ii. METHANISATION

A process for increasing the methane content of coke oven gas by conversion of carbon monoxide and dioxide was carried out at Sterkrade Holten by Ruhrchemie AG. The catalyst was nickel, magnesium oxide and kieselguhr in the ratio of 100 : 10 : 50.

For the preparation of the catalyst, 24 litres of a solution of nitrate containing 42gm/litre nickel and 6·2gm/litre magnesium oxide and 40 litres of a solution of sodium carbonate containing 80gm/litre, were heated to boiling and the nitrate added to the soda solution with stirring. After precipitation was complete, 0·5kg kieselguhr was added and well mixed by stirring. The catalyst was then filtered off in a press and washed with 220 litres hot water and the moist cake extruded on to a belt heated by an open flame. Some magnesia is lost during the washing process. The product was then broken to 3–5mm in a special mill and reduced for one hour at 350°C with a 3 : 1 H_2/N_2 mixture at a space velocity of 6,000–8,000/hr, and cooled to below 100°C in the same gas. It was then saturated with carbon dioxide.

In the process, coke oven gas from which the organic sulphur compounds had been removed passed over the catalyst at 160–215°C; as low a temperature as possible was used, control being to within 1–2°C. Increase in temperature was made only to compensate for decreasing catalyst activity. The catalyst was contained in the 28mm diameter tubes of a multi tubular vessel. Steam generation in the shell provided good temperature control.

iii. SEPARATION OF ETHYLENE AND METHANE FROM COKE OVEN GAS

A plant designed by Still for the extraction of ethylene and methane from the coke oven gas at Nordstern was in course of erection, and was very nearly complete when the works was put out of action by bombing in February, 1945. The process was new and was in the nature of an experiment.

1,700,000m³/day of purified gas were to be cooled to 4°C and scrubbed with sulphur-free benzole at 8ats. The rate of benzole circulation was to be 500m³/hr. The rich benzole was to be distilled, and the vapours compressed to 42ats before fractionation into ethylene, methane and other hydrocarbons. The cooling was to be effected by an ammonia refrigeration plant.

It was intended to send the ethylene to Hüls for rubber synthesis, while the methane and higher molecular weight hydrocarbon gases were to be compressed into cylinders for any suitable purpose.

The estimated daily yields were as follows:—

Ethylene	.. ..	24te
Methane	.. ..	28te
Other hydrocarbons	..	7½te

The estimated consumptions were:—

Steam ..	.. ..	26te/hr
Electricity	.. ..	2,060kw/hr
Water ..	.. ..	845m³/hr
Recirculated water	..	735m³/hr

Documents found at the offices of the Lurgi Gesellschaft für Wärmetechnik, Frankfurt-am-Main, showed that this Company had also made an intensive laboratory study of this problem. Their conclusion was that up to 10ats operating pressure, it is preferable to absorb ethylene and methane with active carbon, preferably nutshell charcoal, at a reduced temperature. When operating at higher pressures, a preliminary concentration by oil washing, e.g. with benzole, was preferred.

C—Hydrogenation Processes

1. INTRODUCTION

In this report, the term "hydrogenation" is taken to cover all the activities of the German factories which were classified as "Hydrierwerke" for the purpose of control and co-ordination of liquid fuel production.

The chief activity at most of these factories was production of aviation and motor petrol from indigenous raw material such as coal and coal tar, using the process of destructive hydrogenation. During the war, the necessity to produce maximum quantities of high quality special aviation fuels resulted in the erection of plant for "hydroforming" both hydrogenation and natural petroleum petrol products, and for the synthesis of branched paraffin aviation fuel components such as iso-octane and alkylate. Usually these plants were built as auxiliaries to destructive hydrogenation factories, and used hydrogenation products as their raw material. Exceptions were Mooshierbaum, which operated only the hydroforming process, and Heydebreck and Auschwitz, whose contribution to fuel production was limited to synthesis of iso-octane from isobutyl alcohol.

The interdependence of destructive hydrogenation, hydroforming and branched paraffin synthesis processes in the German oil production programme is shown in the attached chart (Fig. 26), and these three groups of processes, as operated in Germany, are described in detail in the separate sections which follow.

2. EXTENT OF GERMAN HYDROGENATION ACTIVITIES

At the outbreak of war, Germany already had seven destructive hydrogenation plants in operation, six of which were working substantially to the full capacity of the installed equipment while the seventh was just starting up. The total installed capacity of these plants was about 1,400,000te/yr of oil plus liquefied gas products, and the actual production rate in the latter part of 1939 was about 1,150,000te/yr.

Table XXV lists the plants operating before the war, and shows the raw materials employed and the individual plant outputs.

At the beginning of the war, none of the plants was equipped for secondary processes such as hydroforming of petrol naphtha or synthesis of octane or alkylate from by-product butane.

The erection of three additional destructive hydrogenation plants at Stettin-Pölitz, Lützkendorf and Wesseling had been started before the war. The first two came into production in mid 1940, and Wesseling started up at the end of 1941. Later, two large factories were erected at Brüx and Blechhammer, and these first came on to line in late 1942 and early 1944 respectively. All the older hydrogenation plants were greatly extended during the war, and in many cases auxiliary plant for

TABLE XXV

GERMAN HYDROGENATION PLANTS OPERATING IN 1939

Name of plant	Main raw material	Liquid product capacity te/yr	Liquid product production te/yr
Leuna	Brown coal	440,000	440,000
Böhlen	Brown coal tar	155,000	155,000
Magdeburg	Brown coal tar	145,000	145,000
Zeitz	Brown coal tar	170,000	170,000
Scholven	Bituminous coal	145,000	145,000
Welheim	Bituminous coal tar pitch	100,000	70,000
Gelsenberg	Bituminous coal	200,000	30,000

FIGURE 26
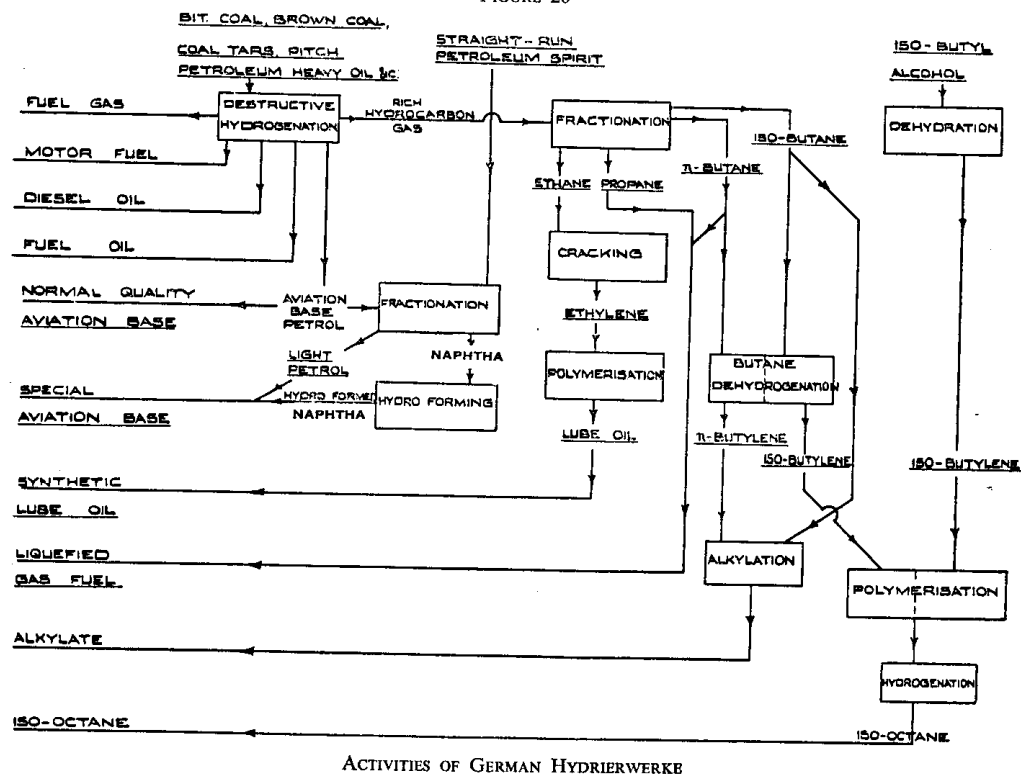
ACTIVITIES OF GERMAN HYDRIERWERKE

hydroforming petrol naphtha and for synthesis of alkylate was either installed or was in course of erection.

Immediately after the start of the war, the experimental hydrogenation equipment at Ludwigshafen-Oppau was converted to a small hydroforming plant for treatment of petroleum naphthas, and a new plant for the same purpose was erected at Moosbierbaum, and came on line in 1942.

Plants for synthesis of iso-octane and aviation base petrols from higher alcohols were erected at Heydebreck and Auschwitz. The former began production in 1944, but the Auschwitz plant had not been completed at the time it was overrun. Small quantities of oil products were also made at the synthetic rubber plants at Schkopau and Hüls.

Table XXVI summarises the available data concerning the 18 Hydrierwerke which Germany possessed at the end of the war.

The maximum rate of production of oil products by the German Hydrierwerke was obtained in the first four months of 1944. Production in these months corresponded to a yearly rate of 3,600,000te, including 350,000te liquefied gases. The serious bombing which began in May, 1944, rapidly reduced output until by the end of August, production was at the rate of only 120,000te/yr. There was a slight improvement from September to November when production reached the rate of 800,000te/yr, but further bombing brought about another decline and by February, 1945, there was a negligible output. The complete story of oil production by the individual Hydrierwerke from the beginning of 1938 to March, 1945, is shown in Tables XXVII and XXVIII.

Aviation base petrol and aviation components were the most important Hydrierwerke products. During the period of maximum production at the beginning of 1944, aviation fuel was made at a rate corresponding

TABLE XXVI

LIST OF GERMAN HYDROGENATION PLANTS OPERATING IN 1945

Name of plant	Basic process employed	Main raw material	Auxiliary processes operated		Nominal capacity for production of total liquid products, including liquefied gases	Maximum output rate achieved over reasonable extended period
			Hydroforming	Alkylate synthesis	te/yr	te/yr
Leuna	Destructive hydrogenation	Brown coal and brown coal tar	Plant installed for production of 400,000 te/yr aviation naphtha—only 25% operated	Plant of 60,000 te/yr capacity in operation	620,000	640,000
Böhlen	,,	Brown coal tar	Plant of 200,000 te/yr capacity in course of erection	Plant of 30,000 te/yr capacity in course of erection	250,000	275,000
Magdeburg ..	,,	,,	None	None	220,000	275,000
Zeitz	,,	,,	Plant of 200,000 te/yr capacity in course of erection	,,	250,000	250,000
Scholven	,,	Bituminous coal	Plant of 200,000 te/yr capacity in operation	Plant of 60,000 te/yr capacity in operation	220,000	240,000
Gelsenberg ..	,,		None	None	400,000	435,000
Welheim	,,	Pitch and tar			130,000	145,000
Stettin-Pölitz ..	,,	Bituminous coal, pitch, tar and petroleum residues	Plant of 400,000 te/yr capacity in operation	Plant of 64,000 te/yr capacity in operation	700,000	750,000
Lützkendorf ..	,,	Petroleum residues and tar	None	None	50,000	12,000
Wesseling ..	,,	Rhine brown coal	,,	Plant of 20,000 te/yr capacity in course of erection	200,000	230,000
Brüx	,,	Brown coal tar	Plant of 300,000 te/yr capacity in course of erection	Plant of 24,000 te/yr capacity in course of erection	400,000	360,000
Blechhammer ..	,,	Bituminous coal	Plant of 200,000 te/yr capacity in course of erection	Plant of 40,000 te/yr capacity in course of erection	425,000	65,000
Moosbierbaum ..	Hydroforming	Petroleum naphtha	None	None	105,000	85,000
Ludwigshafen/ Oppau	,,	,,	,,	,,	50,000	60,000
Heydebreck ..	Saturation	Higher alcohols	,,	,,	60,000	30,000
Auschwitz ..	,,	,,	,,	,,	24,000	—

to about 1,900,000te/yr. Other products were made at the following rates:—

Motor spirit	.. ..	350,000te/yr
Diesel oil	.. ..	680,000te/yr
Fuel oil ..	.. ..	240,000te/yr
Lube oil, etc.	.. ..	80,000te/yr
Liquefied gases ..	..	350,000te/yr

In order to appreciate the importance of hydrogenation in the German war effort, it is interesting to compare the production by these plants with the output of the various oils from Fischer-Tropsch plants, refining of German crude petroleum, etc. This is done in Table XXIX, the figures again referring to the early part of 1944.

3. DESTRUCTIVE HYDROGENATION

i. INTRODUCTION

Destructive hydrogenation is a method of production of hydrocarbon oils from higher molecular weight organic substances by heating these with hydrogen under high pressure and in the presence of suitable catalysts. The chemical reactions involved are complex. In the case of raw materials such as coal, which contain substantial quantities of combined oxygen, nitrogen and sulphur, the first effect is to remove the greater part of these elements as water, ammonia and hydrogen sulphide, leaving what is substantially a high-boiling "hydrocarbon." Under the influence of heat, this hydrocarbon splits or cracks into lower molecular weight substances, some at least

of which are necessarily unsaturated or deficient in hydrogen. The essential feature of the destructive hydrogenation process is that, in the presence of a suitable catalyst and of hydrogen at high pressure, the primary products of the cracking reaction are saturated with hydrogen as soon as formed, thereby avoiding polymerisation to heavier products and ultimate formation of solid carbon which are characteristic of ordinary thermal cracking processes. Satisfactory hydrogenation depends, therefore, on the choice of temperature hydrogen pressure, reaction time and, most important, of all, the catalyst which ensures a proper balance between the cracking and hydrogen absorption reactions.

Theoretically, any organic substance capable of thermal disintegration can be converted into light hydrocarbons by destructive hydrogenation. This has been largely confirmed in practice and a wide range of raw materials, including coal, coal tar pitch, etc., has now been processed in large commercial-scale plants. A characteristic of the process is that by suitable choice of conditions including the extent of recycle of intermediate products for further breakdown, it can be arrested at any desired stage so as to produce a variety of oil products. For example, coal may be hydrogenated to give heavy fuel oil with a comparatively small amount of by-product petrol and hydrocarbon gas, or conditions can be chosen so that the final product consists entirely of high volatility aviation petrol and hydrocarbon gases.

TABLE XXVII

PRODUCTION OF TOTAL OIL PRODUCTS BY INDIVIDUAL HYDROGENATION PLANTS—THOUSAND TONNES/MONTH

(These figures include liquefied gas)

Name of plant	1938 Average for			1939 Average for			1940 Average for			1941 Average for			1942 Average for			1943 Average for		
	1st third	2nd third	3rd third	1st third	2nd third	3rd third	1st third	2nd third	3rd third	1st third	2nd third	3rd third	1st third	2nd third	3rd third	1st third	2nd third	3rd third
Leuna	32·5	32·5	32·5	36·6	36·6	36·6	39·8	39·8	39·8	48·5	48·5	48·5	53·8	53·8	53·8	52·0	52·0	52·0
Böhlen	12·0	12·0	12·0	13·0	13·0	13·0	16·0	16·0	18·0	18·0	18·0	18·0	20·0	20·0	20·0	22·0	22·0	22·0
Magdeburg	11·0	11·0	11·0	12·0	12·0	12·0	14·0	14·0	14·0	15·0	15·0	15·0	16·0	16·0	16·0	18·0	18·0	18·0
Zeitz	—	—	—	7·0	10·0	14·0	16·0	14·0	14·0	18·0	18·0	18·0	20·0	20·0	20·0	21·0	21·0	21·0
Scholven	10·0	10·0	10·0	12·0	12·0	12·0	14·0	14·0	15·0	16·0	17·0	17·0	18·0	18·0	18·0	19·0	19·0	19·0
Gelsenberg	—	—	—	—	—	2·5	5·0	10·0	16·0	20·0	20·0	25·0	25·0	36·0	36·0	36·0	36·0	36·0
Welheim	—	—	2·0	6·0	6·0	6·0	8·0	8·0	8·0	8·0	8·0	8·0	9·0	9·0	9·0	10·0	10·0	10·0
Stettin-Pölitz	—	—	—	—	—	—	—	3·0	10·0	20·0	25·0	25·0	30·0	30·0	30·0	40·0	50·0	60·0
Lützkendorf	—	—	—	—	—	—	1·0	1·0	1·0	1·0	1·0	1·0	1·0	1·0	1·0	1·0	1·0	1·0
Wesseling	—	—	—	—	—	—	—	—	—	—	—	4·0	6·0	7·0	9·0	12·0	14·0	16·0
Ludwigshafen/Oppau	—	—	—	—	—	—	0·2	0·2	0·2	0·2	0·2	0·2	3·0	3·0	3·0	4·0	5·0	5·0
Moosbierbaum	—	—	—	—	—	—	—	—	—	—	—	—	—	—	2·5	4·0	5·0	6·0
Brüx	—	—	—	—	—	—	—	—	—	—	—	—	—	—	5·0	23·0	25·0	30·0
Blechhammer	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Heydebreck	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Auschwitz	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Hüls	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Schkopau	—	—	—	—	—	—	—	—	—	—	—	—	0·1	0·1	0·1	0·3	0·3	0·3
TOTAL	65·5	65·5	67·5	86·6	89·6	96·1	114·0	120·0	136·0	164·7	170·7	179·7	201·9	216·4	224·9	262·3	278·3	296·3

Name of plant	1944 Jan.	Feb.	Mar.	April	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.	1945 Jan.	Feb.	Mar.
Leuna	53·7	46·5	51·5	50·5	21·6	14·9	21·1	0·2	0·9	4·0	14·0	—	—	—	3·1
Böhlen	22·0	20·0	23·0	23·0	9·1	17·5	—	5·2	11·4	3·4	13·0	14·0	11·0	10·0	5·0
Magdeburg	18·0	16·0	19·0	18·1	16·5	5·4	—	—	—	—	—	—	2·0	—	—
Zeitz	20·0	18·0	20·0	22·0	4·3	—	—	0·8	0·8	12·4	14·0	7·0	5·0	—	—
Scholven	19·0	16·0	19·0	20·0	20·3	14·6	7·4	—	—	—	—	—	1·0	—	—
Gelsenberg	35·0	30·0	36·0	36·0	37·0	14·0	—	—	0·3	—	—	—	—	—	—
Welheim	10·0	9·0	10·0	12·0	12·1	11·9	5·8	—	0·6	—	—	—	—	—	—
Stettin-Pölitz	60·0	55·0	58·0	62·0	63·8	—	2·8	5·4	2·3	6·7	11·0	6·0	—	—	2·0
Lützkendorf	1·5	1·0	—	—	—	—	—	—	—	—	—	—	—	—	—
Wesseling	18·0	19·0	19·0	20·0	20·7	16·6	11·6	0·6	—	—	—	—	—	—	—
Ludwigshafen/Oppau	5·0	4·0	4·7	4·5	4·7	4·4	4·8	2·2	—	—	—	—	—	—	—
Moosbierbaum	6·0	5·0	6·5	7·0	7·5	3·9	—	3·8	—	4·9	1·0	—	—	—	—
Brüx	32·0	28·0	33·0	30·0	14·7	—	—	—	0·7	—	8·0	11·0	—	—	—
Blechhammer	—	1·0	2·0	2·0	—	5·4	5·2	2·6	—	1·2	11·0	2·0	—	—	—
Heydebreck	—	—	—	1·0	3·4	2·5	1·1	0·8	—	—	—	—	—	—	—
Auschwitz	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Hüls	0·3	0·2	0·3	0·4	0·3	0·2	0·1	0·1	0·1	0·1	0·1	0·1	0·1	0·2	0·1
Schkopau	—	—	—	—	—	0·2	0·2	0·2	0·2	0·2	0·2	0·2	0·2	—	—
TOTAL	300·5	268·7	302·0	308·5	235·7	111·5	60·1	21·9	17·3	32·9	72·3	40·3	19·3	10·2	10·2

Most of the more complex hydrogenation raw materials, such as coal or coal tar, contain small quantities of inorganic and unreactive organic substances. These have to be purged from the hydrogenation system and small quantities of oil product are inevitably lost in the operation. Apart from these purge losses, all the carbon in the original raw material appears as hydrocarbon oil or hydrocarbon gas. The amount of hydrocarbon gas made naturally increases with the extent of the hydrogenation treatment, but it is by no means a waste product. It consists largely of butanes and propane which can be sold in the liquid form as domestic or motor fuel. A more important use for butanes in war-time lies in their conversion into iso-octane or alkylate, *i.e.* branched-chain paraffin hydrocarbons of high anti-knock quality, which are required for blending with high-volatility petrols to produce aviation fuels. Alternatively, by-product hydrocarbon gas may be reacted catalytically with steam to give a part, or, in some cases, all the hydrogen required for the hydrogenation process itself.

A further important feature of the destructive hydrogenation process, particularly when applied to aromatic raw materials, is that it gives rise to petrol products having extremely good anti-knock qualities. Hydro-petrols also have a considerably lower sulphur content

than corresponding products obtained by conventional petroleum refining, and for this reason they show a maximum increase of knock rating on addition of tetraethyl lead. When the process is arrested at an intermediate stage, so as to produce oils boiling in the gas oil range (240–320°C), such products are usually too aromatic or naphthenic to be very good diesel oils. Likewise the higher boiling hydrogenation products do not provide a source of good quality lubricating oil. It follows that normally the most advantageous use of the hydrogenation process is in the production of petrol products.

The reason for Germany's concentration on destructive hydrogenation, particularly for production of aviation fuels, will be appreciated from the above very brief review of the characteristics of the process. It was, in fact, the only method which could secure adequate quantities of suitable fuels from her indigenous raw materials; economics had to be completely ignored.

Before giving a detailed description of the various hydrogenation processes as practised in Germany, it is preferable to give the theoretical background to an important technical feature which is common to the majority of these processes. It has been pointed out that it is essential in any hydrogenation process to balance the splitting and hydrogen saturation reactions.

TABLE XXVIII

PRODUCTION OF AVIATION PETROL AND COMPONENTS BY INDIVIDUAL HYDROGENATION PLANTS—THOUSAND TONNES/MONTH

Name of plant	1938 Average for			1939 Average for			1940 Average for			1941 Average for			1942 Average for			1943 Average for		
	1st third	2nd third	3rd third	1st third	2nd third	3rd third	1st third	2nd third	3rd third	1st third	2nd third	3rd third	1st third	2nd third	3rd third	1st third	2nd third	3rd third
Leuna	5·3	5·3	5·3	12·9	12·9	12·9	19·8	19·8	19·8	20·3	20·3	20·3	24·0	24·0	24·0	21·0	21·0	21·0
Böhlen	—	—	—	—	—	—	—	—	12·0	14·0	7·0	—	14·0	16·0	16·0	—	16·0	10·0
Magdeburg	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Zeitz	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Scholven	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Gelsenberg	—	—	—	—	6·0	10·0	12·0	12·0	13·0	13·0	14·0	14·0	15·0	16·0	17·0	17·0	17·0	17·0
Welheim	—	—	—	—	—	—	—	7·0	12·0	15·0	15·0	18·0	18·0	29·0	29·0	30·0	30·0	30·0
Stettin-Pölitz	—	—	—	—	—	—	2·0	2·5	2·5	2·5	2·5	2·5	3·0	3·0	3·0	4·0	4·0	4·0
Lützkendorf	—	—	—	—	—	—	—	2·0	8·0	15·0	19·0	19·0	22·0	22·0	22·0	39·0	38·0	46·0
Wesseling	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Ludwigshafen/Oppau	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Moosbierbaum	—	—	—	—	—	—	0·2	0·2	0·2	0·2	0·2	0·2	3·0	3·0	—	—	7·0	11·0
Brüx	—	—	—	—	—	—	—	—	—	—	—	—	—	2·5	3·0	4·0	5·0	5·0
Blechhammer	—	—	—	—	—	—	—	—	—	—	—	—	—	—	4·0	4·0	5·0	6·0
Heydebreck	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	15·0	17·0	22·0
Auschwitz	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Hüls	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Schkopau	—	—	—	—	—	—	—	—	—	—	—	—	0·1	0·1	0·1	0·3	0·3	0·3
TOTAL	5·3	5·3	5·3	12·9	18·9	22·9	34·0	43·5	67·5	80·0	78·0	74·0	99·1	115·6	118·1	127·3	160·3	172·3

Name of plant	1944												1945		
	Jan.	Feb.	Mar.	April	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.	Jan.	Feb.	Mar.
Leuna	9·5	8·4	9·6	8·8	3·6	—	7·6	—	—	2·1	9·4	—	—	—	—
Böhlen	14·0	15·0	—	—	—	—	—	—	—	—	—	—	—	—	—
Magdeburg	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Zeitz	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Scholven	17·0	13·0	17·0	18·0	18·0	12·0	1·0	—	—	—	—	—	—	—	—
Gelsenberg	29·0	26·0	31·0	31·0	32·0	12·0	—	—	—	—	—	—	—	—	—
Welheim	4·0	3·0	4·0	4·5	4·5	4·0	2·0	—	—	—	—	—	—	—	—
Stettin-Pölitz	46·0	41·0	43·0	48·0	49·0	—	2·5	5·0	2·0	6·2	10·0	5·5	—	—	—
Lützkendorf	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Wesseling	13·0	14·0	14·0	15·0	15·0	11·0	5·0	—	—	—	—	—	—	—	—
Ludwigshafen/Oppau	5·0	4·0	4·7	4·5	4·7	4·4	4·8	2·2	—	—	—	—	—	—	—
Moosbierbaum	6·0	5·0	6·5	7·0	7·5	3·9	—	3·8	—	4·9	1·0	—	—	—	—
Brüx	22·0	20·0	24·0	21·0	11·0	—	—	—	0·5	—	7·0	9·0	—	—	—
Blechhammer	—	—	—	1·0	—	2·2	2·1	1·3	—	0·6	5·5	1·0	—	—	—
Heydebreck	—	—	—	0·8	2·2	1·6	0·7	0·5	—	—	—	—	—	—	—
Auschwitz	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Hüls	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Schkopau	0·3	0·2	0·3	0·4	0·3	0·2 / 0·2	0·1 / 0·2	0·1 / 0·2	0·1 / 0·2	0·1 / 0·2	0·1 / 0·2	0·1 / 0·2	0·1 / 0·2	0·2	0·1
TOTAL	165·8	149·6	153·5	160·0	147·8	51·5	31·0	13·1	2·8	14·0	33·2	15·8	0·3	0·2	0·1

TABLE XXIX

SUMMARY OF GERMAN OIL AVAILABILITY FROM VARIOUS SOURCES AT THE BEGINNING OF 1944

(Figures in tonnes)

Type of oil product	Annual rate of production by						TOTAL
	Hydrogenation	Fischer-Tropsch synthesis plants	Refining of German and Austrian petroleum	Brown coal and bituminous coal tar distillation	Benzole	Imports from Rumania and Hungary	
Aviation fuel	1,900,000	—	—	—	50,000	100,000	2,050,000
Motor spirit	350,000	270,000	160,000	35,000	330,000	600,000	1,745,000
Diesel oil	680,000	135,000	670,000	110,000	—	480,000	2,075,000
Fuel oil	240,000	—	120,000	750,000	—	—	1,110,000
Lubricating oil	40,000	20,000	780,000	—	—	—	840,000
Miscellaneous	40,000	160,000	40,000	50,000	—	—	290,000

The temperature required for the former reaction to proceed at a satisfactory speed is lower the higher the molecular weight of the molecule being cracked. It is thus more difficult to ensure balanced hydrogenation conditions when attempting to convert a very complex raw material into petrol in a single stage, than is the case when the process is sub-divided into two or more stages, in each of which optimum conditions can be chosen for cracking material in a relatively narrow range of molecular size.

This argument in favour of multi-stage hydrogenation processes is supported by a further consideration. From the standpoint of maximum throughput and maximum yield of any particular oil product, the use of an active catalyst is all-important. The best catalysts give optimum results when used in high concentration in

TABLE XXVIII

PRODUCTION OF AVIATION PETROL AND COMPONENTS BY INDIVIDUAL HYDROGENATION PLANTS—THOUSAND TONNES/MONTH

Name of plant	1938 Average for			1939 Average for			1940 Average for			1941 Average for			1942 Average for			1943 Average for		
	1st third	2nd third	3rd third	1st third	2nd third	3rd third	1st third	2nd third	3rd third	1st third	2nd third	3rd third	1st third	2nd third	3rd third	1st third	2nd third	3rd third
Leuna	5·3	5·3	5·3	12·9	12·9	12·9	19·8	19·8	19·8	20·3	20·3	20·3	24·0	24·0	24·0	21·0	21·0	21·0
Böhlen	—	—	—	—	—	—	—	—	12·0	14·0	7·0	—	14·0	16·0	16·0	—	16·0	10·0
Magdeburg	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Zeitz	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Scholven	—	—	—	—	6·0	10·0	12·0	12·0	13·0	13·0	14·0	14·0	15·0	16·0	17·0	17·0	17·0	17·0
Gelsenberg	—	—	—	—	—	—	—	7·0	12·0	15·0	15·0	18·0	18·0	29·0	29·0	30·0	30·0	30·0
Welheim	—	—	—	—	—	—	2·0	2·5	2·5	2·5	2·5	2·5	3·0	3·0	3·0	4·0	4·0	4·0
Stettin-Pölitz	—	—	—	—	—	—	—	2·0	8·0	15·0	19·0	19·0	22·0	22·0	22·0	39·0	38·0	46·0
Lützkendorf	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Wesseling	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	7·0	11·0
Ludwigshafen/Oppau	—	—	—	—	—	—	0·2	0·2	0·2	0·2	0·2	0·2	3·0	3·0	3·0	4·0	5·0	5·0
Moosbierbaum	—	—	—	—	—	—	—	—	—	—	—	—	—	2·5	4·0	4·0	5·0	6·0
Brüx	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	15·0	17·0	22·0
Blechhammer	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Heydebreck	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Auschwitz	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Hüls	—	—	—	—	—	—	—	—	—	—	—	—	0·1	0·1	0·1	0·3	0·3	0·3
Schkopau	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
TOTAL	5·3	5·3	5·3	12·9	18·9	22·9	34·0	43·5	67·5	80·0	78·0	74·0	99·1	115·6	118·1	127·3	160·3	172·3

Name of plant	1944												1945		
	Jan.	Feb.	Mar.	April	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.	Jan.	Feb.	Mar.
Leuna	9·5	8·4	9·6	8·8	3·6	—	7·6	—	—	2·1	9·4	—	—	—	—
Böhlen	14·0	15·0	—	—	—	—	—	—	—	—	—	—	—	—	—
Magdeburg	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Zeitz	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Scholven	17·0	13·0	17·0	18·0	18·0	12·0	1·0	—	—	—	—	—	—	—	—
Gelsenberg	29·0	26·0	31·0	31·0	32·0	12·0	—	—	—	—	—	—	—	—	—
Welheim	4·0	3·0	4·0	4·5	4·5	4·0	2·0	—	—	—	—	—	—	—	—
Stettin-Pölitz	46·0	41·0	43·0	48·0	49·0	—	2·5	5·0	2·0	6·2	10·0	5·5	—	—	—
Lützkendorf	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Wesseling	13·0	14·0	14·0	15·0	15·0	11·0	5·0	—	—	—	—	—	—	—	—
Ludwigshafen/Oppau	5·0	4·0	4·7	4·5	4·7	4·4	4·8	2·2	—	—	—	—	—	—	—
Moosbierbaum	6·0	5·0	6·5	7·0	7·5	3·9	—	3·8	—	4·9	1·0	—	—	—	—
Brüx	22·0	20·0	24·0	21·0	11·0	—	—	—	0·5	—	7·0	9·0	—	—	—
Blechhammer	—	—	—	1·0	—	2·2	2·1	1·3	—	0·6	5·5	1·0	—	—	—
Heydebreck	—	—	—	0·8	2·2	1·6	0·7	0·5	—	—	—	—	—	—	—
Auschwitz	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Hüls	0·3	0·2	0·3	0·4	0·3	0·2	0·1	0·1	0·1	0·1	0·1	0·1	0·1	0·2	0·1
Schkopau	—	—	—	—	—	0·2	0·2	0·2	0·2	0·2	0·2	0·2	0·2	—	—
TOTAL	165·8	149·6	153·5	160·0	147·8	51·5	31·0	13·1	2·8	14·0	33·2	15·8	0·3	0·2	0·1

TABLE XXIX   ᴸ∕

SUMMARY OF GERMAN OIL AVAILABILITY FROM VARIOUS SOURCES AT THE BEGINNING OF 1944

(Figures in tonnes)

Type of oil product	Annual rate of production by						
	Hydrogenation	Fischer-Tropsch synthesis plants	Refining of German and Austrian petroleum	Brown coal and bituminous coal tar distillation	Benzole	Imports from Rumania and Hungary	TOTAL
Aviation fuel	1,900,000	—	—	—	50,000	100,000	2,050,000
Motor spirit	350,000	270,000	160,000	35,000	330,000	600,000	1,745,000
Diesel oil	680,000	135,000	670,000	110,000	—	480,000	2,075,000
Fuel oil	240,000	—	120,000	750,000	—	—	1,110,000
Lubricating oil	40,000	20,000	780,000	—	—	—	840,000
Miscellaneous	40,000	160,000	40,000	50,000	—	—	290,000

The temperature required for the former reaction to proceed at a satisfactory speed is lower the higher the molecular weight of the molecule being cracked. It is thus more difficult to ensure balanced hydrogenation conditions when attempting to convert a very complex raw material into petrol in a single stage, than is the case when the process is sub-divided into two or more stages, in each of which optimum conditions can be chosen for cracking material in a relatively narrow range of molecular size.

This argument in favour of multi-stage hydrogenation processes is supported by a further consideration. From the standpoint of maximum throughput and maximum yield of any particular oil product, the use of an active catalyst is all-important. The best catalysts give optimum results when used in high concentration in

the form of a fixed bed of pellets placed in the reaction vessel. The use of catalysts in this way is obviously restricted to conditions in which catalyst deterioration is limited, and such conditions are normally obtained only when the feed material is a comparatively light distillate oil, consisting mainly of hydrocarbons which can be processed in the vapour phase.
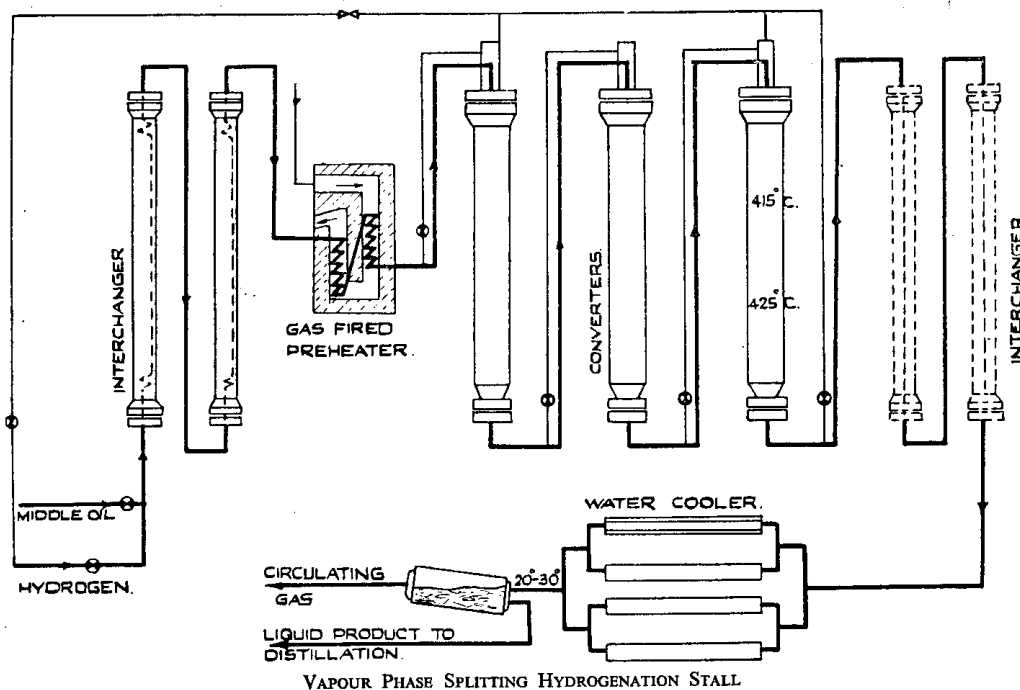
Consequently, destructive hydrogenation to petrol of complex raw materials is carried out in at least two stages:—

(1) Treatment in the liquid phase, usually with a dispersed powder catalyst, to a product consisting mainly of middle oil (boiling up to about 325°C), and

(2) vapour phase hydrogenation of this middle oil to petrol over an active fixed catalyst.

intermediate gas mixing chambers into which cold hydrogen is introduced in order to control the exothermic reaction. The maximum reaction temperature is about 450°C.

The products leaving the converter pass through the shells of the two interchangers and thence via a water cooler to a high pressure cold separator vessel. Here the condensed oil product is separated from unreacted hydrogen. The latter is circulated to the inlet of the plant and the liquid product is let down to atmospheric pressure in two or three stages. The purpose of the multi-stage let-down is to separate the hydrocarbon gas which comes out of solution in the oil into a "lean gas," consisting mainly of hydrogen and methane and used as fuel, and "rich gas," which is treated for separation of the butanes and propane. Normally, hydrocarbon gas

FIGURE 27

VAPOUR PHASE SPLITTING HYDROGENATION STALL

ii. HYDROGENATION OF VAPORISABLE MIDDLE OIL
    TO PETROL

a. *General Description of Normal Process*

As explained in the Introduction, this is the simplest and most efficient application of the destructive hydrogenation process. The procedure adopted in Germany for treatment of a highly refined hydrocarbon middle oil may be followed from the line diagram shown in Fig. 27. The oil is pumped into the plant against an operating pressure of 250–300ats. It is joined by a stream of high pressure hydrogen and the two reactants are heated, first by passage through the tubes of two tubular heat exchangers and finally in a gas-fired tubular preheater, to a temperature of about 400°C. The hydrogen : oil ratio is maintained sufficiently high (usually 2,000m³ hydrogen/te oil) to ensure complete vaporisation of the oil before it leaves the preheater. The middle oil vapour and hydrogen are then passed downflow through a series of converters packed with pelleted catalyst. The catalyst is arranged in beds with

dissolved in the liquid product represents the whole of that gas made in the reaction and there is therefore no need to wash the recycle high pressure hydrogen with oil in order to effect a further hydrocarbon gas purge. Recycle gas is, however, frequently washed with water to remove ammonia which, as will be seen later, has a repressive effect on the reaction.

The liquid product, which contains 50–70% of petrol, is distilled to give petrol of the desired end-point or volatility as overhead and middle oil bottoms which are recycled for further treatment. The petrol is finally stabilised, *i.e.* fed to a pressure still for removal of dissolved butane and propane, to the extent necessary to reduce the vapour pressure of the petrol to the required figure.

The catalyst employed in Germany in the above process, which is usually referred to as "vapour phase splitting hydrogenation," is 10% of tungsten sulphide (WS₂) supported on activated Terrana Earth (Catalyst No. 6434). In order to maintain the catalyst at maximum

activity, it is necessary to keep it in a sulphided condition. In cases where the make-up middle oil has a low sulphur content, this is achieved by dissolving a suitable quantity of hydrogen sulphide in the oil fed to the stall.

The single-stage vapour phase splitting hydrogenation process described above is, however, only satisfactory with refined hydrocarbon middle oil feedstocks which are substantially free from nitrogen compounds. Such feeds are of very limited availability and most middle oils processed in Germany—for example those obtained by distillation of crude tars or by hydrogenation of heavier materials—contain an appreciable amount of nitrogen derivatives which have a very marked repressive effect on the splitting hydrogenation catalyst. The oxygen-containing compounds present in these feeds also have a repressive and probably a permanent deteriorating effect on the catalyst. It is therefore customary to refine such feedstocks by a mild hydrogenation, which process is usually referred to as "presaturation."

Presaturation is carried out in plant identical to that described above for vapour phase splitting hydrogenation, but it is a once-through as distinct from a recycle process. The catalyst employed is tungsten sulphide (5058), or 25% tungsten sulphide + 3% nickel sulphide supported on activated alumina (8376). The latter is a new catalyst developed by IG during the war. It is alleged to remove impurities from the oil with less accompanying saturation of the aromatic components, but there is evidence that it is inferior to 5058 as regards catalyst life and that the main reason for its use in Germany was shortage of tungsten. Reaction temperature is controlled at 400–410°C by introduction of cold hydrogen between catalyst beds. Reaction pressure is 250–300ats. When the two-stage vapour phase process is used, the life of the catalyst in both stages is at least one year.

Although conditions in presaturation are adjusted to give a minimum of splitting between carbon atoms, there is, nevertheless, a marked reduction in boiling range of the oil, due, for example, to conversion of phenols to corresponding hydrocarbons and to the saturation of aromatics to lower-boiling naphthenes. It follows that, even with a middle oil feed free from constituents boiling in the petrol range, the presaturated products contain a substantial amount (up to 30%) of "petrol." In the German plants the feed to vapour phase treatment is frequently the total petrol plus middle oil product obtained by hydrogenation of heavier materials, and with such feeds the petrol content of the presaturated oil can be as high as 50%. It is therefore customary in Germany to fractionate the product from the presaturation stage into petrol and middle oil, before subjecting the latter to splitting hydrogenation over catalyst 6434. The normal combination of presaturation, fractionation and vapour phase splitting hydrogenation can be followed from Fig. 31 (p. 56), which shows the Leuna flowsheets for conversion of the "middle oil" product from brown coal tar hydrogenation into motor and aviation petrols respectively. The same two-stage process was operated in all the German hydrogenation plants with the exception of Böhlen, Welheim and Lützkendorf. These exceptions will be discussed later.

b. Yields

The amount of hydrocarbon gases (butanes and lighter) made in the presaturation stage corresponds to 2–3% of the carbon in the feed oil. In the splitting hydrogenation stage about 15% of the carbon in the make-up oil appears as hydrocarbon gas when making motor petrol of about 30% volatility at 100°C and 190°C final boiling point. When aviation petrol of 150°C final boiling point and 60–70% volatility is the final product, loss of carbon as gas is increased to 20% of that in the feed.

Practically no butane can be included in aviation petrol because of its limited allowable vapour pressure. Motor spirit, on the other hand, can contain up to 5% by weight of butane, so that the effective difference in by-product gas make when producing these two grades of petrol is substantially greater than indicated by the above figures for total gas yields.

The overall yield of petrol from the two-stage vapour phase hydrogenation process varies not only with its volatility, but also to a less extent with the nature of the feed oil. For example, a feed, consisting entirely of hydrocarbons and containing a high proportion of low-boiling components, gives a higher petrol yield than a heavier feedstock containing a substantial amount of, say, phenols. In general, however, motor petrol yield is 92–95% and that of aviation base spirit 80–83% by weight on the feed oil.

The quantity of hydrogen consumed varies much more markedly with the character of the feedstock. With a highly paraffinic feed, it can be as low as 3% and with a highly aromatic oil, such as a high-temperature coal tar distillate, as high as 9% by weight on the feed oil. These figures refer to motor petrol production; when making aviation petrol they are increased by about 0·5% weight on the feed.

c. Plant Capacity

The rate at which oil can be fed to both presaturation and splitting hydrogenation stages is dependent on the character of the oil, the catalyst activity and the desired volatility of the final petrol product. The factor which most frequently limits throughput, particularly in the presaturation stage, is, however, difficulty in temperature control, which increases with the extent of hydrogen absorption and is, therefore, most marked with highly aromatic or unsaturated feed oils.

In the German plants, oil feed to the presaturation stage varies from about 0·6te/hr per m^3 catalyst for oils such as distillates from high-temperature bituminous coal tar, to 1·5te/hr per m^3 catalyst for highly paraffinic oils.

Total oil feed rates to the splitting stage do not show such wide variation, since the presaturation treatment brings most oils up to more or less the same level of hydrogen content. The usual figure is 0·80 to 1·00te/hr total oil feed per m^3 catalyst. When making motor petrol some 70–75% of this feed is fresh make-up middle oil and the rest recycle bottoms from product distillation. Fresh feed amounts to only about 50% on the total feed when aviation petrol is being produced.

In Germany, vapour phase hydrogenation units usually have three converters, each of 8m^3 catalyst capacity. A saturation unit or "stall" can thus treat between 360 and 870te/day of feed oil, depending on its hydrogen content. A splitting hydrogenation stall can cope with some 350–430te/day make-up middle oil (usually corresponding to 500–630te/day feed to the saturation stage) when making motor spirit. This throughput is reduced by about 30% when aviation petrol is required.

d. Utility Consumption and Costs of Normal Vapour Phase Hydrogenation

The consumption of the various services in the two-stage vapour phase hydrogenation processes does not vary appreciably with different "middle oil" feeds. The

IG Central Technical Department at Ludwigshafen supplied the following average figures:—

HP steam	.. ..	0·20te/te motor petrol
LP steam	.. ..	0·59 „ „
Fuel gas	.. ..	700te.cal/te motor petrol
Electric power	..	146kwh/te „ „
Cooling water	..	80m³ „ „

The capital cost of the plant, excluding hydrogen production and power station, was stated by the same authority to be about RM106 for each ton of annual capacity for production of motor petrol. The capital value of associated hydrogen production plant obviously varies with the type of feed oil. It is approximately RM850–900 per te/yr of hydrogen consumed.

Operating charges, excluding hydrogen and feed oil costs, and before inclusion of obsolescence and other

low, *e.g.* yield of motor petrol at Böhlen was only 85% by weight of the middle oil fed and that of aviation base only 78%.

The vapour phase units at Böhlen were also frequently operated to give motor petrol and diesel oil as final product. Middle oil from the liquid phase treatment of brown coal tar was given a straight-through treatment over catalyst 5058, and the product fractionated to give 60% motor petrol as overhead, and 40% diesel oil as still residue. Expressed as weight % yield on middle oil treated, petrol amounted to 52% and diesel oil to 36–37%. Fig. 28 shows typical flowsheets for the Böhlen vapour phase operations.

f. Vapour Phase Splitting Hydrogenation at 700ats Pressure

At two of the German hydrogenation plants, Welheim

FIGURE 28
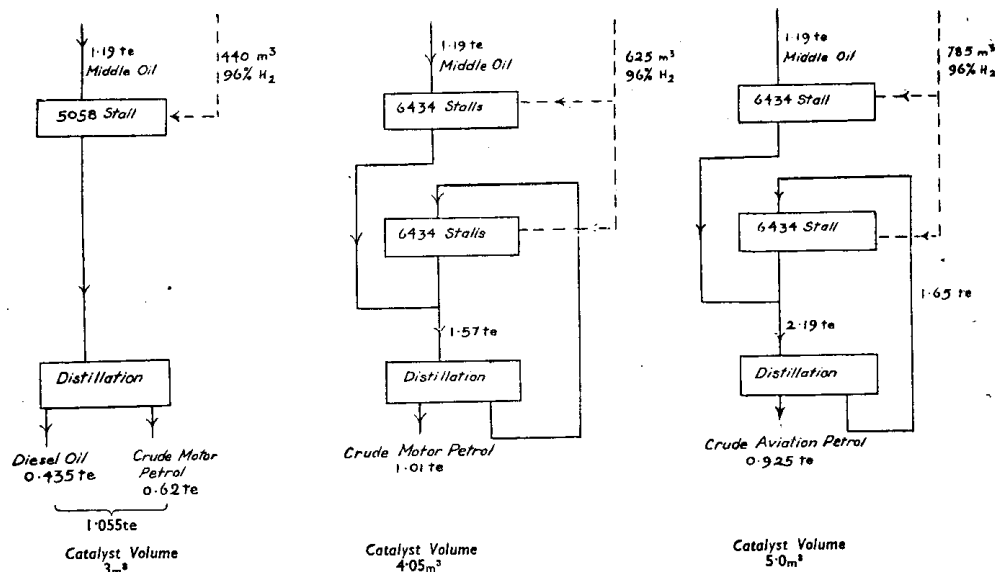
VAPOUR PHASE HYDROGENATION. 1943—BÖHLEN

capital charges, were given by the IG Technical Department at RM22·0/te motor petrol. Both capital and operating costs refer to a plant of 200,000 te/yr motor petrol capacity.

The question of costs is dealt with more fully in later sections dealing with the overall treatment of coal, tar, etc., to produce petrol.

e. Modified Vapour Phase Hydrogenation Process Operated at Böhlen

The Brabag plant at Böhlen did not take full advantage of a presaturation treatment. Middle oil and petrol from the liquid phase treatment of brown coal tar were fed direct to a stall filled with catalyst 6434 and operating under mild splitting conditions. The product was distilled and the residual middle oil used as make-up feed to a second 6434 splitting stall operating under recycle conditions.

The above method was adopted in order to improve the petrol quality, petrol made by catalyst 5058 or 8376 presaturation of brown coal middle oils being of low octane number. Compared with the normal process, gas makes were high and petrol yields correspondingly

and Lützkendorf, the saturation stage of vapour phase hydrogenation was omitted, and liquid phase middle oil or middle oil obtained by distillation of tar products, was hydrogenated directly to petrol at 700ats.

At Lützkendorf, the normal 6434 catalyst was employed. Reaction temperature was 460°C, compared with 410–430°C in the normal 300ats splitting of pre-saturated oil. Feed rate was approximately 0·8te/hr per m³ catalyst, and conversion per pass about 40%. The yield of petrol was the same as that obtained by the two-stage 300ats process.

At Welheim, a special catalyst was used consisting of 0·6% molybdenum, 2% chromium, 5% zinc, supported on activated Terrana Earth. The catalyst was used in a sulphided form and contained 5% of sulphur. A reaction temperature of about 480–500°C was employed and the rate of petrol production was much the same as at Lützkendorf—0·4te/hr per m³ catalyst. Petrols cut to aviation volatility contained 50–60% aromatics. The production of highly aromatic high anti-knock petrols by direct treatment of middle oil at 700ats is limited to highly aromatic feed stocks, such as those

obtained by liquid phase hydrogenation of bituminous coal and pitch, or by distillation of bituminous coal tar. It is possible to obtain similar petrols by hydroforming the higher boiling fractions of hydropetrols produced by normal 300ats vapour phase hydrogenation. This alternative method is applicable to a much wider range of feed stocks, but it has the disadvantage that it leads to a loss as hydrocarbon gas of 20-25% of the naphtha treated. The wider applicability of the process, coupled with the difficulty of providing special construction materials for 700ats operation, probably explains why the Germans adopted the hydroforming process much more extensively than the high pressure direct hydrogenation method.

iii. HYDROGENATION OF HEAVY OILS OVER FIXED CATALYSTS, TTH AND MTH PROCESSES

It is possible to hydrogenate certain heavy oils in the liquid phase over fixed active catalysts using plant

is 300ats. The average reaction temperature is 360°C in the low-temperature or TTH process and 390°C in the medium temperature version (MTH). The tar feed rate is 1·0te/hr per m³ catalyst in the TTH and about 0·6te/hr per m³ catalyst in the MTH process.

The crude product from the TTH process amounted to about 95% and that from the MTH method to 90-92% by weight on the raw brown coal tar treated. The crude product was distilled to give the products shown in Table XXX below, which also shows the hydrocarbon gas make, and the hydrogen consumed by the two processes.

In spite of the careful fugalling and filtering of the feed, catalyst deteriorated fairly rapidly, and had to be renewed every 4-6 months.

No cost data for the TTH and MTH processes are available but it would be reasonable to assume, on the basis of the vapour phase hydrogenation costs that operating charges, exclusive of raw material, hydrogen

FIGURE 29
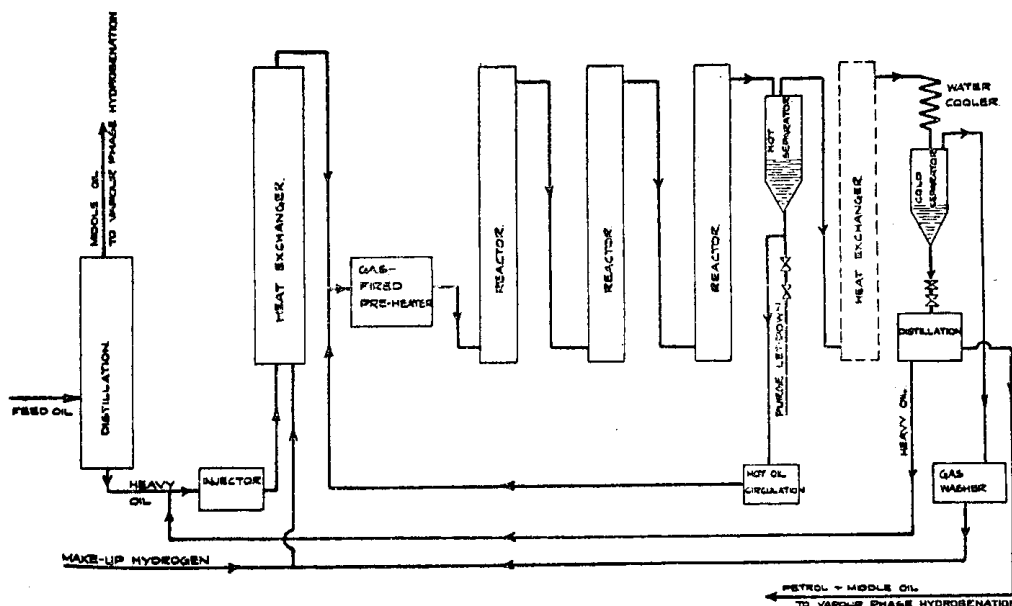
PLANT FOR LIQUID PHASE HYDROGENATION OF HEAVY OILS

practically identical with that used for vapour phase hydrogenation. The essential requirement is that the feed oil must not contain materials which rapidly "poison" the catalyst. Conditions must also be such that no polymerisation of intermediate unsaturated products to catalyst-poisoning substances occurs and, for this reason, it is usually necessary to restrict the extent of hydrogenation in a single-stage treatment. The only example of this type of hydrogenation process encountered in Germany was at Zeitz where brown coal tar is hydrogenated to lube oil, diesel oil and petrol by the so-called TTH and MTH processes.

The brown coal tar is fugalled and filtered to reduce its solids content to less than 0·1%. The hydrogenation process is a once-through operation without any recycle. The oil is injected into the plant and together with hydrogen in the ratio of about 2,500m³ H₂ (normal temperature and pressure) per ton of oil, passes via interchangers and a preheater to converters containing pellets of 5058 or 8376 catalyst. The operating pressure

and capital charges, would be of the order of RM15/te of finished products.

TABLE XXX

PRODUCTS FROM TTH AND MTH PROCESSES

		Temperature 360°C TTH process	Temperature 390°C MTH process
Petrol		25	35
Diesel oil	% wt on	50	60
Refined wax	crude	10-15	—
Lube oil	product	10-15	—
Heavy bottoms		—	5
Hydrocarbon gas, % wt on original tar		1-2	6
Hydrogen used, % wt on original tar		4·4	5·6

The MTH process was not employed in Germany as a first step in the conversion of brown coal entirely to petrol. The reason for this is that middle oil from the MTH process is highly saturated with hydrogen and gives

rise to a comparatively poor quality petrol when subjected to vapour phase hydrogenation. This is not necessarily a serious disadvantage under peace-time conditions, and when motor fuel is the required product.

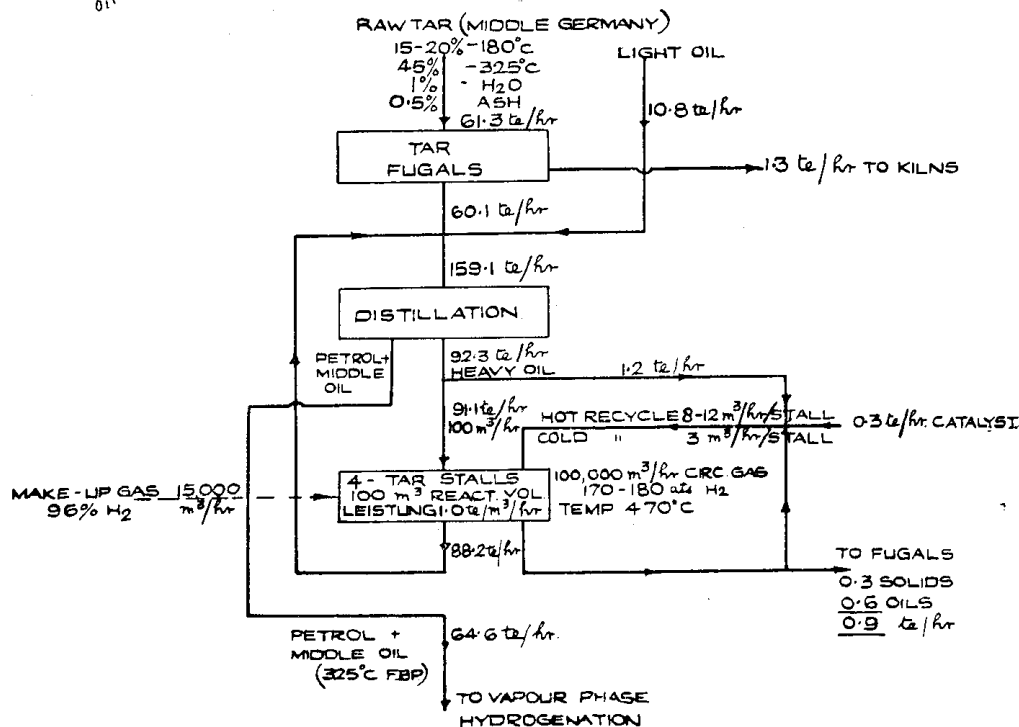### iv. HYDROGENATION OF BROWN COAL TAR

a. Process

The usual method for hydrogenation of brown coal tar in Germany is a multi-stage process. The crude tar is fugalled to remove solids which would foul interchanger and preheater tubes. It is then distilled to give a light clean boiling below 325°C as overhead and a heavy oil residue. The latter is subjected to liquid phase

and the tubes of a gas-fired preheater. The reactants then enter the first of two to four converters which are cylindrical forgings or wound pressure vessels 12–18m long and 800–1,200mm diameter. Cold gas is introduced at suitable points in the converter system to maintain reaction temperature at about 480°C.

The product leaving the last converter passes to a high pressure hot catchpot operating at about 450°C for separation of vapour and liquid products. The greater part of the liquid product is usually circulated back to the preheater inlet under pressure and without any appreciable cooling. The remainder is let down to atmospheric pressure via air coolers. Part of the

FIGURE 30

FLOWSHEET FOR PETROL FROM BROWN COAL TAR

hydrogenation in the presence of finely divided catalyst which is suspended in the reacting liquid. The end-product of this reaction is an oil boiling below 325°C and consisting mainly of 180–325°C middle oil. This, together with the light distillate from the crude tar distillation, is then passed on to the conventional two-stage vapour phase hydrogenation process for conversion to petrol. When, as is usually the case, light oil obtained by scrubbing the gas from brown coal carbonisation is available along with the brown coal tar, this is fed direct to the vapour phase process along with the other light oils. This process was employed at Böhlen, Magdeburg, Leuna and Brüx.

The liquid phase stage of the process can be followed by reference to Fig. 29. The heavy oil and a small quantity of make-up catalyst in the form of an oil paste are injected separately to the plant which operates at 220–300ats. The liquid feed is joined by a stream of compressed hydrogen (1,000m³ H₂ measured at atmospheric temperature and pressure for each tonne of oil) and is heated to 460°C by passage through interchangers

let-down is used for making up fresh catalyst paste and the remainder is carbonised in rotating kilns (Schneckenofen) in order to provide a purge from the system of spent catalyst and the more difficultly hydrogenable components of the original feed stock. The recovered distillate oil from the kilns is recycled to feed.

The vapour product from the hot catchpot passes through the interchanger heating up the reactants and then, via a water cooler, to a cold high pressure separator. Gas from the top of the cold catchpot is recycled to the plant inlet after being washed with oil to remove hydrocarbon gas. The liquid product is let down in three stages in order to separate the hydrocarbon gas which comes out of solution on release of pressure into lean gas which is used as fuel, and rich gas from which propane and butane are eventually separated. The final liquid product is distilled to give petrol and middle oil as overhead, and a heavy oil residue, which is recycled for further treatment, or is sold as fuel oil. The distillate is worked up to give petrol and diesel oil or, more

frequently, is passed on to the vapour phase hydrogenation stage.

It is usual to distil the liquid phase product in admixture with the crude fugalled tar. This avoids the decomposition of the heavier tar components which tends to occur when tar is distilled alone.

The catalyst is prepared by impregnation of finely

is about 35%, so that the make-up heavy oil consumption rate is approximately 0·33te/hr per m³ reaction volume.

b. Yields

The raw material usually available in German plants processing brown coal tar consists of 75–85% weight of brown coal tar, and 15–25% of light oil obtained by scrubbing gas from brown coal carbonisation. The

FIGURE 31
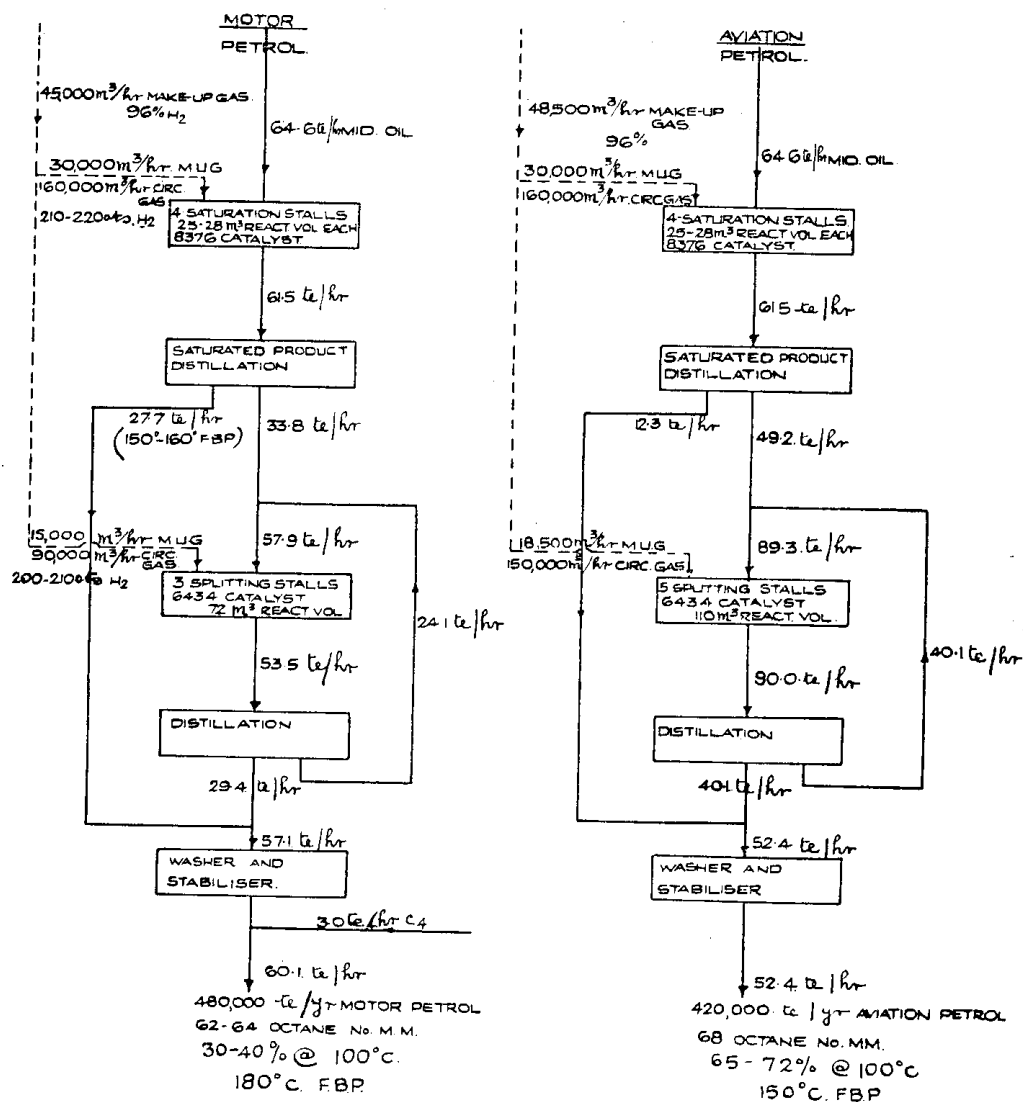
FLOWSHEET FOR PRODUCTION OF MOTOR OR AVIATION PETROL FROM BROWN COAL MIDDLE OIL

divided active coke, obtained from brown coal in Winkler generators, with stoichiometric proportions of ferrous sulphate and caustic soda solutions. The impregnated material is dried without washing out sodium sulphate, and contains 5–6% by weight of iron. Catalyst make up is 1% by weight on the make-up brown coal tar heavy oil.

The total rate of feed of heavy oil is equivalent to 0·9–1·0te/hr per m³ reaction volume. The pass conversion of heavy oil to products boiling below 325°C

tar contains 25–30% of material boiling below 325°C, about 5% phenolic material, 5% asphalts, and 1·0% solids. Heavy oil to be converted by liquid phase hydrogenation amounts to 55–62% of the total raw material.

The hydrocarbon gas make in the liquid phase hydrogenation stage, when converting heavy oil completely into oils boiling below 325°C is 17–18% by weight on the heavy oil treated. 2–3% of the heavy oil fed is lost in carbonisation of purge sludge. The

yield of new-formed petrol plus middle oil is 79%, and the hydrogen consumed 3·8% by weight on the fresh heavy oil feed.

The overall yield of motor or aviation petrol, and the corresponding hydrogen consumption for the multi-stage brown coal tar process, are given in Table XXXI. All figures are % wt on the brown coal tar plus scrubber oil feedstock.

TABLE XXXI

YIELDS OF PETROL AT LEUNA—BROWN COAL TAR
HYDROGENATION

	Motor petrol	Aviation petrol
Leuna—using a feed with 15% scrubber oil:		
Petrol yield	83·4	72·7
Hydrogen used	6·72	7·1
Böhlen—using a feed with 26% scrubber oil:		
Petrol yield	75·0	68·6
Hydrogen used	5·8	6·2

At Böhlen the less efficient vapour phase process was in use as described in Section C3(ii)*e*.

Figures 30 and 31 show the complete flowsheet for the Leuna operations. Magdeburg operated in the same way as Leuna.

c. Petrol Quality

The final blend of motor petrol made from brown coal tar has an octane number (CFR Motor Method) of 62–64. The corresponding aviation petrol has 68 octane number, which can be brought up to 86 by addition of 1·15ml tetraethyl lead per litre. Petrol obtainable by distillation of the pre-saturation stage product is about five units lower in octane number than the complete blend; that from the splitting hydrogenation stage is 1–2 units better than the blend.

d. Special Conditions Relating to the Brüx Plant

The tar obtained by carbonisation of the local brown coal at Brüx is entirely different from the middle German brown coal tar. It has a higher phenol and asphalt content and frequently contains arsenic compounds, which form deposits in interchangers and preheaters, and also lead to rapid catalyst poisoning. These troubles were being overcome by cleaning the coal from pyritic inclusions prior to carbonisation.

e. Utility Consumptions

The following data were obtained at Böhlen:—

	Motor petrol	Aviation petrol
HP steam	0·66te/te	0·75te/te
LP steam	4·00te/te	4·50te/te
Electric power ..	1,500kwh/te	2,150kwh/te
Fuel gas	1·06te.cal/te	1·30te.cal/te
Water..	67m³/te	88m³/te

No detailed costs for brown coal tar hydrogenation were obtained, but it was stated at Leuna that, charging this raw material at RM80/te, the full cost of motor petrol inclusive of obsolescence charges was about RM190/te.

V. HYDROGENATION OF BITUMINOUS COAL TAR, PITCH AND HEAVY PETROLEUM RESIDUUM

a. Process

The components of the above materials boiling above 325°C are more difficult to hydrogenate in the liquid phase than brown coal tar heavy oil. Their main constituents are less reactive than those of brown coal tar and, further, they contain an appreciable quantity of high molecular weight asphaltic substances which are still more resistant to breakdown to lighter products. Increase in reaction temperature, while maintaining

hydrogen partial pressure at about 200ats, is not an effective means of preventing build-up of asphalt in recycle oil. It destroys the balance of the hydrogen saturation and thermal splitting reactions, and intermediate products from the main components of the tar tend to polymerise to form secondary asphalts which are even more refractory than those originally present in the feed. Control of asphalt content of recycle oil by purge is uneconomic because of the large amount of good heavy oil which is lost along with the purged asphalt in the carbonisation kilns.

In order to prevent secondary asphalt production, and because higher pressures are also beneficial for hydrogenation of complex components of the feeds, bituminous coal tar heavy oils, pitch and heavy petroleum residuum were treated in Germany at 700ats. The plants involved were Stettin-Pölitz (bituminous coal tar, pitch and heavy petroleum residuum, Welheim (pitch), and Lützkendorf (bituminous coal tar and heavy petroleum).

Apart from the difference in pressure in the liquid phase stage, the process is practically identical with that described for brown coal tar. The same catalyst is used but the make-up requirement is increased to about 2% on the fresh heavy oil feed. Reaction temperature is increased slightly to 480–490°C. The consumption rate of make-up heavy oil varies widely with the source of the feedstock. For example, when converting bituminous coal tar heavy oil completely into products boiling below 325°C, it is 0·33te/hr per m³ reaction volume, *i.e.* the same as in brown coal tar hydrogenation. The corresponding figure for 700ats hydrogenation of heavy petroleum residuum is 0·63te/hr per m³ reaction volume. At Welheim a feed consisting of 70% pitch and 30% tar oil was consumed at a rate of 0·51te/hr per m³ reaction volume, but the final product contained a large proportion of heavy oil boiling above 325°C which was disposed of as fuel oil.

b. Yields

Crude bituminous coal tar is first distilled to give 30% distillate boiling below 325°C and therefore suitable for direct vapour phase treatment. Only 70% of the feed stock in this case has to be treated in the liquid phase. In the case of pitch and heavy petroleum residuum, all the raw material is fed in the first place to the 700ats hydrogenation stall.

Yield data for the liquid phase operation are given in Table XXXII. The figures for bituminous coal tar heavy oil and heavy petroleum residuum were supplied by the Central IG Technical Department atLudwigshafen. The data for pitch were obtained at Welheim.

The hydrocarbon gas is composed of approximately equal proportions by weight of methane, ethane, propane and butane, the latter being chiefly normal butane.

Yield data for the complete multi-stage processes converting coke oven tar or heavy petroleum residuum into motor petrol as the sole liquid product are shown in Table XXXIII. Corresponding data for pitch hydrogenation at Welheim are not available.

If aviation base petrol is made, the above petrol yields will be reduced by approximately 9% on the raw material. The hydrogen consumption figures given for heavy petroleum residuum assume that this material has a hydrogen content of 11·0% by weight. At Stettin-Pölitz, a lower hydrogen content oil was used and, although the yield of aviation petrol was 70% weight the hydrogen used was 8·6% weight on the feed material.
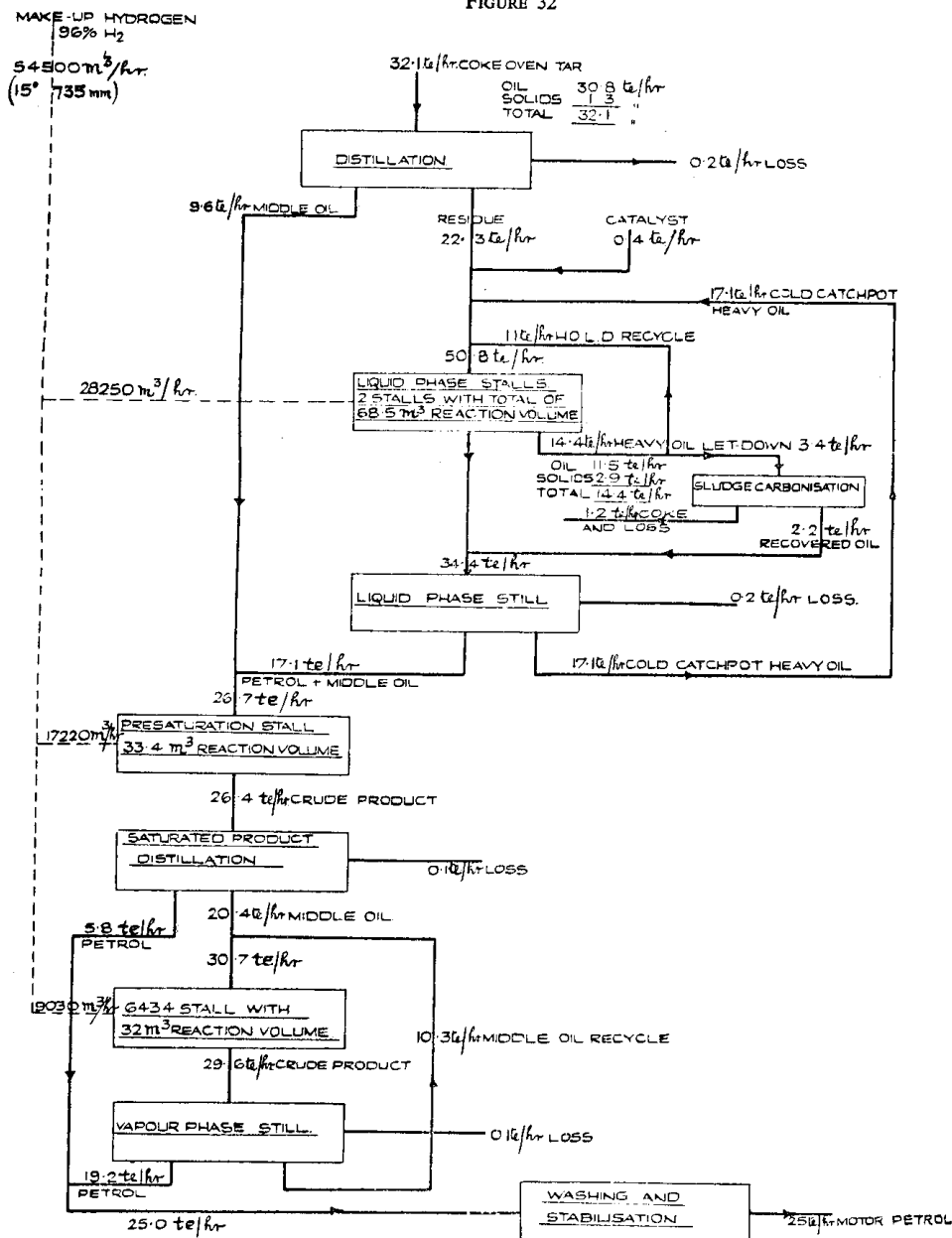
Complete flowsheets for the conversion of bituminous coal tar and heavy petroleum residuum to motor petrol

TABLE XXXII

YIELD DATA FOR LIQUID PHASE HYDROGENATION OF HEAVY OILS AT 700ATS PRESSURE
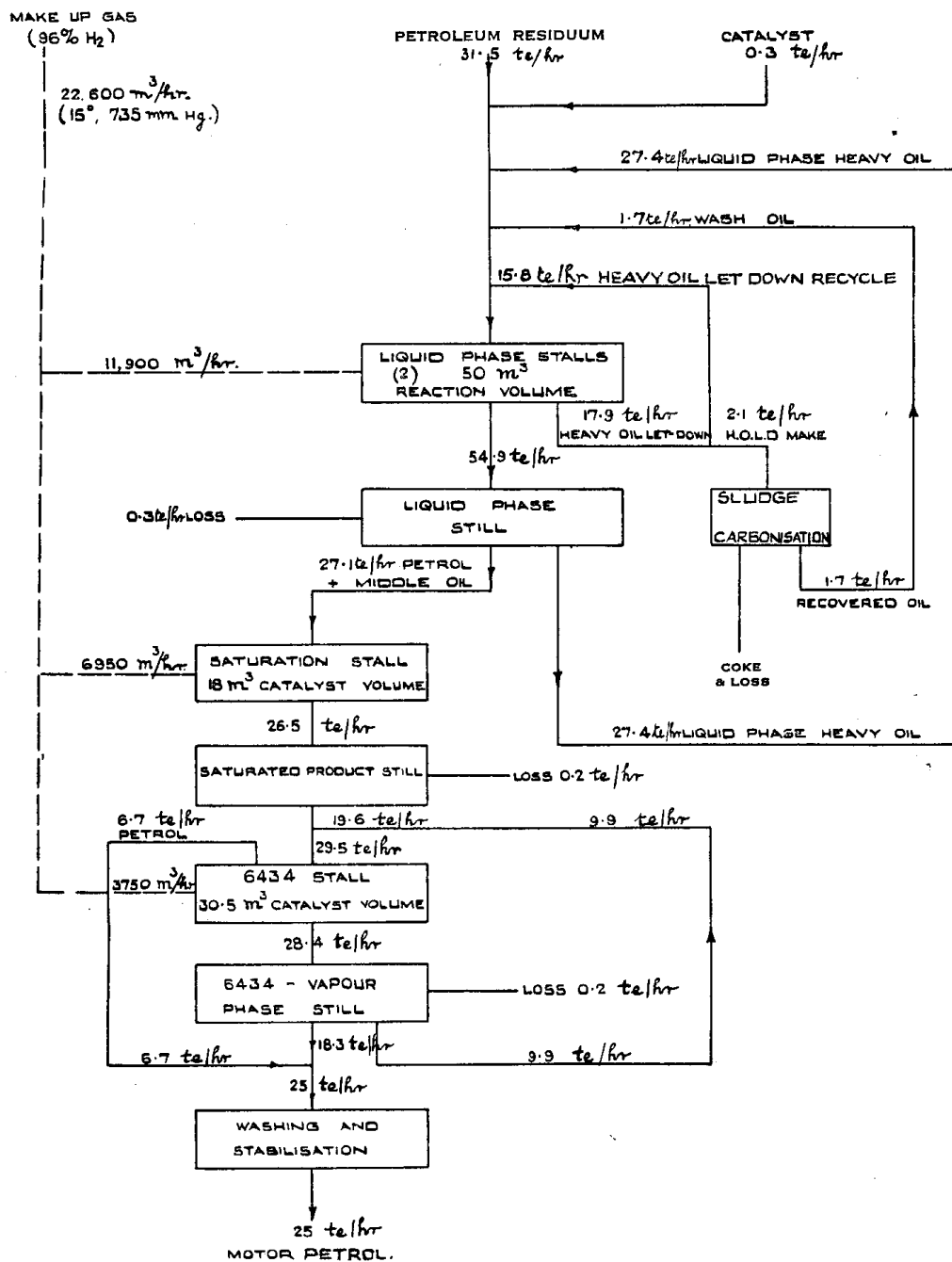
(Weight % on make-up heavy oil)

Heavy oil treated	Bituminous coal tar heavy oil	Bituminous coal tar pitch	Petroleum residuum
Petrol + middle oil boiling below 325°C ..	77	28–29	86
Fuel oil > 325°C	—	45–46	—
Hydrocarbon gas	21·5	9·0	12·0
Losses in purge	3·5	11·0	0·5
Hydrogen consumed	10·3	7·1	3·2

FIGURE 32

MAKE-UP HYDROGEN
96% H₂

54500 m³/hr.
(15° 735 mm)

32·1 te/hr. COKE OVEN TAR

OIL   30·8 te/hr
SOLIDS   1·3
TOTAL   32·1

DISTILLATION → 0·2 te/hr LOSS

9·6 te/hr MIDDLE OIL

RESIDUE   CATALYST
22·3 te/hr   0·4 te/hr

17·1 te/hr COLD CATCHPOT HEAVY OIL

11 te/hr HOLD RECYCLE

50·8 te/hr

LIQUID PHASE STALLS
2 STALLS WITH TOTAL OF
68·5 m³ REACTION VOLUME

28250 m³/hr.

14·4 te/hr HEAVY OIL LET DOWN 3·4 te/hr

OIL   11·5 te/hr
SOLIDS 2·9 te/hr
TOTAL 14·4 te/hr

SLUDGE CARBONISATION

1·2 te/hr COKE
AND LOSS

2·2 te/hr
RECOVERED OIL

34·4 te/hr

LIQUID PHASE STILL → 0·2 te/hr LOSS.

17·1 te/hr COLD CATCHPOT HEAVY OIL

17·1 te/hr
PETROL + MIDDLE OIL

26·7 te/hr

PRESATURATION STALL
33·4 m³ REACTION VOLUME

17220 m³/hr

26·4 te/hr CRUDE PRODUCT

SATURATED PRODUCT
DISTILLATION → 0·1 te/hr LOSS

5·8 te/hr
PETROL

20·4 te/hr MIDDLE OIL

30·7 te/hr

6434 STALL WITH
32 m³ REACTION VOLUME

12030 m³/hr

10·3 te/hr MIDDLE OIL RECYCLE

29·6 te/hr CRUDE PRODUCT

VAPOUR PHASE STILL. → 0·1 te/hr LOSS

19·2 te/hr
PETROL

25·0 te/hr

WASHING AND
STABILISATION → 25 te/hr MOTOR PETROL

FLOWSHEET FOR HYDROGENATION OF COKE OVEN TAR TO GIVE 200,00TE/YR MOTOR PETROL

FIGURE 33

MAKE UP GAS
(96% H₂)

22.600 m³/hr.
(15°, 735 mm Hg.)

PETROLEUM RESIDUUM
31·5 te/hr

CATALYST
0·3 te/hr

27·4 te/hr LIQUID PHASE HEAVY OIL

1·7 te/hr WASH OIL

15·8 te/hr HEAVY OIL LET DOWN RECYCLE

11,900 m³/hr.

LIQUID PHASE STALLS
(2)   50 m³
REACTION VOLUME

17·9 te/hr
HEAVY OIL LET DOWN

2·1 te/hr
H.O.L.D MAKE

54·9 te/hr

0·3 te/hr LOSS

LIQUID PHASE
STILL

SLUDGE

CARBONISATION

1·7 te/hr
RECOVERED OIL

27·1 te/hr PETROL
+ MIDDLE OIL

6950 m³/hr

SATURATION STALL
18 m³ CATALYST VOLUME

COKE
& LOSS

26·5 te/hr

27·4 te/hr LIQUID PHASE HEAVY OIL

SATURATED PRODUCT STILL

LOSS 0·2 te/hr

6·7 te/hr
PETROL

19·6 te/hr

9·9 te/hr

29·5 te/hr

3750 m³/hr

6434 STALL
30·5 m³ CATALYST VOLUME

28·4 te/hr

6434 - VAPOUR
PHASE STILL

LOSS 0·2 te/hr

6·7 te/hr

18·3 te/hr

9·9 te/hr

25 te/hr

WASHING AND
STABILISATION

25 te/hr
MOTOR PETROL.

FLOWSHEET FOR THE HYDROGENATION OF PETROLEUM RESIDUUM TO 200,000 TE/YR MOTOR PETROL

are shown in Figs. 32 and 33. Fig. 34 is a flowsheet of the liquid phase treatment of 70% pitch + 30% tar heavy oil at Welheim.

c. Petrol Quality

Motor petrol from bituminous coal tar has a CFR Motor Method octane number of 69. The corresponding aviation grade, unleaded, has 73-74 octane number, which can be increased to 90–91 by addition of 1·15ml TEL/litre. No data on quality of petrol from petroleum residuum are available; it will obviously vary widely with the character of the oil used.

E

TABLE XXXIII

YIELDS FOR COMBINED LIQUID AND VAPOUR PHASE HYDROGENATION OF BITUMINOUS
COAL TAR AND PETROLEUM RESIDUUM TO MOTOR PETROL

(Weight % on original raw material)

Raw material	Bituminous coal tar	Petroleum heavy residuum
Motor petrol	78·0	79·5
Hydrocarbon gas, excluding C_4 in petrol ..	23·0	18·5
Loss in purge	2·5	0·5
Hydrogen consumed	13·7	5·8

d. Utilities Consumptions and Costs

The IG Technical Department at Ludwigshafen provided details of services and labour requirements for a plant to produce 200,000te/yr motor petrol from bituminous coal tar or heavy petroleum residuum (11% H_2) and also gave an estimate of the cost of the

FIGURE 34

263,000 te/yr (70%pitch, 30% tar)

FLOWSHEET FOR PITCH AND TAR HYDROGENATION
(700ats—Welheim)

process, based mainly on the achieved performance of the Stettin-Pölitz plant. Independent examination of the Stettin-Pölitz achieved cost shows the Ludwigshafen estimate to be reasonable at the assumed raw material prices.

The Ludwigshafen estimates are summarised in Tables XXXIV and XXXV.

The capital cost figures do not include hydrogen production plant or power station. Inclusion of the former would bring up the capital cost of a plant to make 200,000te/yr motor petrol from bituminous coal tar to about RM91,000,000, or RM455 per te/yr motor petrol. The corresponding figures for heavy petroleum residuum are RM72,000,000 for a 200,000te/yr plant, or RM360 per te/yr motor petrol.

It is interesting to compare these capital cost figures with that for a plant operating only the comparatively simple vapour phase process. Even in the case of a

middle oil feed stock requiring a high hydrogen absorption (9% by weight on the feed) the latter figure is only about RM190 per te/yr motor spirit, i.e. less than half the cost of a plant to treat the more complex feed stocks by a multi-stage process.

Operating costs show a similar relationship. Excluding raw material and hydrogen costs, by-product credits and obsolescence charges, they amount to about RM60/te motor petrol in the case of the multi-stage treatment of heavy feedstocks compared with a figure of RM22/te for the production of motor petrol from a vaporisable oil.
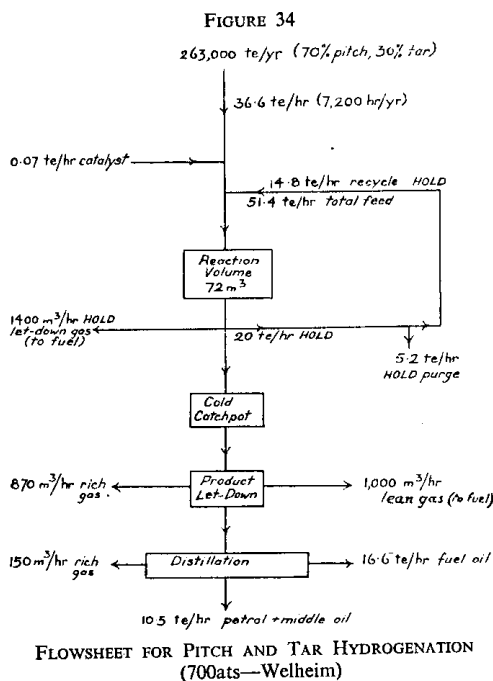
The total production costs for motor petrol of RM206/te and RM181/te from bituminous coal tar and petroleum residuum are not of great significance since they depend to such a large extent on the price assumed for raw materials and the credit allowed for hydrocarbon gases. At Stettin-Pölitz, the full cost of production of aviation petrol from these raw materials was RM360–390te, whereas correction of the Ludwigshafen estimates to an aviation petrol basis would suggest a figure of RM200–220/te. The reason for the high Stettin-Pölitz costs was the high price paid for raw material (RM85/te bituminous coal tar and RM123/te petroleum residuum), a comparatively low credit for hydrocarbon gas, and extremely high obsolescence charges (RM30–50/te). There are indications that in the case of hydrogenation plants treating several raw materials, including coal, the price paid for these was that at which petrol could be produced from them at the coal hydrogenation petrol cost. At Leuna, for example, the price paid for brown coal tar was RM80/te, at which figure motor petrol could be made at RM190/te, i.e. the cost from brown coal.

vi. HYDROGENATION OF MIDDLE GERMAN BROWN COAL

a. Process

This is the simplest of the coal hydrogenation processes, and was in operation at Leuna as early as 1927. The plant employed for the liquid phase stage is essentially the same as that used for brown coal tar heavy oil hydrogenation, except that there is no hot recycle of liquid from the hot catchpot to the preheater inlet.

The wet coal containing about 54% of water and 5·5% of ash is mixed with 4% by weight of catalyst (Bayermasse—crude iron oxide obtained as a by-product in aluminium manufacture). The mixture is dried down to 5% water content, and fed to grinding and pasting mills where it is made into a paste (44% dry coal, 49% total solids) with recycle heavy oils from the process. The paste is injected to the plant operating at 230ats, and is preheated, together with hydrogen (900–1,000m³ per m³ of paste) by passage through a heat interchanger and a gas-fired preheater. The reactants enter the first of four converters at a temperature of about 430°C and are rapidly heated up to 490°C as a result of the exothermic reaction. The reaction temperature in the first

TABLE XXXIV

ESTIMATED COSTS OF MOTOR PETROL PRODUCTION BY HYDROGENATION OF BITUMINOUS
COAL TAR AND PETROLEUM RESIDUUM

(Scale 200,000 te/yr Motor Petrol)

Raw material	Bituminous coal high-temperature tar	RM/te motor petrol	Petroleum residuum	RM/te motor petrol		RM/te motor petrol
Materials:						
Feed ..	1·29te HT tar at RM40/te	51·50	1·26te residuum at RM40/te	50·50	1·26te residuum at RM60/te	75·50
Hydrogen (100%) ..	2090m³ at 4·5pfg/m³	94·90	870m³ at 4·5pfg/m³	39·20	870m³ at 4·5pfg/m³	39·20
Catalyst and chemicals ..	—	7·20	—	3·00	—	3·00
Operating costs ..		87·20		85·10		85·10
Less Credits:						
Liquefied gases ..	186kg at RM193/te	35·80	143kg at RM148/te	21·00	143kg at RM170/te	24·80
Fuel gases ..	2·0 × 10⁶k.cal at RM6/10⁶k.cal	12·00	1·44 × 10⁶k.cal at RM6/10⁶k.cal	8·60	1·44 × 10⁶k.cal at RM6/10⁶k.cal	8·60
Production costs ..		193·00		148·20		169·40
Export costs ..		3·00		3·00		3·00
General costs and licence ..		9·65		7·40		8·50
TOTAL COSTS (Loaded) ..		205·65		158·60		180·90
			(Residuum at RM80/te gives total cost of			204·60)

TABLE XXXV

ANALYSIS OF OPERATING COSTS GIVEN IN TABLE XXXIV

Raw material	Bituminous coal high-temperature tar			Petroleum residuum		
	Liquid phase	Vapour phase	Total	Liquid phase	Vapour phase	Total
Capital cost in RM × 10⁶:						
Hydrogenation proper (exclusive of hydrogen production) ..	31·5	17	48·5	30	17	47·0
Associated buildings, 25%* ..	—	—	12·0	—	—	12·0
			60·5			59·0
Labour:						
Man-hours/te petrol ..	4·2	3·2	7·4	3·8	3·2	7·0
	RM/te motor petrol			RM/te motor petrol		
Labour Costs:						
Wages at RM1·30/hr ..	5·45	4·15	9·60	4·95	4·15	9·10
Salaries, 20% of wages ..	1·10	0·85	1·95	1·00	0·85	1·85
Energy costs:						
Water at RM0·01m³ ..	(80m³) 0·80	0·80	1·60	(80m³) 0·80	0·80	1·60
HP steam at RM3·0/te ..	(0·33te) 1·00	0·60	1·60	(0·23te) 0·70	0·60	1·30
LP steam at RM2·25/te ..	(0·76te) 1·70	1·30	3·00	(0·69te) 1·55	1·30	2·85
Electricity energy at RM0·015/kwh ..	(400kw) 6·00	2·10	8·10	(420kw) 6·30	2·10	8·40
Fuel gas at RM6·0/10⁶k.cal ..	(1·2×10⁶ k.cal) 7·20	4·20	11·40	(1·2×10⁶ k.cal) 7·20	4·20	11·40
Maintenance costs:						
6% of the plant ..	9·40	5·10	14·50	9·00	5·10	14·10
2% of the associated buildings ..	0·80	0·40	1·20	0·80	0·40	1·20
Working materials:						
10% of wages ..	0·55	0·40	0·95	0·50	0·40	0·90
Amortisation:						
10% of the plant ..	15·75	8·50	24·25	15·00	8·50	23·50
5% of the associated buildings ..	1·95	1·05	3·00	1·95	1·05	3·00
Taxes, fire protection, etc.:						
2% of capital costs ..	3·95	2·10	6·05	3·80	2·10	5·90
TOTAL OPERATING COSTS ..	55·65	31·55	87·20	53·55	31·55	85·10

* 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.

three converters is controlled at 490°C by introduction of cold circulating gas at suitable points. Under the latest operating conditions the reactants are cooled on entering the last converter so that the average reaction temperature in this vessel is about 475°C. The total circulating gas used for temperature control is about 1,000m³ per m³ of paste.

A small amount (100litres/hr) of sludge is withdrawn continuously from the bottom of the first converter in order to prevent the build-up of sand and the formation of "caviare," i.e. small spheres consisting of coke formed round a central sand particle. This draw-off is automatically controlled. On leaving the fourth converter, the products pass, as in the case of heavy oil hydrogenation, to a hot catchpot operating at about 440°C. The liquid product from this vessel contains the whole of the ash introduced with the coal, the catalyst, and any coal constituents which have resisted conversion to liquid products. After cooling and letting down to atmospheric pressure, about two-thirds of the liquid product is diluted with 75% of its weight of distillate heavy oil obtained by topping the cold catchpot product, and the mixture is centrifuged. The filtrate is recycled as pasting oil and the concentrate, mixed with the remaining portion of the liquid let down from the hot catchpot, is carbonised in a rotating kiln for recovery of its vaporisable oil content.

The vapour products from the hot catchpot are passed through the interchanger and water cooler to a cold high pressure catchpot exactly as in the case of heavy oil hydrogenation.

The cold catchpot product is distilled to give oil boiling below 325°C as overhead, and a heavy oil residue. The latter is recycled as pasting oil for the brown coal feed, and the former is passed on to the conventional two-stage vapour phase process for conversion to petrol.

b. Capacity of Liquid Phase Plant

The normal practice in coal hydrogenation is to adjust conditions of throughput and temperature so that the amount of recoverable heavy oil in the exit products is just sufficient to provide the necessary pasting oil for the ingoing coal. In the case of brown coal hydrogenation it was found at Leuna that the maximum throughput of brown coal through a liquid phase stall is obtained under rather more severe conditions which necessitate a small make-up of heavy pasting oil from an external source. Such oil is readily available in the form of brown coal tar, and the normal raw material feed at Leuna consists of 95–96% by weight of raw brown coal and 4–5% of raw brown coal tar. Under these conditions, a throughput of 1·2m³/hr coal paste per m³ reaction volume is obtained at Leuna. This corresponds to 0·46te/hr of ash- and moisture-free brown coal per m³ reaction volume, which represents an improvement of about 70% on the pre-war capacity of the same stalls.

The marked improvement resulted from detailed attention to the problem of asphalt formation and purge.

Under the old 1939 conditions, the reaction temperature was controlled at 460–470°C throughout the converter system. The use of a higher reaction temperature was prohibited by the formation of asphaltic materials by polymerisation of intermediate products. It was found, however, that most of the asphalt formation occurred in the last converter and that provided the temperature in this vessel is kept to 465–475°C, that of preceding converters can be increased to 480–490°C, with a consequent increase in rate of hydrogenation, and therefore of coal throughput.

The latest conditions of operation also permit a higher

concentration of asphalts and solids in recycle oil to be used than was possible in 1939. At that time, one of the most serious practical difficulties associated with the hydrogenation of brown coal was coke formation in the hot catchpot. This was greatly encouraged by increase in asphalt and solids content of the liquid product, and by the periodic drying out of the walls of the vessel, resulting from a varying liquid level. One of the improvements made during the war was the adoption of automatic level control and this, together with improved hot catchpot design, has greatly reduced the coking difficulty. Automatic control was also adopted for mixing hot catchpot liquid product and fugalled concentrate, thereby ensuring a constant asphalt content of feed to the carbonisation kilns. The kilns coke up when the asphalt content of feed is too high, and under the old conditions of working the average asphalt content of feed had to be maintained considerably below the safe limit in order to provide a margin for error in mixing the feed components.

c. Yields

When a correction is made for the simultaneous hydrogenation of the small proportion of brown coal tar, the yield data for liquid phase hydrogenation of middle German brown coal at Leuna are as follows:—

	% wt on amf coal
Petrol + middle oil < 325°C	50·0
Hydrocarbon gas	15·2
Carbon monoxide and carbon dioxide	10·6
Unconverted coal	1·5
Oil lost in sludge carbonisation	8·5
Water, ammonia, H₂S, etc.	20·9
H₂ chemically absorbed, i.e. not including losses as dissolved gas	6·7

The noteworthy feature of these yield figures when compared with those for liquid phase hydrogenation of heavy oils is the greatly increased oil losses in purge carbonisation. The reason for this is the large increase in amount of solids—coal ash, unconverted coal, catalyst —which have to be removed from the system.

The overall yields of motor or aviation petrol obtainable from brown coal, again after making suitable adjustment for brown coal tar included in the Leuna feed, are:—

	% wt on amf coal	
	Motor petrol	Aviation petrol
Petrol	46·2	40·2
Hydrocarbon gas	19·3	25·7
Total hydrogen used	9·13	9·34

The full flowsheet for Leuna hydrogenation of brown coal, with the addition of a small amount of brown coal tar, is shown in Fig. 35.

d. Petrol Quality

Petrols obtained by hydrogenation of brown coal have CFR Motor Method octane numbers about two units higher than the corresponding brown coal tar petrols.

e. Utility Consumptions and Costs

Very complete data are available on services, labour requirements and costs for the production of 580,000te/yr motor, or 505,000te/yr aviation base petrol, at Leuna. These data are summarised in Tables XXXVI and XXXVII. (For further details, reference should be made to CIOS Report XXXII–107.)

Leuna being an old plant, no reliable figure for the present-day capital cost of a brown coal hydrogenation plant is available for comparison with that of other types of hydrogenation plant. For the same reason it must be borne in mind that obsolescence charges included in the Leuna production costs are based on a written-down capital figure, and are abnormally low.

FIGURE 35
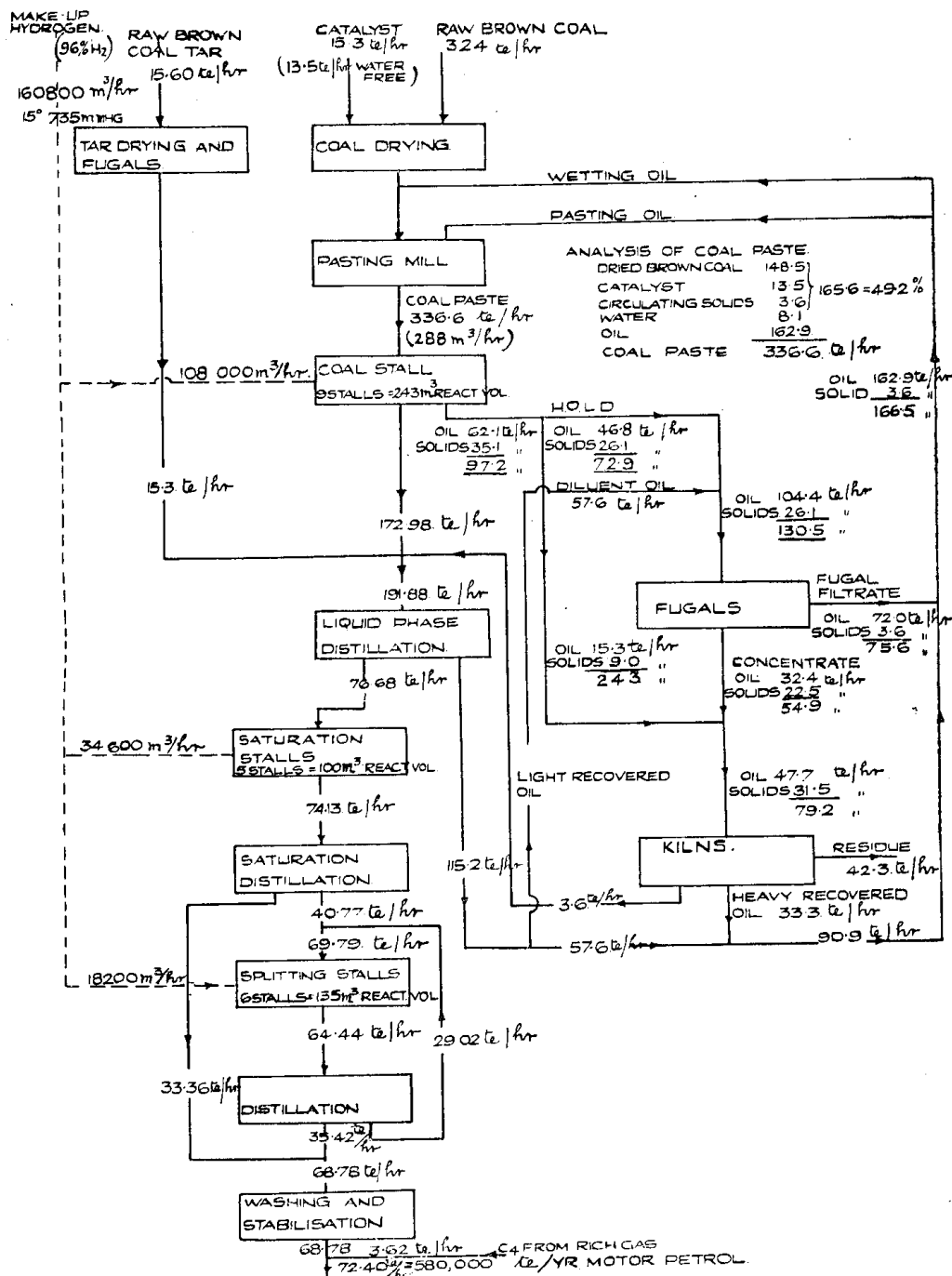
FLOWSHEET FOR MOTOR PETROL FROM BROWN COAL BY HYDROGENATION

(All fluid products are gas-free but include C₅)

TABLE XXXVI

COST CALCULATION FOR PRODUCTION OF PETROL FROM BROWN COAL

| | Unit | Cost per unit RM | Motor petrol production | | | | Aviation petrol production | | | |
| | | | Per hour | | Per te motor petrol | | Per hour | | Per te aviation petrol | |
			Quantity	RM	Quantity	RM	Quantity	RM	Quantity	RM
Raw materials:										
Brown coal	te	3·00	324	972·00	4·475	13·43	324	972·00	5·138	15·41
Brown coal tar	,,	80·00	15·60	1,248·00	0·215	17·24	15·6	1,248·00	—	—
Other materials:										
Make-up gas (96%H₂) ..	m³	0·042	160,800	6,753·60	2,221	93·27	165,000	6,930·00	2,167	109·90
Red earth (dried) ..	te	20·00	15·3	306·00	0·211	4·23	15·3	306·00	0·243	4·85
Catalyst and other chemicals	—	—	—	144·80	—	2·00	—	182·00	—	2·89
Operating costs	—	—	—	6,637·43	—	91·67	—	6,916·89	—	109·69
Less credits:										
Butane*	te	170·14	5·35	910·25	0·074	12·57	13·48	2,293·49	0·214	36·37
Propane*	,,	170·14	6·65	1,131·43	0·092	15·63	7·39	1,257·33	0·117	19·94
Ethane	,,	110·00	2·87	315·70	0·040	4·36	2·90	319·00	0·046	5·06
Hydrogenation gas ..	te.cal × 10³	7·00	198·00	1,386·00	2·735	19·14	204·00	1,428·00	3·235	22·65
PRODUCTION COSTS ..	—	—	72·40	12,318·45	1·000	170·14	63·06	11,257·07	1·000	178·51
Loading and evaporation ..	te	3·00	72·40	217·20	1·000	3·00	63·06	189·18	1·000	3·00
On-costs— IG direction, research, etc.	—	—	—	1,220·66	—	16·86	—	1,220·66	—	19·36
TOTAL COSTS	—	—	72·40	13,756·31	1·000	190·00	63·06	12,666·91	1·000	200·87

* Valued at cost of production of motor petrol.

TABLE XXXVII

ANALYSIS OF OPERATING COSTS GIVEN IN TABLE XXXVI

| | Unit | Motor petrol production per hour | | | Aviation petrol production per hour | | |
		Quantity	RM		Quantity	RM	
Labour costs:							
Wages	hr	447·51	524·65		459·01	538·47	
Salaries	—		111·98			115·07	
Social insurance	—		40·99	677·62		42·21	695·75
Energy costs:							
Water	m³	10,253·2	147·71		11,342·73	163·87	
HP steam	te	280·15	849·77		303·20	919·57	
LP steam	,,	150·54	337·19		152·59	341·76	
Electricity, high tension ..	kwh	15,460·47	317·86		16,451·88	332·85	
,, low tension ..	,,	3,761·12	77·82		3,929·78	81·31	
Fuel gas	te.cal 10³	83,747·51	743·82		87,991·65	781·62	
Brown coal	te	45·063	139·46			139·46	
Other forms (gas)	—		7·19			4·58	
			2,620·82			2,765·02	
Less credit LP steam	te	112·93	225·83	2,394·99	125·66	251·28	2,513·74
Repair costs:							
Wages	hr	371·97	451·61		383·60	465·56	
Material	—		299·45			321·52	
Workshop and material on cost	—		745·79	1,496·85		774·63	1,561·71
Working materials	—		57·63			59·35	
Traffic charges	—		154·53			154·90	
Works general charges ..	—		297·93			308·11	
Capital charges	—		1,139·34			1,190·10	
Taxes	—		154·04			158·53	
Various costs	—		323·81			334·01	
			6,696·74			6,976·20	
Less credits	—		59·31			59·31	
TOTAL OPERATING COSTS ..			6,637·43			6,916·89	

Operating costs, exclusive of raw materials, hydrogen and obsolescence charges, amount to RM76/te motor petrol, or RM91/te aviation base. It will be noted that in spite of the very large scale of operation and the low pressure, these production costs are higher than those given in Section C3(v) *d* for heavy oil hydrogenation at 700ats. The reason is the additional cost of auxiliary operations such as coal drying and pasting, purge of solids and recovery of oil from purges.

vii. HYDROGENATION OF BITUMINOUS COAL AT 300 ATS PRESSURE

a. Process

Hydrogenation of bituminous coal is more difficult than treatment of brown coal, for much the same reasons that bituminous coal tar hydrogenation is less easy than that of brown coal tar. Bituminous coals leave a greater amount of non-hydrogenable solid residue, and their primary hydrogenation products contain a greater proportion of asphaltic and relatively unreactive materials. In coal hydrogenation, adequate destruction of asphaltic primary products and prevention of formation of secondary asphalts is even more important than in heavy oil hydrogenation. A comparatively large amount of solids, including organic solids, has to be purged from the system as a sludge with oil, which has to be recovered by carbonisation of the sludge. A high concentration of asphalts in the sludge purge brings about the formation of sticky semi-coke which renders the carbonisation kilns unworkable. Thus a large asphalt purge in coal hydrogenation is impracticable as well as being uneconomic. There is also a definite limitation to the extent to which asphalts can be allowed to build up in the recycle pasting oils, because of the limited viscosity of a pumpable coal paste.

One method of securing adequate asphalt destruction in the liquid phase hydrogenation of bituminous coal is to use more active catalysts than are necessary for brown coal hydrogenation. A suitable catalyst is finely divided tin, usually introduced in the form of tin oxalate. This catalyst exerts its maximum effect when employed under non-alkaline and preferably' acid reaction conditions, which are achieved by introducing ammonium chloride. Under reaction conditions, this dissociates and the resulting hydrochloric acid neutralises alkaline ash constituents of the coal. An excess of ammonium chloride is necessary and introduces the difficulty of corrosion by the exit products. Fortunately the corrosion danger, when working at pressures of the order of 300ats, is limited to those parts of the plant operating at temperatures below about 350°C. Hydrogen sulphide is always present in the exit hydrogenation products in sufficient concentration for the $Fe/H_2S/H_2/HCl$ equilibrium to be such that the iron sulphide surface of the plant is not decomposed at temperatures above 350°C. It is thus possible to neutralise the products by scrubbing with an oil suspension of alkali before passing to the interchangers and coolers.

A process based on the principles described in the above paragraph is operated at Scholven. Ruhr coal containing 82–83% carbon on an ash- and moisture-free basis is cleaned in a Baum washer to reduce ash content to 4·5–5·5%. The washed coal with a moisture-content of 8 to 12% is ground and at the same time dried down to 2% water in Knapp Grison mills.

The powdered coal is made into a 45% coal paste with recycle heavy oils and to this paste is added 0·07% by weight of tin oxalate, reckoned on the dried coal. Ammonium chloride in the form of a 20% oil suspension

is injected directly into the first converter of the coal hydrogenation stall. The amount of ammonium chloride used is approximately 1% on the dry coal feed. Neutralisation of the exit products is effected in the upper portion of the last converter by injection of a 20% suspension of sodium carbonate in oil at a point 3m from the top. Approximately 1·1% by weight of sodium carbonate, on the dry coal feed, is required. Apart from these differences in catalyst and the precautions against corrosion, the process is much the same as that used for brown coal hydrogenation. Reaction temperature is about 460°C and working pressure 300ats.

b. Capacity of Liquid Phase Plant

Operating under conditions in which recoverable heavy oil in the exit products just balances pasting oil requirement, the throughput of ash- and moisture-free coal is 0·264te/hr per m^3 reaction volume. The Scholven stalls consist of three converters, each of 13m^3 capacity. Each stall is thus capable of dealing with 10·3te/hr of ash- and moisture-free coal (amf coal).

c. Yields

The yield data for hydrogenation of Ruhr coal by the above process, using conditions under which petrol plus middle oil suitable for vapour phase treatment is the sole recovered liquid product, are as follows:—

	% wt on amf coal
Petrol + middle oil	60–61
Unconverted coal	8
Heavy oil lost in solids purge	6
Hydrocarbon gas liquor	24–25
Hydrogen used (including losses)	9–10

These are the achieved yields at Scholven during the latter part of the war. They are probably rather worse than could be obtained under settled conditions, allowing of selection of the coal used and more careful coal cleaning. In particular, it should be possible to reduce the unconverted coal figure. The overall yields of motor or aviation petrol obtainable by the combined 300ats liquid phase and vapour phase processes are:—

	% wt on amf coal	
	Motor petrol	Aviation petrol
Petrol yield	56–57	47–48
Hydrocarbon gas, excluding C_4 in petrol	29–30	37–38
Hydrogen used	14·6	15·0

d. Utility Requirements and Costs

No data are available for the Scholven process.

viii. HYDROGENATION OF BITUMINOUS COAL AT 700ATS PRESSURE AT GELSENBERG AND STETTIN-PÖLITZ

a. Process

An alternative method of securing adequate asphalt destruction in bituminous coal hydrogenation is to operate the process at higher pressure. This method was actually adopted in Germany for all the new coal plants, namely, those at Gelsenberg, Stettin-Pölitz, Blechhammer and Wesseling. The raw material used in the latter plant is Rhine brown coal, which, however, from the standpoint of reactivity and asphalt formation, is much more like bituminous coal than middle German brown coal. Wesseling and Blechhammer, which also operated under special conditions, will be dealt with separately.

At Gelsenberg and Stettin-Pölitz the process, except for the higher pressure and for the use of different catalysts, is essentially the same as the coal hydrogenation processes previously described. 1·2%wt $FeSO_4.7H_2O$ is mixed with the coal, usually before the drying stage. After drying, 1·5%wt on the dried coal of Bayermasse is

FIGURE 36
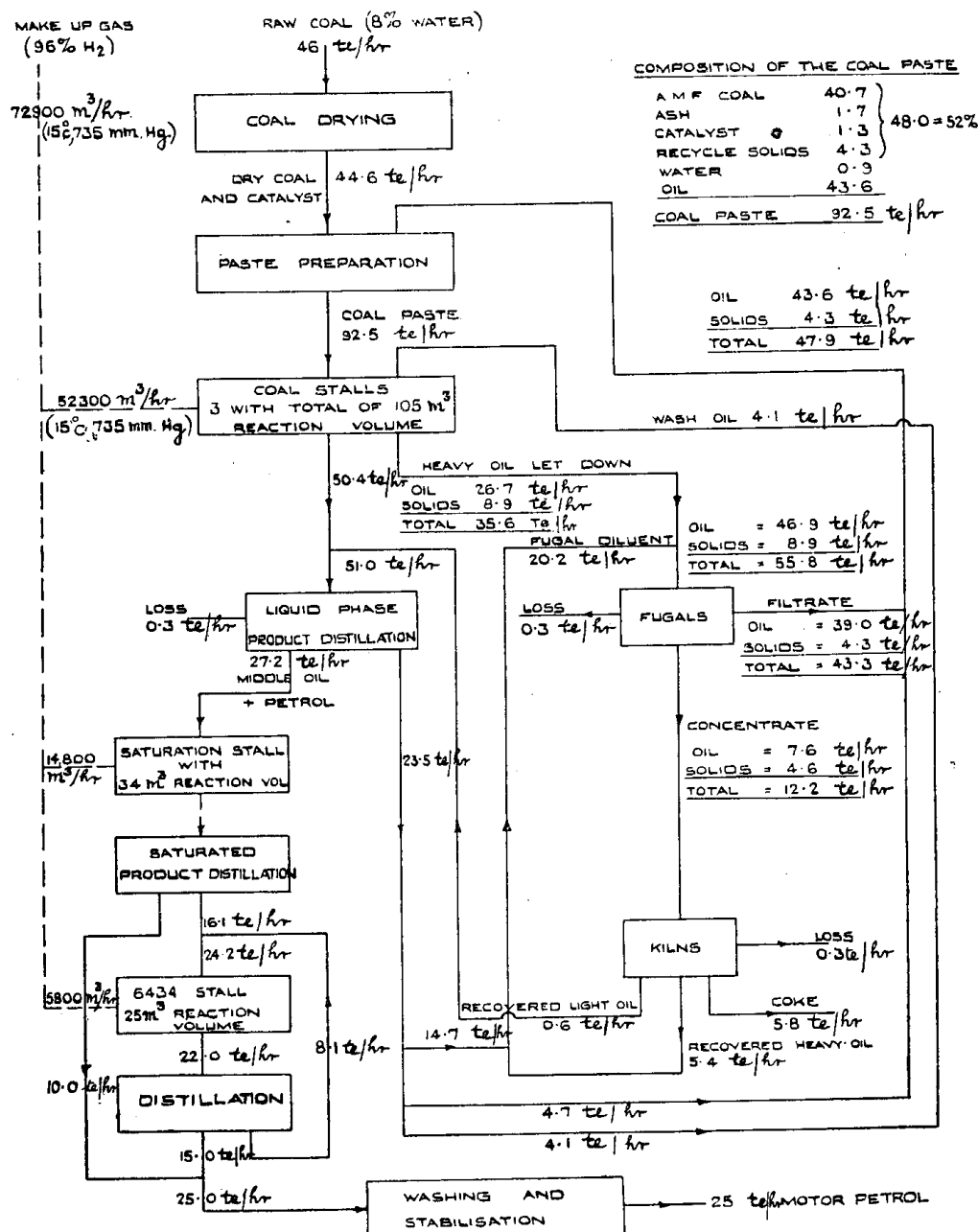
FLOWSHEET FOR BITUMINOUS COAL HYDROGENATION (RUHR COAL) TO 200,000TE/YR MOTOR PETROL

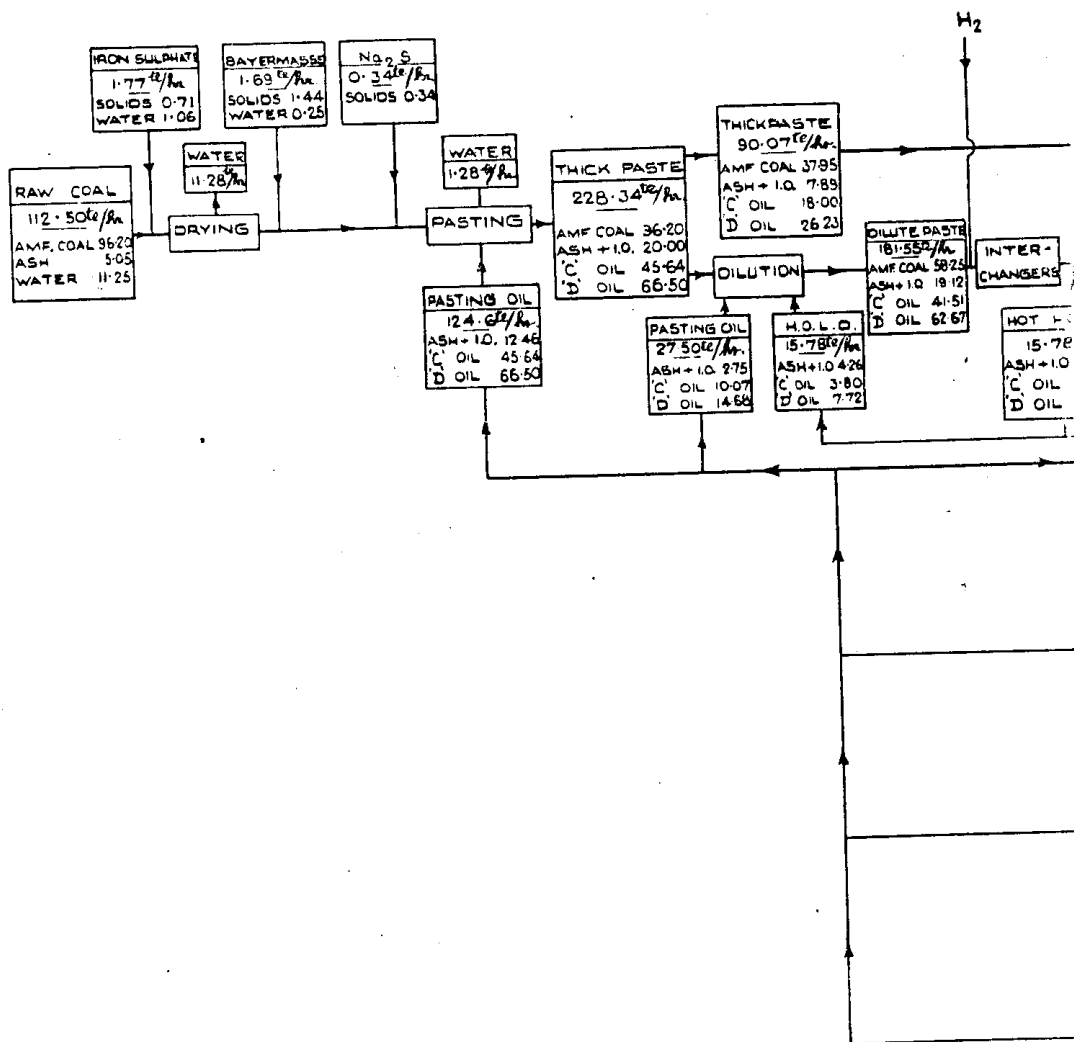added. Finally, in the pasting stage, 0·3%wt sodium sulphide on the dry coal is introduced.

Reaction temperature in the 700ats process is rather higher (480°C) than is used at Scholven.

b. *Capacity of Liquid Phase 700ats Coal Hydrogenation Plant*

At Gelsenberg, using Ruhr coal, and at Stettin-Pölitz, where Upper Silesian coal was processed, the allowable coal feed rate is about 0·39te/hr amf coal per m³ reaction volume. The reaction volume provided by a 700ats standard converter is, however, only 70% of that of the corresponding 300ats vessel and the improvement in throughput per converter by increase in pressure is thus negligible.

At Gelsenberg, the stalls consisted of four converters, each of 9m³ capacity and had a throughput of about 340te/day amf coal.

H₂

IRON SULPHATE
1·77 te/hr
SOLIDS 0·71
WATER 1·06

BAYERMASSE
1·69 te/hr
SOLIDS 1·44
WATER 0·25

Na₂S
0·34 te/hr
SOLIDS 0·34

WATER
11·28 te/hr

WATER
1·28 te/hr

RAW COAL
112·50 te/hr
AMF. COAL 96·20
ASH 5·05
WATER 11·25

DRYING

PASTING

THICK PASTE
228·34 te/hr
AMF COAL 36·20
ASH + I.O. 20·00
'C' OIL 45·64
'D' OIL 66·50

THICKPASTE
90·07 te/hr
AMF COAL 37·95
ASH + I.O. 7·89
'C' OIL 18·00
'D' OIL 26·23

PASTING OIL
124·6 te/hr
ASH + I.O. 12·46
'C' OIL 45·64
'D' OIL 66·50

PASTING OIL
27·50 te/hr
ASH + I.O. 2·75
'C' OIL 10·07
'D' OIL 14·68

H.O.L.O.
15·78 te/hr
ASH + I.O. 4·26
'C' OIL 3·80
'D' OIL 7·72

DILUTION

DILUTE PASTE
181·55 te/hr
AMF COAL 58·25
ASH + I.O. 19·12
'C' OIL 41·51
'D' OIL 62·67

**INTER-
CHANGERS**

HOT H
15·78
ASH + I.O.
'C' OIL
'D' OIL

PRODUCTION OF AVIATION PETROL & FUEL OIL FROM U'

FLOWSHEET OF THE BLECHHAMMER HYDROGENA

LØ PETROL
7.93 ᵗ/hr
A OIL 7.93

PHENOLIC CUT
5.85 ᵗ/hr
B OIL 5.85

PHENO-SOLVAN PLANT

SATⁿ STALL FE
34.28 ᵗ/ʰ
A OIL 7.93
B OIL 5.85
C OIL 20.50

LØ STILL

LØ M.O
64.26 ᵗ/hr
C OIL 64.26

LØ M.O
20.50 ᵗ/ʰ
C OIL 20.50

TOTAL FEED
292.66 ᵗ/hr
AMF COAL 96.20
ASH + I.O 31.80
C OIL 65.24
D OIL 99.42

PRE-HEATERS

LØ STALLS REACTION VOL. 148m³

HOT C/P

COLD C/P

LIQUOR

TER-NGERS

GLEITOL
5.26 ᵗ/hr
ASH + I.O 0.53
C OIL 1.93
D OIL 2.80

HOT H.O.L.D.
15.78 ᵗ/hr
ASH + I.O 4.26
C OIL 3.80
D OIL 7.72

WASH OIL
5.26 ᵗ/hr
D OIL 5.26

H.O.L.D
132.60 ᵗ/hr
ASH + I.O 35.83
C OIL 31.93
D OIL 64.84

LØ M.O.
66.09 ᵗ/hr
D OIL 66.09

H.O.L.D TO FUGALS
101.04 ᵗ/hr
ASH + I.O 27.31
C OIL 24.33
D OIL 48.40

FUGAL DILUENT
40.16 ᵗ/hr
D OIL 40.16

FUGAL DILUENT
33.13 ᵗ/hr
C OIL 33.13

FUGAL FILTRATE
143.34 ᵗ/hr
ASH + I.O. 15.74
C OIL 49.87
D OIL 77.73

FUGALS

LOSS
0.89 ᵗ/hr
ASH + I.O 0.14
C OIL 0.29
D OIL 0.46

TO FUEL OIL
20.67 ᵗ/hr
D OIL 20.67

TO FUEL OIL
10.63 ᵗ/hr
C OIL 10.63

CONCENTRATE
30.10 ᵗ/hr
ASH + I.O. 11.43
C OIL 7.30
D OIL 11.37

DISTILLATE
7.55 ᵗ/hr
C OIL 6.60
D OIL 0.95

STILLS

RESIDUE
22.05 ᵗ/hr
ASH + I.O. 11.37
C OIL 0.53
D OIL 10.15

LOSS
0.15 ᵗ/hr
ASH + I.O 0.06
C OIL 0.04
D OIL 0.05

FUEL OIL
31.30 ᵗ/hr
C OIL 10.63
D OIL 20.67

RECOVERED OIL
6.47 ᵗ/hr
C OIL 1.07
D OIL 5.40

KILNS

RESIDUE
13.20 ᵗ/hr
ASH + I.O 2.74
C OIL 0.05
D OIL 0.41

FUEL OIL FROM UPPER SILESIAN COAL

...MER HYDROGENATION PLANT

H₂

H₂

```
...ROL          ┌──────────┐
...93           │ PHENO.   │        ┌──────────────┐
...CUT          │ ISOLVAN  │        │ SATⁿ STALL FEED│
...85           │ PLANT    │        │  34.28 te/hr  │        ┌──────────────┐
               └──────────┘        │ A OIL  7·93  │        │  SATⁿ STALL  │      ┌──────┐
...O           ┌──────────┐        │ B OIL  5·85  │        │ CATALYST VOL │      │ COLD │
.../hr          │ L.Ø.M.O. │        │ C OIL 20·50  │        │   48 m³      │      │ C/P  │
.26            │ 20·50/hr │        └──────────────┘        └──────────────┘      └──────┘
               │ C OIL 20·50│                                                        │
               └──────────┘                                                    ┌──────────┐
                                                                               │  LIQUOR  │
                                                                               └──────────┘
```

```
        ┌──────────┐     ┌──────────────┐
        │  PETROL  │     │ SPLITTING STALL│     ┌──────┐
        │ 15·58 te/hr│   │ CATALYST VOL │     │ COL. │
        │ (< 155°C)│     │   32 m³      │     │ C/F  │
        └──────────┘     └──────────────┘     └──────┘

 SAT    ┌──────────┐     ┌──────────────┐
 PROD.  │ SATⁿ M.O.│     │ RECYCLE M.O. │
 S      │ 17·55 te/hr│   │ 14·40 te/hr  │
 T      │ (> 155°C)│     │  (> 155°C)   │
 I      └──────────┘     └──────────────┘
 L
 L
```

...UENT
.../hr
.13

```
┌──────────────┐
│ TO FUEL OIL  │
│ 10·63 te/hr  │
│ C OIL  10·63 │
└──────────────┘
```

```
┌────────┐
│  OIL   │
│ ./hr.  │
│ 10·63  │
│ 20·67  │
└────────┘
```
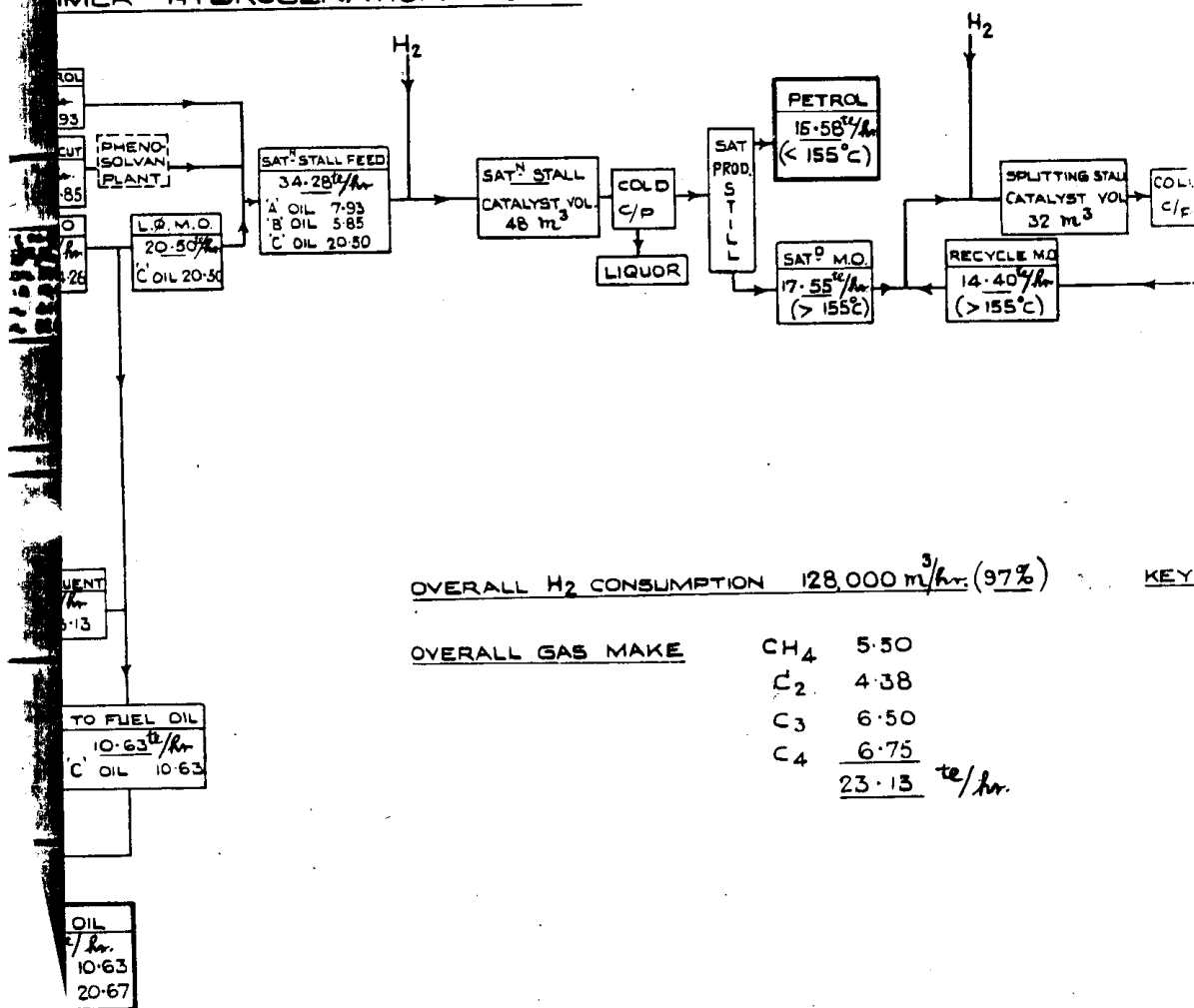
OVERALL H₂ CONSUMPTION   128,000 m³/hr. (97%)   KEY

OVERALL GAS MAKE CH_4 5·50
                        C_2 4·38
                        C_3 6·50
                        C_4 $\underline{6·75}$
                                  $\underline{23·13}$ te/hr.

IAN COAL

IT

FIG. 37.

H₂

ALL $_3$ VOL	COLD C/P	SAT PROD. STILL

LIQUOR

PETROL 15·58 te/hr (< 155°C)

SAT^D M.O. 17·55 te/hr (> 155°C)

RECYCLE M.O. 14·40 te/hr (> 155°C)

SPLITTING STAGE CATALYST VOL 32 m³

COLD C/P

STILL

PETROL 14·26 te/hr (< 155°C)

H₂ CONSUMPTION   128,000 m³/hr. (97%)
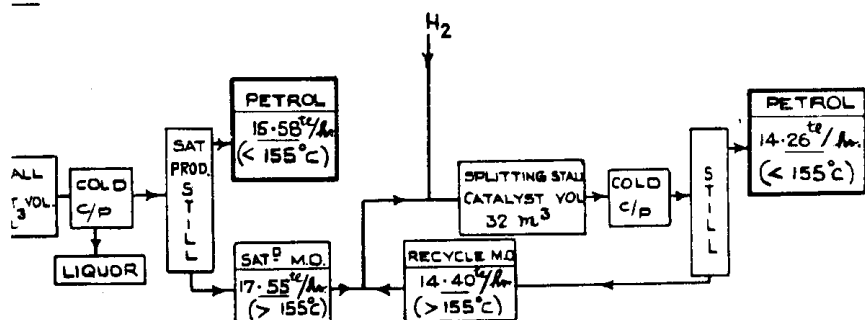
GAS MAKE   CH₄   5·50
               C₂   4·38
               C₃   6·50
               C₄   6·75
                    ─────
                    23·13 te/hr.

KEY TO OIL CODE   'A' OIL   0-160°C
                  'B' OIL   160-210°C
                  'C' OIL   210-325°C
                  'D' OIL   > 325°C

TABLE XXXVIII

COST CALCULATION FOR PRODUCTION OF MOTOR PETROL BY
HYDROGENATION OF BITUMINOUS COAL

(Scale: 200,000te/yr motor petrol)

		RM/te motor petrol
Raw materials		
Coal	1·84te bituminous coal* at RM21·50/te	·39·50
Hydrogen (100%)	2,800m³ at 4·5pfg/m³	126·00
Catalysts and chemicals ..	—	5·00
Operating costs		121·35
Less Credits:		
Liquefied gases	230kg at RM220·65/te†	50·80
Fuel gases	3.4 × 10⁶k. cal at RM6/10⁶k. cal.	20·40
Production cost ..		220·65
Export costs		3·00
General costs and licence ..	5% of production costs	11·05
TOTAL COSTS		234·70

* Bituminous coal with 8% water and 4% ash.   † Valued at the production cost of motor petrol.

TABLE XXXIX

ANALYSIS OF OPERATING COSTS GIVEN IN TABLE XXXVIII

	Liquid phase		Vapour phase		Total
Capital cost in RM × 10⁶:					
Hydrogenation proper	46		17		63
Associated buildings, 25%	—		—		16
					79
Labour:					
Man-hours/te petrol	7·75		3·2		10·95
	RM/te motor petrol				
Labour costs:					
Wages at RM1·30/hr	10·00		4·15		14·15
Salaries, 20% of wages	2·00		0·85		2·85
Energy costs:					
Water at RM0·01/m³	(110m³)	1·10	(80m³)	0·80	1·90
HP steam at RM3·0/te	(0·43te)	1·30	(0·2te)	0·60	1·90
LP steam at RM2·25/te	(1·64te)	3·70	(0·59te)	1·30	5·00
Electricity energy at RM0·015/kwh	(800kwh)	12·00	(146kwh)	2·10	14·10
Fuel gas at RM6·0/10⁶k.cal	(2 × 10⁶k.cal)	12·00	(0·7 × 10⁶)	4·20	16·20
Maintenance costs:					
6% of the plant	13·90		5·10		19·00
2% of the associated buildings	1·15		0·45		1·60
Working materials:					
10% of wages	1·00		0·40		1·40
Amortisation:					
10% of the plant	23·00		8·50		31·50
5% of the associated buildings	2·85		1·05		3·90
Taxes, fire protection, etc.:					
2% of the capital cost	5·75		2·10		7·85
TOTAL OPERATING COSTS	89·75		31·60		121·35

c. Yields

Gelsenberg.—Using Ruhr coal similar to that treated at Scholven, the chief yield benefits obtained by the 700ats process appear to be reduction in the amount of coal substance resisting hydrogenation, a slight reduction in hydrocarbon gas make, and a reduced oil loss in sludge treatment. The latter is due to the smaller quantity of organic solids which have to be purged and to a slightly lower asphalt content in the oil fed to sludge carbonisation.

A flowsheet for Ruhr coal (Fig. 36) provided by the IG Central Technical Department at Ludwigshafen, which an examination of Gelsenberg plant records shows to be reasonably in line with achieved results, shows the

following yields for the 700ats liquid phase hydrogenation stage:—

				% wt on amf coal
Petrol + middle oil	..	..	..	66·8
Hydrocarbon gas	..	..	..	20·5
Unconverted coal..	..	..	..	4·0
Loss of oil in fugals and kilns	..	..	4·7
Hydrogen used	..	..	..	10·3

The overall yields of liquid phase plus vapour phase hydrogenation treatment to make motor or aviation petrol as the sole recovered liquid product from Ruhr bituminous coal are:—

				% wt on amf coal	
				Motor petrol	Aviation petrol
Petrol	..	..	..	61·4	53·5
Hydrocarbon gas, exclusive of C₄ in petrol..	..	..	..	25·9	35·0
Hydrogen used	..	..	..	14·45	14·7–15·0

Stettin-Pölitz.—The Stettin-Pölitz plant, using Upper Silesian coal, gives much inferior yields. This was presumed to be due to an inferiority of the coal used, but it introduces a doubt as to whether all the difference between the Gelsenberg and Scholven yields is due to the difference in process, as distinct from comparatively slight differences in coal. This doubt is strengthened by the fact that, as will be shown later, the Upper Silesian coal hydrogenated at Blechhammer gives better results than that treated at Stettin-Pölitz. It would thus appear that coals from the same area can give very different results. ·

Yields in the liquid phase stage at Stettin-Pölitz are:—

				% wt on amf coal
Petrol + middle oil	..	..	..	57–59
Hydrocarbon gas	..	..	..	23–25
Unconverted coal	..	..	..	8
Oil lost in fugals and kilns	..	..	7–9

The yield of aviation petrol obtained at Stettin-Pölitz when made as the sole recovered liquid product from coal is only 47–48% wt on the amf coal treated. Hydrogen consumption is given as 14·3% wt on the amf coal.

d. Petrol Quality

The aviation petrol made from Ruhr bituminous coal at Gelsenberg has a CFR Motor Method octane number of 72, which is increased to 90 on addition of 1·15ml TEL/litre. Aviation volatility petrol obtained by distillation of the product of the presaturation stage of vapour phase treatment has a clear rating of 66–67 and a leaded octane number of 84–85. Petrol of the same volatility from the splitting stall product rates at 73–74 clear, and 91–92 octane number leaded.

e. Utility Consumptions and Costs

The IG Technical Department at Ludwigshafen prepared a statement of services and labour requirements, and operating costs, for 700ats bituminous coal hydrogenation to give motor spirit, which is summarised in Tables XXXVIII and XXXIX.

Hydrogen consumption amounts to 0·236te/te of motor petrol. The coal required to produce this hydrogen, plus that equivalent to the steam and electric power, but deducting the coal equivalent of the hydrocarbon gas by-products, amounts to about 4·1te amf coal/te of motor petrol. The amf coal actually consumed as a reactant in the hydrogenation process is 1·6te/te motor petrol, making the total effective amf coal consumption 5·7te/te motor petrol.

When the cost of the hydrogen production plant is included, capital cost of a plant to produce 200,000te/yr motor petrol is about RM120,000,000 or RM600 per te/yr motor petrol, i.e. a 30% increase on the cost of a plant to make the same product from coke oven tar and a 200% increase on that of a plant dealing only with vaporisable aromatic middle oils.

The operating costs, excluding raw materials, hydrogen and obsolescence charges and by-product credits, amount to RM86/te motor petrol, i.e. four times the cost of producing this product from vaporisable middle oils, and 40% in excess of that using crude tar or petroleum residuum.

The corresponding achieved operating cost at Stettin-Pölitz was RM123/te of aviation petrol, which when corrected to a motor petrol basis would be about RM108. As explained earlier, the yield of petrol for Upper Silesian coal at Stettin-Pölitz was abnormally low. Correcting for this yield difference between Stettin-Pölitz and Gelsenberg, the operating cost becomes RM96/te motor petrol, suggesting that the Ludwigshafen estimate may be somewhat optimistic. The full cost of aviation petrol from coal costing RM27/te at Stettin-Pölitz and allowing RM56/te obsolescence charges, amounted to RM361/te.

ix. MODIFIED 700ATS PRESSURE PROCESS FOR BITUMINOUS COAL HYDROGENATION OPERATED AT BLECHHAMMER

a. Process

At Blechhammer, Upper Silesian coal is hydrogenated in the liquid phase at 700ats pressure under such conditions that the amount of heavy oil boiling above 325°C present in the cold catchpot product is greater than is required for coal pasting. This "excess" heavy oil, blended with some middle oil, is sold as Navy fuel oil.

This result is achieved by reducing the extent of heavy oil hydrogenation by partially replacing the heavy oil in the coal paste by "middle oil." This use of middle oil pastes introduces difficulties with regard to settling of solids in interchangers and preheaters. At Blechhammer the ground coal is made up into two kinds of paste. The first, containing a comparatively low coal and a high asphalt concentration, is fed in the normal way to an interchanger and to the preheater. The second, which has a high coal and middle oil content, is fed direct to the inlet of the preheater. In order to avoid settling in the preheater, part of the heavy liquid product from the hot catchpot is circulated to the preheater inlet without let-down of pressure.

Special precautions are also taken to avoid loss of valuable middle oil in the purge of solids from the system. The concentrate from the fugals is fed to a flash distillation apparatus for recovery of the greater part of its oil content and the residues are fed hot to the carbonisation kilns.

It is also necessary to modify the distillation of the cold catchpot product in order to provide a middle oil for pasting which is free from very volatile components. At Blechhammer, the cold catchpot product is distilled to give four fractions—petrol boiling below 160°C, a light middle oil of boiling range 160–210°C from which phenolic by-products are extracted, a 210–325°C cut used for pasting and for blending with heavy oil to give fuel oil to Navy specifications and the usual heavy oil bottoms boiling above 325°C.

Apart from the above special fractions, the Blechhammer process is substantially the same as that operated at Gelsenberg.

b. Capacity of the Liquid Phase Plant

Because of the reduced extent of the breakdown of heavy to light oil products, the coal throughput per stall obtainable at Blechhammer is considerably greater

TABLE XL

SUMMARY OF HYDROGENATION DATA FOR THE PRODUCTION OF MOTOR PETROL FROM VARIOUS RAW MATERIALS

	Raw material requirement, te amf material per te petrol	Hydrogen consumption, te/te petrol	Surplus hydrocarbon gas make, te/te petrol	Oil losses in sludge kiln, etc., te/te petrol	Unconverted solid residue, te/te petrol	Operating cost excluding raw material hydrogen and obsolescence charges, RM/te petrol	Liquid phase reaction volume requirement for 200,000 te/yr petrol	Vapour phase saturation stall reaction volume requirement for 200,000 te/yr petrol	Vapour phase splitting hydrogenation reaction volume requirement for 200,000 te/yr petrol	Capital cost including hydrogen plant, RM/te/yr petrol
Vaporisable middle oil, distilled from natural petroleum..	1·06	0·032	0·09	—	—	22	—	18m³	30m³	135
Vaporisable aromatic middle oil, e.g. from coal tar distillation	1·07	0·097	0·09	—	—	22	—	45m³	32m³	190
Brown coal tar + associated scrubber oil (Leuna)	1·20	0·081	0·23	0·03	—	—	42m³	45m³	30m³	—
Petroleum residuum (containing 11% hydrogen)	1·26	0·073	0·23	0·01	—	60	50m³	18m³	31m³	360·
Coke oven tar..	1·28	0·176	0·29	0·03	—	60	68m³	34m³	32m³	455
Middle German brown coal..	2·07	0·198	0·41	0·18	0·03	76	84m³	35m³	46m³	—
Ruhr bituminous coal, 700ats pressure process	1·63	0·236	0·43	0·08	0·07	86	105m³	34m³	25m³	600
Ruhr bituminous coal, 300ats pressure process	1·77	0·258	0·52	0·11	0·14	—	168m³	34m³	25m³	—

than at Gelsenberg and Stettin-Pölitz. The Blechhammer stalls, which are identical with those at Gelsenberg (four converters each of 9m³ capacity), process 560te/day amf coal, which is equivalent to 0·65te/hr amf coal/m³ reaction volume.

c. Yields

The yields achieved at Blechhammer in the liquid phase stage are:—

	% wt on amf coal
Petrol + middle oil boiling below 325°C	46·7
Heavy oil boiling above 325°C	21·5
Hydrocarbon gas	19–20
Unconverted coal..	4
Oil lost in fugals and kilns	5·5–6·0

Part of the middle oil product is blended with heavy oil for sale as fuel oil. The remaining petrol and middle oil is passed on to a conventional two-stage vapour phase process for conversion to aviation petrol.

Fig. 37 is a flowsheet showing the complete operations at Blechhammer to make aviation petrol and fuel oil as the final products. The overall yield data may be summarised as follows:—

	% wt on amf coal
Aviation petrol	31·0
Fuel oil	32·5
Hydrocarbon gas	24·0
Hydrogen used	10·8

d. Possible Applications of the Blechhammer Method

Workers in the hydrogenation field have for a long time held the view that, theoretically, the best way to obtain an increased yield of light oil by hydrogenation of bituminous coal is to conduct the liquid phase hydrogenation in two stages, i.e. conversion of coal primarily to an asphalt-free heavy oil followed by conversion of the heavy oil, preferably over a fixed catalyst, to a material suitable for vapour phase hydrogenation. In practice, the first stage of this process, when conducted at 300ats, is not easily operable because of the difficulty of conversion of asphalts at an adequate rate. The Blechhammer operations have shown that this stage of the process is workable at 700ats.

IG were conducting experiments on the secondary hydrogenation of the heavy oil product of coal hydrogenation over fixed catalysts at 700ats, but the work had not gone very far, and no results have been found. Even assuming that a fixed catalyst process is not feasible, the conventional dispersed catalyst process

will give an 80% yield of petrol plus middle oil from asphalt-free coal heavy oil. Combining this with the Blechhammer results, it should therefore be possible to produce petrol + middle oil from Silesian coal by a two-stage process with a yield of 64%. This is 7% better than the yield from Upper Silesian coal at Stettin-Pölitz, but part at least of the difference must be attributed to differences in the coal used at the two plants.

x. SUMMARY OF DATA ON HYDROGENATION OF VARIOUS RAW MATERIALS TO MOTOR PETROL

Table XL summarises the more important data on yield of motor petrol, by-product hydrocarbon gas, hydrogen consumption, reaction volume requirement, and capital and operating costs for hydrogenation of various raw materials. It clearly demonstrates the increase in complexity and cost of the process as the raw material is changed from the vaporisable middle oil to a heavier feed stock and from a heavy oil to coal.

xi. NOTES ON HYDROGENATION PLANT EQUIPMENT

a. Oil and Paste Injectors

Clean oils are injected to the hydrogenation stalls by means of electrically-driven three-throw pumps. SEA rings for gland packing had not been very satisfactory, and acacia wood packing was employed in Germany with considerable success, the life being about 1,800 hours.

Injection of coal paste was by horizontal hydraulically-operated ram pumps, the injection rate being varied by controlling the rate of entry of water to the hydraulic cylinder. Originally, tin packings were used in these injectors, but latterly lead alloyed with 0·1% cadmium had been found to be satisfactory. Because of the great variation in quality of nitrided rams in Germany, ordinary case-hardened rams of 400 Brinell hardness were usually employed.

b. Interchangers

These were of the tube and shell type, the shell being usually a low-chromium steel forging 18m long and 600mm internal diameter (see Fig. 38). The number of tubes for an interchanger operating on paste was of the order of 190 and this number was increased with clean oil feeds to 240. The tubes were zinc-treated to withstand H_2S attack. The heat transfer coefficient of these interchangers when operated with coal paste was of the
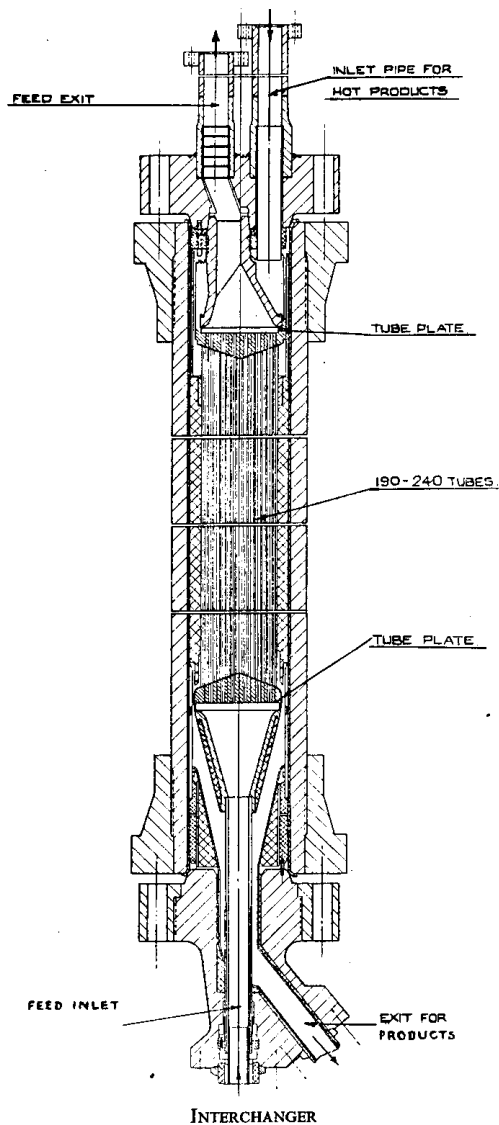
order of 150, and when employed with fluid oils 250k.cal/m²/°C/hr.

c. Preheaters

These consisted of a series of hairpin tubes placed in a rectangular brickwork chamber and heated by hot flue gas produced in a separate combustion chamber and circulated by means of a fan.

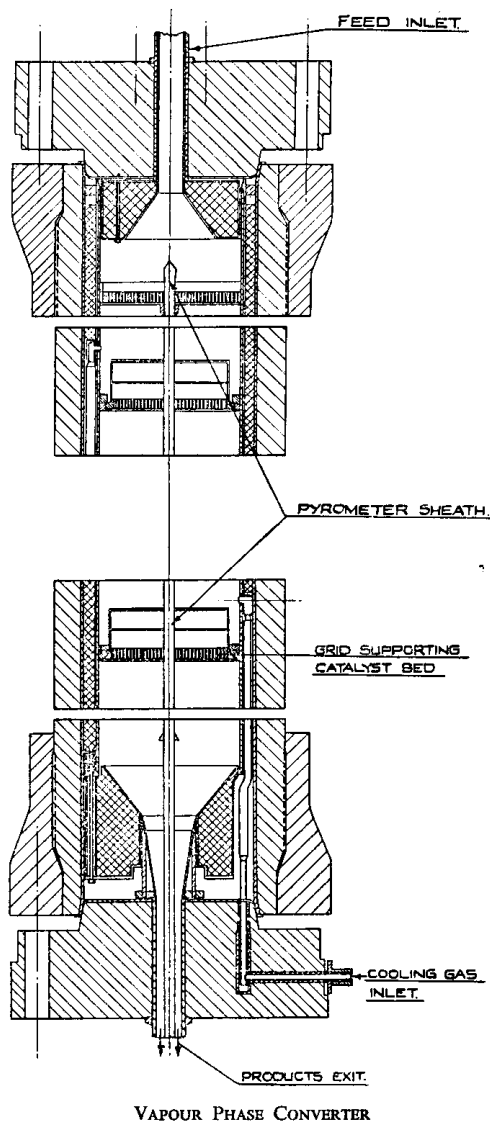At Leuna the hairpins were 15·5m long, 120mm bore, and 171mm external diameter. They were fitted with

The most suitable material for preheater tubes, particularly for 700ats operation, was considered to be V2A steel. The shortage of nickel and chromium had necessitated the use of substitute material (N10) of the following approximate analysis:—

Carbon	..	.. 0·2%
Chromium	..	.. 3–4%
Molybdenum		.. 0·5–1%
Tungsten	..	.. 0·5%
Vanadium	..	.. 0·8%

FIGURE 38

INTERCHANGER

FIGURE 39

VAPOUR PHASE CONVERTER

fins 4mm thick and 10mm apart, which provided a 1 : 20 internal : external surface ratio. Average overall heat transfer coefficient at Leuna was stated to be 150k.cal/m²/°C/hr.

Much larger preheaters were used in the new bituminous coal hydrogenation plants. These contained up to 25 hairpins and were fed with twin gas circulation fans.

d. Converters

These are chrome steel forgings, fitted with a V2A liner with a layer of 64mm cement asbestos lagging between the liner and the inner forging wall. The largest 300ats converters are 18m long and 1,200mm internal diameter, and provide 13m³ liquid phase reaction volume, or 9·5m³ of fixed catalyst volume, with provision for

cold gas mixing chambers. Converters 18m long and 1,000mm internal diameter were in common use, particularly for vapour phase operations, and provided a packed catalyst volume of 8m³. The largest 700ats liquid phase converters gave a liquid phase reaction volume of 9m³. Fig. 39 is a diagram of a vapour phase converter showing the method of introduction of cold gas through the bottom flange for intermediate cooling between catalyst beds. Some of the liquid phase converters were fitted with a central stand-pipe for introduction of the feed to the top of the converter.

e. Wickel Vessels

In some of the German plants, forgings for interchangers, catchpots, etc., were replaced by wound pressure vessels. These, which were called Wickel vessels, are made by winding the necessary number of layers of steel tape on the outside of a comparatively thin-walled tube. For a full description of the manufacture of Wickel vessels, see CIOS Report XXX–103, page 53.

f. Hot Catchpots

These were cone-bottom vessels fitted inside a pressure chrome steel forging in much the same way as the liner of a converter, as shown in Fig. 40. The detailed design varied considerably from plant to plant, according to the difficulty experienced in separation of solids and coke formation in this vessel. In some cases, hydrogen was introduced at the bottom of the cone in order to stir the liquid contents. In others, cold gas was circulated through cooling coils placed between the inner vessel and the forging. These coils were usually placed at the bottom of the vessel, round the inlet pipe, and at the top of the vessel, in order to provide a cleaning action by refluxed oil (Fig. 41).

g. Sludge Carbonisation Kilns

There were two types of sludge carbonisation kilns operating in Germany—Schneckenofen and Kügelofen.

A Schneckenofen unit consists of two horizontal steel tubes 1m diameter and 16m long, arranged one above the other inside a brickwork gas-fired furnace. Each tube is fitted with paddles fixed with a slight pitch on to a central rotating shaft, and these scrape the inner walls of the tube free from adhering coke. Loose iron bars are attached to the paddles so that, as it rotates, the bars are lifted to fall later with sufficient force to dislodge coke deposited on the paddle.

The central shaft is rotated at about 1rpm. The average feed rate for a Schneckenofen, which is usually employed in conjunction with brown coal hydrogenation, is 2·5–3 m³/hr sludge when clean, falling to 1·8m³/hr after 50 hours' operation, when the unit is taken off line for cleaning. A rough sketch of a Schneckenofen is shown in Fig. 42.

The Kügelofen illustrated in Fig. 43 consists of a rotating tube, 2·2m diameter and 11m long, slightly inclined to facilitate the removal of coke. This tube rotates at about 9rpm inside a brickwork chamber, heated by 12 gas burners. The sludge is preheated before entering the kiln by means of a preheater arranged above the kiln itself. Steam is also superheated in this preheater and introduced into the kiln. About three-quarters of the kiln length is occupied in the coking operation and this part is filled with 9te of grinding balls, each weighing 1·8kg. In the remaining length of the kiln there are 24 grinding balls, each weighing 10kg. Coke from the delivery chamber is dumped into a water seal, and the quenched coke carried by a continuous band conveyor to railroad cars for disposal.

The normal sludge feed is 2·5–3·0te/hr. 150–250kg steam preheated to 450°C is required. The operating period between cleaning operations varies considerably with the nature of the sludge. At Gelsenberg it was stated that a run of 6–12 weeks was possible whereas only one month runs were obtained at Scholven.

FIGURE 40

HIGH-PRESSURE HOT CATCHPOT
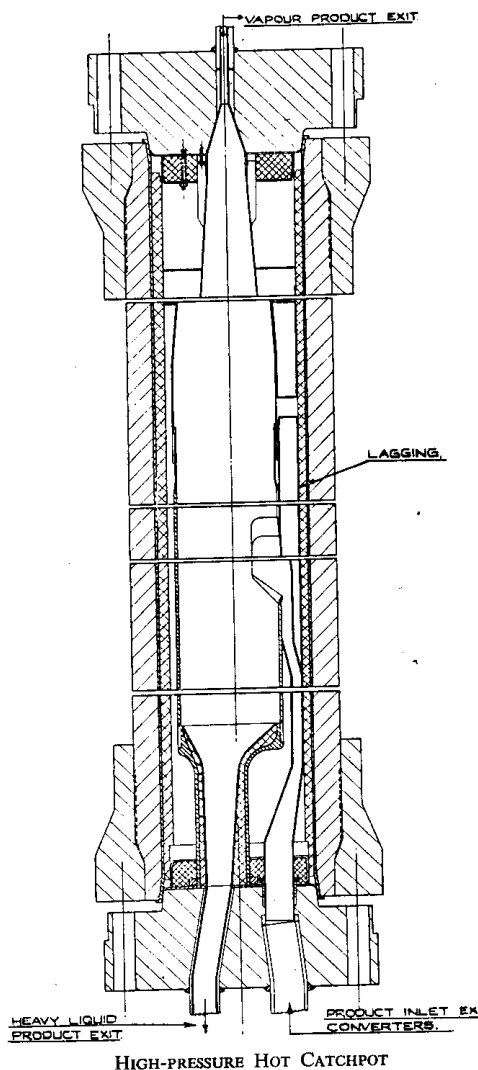
xii. GENERAL COMMENTS ON THE VALUE OF GERMAN HYDROGENATION INFORMATION

Hydrogenation was the only process by which Germany's war-time requirements of petrol, and, in particular, aviation petrol, could be supplied. The most favourable raw materials for the process, i.e. middle oils and high hydrogen content heavy oils, were not available in the necessary quantities, and the process had therefore to be applied in its more complicated forms to the treatment of complex materials such as coal and pitch. It is not surprising, in these circumstances, that the German technicians were so preoccupied with the erection and operation of new plants
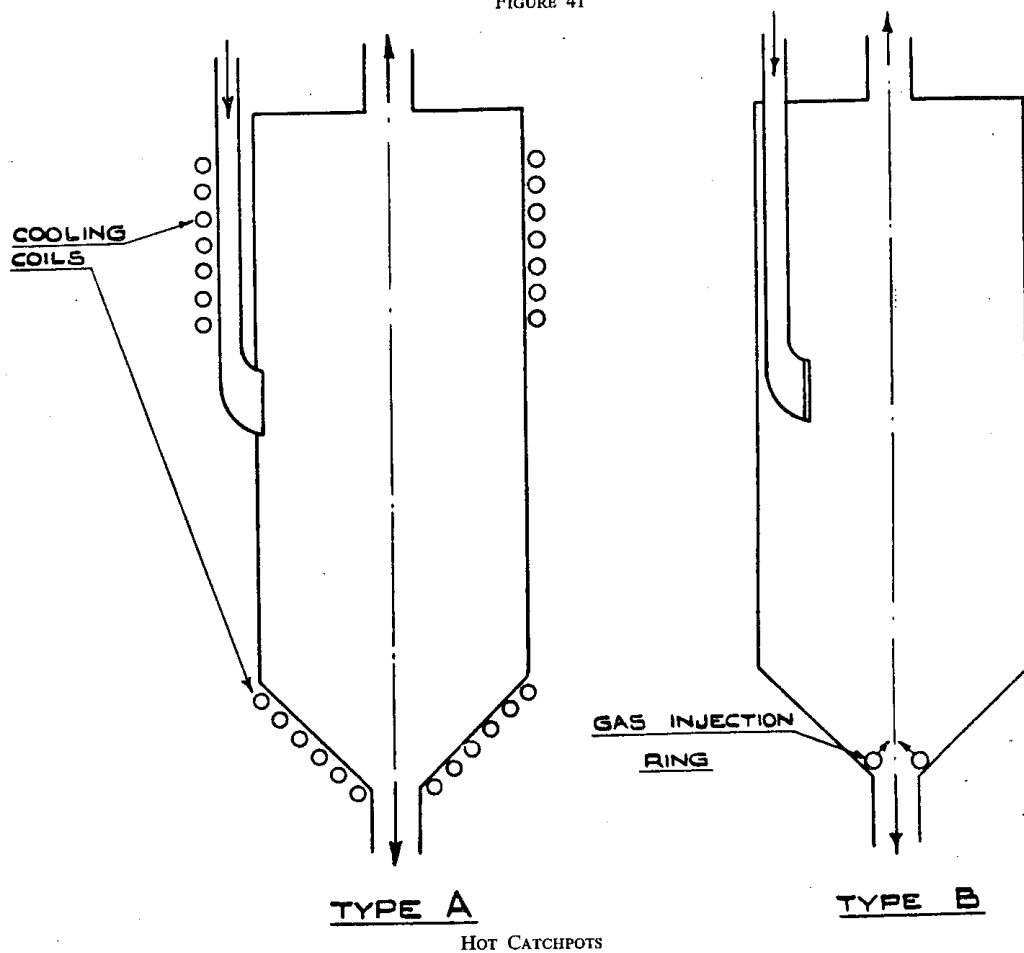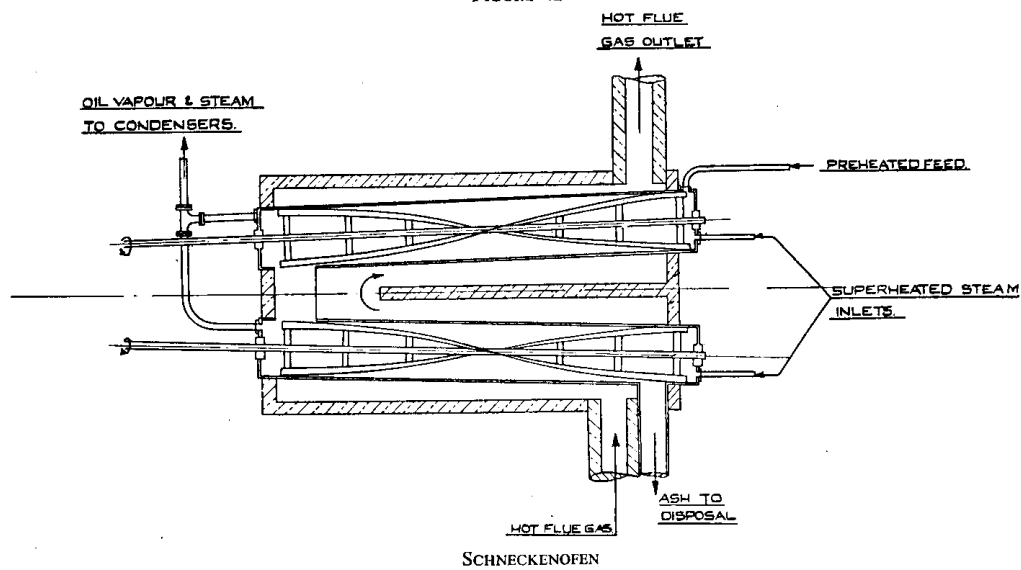
FIGURE 41

COOLING
COILS

GAS INJECTION
RING

TYPE A   TYPE B

Hot Catchpots

FIGURE 42

HOT FLUE
GAS OUTLET

OIL VAPOUR & STEAM
TO CONDENSERS.

PREHEATED FEED.

SUPERHEATED STEAM
INLETS.

ASH TO
DISPOSAL

HOT FLUE GAS

SCHNECKENOFEN

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

KÜGELOFEN
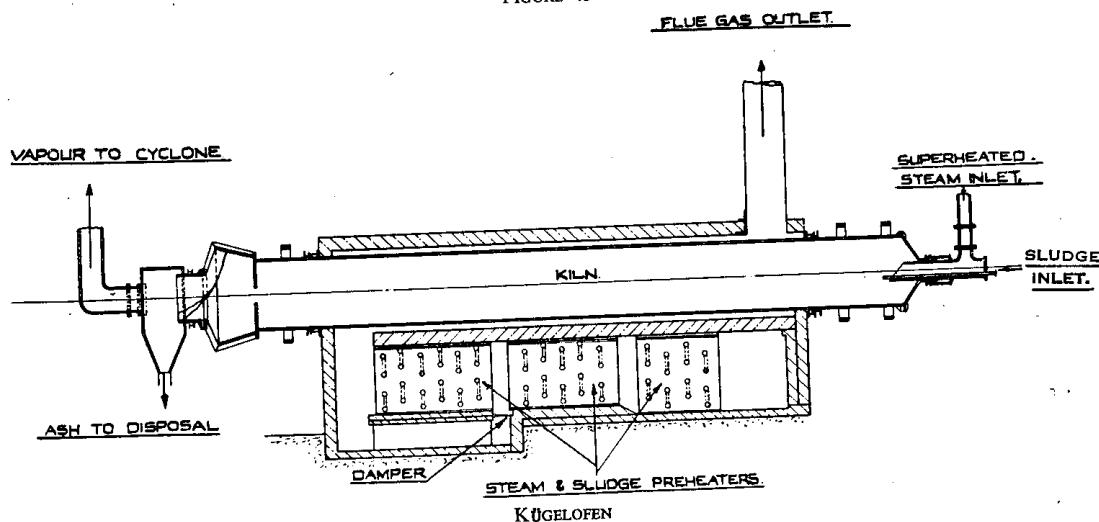
be expected to give about a 5% higher yield of petrol than processes used at present. Such improvement is not nearly sufficient, however, to alter the economic picture of coal hydrogenation at the existing level of coal and petrol prices. A second point of interest in the German work which, if followed 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 600–1,000m³ 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