Germans made no noteworthy advance. The only new catalyst reported (8376) is a substitute material developed in order to reduce the consumption of tungsten. Similarly, there has been no major improvement in the design of hydrogenation equipment, e.g. vapour phase converters which permit of higher outputs per stall.

#### 4. HYDROFORMING

##### i. INTRODUCTION

The availability of alkylate and iso-octane in Germany was not sufficient to blend up aviation base petrol, as produced by direct hydrogenation, to the quality desired

##### ii. HF PROCESS

A simplified flow diagram of this process as operated in the Leuna pilot plant is shown in Fig. 44. This pilot plant was the forerunner of the large-scale Moosbierbaum unit.

There are two reactor systems, each consisting of three reaction vessels arranged in series. One system is on stream while catalyst regeneration is carried out in the other. The German HF process differs from that employed in American refineries in several detailed respects. For example, the catalyst (ammonium molybdate on alumina) in different parts of the reactor system varies in molybdenum content from 5% to 10%, and also in particle size. The object is to obtain a more uniform deposition of carbon on the catalyst.

The naphtha charge, obtained by removing 0-90°C fraction from straight-run petrols by distillation, is heated by interchange with the products and mixed with 600-1,000m<sup>3</sup> circulating gas per tonne of feed before being preheated to 520°C under 15ats pressure. The reactants then pass through three reactors arranged in series with reheating coils between each reactor. The final product exit temperature is about 510°C. The products are passed via the interchanger and a cooler to a cold catchpot where the liquid product is separated from the gas. Part of the latter is recycled and the rest

FIGURE 44

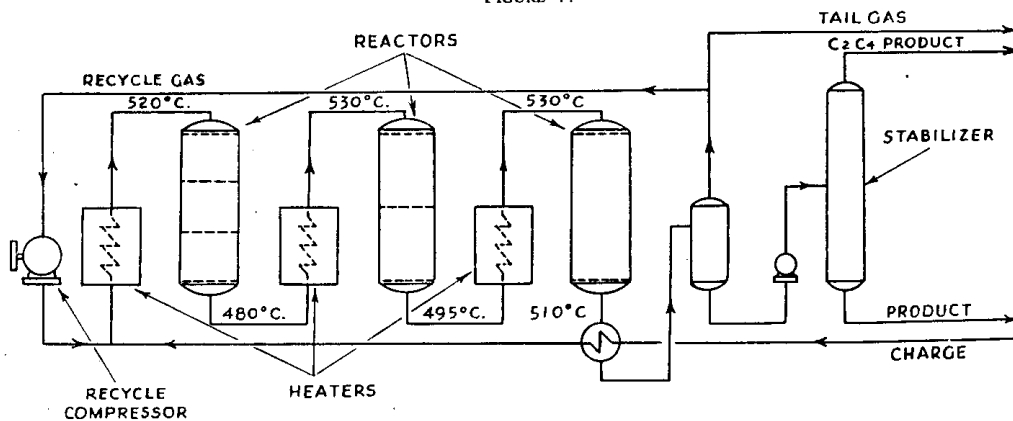


FIGURE 45

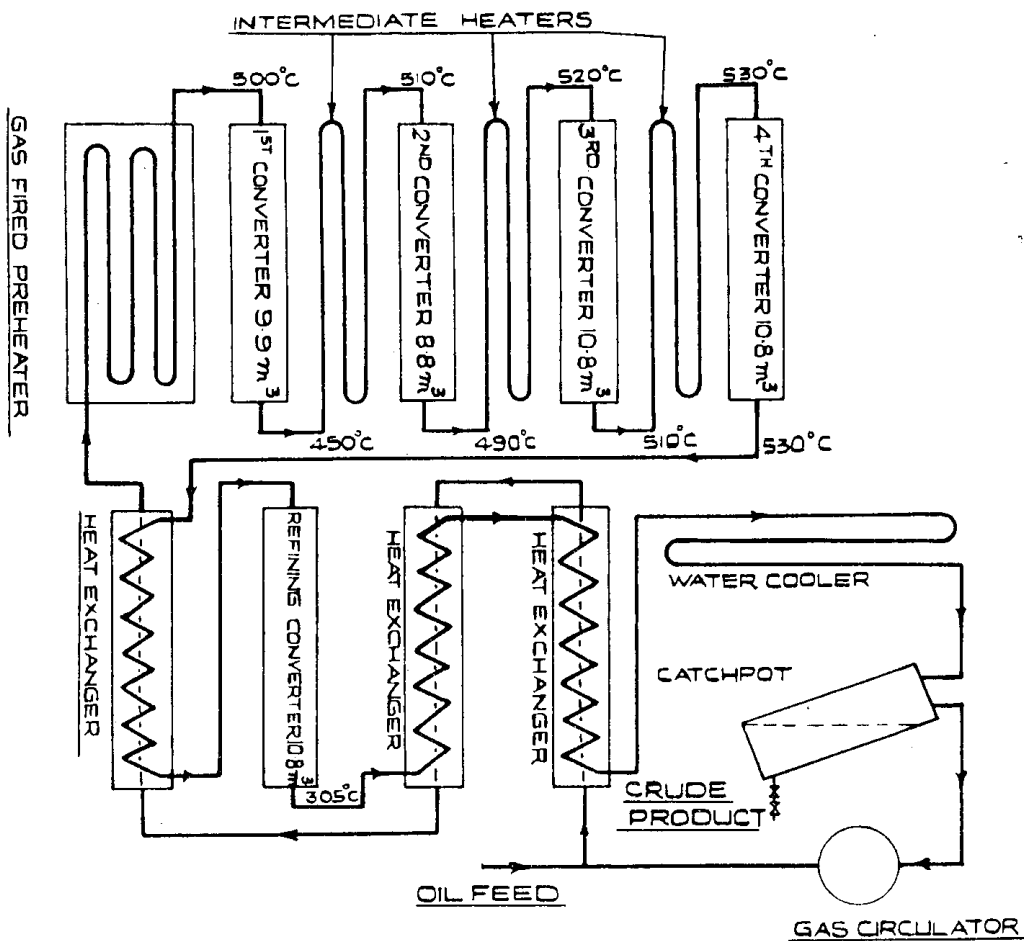


TABLE XLI

LEUNA DHD PLANT—PROPERTIES OF FEED AND PRODUCTS

	0-85°C light petrol	85°-180°C naphtha feed to DHD process	Stabilised DHD product	Final DHD petrol blend
Aniline point .. .. . °C	52	45	1.6	6.9
Aniline point after treatment with sulphuric acid °C	55.4	—	63.2	61.0
Aromatics .. .. . % wt	4.5	9.5	66.0	52.0
Naphthenes .. .. . % wt	46.2	51.2	7.9	14.4
Paraffins .. .. . % wt	48.7	38.1	25.9	33.0
Olefins .. .. . % wt	0.6	1.2	0.6	0.6
Motor Method octane no. ..	73.5	52.0	82.5	80.5
Motor Method octane no. with 0-12% by vol TEL	—	—	—	91.5

TABLE XLII

CALCULATED COSTS FOR DHD PETROL  
(Based on Costs for First Quarter, 1944)

	Unit	Cost RM/unit	Per hour		Per te DHD petrol	
			Quantity	RM	Quantity	RM
<b>Materials:—</b>						
Petrol .. .. .	te	170.14	13.35	2,271.37	1.379	234.65
Catalysts and chemicals .. .. .	—	—	—	29.04	—	3.00
<b>Operating costs*</b> .. .. .	—	—	—	594.26	—	61.39
<b>Less Credits:—</b>						
By-products circulating gas purge .. .. .	te.cal × 10 <sup>6</sup>	7.00	14.2	99.40	1.467	10.27
Rich gas .. .. .	"	11.35†	20.5	232.68	2.118	24.04
Redistillation residue .. .. .	te	100.00	0.47	47.00	0.049	4.86
<b>Production cost</b> .. .. .	—	—	9.68	2,515.59	1.000	259.87
Loading and evaporation .. .. .	te	3.00	9.68	29.04	1.000	3.00
Oncosts .. .. .	—	—	—	262.62	—	27.13
<b>Total cost (without conversion and oil taxes and other special costs)</b> .. .. .	—	—	9.68	2,807.25	1.000	290.00

\* It is estimated that for four DHD stalls, the operating costs would be RM42/te DHD petrol and the total costs RM270/te DHD petrol.

† Butane and propane in rich gas valued at motor petrol valuation less cost of separation.

purged. Recycle gas usually contains 50-60% hydrogen. The liquid product from the cold catchpot is stabilised, re-run, and blended with a light petrol fraction.

Reaction and revivification periods are equal at 6-12 hours. The throughput of the plant, while on reaction, is equivalent to 0.6te/hr naphtha per m<sup>3</sup> of catalyst.

Catalyst is regenerated by burning off carbon with a controlled quantity of air. Regeneration gas at the beginning of the burning period contains 1-14% air, this concentration being increased to 10-15% at the end of the regeneration period. Temperatures during reaction must not exceed 550°C if catalyst life is to be maintained. Even with this precaution, however, a batch of catalyst rarely lasts more than 6 months.

The HF process is used at Moosbierbaum entirely in connection with straight-run petroleum naphthas. The yield of hydroformate is 72-73% by weight on the charge. The yield of light petrol distillate plus stabilised hydroformate is about 76% by weight on the original straight-run petrol. The final blended product has an aromatic content of 50-55% and a CFR Motor Method octane number of 80 clear. This can be increased to 91 by the addition of 0-12% TEL.

The new-formed gas amounts to about 21% by weight on the original straight-run petrol, and consists of 6.0% hydrogen, 18% methane, 25% ethane and ethylene, 30% propane and propylene, and 21% butane and butylene, all these figures being %wt.

Carbon deposited on the catalyst amounts to approximately 1% on the straight-run petrol.

### iii. DHD PROCESS

#### a. Process Conditions

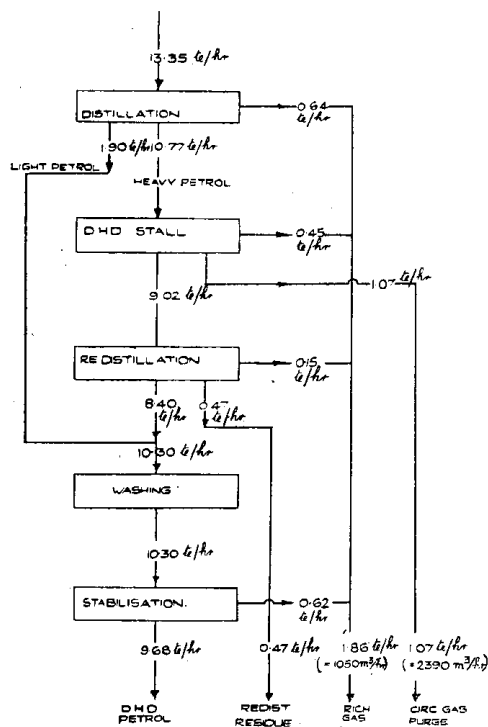
The Germans found that naphthas from the hydrogenation processes give a much lower carbon deposit when subjected to hydroforming than do straight-run petroleum naphthas. Mainly for this reason, IG developed a modified process employing only one reactor system which is off stream for catalyst revivification for only about one-tenth of the time.

A line diagram of this process is shown in Fig. 45. Hypopetrol is first fractionated to remove material boiling up to 85°C, and the bottoms are fed to the DHD process. The feed is mixed with 1,000m<sup>3</sup>/te recycle gas. It is heated first by interchange with outgoing products, and finally by means of a gas-fired preheater to a temperature of about 500°C. It passes through three or four converters arranged in series with intermediate re-heat coils. The product leaving the last converter at a temperature of about 530°C is cooled by interchange with incoming feed to a temperature of about 300°C and passes through a refining converter for saturation of polymerisable unsaturated components. It is then cooled by further interchange and by water cooling on its way to a cold catchpot in which the recycle gas and crude liquid product are separated.

The reaction is carried out at a pressure varying

between 25 and 70ats according to the nature of the feed. The higher pressures are used with the more naphthenic feed stocks such as those derived from bituminous coal and bituminous coal tar. Catalyst is 8-10% molybdic acid supported on activated alumina. The throughput was originally expected to be 0.5te/hr per m<sup>3</sup> of catalyst, but in practice it seldom exceeds 0.3. The on-stream period varies from 120-240 hours according to the nature of the feed. Highly naphthenic hydropetrols treated at the higher pressures give rise to the lowest rate of catalyst deterioration. Catalyst revivification, including the necessary purging operations, is usually completed in less than 24 hours.

FIGURE 46



FLWSHEET FOR DHD BASED ON ACHIEVED  
RESULTS 1ST QUARTER, 1944

The final DHD petrol output is of the order of 80,000te/yr for a four-converter and 100,000te/yr for a five-converter unit.

For the revivification step, the reactors are first depressured, filled with nitrogen to 10ats and depressured again. They are then filled with nitrogen, usually at 70ats pressure, and gas circulation is started. Air is admitted to the recycle gas stream at first in a quantity which restricts the oxygen content at the inlet of each reactor to 1%. Later, oxygen concentration is increased, the controlling factor being that the catalyst temperature must not exceed 540°C. During regeneration about 1m<sup>3</sup>/hr water or dilute caustic solution is introduced into each stall, either at the second heat exchanger or at the cooler, in order to remove acidic compounds produced during the oxidation. SO<sub>2</sub> must be removed completely from the recycle gas, but CO<sub>2</sub> can build up to at least 13% without harmful effect. At the end of the regeneration

treatment, the inert gas is pumped to high-pressure storage for re-use in the next regeneration stage. The converter system is depressured and normal process recycle gas introduced from storage.

#### b. Yields

The yields of final DHD 80 octane petrol blend, hydrocarbon gas, etc., vary with the type of feedstock used, the more naphthenic petrols, such as those derived from hydrogenation of bituminous coal, tar, etc., giving a higher DHD petrol yield than the more paraffinic raw materials. Carbon deposition on the catalyst is also lowest with naphthenic type feedstocks, i.e. about 0.2% by weight on the feed material. Using paraffinic petrols such as straight-run petroleum products or hydropetrols derived from brown coal and brown coal tar, carbon deposition amounts to 1.0% by weight on the original feed.

Fig. 46 is a flowsheet for the plant at Leuna operating on hydropetrol from brown coal and brown coal tar. It shows the yield of final DHD petrol blend to be 72.5% by weight on the original feed. 3.5% by weight appears as heavy naphtha residue suitable as feed to destructive hydrogenation processes. The remaining 24% is accounted for by hydrocarbon gas make, carbon and handling losses. The hydrocarbon gas is composed of approximately equal proportions by weight of ethane, methane, propane and butane.

A design flowsheet dated February, 1941, for the Schoiven plant operating on 6434 splitting stall hydropetrol obtained from coal, plus a small proportion of polymer bottoms from iso-octane manufacture, is shown in Fig. 47. The expected yield of finished DHD petrol blend is 76.5% by weight on the feed, and that of heavy naphtha residue, 3.4%. Most of the polymer bottoms would be expected to be converted into butane and, allowing for this, the yield of finished DHD petrol on the original hydropetrol feed might be as high as 79% by weight.

Captured documents are available giving the achieved results at Stettin-Pöhlitz. Feed stock varied considerably, but was usually principally composed of hydropetrol from bituminous coal, coal tar or pitch and petroleum heavy oil. 5058 saturation stall hydropetrol was normally the main component. The average yield of DHD petrol over 10 months in 1943 was 77.5% by weight. Heavy naphtha residue accounted for 4.7% by weight of the feed, and recovered liquefied hydrocarbon gas, 7.5%.

DHD petrol blends have a clear octane number of 80-81, which can be increased to about 91 by the addition of 0.1% by volume of TEL. Details of the properties of feed and DHD product obtained at Leuna are shown in Table XLI.

#### iv. UTILITY CONSUMPTIONS AND COSTS

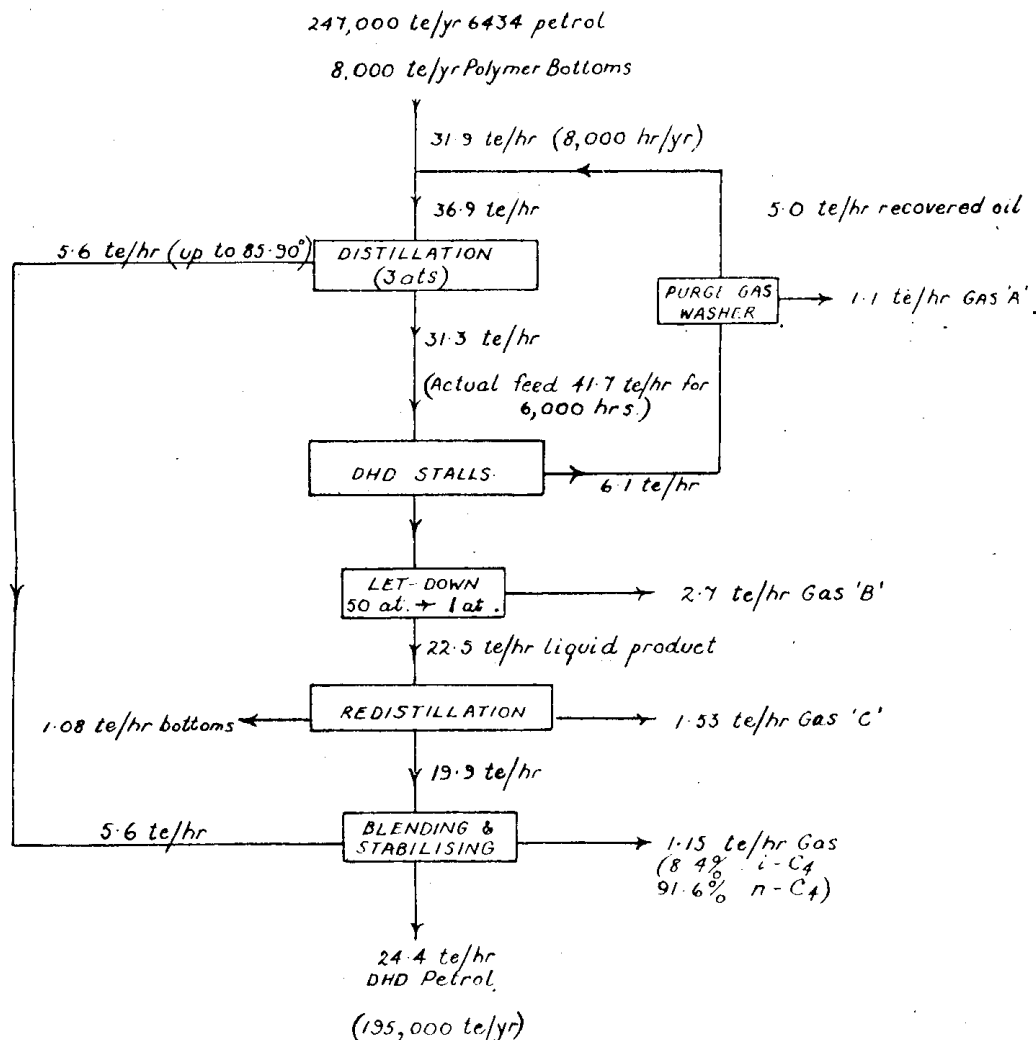
Full details of utility consumptions and costs at the Leuna plant were obtained during the investigation. They are shown in Tables XLII and XLIII. They refer to the operation of 1 four-converter unit with an annual output of about 75,000te/yr of DHD petrol blend. Operating costs alone, exclusive of capital charges, amount to RM32/te finished blend, or about 50% more than the operating costs involved in the production of the original petrol by vapour phase hydrogenation of middle oil. The total cost, even assuming a very high credit value for hydrocarbon gas by-products, is 70% higher than that of the original hydropetrol. It was estimated at Leuna that at four times the above scale the cost of finished DHD blend would still be 160% of that of the normal hydropetrol.

Captured documents show that the full cost of DHD petrol blend at Stettin-Pölitz in 1943 averaged RM500/te compared with an average cost of RM370/te for the ordinary quality aviation petrol obtained by hydrogenation of various raw materials. The scale of operation at Stettin-Pölitz in 1943 was about 165,000te/yr DHD petrol blend.

some surprise that the Germans adopted the process as a means of up-grading their aviation petrol more extensively than they employed iso-octane or alkylate synthesis. The reasons were probably:—

- (1) In the early stages of the war, hydroforming was much further developed in Germany than was the butane dehydrogenation process.

FIGURE 47



## ABSTRACT FROM SCHOLVEN DHD FLOWSHEET DATED 14.2.41

DHD feed.—Sp.gr 0.78. IBP, 85–100°C. 75%, 150°C. FBP, 180°C.

DHD stall.—Circulating gas, 1,500m³/te feed. Regeneration gas, 30,000–35,000m³/hr per stall.

Yield.—Final DHD petrol, 76.5% of total feed or 79% on petrol feed. Yield from DHD stall feed alone 71.5%.

In view of the obvious high cost of the process and the absence of interest in it on technical grounds in this country, no attempt has been made to estimate a cost under UK conditions.

## V. GENERAL NOTES ON GERMAN HYDROFORMING ACTIVITIES

In view of the great loss of output involved in the hydroforming of petrols, it is at first sight a matter for

- (2) The aircraft engine manufacturers and the Luftwaffe insisted on high rich mixture rating of aviation fuels, and in this respect aromatics are preferable to branched-chain paraffins.

As the war developed, there are indications that enthusiasm for DHD treatment declined. Aero engines capable of taking advantage of the very high rich mixture ratings of DHD fuels were not produced in any quantity and in any case it was found that high rich mixture

TABLE XLIII  
ANALYSIS OF OPERATING COSTS FOR DHD PETROL GIVEN IN TABLE XLII

	Cost per hour		Per te DHD petrol	
	Quantity	RM	Quantity	RM
<b>Labour costs :</b>				
Wages .. .. . hr	21.76	26.56	2.25	2.74
Salaries .. .. .	—	7.07	—	0.73
Social insurance .. .. .	—	2.31	—	0.24
		35.94		3.71
<b>Energy costs :</b>				
Water .. .. . m <sup>3</sup>	805.38	13.35	83.20	1.38
HP steam .. .. . te	21.43	67.44	2.21	6.97
IP steam .. .. . te	9.76	20.10	1.01	2.08
LP steam .. .. . te	5.63	13.41	0.58	1.39
Electricity, high tension .. .. . kwh	1,881.31	26.47	194.35	2.73
Electricity, low tension .. .. . kwh	267.52	5.23	27.64	0.54
Fuel gas .. .. . te.cal × 10 <sup>3</sup>	6,461.04	58.13	667.46	6.01
Other forms .. .. .	—	0.28	—	0.03
		163.65		16.91
<b>Maintenance costs :</b>				
Wages .. .. . hr	13.19	15.62	1.36	1.61
Material .. .. .	—	6.98	—	0.72
Workshop and material oncost .. .. .	—	26.57	—	2.75
		49.17		5.08
<b>Working materials</b> .. .. .	—	1.71	—	0.18
<b>Traffic charges</b> .. .. .	—	0.25	—	0.03
<b>Works general charges</b> .. .. .	—	20.04	—	2.07
<b>Capital charges :</b>				
Writing off .. .. .	—	192.78	—	19.90
Obsolescence .. .. .	—	104.51	—	10.80
		297.29		30.70
<b>Taxes</b> .. .. .	—	20.88	—	2.16
<b>Various costs</b> .. .. .	—	6.01	—	0.62
<b>Less Credits</b> .. .. .	—	0.68	—	0.07
<b>TOTAL OPERATING COSTS</b> .. .. .	—	594.26	—	61.39

rating could be obtained by more economical means, such as the addition of monomethyl-aniline. The speed of erection of DHD units appears to have been slowed down and in some cases—for example—Leuna, no serious attempt appeared to have been made to operate all the units available.

## 5. ISO-OCTANE AND ALKYLATE PRODUCTION

### i. GENERAL

The method originally adopted in Germany for production of high octane number branched-paraffin components of aviation fuels was manufacture of iso-octane from isobutyl alcohol. The latter is made from carbon monoxide and hydrogen by the well-known higher alcohols process described in CIOS reports on Oppau and Leuna. The first step consists of dehydration of isobutyl alcohol to isobutylene by treatment at 330–360°C over alumina catalyst. Isobutylene, obtained in 96% of theoretical yield, is next polymerised over a catalyst consisting of either 10% phosphoric acid on coke or magnesium silico phosphate. This stage is carried out at about 20ats and 120–160°C. The polymer is fractionated to give dimer and trimer overhead and higher polymers as residue. The distillate is finally saturated to the corresponding iso-octanes and isododecanes by treatment with hydrogen at 300ats over a nickel tungsten sulphide catalyst (5615). The overall yield of iso-octane plus isododecane is about 70% by weight on the original isobutyl alcohol.

Until comparatively late in the war, the greater part of the isobutyl alcohol produced at Oppau and Leuna (14,000 and 17,000te/yr respectively) was converted into iso-octane. New plants were erected at Heydebreck and Auschwitz with capacities of 50,000 and 25,000te/yr iso-octane. The former plant was put into operation in 1944 but never produced more than half its design output. The Auschwitz plant was never in production.

By 1940 IG had developed a process for production of butylenes by dehydrogenation of butanes made in the destructive hydrogenation processes. Plant for this process was installed at Leuna, Stettin-Pöhlitz and Scholven. Erection of other plants at Wesseling, Böhlen, Brüx and Blechhammer was put in hand, but they were not completed before the end of the war. The Leuna, Stettin-Pöhlitz and Scholven plants operated initially on dehydrogenation of isobutane to isobutylene which was polymerised in the same way as isobutylene derived from isobutyl alcohol. The achieved yield of iso-octane plus isododecane was 65–70% on the isobutane fed to dehydrogenation. The actual production was:—

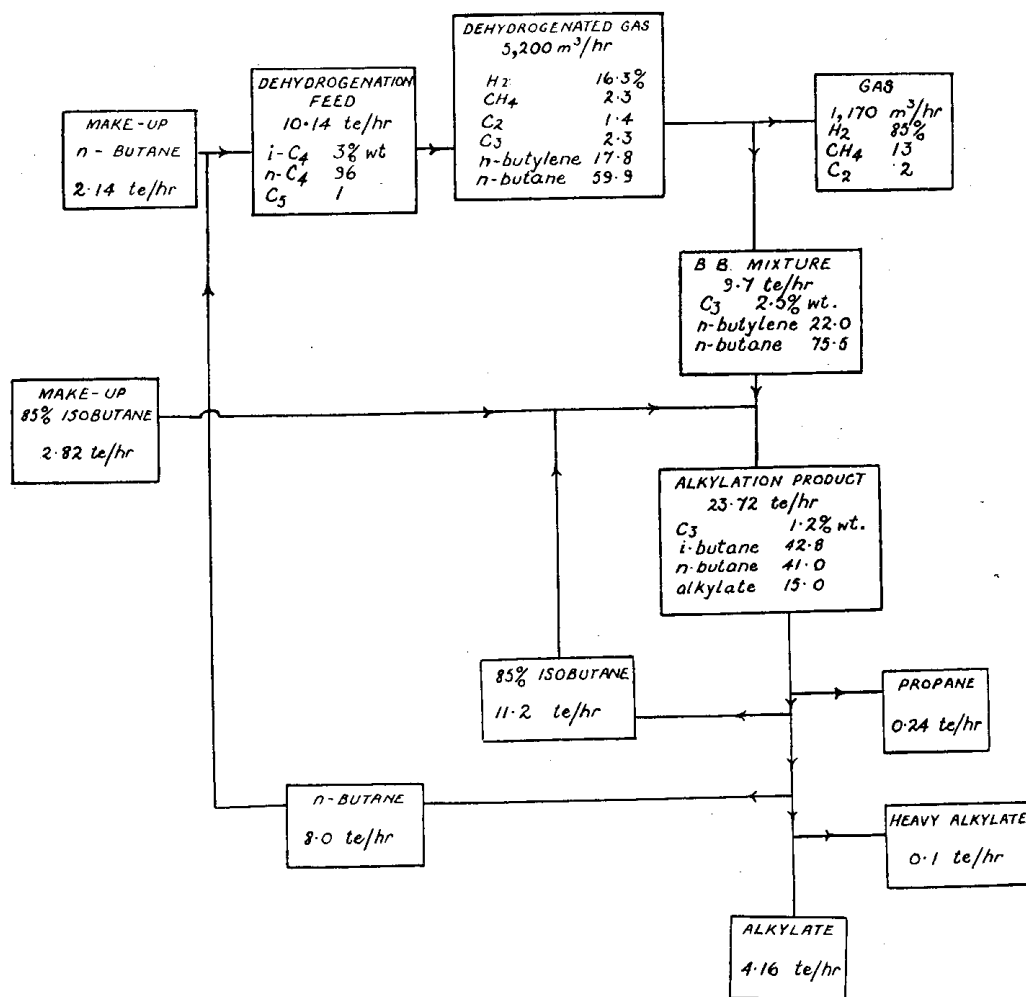
Stettin-Pöhlitz ..	17,000te/yr
Scholven .. .. .	23,000 „
Leuna .. .. .	20,000 „

At a later stage, a process was developed for alkylation of isobutane with normal butylene obtained by dehydrogenation of normal butane from the hydrogenation plants. Alkylation plants were erected and operated at Leuna and Scholven in 1944. A similar plant may have been

completed at Stettin-Pölitz, but it was certainly not in operation by April, 1944. The effect of the change was to increase by some 130% the production of branched-paraffin aviation petrol components obtainable from a given dehydrogenation capacity. The yield of alkylate was 80-85%wt on the total butane used. A quantity flowsheet for alkylate production at Leuna is given in Fig. 48; the flowsheet has been compiled from typical analyses and rates, which are in some cases not mutually consistent.

lined in such a way as to form a venturi tube which passes the heating gas into the upper part of the furnace from which it flows downwards around each of the reactor tube bundles. Heating gas is obtained by burning fuel gas in a chamber situated below the central part of the furnace. The combustion gases are collected in a firebrick ring and thence leave the reaction chamber. Before passing to the stack, the combustion gases are used to preheat the n-butane feed. The flow of catalyst, butane and combustion gases is concurrent.

FIGURE 48



QUANTITY FLOWSHEET FOR ALKYLATE PRODUCTION AT LEUNA

## ii. BUTANE DEHYDROGENATION

The method adopted by the Germans for dehydrogenation of butane is of considerable interest because it employs the moving burden catalyst technique. Fig. 49 is a line diagram of the plant employed at Leuna. Seven dehydrogenation reactors are installed, of which five are in use at any time, one being under repair and one spare. Each reactor consists of a vertical firebrick-lined circular furnace containing eight catalyst tube bundles with 16 tubes per bundle. The tube bundles are arranged around an annular central heating space which is brick-

The tube bundles, which represent the reaction space proper, consist of 16 Sicromal-8 tubes (about 8% Cr, 1-2% Si), each of which has an internal diameter of 70mm and a length of 5m; the tubes are arranged in a circle around a centre core which is dead space. The total catalyst capacity of each reactor is 2.2m³. The catalyst is introduced at the top of the reactor and distributed to the individual tube bundles by means of a cone. The catalyst moves downwards through the tubes and the flow is controlled by means of 16 horizontal cylindrical pocket valves connected with bevel

gears and driven simultaneously by an electric motor. A vertically slotted tube (about 50cm long) is placed between the reactor tubes and the pocket valves to permit separation of the reaction products from the catalysts. In the beginning, catalyst flow was checked audibly by letting the catalyst drop on tuning forks and listening to the sound so produced by means of a stethoscope held to the outside of the reactor. This practice appears to have been found unnecessary and has been abandoned. The cylinders are filled with catalyst in the top position and are emptied by rotation to the bottom position. The catalyst is discharged into a catalyst receiver provided with motor-driven slide valves at the inlet and outlet. The catalyst tubes are kept completely filled with catalyst by continuously replacing from the top hopper the catalyst discharged into the catalyst receiver. When the receiver is filled, the top slide valve connecting it with the reactor is closed and simultaneously the connection between the top catalyst hopper and the reactor is closed. The flow of catalyst through the tubes is thereby stopped, but gas continues to flow through the reactor tubes which, of course, are full of catalyst. The catalyst in the receiver is stripped from hydrocarbons with nitrogen and transferred to the regenerator by means of a bucket conveyor, and the top catalyst hopper is refilled in the same way with regenerated catalyst. The operation of the slide valves on the catalyst receiver and hopper is controlled by means of a photocell indicating when the catalyst receiver has been filled. The residence time of the catalyst in the reactor is four hours, during which time the catalyst moves for 3.5hr and remains stationary for 0.5hr; the time to transfer spent catalyst to the regenerator and simultaneously refill the fresh catalyst hopper consequently is 0.5hr. A catalyst make-up of 165kg/day per reactor is required.

Liquid butane is vaporised with indirect steam and brought to a temperature of 500–550°C by heat exchange with the product gas from the reactor and with combustion gases leaving the reactor. The preheated gas enters the reactor tube at the top and is heated to 560–580°C by combustion gases at about 800°C. The conversion of butane amounts to 20–25% by weight.

The dehydrogenated gas is cooled by heat exchange and then by indirect water cooling. The cooled gas is next passed through a coke filter to remove high-boiling hydrocarbons, mainly aromatics, as well as dust. The filter contains 6.5m<sup>3</sup> of coke and can be operated for 3–6 months. The gas is finally cooled indirectly to about 25°C and passed into a gas holder.

The spent catalyst contains about 3–4% carbon and is regenerated at 560–580°C to give a regenerated catalyst containing 1–2% carbon. Four regenerators are installed; each consists of a circular firebrick-lined vertical shell, about 2.75m diameter and 3.6m long. The catalyst is fed from a hopper over a conical distributor to the annular space formed by metal screens around a hollow centre duct. The catalyst space ends in eight tubes which are provided with the same type of pocket valves for flow control as used in the reactor. The flue gas enters with a temperature of 500°C, passes through the catalyst where the heat of reaction raises the temperature to 560–580°C, flows into the centre duct which acts as dust separator and, by means of vertical slots, enters a collecting ring, from where it leaves the regenerator. The flue gas is circulated by means of a blower at the rate of 40,000–48,000m<sup>3</sup>/hr. The catalyst receiver and top hopper of the regenerator are equipped with motor-driven slide valves of the same design as the corresponding valves on the dehydrogenation

reactors. The catalyst hopper on top of the regenerator is provided with vibrating screens for the removal of fines. The catalyst receiver is equipped likewise.

The catalyst, which consists of activated alumina impregnated with 8% CrO<sub>3</sub> and 1–2% K<sub>2</sub>O is prepared as follows.

Activated alumina is obtained by the precipitation of sodium aluminate with HNO<sub>3</sub>. The precipitate is filtered, washed carefully and dried at about 104°C. It is then kneaded with HNO<sub>3</sub> in a stainless steel kneading machine, dried again and heated to 420–450°C. The material so obtained is mixed with such an amount of K<sub>2</sub>CrO<sub>4</sub> that the mixture contains 8% CrO<sub>3</sub> and 1–2% KOH. Sufficient water is added to obtain a plastic mass which is pressed and subsequently formed into spheres of about 7mm diameter on a candy manufacturing machine (Frankonia machine). The spheres are dried in air, further dried in a steam chest and finally heated to 400–450°C. The finished catalyst is classified and only the spherical material is used; plugging of the catalyst tubes, which results in excessive carbon formation, is thereby prevented.

The exit gas from the dehydrogenation is picked up from intermediate storage and compressed to 8ats. It is then cooled indirectly with water to about 25°C and subsequently cooled with brine to 5°C. The uncondensed portion of the gas is passed into an absorber and washed with oil at 8ats and 10°C. The absorber is jacketed and is cooled by circulating brine at 5°C through the jacket. The gas stripped from the absorption oil is returned to the compressor and recycled. High pressure steam is used for heating the absorption oil regenerator. This separation process is illustrated in Fig. 50.

When isobutane is being dehydrogenated for the production of iso-octane, the liquefied gas obtained as described above is fed to a depropaniser and the stabilised bottoms are used as feed to the polymer unit. When n-butane is dehydrogenated for the production of alkylate, the liquefied mixture (n-butane, n-butylene and propane) is fed direct to the alkylation plant and propane is removed prior to recycle of the butanes.

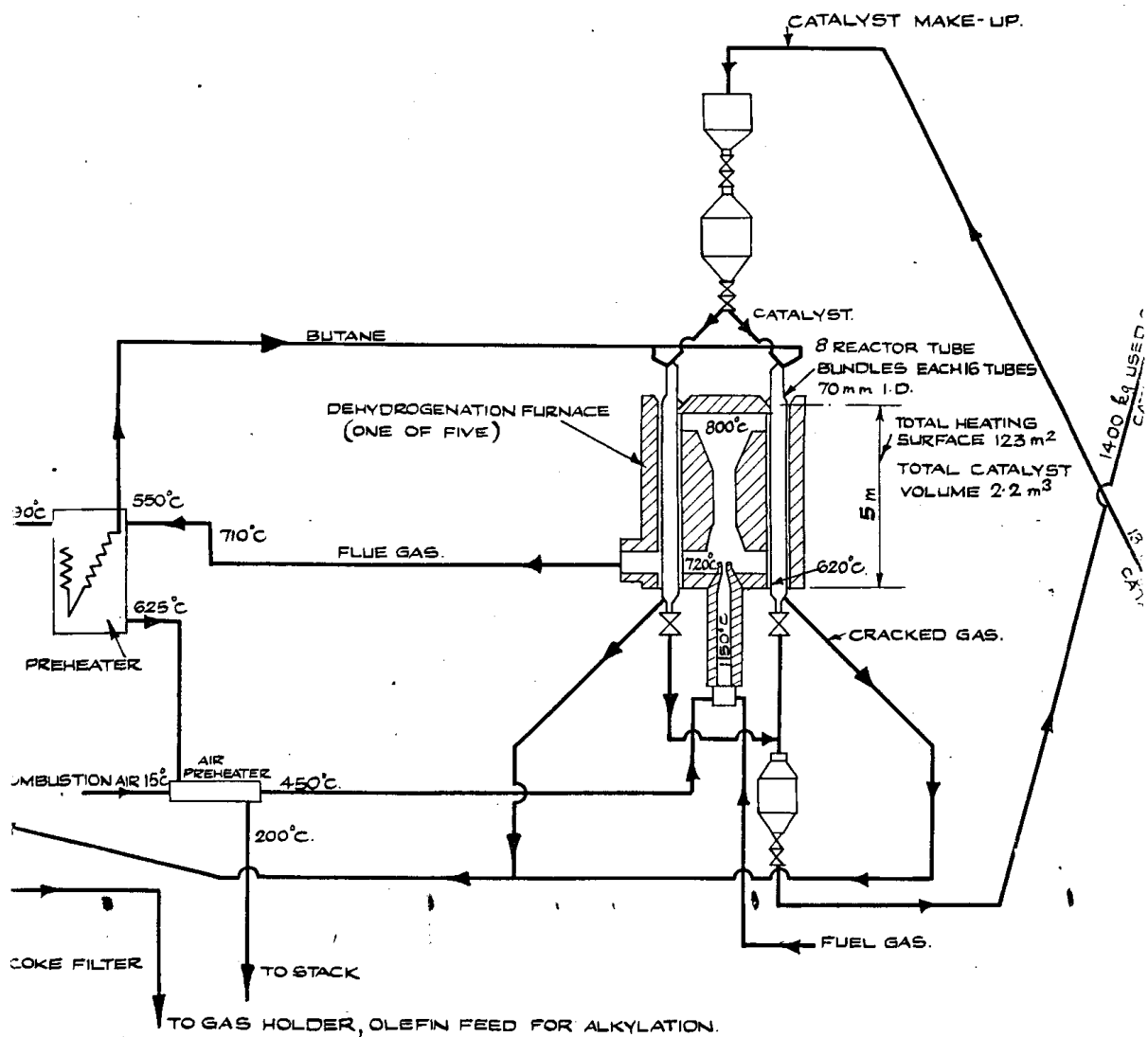
### iii. ALKYLATION PROCESS

A line diagram of this process as employed at Leuna is shown in Fig. 50. Each of the alkylation reactors (of which there are 12; five being in use at any one time) consists of an insulated vertical cylindrical vessel, 3.5m high with capacity of 25m<sup>3</sup>. The reactors are equipped with motor-driven stirrers having blades 80cm long rotating at 120rpm. The volume of a reactor up to the emulsion outlet is approximately 10m<sup>3</sup>. The nett rate of feed is 36m<sup>3</sup>/hr of hydrocarbon per reactor and 8m<sup>3</sup>/hr sulphuric acid. The feed is cooled by interchange with outgoing product to about 8°C and the temperature of the reacting mixture is maintained at 0°C by evaporation of butane. A pressure of about 0.5ats (gauge) is maintained in the reactor and 650–700m<sup>3</sup>/hr butane is circulated for refrigeration of each reactor. 96% H<sub>2</sub>SO<sub>4</sub> is used as make-up and concentration of the recycle acid is maintained at 90%. Acid consumption amounts to 20% by weight of 96% acid on the alkylate produced. The isobutane : olefin ratio is maintained at 6 : 1 and the residence time in the reactor is 40min.

The acid hydrocarbon emulsion is allowed to settle for two hours in settlers of 30m<sup>3</sup> capacity. The upper hydrocarbon layer which is drawn off through heat exchangers (cooling the hydrocarbon feed to alkylation) passes to a final settler and caustic washer. The washed product is fed to a debutaniser, and the crude alkylate







BUTANE DEHYDROGENATION LEUNA.

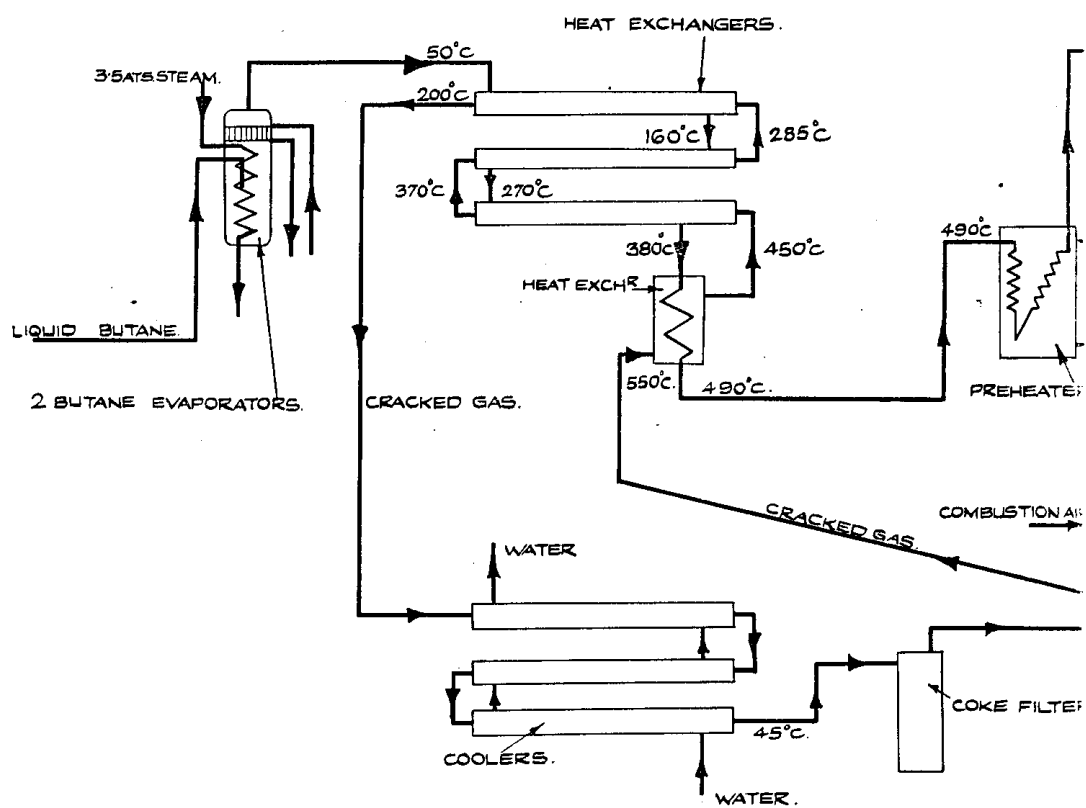
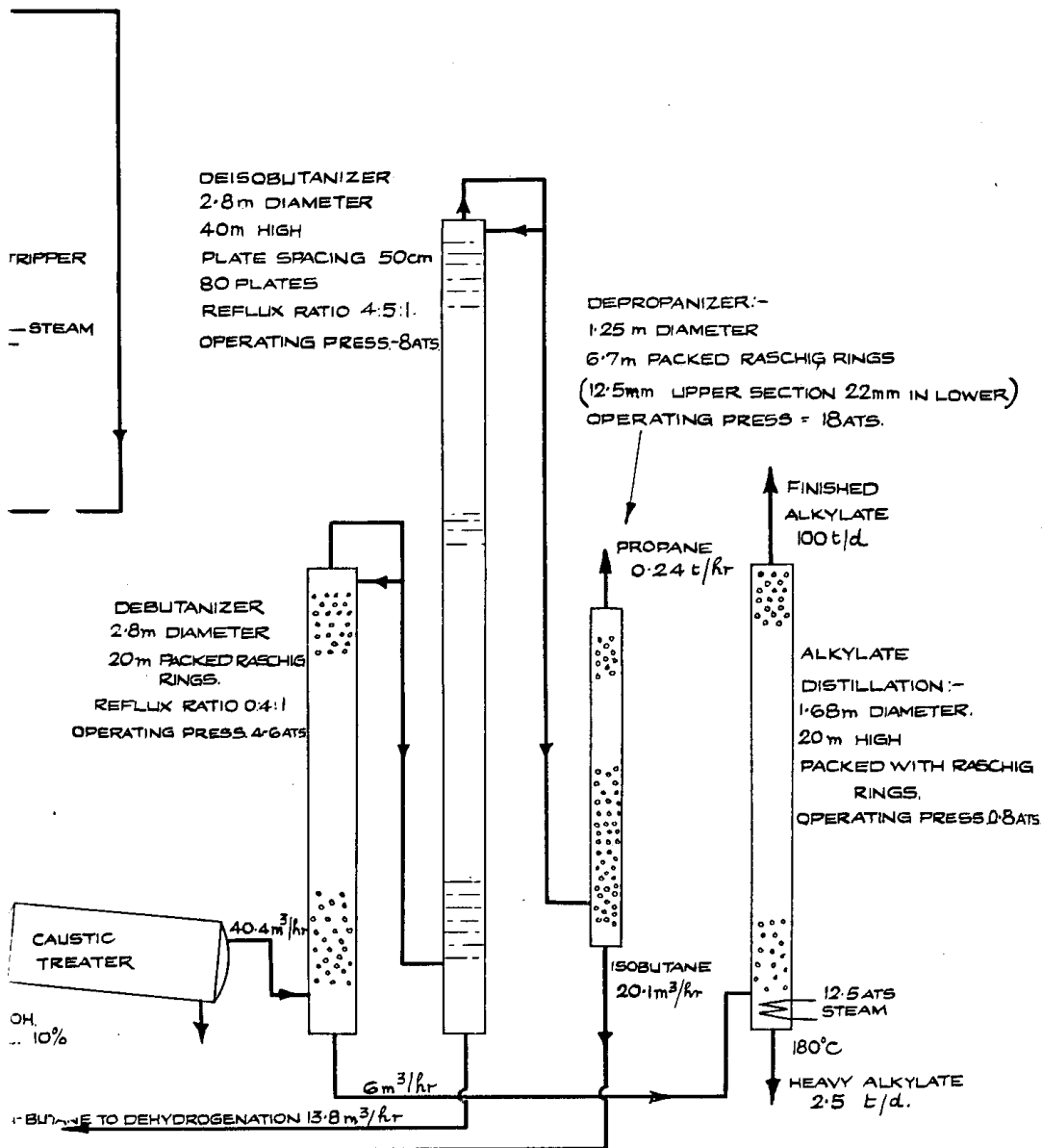
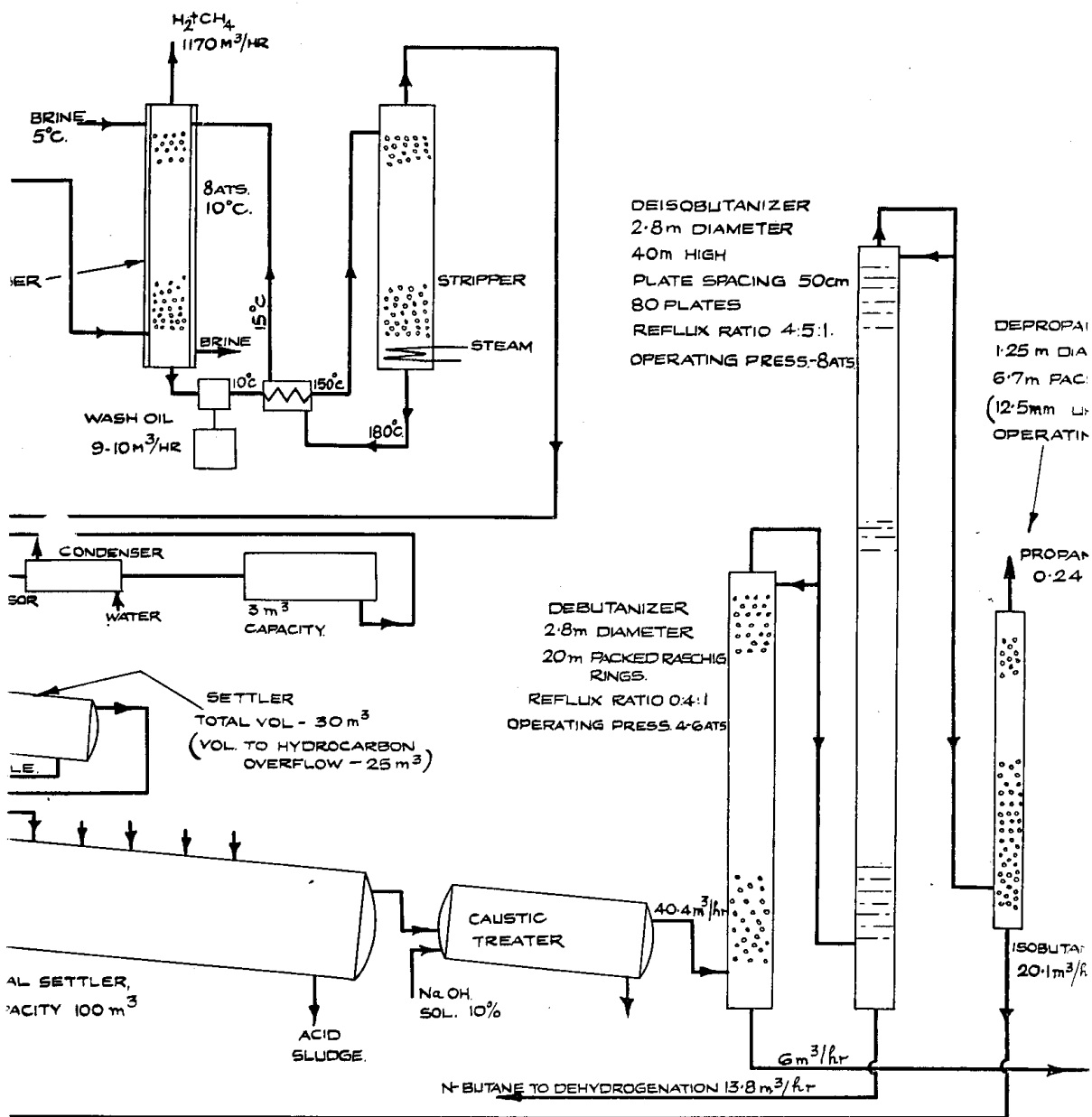


FIG.50.

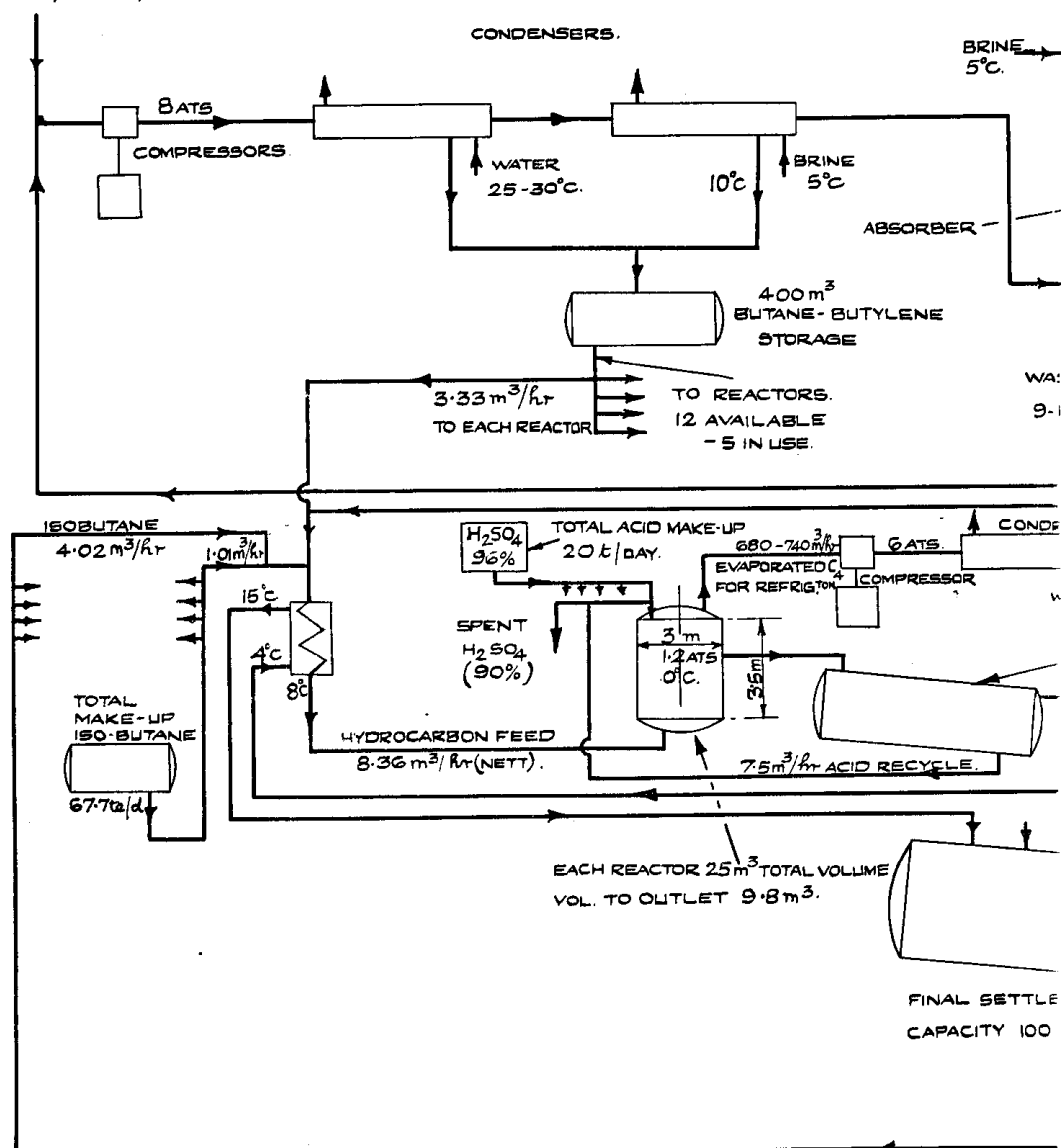




ION, LEUNA.

OLEFIN CONTAINING FEED  
FROM GAS HOLDER

5,200 m<sup>3</sup>/hr



SULPHURIC ACID ALKYLATION ,

is redistilled to give finished alkylate overhead and heavy alkylate bottoms. The overhead from the debutaniser is fractionated in a high efficiency column to separate isobutane and propane from n-butane. The latter is recycled to the dehydrogenation plant. The isobutane-propane mixture is fed to a depropaniser and the isobutane bottoms recycled to the alkylation plant.

Full details of these columns are given in the CIOS Report on Leuna (XXXII-107).

#### iv. YIELDS

##### a. Iso-octane from isobutane

A flowsheet found on the Scholven plant indicated that the expected yield of isobutane plus isododecane was 70.5% by weight on the make-up isobutane to dehydrogenation.

The make-up of the losses is shown in Table XLIV.

TABLE XLIV

EXPECTED LOSSES ON THE ISOBUTANE-ISO-OCTANE PLANTS

	% wt on isobutane fed
Handling loss and carbon deposition in the dehydrogenation plant	2.5%
As hydrogen, C <sub>1</sub> , C <sub>2</sub> , C <sub>3</sub> and C <sub>4</sub> in compression, oil washing and depropanising of dehydro product	22.5
As butane and butylene lost in polymerisation and debutanisation of polymer product	2.5
As tetramer and handling losses in polymer distillation	1.5
As handling losses and hydrocarbon gas make in saturation, less hydrogen absorbed	0.5
	<u>29.5</u>

mination of the production statistics at Stettin-Pö. shows that, in practice, higher losses were obtained and that the yield of finished iso-octane + isododecane was only 66.2% by weight on the make-up isobutane. Analysis of the average losses incurred in 1943 is given in Table XLV.

TABLE XLV

ACTUAL LOSSES ON THE ISOBUTANE-ISO-OCTANE PLANTS

	% wt on isobutane fed
Handling loss and carbon deposition in the dehydrogenation plant	8.0
As hydrogen, C <sub>1</sub> , C <sub>2</sub> , C <sub>3</sub> and C <sub>4</sub> in compression, oil washing and depropanising of dehydro product	24.0
As butane and butylene lost in polymerisation and debutanisation of polymer product	0.8
As tetramer and handling losses in polymer distillation	0.8
As handling losses and hydrocarbon gas make in saturation, less hydrogen absorbed	0.2
	<u>33.8</u>

##### b. Alkylate from Iso- and n-butane

A captured Scholven flowsheet anticipated a yield of 82-83% finished alkylate on make-up butane. The expected losses are given in Table XLVI.

TABLE XLVI

PECTED LOSSES AT SCHOLVEN ALKYLATE PLANT

	% wt on total butane fed
In dehydrogenation of butane and compression and oil washing of dehydro product	7.7
Handling loss and loss to acid in alkylation	0.4
As C <sub>3</sub> , etc. in depropaniser	2.0
In isomerisation of recycle normal butane	0.4
As heavy alkylate residue	4.6
As gas loss in final stabilisation of distilled alkylate	2.6
	<u>17.7</u>

The achieved yield of alkylate at Leuna (83.9%) is similar to that expected at Scholven. The principle losses in the Leuna plant are given in Table XLVII.

TABLE XLVII

ACTUAL LOSSES ON THE LEUNA ALKYLATE PLANT

	% wt on total butane fed
Handling loss, carbon, etc., in dehydrogenation of normal butane	2.5
As hydrogen, C <sub>1</sub> , C <sub>2</sub> , C <sub>3</sub> and C <sub>4</sub> in condensation and oil washing of dehydro product	6.4
As C <sub>3</sub> , etc., in depropaniser	4.8

#### v. UTILITY CONSUMPTIONS AND COSTS

Details of utility consumptions in the production of alkylate were obtained at Leuna. These are shown in Table XLVIII.

Labour requirements at Leuna for a plant producing 100te/day alkylate were reported to be:—

	Foremen	Process workers
Dehydrogenation and compression and oil washing of dehydro gas	4	35
Alkylation, including refrigeration	3	20
Butane, isobutane separation, depropaniser, debutanising of alkylation distillation	4	28

In addition to the above, one laboratory technician and three "machinists" were employed on the plant.

No information on maintenance costs was obtained.

Captured Stettin-Pölit documents show that for the year 1943 the production costs of iso-octane + isododecane made by dehydrogenation of isobutane averaged RM927/te of product. This cost was made up as follows:—

Isobutane	RM518
Hydrogen	RM14
Catalysts	RM38
Gas credits	less RM24
Operating costs, including obsolescence of the plants concerned	RM381

A split of the operating costs was given as:—

	Finished iso-octane + isododecane
Butane dehydrogenation plant	RM181/te
Compression, oil washing and depropanising of dehydro gas	RM83/te
Polymerisation	RM24/te
Debutanising of polymer and polymer distillation	RM42/te
Saturation of octenes	RM29/te
Miscellaneous costs	RM22/te

After adding charges for licences and central administration charges, the full cost of finished iso-octane for the year 1943 was brought up to RM1,030/te.

The above costs refer to production at the rate of 17,300te/yr. The same documents provide similar data for 1942 when the production was only 8,000te. Production costs amounted to RM1,499/te, to which raw materials, less credits, contributed RM771 and operating costs RM728/te.

No breakdown of the operating costs for either 1942 or 1943 into labour, energy, maintenance and obsolescence charges has been found.

#### 6. COMPOSITION OF CATALYSTS USED ON THE INDUSTRIAL SCALE

Details of the catalysts mentioned in this Report and particularly in this Section, as well as of others also used industrially are given in Table XLIX.

TABLE XLVIII  
UTILITY CONSUMPTIONS IN ALKYLATE MANUFACTURE

Operation	HP steam 12.5-15.5ats te/te alkylate	LP steam 2-6ats te/te alkylate	Electric power kwh/te alkylate	Circulating water m <sup>3</sup> /te alkylate	Fuel gas te.cal/te alkylate
Dehydrogenation	—	1.27	98	24	2,000
Compression of dehydrogenated gas and absorption unit	0.14	—	216	84	—
Alkylation, including refrigeration	4.88	—	72	128	—
Butane-isobutane separation and depro- paniser	—	4.4	24	128	—
Debutanising of alkylate, and alkylate distillation	1.20	1.53	186	128	—

TABLE XLIX  
COMPOSITIONS OF CATALYSTS USED ON THE INDUSTRIAL SCALE

Code number	Use	Analysis
(Methane steam) (Brown oxide)	H <sub>2</sub> + CO from hydrocarbons	25% Ni <sub>2</sub> O <sub>3</sub> , 14% MgO, 28% cement, 33% kaolin
—	CO conversion	85% Fe <sub>2</sub> O <sub>3</sub> , 15% Cr <sub>2</sub> O <sub>3</sub>
10927	Methanisation of H <sub>2</sub> + CO	61% Ni, 9% MgO, 30% kieselguhr
—	Hydrogenation of tar, pitch and petroleum residuum	5% Fe on "grude" (Winkler coke from brown coal)
Bayermasse	Brown coal hydrogenation	Crude hydrated iron oxide (by-product of aluminium industry)
—	300ats bituminous coal hydrogenation	0.07% stannous oxalate + 1.0% NH <sub>4</sub> Cl, on dry coal fed
—	700ats bituminous coal hydrogenation	1.2% FeSO <sub>4</sub> ·7H <sub>2</sub> O, 1.5% Bayermasse, 0.3% Na <sub>2</sub> S, on dry coal fed
5058	Vapour phase presaturation, also MTH and TTH processes	100% WS <sub>2</sub>
7846	Early 5058 substitute	10% WS <sub>2</sub> , 3% Ni <sub>2</sub> O <sub>3</sub> , 87% Al <sub>2</sub> O <sub>3</sub>
8376	Final 5058 substitute	25% WS <sub>2</sub> , 3% NiS, 72% activated Al <sub>2</sub> O <sub>3</sub>
6434	Vapour phase splitting	10% WS <sub>2</sub> on activated Terrana earth
—	Welheim 700ats splitting	0.6% Mo, 2% Cr, 5% Zn on activated Terrana, sulphided to 5% S
7360	DHD	} 10-12% MoO <sub>3</sub> on Al <sub>2</sub> O <sub>3</sub>
5436	Hydroforming	
5931	Hydroforming	15% MoO <sub>3</sub> on activated Al <sub>2</sub> O <sub>3</sub>
7935	Improved DHD	5% MoO <sub>3</sub> on activated Al <sub>2</sub> O <sub>3</sub>
5939	Hydroforming	5% MoO <sub>3</sub> on technical Al <sub>2</sub> O <sub>3</sub> , with up to 0.7% Na <sub>2</sub> O
5635	Hydroforming	8% Cr <sub>2</sub> O <sub>3</sub> , 2% K <sub>2</sub> O, 90% Al <sub>2</sub> O <sub>3</sub>
6448	Butane dehydrogenation	75% P <sub>2</sub> O <sub>5</sub> , 4-5% H <sub>2</sub> O on asbestos
4821	Butylene polymerisation	65% P <sub>2</sub> O <sub>5</sub> , 26.75% H <sub>3</sub> PO <sub>4</sub> , 1.23% H <sub>2</sub> O, 11.09% MgO, 6.45% SiO <sub>2</sub> , 0.71% CaO, 0.30% Al <sub>2</sub> O <sub>3</sub> , 0.28% Fe <sub>2</sub> O <sub>3</sub> , 0.09% Na <sub>2</sub> O, 0.1% SO <sub>2</sub>
—	Butylene polymerisation	
5615	} Iso-octene saturation	2WS <sub>2</sub> -NiS
6718		2WS <sub>2</sub> -NiS
3076		WS <sub>2</sub> -2NiS
1132	Isobutanol synthesis	33% Cr <sub>2</sub> O <sub>3</sub> , 60% ZnO, 1% K <sub>2</sub> O, 1% graphite, 5% H <sub>2</sub> O
5780	Isobutanol dehydration	γ-Al <sub>2</sub> O <sub>3</sub> , with 0.03-0.04% Na <sub>2</sub> O, 4% H <sub>2</sub> O
2730	Isobutylene polymerisation	35% H <sub>3</sub> PO <sub>4</sub> , 5% H <sub>2</sub> O on activated C
—	Organic S removal	70% Luxmasse, 30% Na <sub>2</sub> CO <sub>3</sub>
—	Fischer catalyst	31.9% Co, 1.6% ThO <sub>2</sub> , 2.6% MgO, 63.9% kieselguhr

## D—Fischer-Tropsch Process

### I. INTRODUCTION

The process usually associated with the names of Fischer and Tropsch, the discoverers of the basic reaction, comprises the synthesis of liquid and solid aliphatic hydrocarbons from mixtures of carbon monoxide and hydrogen. The object of the present Section is to give an account of the industrial operation of this process in Germany together with a summary of the research and development work which was carried out in this field during the war.

### i. HISTORY OF THE PROCESS

In 1925, F. Fischer and H. Tropsch, of the Kaiser Wilhelm Institut für Kohlenforschung, Mülheim, Ruhr, published an account of their synthesis of a mixture of liquid and solid aliphatic hydrocarbons from water gas at temperatures in the region of 200°C at atmospheric pressure in the presence of catalysts based on iron, cobalt or nickel. The synthetic oil consisted almost entirely of straight-chain paraffin and olefine hydrocarbons and somewhat resembled a paraffin-base