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

Edited by

DR. R. HOLROYD

on behalf of

MIN. of F. and P. and T. I. I. C.

INFORMATION SUPPLIED

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of

THE PETROLEUM INDUSTRY WAR COUNCIL

PERSONNEL OF VISITING TEAMS

1st Visit April 21st - 26th 1945.

Lt. Col. H. Hollings	British Ministry of Fuel and Power.
Major J. F. Ellis	
Capt. H. G. Simpson	
Capt. G. U. Hopton	
Mr. E. B. Peck	U. S. Petroleum Administration for War
Mr. P. K. Kuhne	
Mr. H. M. Weir	
Mr. V. Haensel	
Mr. E. Cotton	
Mr. L. L. Hirst	U. S. Bureau of Mines Mines
Mr. W. W. Odell	

2nd Visit May 8th - 24th 1945.

Lt. Col. R. Holroyd	British Ministry of Fuel and Power
Major M. A. G. Banks	
Major D. A. Howes	
Major A. J. V. Underwood	
Major R. A. Taylor	
Major R. J. Morley	
Major J. F. Ellis	
Mr. W. F. Faragher	U. S. Petroleum Administration for War
Mr. J. G. Allen	
Mr. H. Schindler	

Amongst those visiting the plant later, the following submitted notes for inclusion in the present report:

Mr. L. L. Newman	U. S. Bureau of Mines
Mr. W. A. Horne	U. S. Petroleum Administration for War
Mr. J. P. Jones	

Although not a member of any visiting team, Dr. H. Clough (British) has made a valuable contribution to the above report by studying evacuated documents and by his assistance in editing the final document.

INTRODUCTION

The Leuna Factory of the I. G. Farbenindustrie A. G. situated near Merseburg, is the biggest heavy chemical plant in Germany and produces a very wide range of products, mainly based on hydrogen or hydrogen and carbon monoxide. Its principal products are ammonia, synthetic petrol derived from the hydrogenation of brown coal, and synthetic alcohols made from hydrogen and carbon monoxide.

The plant was first visited on the 21st April 1945 by a team including E. Cotton, V. Haensel, E. B. Peck, P. K. Kuhne, H. M. Weir, L. L. Hirst, W. W. Odell, G. U. Hopton, H. Hollings, J. F. Ellis, and H. G. Simpson. It was again visited on the 8th - 24th May 1945, by a combined British and American team consisting of R. Holroyd, M. A. G. Banks, D. A. Howes, A. J. V. Underwood, R. A. Taylor, W. F. Faragher, H. Schindler, and J. G. Allen. This team was later joined by J. F. Ellis and R. J. Morley.

A third visit with particular reference to catalyst manufacture was made by W. F. Faragher and W. A. Horne and the notes of these latest investigators have been taken into account in preparing the report.

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Editor's Note: In preparing the following report, many of the sections have had to be written on the basis of notes supplied by two or three separate investigators. Although in these cases the names of the people supplying the basic notes have been put down as "authors" of the section, it has not, in every case, been possible for them to see and approve the final documents. Every effort has, however, been made to include all the information obtained and to keep as closely as possible to the tone of the individual notes.

I GAS PRODUCTION

The interrogation of Dr. Sabel (Engineer in charge of gas production) and Dr. Jeltsch (Chemist in charge of H_2S removal) was carried out by Hollings, Weir, Odell and Hopton on April 22nd and 23rd, 1945. Additional information was obtained by C. A. F. T. about the same time and by Ellis and Morley on May 16th. Newman interrogated Oberingenieur Ohler, Dr. Schroeter, Dipl.-Ing. Stingl and Obermeister Heuer on May 14th and 15th, 1945, in regard to the detailed operation of the slagging gas producers (abstich-generatoren).

Gas Production

Water gas for NH_3 and methanol synthesis and for H_2 production was made in three distinct ways. The bulk was still made on water gas generators, of the usual design, working a cycle and using oven coke, and the rest was divided between Winkler generators, using O_2 and grude coke, and ~~slagging producers, using O_2 and oven coke, or Rohschlacke (refuse from~~ the Brassert generators). A rough summary of the plant can be seen in the following table:

Type	No. of Units	Unit Capacity M^3/hr Gas	Normal Output from Plant M^3/hr. H_2 + CO
"Pintsch-Drehrost"	10	5,000)	240,000
"Pintsch-Brassert"		10-12,000?)	
Winkler	1	40,000)	55,000 (Limited by (oxygen available: (a second Winkler (ran to make (producer gas for (power.)
	4	80,000)	
Slagging producers	6	15,000(coke)	?
		8,200 (Rohschlacke)	30,000
Pintsch producers	10	?	Not used

Water Gas Generators

The original generators were of an old Humphreys and Glasgow design built by Pintsch (now referred to as "Drehrost-generatoren"), but most of them had been modified by Brassert (now referred to as Pintsch-Brassert-Generatoren). Very little attention was paid to this plant, as it was old and contained little novel. Only a few of the generators were seen, and as a number of changes had been carried out on various generators it was difficult in the short time available to get any clear idea of how many generators included each modification or indeed what was the effect of each modification. The following notes are therefore very incomplete.

All generators had concentric ring rotary grates, but whilst some were brick-lined others had jacket boilers. They had an I. D. of 3 m, so that the stated output of 10,000 to 12,000 M^3/hour must be considered very high and possibly in error. They were enabled to achieve high outputs without clinker troubles by extracting ash with a high coke content (50%C), the theory being that troublesome clinker could not form if ash were not allowed to accumulate in high concentration; the carbon in ashes was not lost, as it was used on the slagging producers. At least some of the generators actually in use were hand-operated.

The fuel used was oven coke, made from bituminous coal, and brought by rail from the Ruhr, a distance of 275 miles. The daily consumption of coke was 3,000 T/D.

We were told that until very recently the Winkler generators, using oxygen and local brown coal or grude coke, were more expensive to run than the coke water gas generators, despite the high cost of coke after ~~its long haul and this had been the reason for the continued existence~~ of the old method of gas manufacture. Only in the last years of the war, apparently, had the cost of Ruhr coke become high enough to make the Winkler generator cheaper to run. We do not know how far these arguments include considerations of the high capital cost needed for a new plant, remembering the old generators were in existence.

Winkler Generators (Site 279 on Works plan)

These generators were built in 1929-31 and since then have been subjected only to minor modifications. Since more modern installations were seen elsewhere (e.g. Zeitz) the plant was not covered in much detail. They have been used to gasify both dried brown coal and "grude" coke (brown coal low temperature coke), and have been used for the manufacture of power gas, producer gas for NH_3 synthesis and water gas. In recent years the fuel has been almost entirely grude coke, with one Winkler run to make power gas and one run to make water gas. Shortage of oxygen limited the plant output of water gas to one Winkler.

The principle of the Winkler generator is well known: particulate fuel was used, the most suitable size being 3 mm diameter, with less than 10% above 5 mm and the blast of air alone (when making power gas) or of a mixture of oxygen and steam (when making water gas) was sufficient to make the fuel "dance" or boil. As a result very high outputs could be obtained from a given cross-section in comparison with orthodox water gas generators.

There were five Winkler generators in all; the oldest and smallest one had an output of 40,000 M^3/hour water gas for a cross-section area of 12 sq.m. and the other four each had an output of 80,000 M^3/hour wate gas for a grate area of 25 sq.m.

~~The change over from dry brown coal to grude coke probably took~~ place because of the increased demands of hydrogenation for dry brown coal, thus causing a limitation of drying capacity, and also because of the availability of grude coke from various neighbouring brown coal L. T. carbonization plants, set up primarily to recover tar from the coal. Both fuels were quite satisfactorily gasified, although dry brown coal gave a higher CH_4 content of synthesis gas. The fuel was fed into the side of the conical base by four screw conveyors.

All the generators originally had stationary grates, over which swept a rotating water-cooled arm, to remove ash through an opening on one side. The blast passed through this grate. In recent years however the small generator (1943) and one large generator (1944) were modified and the grate and rotating arm eliminated, the oxygen and steam mixture then being added through tuyeres entering the side of the conical base; this successfully eliminated all shut-downs for repairs of the rotating arm, although by then the earlier rather serious troubles due to leaks from the arm, had been much reduced; more important however, it was ~~claimed that the modification had reduced the consumption of fuel and~~ oxygen by about 10%, although no reason was given. The grateless generator was fitted with two screw conveyors at the base, which could be run intermittenly to remove that ash, foreign material, etc., which was not blown over and had collected at the base. A grateless generator has been installed at Brüx.

In operation of generators with grates only about 10% of the ash was withdrawn at the base through screw conveyors: the remainder passed overhead. It was possible to run for 1 to 2 weeks without these screw conveyors, large material merely collecting slowly on the grate. The overhead ash contained 50 to 55% carbon and had a maximum size of 0.3 to 0.4 mm. It could either be returned to the generator or burnt on boilers: it had also been used as an active carbon for the dephenolation of effluents.

The blast, when making water gas, consisted of a mixture of 40 to 50% oxygen with 60 to 50% steam. About two-thirds of the oxygen was blown through the bed and one-third, mixed with 20% steam to prevent explosions in the tuyere main, was blown through tuyeres into the gas space about 3 to 4 m above the bed, with the object of gasifying carbon in dust entrained in the gas and cracking any tar and hydrocarbons. The original design had the top half of the generator enlarged to a bulb, designed to give a longer time contact for these reactions, but in later designs this was eliminated and the straight cylindrical portion heightened to give the same effect; the reason for the change was given as capital cost. Some of the generators at Leuna still had these bulbs, but some had not; the exact number of each was not obtained with any certainty. In all later plants the straight-sided generators were installed, e.g. three at each of the Brabag plants at Böhlen, Magdeburg and Zeitz, and five at Brüx (but including one grateless type as mentioned before). The most detailed account of this design is given in the report on Zeitz. Three such generators were also built by I. G. at Ludwigshafen for Japan, designed to work on a grain size mineral coal of particularly active character.

The whole generator was brick-lined and no trouble was obtained with clinker. The fuel bed temperature was about 900° C, but this depended on the nature of the fuel. The bed depth was about 1 m. and had a back pressure of about 0.5 m. water gauge.

With less reactive fuels, such as bituminous coal derivatives, the Winkler generator was said to be much less satisfactory. Much higher bed temperatures had to be used and the CO_2 in water gas was high.

Typical performance figures were given as follows:-

		Water Gas		Power Gas	
		Dry Brown Coal	Grude	Dry Brown Coal	Grude
Gas Analysis	$\%CO_2$	19	20	10	11
(H_2S free)	$\%CO$	38	38	22	27
	$\%H_2$	40	40	12	7
	$\%CH_4$	2	1.5	0.7)	55
	$\%N_2$	1	0.5	55)	
Net C.V.T.cals/M		-	-	950	956
Fuel	kg/M3	0.625	0.50	0.335	?
Oxygen	M3/M3	0.25-0.26	0.25-0.26	nil	nil
Steam	M3/M3	0.39	0.375	nil	nil

Typical analyses of the fuels, not necessarily corresponding with the above figures, were:

	Dry Brown Coal (dry basis)	Grude Coke (dry basis)
C	61.1	68
H	4.7	2.0
O	17.0	2.2
N	0.1	-
Volatile S	3.3	1.3
Ash	13.8	26.5
H_2O	(6.0)	(2.0)

The major thermal losses were as carbon carried away as dust and as sensible heat carried away in the water gas at about 900° C. The flue gas was passed through a cyclone to recover any coarse dust, was cooled to about 200° C in a waste heat boiler, and passed through a hydraulic seal; it was then dedusted in a direct contact water washer and a Theisen disintegrator. It was stated that unsuccessful attempts had been made to build recuperators and heat exchangers in the top of the generator, presumably to preheat the blast.

To avoid explosions when using oxygen-steam blasts it was essential to get good mixing; on the Winklers it was present practice to mix at a minimum distance of 30 to 40 m. from the point of entry into the generator, with several bends to promote turbulence.

Slagging Producers ("Abstichgeneratoren")

The original slagging producers at Leuna were three Würth producers, using coke breeze, "ashes" from the water gas generators or simply coke, blown with air only to make producer gas for NH_3 synthesis; the producers were completely brick-lined and ash was removed as molten slag. Steam or oxygen could be added as conditions permitted.

Owing presumably to brickwork failures the Würth type was replaced by another, in which the whole of the lower part of the producer was water-cooled. There were six of these producers, five of I. G. design and one by Pintsch. One had been built during the war. The producers were blown with oxygen and steam and the capacity of each unit was 15,000 M^3/hour of substantially nitrogen-free producer gas.

The producer was built of 1/2" to 5/8" iron plate, having a diameter of 2.5 metres at the tuyeres and 3.8 metres higher up, with the inside ~~diameter of the brickwork 1.7 metres at the tuyeres and 3.3 metres at the~~ top. The total height was 7 m. above the tuyeres and the fuel bed was 4 m. deep above the tuyeres. Only the top part, above the fuel bed, and the lower part, below the tuyeres, were brick-lined; the rest was bare metal. In five generators the producer was water jacketed but in the last one built the jacket had been omitted and the metal was cooled merely by trickling water down over the outside. This modification had been carried out as the result of a serious accident on one of the old type; a piece of clinker became lodged just above a tuyere and as a result the incoming oxygen caused a very high local temperature, which burnt a hole in the jacket; the producer became flooded and quenched and before it was noticed oxygen had broken through, causing a serious explosion in the gas mains and gas coolers. This could not happen with the latest design; it was said that there was no trouble with evolution of steam as the water merely became warm.

It was very difficult to make power gas on these producers, using air only; the difficulty was presumably insufficiently high temperature to permit slagging, owing to heat abstracted through the generator walls, since the old brick-lined Würth producers could be run successfully on air.

When making producer gas, a mixture of oxygen and steam was introduced at the tuyeres and a temperature of 1,700° C was obtained, although the exit gas temperature was only 400° C. Limestone could be added to act as a flux for the liquid slag. Depending on the fuel, slag was run off at intervals of 20 to 60 minutes. One method of slagging was to run the liquid slag first into troughs, where any iron sank (and was dug out at intervals), and then into cold water; another method was to tap off molten iron from the extreme bottom of the generator and molten slag from a tap somewhat higher.

A wide variety of fuels could be used, but Rohschlacke (refuse) containing 50% carbon, from the Brassert generators was normally used. The fuel should be above 30 mm, and could be as large as 1 to 2 feet. When using metallurgical coke it was common practice to add 3% of limestone and 20% of solid slag from previous working to assist in the formation of slag. When using coke the blast mixture was 35% O_2 and 65% steam: when using Brassert Rohschlacke the mixture contained 50 to 58% O_2 and 50 to 42% steam.

Typical operating figures were:

		Brassert Refuse	Grude from Deuben	Met. Coke	Met. Coke with CO_2
CO_2	%	9.7	5.4	6.8	3.0
CO	%	66.5	62.4	61.4	92.5
H_2	%	22.9	31.2	31.0	3.0
CH_4	%	0.0	0.0	0.0	0.0
N_2	%	0.9	1.0	0.8	1.5
H_2S	g/M^3	2.7	13	4.3	2.2
O_2	M^3/M^3 $H_2 + CO$	0.347	0.276	0.262	0.310
~~H_2O~~	~~kg/M^3 $H_2 + CO$~~	~~0.207~~	~~0.266~~	~~0.346~~	~~nil~~
CO_2	M^3/M^3 $H_2 + CO$	nil	nil	nil	0.258
Fuel	kg/M^3 $H_2 + CO$	?	0.80	0.490	0.330
Carbon	" $H_2 + CO$	?	0.482	0.424	0.460
Fuel Analysis	C %	45-50	54	86.8	87.2
	ash %	55-40	16.9	9.1	11.8
	H_2O	0	22	1.8	1.0

The figures in the last column are interesting; here steam in the blast was replaced by CO_2, resulting in a very high content of CO in the gas made.

Smaller slagging producers were available and used for testing various fuels and various methods of running.

Pattenhausen Generator

This generator was not inspected, although the installation was seen from a distance. The principle of this generator was that all the heat of reaction was added in the form of highly preheated steam at about 900° C. A large excess (fourfold?) of steam was used and gasification of dry brown coal proceeded at about 600° to 700° C, a temperature only possible with a highly reactive fuel. We gathered that the plant was not a great success and certainly no other units had been built, although the original one started up in 1937.

Oxygen Plant

This consisted of Linde-Frankl units of conventional design and was not studied in detail. There were 9 units in all, having a total capacity of 23,700 M^3/hour of 98% O_2, the two oldest units producing 1,900 and the other seven 2,850 M^3/hour. The actual output over the five years 1938-42 averaged 22,000 M^3/hour 100% O_2. A somewhat smaller quantity of nitrogen was also recovered, and used before the war approximately equally for purging and for NH_3 synthesis: during the war a drop in NH_3 output caused less N_2 to be used for the latter purpose; the maximum capacity of pure N_2 was 32 to 36,000 M^3/hour, limited to that obtainable from four units.

The energy consumption varied from 0.5 to 0.6 KWH/M^3 oxygen, averaging about 0.55 KWH/M^3 100% oxygen. With the cost of power at 1.1 to 1.2 pfg/KWH, the cost of oxygen was said to be 1.6 to 2.0 pfg/M^3; a separate set of figures were given, stating this cost to be made up of 60% power (the above figures give only 41% at most), 30% amortisation and 10% labour repairs, etc.

A small quantity of krypton was also made as a by-product. The capacity was about 30 M^3/month, containing about 75% krypton, with the impurities mainly oxygen.

Documents in Connection with Gas Production

The following documents give additional information:

(1) Drawings of the Winkler generator, which had been deposited at Bottendorf, were taken by the U. S. Navy team.

(2) Files relating to the Winkler plant were collected by Mr. Hopton from engineer Sauer's office and placed with the official documents.

(3) Leuna report 837, entitled "10 Jahre Sauerstoff-Vergasung in Leuna" by Sabel, dated 15.9.42, was arranged by Dr. Morley to be sent to London through the Military Governor of Merseburg.

(4) Leuna report 916, entitled "Jahresbericht der Stickstoff und Sauerstoff - Fabrik und Nebenbetriebe 1938-42" by Koppe, dated May 1944, was arranged by Dr. Morley to be sent to London through the Military Governor of Merseburg.

(5) A drawing of the slagging producer was obtained by Mr. Ellis and placed with the official documents.

H_2S Removal

Two methods were used: an Alkacid process, purifying Winkler gas and the old active carbon process, purifying Pintsch-Brassert generator gas and some half-purified Winkler gas.

Alkacid Process

Winkler gas contained 15 to 20 g/M^3 S (or 1 to 1.5% H_2S); it was purified by alkacid in two stages: after the coarse purification it contained 2 g/M^3S and after the fine purification it contained 150 mg/M^3 S.

~~The liquor normally used was a solution of sodium glycocoll,~~ $NH_2.CH_2.COONa$, of S. G. 1.17, containing 200 g/l, calculated as Na_2CO_3 or 45 g/l calculated as nitrogen (these two figures indicate the presence of some Na_2CO_3 as such). It was a selective solvent for H_2S, so that for example with a gas containing 20% CO_2 and 2% H_2S it would remove nearly all the H_2S but only about 2% CO_2. The absorbers of the coarse purification each had a diameter of 3 m for a gas rate of 20,000 M^3/hour, and contained 7 to 9 bubble-cap trays. The gas/circulating liquor ratio was 500 in hot weather, rising to 1,500 in cold weather. In the regenerators direct steam and indirect steam were both used, the steam consumption being 80 kgs/M^3 liquor in the coarse purification and 150 kg/M^3 liquor in the fine purification. The mixture of H_2S, CO_2 and steam leaving the regenerator was condensed at 50° to 60° C, to reduce the H_2S content of the condensate, and the H_2S was finally burnt in a Claus kiln; the recovered sulphur was eventually used to make H_2SO_4.

Iron was used for the cold parts of the Alkacid plant, brick-lined iron for the regenerator, aluminium for the indirect heater and hot pipes, and an aluminium-silicon alloy, called Silumin or Alpax, for the pumps. No appreciable corrosion was experienced at Leuna.

An alternative solvent was sodium alanine, $CH_3.CH(NH_2).COONa$, but this also dissolved CO_2; it was used at Leuna only for purification of tail gases from hydrogenation. This liquor could be used for CO_2 removal, when its capacity (in the same concentration as used for glycocoll) was 25 M^3 liquor, the steam consumption being 120 kg/M^3 liquor; over 95% removal of CO_2 was possible.

Active Carbon Process

The whole of the Pintsch-Brassert water gas, containing 3 to 4 g/M^3 S, together with a varying fraction of Winkler gas, was purified down to 1 to 2 mg/H_2S/M^3 in the active carbon process, which had been in use for 20 years. Raw Winkler gas could not be used in this process because it's high sulphur content caused excessive temperature rise.

The carbon was prepared from brown coal carbonised at 900° C and then steamed. Air or oxygen was added to the inlet gas, so that in effect H_2S was oxidized to sulphur, which was left on the charcoal; NH_3 was also added to the gas to act as catalyst. After passing gas for about 10 days the sulphur was extracted with ammonium sulphide solution at 40° in the absence of air. The polysulphide solution was then distilled at 2 ats, with a top temperature of 111° C; the vapours were condensed and used again, whilst molten sulphur and water separated into two layers at the bottom of the still and were run off separately. It was stated that the still effluent was not obnoxious.

This process apparently was widely used in Upper Silesian plants: it was, however, unsuccessful on coal gas at Huls, because of gum-forming compounds.

Organic Sulphur

Gas after H_2S removal contained 250 mg. organic sulphur/M^3. This was converted to H_2S in the CO conversion plant, and this H_2S was almost completely removed during the removal of CO_2 and CO.

CO Conversion

The plant in which the water gas shift reaction was carried out was seen but not inspected in detail.

$$CO + H_2O \longrightarrow CO_2 + H_2$$

It was an old plant, working at atmospheric pressure. The development work on this process has been done at Oppau and an account is given in the report on that target. Converted gas for NH_3 and H_2 contained 3 to 4% CO, whilst converted gas for methanol contained 30% CO. The catalyst was Fe_2O_3 with 6 to 7% Cr_2O_3.

II. AMMONIA SYNTHESIS

This section was not discussed in much detail, as the plant was old and largely out-of-date. A much better knowledge of I. G.'s latest ideas could be obtained from a visit to the NH_3 synthesis plant of the Ostmarkische Stickstoff Werke at Linz, Austria, or at least from a study of the designs and drawings, which were carried out by Oppau; the plant at Linz commenced operation in 1940.

General

The gases received were catalysed gas i.e. water gas, which had been subjected to CO conversion with steam over brown oxide; part of the gas, ex Winkler and water gas generators, had low N_2 and CO, and eventually went as H_2 mostly to hydrogenation; another part had low N_2 but higher CO and eventually went to synthesis of methanol and iso-butanol; a third part, ex water gas generators, had high N_2 and low CO, and eventually went to NH_3 synthesis. It was possible to compress and purify these three gases in three parallel streams, but it was also possible under certain conditions ~~to unite the gases for NH_3 and H_2 into one stream of low N_2, the necessary~~ N_2 being added to NH_3 synthesis gas after compression and purification had been completed; such N_2 came from the Linde-Frankl oxygen plant.

Staff Interviewed

Dr. Paul Koppe, chemist in charge of H.P. Division, and Dipl. Ing Martin Rabes, NH_3 synthesis and O_2 plant engineer, were interviewed on May 12th and Dr. Koppe alone on May 16th.

Compression

The compressors were contained in at least five buildings. They were 5-stage horizontal machines, some of old design; they were driven by steam gas engines and electricity and had capacities respectively of 3,300, 10,000 and 15,000 M^3/hour catalysed gas and the total installed capacity was 660,000 M^3/hour, although the maximum rate used was about 550,000 M^3/hour. A complete list of machines was obtained by U. S. S. B. S. The first three stages of compression brought the gas up to 25 ats. at which pressure CO_2 was removed by water washing. The last two stages brought the gas to the final pressure of 250 ats: the original plant design pressure of 200 ats. had been raised as the result of revision of ratio of test pressure/working pressure. Additional compressors were used to compress part of the gas to 25 ats. to cover the gas removed in CO_2 removal.

It was stated that no oil emulsion trouble was experienced in the CO Removal Plant at Leuna and, therefore, a particular point was made to interrogate the compression plant engineers - Ober Ing Gleitz and Ober Ing. Weissenfels on the subject of lubrication.

Superheated steam oil of 320° C Flash point, 50-55° Engler viscosity at 50° C and 0.01-0.02% asphalt content is fed to the steam cylinders of the main steam engines. These machines take steam at 15 ats. and 320° C and discharge either to the LP steam system or to condensers. Oil is extracted from the steam before it reaches the condensers and is heated to 90°C and cleaned and dewatered in a centrifuge. The cleaned oil is mixed with a machine oil of 3° Engler viscosity at 50°C and is used as make-up oil to the compressors. It has a flash point of 230°C, a 50°C Engler viscosity of 22-30° and a 100°C Engler viscosity of 3-4°. This latter property is considered to be particularly important.

A compressor of 16,000 M^3/hour capacity uses about 2.2 kgs/hour of lube oil.

There is a catchpot of 500 mm diameter and 4 M long immediately after each compressor and this is blown every two hours. At the inlet to the CO Removal Plant there is a further catchpot 600 mm diameter and 10 M long for each 100,000 M^3/hour of gas for collection of oil and condensate.

In order to avoid condensation gases are never allowed to cool below 30°C. In the third stage of compression, gas temperature may be as high as 48-50°C. Piston rings are made of material in the pearlitic state ~~with long graphitic inclusions to hold the oil to the surface of the ring.~~

The Leuna engineers gave the following general data on lube oil consumption in compressors:

TABLE 1A.

Pressure	Lube Oil Consumption grms/1000 M^2 swept surface of	
	(a)	(b)
ats.	cylinder	piston rod
2.5	1.9	7.0
11.0	3.25	10.0
28	7	17.5
70	20	25.0
170	20	-
250	20	-

CO_2 Removal

The largest absorption towers were 2.4 m. I. D., but there were 60 to 70 old ones of 1.4 m. I. D. They were packed with ceramic rings; Leuna had never tried bubble plates. A rose-type distributor was used and with a constant water-rate there was no trouble with mal-distributions; they had tried re-distributing water half-way down the tower, but this had brought no advantage. There was no chlorination of circulating water and no trouble with algae. The exit gas contained 1.5% CO_2.

Water from the towers was let-down in one stage through Pelton wheels. The let-down gas contained 93% CO_2. Part of this was used as an inert gas and part in the ammonium sulphate plant, the rest being blown to atmosphere. No urea was made at Leuna and only a little dry ice, and this only for internal use: no dry ice could be sold, because of the difficulty in eliminating the smell, said to arise from organic sulphur compounds originating in the Winkler generators.

The let-down water was used for gas-cooling at the CO conversion plant before being sent for regeneration. This was done to eliminate O_2 from catalysed gas, which in the presence of H_2S and H_2O was said to cause corrosion in the gas compressors. This system had been used for 15 years, with no corrosion.

CO Removal

This plant used copper liquor at 250 ats. The liquor contained only carbonate, with no formate (last used 1925). It was regenerated at a maximum temperature of 40°C, using a vacuum in two stages, ending at 160-to 200 mms. Hg. absolute pressure.

They had not used refrigeration of the liquor, as cooling below 5°C caused deposition of ammonium carbonate. No vapour pressure curves were available.

There was no difficulty in controlling the cuprous/ cupric ratio. An automatic measurement of cupric, depending on the colour, was used.

There was said to be no difficulty with sludge deposition of any sort. Dr. Koppe ascribed this to the low temperature of regeneration. The oil separators on the 5th stage delivery of the compressors were very simple but were said to be very effective; they consisted merely of a pipe dipping into a forging, with the gas outlet at the top.

Let-down engines for power recovery from copper liquor were used, but only old-type machines were seen.

Final NH_3 Make-Up Gas Purification

Gas leaving the CO removal plant was washed with NH_3 liquor, to reduce the CO_2 content from 0.04% to <1 mg/M^3. Active charcoal (to remove organic sulphur poisons) had never been used.

NH_3 Synthesis

The capacity was originally 1200 T/D NH_3, but according to I. G. staff, even after extensive repairs lasting 10 months, only 1000 T/D NH_3 could be made in the future.

The gas circulating system was conventional. Exit gas from the converter was cooled first in a water cooler and then in a cold exchanger before entering a condenser refrigerated by evaporation of liquid ammonia. Liquid NH_3 was condensed out of the gas and unconverted gases returned to the converter via the cold exchanger and a circulator. Liquid NH_3 was let down from a catchpot after the refrigerated condenser. If ammonia gas could be used as such, part of the make of liquid ammonia was used for refrigeration purposes; otherwise the NH_3 gas from the refrigerator was re-liquefied and returned to the refrigerator system. Under the former method of working, the yields of gaseous and liquid NH_3 were approximately equal, averaged over the year. Make-up gas entered the circulating system at a point between the converters and water-coolers; this gave a minimum water content in the gas returned to the convertor.

The plant was arranged as a number of separate gas circulating systems. The first system consisted of a number of units in parallel, each taking make-up gas containing 1% Argon + CH_4; the circulating gas in this system contained 4 to 6% Argon + CH_4 and the NH_3 content of the gas rose from 3-4% to 8-10% during passage through the converters. Purge gas from this system was used as make-up to another system working with circulating gas containing more impurities. In turn, purge gas from this system was used as make-up for the next, and this procedure was repeated until, in the final system, the inert content of the circulating gas was some 20-30%.

Circulator

A point of interest was use of a centrifugal circulator at Leuna, drawings of which were obtained. It was stated that at the Ammonia plant at Linz this type of circulator had been adopted throughout. It was reported that this circulator ran perfectly satisfactorily with a routine dismantling every 3 months for examination of bearings.

~~The machine is an ordinary electric driven centrifugal pump totally~~ enclosed in a high pressure vessel in a way similar to that used in the oil industry for dealing with hot-oil pumps. The difference is that the electric motor is also enclosed. This means that there is no gland problem but there is instead a bearing lubrication problem, which is said to be much easier to overcome. For a capacity of 80,000 M^3/hr. the forging containing the circulator is about 14 feet long and about 2 feet internal diameter. The machine was built so that, if the pump did not have the required performance, the number of stages could be increased. The use of such a pump for the circulation of gas on hydrogenation plants was not considered practicable because of the great difficulties of ensuring the proper lubrication of the bearings in the presence of hydrocarbon vapours.

Catalyst

This was the usual iron-type catalyst, promoted with alumina and potassia and sometimes a little lime. Preparation was as follows: 19 kgs of small pieces of Swedish iron (or sometimes charcoal iron during the war) were placed in a shallow water-cooled iron pan, 50 cm diameter and 15 cm deep. Pure oxygen was then played on it after ignition by a "Zündkirsche": after 10 minutes 1 kg of the promoter was added to the now molten mass and the oxidation completed in another 20 minutes. The mass was poured on to an iron pan and allowed to cool, when it was broken up and screened. Material between 5 and 12 mms was used in the converters, whilst the fines were remelted.

The promoter was made by dissolving 16 kgs pure Al_2O_3 and 4 kgs KNO_3 in 2 litres 60° Baume HNO_3 and 2 to 4 litres water: this was boiled and cooled to a solidified cake. Sometimes a little lime was also added.

The final catalyst had the composition; 97% Fe_3O_4, 2.5% Al_2O_3, 0.16% S and 0.03% C, with a bulk density of 2.0. No sample was obtained.

It was said that this was the same recipe as for the so-called Mittasche catalyst, except that the latter contained more lime; the Mittasche catalyst was better for water-containing gases, but the I. G. catalyst was to be preferred for the dry gases used at Leuna. The same catalyst was used at Leuna for the SYNOL process.

Catalyst removed from the converters was re-fused in an electric furnace and was said to be as good as the new catalyst.

About 30 T/D N (≡ 36 T/D NH_3) was made per converter, containing 6 T catalyst. The normal life was about one year if purge gas from methanol and iso-butanol entered the system, even with a guard converter; thus about 2000 T NH_3 were obtained per T catalyst. With no methanol purge gas longer life was obtained.

The poisons in methanol purge gas were said to be oxygen-containing ~~substances, such as CH_3OH and R_2O. The sulphur content of make-up gas was~~ said to be $<$0.1 mg S/M^3.

Converters

Converter design had by no means reached finality, and both Leuna and Oppau had tried out a number of designs.

The normal design used at Leuna was as follows. An internal interchanger was fitted under the catalyst, contained in tubes, touching one another for good heat transfer, and narrowed down at the bottom, for fitting into a tube plate. The incoming gas passed up over the outside of the interchanger tubes and over the outside of the catalyst tubes, cooling the catalyst and so maintaining a more favourable temperature gradient; the gas then passed down through the catalyst and then through the interchanger tubes.

In another type which had been tried the catalyst was cooled, not by being placed in tubes, but by placing tubes in the catalyst bed. The cooling gas passed through these tubes, which were either in the form of hairpins passing up and down the catalyst, or in the form of tubes carrying a central leg, up which passed the gas after carrying out the cooling in passing down the annulus.

More fundamental changes in design had been carried out at Oppau: they had built one or two "stalls", both with internal and with external interchangers, but Dr. Koppe said they had encountered constructional difficulties; such converters had inter-tray cooling with cold gas, as in a hydrogenation stall.

Leuna had not carried out any fundamental research on catalysts or on the kinetics of reaction: this had all been done at Oppau.

III. METHANOL AND HIGHER ALCOHOL SYNTHESIS

Dr. Halmut Hanisch and Dr. Erich Sackmann, respectively head and engineer of the Organic Division, were interrogated on May 12th.

Methanol

The converter was of the cold-shot type, with external interchanger. Each forging had an I. D. of 800 mm. and was 12 m high; the internals were made either of pure copper or of copper-covered steel. The catalyst basket had an I. D. of 650 mm. and contained 5 or 6 equal beds, holding a total of 3 M^3 catalyst. The circulating gas rate was about 100,000 M^3/hr. giving an output of 120 T/D crude methanol, containing 4 to 5% H_2O, dependent on the CO_2 content of the gas. The compositions of make-up and circulating gas were:

	Make-up gas	Circulating gas
CO_2	1 to 1.5%	
CO	30%	18%
H_2	65 to 68%	
N_2	1 to 2%)	10 to 15%
CH_4	0.5 to 1%)	

The maximum catalyst temperature was given as 390°C, reached towards the end of the converter.

A sample of the catalyst was obtained; it was in the form of 9 mms pellets and was based on zinc and chromium. No CH_4 formation occurred to any measurable extent.

Plant output was of the order of 12,000 T/month crude. Reciprocating circulators were used, not centrifugal ones as used for ammonia.

Water-free methanol was used instead of ethanol in motor fuels. Purified methanol was used for formaldehyde manufacture and for solvents.

Higher Alcohols

The name given to higher alcohols was "iso-butanol", although this was the main and not the only substance synthesized.

The plant used was very similar to that used for methanol synthesis, although the interchanger was a little smaller, having an I. D. of only 500 mm.

The circulating gas rate was only 35,000 M^3/hr., giving an output of 40 T/D crude higher alcohols, containing about 12% iso-butanol.

The composition of the gases was:

	Make-up gas	Circulating gas
CO_2	1 to 15%	3 to 5%
CO	30%	25 to 26%
H_2	65 to 68%	
N_2	1 to 2%)	10 to 15%
CH_4	0.5 to 1%)	

Thus higher alcohol circulating gas contained more CO and CO_2 than did methanol circulating gas; CO_2 presumably was produced by reaction between CO and water made in the reaction.

The maximum catalyst temperature was given as 450°C. About 2% methanation occurred. The catalyst was the same as methanol catalyst, but with 2% K_2O added; a sample was obtained.

~~Plant output was of the order of 12,000 T/month crude, i.e. about~~ 1,400 T/month iso-butanol.

Methanol made up half the crude and after separation it was injected into the inlet of the interchanger and re-passed through the converter, where it was converted into higher alcohols. By using stocks of crude higher alcohols the synthesis plant could be run for some time without make-up gas, using only this crude methanol as feed. Such methanol was difficult to purify on account of the hydrocarbons, mostly olefins, it contained.

The composition of crude was given as:

50 to 55% methanol
22 to 25% water
1 to 3% dimethyl ether
1 to 2% n-propanol
11 to 12% iso-butanol
2% C_5
2.5% C_6 and C_7)
1 to 2% C_8 and C_9) alcohols, ketones, hydrocarbons, etc.
1% C_{10} up to C_{14})
1 to 2% hydrocarbons (yellow oil containing 70% olefins)

The fraction 110° to 160°C amounted to 3 to 4% and the fraction 160° to 250°C also amounted to 3 to 4%.

The working up of the crude can be followed by reference to Figure I. First dimethyl ether was removed in a ring-packed tower working at 10 ats. Then methanol was removed in a bubble-plate column working at 10 ats.; "yellow oil", i.e. the hydrocarbons, was taken overhead and methanol was taken as a side-stream near the top; to obtain an isobutyrone fraction $[(CH_3)_2\,CH.\,CO.\,CH\,(CH_3)_2]$, amounting to 0.5% on crude, a side-still was used as shown. The bottoms from this column separated in two layers; the

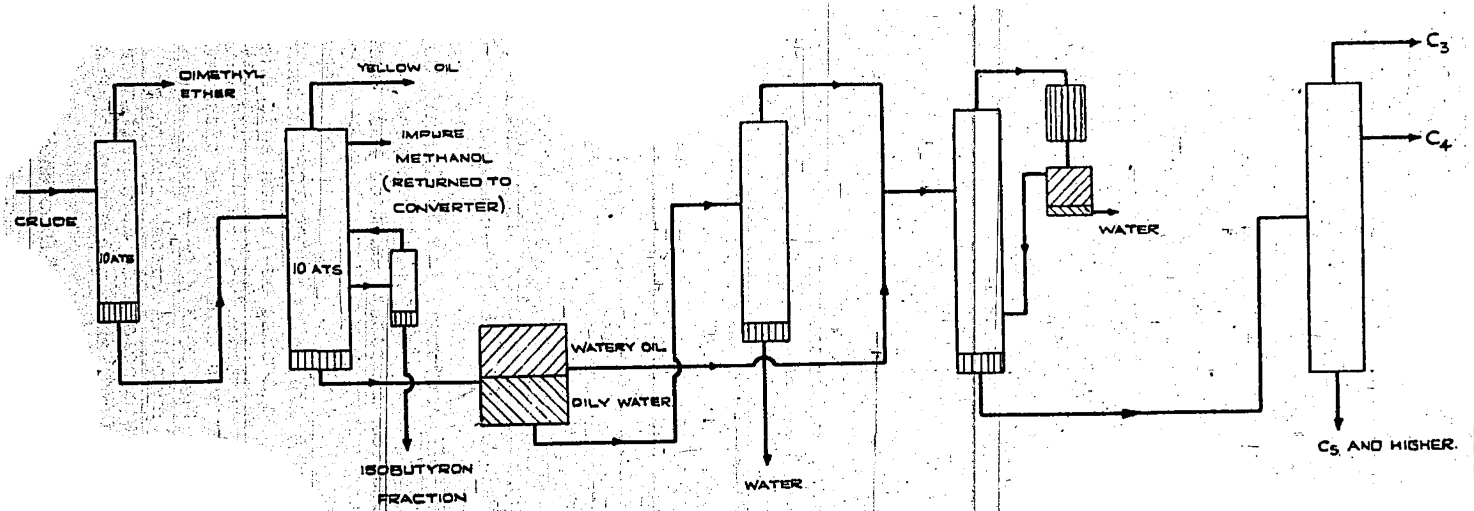
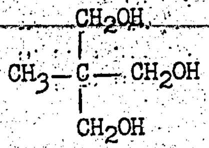


FIG I SEPARATION OF CRUDE HIGHER ALCOHOLS bottom layer, rich in water, was distilled at 1 at. in a ring-packed column to remove water, the overheads being mixed with the top layer, poor in water. Gasoline was added, to form an azeotrope, and the mixture fed to a bubble-plate column operating at 1 at. The overheads from this still on cooling formed two layers; the aqueous one was discarded and the other one was returned to the still. The bottoms from the still were fed to a final bubble-plate column operating at 1 at., with iso-butanol taken off as the main product, propanol taken off overhead, leaving C_5 and greater in the bottoms.

Dimethylether was redistilled in a pressure column and the 98% pure material used for making dimethylsulphate and dimethylaniline.

The propanol fraction was further purified and the purest material was used for cosmetics and in solvents. Other material was converted to propionic acid, but the greater part (100 to 120 T/month) was reacted with formaldehyde to yield trimethylolethane.



$$\begin{array}{ccc} & CH_2OH & \\ & | & \\ CH_3- & C & -CH_2OH \\ & | & \\ & CH_2OH & \end{array}$$

which when reacted with higher acids (see below) gave a substitute for castor oil. A small amount was also used in the manufacture of glycerine, but this process was carried out to a greater extent at Heydebreck (Upper Silesia) and Oppau, the former using 300 to 350 T/month propanol.

Until July 1944 isobutanol was mostly converted to isobutylene and thence to iso-octane, but then the demand for Oppanol (polyisobutylene) became so great that the butanol was practically all shipped to Oppau and Frose for this purpose. About 80 to 100 T/month were used as acetates as solvents ("Polysolvan")for lacquers; some iso-butylene was used for making butyl phenol at Ludwigshafen, used for laquer resins. About 80 to 100 T/month were used for making Koresin at Ludwigshafen, a formaldehyde resin. About 100 T/year were converted to isobutylamine.

50 to 60 T/month of the fractions 110°-130° and 130°-160° were used as acetates as solvents (e.g. "Intrasolvane"). 400 T/month of the fraction 110°-160° were used to make Palatinol HS, esters of phthalic acid, used as plasticisers.

The fraction 160°-200° was oxidized to acids and combined with trimethylolethane (see above) to give a substitute for castor oil. The fraction 200°-250° was used in the manufacture of esters, lubricants and drying aids: the available notes on this are not entirely clear but it appears that the fraction was treated with NaOH and in some way made to yield acids (possibly a naphthenic acid, although this is an obscure reaction), which were then esterified with high alcohols and used as plasticisers or used as Co, Mn or Pb salts as drying aids for lacquers.

Higher fractions could not be used.

IV. HYDROGENATION

A. General

Leuna was the world's first commercial scale hydrogenation plant and also the first to operate on coal (brown coal). In its present form, the Leuna hydrogenation plant consists of 10 liquid phase coal or heavy oil stalls, 5 vapour phase presaturation units and 3 stalls for splitting hydrogenation of middle oils to gasoline. In 1943 and the first half of 1944, the average rates of consumption of the various feedstocks were:

Dry Brown coal	1,100,000 Tons/year
Brown coal Tar	120,000 "
Bituminous coal tar oil	40-50,000 "

Production of final liquid products was slightly more than 600,000 T/yr. and, according to Dr. Buterfisch, these products were made up of 40% aviation base gasoline, 20% motor gasoline, and 40% Diesel oil. In addition, some 150,000 Tons/year of by-product hydrocarbon gases were obtained and these were used for synthesis of isooctane or alkylate (butane), for liquefied gas fuels (propane or propane + butane) and for manufacture of synthetic lube oils (ethane).

In July 1944, Leuna suffered a surprise air attack and, because of the absence of facilities for safe emergency draining of the coal hydrogenation converters, the plant was coked up. The coal-paste preparation plant was also badly damaged. At the same time, damage to the nearby Brabag hydrogenation plants prevented them from hydrogenating all the available brown coal tar. It was therefore decided to change over Leuna from brown coal to brown coal tar and 5 or 6 coal stalls were modified for hydrogenation of liquid phase heavy oil. During the second half of 1944 it was possible to operate the normal liquid phase and vapour phase process for conversion of brown coal tar to gasoline but production was interrupted more and more by continued air raids and, following particularly heavy attacks in January 1945 in which the tar fugals were put out of action, operations had to be limited to a single stall working a modified T.T.H. process (see Ludwigshafen and Zeitz reports). Crude tar input was only 250-300 Tons/day.

The information given in the following sections was obtained from Dr. ~~Schunck, Director and Manager of the hydrogenation section of Leuna, Dr.~~ Becker, his principal assistant and stalls manager, Ing. Cron, hydrogenation section engineer, and Dr. Pichler, a costs expert attached to the hydrogenation section.

B. Brown Coal Hydrogenation

(i) Outline of present process

The brown coal hydrogenated at Leuna is obtained from local open workings owned and operated by the I. G. As delivered to the plant, it contains 54% water and 5.5% ash. The ash and moisture free coal substance

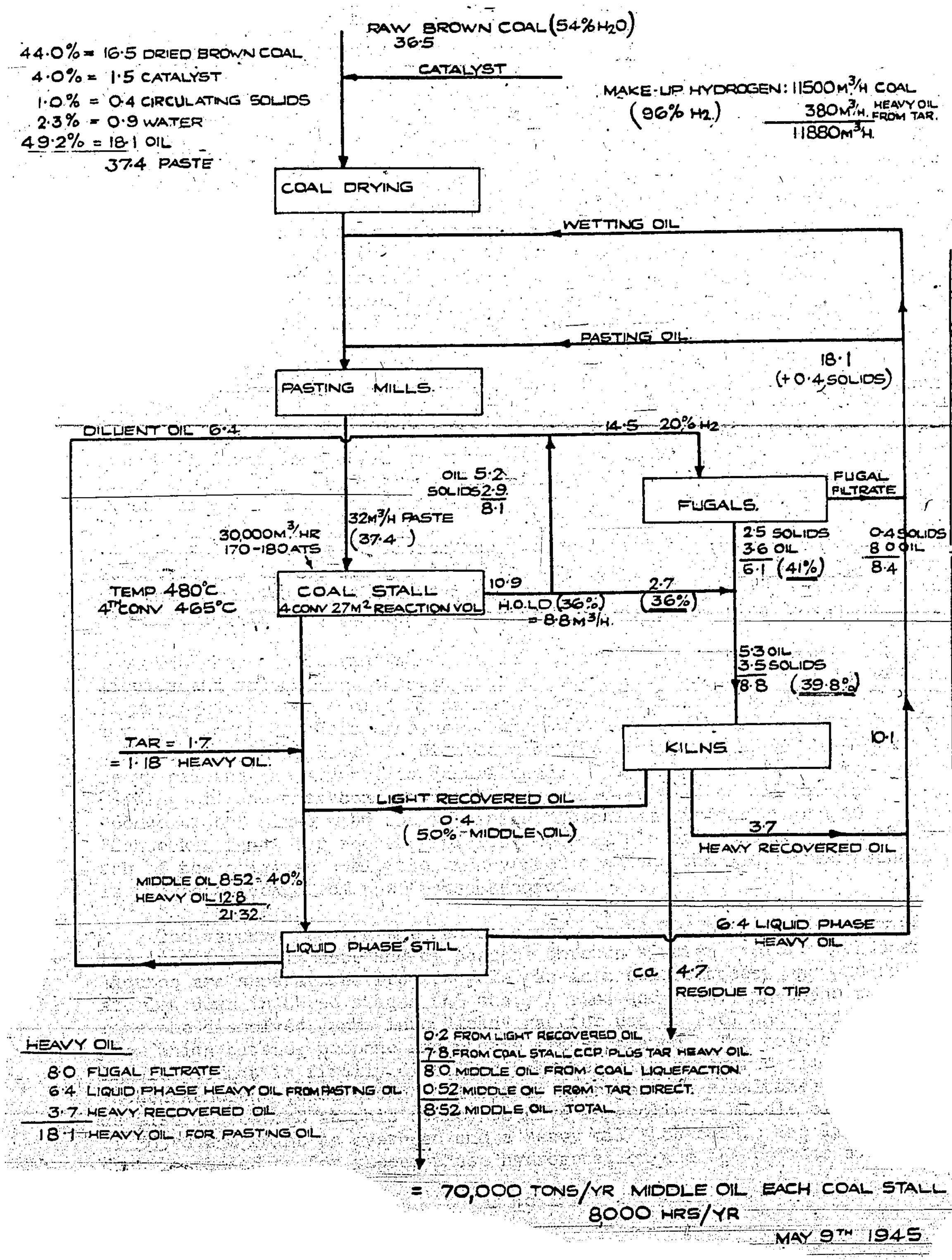


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FIG. 11

HYDROGENATION OF BROWN COAL 1944

ALL QUANTITIES IN TONNES/HR EXCEPT WHERE STATED has the analysis - 71% carbon, 5% hydrogen, 5-6% sulphur, 17-18% oxygen and 1% nitrogen. A high proportion of the ash constituents of the coal is sand with very errosive properties.

The hydrogenation process as applied to brown coal is summarised in the flowsheet shown in Fig. II. The wet coal together with about 4% of its weight of catalyst (Bayermasse obtained as a byproduct in the manufacture of aluminium) is dried down to 5% water. The product is immediately wetted with part of the recycle pasting oil in order to avoid dust difficulties and explosion risks and is fed to the grinding and pasting mills where it is mixed with the rest of the recycle pasting oil. The resulting "paste" containing some 44% dry coal (49% total solids) is injected into the hydrogenation stall which operates at a pressure of 230 atmospheres. It is heated together with circulating gas (900 - 1,000 M^3 circulating gas/M^3 paste) firstly by interchange with outgoing vapour products and finally in a gas-fired tube preheater. The reactants then enter the first of (usually) 4 converters at a temperature of about 430°C. This temperature is quickly raised by the heat of reaction to 490°C and is then controlled at this figure, by introduction of cold circulating gas at suitable points, until the reactants leave the third reactor. Under the latest operating conditions, this average reaction temperature in the last reactor is dropped to 475°C by introduction of more cold circulating gas. The total circulating gas used for temperature control is about 1000 M^3/M^3 paste fed.

A small amount (100 litres/hour) of reactant is continuously drawn off at the bottom of the first reactor in order to prevent the build up of sand and the formation of "Caviar" i.e. small spheres consisting of coke formed round a central sand particle. This draw off is automatically controlled.

The products leaving the last converter pass to a hot catchpot where liquids and vapours are separated at a temperature of about 440°C. The liquid products are cooled by passage through finned air coolers and are let down to atmospheric pressure. Approximately two thirds of this heavy oil let down (Abschlamm) is diluted with 75% of its weight of distillate heavy oil and the mixture is centrifuged. The "filtrate" is recycled as pasting oil and the "concentrate" is recycled as pasting oil and the "concentrate" mixed with the remaining "Abschlamm" is carbonised in "Schneckenofen" for recovery of its vapourisible oil content. All the ash of the original coal, the unconverted coal and the new formed asphalt is purged as coke from the "Schneckenofen.

The vapours leaving the hot catchpot are cooled by interchange with the incoming coal paste and by passage through a water cooler. Condensed liquids are separarated from recycle gas in a cold catchpot and the former are let down in three stages (45 ats., 4 ats. and 1 at.) in order to separate the dissolved gases into "lean" gas for use as fuel and "rich gas" from which butane, propane and ethane are separated. The cold catchpot liquid product is finally distilled together with recovered oils from the "Schenckenofen" (when brown coal tar is hydrogenated simultaneously, this is also introduced at this stage) to give a gasoline + middle oil fraction of 335°C end point as overhead and a heavy oil "bottoms". The light product is passed on for vapour phase hydrogenation and the bottoms are recycled either directly to coal pasting or indirectly as "Abschlamm" diluent oil via the fugals. Gas from the cold catchpot is boosted back to the inlet of the plant via a gas washing plant in which hydrocarbons and nitrogen are dissolved in oil (heavy middle oil ex cold catchpot liquid product) in order to maintain the required hydrogen partial pressure (170-180 ats.).

Under these latest operating conditions this paste throughput is slightly under 1.2 M^3/M^3 of reaction space/hour corresponding to 0.46 Tons ash and moisture free coal/M^3 reaction volume/hour. Throughput and reaction temperature are adjusted so that there is no net make of heavy oil. The yield of 0-335°C light product is 49-50% by weight on the ash and moisture free coal fed. Unconverted coal purged in the Schneckenofen coke amounts to 1.5% on the original ash and moisture free coal. (This is not apparent from the flowsheet in Fig. II since no distinction is made between organic and inorganic solids and no indication is given of the change in weight of the latter due to chemical reduction during the hydrogenation reaction). Gas make in the hydrogenation of brown coal is 25.75% on the amf. coal. This is made up as follows:

Carbon monoxide	1.45%
Carbon dioxide	9.15%
Methane	4.15%
Ethane	3.60%
Propane	4.75%
Butane	2.65%
Total	25.75%

Oil lost in the carbonisation of Abschlamm and Abschlamm concentrate amounts to 8.5% by weight on the ash and moisture free coal.

The following figures show roughly the carbon balance for this process:

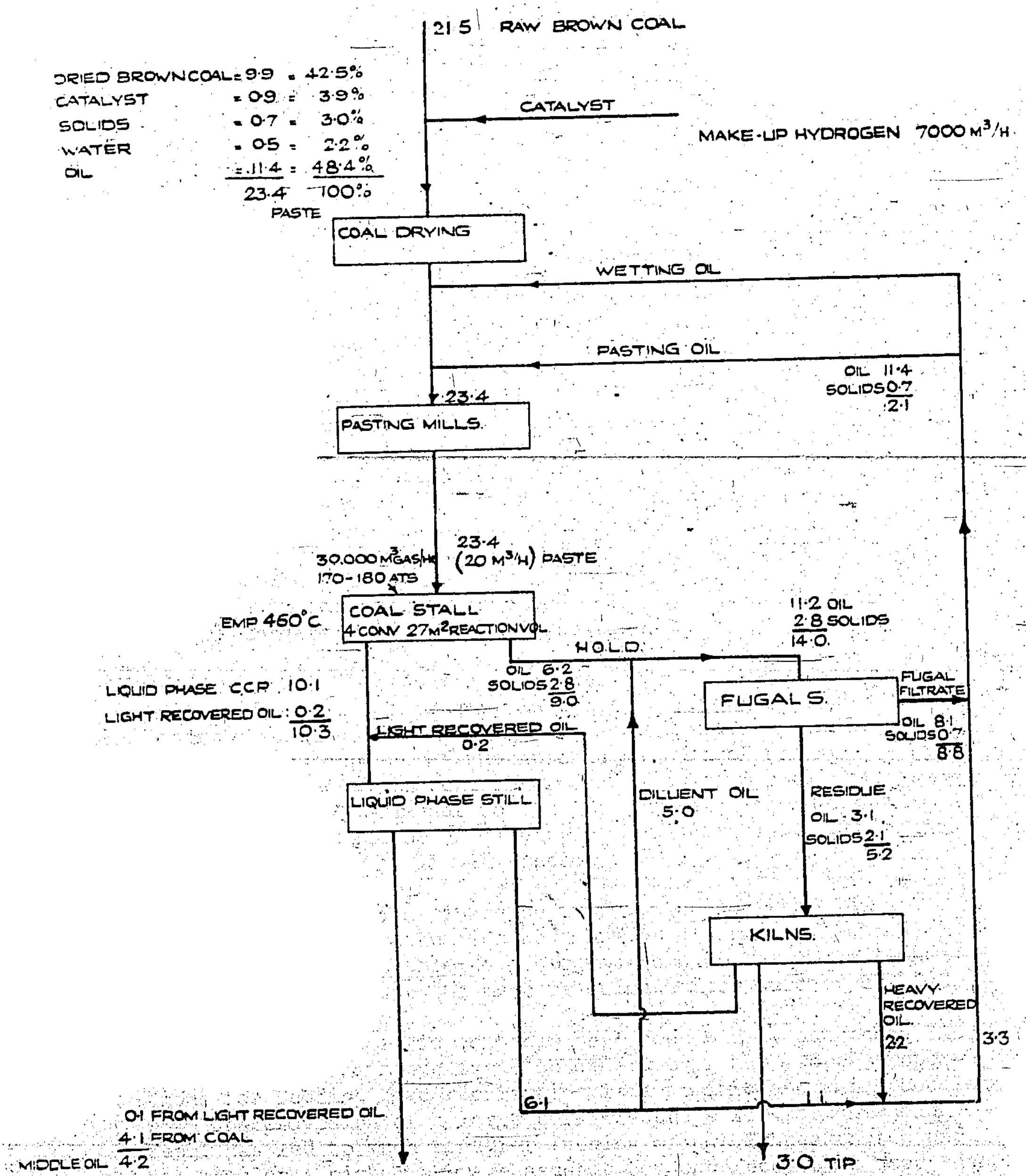
IN	Carbon in brown coal	100
OUT	Carbon in unconverted coal	2.0
	Carbon in coke and gas made by decomposition of asphalts in sludge carbonisation.	11.5
	Carbon in CO and CO_2	4.4
	Carbon in hydrocarbon gases	17.6
	Carbon in sundry losses	1.0
	Carbon in Petrol + Middle oil product	63.5
	Total	100.0

Hydrogen consumption is 800 M^3/Ton of ash and moisture free coal hydrogenated or 6.6-6.7% by wt.

(ii) Consideration of process improvements made since the war.

FIG II. HYDROGENATION OF BROWN COAL 1939-1940

ALL QUANTITIES IN TONNES/HR EXCEPT WHERE STATED.



DRIED BROWN COAL	= 9·9	= 42·5%
CATALYST	= 0·9	= 3·9%
SOLIDS	= 0·7	= 3·0%
WATER	= 0·5	= 2·2%
OIL	= 11·4	= 48·4%
	23·4	100%

= 34000 TNES/YR MIDDLE OIL EACH COAL STALL
(8,000 HRS/YR)

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The process described above, although much the same as regards yields as that operated before the war, shows a marked improvement in output per stall. Fig. III is a typical Leuna flowsheet for brown coal hydrogenation in a single stall in 1939-1940 and it shows that the coal throughput rate then obtainable was only 0.32 Tons amf. coal/M^3 reaction volume/hour or 70% of that achieved in more recent times. The improvement which has been made is actually greater than this, because in addition to a throughput of 0.46 T. of amf. coal, 0.047 T/hr. of tar heavy oil is now hydrogenated in each M^3 of reaction space.

With fixed pressure and catalyst conditions the only method for increasing the rate of hydrogenation of a given raw material to a given extent is to increase reaction temperature. The extent to which this can be done is, however, limited because of the following considerations:

(a) For a given extent of hydrogenation, (i.e. in this case, complete conversion of coal to petrol and middle oil with only sufficient new formed heavy oil to replace sludge carbonisation losses) increase in temperature increases the yield of gas, asphalt and unconverted oil at the expense of petrol and middle oil. The increase in asphalt make is particularly serious because, in order to keep the viscosity of the recycle pasting oils down to a workable figure all new formed asphalt must be destroyed in sludge carbonisation and this results in an appreciable loss of carbon from the hydrogenation system. Further, the carbonisation plant itself gets into operating troubles when the asphalt content of the feed is too high.

(b) Unless special precautions are taken to cool the products before they enter the hot catchpot, increase in reaction temperature leads to a reduction in the amount and, therefore, an increase in the solids content of the Abschlamm. One of the most serious practical difficulties encountered in the brown coal hydrogenation process has been due to coke formation on the hot catchpot walls and this is more difficult to avoid the higher the solids concentration in the liquid product.

The secret of the increase in throughput of the Leuna stalls is that, by attention to a number of process details, the I. G. have been able to get round some of the above limitations and so increase the mean reaction temperature by 20-25°C.

Firstly, automatic controls have been widely adopted. The mixing of Abschlamm and fugal concentrate in the proper proportions for feeding to carbonisation is automatic and this, coupled with the provision of a large buffer storage for carbonisation feed, has led to much steadier running of the Schneckenofen and has enabled a higher <u>average</u> asphalt content feed to be used than was the case when a margin had to be allowed for possible errors in hand mixing. The hot catchpot level is also automatically controlled; this eliminates the danger of the periodic drying out of the walls of this vessel which greatly encourages coke formation and, therefore, allows a higher solids content of Abschlamm to be tolerated.

Secondly, the I. G. staff have found that, when the hydrogenation process is operated in the normal way using a gradual upward temperature gradient in the reactor system, much of the asphalt make is produced in the last converter where temperature is at a maximum and hydrogen partial pressure is at its lowest. Dropping the temperature in the last converter materially reduces the asphalt make and it also helps to reduce the solids content of Abschlamm and, therefore, the hot catchpot coking danger.

At Leuna, this reduction of temperature in the last converter can be practised only in conjunction with high feed rates resulting in a high rate of heat evolution per stall. At lower throughputs, the loss of recoverable heat by cooling the last converter introduces a preheater capacity limitation.

The Leuna staff feel that still greater throughputs would be possible if it were not for two other limiting factors, (1) erosion of preheater tubes and (2) the capacity of the existing Schneckenofen. With the present high rates preheaters have to be shut down for examination every 120-150 days and this shut-down takes 6 days. Incidentally, the general maintenance shut-down of a brown coal stall takes 25 days and occurs, normally, every 15 months. Kugel ovens are considered to be superior to Schneckenofen and several were on order for installation on the Leuna plant.

(iii) Details of Plant Equipment

Paste Mills. These are simply horizontal rotating ball mills fed from each end with the appropriate quantities of dried coal and pasting oil, measurement of both being automatically controlled. The paste leaves the mill via slots cut in the side and passes through a 1 mm. screen for removal of nibs of coal, tramp iron, etc.

Paste Injectors. These are ram pumps, the power for both injection and suction strokes being hydraulically supplied. Injection rate is varied by controlling the rate of entry of water into the hydraulic cyclinder.

The gland packing for these injectors had latterly been lead alloyed with 0.1% Cadmium and this had been satisfactory. Before the war, tin packings were used.

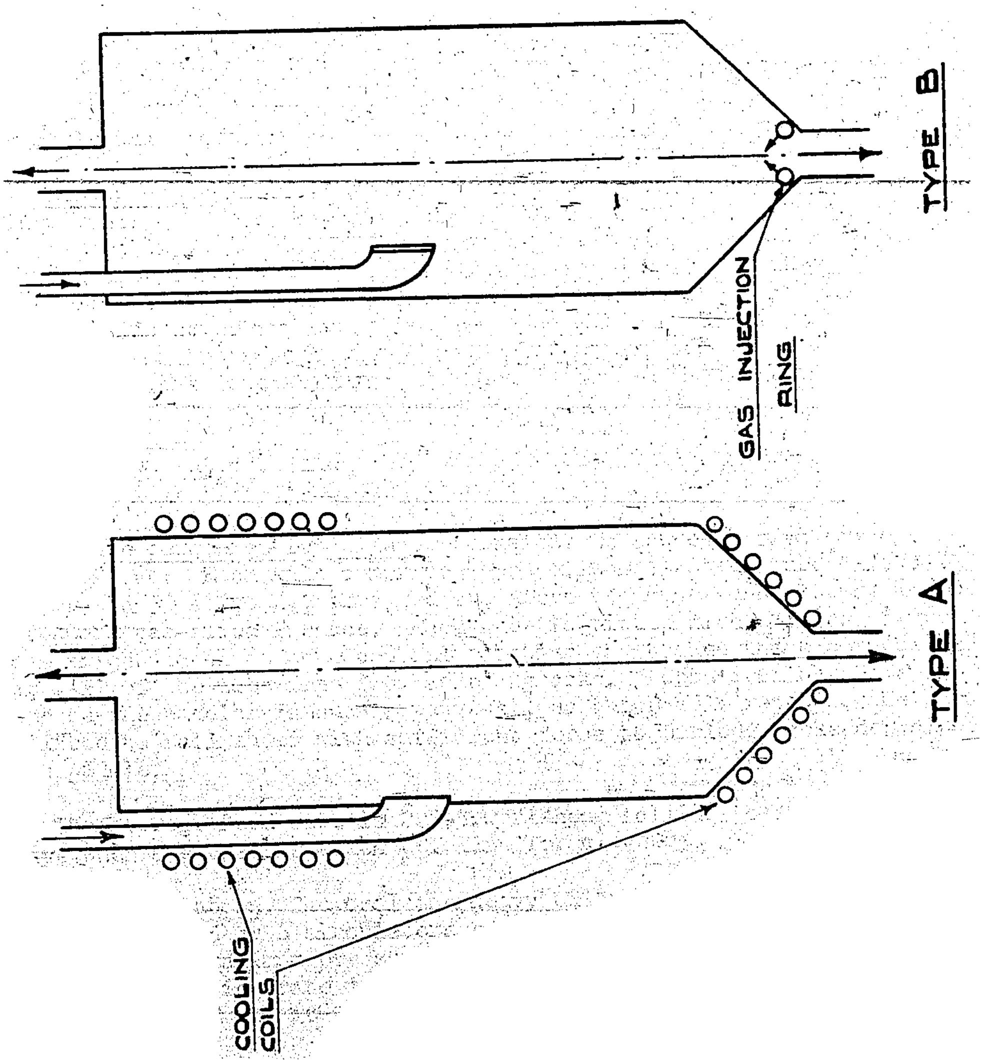
The I. G. had ceased to use nitrided rams because of the wide variation in quality which had been experienced. Ordinary case hardened rams of 400 B.H. were being used.

Paste Interchangers consist of a bundle of 199 tubes in a forging 600 mm. diameter and 18 M long. Formerly 241 tubes were used but trouble was experienced with chokes. The tubes are zinc treated.

With a paste feed rate of 30 M^3/hour and a gas rate of 20,000 M^3/hour the K value is 250-200. Units for K value: Kg. cals/M^2/°C/hr. Interchangers are stripped every two years.

FIG. IV

HOT CATCHPOTS



Paste Preheaters. These are gas-fired convection type heaters of the standard I. G. rectangular design. The tube hairpins are 15.5 M long, 120 mm. bore and 171 mm. external diameter. They are fitted with fins 4 mm. thick and 10 mm. apart and which give the tubes an internal/external arearatio of 1 : 20. 6-7 hairpins are used in a normal preheater the average overall K value of which is 180-150. With high feed rates erosion of the hairpin bends is appreciable and the average life of a bend had fallen to 18 months. It was proposed to change to tubes of 160 mm. bore and 229 mm. external diameter with fins 4 mm. thick and 320 mm. square spaced 16 mm. apart. The hairpins were to have been made with a pitching of 500 mm. instead of the standard 400 mm.

Brown coal stall Converters. Leuna used converter forgings of a variety of sizes varying from 800 - 1200 mm. diam. and from 11-18 M. in length. A stall had four converters and the size was usually such that the total stall reaction volume was roughly 27 M^3.

Hot Catchpot. Several designs have been tried in an attempt to reduce coking. The type most commonly adopted is shown in Fig. IV A. It is fitted with gas cooling coils between the forging and inner catchpot wall and the inlet pipe for reactants is outside the inner vessel. The idea of the cooling tubes at the top of the catchpot is to ensure sufficient condensation that the walls never dry out. Another type (Fig. IV B) has no cooling coils but cold gas is introduced at the bottom of the vessel via a ring distributor. It is claimed that the stirring provided by this method helps to reduce coke formation.

Let down valves. These are fitted with "Widia" inserts but even so they have a life of only 200-400 hours.

Sludge carbonisation kilns. Leuna has 26 Schneckenofen arranged in sets of two. Each kiln comprises two horizontal steel tubes 2 ft. in diameter and 30 ft. long, arranged one above the other and sitting 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 wall of the tube free from adhering coke. Loose iron bars are attached to the paddles in such a way that, as the paddle rotates, the bars are lifted to fall later with sufficient force to dislodge coke deposited on the paddle.

The average feed rate is 2.5-3.0 M^3/hour falling to 1.8 M^3/hour after 50 days when the unit is taken off line for cleaning.

Gas Circulators. The coal and heavy oil hydrogenation system at Leuna normally employs 5 or 6 circulators each of 80-85,000 M^3/hour capacity. The machines throw a maximum pressure of 30 ats. They are operated at constant speed and circulation rate is varied by controlled bypass. Stall pressure is hand controlled and it was stated that swings of up to 20 ats. are observed.

Gas washing. Purification of the circulating gas is carried out in 9 towers each 1300 mm. diameter. Wash oil (a heavy cut of liquid phase hydrogenation middle oil) is injected partly with three throw pumps and partly by means of three machines driven by let down engines operating on the saturated wash oil. The wash oil feed rate was controlled automatically in order to maintain a constant hydrogen content of circulating gas.

Automatic Controls. Full details of the various automatic controls were obtained but these are amongst the documents (2nd Leuna visit) which have not yet reached London.

C. Brown Coal Tar Hydrogenation

The Leuna flowsheet for hydrogenation of Central German brown coal tar is shown in Fig. V. The crude tar which contains 1% water, 0.5% solids and 1-3% asphalts, is fugalled to remove slightly over 2% of it's weight of sludge which is sent to carbonisation for oil recovery. The cleaned tar is mixed with "Leuchtöl", i.e. recovered oil from brown coal carbonisation gases ~~(the crude tar + Leuchtöl mix usually contains 45% by weight of heavy~~ oil boiling above 325°C, ~~35-40% distilling between 180 and 325°C and 15-20%~~ boiling below 180°C) and with the crude product from the liquid phase hydrogenation of heavy oils. This mixture is distilled to give a 0-325°C fraction as overhead and a heavy oil bottoms which is the feed to the hydrogenation stalls.

The plant employed is substantially the same as in the case of coal hydrogenation with the exception that a special pump is installed for hot recycle of liquid from the hot catchpot to the inlet of the preheater.

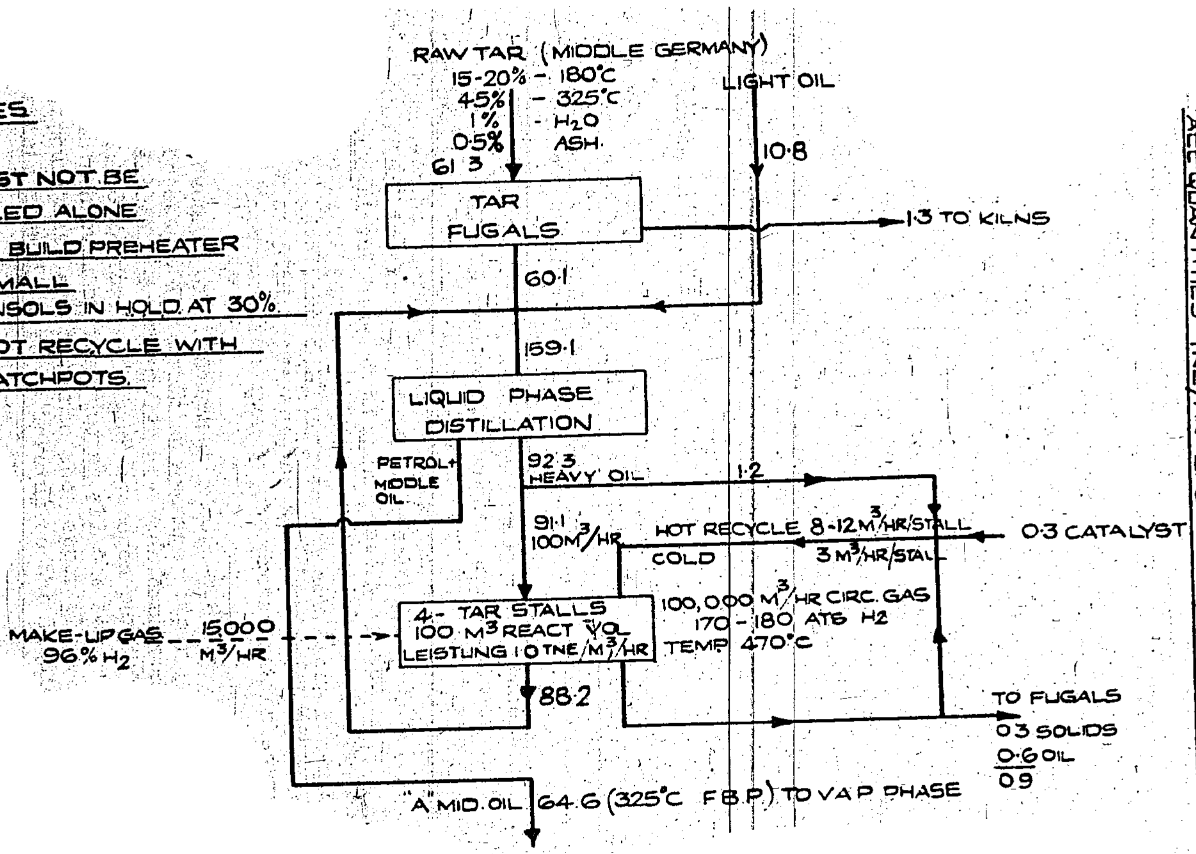
Hydrogenation conditions for heavy oil are:

Circulating gas/Oil feed	1,000 M^3/Ton
Mean Reaction Temperature	480°C
Oil feed rate	0.9 - 1.0 kg/litre catalyst/hour.
Pass Conversion of heavy oil into lighter products.	35%
Total Pressure	230 ats.
Hydrogen Partial Pressure	170-180 ats.
Catalyst	5 - 6% Iron on Crude coke in suspension in the reactants.

The catalyst (10927) is made by impregnation of the coke obtained from Winkler generators with the necessary amount of ferrous sulphate and caustic soda solutions in stoichiometric proportions. The impregnated coke is dried and ground so that not more than 2% remained on a 10,000 mesh screen. There is no washing step in the preparation of this catalyst. Make up catalyst is introduced as a suspension in part of the heavy oil feed usually injected into the hot liquid recycle system. Catalyst consumption is roughtly 1% by weight on the fresh > 325°C heavy oil feed.

FIG. V FLOWSHEET FOR PETROL FROM BROWN COALTAR

ALL QUANTITIES TNE/HR EXCEPT WHERE STATED



NOTES.

1. TAR MUST NOT BE DISTILLED ALONE
2. DO NOT BUILD PREHEATER TOO SMALL
3. KEEP INSOLS IN HOLD AT 30%.
4. USE HOT RECYCLE WITH OLD CATCHPOTS.

The main purpose of the hot liquid recycle from the hot catchpot to the preheater is to increase the velocity of liquid in the former and so reduce the coke formation. The rate of recycle necessary depends on the hot catchpot design. With the later types, hot recycle can be eliminated and it was stated that Brux operated in this way.

In order to purge spent catalyst and non hydrogenable material in the tar, there is a small let down from the hot catchpot. Part of this product is recycled direct and the remainder treated in fugals to give a concentrate which is carbonised for oil recovery.

The yield of petrol and middle oil obtained by liquid phase hydrogenation of brown coal tar heavy oil is just over 80% by weight. Hydrogen consumption is 3.9 to 4.0% by weight. It is interesting to note that the petrol + middle oil production "leistung" per M^3 reaction volume is lower from brown coal tar heavy oil than from brown coal. The figures are 0.25-0.26 Tons/M^3/hour for tar heavy oil and 0.29-0.30 for coal.

D. Vapour Phase Hydrogenation of Middle Oils

(i) Process conditions and yields

Leuna operates the two-stage process, i.e. straight through presaturation to convert nitrogen compounds to ammonia and to hydrogenate the greater part of the oxygenated components followed by splitting hydrogenation with recycle of unconverted middle oil.

For each stage the plant consists simply of a preheater, two interchangers, three or four converters, a cooler and a cold catchpot. Reaction volume per stall is usually about 25 M^3. For the first stage, Leuna, in common with most other German hydrogenation plants, have changed from 5058 (tungsten sulphide) in the form of 10 mm. pellets, to 8376 (25% tungsten sulphide + 3% nickel sulphide on alumina) catalyst used in the form of cubes. This was found to be as good as 5058 for reduction of phenols and superior to 5058 in that it gave less splitting to comparatively low quality petrol. It was not as good as 5058, however, for destruction of nitrogen compounds which is the most important function of the presaturation stage.

Leuna achieved an oil throughput of 0.6-0.8 Tons/M^3 catalyst/hour in the presaturation stage, for which an average temperature of 410°C and a hydrogen partial pressure of 210-220 ats. was employed. Circulating gas to oil ratio was 2,500 M^3/Ton. The high hydrogen partial pressure in the vapour phase stalls is achieved by introducing all the make up hydrogen for both liquid and vapour phase systems into the vapour phase circulating gas. A purge from this system is used as make up to the liquid phase.

Gas made in the presaturation step is the equivalent of 3% of the carbon in the feed. Roughly half this gas (by weight) is butane, a third propane and the remainder ethane and methane in approximately equal proportions. The yield of butane-free product depends of course on the oxygen, nitrogen and sulphur content of the feed. In the case of total 0-325°C product from brown coal tar it is 95% and hydrogen consumption is 3.9%

by weight. Using petrol + middle oil from brown coal hydrogenation as feed, the yield of saturated product is 97% and hydrogen consumption 3.7-3.8%.

The saturated product from both brown coal and brown coal tar contains an appreciable amount of material boiling in the petrol range. This fraction has a comparatively poor knock rating and it is desirable to keep it separate from the better quality product obtained by splitting hydrogenation. It is, therefore, usual to distil the saturation product, taking overhead a 0-150 or 160°C cut if motor gasoline is the desired end product or a 0-120°C fraction if aviation base petrol is being made. It was stated that 0-120°C saturation stage petrol ex brown coal hydrogenation has a motor method octane number of 70-71 while the rating of the corresponding product from brown coal tar was only 68-70. Presaturation stage petrol is frequently used as feed for the D.H.D. process.

The middle oil from the presaturation stage contains 2-3 mgs. nitrogen per litre. It can be used direct as a Diesel fuel and has a Cetane number of 40-42 and a pour point of -15°C. The pour point can be lowered to -40°C by cutting 15% from the higher boiling end but this reduces the Cetane number to 38.

Splitting hydrogenation of saturated middle oil is carried out over a tungsten sulphide on Terrana earth catalyst (6434). Other process conditions are:

	For Motor Gasoline	For Aviation Base Gasoline
Oil throughput Kgs/litre catalyst/hour	0.8	0.8
Conversion/pass	60%	55%
Circulating gas/oil feed ratio. M^3/Ton	1,500	1,700
Hydrogen Partial Pressure	210 - 220 ats.	210 - 220 ats.
Temperature	400°C	410°C

Circulating gas is water washed before entering the stall to reduce nitrogen to less than 0.1 mgrm/litre oil feed. Motor gasoline is cut to an end point of 190°C and has a volatility of about 30-35% at 100°C. Aviation base gasoline distils 65-70% at 100°C and has an end point of 150°C.

When making motor gasoline, 15% of the carbon in the 150-325°C saturated middle oil feed is converted into hydrocarbon gas consisting of 83% by weight of butane, 15% propane, 1% ethane and 1% methane. It is possible, however, to include 40-50% of the butane in the final petrol so that the net weight yield of motor gasoline is 91-92% on the feed.

20% of the carbon in the 120-325°C feed is converted into hydrocarbon gas of the same composition as given above when making aviation base petrol. It is not possible to include butane in the liquid product and the net yield is thus only 81% by weight.

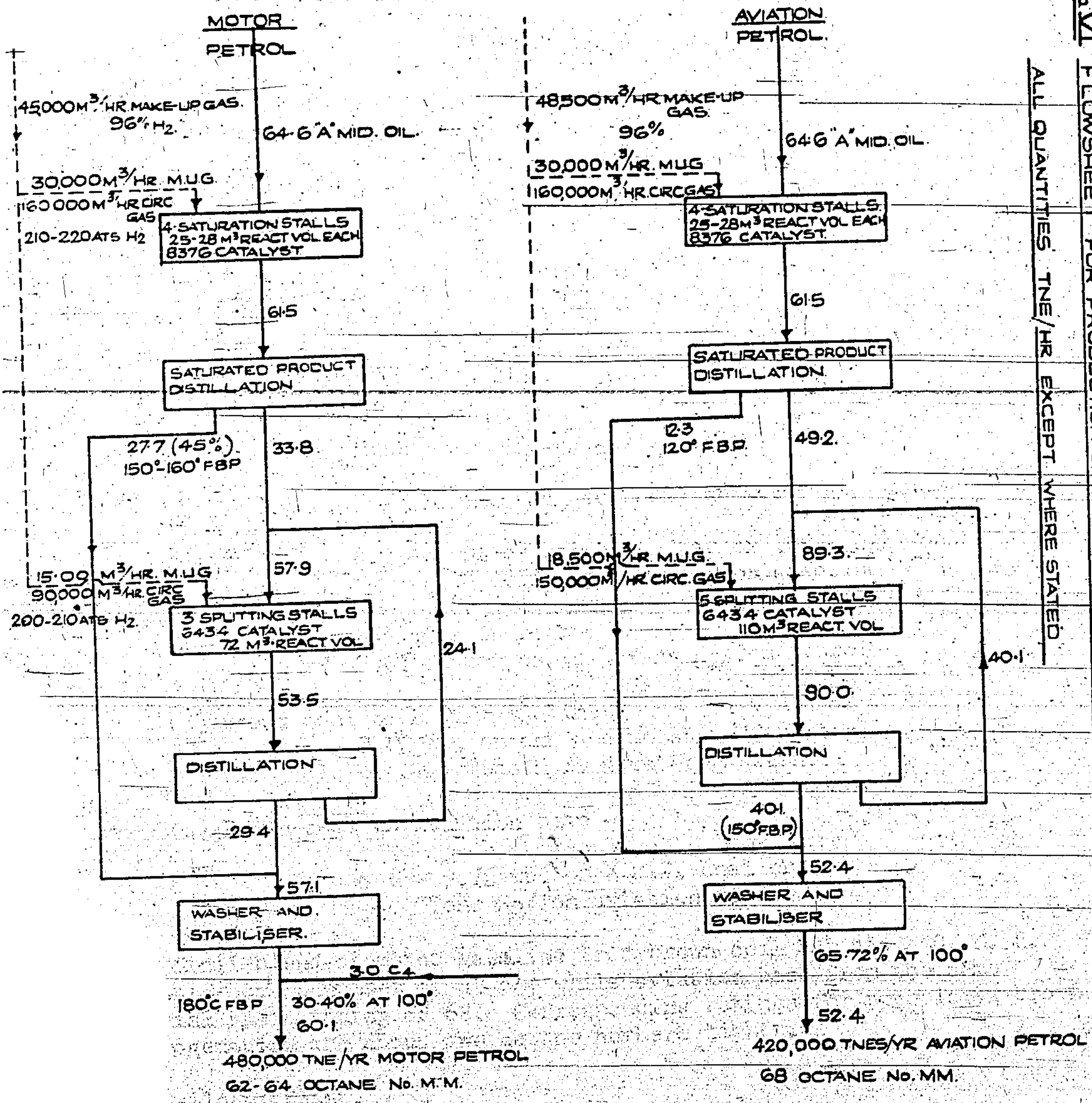


FIG VI FLOWSHEET FOR PRODUCTION OF MOTOR OR AVIATION PETROL FROM BROWN COAL MIDDLE OIL.

ALL QUANTITIES TNE/HR EXCEPT WHERE STATED

Figs. VI and VIII show diagrammatically the conversion to two grades of petrol + middle oil from liquid phase hydrogenation of brown coal tar (including Leuchtöl) and brown coal respectively. They show that the following overall yields are obtained:

	Motor Gasoline	Aviation Base Petrol
Brown coal tar		
(a) wt.% on crude tar including Leuchtöl	83	72.5
(b) wt.% on liquid phase petrol + middle oil	93	81
Brown coal		
(a) wt.% on ash and moisture free coal	46	40
(b) wt.% on liquid phase petrol + middle oil.	95	83

Overall hydrogen consumption figures are:

(1) Brown coal tar (including Leuchtöl) to Motor gasoline -
6.9 - 7.0% by weight on tar or .083-.084 Tons Hydrogen per Ton Motor gasoline.

(2) Same feed to Aviation petrol -
7.3% on tar or .1 Tons H_2/Ton petrol.

(3) Brown coal to Motor gasoline -
9.4% wt. on ash and moisture free coal or .203 Tons H_2/Ton motor gasoline.

(4) Brown coal to Aviation base -
9.6 - 9.7% wt. on a.m.f. coal or .24 Tons H_2/Ton aviation base.

The final blend of motor gasoline from brown coal tar has a C. F. R. motor method octane number of 62-64, while aviation base from the same raw material has a rating of 68. Corresponding ratings for petrols ex brown coal hydrogenation are about two octane numbers higher.

(ii) <u>Details of Plant.</u>

<u>Injectors.</u> Normal three throw pumps are used with electric drives. S. E. A. rings for gland packing had not been very satisfactory and the I. G. had used ACACIA wood packing with considerable success. These new packings had a life of about 1,800 hours.

Interchangers were similar to those in use in liquid phase stalls except that those in use in saturation stalls had 241 tubes. K value for both was 300-200.

Preheaters. On the saturation stalls the preheater consisted of 4 or 5 elements of 90 mm. bore, 127 mm. external diameter tube heated electrically. Normal gas-fired preheaters were used in splitting stalls - each contained about 25 elements of 90 mm. bore tube and had a K value of 200-180.

Reactors. The main feature of vapour phase hydrogenation reactors is the arrangement of the catalyst in beds with intermediate mixing chambers into which cold circulating gas is introduced in order to give the necessary temperature control. The Leuna engineers do not appear to have been very progressive as regards improvements in design of these bed converters and the operating staff seemed satisfied with the present reactors although they are capable of much smaller throughputs than those in use, for example, at Billingham.

The forging body was formerly lined with stamped-cement asbestos. During the war, Leuna has used fired bricks of "Schammote stein" with apparent success.

Coolers. The K value of vapour phase hydrogenation stall coolers was stated to be 400-500 kg. cals/°C/M^2/hour.

E. Vapour Phase Splitting Hydrogenation at 700 atmospheres Pressure

This was not practised at Leuna but the research for the Dutzkendorf plant of the Wintershalle A. G. was done in the Leuna laboratories. Dr. Becker supplied comparative data for 300 ats. two stage (presaturation followed by splitting hydrogenation) and 700 ats. direct treatment over 6434 when using bituminous coal tar middle oil (creosote middle oil) as feed. These data are given in Fig. VII.

It will be seen that the weight yield of petrol of 30% volatility at 100°C is substantially the same in the two processes but that the high pressure method gives a product higher in anti-knock rating by 5-10 octane numbers. Dr. Becker was unable to give figures for hydrogen consumption but presumably the 700 ats. process requires less hydrogen because of the greater concentration of aromatics in the final product. Incidently this aromatic content and also the octane number of the petrol could be increased still further using a "diluted" catalyst such as is employed at Welheim instead of 6434.

In the 700 ats. process overall petrol production leistung is 0.37-0.38 kgs./litre catalyst/hour. This compares with 0.29 kgs./litre 5058 + 6434 catalyst/hour for the 300 ats. two stage method. Since 700 ats. converters have only 75% of the catalyst capacity of vessels of weight used for 300 ats., there is no saving in reaction vessels using the higher pressure process. Because the conversion/pass using 700 ats. and non-saturated feed is low - 43%, the amount of distillation involved is rather

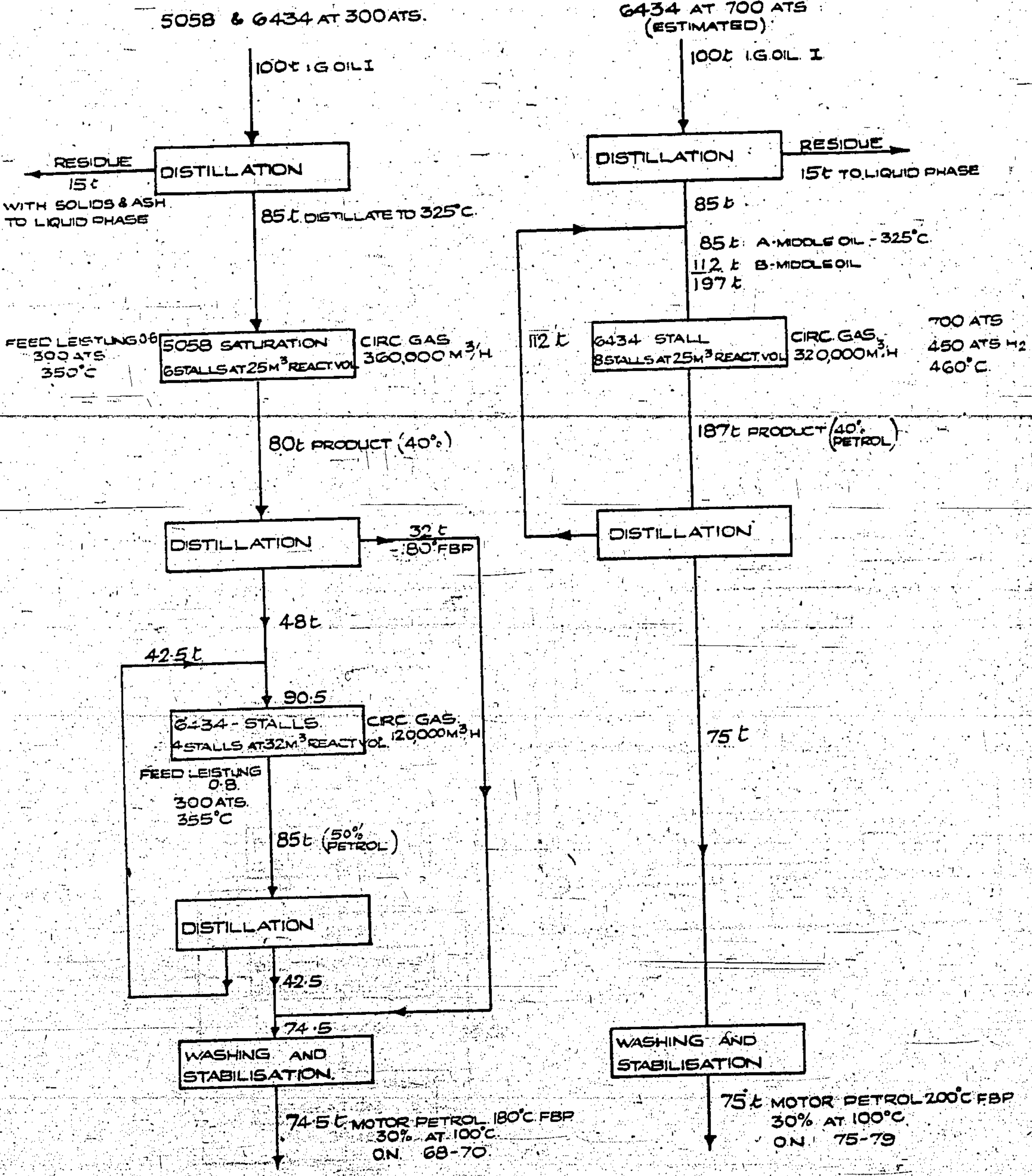


FIG VII. COMPARATIVE FLOWSHEETS FOR PETROL FROM BITUMINOUS COAL TAR MIDDLE OIL

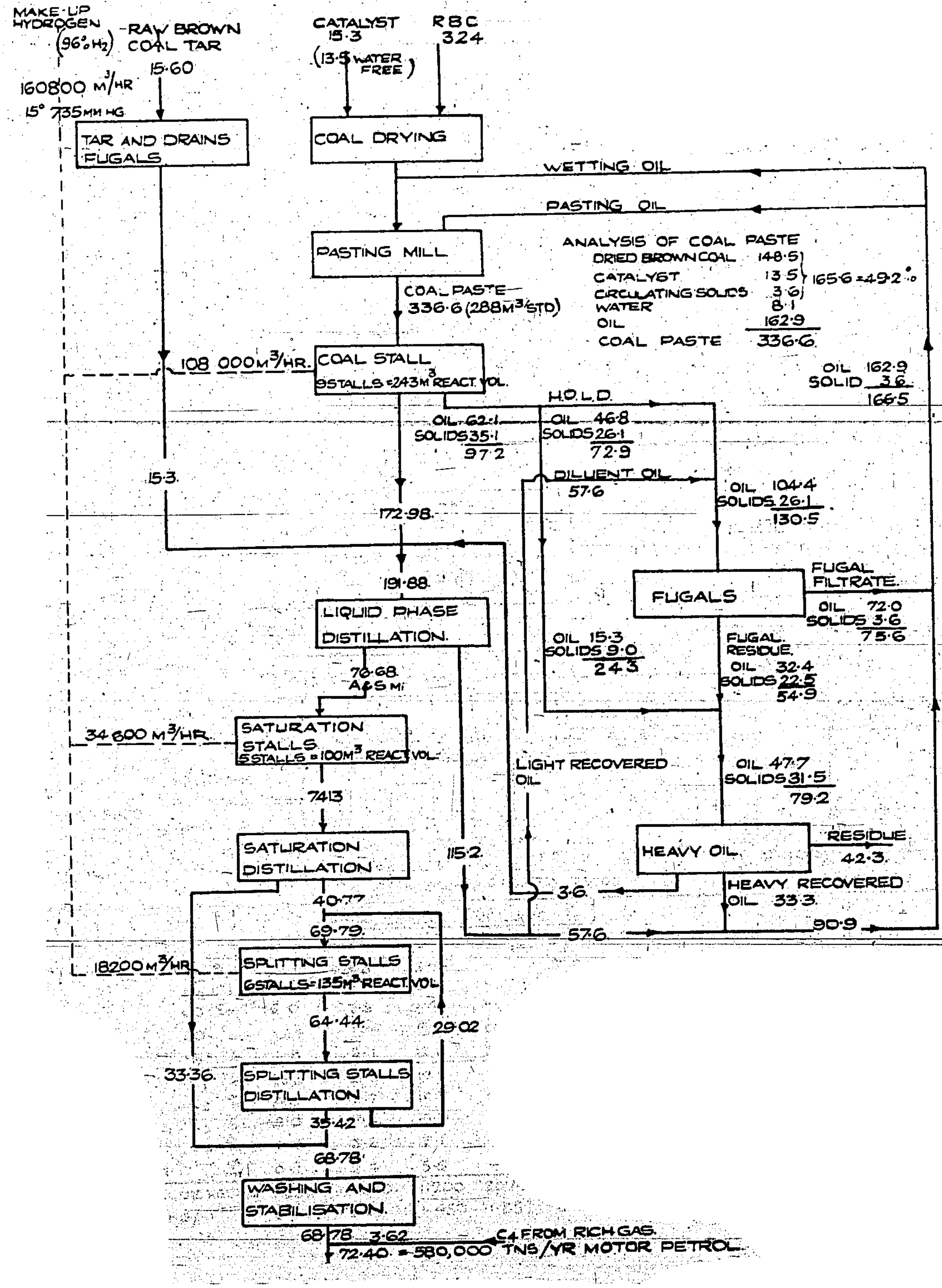


FIG VIII FLOWSHEET FOR MOTOR PETROL FROM BROWN COAL BY HYDROGENATION

ALL QUANTITIES IN TNES/HR UNLESS STATED

ALL FLUID PRODUCTS ARE GAS FREE BUT INCLUDE C_5

ALL FIGURES IN M³/HR. AT 15°C 735 MM UNLESS STATED.

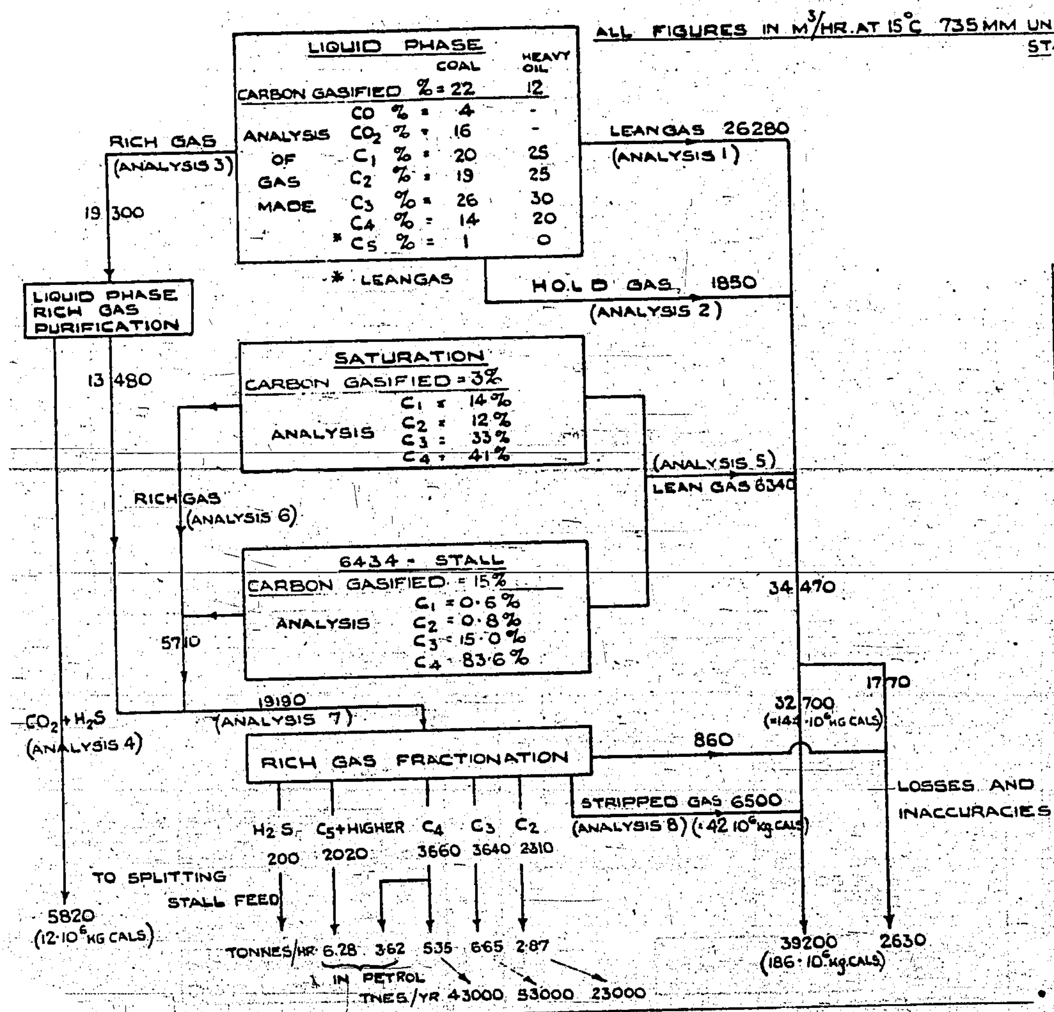


FIGURE IX

HYDROCARBON GAS FLOWSHEET

MOTOR PETROL FROM BROWN COAL

ANALYSES (VOLUME %)

	1	2	3	4	5	6	7	8
H_2 %	42·1	26·8	5·7	-	67·0	6·8	7·8	21·9
N_2 %	8·5	5·7	2·1	-	17·6	3·5	3·1	8·7
CO %	5·0	3·5	1·4	-	-	-	1·4	3·9
CO_2 %	10·7	13·8	18·2	60·1	-	-	-	-
H_2S %	1·8	6·1	12·0	39·9	0·6	3·6	1·1	-
C_1 %	25·3	21·9	17·2	-	14·9	8·3	19·7	55·5
C_2 %	4·3	8·7	14·7	-	1·3	3·5	15·9	8·9
C_3 %	2·0	7·9	16·0	-	2·2	14·6	20·3	1·1
C_4 %	0·3	3·2	7·1	-	2·0	43·3	20·1	-
C_5 + HIGHER %	0·1	2·4	5·6	-	0·4	16·4	10·6	-
HEATING VALUE KG CALS/M³	4330	7240	11200	2070	3910	21400	17000	6460
DENSITY KG/M³	0·67	1·01	1·480	1·65	0·475	2·03	1·59	0·659

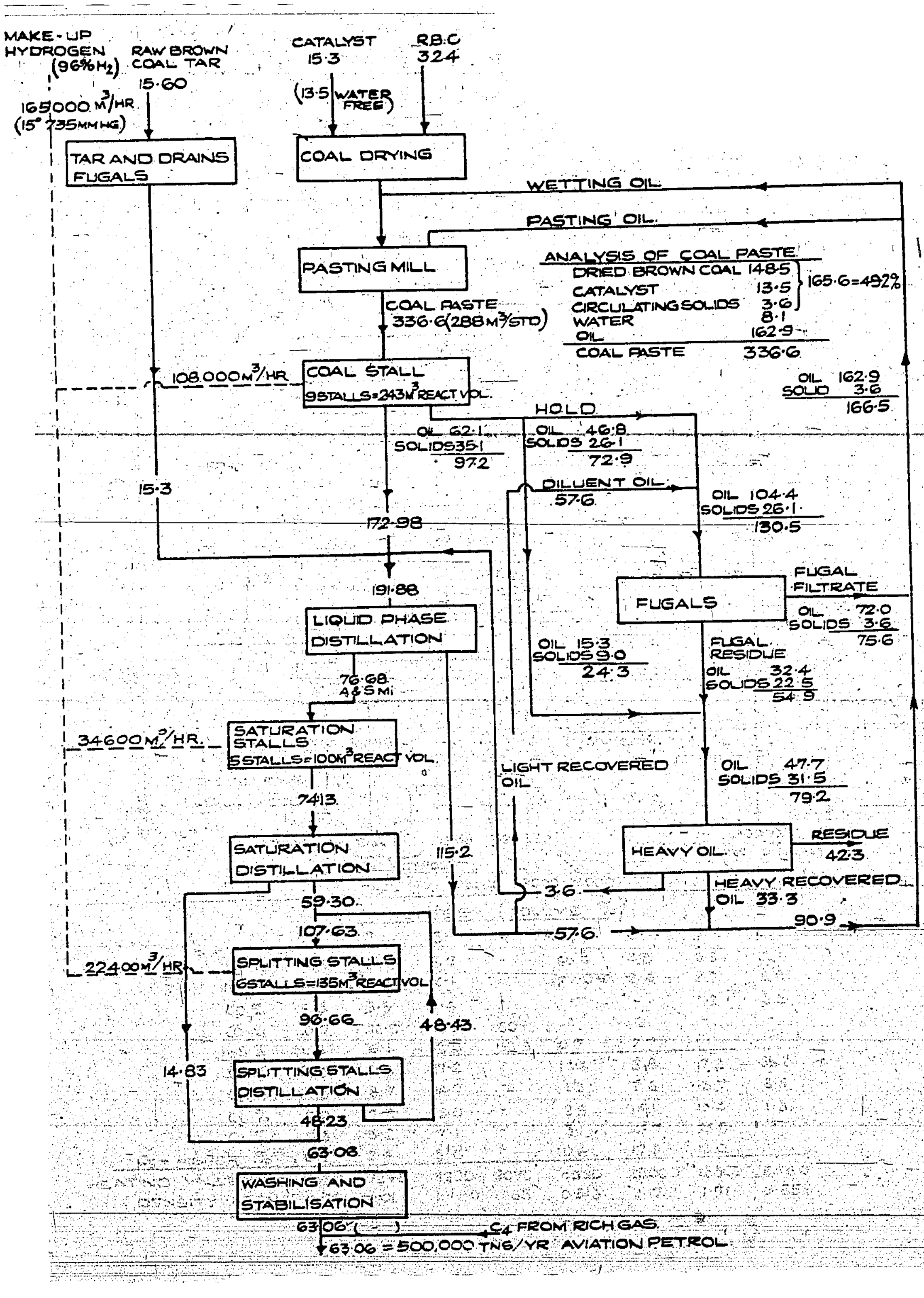


FIG. X FLOWSHEET FOR AVIATION PETROL FROM BROWN COAL BY HYDROGENATION

ALL QUANTITIES IN TNES/HR UNLESS STATED
ALL FLUID PRODUCTS ARE GAS FREE BUT INCLUDE C_5

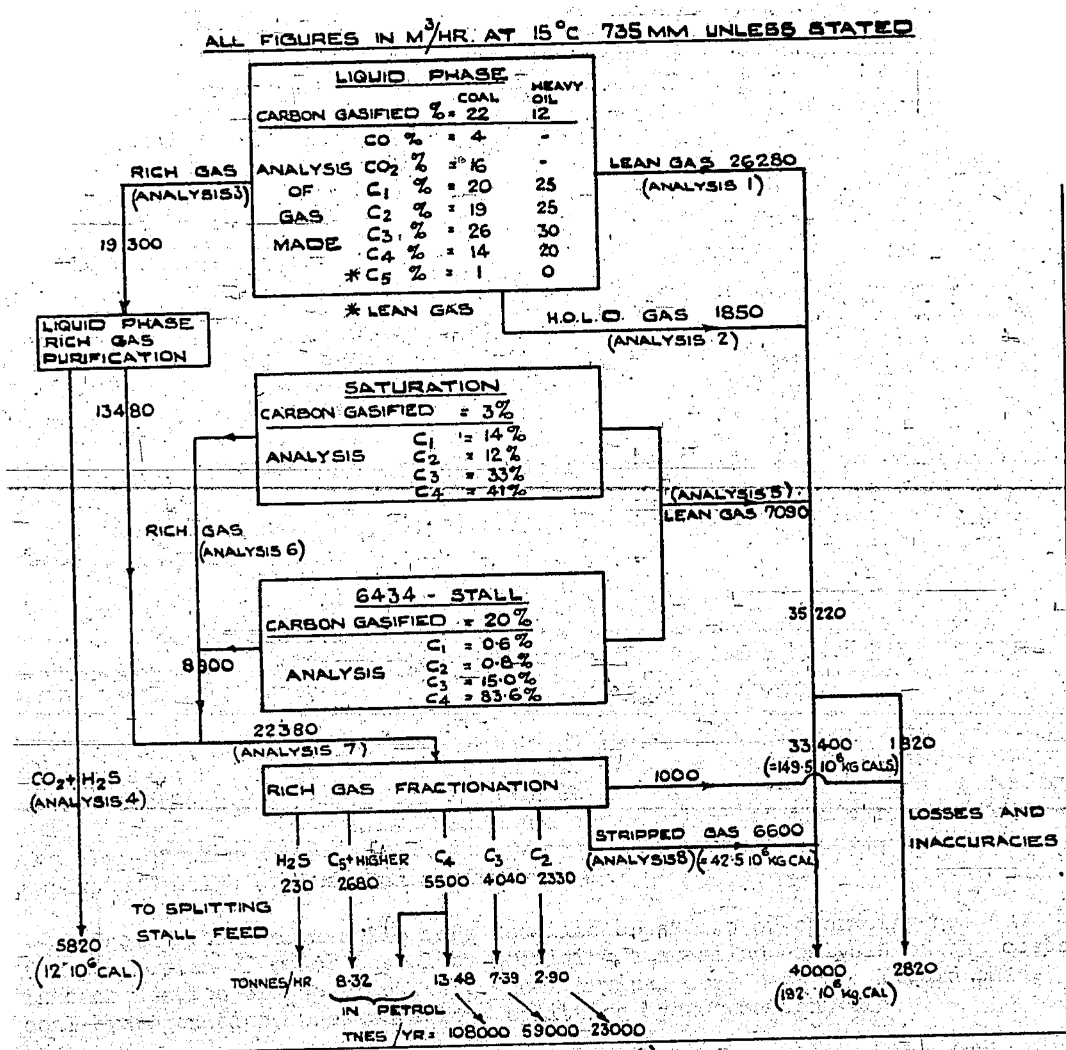


FIGURE XI

HYDROCARBON GAS FLOWSHEET AVIATION PETROL FROM BROWN COAL

ANALYSES (VOLUME %)

	1	2	3	4	5	6	7	8
H_2 %	42·1	26·8	5·7	-	60·0	4·8	6·9	22·1
N_2 %	8·5	5·7	2·1	-	77·0	2·4	2·7	8·8
CO %	5·0	3·5	1·4	-	-	-	1·2	3·8
CO_2 %	10·7	13·8	18·2	60·1	-	-	-	-
H_2S %	1·8	6·1	12·0	39·9	0·7	2·7	1·1	-
C_1 %	25·3	21·9	17·2	-	14·4	5·8	17·2	55·2
C_2 %	4·3	8·7	14·7	-	1·3	2·6	13·7	8·8
C_3 %	2·0	7·9	16·0	-	2·9	14·1	19·4	1·3
C_4 %	0·3	3·2	7·1	-	3·1	49·7	25·8	-
C_5 + HIGHER %	0·1	2·4	5·6	-	0·6	17·9	12·0	-
HEATING VALUE KG.CALS/M³	4330	7240	11200	2070	4390	23000	18300	6460
DENSITY KG./M³	0·67	1·01	1·480	1·65	0·513	2·17	1·71	0·659

higher than is the case in the normal two stage 300 ats. process. If it is essential to produce petrol of high aromatic content and an octane number of 75-79, there is clearly an advantage in using the 700 ats. method (possibly with a less saturating catalyst than 6434) instead of the conventional two-stage method followed by D. H. D. treatment of the saturation stage naphtha.

F. Hydrogenation Costs

On the instructions of the Ministry of Fuel & Power a special effort was made to get detailed information on the economics of the hydrogenation activities at Leuna. During our visit, Dr. Pichler went through the whole of the available records and made the following summary of brown coal hydrogenation costs.

Figs. VIII to XI present the basic flowsheet data for hydrogenation of brown coal to motor and aviation petrols using the latest Leuna high-throughput conditions. They are typical of the Leuna operations during 1943 and early 1944.

Table I gives an analysis of the cost of production of motor and aviation petrols according to these flowsheets in terms of raw material costs, operating costs and capital charges, credits for hydrocarbon gases being taken into account.

Table II shows a breakdown of the operating costs in terms of operating labour, labour and materials for repairs, electric power, fuel gas, steam, etc. "Overhead charges" and obsolescence are shown as part of the operating cost. Labour is given in man/hours and consumptions of the various utilities are also quoted so that it is an easy matter to translate these costs to apply to British or American conditions.

Table III gives a still more detailed breakdown of operating costs for production of motor petrol by providing a detailed analysis of the costs in each section of the plant, e.g. coal drying, coal pasting, liquid phase coal hydrogenation, presaturation, splitting hydrogenation, etc.

Table IV shows the costs additional to those set out in Table III which are incurred when aviation base petrol is made.

These cost data will be analysed in a later report.

It is interesting to note that although the full cost of production of aviation base petrol was only 200 RM/Ton, the Leuna realisation was stated to have been 340 RM for this grade and 310 RM for motor gasoline. On the basis of these figures, the I. G. had a profit margin of about 80 x 10^6 RM/year in respect of Leuna hydrogenation activities alone. Dr. Pichler said that this very high return was allowed in order to compensate the I. G. for its heavy expenditure in developing the hydrogenation process.

TABLE I. - COST CALCULATION FOR PRODUCTION OF PETROL FROM BROWN COAL

	Unit	Cost per Unit.RM	Motor Petrol Production				Aviation Petrol Production			
			Per hour		Per Tne Motor Spirit		Per hour		Per Tne Aviatn. Spirit	
			Quantity	RM	Quantity	RM	Quantity	RM	Quantity	RM
A. Materials										
1) Raw materials										
Brown Coal	Tne	3.00	324	972.00	4.475	13.43	324	972.00	5.138	15.41
Brown Coal Tar	"	80.00	15.60	1248.00	0.215	17.24	15.6	1248.00	0.247	19.79
2) Other Materials										
Make-up Gas (96% H_2)	M^3	0.042	160800	6753.60	2221	93.27	165000	6930.00	2617	109.90
Red Earth (dried)	Tne	20.00	15.3	306.00	0.211	4.23	15.3	306.00	0.243	4.85
Catalyst and other chemical				144.80		2.00		182.00		2.89
3) By-Products										
Butane x	Tne	170.14	5.35	1/910.25	0.074	1/12.57	13.48	1/2293.49	0.214	1/36.37
Propane x	"	170.14	6.65	1/1131.43	0.092	1/15.63	7.39	1/1257.33	0.117	1/19.94
Ethane	"	110.00	2.87	1/315.70	0.040	1/4.36	2.90	1/319.00	0.046	1/5.06
Hydrogenation Gas	10^3 T.Cals	7.00	198	1/1386.00	2.735	1/19.14	204	1/1428.00	3.235	1/22.65
B. Running Costs (See Table II)				6637.43		91.67		6916.89		109.69
Production Cost			72.40	12318.45	1.000	170.14	63.06	11257.07	1.000	178.51
C. Loading & Evaporation	Tne	3.00	72.40	217.20	1.000	3.00	63.06	189.18	1.000	3.00
D. On-Costs (I.G. direction, research, etc.				1220.66		16.86		1220.66		19.36
WORKS COST			72.40	13756.31	1.000	190.00	63.06	12666.91	1.000	200.87

x Valued at cost of production of Motor Petrol.

1/ Designates credit against operating costs.

TABLE II

BUILD UP OF RUNNING COSTS

	Motor Petrol Production per hour		Aviation Petrol Prodn. per hour	
	Quantity	RM	Quantity	RM
Labour Costs		677.62		695.75
Wages hrs.	447.51	524.65	459.01	538.47
Salaries		111.98		115.07
Social Insurance		40.99		42.21
Energy Costs		2,394.99		2,513.74
Water M^3	10,253.2	147.71	11,342.73	163.87
H. P. Steam Tne.	280.15	849.77	303.20	919.57
I. P. Steam Tne.	112.93	1/ 225.83	125.66	1/ 251.28
L. P. Steam Tne.	150.54	337.19	152.59	341.76
H.T. Electricity KW/hr.	15,460.47	317.86	16,451.88	332.85
L.T. Electricity KW/hr.	3,761.12	77.82	3,929.78	81.31
Fuel Gas 10^3 Tne Cals.	83,747.51	743.82	87,991.65	781.62
Brown Coal Tne.	45.063	139.46		139.46
Other Forms (Gas)		7.19		4.58
Repair Costs		1,496.85		1,561.71
Wages hrs.	371.97	451.61	383.60	465.56
Material		299.45		321.52
Workshop & Material oncost.		745.79		774.63
Working Material		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
Credits		59.31		1/ 59.31
		6,637.43		6,916.89

1/ Designates credit against operating costs.

Remarks: 1. The supplementary charges are based on calculations made in Feb. 1943 for Motor Petrol or Aviation Petrol.

2. The rates for wage earners average 1 RM/hr. Owing to surcharges for holidays-with-pay, payment during illness, etc., the actual running cost rate averages 1.17 RM/hr. In peace time this surcharge was less. In the repair charges the payment for unworked hours has been included in the Workshops charges; the hourly rate of 1.20 RM/hr., therefore, is the actual rate of payment.

3. In a modern plant it is estimated that the Wages, Energy Requirements and Repair Charges would be 10-20% less.

TABLE III. - BUILD-UP OF HYDROGENATION COSTS

(Based on values of Nov. 1943 and a Motor Fuel Production of 72.40 Tnes/hr)

		Coal-Steam Drying		Coal - Gas-fired drying		Paste Preparation		Paste Injection		Coal Stalls		H.O.L.D. Fugals	
		Qty/hr	RM/hr	Qty/hr	RM/hr	Qty/hr	RM/hr	Qty/hr	RM/hr	Qty/hr	RM/hr	Qty/hr	RM/hr
01. **Wages**			25.69		90.20		51.31		34.84		78.73		22.69
Wages to IG workers.	hrs.	12.73	15.42	48.40	60.96	27.42	33.42	22.92	27.32	51.33	61.87	12.38	14.52
" " foreign "	"	4.37	3.50	11.66	11.74	6.10	6.13	0.24	0.20	0.02	0.02	3.86	3.55
Salaries			3.40		12.67		8.81		4.98		11.53		3.34
Social Insurance, etc.			1.37		4.83		2.95		2.34		5.31		1.28
02. **Energy Costs**			96.73		236.98		78.47		97.86		256.13		17.26
L.P. Water (Take	M^3	1.47	0.01										
L.P. Water (Cr.	M^3												
H.P. Water	"			0.47	0.01	6.66	0.10	238.93	3.53	1895.48	27.98	6.67	0.10
Drinking Water	"	0.93	0.09	2.52	0.24								
Cooling Water (Take	"									1/302.64	1/10.14		
Cooling Water (Cr.	"												
Condensate, Oil free	"	1/35.82	1/9.29	1/0.34	1/0.09	1/4.51	1/0.61	1/0.53	1/0.07	1/7.49	1/1.01	1/1.51	1/0.18
" Oily	"												
H.P. Steam	Tne	3.35	10.15	0.57	1.73	12.65	38.31			12.83	38.85	6.31	19.11
Back Pressure Steam	"			1/0.35	1/0.69	1/3.89	1/7.78					1/3.11	1/623
L.P. Steam	"	37.88	85.24	0.93	2.08	2.19	4.93	1.29	2.91	5.39	12.13		
H.T. Electricity	KWH	20.20	0.30	2760.69	41.71	1222.19	18.46	5971.41	90.20	1112.28	16.80	185.65	2.85
L.T. " Power	"	137.25	2.84	471.76	9.76	443.90	9.19	56.56	1.17	42.28	0.87	68.89	1.43
" " Light	"	8.81	0.18	32.28	0.67	11.20	0.23	5.87	0.12	2.04	0.04	2.33	0.05
Fuel Gas	M^3			3385.25	30.06					19283.33	170.52	0.43	0.01
Workshops Gas	"												
Nitrogen 90 lbs/in²	"	263.89	4.30	45.25	0.74	866.53	14.13			55.34	0.06	191.89	0.17
CO_2 7 lbs/in²	"	5020.06	2.60	5686.36	4.90	1754.30	1.51						
Towns Gas	"												
Acetylene	"									10.18	-0.03		
Compressed Air	"	90.65	0.31	1921.90	6.40								
Raw Brown Coal	Kg			45062.94	139.46								
Bit. Coal and Coke	"												
03. **Repair Costs**			27.86		95.86		173.79		37.93		346.81		38.22
Foreign Wrkrs. Wages.	hrs.	0.63	1.04	6.88	8.96	0.45	0.55	0.07	0.07	0.59	0.64	0.92	1.83
" " Material & oncosts.	hrs.		0.04		5.20		42.20		8.41		10.95		2.72
Stores Material			1.11		7.76		8.53		2.37		50.43		3.02
" " supplement			0.18		1.27		1.38		0.30		8.29		0.49
Workshops Wages.	hrs.	8.73	10.73	24.38	29.79	38.12	46.09	8.25	10.09	82.82	99.98	9.74	11.63
Workshops Costs. s'ment			14.69		41.95		72.50		16.53		170.98		18.26
Repairs-Transport charges			0.07		0.93		2.54		0.07		5.54		0.27
04. **Running Materials**			0.65		3.27		11.32		0.66		1.33		1.40
Materials			0.59		2.86		11.00		0.57		1.31		1.24
Stores supplement			0.06		0.41		0.32		0.09		0.02		0.16
05. **Traffic Costs**			0.02		12.05		41.84		0.10		1.21		0.78
06. **Works General Charges**			9.28		35.06		22.21		14.14		37.16		9.26
Wage & Salary s'ment.			7.02		26.83		15.12		10.01		22.73		6.74
Fire Brigade			1.50		5.68		1.63		0.79		7.14		0.61
Post Office Costs			0.76		2.55		5.46		3.34		7.29		1.91
07. **Capital-Charges**			20.60		145.83		68.17		15.49		168.21		23.29
Writing off			15.68		113.00		50.69		12.94		142.04		18.94
Interest			4.74		32.83		17.48		2.55		26.17		4.35
08. **Taxes**			4.93		21.18		11.98		6.40		17.72		4.76
09. **Various Costs**			2.14		59.23		8.68		0.37		24.39		7.59
Laboratory			2.02		20.71		7.70				23.84		7.17
Other Costs			0.12		0.68		0.98		0.37		0.55		0.42
Raw Material Stores					37.84								
Part cost Pipe Bridges													
" " Factory Wtr. System					43.76								
" " Tip Charges					4.43								
10. **Credits**													
Production: Total			185.90		747.85		467.67		207.79		931.76		125.25

1/ Designates credit against operating costs.

TABLE III. - BUILD-UP OF HYDROGENATION COSTS (Cont'd)
(Based on values of Nov. 1943 and a Motor Fuel Production of 72.40 Tnes/hr)

		H.Q.L.D. Kilns		Tar Fugals.		Liquid Phase Distillation		Gas Washing Plant		Circulation	
		Qty/hr	Rm/hr	Qty/hr	RM/hr	Qty/hr	RM/hr	Qty/hr.	RM/hr	Qty/hr	RM/hr
01. Wages			77.89		24.38		21.65		23.31		20.89
Wages to IG workers. hrs.		43.75	51.53	13.34	15.94	12.35	14.83	12.60	14.88	11.69	13.93
" "foreign " "		14.83	15.31	3.19	3.28	0.80	0.92	1.03	0.99	1.92	1.83
Salaries			6.71		3.75		4.55	0.00^3	6.02	0.00^2	3.87
Social Insurance, etc.			4.34		1.41		1.35		1.42		1.26
02. Energy Costs			388.75		23.24		230.08		23.84		132.75
(Take	M^3										
L.P. Water (Cr.	"										
H.P. Water	"	566.20	8.36	23.79	0.35	540.62	7.98	13.67	0.20	11.93	0.18
Drinking Water	"	0.32	0.03			0.96	0.09				
(Take	"										
Cooling Water (Cr.	"										
Condensate - Oil free	"										
" Oily	"	1/14.26	1/1.93	1/2.92	1/0.40	1/1.81	1/0.25	1/0.17	1/0.02	1/12.17	1/1.64
H.P. Steam	Tne	8.86	26.82	3.53	10.68	1.12	3.40	2.18	6.61	28.46	86.17
Back-Pressure Steam	"							1/1.96	1/3.92		
L.P. Steam	"	25.79	58.03	3.59	8.08	8.64	19.44	0.20	0.45	1.05	2.37
H.T. Electricity	KWH	180.34	2.72	3.21	0.07	1116.73	16.87	1330.07	20.08	2957.83	44.68
L.T. " Power	"	67.61	1.40	198.20	4.10	118.69	2.46	10.87	0.23	45.65	0.94
" " Light	"	0.71	0.01			0.47	0.01	2.02	0.04	2.63	0.05
Fuel Gas	M^3	23431.90	208.10			19721.42	174.96				
Workships Gas	"					6.90	0.16				
Nitrogen 90lbs/in^2	"					304.20	4.96	10.52	0.17		
CO$_2$ 7 lbs/in^2	"	205.61	0.18	410.69	0.36						
Towns Gas	"										
Acetylene	"										
Compressed Air	"	9.25	0.03								
Raw Brown Coal	Kg.										
Bit. Coal & Coke	"										
03. Repair Costs			143.23		21.60		62.80		50.94		55.90
Foreign workers wages, hrs.		0.73	1.35			2.32	3.80	0.20	0.37	0.01	0.01
" " material & oncosts.			6.80		0.56		6.00		3.04		5.02
Stores Material			14.12		1.71		1.44		5.32		6.43
" " supplement			2.30		0.27		0.17		0.85		1.06
Workshops wages. hrs.		38.36	45.51	5.76	7.08	16.50	19.68	13.08	15.91	13.56	16.62
" costs supplement			71.22		11.62		30.94		25.90		26.58
Repairs - Transport charges			1.93		0.36		0.77		0.15		0.18
04. Running Materials			4.46		0.85		1.17		0.85		3.45
Materials			3.96		0.76		1.05		0.74		2.97
Stores supplement			0.50		0.09		0.12		0.11		0.48
05. Traffic Costs			92.50		0.38		0.04		0.04		0.08
06. Works General Charges			36.01		0.08		10.16		10.02		9.94
Wage & Salary S'ment.			22.91		7.21		6.25		6.70		6.10
Fire Brigade			2.65		0.14		1.64		2.09		1.81
Post Office Costs			10.45		1.73		2.27		1.23		2.03
07. Capital Charges			115.99		3.52		48.21		57.78		45.44
Writing off			94.12		2.64		42.10		50.15		32.67
Interest			21.87		0.88		6.11		7.63		12.77
08. Taxes			16.84		4.55		4.97		5.46		5.93
09. Various Costs			10.84		26.10		9.02		1.33		0.28
Laboratory			3.69		3.29		0.91		1.31		
Other Costs			7.15		0.67		0.10		0.02		0.28
Raw Material Stores					22.14		8.01				
Part Cost Pipe Bridges											
" " Factory Wtr. System											
" " Tip Charges											
10. Credits											
Production: Total:			801.51		113.70		388.10		173.57		274.66

1/ Designates credit against operating costs.

TABLE III. - BUILD-UP OF HYDROGENATION COSTS (Cont'd)
(Based on values of Nov. 1943 and a Motor Fuel Production of 72.40 Tnes/hr)

		Vapour Phase Injection		Vapour Phase Stalls		Vapour Phase Distillation		Petrol Wash		Depropanising Plant	
		Qty/hr	RM/hr	Qty/hr	RM/hr	Qty/hr	RM/hr	Qty/hr	RM/hr	Qty/hr	RM/hr
01. Wages			21.70		48.72		27.96		2.61		9.13
Wages to IG workers, hrs.		13.82	16.52	30.70	37.08	16.22	19.75	1.69	1.98	7.05	8.47
" "foreign " "		0.14	0.12	0.01	0.01	0.45	0.44				
Salaries		0.00^2	3.63	0.004	8.40	0.00^2	5.98		0.46		
Social Insurance, etc.			1.43		3.23		1.79		0.17		0.66
02. Energy Costs			33.50		83.87		176.00		11.42		24.40
L.P. Water (Take	M³										
(Cr.	"										
H.P. Water	"			1817.18	26.83	529.40	7.82	126.75	1.87	32.34	0.48
Drinking Water	"					3.93	0.37				
Cooling Water (Take	"										
(Cr.	"			1/293.77	1/9.85						–
Condensate, Oil free	"										
" Oily	"	1/6.87	1/0.12	1/0.21	1/6.03	1/1.80	1/6.24	1/1.71	1/0.23	1/3.02	1/0.41
H.P. Steam	Tne	21.20	64.19	0.51	1.55	2.85	8.62			7.36	22.29
Back Pressure Steam	"	1/19.07	1/38.13								
L.P. Steam	"					7.31	16.45	4.15	9.34		
H.T. Electricity	KWH	488.27	7.38	1784.68	26.96	570.90	8.62				
L.T. " Power	"			40.83	0.84	490.26	10.15	17.64	0.36	98.00	2.03
" " Light	"	5.55	0.11	1.96	0.04	5.68	0.12	3.92	0.08	0.39	0.01
Fuel Gas	M³			4244.73	37.39	13598.41	120.77				
Workshops Gas	"			3.76	0.09	54.03	1.28				
Nitrogen 90 lbs/in²	"					12.23	0.20				
CO_2 7 lbs/in²	"	80.58	0.07	21.85	0.02						
Towns Gas	"										
Acetylene	"										
Compressed Air	"			9.77	0.03	554.19	1.84				
Raw Brown Coal	Kg										
Bit. Coal & Coke	"										
03. Repair Costs			36.98		214.99		28.24		6.97		20.53
Foreign workers wages. hrs.		0.22	0.29	0.25	0.26	0.21	0.26			0.21	0.22
" " material & oncosts			3.64		12.16		0.38		3.68		0.03
Stores material			4.95		64.97		1.29		0.17		1.42
" " supplement			0.83		10.88		0.22		0.03		0.21
Workshops wages hrs.		8.55	10.44	36.19	43.21	8.48	10.26	1.07	1.26	5.59	6.83
" costs supplement			16.61		82.19		15.07		1.83		10.64
Repairs - Transport charges			0.22		1.32		0.76				1.18
04. Running Materials			2.93		3.76		0.64				
Materials			2.52		3.39		0.55				
Stores supplement			0.41		0.37		0.09				
05. Traffic Costs			0.05		1.37		0.13				0.04
06. Works General Charges			10.79		28.77		13.07		0.99		2.90
Wage and salary s'ment.			6.37		14.03		8.04		0.75		2.68
Fire Brigade			0.96		8.50		2.15		0.09		0.22
Post Office costs			3.46		6.24		2.88		0.15		
07. Capital Charges			17.54		179.66		27.98		2.62		8.49
Writing Off			14.52		150.48		22.84		1.88		7.57
Interest			3.02		29.18		5.14		0.74		0.92
08. Taxes			4.33		13.13		6.90		0.65		1.69
09. Various Costs			0.28		39.34		2.58		0.88		0.22
Laboratory			0.02		27.34		2.21		0.88		0.01
Other Costs			0.26		1.09		0.37				0.21
Raw Material Stores					10.91						
Part Cost Pipe-Bridges											
" " Factory Wtr. System											
" " Tip Charges											
10. Credits							etc 1/0.01				
Production: Total:			128.11		613.61		283.49		26.14		67.40

1/ Designates credit against operating costs.

TABLE III. - BUILD-UP OF HYDROGENATION COSTS (Cont'd)

(Based on values of Nov. 1943 and a Motor Fuel Production of 72.40 Tnes/hr)

		Liquid Phase Rich Gas Purification		Rich Gas Fractionation		Petrol Testing		Liquid Phase Intermediate Storage		Vapour Phase Intermediate Storage	
		Qty/hr	RM/hr	Qty/hr	RM/hr	Qty/hr	RM/hr	Qty/hr	RM/hr	Qty/hr	RM/hr
01. Wages			20.97		40.11	–	0.76		16.0		3.39
Wages to IG workers, hrs.		8.80	9.62	24.47	29.34			10.15	12.01	2.18	2.49
" "foreign " "		5.54	4.08	0.53	0.44						
Salaries		0.00^{3}	6.28	0.00^{4}	7.70		0.72	0.001	2.93		0.69
Social Insurance, etc.			0.99		2.63		0.04		1.06		0.21
02. Energy Costs			152.77		294.30		0.15		73.26		19.34
Low Pressure Water (Take	M³	735.00	5.35								
(Cr.	"	1/19.76	1/0.09								
High Pressure "	"	67.21	0.99	3623.55	53.50	5.49	0.08	14.35	0.21	1.42	0.02
Drinking Water	"	0.26	0.02								
Cooling Water (Take	"										
(Cr.	"										
Condensate - Oil free	"										
" - Oily	"	1/1.75	1/6.24	1/17.49	1/2.36	1/0.01		1/9.41	1/1.27	1/2.61	1/0.35
High Pressure Steam	"	42.74	130.87	99.78	302.17			14.46	43.79	5.44	16.47
Back " "	"	1/36.94	1/73.87	1/47.04	1/94.08			1/0.57	1/1.13		
Low " "	"	36.68	82.16	4.48	10.05	0.03	0.06	8.92	20.06	0.89	1.99
H.T. Electricity	KWH		–	857.44	16.10			219.20	3.31		
L.T. " Power	"	357.77	7.41	419.15	8.67	0.30	0.01	335.51	6.94	57.05	1.19
" " Light	"	1.16	0.02	4.21	0.09	0.04		0.35	0.01		
Fuel Gas	M³										
Workshops Gas	"							82.42	1.34		
Nitrogen 90 lbs/in²	"	5.08	0.08								
CO_2 7 lbs/in²	"	57.47	0.05								
Towns Gas	"										
Acetylene	"									6.87	0.02
Compressed Air	"	6.94	0.02	62.19	0.20						
Raw Brown Coal	Kg										
Bit. Coal & Coke	"										
03. Repair Costs			37.63		42.31		3.31		23.40		6.64
Foreign Workers wages, hrs.		0.30	0.42	0.31	0.31			0.26	0.26 0		
" " material & oncosts			0.76		0.35		0.01		2.84		
Stores Material			3.46		2.87		0.01		1/0.46		0.28
" " supplement			0.74		0.76				1/0.08		0.05
Workshops Wages. hrs.		10.53	12.47	12.04	14.40	1.03	1.27	6.91	8.19	2.00	2.49
" Costs supplement			19.76		23.26		2.02		12.54		3.81
Repairs - Transport charges			0.02		0.36				0.11		0.01
04. Running Materials			1.04		1.46		1.00		0.39		0.01
Materials			1.03		1.45		1.00		0.33		0.01
Stores supplement			0.01		0.01				0.06		
05. Traffic Costs			0.61		2.98		0.04		0.12		
06. Works General Charges			8.62		16.59		0.23		6.66		1.46
Wage & Salary s'ment			7.41		13.14		0.20		4.60		0.98
Fire Brigade			1.00		2.34		0.02		0.87		0.48
Post Office Costs			0.21		1.11		0.01		1.19		
07. Capital Charges			42.34		101.92		0.63		20.88		4.67
Writing off			32.59		78.30		0.49		17.51		3.92
Interest			9.75		23.62		0.14		3.37		0.75
08. Taxes			4.71		9.88		0.17		3.36		0.73
09. Various Costs			7.82		7.10		1/0.02		1.70		0.88
Laboratory			7.25		6.22		1/0.02		1.37		0.88
Other Costs			0.16		0.79				0.33		
Raw Material Stores			0.41		0.09						
Part cost Pipe-Bridges			5.89						6.46		4.31
" " Factory Wts. System			3.82								
" " Tip charges		Transferred to 5058 Catalyst Plant H.S. gas section									
10. Credits					1/2.47						
Production: Total:			286.22		524.18		6.27		152.23		41.43

1/ Designates credit against operating costs.

TABLE III. - BUILD-UP OF HYDROGENATION COSTS (Cont'd)

(Based on values of Nov. 1943 and a Motor Fuel Production of 72.40 Tnes/hr)

		Hydrogenation Drain Wtr. Treatment		Hydrogenation Phenol Separation		Hydrogenation Phenol Washing		Total	
		Qty/hr	RM/hr	Qty/hr	RM/hr	Qty/hr	RM/hr	Qty/hr	RM/hr
01. Wages			3.39		2.02		11.28		677.62
Wages to IG workers, hrs.		0.21	0.28	1.11	1.15	6.00	7.23	391.21	470.54
" "foreign " "		1.61	1.55					56.30	54.11
Salaries			1.47		0.74		3.35		111.98
Social Insurance, etc.			0.09		0.13		0.70		40.99
02. Energy Costs			3.54		6.15		19.20		2394.99
Low Pressure Water (Take	M^3					356.64	2.60	1093.11	7.96
Low Pressure Water (Cr.	"					1/351.33	1/1.60	1/371.09	1/1.69
High Pressure Water	"							9522.11	140.59
Drinking Water	"					0.15	0.01	9.07	0.85
Cooling Water (Take	"			2.66	0.10			2.66	0.10
Cooling Water (Cr.	"							1/596.41	1/19.99
Condensate - Oil free	"					1/3.82	1/1.11	1/39.98	1/10.49
" - Oily	"	1/0.23	1/0.03					1/84.28	1/11.39
High Pressure Steam	Tne	0.37	1.13			5.58	16.90	280.15	849.77
Back " "	"							1/112.93	1/225.83
Low " "	"	0.41	0.09	0.58	1.30	0.14	0.03	150.54	337.19
H.T. Electricity	KWH			53.11	0.80			15460.47	317.86
L.T. " Power	"	113.67	2.35	0.46	0.01	75.10	1.55	3667.38	75.90
" " Light	"			1.17	0.02	0.95	0.02	93.74	1.92
Fuel Gas	M^3							83665.04	741.80
Workshops Gas	"							65.72	1.54
Nitrogen 90 lbs/in^2	"					43.50	0.71	2633.62	26.63
CO_2 7 lbs/in^2	"			3240.38	2.79	10.53	0.01	14735.06	12.72
Towns Gas	"			16.48	0.47	0.27	0.01	16.75	0.48
Acetylene	"			196.89	0.66	22.21	0.07	2881.04	9.61
Compressed Air	"							45062.94	139.46
Raw Brown Coal	Kg								
Bit. Coal & Coke	"								
03. Repair Costs			7.18		1.31		12.42		1496.85
Foreign Workers Wages, hrs.		0.17	0.18					14.73	20.82
" " material & oncosts			0.86		0.08		0.53		116.26
Stores material			0.95		0.06		0.98		188.19
" " supplement			0.15		0.01		0.15		30.60
Workshops Wages hrs.		1.62	2.00	0.41	0.49	3.52	4.37	357.24	430.79
" Costs, supplement			3.04		0.67		6.30		698.31
Repairs - Transport Charges							0.09		16.88
04. Running Materials			0.25		0.70		16.04		57.63
Materials			0.22		0.68		15.96		54.19
Stores supplement			0.03		0.02		0.08		3.44
05. Traffic Costs			—				0.24		154.53
06. Works General Charges			1.34		0.77		3.42		297.93
Wage & Salary supplement			1.03		0.77		3.20		200.62
Fire Brigade			0.27		0.20		0.19		42.97
Post Office Costs			0.04				0.03		54.34
07. Capital Charges			10.25		4.63		5.20		1139.34
Writing off			7.94		3.83		4.08		921.10
Interest			2.31		0.80		1.12		218.24
08. Taxes			1.01		0.48		2.21		154.04
09. Various Costs			7.72				0.39		228.86
Laboratory			7.38				0.04		134.24
Other Costs			0.34				0.35		14.87
Raw Material Stores									79.75
Part cost Pipe-Bridges									16.66
" " Factory Wtr. System			26.28						73.86
" " Tip charges									4.43
10. Credits				For H_2S make Tne Cal.	1/7.04	For Creosote Oil "S" Kg	1/49.79		1/59.31
Production: Total			60.96		9.02		20.61		6637.43

1/ Designates credit against operating costs.

TABLE IV. - EXTRA CHARGES FOR AVIATION PETROL

		Circulation		Vapour Phase Injection		Vapour Phase Stalls		Vapour Phase Distillation		Rich Gas Fractionation		Total	
		Qty/hr	RM/hr	Qty/hr	RM/hr	Qty/hr	RM/hr	Qty/hr	RM/hr	Qty/hr	RM/hr	Qty/hr	RM/hr
01. Wages					5.59		12.54						18.13
Wages to IG workers.	hrs.			3.56	4.25	7.90	9.54					11.46	13.79
" " foreign "	"			0.04	0.03							0.04	0.03
Salaries					0.93		2.16						3.09
Social Insurance, etc.					0.38		0.84						1.22
02. Energy Costs			10.23		8.62		21.59		40.62		37.69		118.75
(Take	M³												
L.P. Water (Cr.	"	0.92	0.01			467.74	6.91	122.17	1.80	497.79	7.35	1088.62	16.07
H.P. Water	"							0.91	0.09			0.91	0.09
Drinking Water	"												
(Take	"												
Cooling Water (Cr.	"					1/75.62	1/2.53					1/75.62	1/2.53
Condensate, Oil free	"	1/0.94	1/0.13	1/0.22	1/0.03	1/0.05	1/0.01	1/0.42	1/0.06	1/2.91	1/0.39	1/4.54	1/0.62
" Oily	"	2.19	6.65	5.46	16.51	0.13	0.40	0.66	1.99	14.61	44.25	23.05	69.80
H.P. Steam	Tne			1/4.91	1/9.81					1/7.82	1/15.64	1/12.73	1/25.45
Back Pressure Steam	"	0.08	0.18					1.69	3.80	0.28	0.59	2.05	4.57
L.P. Steam	"	227.82	3.45	125.68	1.90	459.38	6.94	131.75	1.99	46.78	0.71	991.41	14.99
H.T. Electricity	KWH	3.52	0.07			30.51	0.22	113.14	2.34	37.55	0.78	164.72	3.41
L.T. " Power	"			1.43	0.03	0.50	0.01	1.31	0.03	0.70	0.01	3.94	0.08
" " Light	"					1092.59	9.62	3138.11	27.86			4230.70	37.48
Fuel Gas	M³					0.97	0.02	12.47	0.30			13.44	0.32
Workshops Gas	"							2.82	0.05			2.82	0.05
Nitrogen 90 lbs/in²	"			20.74	0.02							20.74	0.02
CO_2 7 lbs/in²	"												
Towns Gas	"												
Acetylene	"					2.51	0.01	127.89	0.43	10.34	0.03	140.74	0.47
Compressed Air	"												
Raw Brown Coal	Kg												
Bit. Coal & Coke	"												
03. Repair Costs					9.52		55.34						64.86
Foreign Workers Wages.	hrs.			0.06	0.07	0.06	0.07					0.12	0.14
" " Material & oncosts.	hrs.				0.94		3.13						4.07
Stores material					1.28		16.72						18.00
" " supplement					0.20		2.80						3.00
Workshops Wages.	hrs.			2.20	2.69	9.31	11.12					11.51	13.81
Workshops Costs Supplement					4.28		21.16						25.44
Repairs-Transport charges					0.06		0.34						0.40
04. Running Materials					0.75		0.97						1.72
Materials					0.65		0.87						1.52
Stores supplement					0.10		0.10						0.20
05. Traffic Costs					0.02		0.35						0.37
06. Works General Charges					2.78		7.40						10.18
Wages & Salary supplement					1.64		3.61						5.25
Fire Brigade					0.25		2.19						2.44
Post Office Costs					0.89		1.60						2.49
07. Capital Charges					4.52		46.24						50.76
Writing off					3.74		38.73						42.47
Interest					0.78		7.51						8.29
08. Taxes					1.11		3.38						4.49
09. Various Costs					0.07		10.13						10.20
Laboratory							7.04						7.04
Other Costs					0.07		0.28						0.35
Raw Material Stores							2.81						2.81
Part cost Pipe-Bridges													
" " Factory Water system													
" " Tip charges													
10. Credits													
Production: Total			10.23		32.98		157.94		40.62		37.69		279.46

1/ Designates credit against operating costs.

V. D.H.D. (DEHYDRIERUNG-HOCH-DRUCK) PROCESS

(i) Description of Process and Leuna operating results.

The DHD process was developed in Germany by the I. G. Farbenindustrie A.G. for the catalytic dehydrogenation of naphthenes to aromatics and was intended primarily for the use on hydrogasolines. The catalyst employed is 10% molybdic oxide on alumina and the reaction is carried out with recycle hydrogen under a pressure of 30-40 ats at a temperature slightly above 500° C.

Two DHD units had been completed at Leuna and one of them had operated for 3 months. Two further units were in course of erection.

The method of operating the process is shewn in the simplified flow diagram in Fig. XII. & XIII.

Full boiling range (IBP-185°C) hydrogasoline is first fractionated to ~~remove, as an overhead cut, the lower boiling material boiling up to 85°C.~~ The bottoms from this prefractionator are mixed with recycle gas containing 55-65% hydrogen. 1 cu.m. of recycle gas is used per kg. of liquid feed.

The mixture of gasoline and recycle gas is first preheated by heat exchange with the product from the end reactor; then by heat exchange with material from the fourth reactor, and finally by convection heating to a four-chamber convection heater. The pressure at the inlet of the first exchanger is 42 ats, and at the inlet of the first reactor it is 37 ats.

The feed enters the first reactor at 500°C and passes downward through the catalyst bed and leaves at 450°C. The mixture is then reheated in one section of the heater to 510°C, and enters the second reactor under 34 ats pressure. The material leaves the bottom of the second reactor at 490°C, is reheated in a third section of the heater and enters the third reactor at a temperature of 520°C and under a pressure of 31 ats. The outlet from this reactor at 510°C is again reheated in the fourth section of the heater and enters the fourth reactor at 530°C under a pressure of 30 ats. Each section of the preheater has its own burner and independent fuel gas, air and recycle gas supply. At the outlet of the fourth reactor, the dehydrogenation reaction is completed. The effluent from this reactor at 530°C. is cooled to 300°C by heat exchange with the fresh feed and passes to the fifth reactor for hydrogenation of the olefins. The effluent from this fifth reactor exchanges heat with the fresh feed and passes through a cooler to a receiver for the separation of the gas from the liquid. The gas is principally methane and hydrogen with some ethane and very little C_3-C_4. At the beginning of the cycle, the gas contains about 65% hydrogen, and at the end of the cycle about 55% hydrogen. The density of the recycle gas at 15°C and 735 mm. is 0.38-0.45 kg per cubic metre. A part of this gas is recycled with the fresh feed, as explained above, and the remainder removed from the system as tail gas.

The liquid product from the receiver is let down, fractionated to remove the heavy materials and then sent to a stabilizer along with the LBP-85°C cut from the initial charge. In the stabilizer, the ethane to butane product is taken overhead and the DHD gasoline is made as bottoms.

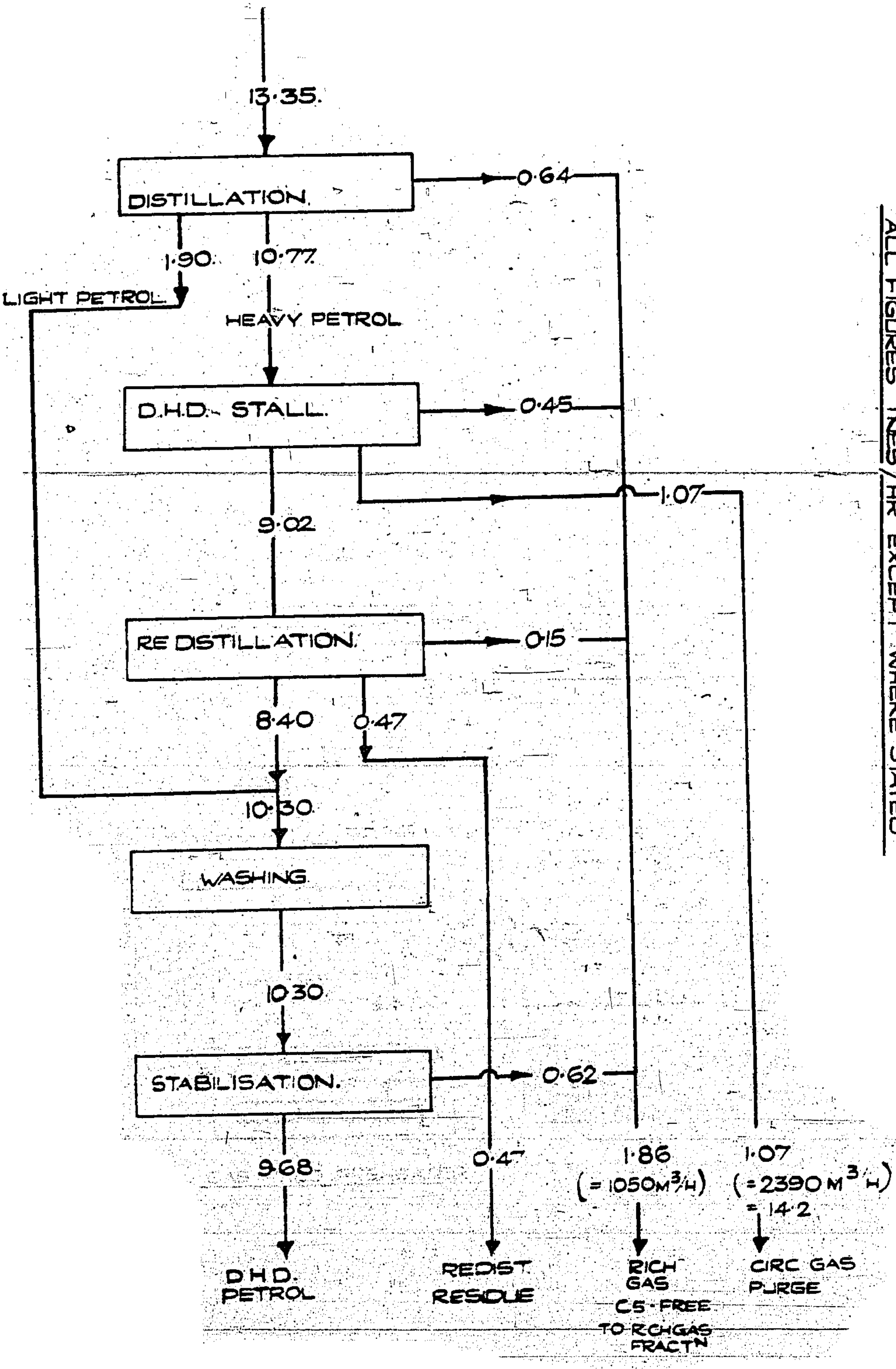


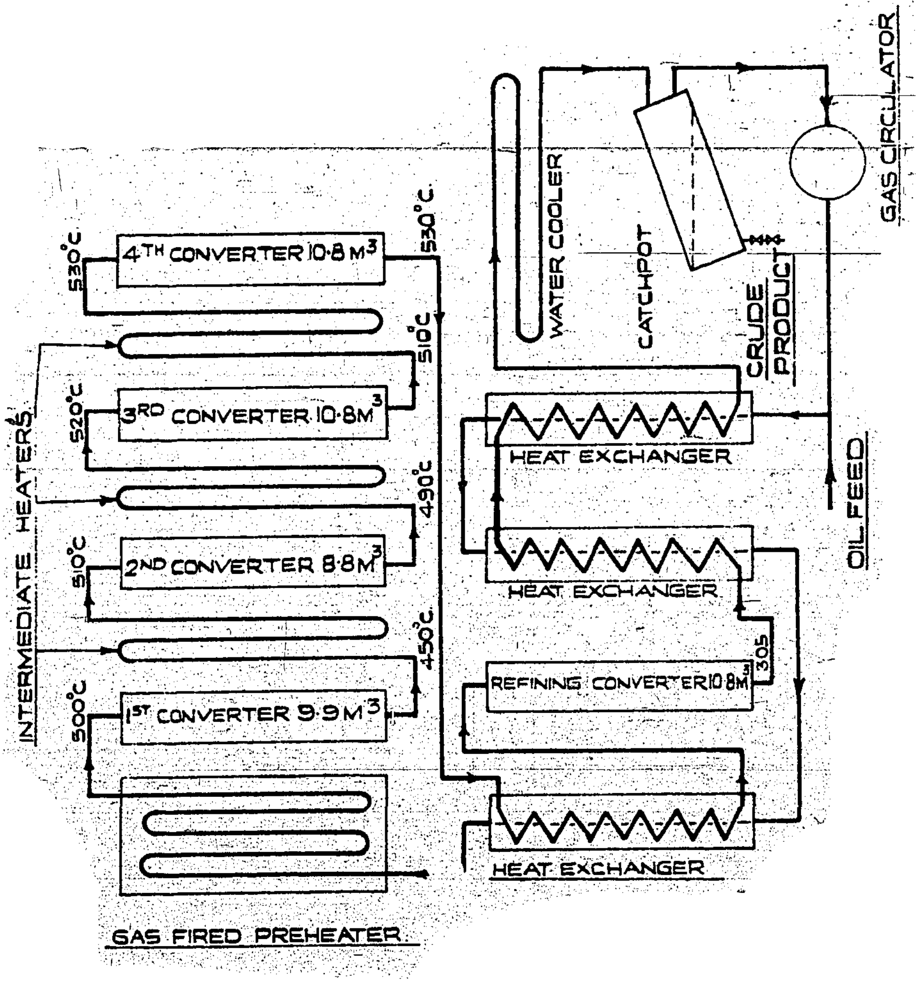
FIG XII FLOWSHEET FOR D.H.D.

BASED ON ACHIEVED RESULTS 1ST QTR. 1944.

ALL FIGURES TNES/HR EXCEPT WHERE STATED

FIG. XIII

FLOW DIAGRAM, D.H.D PROCESS



The total hydrocarbon gas made is purged from the circulating gas and evolved on let down of the liquid product and on its subsequent stabilization amounts to 19-20% by weight of the original hydropetrol, i.e. about 25% by weight of the naphtha fed to the process. The gas is comprised of roughly equal proportions by weight of methane, ethane, propane and butane.

The catalyst used in all five reactors is active alumina on which has been deposited 8-10% MoO_3. It is prepared by the impregnation of activated alumina with ammonium molybdate solution. The catalyst is used in the form of 8-12 mm. cubes and is placed in the reactors in a single bed. It was originally planned to operate the DHD unit with a liquid space velocity of 0.38 kgs of liquid per litre of catalyst. In actual operation, space velocities of 0.25-0.32 were the highest obtainable. The length of the on-stream cycle on the catalyst depends upon the charge stock and varies from 120-240 hours. The regeneration period with the necessary purging operation requires about 24 hours.

At the end of the on-stream cycle, the reactors are first depressured and filled with nitrogen to 10 atmospheres pressure, depressured again and filled with nitrogen to 70 ats pressure. The recycle compressor is then started and air is admitted to the recycle gas stream until the oxygen conten at the inlet of each reactor reaches 1%. 20,000 cu.m. of gas are recycled per hour through each reactor. The normal time of regeneration is about 12 hours. Oxygen concentration in the recycle gas is controlled to hold the regeneration temperature to slightly less than 540°C. During regeneration, 1 cu.m. of water is added per hour, either at the second heat exchanger or at the cooler, for removal of acidic compounds produced during regeneration. In some cases, it has been necessary to use dilute caustic at this point. It is necessary to remove SO_2 sulphur dioxide completely from the recycle gas, but the carbon dioxide concentration can go up to 8-13% without harmful effects. At the end of the regeneration cycle, the inert gas is stored in cylinders for re-use on the next regeneration. The catalyst chambers are depressured and then filled with the regular recycle gas from storage for the subsequent on-stream cycle.

The reactors are the usual high pressure reaction vessels having a flanged top head. The inside diameter of the reactor is 1320 mm. The first reactor is 11 metres in length and the remaining four reactors are 13 metres in length. The reactors are lined with firebrick in order that the outer reactor wall temperature does not exceed 200°C. The exchangers are conventional tube and shell units with the fresh feed in the shell in all cases. The convection heater employs flue gas recirculation and all heating is done by convection heat rather than by radiant heat. The fractionating system is the conventional bubble plate tower type.

The finished debutanized DHD gasoline, which includes front ends from the gasoline charge, contains 50-52% by weight of aromatics. The octane number is 80.5 CFR motor method. It appears that some paraffins are converted to aromatics in the process. Other properties of DHD Plant feed materials and products are given in Table V.

TABLE V. - LEUNA D.H.D. PLANT PROPERTIES OF FEED AND PRODUCTS

	0-85°C Light Petrol	85°-180°C Naphtha feed to D.H.D. Process	Stabilised D.H.D. Product	Final DHD Petrol Blend
Aniline Point	52	45	1.6	6.9
Aniline Point after treatment with sulphuric acid	55.4	-	63.2	61.0
Wt.% aromatics	4.5	9.5	66.0	52.0
Wt.% Naphthenes	46.2	51.2	7.9	14.4
Wt.% Paraffins	48.7	38.1	25.9	33.0
Wt.% Olefines	0.6	1.2	0.6	0.6
Motor Method Octane No.	73.5	52.0	82.5	80.5
Motor Method Octane No. with 0.12% by vol. TEL.	-	-	-	91.5

(ii) Costs

Dr. Pichler provided the following cost data for the DHD process.

The basic flowsheet assumed for the cost calculation is shown in Fig. XIII.

Table VI analyses the cost of manufacture of DHD gasoline in terms of raw material charges and operating costs and shews the credit for hydrocarbon gas.

Table VII gives a breakdown of the operating costs and provides the data on labour requirements, utilities consumption, etc., for calculation of the costs of the process if operated in U.S.A. or Britain.

TABLE VI. - CALCULATED COSTS FOR D.H.D. PETROL

(Based on Works Costs for 1st Qr., 1944)

	Unit	Cost RM/Unit	Per Hour		Per Tne DHD Petrol	
			Quantity	RM	Quantity	RM
A. Materials						
1) Petrol	Tonne	1/170.14	13.35	2,271.37	1.379	234.65
2) Catalysts & Chemicals				29.04		3.00
3) By-Products						
Circ.Gas Purge	10^6 Tne Cal.	7.00	14.2	4/99.40	1.467	4/10.27
Rich Gas	"	2/11.35	20.5	4/232.68	2.118	4/24.04
Redistilln Residue	Tonne	100.00	0.47	4/47.00	0.049	4/4.86
B. Running Costs3/ (See Table VI)				594.26		61.59
Production Cost			9.68	2,515.59	1.000	259.87
C. Loading & Evaporation	Tonne	3.00	9.68	29.04	1.000	3.00
D. Oncosts				262.62		27.13
Works Cost (without conversion and oil taxes and other special costs)			9.68	2,807.25	1.000	290.00

1/ This cost has been taken from Table 1.

2/ Butane and Propane in Rich Gas valued at Motor Spirit valuation less cost of separation.

3/ It is estimated that for 4 DHD Stalls, the running costs would be 42 RM/Tne DHD Petrol and the Works cost, 270 RM/Tne DHD Petrol.

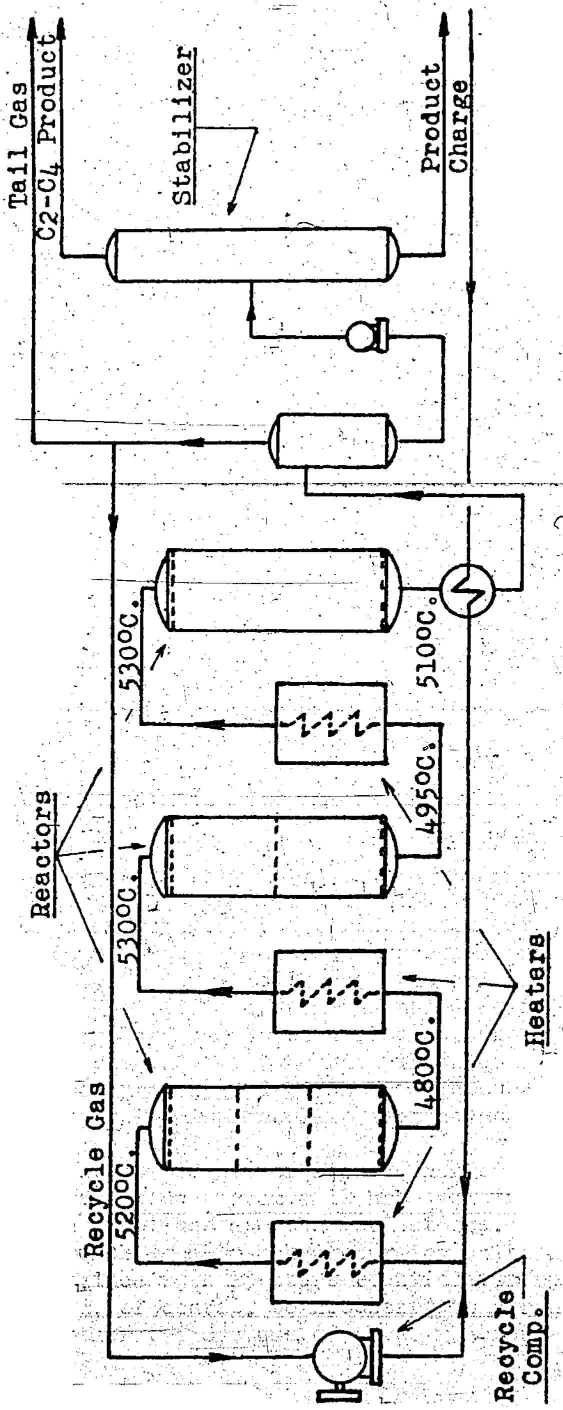
4/ Designates credit against operating costs.

TABLE VII. - BUILD-UP OF RUNNING COSTS FOR DHD PETROL

		Cost per hour		Per Tne DHD Petrol.	
		Quantity	RM	Quantity	RM
Labour Costs			35.94		3.71
Wages	hrs.	21.76	26.56	2.25	2.74
Salaries			7.07		0.73
Social Insurance			2.31		0.24
Energy Costs			163.65		16.91
Water	M³	805.38	13.35	83.20	1.38
H.P. Steam	Tne	21.43	67.44	2.21	6.97
I.P. Steam	Tne	9.76	1/20.10	1.01	1/2.08
L.P. Steam	Tne	5.63	13.41	0.58	1.39
H.T. Electricity	KWH	1,881.31	26.47	194.35	2.73
L.T. Electricity	KWH	267.52	5.23	27.64	0.54
Fuel Gas 10^3	Tne-Cals.	6,461.04	58.13	667.46	6.01
Other forms			1/0.28		1/0.03
Repair Costs			49.17		5.08
Wages	hrs.	13.19	15.62	1.36	1.61
Material			6.98		0.72
Workshop and Material on cost			26.57		2.75
Working Materials			1.71		0.18
Traffic Charges			0.25		0.03
Works General Charges			20.04		2.07
Capital Charges			297.29		30.70
Writing off			192.78		19.90
Obsolescence			104.51		10.80
Taxes			20.88		2.16
Various Costs			6.01		0.62
Credits			1/0.68		1/0.07
TOTAL:			594.26		61.39

1/ Designates credit against operating costs.

FIG. XIV



FLOW DIAGRAM - HYDROFORMING PROCESS

VI. HYDROFORMING PROCESS.

The hydroforming process was invented in Germany by the I.G. Farbenindustrie A.G. before the war and the basic patents were held by the Germans. The process was developed in America for the production of aromatics from straight run gasoline. No commercial units had been built in Germany prior to the war, and the Leuna pilot unit was the forerunner of the only large-scale hydroforming plant now operating in Germany, namely that designed and built by the I.G. at Moosbierbaum. The capacity of the plant is 7,000-7,500 tons of finished product per month; this was to be expanded to 14,000 tons per month, but the project did not materialize. The unit at Leuna is similar in some respects to the units in the United State, but in others, quite different. A simplified flow diagram of the Leuna unit is attached as Fig. XIV.

Charging stocks were primarily straight run gasolines and the catalyst used was a molybdena on alumina catalyst containing 5-10% MoO_3.

The Leuna unit consists of two reactor systems of three reactors each. One system is on stream while the other is on regeneration.

It was thought necessary by the Germans to vary the activities of the catalyst in the different reactors by varying the MoO_3 content and the particle size in order to obtain a uniform coke laydown. The catalyst in the first reactor is divided into three zones, i.e. the top zone containing a catalyst with 5% MoO_3 and with a particle size of 10-15 mm.; a middle zone, also with a particle size of 10-15 mm., containing 10% MoO_3, and a bottom zone containing 10% MoO_3 but with a particle size of 6-10mm. The second reactor has two zones of catalyst, both with a MoO_3 content of 10%, but with a 10-15 mm. size in the upper zone, and a 6-10 mm. size in the bottom zone. The third reactor contains one bed of 6-10 mm. catalyst with 10% MoO_3.

The charge first exchanges heat with the effluent from the third reactor and is then mixed with 600-1000 cu.m. of recycle gas per cu.m. of charge containing 50-60% hydrogen preheated to 520°C. under 15 atms. pressure. The material leaves the bottom of the first reactor at 480°C., is reheated to 530°C., passes down through the second reactor and leaves at 495°C. It is then reheated to 530°C., passes through the third reactor containing the more active catalyst. The effluent from the third reactor at 510°C. exchanges heat with the charge and passes to a receiver where the recycle gas is separated and the gas made is removed. The liquid is then charged to a stabilizer where ethane, propane and butane are removed as an overhead product and the debutanized hydroforming gasoline is made as bottoms.

The throughput is 600 gr. of liquid charge per litre of catalyst volume. The three reactors are on-stream 6-12 hrs. and on regeneration for 6-12 hours when straight run gasolines are the feed stocks. It was reported that, if hydrogasolines are charged to a hydroforming unit, an on-stream time of 100 hrs. would be obtained with 25 hours required for regeneration. With such an operation it would, of course, be necessary to arrange the unit in a different manner from the other two systems of three reactors employed at Leuna.

The catalyst is regenerated in situ by recirculation of inert gas and the introduction of controlled amounts of air. At the beginning of the regeneration cycle, the gas contains 1-1½ % air, and at the end 10-15% air. The regeneration air is controlled so as not to exceed 550°C. during any part of the cycle. It was believed by the Germans that this is highly important in order to obtain a long catalyst life, although the catalyst life obtained was only in the order of 6 months.

The catalyst was prepared by impregnation of activated alumina with ammonium molybdate solution. It was reported that the catalyst was relatively inactive during the first on-stream cycle until the last traces of ammonia were removed by the first regeneration.

The feed stock was prepared by first distilling overhead 10-15% of a material boiling below 90°C.; the remainder was then hydroformed, the hydroformate was blended with the overhead cut from the primary distillation. A yield of 76% hydroformate based on the total straight-run gasoline charge was obtained with a yield of 72-73% based on a case charge. The length of the cycle was controlled to maintain a minimum of 50% concentration of aromatics in the final product. Typical inspection of the charge and product obtained from a mixed base charge is as follows:-

	Charging Stock.	Product.
Sp.gr.@ 20°C.	0.750	0.776
IBP. °C	62	44
% over at 100°C.	18	36
% over at 160°C.	95	94
RVP atms.	-	0.4
Bromine Number	0.51	2.3
Olefins	0.5	1.5
Aromatics	14	54
Naphthenes	44	8
Paraffins	41.5	36.5
% C.	85.46	87.74
% H.	14.53	12.26
Octane No. MM.	58.5	80
Octane No. MM. plus 0.12% TEL.	79.0	91

Information was obtained on the results from the hydroforming of paraffin base, mixed base and brown coal hydrogasoline in the pilot unit. These are as follows:-

Charging Stock.	Paraffin Base.	Mixed Base.	Browncoal Hydrogasoline.
API gravity of charge	51-52	48-50	44
Products % by weight:			
H_2	1.35	1.45	1.5
C_1	3.5	5.1	2.8
C_2	5.0	5.25	4.0
C_3	6.0	5.4	4.1
i-C_4	1.7	4.75	1.1
n-C_4	3.2		2.1
Coke	1.2	0.7	0.2
Gasoline, IBP 165°C.	74.5	78.3	80.9
Residue	3.6	3.4	3.4

It was proposed to subject the heavy hydroformate boiling above 165°C. to a hydrocracking operation described in section VII - Arobin Process.

It should be noted that the Leuna people were not too well satisfied with their present hydroformer design and have made experiments on hydroforming in a tubular reactor. The experimental unit employed consisted of five tubes with a 60 mm. diameter, each tube containing some 25 litres of catalyst. The tubes were heated by flue gas from an auxiliary burner, and a temperature of 510°C. was maintained throughout the length of the tube. In actual operation, of course, the temperature was varied with the charging stock used to give a desired aromatics concentration in the product. The space velocity used in the tubular reactor was 0.8 kg. of feed per litre of catalyst, as compared to 0.6 kg. of feed per litre of catalyst used in the present unit. The same recycle gas to feed ratio was maintained. It is claimed that the use of the tubular reactor resulted in a 5 percent increase in yield for the same aromatic concentration in the product. Furthermore, it was possible to increase the on stream time using straight run to 20-50 hours, the ratio of on stream to regeneration times being 4-5 to 1. It should be emphasized that the above results are those of a relatively small pilot plant, but it is significant that the I.G. had decided on a plant of this type for the projected Moosbierbaum extensions.

VII. AROBIN PROCESS

The Arobin process is a method of manufacture of aromatics from the high boiling residues of the DHD (dehydrogenation of naphthenes) and the HF (hydroforming) processes. The available charge stock consisted of about 5% residues from the distillation. The process was developed to the pilot plant stage only, with a catalyst volume of 25 cubic ft., and a charge rate of 120 gallons hour.

The following details of the process as applied to HF plant residues were secured from Dr. Herold of Leuna, who is in charge of development work on further utilization of products from existing processes.

Charge to Arobin Plant

Bottoms from HF process charging mixed Rumanian and Hungarian straight run gasoline:

API Gravity	21.2
Engler Distillation	
IBP	316°F.
50%	383
E.P.	676
Bromine No.	14.4
Aromatics & Olefins	98.5%
Pour Point	-66°F.
Elementary Analysis:	
Carbon	90.59%
Hydrogen	9.42
Sulphur	0.08

Operating Conditions

Catalyst Temperature (According to Catalyst activity)	752-852°F.
Space velocity (liquid)	0.65 vol. oil/vol. catalyst/hr.
Gasoline concentration at stripper	50% (by volume)
Pressure	2,940 psi
Circulating gas	1000-5000 volumes/volume gasoline/hour, to control the heat of reaction (about 0.360 BTU/lb charge)
Chemical consumption of hydrogen	5.45-6.20 cubic ft./lb of finished gasoline.

Catalyst - "KK" catalyst + 1% MoO_3 (see below for method of preparation)

The MoO_3 acts as a hydrogenation catalyst and thus prevents the formation of polymers which would cause coking.

Yield and Quality of the Product

Average Net Yield	Weight %
Methane	0.2
Ethane	1.7
Propane	4.8
Isobutane	3.8
N-Butane	2.4
Gasoline	85.7
	98.6

Quality of the finished product (Arobin)	
API Gravity	43.2
Octane No. (Motor Method)	86
+ 4.55 cc/gal TEL	93.5
Bromine No.	0.84
Reid Vapour Pressure	5.9
Corrosion	Neg.
Freezing Point	Below -76°F.
Gum (Glass dish)	4.0 mg/100 cc
Aniline Point	Below -4°F.
Aromatics & Olefins	65.0 Vol.%
Naphthenes	27.0
Paraffins	8.0
Elementary Analysis	
Carbon	88.50%
Hydrogen	11.45

Engler Distillation	
IBP	117°F.
7.0% at	176
20.0	212
41.0	248
72.0	284
95.0	320
99.0	333
Residue	0.8%

Preparation of the Arobin Catalyst

1. **Preparation of alumina.** Commercial alumina is dissolved in hot 25% caustic solution, to give about 1.66 lbs. Al_2O_3/gallon. This solution is added to 45% nitric acid to give a pH of 6. Precipitation temperature not over 122°F. After precipitation, the solution is filtered or decanted, the precipitate is washed with pure water until the effluent shows no nitrate, and dried at 248°F, until the ash content is about 70%.

2. **Preparation of silica gel.** Waterglass solution (Sp. g. 1,333, SiO_2 27%) and 10% sulphuric acid are reacted at 50-59°F to give a 3-4 pH. On heating to 158-176°F, the clear sol congeals. This gel is broken into 1-1/4"-2" pieces and washed until the wash water shows no trace of sulphate. The gel is dried at 248°F to an ash content of about 70%. It is pulverized in a mill (Wibratom) until at least 90% of the powder will pass a 10,000 mesh (per unit) sieve.

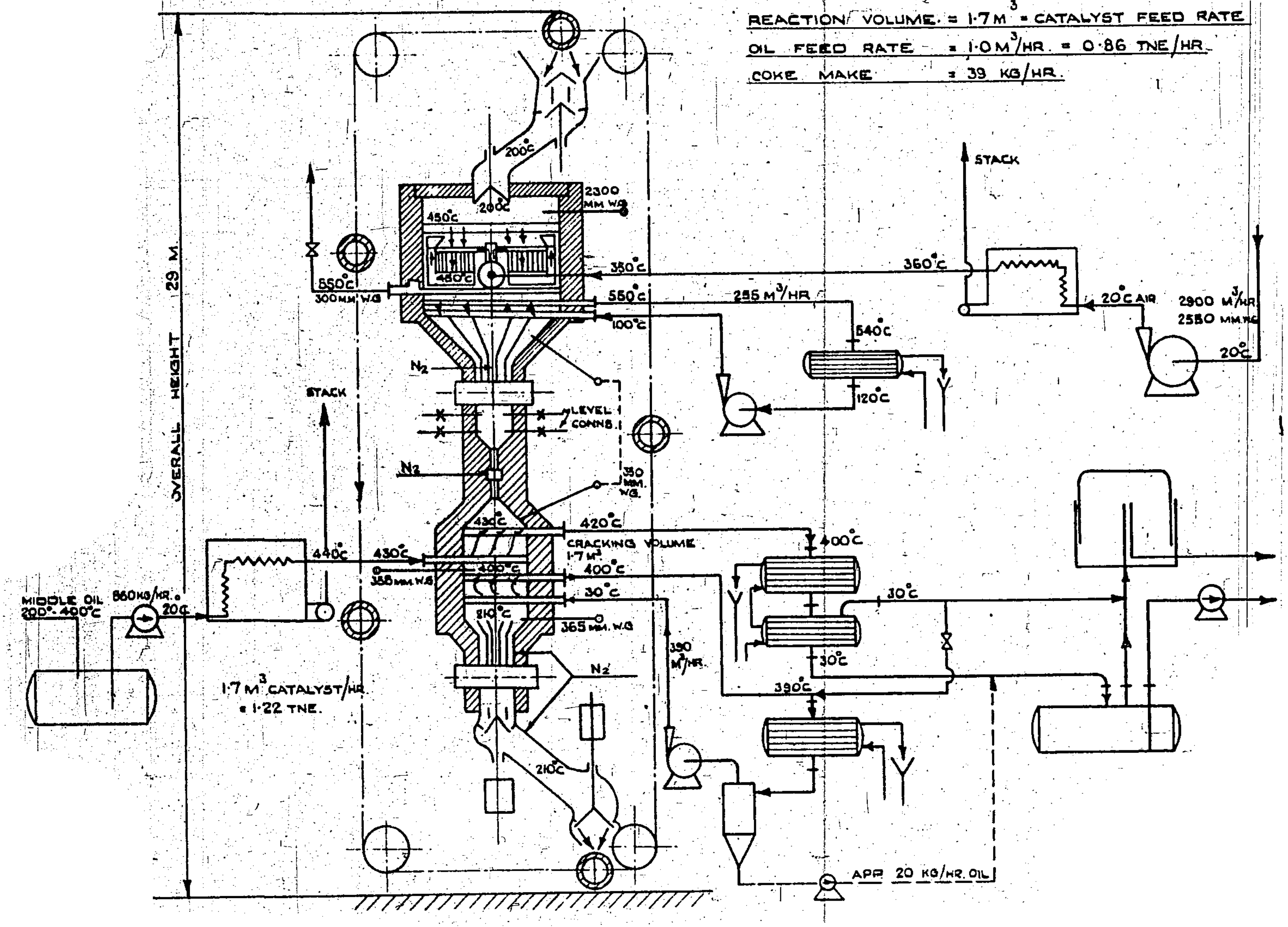
3. Preparation of the "KK" Catalyst from the gel. The alumina is kneaded in a kneading machine with enough water to make a plastic mass. A 45% nitric acid solution is added, the quantity being 10% of that theoretically needed to form aluminium nitrate. Then the powdered silica gel is added with continuous kneading to give a ratio Al_2O_3: SiO_2 = 1:9. The mass if further kneaded for 6 to 10 hours. The mass is then extruded for feed to an adjoining candy manufacturing machine (Franconia), where it is formed into spheres.

4. Preparation of the Arobin Catalyst. The above spheres are soaked with ammonium molybdate solution made up in such proportions that one weight per cent MoO_3 is absorbed. The spheres absorb practically all the liquid. They are then drained and dried at 356°F.

A 5-pound sample of this Arobin catalyst was secured for further testing.

FIGURE XV

CATALYTIC CRACKING RESEARCH UNIT DEUBEN

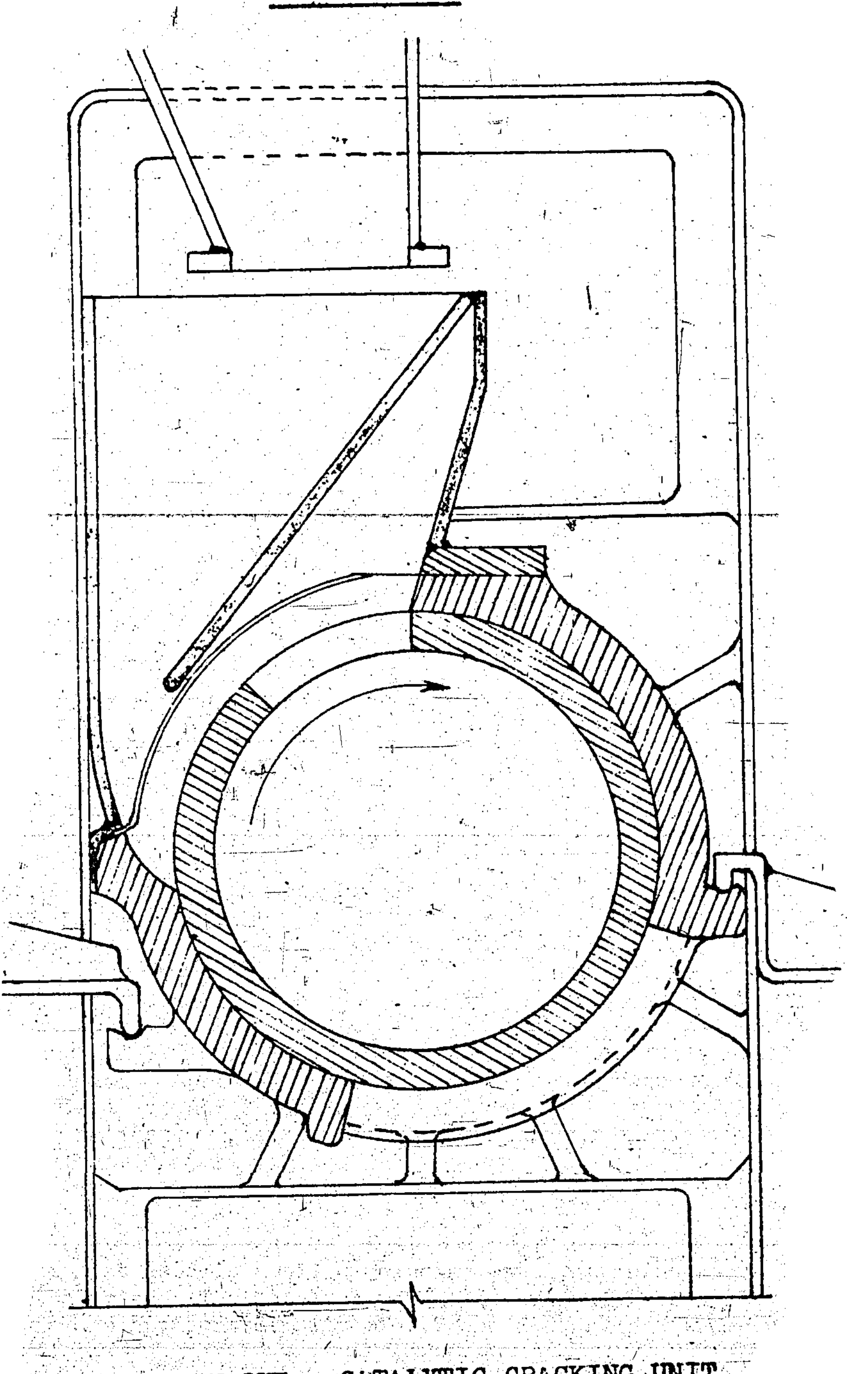


REACTION VOLUME = 1·7 M³ = CATALYST FEED RATE

OIL FEED RATE = 1·0 M³/HR. = 0·86 TNE/HR.

COKE MAKE = 39 KG/HR.

FIG. XVI



CATALYST VALVE - CATALYTIC CRACKING UNIT

VIII. CATALYTIC CRACKING.

Introduction

Catalytic cracking was not being employed on any appreciable scale in Germany. Experimental work was being carried out at Leuna on a catalytic process similar to the TCC process, using a silica alumina catalyst, and there was a pilot unit of 20 litres catalyst capacity which could process 12 litres of oil per hour. A larger unit (at Deuben near Zeitz) was essentially complete, and was designed to process 1,000 litres of oil per hour. The Deuben plant has not been in operation, however. It was also planned to build a commercial unit as part of an underground aviation gasoline plant near Nordhausen. A sketch of the proposed reactor-regenerator set up is attached as Fig. XV.

Reaction Conditions

The regenerator is mounted above the reactor so that the regenerated catalyst is fed to the reactor by gravity. Spent catalyst from the bottom of the reactor is elevated to the top by means of an open bucket elevator. The main regeneration zone consists of an air-catalyst exchanger device where the air for regeneration passes through the inside of reactangular plate sections and is preheated by the catalyst passing on the outside. The preheated air from this section then passes up to the top of the regenerator in an outside duct, and then passes down through the catalyst and leaves the regenerator through a collecting device below the air preheater section. The object of the air preheater section, in addition to that of heat economy, is to control the temperature of regeneration so as not to exceed 550°C. Below the regenerating zone, the catalyst is cooled with recirculated inert gas and then passes through a feeder into the reaction zone. Oil enters the reactor about the middle of the reactor through a distributor and passes upward through the top half of the catalyst bed and leaves through a collecting device. In the bottom half of the reactor, the catalyst is stripped with inert gas and then discharged through a second feeder similar to the one located between the regenerator and the reactor. No steam stripping is used anywhere in the system as it was thought to be detrimental to catalyst activity.

The catalyst feeder mechanism or valve consists of concentric cylinders, the inner cylinder being rotated so that on each revolution, the cylinder is filled with catalyst in an upward position, and the catalyst discharged in a downward position. Apparently, this feeder had not been used on any commercial unit and it was not known what trouble would be encountered with erosion by the catalyst dust. A detail drawing of this feeder was obtained. A cross-section is attached as Fig. XVI.

Catalyst

The catalyst used is a silica alumina catalyst, nine parts of silica to one part of alumina. The catalyst particles are white to yellow round granules with an apparent density of 0.7 and a crushing strength of 10-30 kg.

The alumina for the catalyst is prepared by dissolving technical aluminum oxide in 25% sodium hydroxide solution in the proportions of 1 mol. of Al_2O_3

to 1.5 mols of Na_2O. The solution contains 300 gr. of Al_2O_3 per litre. Water is added to the solution equivalent to one-third of the final total volume. To this solution is added 45% nitric acid while maintaining a pH of 6-7 antimony electrode. The temperature during the precipitation is allowed to rise about 50°C. The precipitate is filtered and the cake is washed either in a filter press or by decantation until the wash water is clear of nitrate ion. The alumina is then dried to a 30% water content by heating at 120°C.

Silica gel is prepared by mixing a water glass solution containing 27% SiO_2 with a specific weight of 1.333 with 2N sulphuric acid at a pH of 3-4 and a temperature of 10-15°.

The silica gel is then produced by heating to 70-80°C. The gel is then broken into pieces of 3-5 cm. size and washed with water by decantation until the wash water is free of sulphate ion. The wash water is either distilled water or steam condensate with 2-3 degrees hardness. 100 kg. of gel require approximately 40 cu.m. of wash water. The gel is then dried at 120°C. to 30% water content, powdered in a vibrating mill to a particle size of 90% through a sieve having 10,000 openings per square cm.

The aluminum hydroxide is kneaded with sufficient water to produce a plastic mass containing 50-60% solids, and then peptized with sufficient 45% nitric acid to convert 10% of the material to aluminum nitrate. The silica gel is then added to this peptized aluminum hydroxide and the mass kneaded for 6-10 hours. The catalyst is then pressed and transferred to a candy-making machine (Frankoma) and formed into spheres of about 1-4 inch diameter. The spheres are dried at 120°C. and then calcined at 450°C. for 4 hours.

An alternative method of catalyst preparation consists of mixing the gels, both containing about 30% water, in a mixer and then kneading them with water for 1 to 3 hours. No nitric acid is used in this preparation to peptize the aluminum oxide.

The catalyst is said to be amorphous since X-ray pictures show a general dark field with a few weak and unclear lines principally from crystalline aluminum oxide. If the catalyst is calcined for a longer period of time at 550°C., the X-ray pictures show definite evidence of recrystallization of the alumina.

Products

A typical pilot plant operation cracking a light Hannover gas oil of 165-350°C. boiling range at a space velocity of 0.6 volumes of oil per volume of catalyst per hour, and a residence time of one hour gave the following results:

Dry gas	3 wt.%
C_3-C_4	14 wt.%
C_5-165°C.	30-33 wt.%
Coke	5%
Residue	45-48%

The C_3-C_4 fraction contains 60% C_3 and 40% C_4, 75% of the C_4 cut being isobutane. The C_5-165°C. gasoline fraction contained 5-8 wt.% olefins, 25%

aromatics and 67-70% paraffins and naphthenes. The octane number of this fraction with 0.12% by volume of TEL was 90-92 MM.

Catalyst Life

Catalyst life tests in a 1.2 litre catalyst testing apparatus indicated that the catalyst life decreased from a yield of 30% C_5-165°C. fraction to a 25% yield in 6-9 months. The oil used for these catalyst life tests was a 200-400°C. mixed base gas oil from the Vienna district.

Pilot plant tests were also made on cracking a brown coal middle oil and a hard coal middle oil. The highest rich-rating gasoline was made from hard coal middle oil. The lowest rating was obtained from cracking gas oil, and the brown coal middle oil gave an intermediate result.

Hydrogenation of Product

Experiments were conducted in the laboratory on hydrogenating the residue from the catalytic cracking unit using a catalyst containing equal molecular proportions of nickel oxide and tungstic acid at a temperature of 400 C. under 200 atms. pressure with 2000 litres of hydrogen per litre of charge. A second catalyst was also tried which contained 10% tungstic acid on activated alumina at 450°C., but this catalyst produced considerable cracking. 5-8% gasoline with a low octane number was obtained. With the nickel oxide-tungstic oxide catalyst, no cracking was obtained. The catalytic cracking of this hydrogenated residue, which was more paraffinic than the original charge, produced results similar to those obtained on the fresh charge.

Some work has been done on the cracking of pure normal decane, normal decene and decalin. It was found that decalin was the easiest to crack, normal decane being the most difficult and normal decene intermediate. There was little difference in the refractivity of the normal decene and the decalin, however.

Conclusions

Apparently the Germans had not been doing any work on a fluid type catalytic cracking process, and are not, at the present time, very familiar with handling any sort of catalytic process in which the catalyst is used for short periods and then regenerated. The proposed catalytic cracking unit for Nordhausen is apparently the first attempt by them to employ a catalytic process of this type. It is doubtful if anything new is to be learnt from the Germans on catalytic cracking of gas oil, with the presumable exception of their low-temperature regeneration of catalysts. The low temperature regeneration apparently gives considerably longer catalyst life, but this of course has not been proven by commercial operation.

IX. DEHYDROGENATION OF BUTANE - ALKYLATION.

Introduction:

In the course of the visit to Leuna, information on catalytic butane dehydrogenation and alkylation of the resulting butylenes was obtained from Dr. Giesen, Dr. Hanisch and Dr. Strätz. Dr. Giesen is in overall charge of the manufacture of organic chemicals, alcohols and lubricating oils; Dr. Hanisch supervises the manufacture of methanol, isobutyl alcohol, amines, ester oils, synthetic lubricating oils and alkylate, as well as the manufacture of catalysts. Dr. Strätz is in charge of the butane dehydrogenation and alkylation plants.

Summary of Operations:

The alkylation plant produced an average of 888 bbls. of finished alkylate per day, together with 20 bbls. of heavy alkylate and 72 bbls. of propane. The necessary amount of n-butylenes was obtained by charging 2,640 bbls./day of n-butane (96%) to the dehydrogenation reactor yielding, after proper separation, 2,510 bbls. of a butane/butylene mixture (535 bbls. n-butylenes, 1,905 bbls. n-butane, 72 bbls. propane) as alkylation feed stock. The total amount of iso-butane (85%) charged to the alkylation step was 3,797 bbls./day. The daily requirements of fresh gas to supplement the recycle gas were 558 bbls. of n-butane and 760 bbls. of isobutane. The isobutane-olefin ratio was about 6:1, the hydrocarbon-acid ratio was 1:1, and the acid consumption amounted to 1.2 lbs. of 96% H_2SO_4 per gallon of finished alkylate (45,700 lbs. of acid/day). The alkylation acid was discarded when the concentration had decreased to 90% H_2SO_4. A summary flowsheet of these operations is given in Fig. XVII.

Dehydrogenation:

The catalytic butane dehydrogenation was carried out at Leuna in 7 reactors of which 5 were operated simultaneously while one was inspected and repaired and one was held in reserve. The catalyst was regenerated in 4 regenerators. The reactor consists of a vertical firebrick-lined circular furnace containing 8 catalyst tube bundles with 16 tubes each. The tube bundles are arranged around an annular central heating space which is brick-lined in such a way as to form a Venturi tube which passes the heating gas into the upper part of the furnace from which it flows downward around each of the reactor tube bundles. Heating gas is obtained by burning waste gas in a chamber situated below the central part of the furnace. The combustion gases are collected in a firebrick ring and thence leave the reaction chamber. Before leaving through the stack the combustion gases are used to preheat the n-butane feed. The flow of catalyst, n-butane and combustion gases is concurrent, as illustrated in Fig. XVIII.

The tube bundles, which represent the reaction space proper, consist of 16 Sicromal-8 tubes (about 8% Cr, 1 - 2% Si) each of which has a diameter of 2-3/4" and a length of 26'3"; the tubes are arranged in a circle around a centre core which is dead space. The total catalyst capacity of each reactor is 81 cu.ft. The catalyst is introduced at the top of the reactor and distributed to the individual tube bundles by means of a cone. The catalyst moves

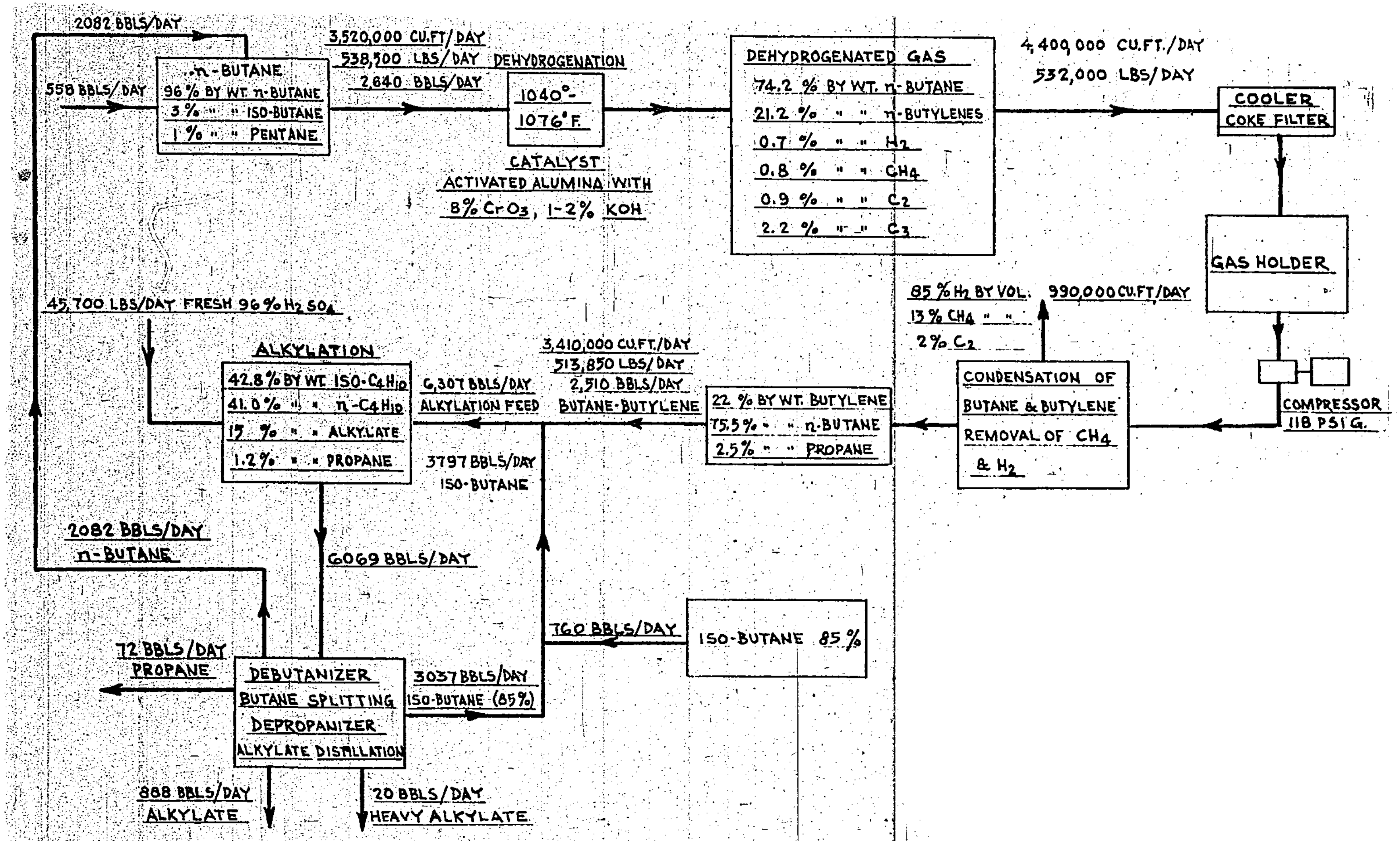


FIGURE XVII - MATERIAL BALANCE - BUTANE DEHYDROGENATION & ALKYLATION LEUNA - WERKE

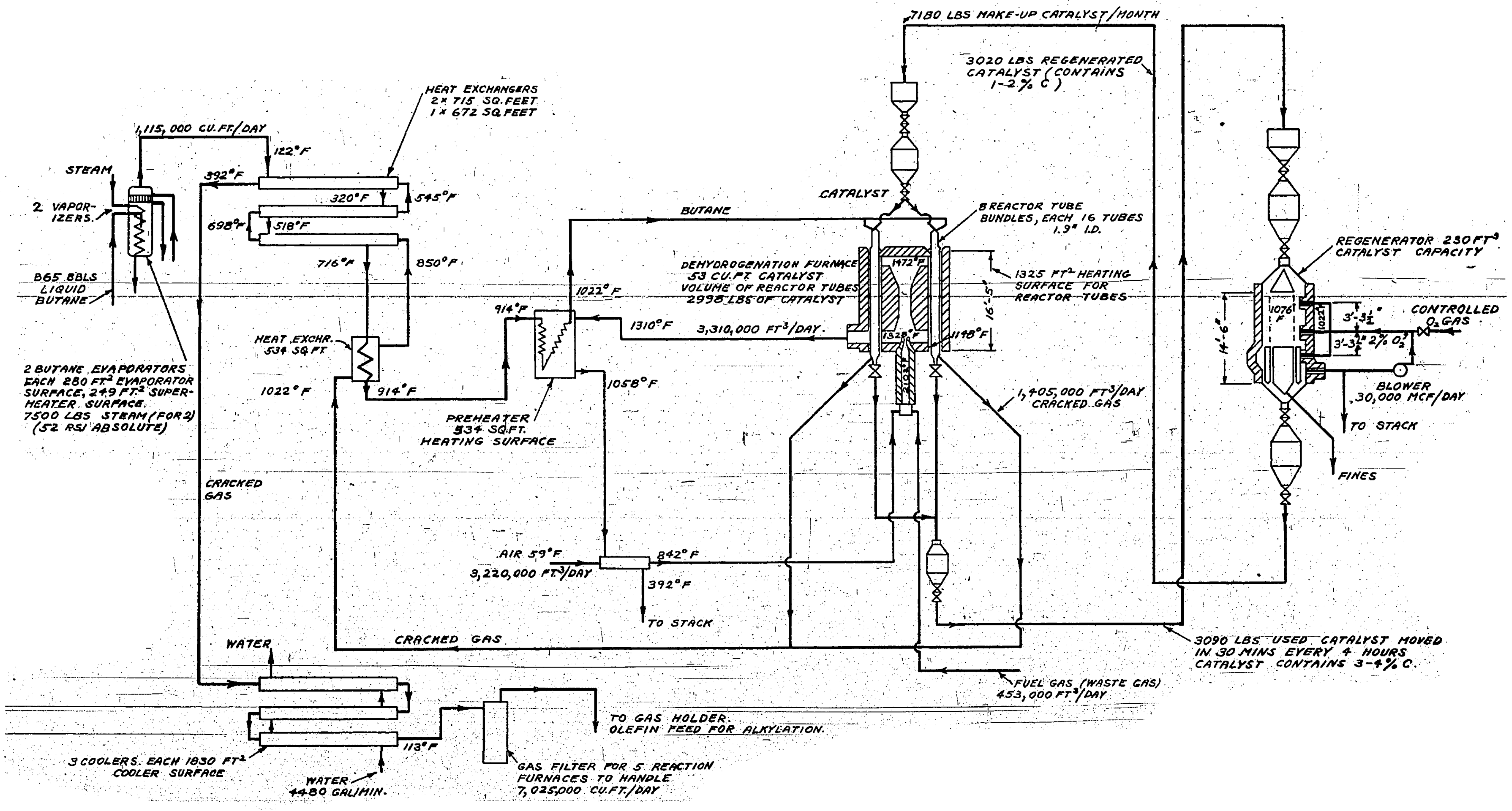


FIGURE XVIII - BUTANE DEHYDROGENATION LEUNA WORKS AMMONIAKWERKE MERSEBURG.

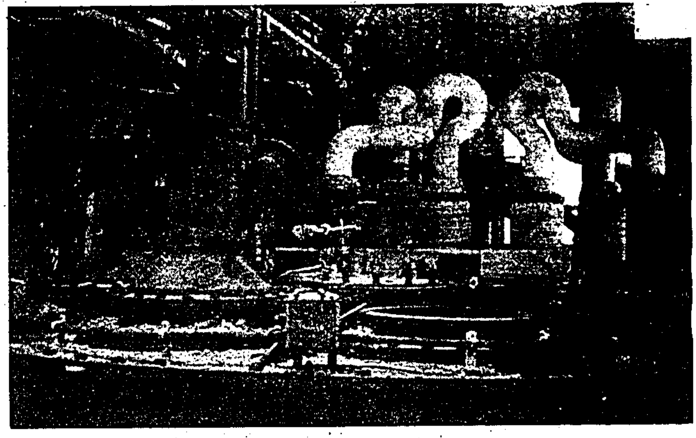


FIGURE XX

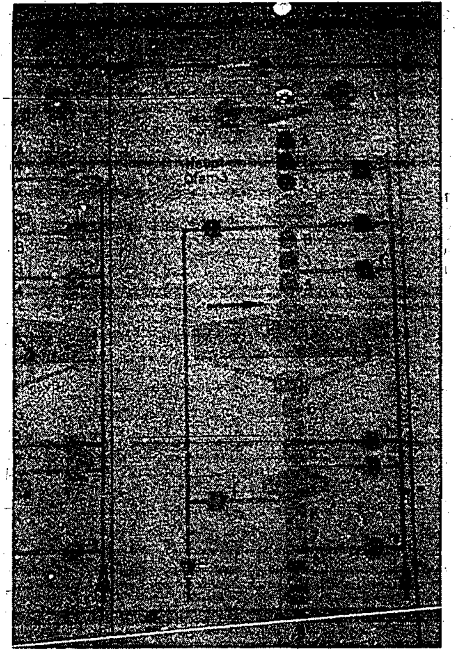


FIGURE XXI

downwardly through the tubes and the flow is controlled by means of 16 horizontal cylindrical pocket valves connected with bevel gears and driven simultaneously by an electric motor. A vertically-slotted tube (about 18" long) is placed between the reactor tubes and the pocket valves to permit separation of the reaction products from the catalyst. In the beginning catalyst flow was checked audibly by letting the catalyst drop on tuning forks and listening to the sound so produced by means of a stethoscope held to the outside of the reactor. This practice appears to have been found unnecessary and has been abandoned. The cylinders are filled with catalyst in the top position and are emptied by rotation to the bottom position. The catalyst is discharged into a catalyst receiver equipped with motor-driven slide valves at the inlet and outlet. The catalyst tubes are kept completely filled with catalyst by continuously replacing from the top hopper the catalyst discharged into the catalyst receiver. When the receiver is filled, the top slide valve connecting it with the reactor is closed and simultaneously the connection between the top catalyst hopper and the reactor is closed. The flow of catalyst through the tubes is thereby stopped but gas continues to flow through the reactor tubes which, of course, are full with catalyst. The catalyst in the receiver is stripped from hydrocarbons with nitrogen and transferred to the regenerator by means of a bucket conveyor and the top catalyst hopper is refilled in the same way with regenerated catalyst. The operation of the slide valves on the catalyst-receiver and hopper are controlled by means of a photocell indicating when the catalyst receiver has been filled. The residence time of the catalyst in the reactor is 4 hours, during which time the catalyst moves for 3.5 hours and remains stationary for 0.5 hours; the time to transfer spent catalyst to the regenerator and simultaneously refill the fresh catalyst hopper consequently is 0.5 hours. Three catalyst charges of a total of 243 cu.ft. per reactor are kept in the dehydrogenation-regeneration system during operation and a catalyst make-up of 367 lbs./day/reactor is required.

In Fig. XX is shewn a photograph of the tops of two dehydrogenation reactors. The side arm, through which the catalyst enters a tube bundle, can be cleerly seen in the foreground. In the background can be seen the inlet lines for the hot butane vapours.

Liquid n-butane (96% by wt. n-butane, 3% isobutane, 1% pentanes) is vaporised with indirect steam at 210°F and brought to a temperature of 932 - 1,022°F by heat exchange with the product gas from the reactor and with combustion gases leaving the reactor. The preheated gas enters the reactor tube at the top and is heated to 1,040-1,076°F by combustion gases at about 1,472° F. The rate of gas flow is 680 cu.ft. of gas/cu.ft. of catalyst/hour. The conversion of n-butane amounts to 20-25% by wt. of which 85% is n-butylene (60% α-butylene, 40% β-butylene). The composition of the effluent gas is given as follows:-

74.2%	by wt.	n-butane	
21.2%	"	"	n-butylene
0.7%	"	"	hydrogen
0.8%	"	"	methane
0.9%	"	"	C_2 hydrocarbons
2.2%	"	"	C_3 "

The volume of the reacted gas has increased by 1.25 as compared to the n-butane feed. The dehydrogenated gas is cooled to 266 to 300°F by heat exchange and to about 100°F by indirect water cooling. It is then passed through a coke filter to remove high boiling hydrocarbons, mainly aromatics, as well as dust. The filter contains 231 cu.ft. coke and can be operated for 3-6 months. The gas is finally cooled indirectly to about 77°F and passed into a gas holder for intermediate storage.

Catalyst Regeneration:

The spent catalyst contains about 3 - 4% carbon and is regenerated at 1,040-1,076°F to give a regenerated catalyst containing 1 - 2% carbon. The regenerator consists of a circular firebrick-lined vertical shell of about 9' diameter and 12' length. The catalyst is fed from a hopper over a conical distributor to the annular space formed by metal screens around a hollow centre duct. The catalyst space ends in 8 tubes which are provided with the same type of pocket valves for flow control as used in the reactor. The flue gas enters with a temperature of 932°F, passes through the catalyst where the heat of reaction raises the temperature to 1,040-1,076°F, flows into the centre duct which acts as dust separator and, by means of vertical slots, enters a collecting ring from where it leaves the reactor. The flue gas is circulated by means of a blower at a rate of 1,400,000 - 1,700,000 c.ft./hr. The catalyst receiver and top hopper of the regenerator are equipped with motor-driven slide valves of the same design as the corresponding valves on the dehydrogenation furnaces. The catalyst hopper on top of the reactor is provided with vibrating screens for the removal of fines. The catalyst receiver is equipped likewise. A photograph of the control panel for one of the regenerators is shown in Fig. XXI. A detailed flowsheet of the dehydrogenation process is given in Fig. XVIII. It should be noted that this flowsheet has been prepared with the aid of design drawings for the dehydrogenation of isobutane since these were the only ones available. The dimensions of the equipment used in actual plant operation are somewhat different. The data and dimensions given in the descriptive part of the report are actual figures for the plant as operated at Leuna.

Catalyst Manufacture:

The catalyst, which consists of activated alumina impregnated with 8% CrO_3 and 1 - 2% K_2O, is prepared as follows:-

Activated alumina is obtained by the precipitation of sodium aluminate with HNO_3. The precipitate is filtered, washed carefully and dried at about 220°F. It is then kneaded with HNO_3 in a stainless steel kneading machine, dried again and heated to 788-842°F. The material so obtained is mixed with such an amount of K_2CrO_4 that the mixture contains 8% CrO_3 and 1 - 2% KOM. Sufficient water is added to obtain a plastic mass which is pressed and subsequently formed into spheres of about 1/4" diameter on a candy manufacturing machine (Frankonia machine). The spheres are dried in air, further dried in a steam chest and finally heated to 752 - 842°F. The finished catalyst is classified and only the material representing spheres is used; plugging of the catalyst tubes, which results in excessive carbon formation, is thereby prevented.

Preparation of Alkylation Feed Stock.

The exit gas from the dehydrogenation is picked up from intermediate storage and compressed to 118 psi. It is then cooled indirectly with water to about 77°F and subsequently cooled with brine to 41°F. The material liquefied under these conditions is stored and represents the olefin feed stock for the alkylation. The composition of this butane-butylene mixture is as follows:

22% by wt. butylenes
75.5% by wt. n-butane.
2.5% " " propane

The uncondensed portion of the gas is passed into an absorber and washed with oil at 118 psi. and 50°F. The composition of the non-absorbed gas is as follows:

Approx. 80 - 85% by vol. H_2
" 12 - 15% " " CH_4
" 3 - 5% " " C_2 hydrocarbons

The absorber is jacketed and is cooled by circulating brine of 41°F through the jacket. The gas stripped from the fat absorption oil is returned to the compressor and recycled. High pressure steam (175-220 psi) is used for heating the absorption oil regenerator.

The mixture of butanes, which is the starting point for alkylate manufacture, is furnished by the high pressure hydrogenation plant. This mixture contains an excess of normal butane and a portion of this excess, separated from the alkylation effluent, is isomerised to isobutane in the isomerisation plant discussed in another section. The material balance of Fig. XVII does not take into consideration the operation of an isomerisation unit, since it is a small proportion of the circulating normal butane.

Alkylation:

The alkylation reactors are insulated vertical cylindrical vessels, 11'6" high, with a capacity of 157 bbls. There was a total of 12 reactors, in two groups of six each, housed in adjoining buildings to protect them from bomb damage. One group has been destroyed by bombing but the other group is undamaged. The volume of a reactor up to the emulsion outlet is 61.5 bbls. and the reactor is equipped with a motor-driven stirrer with a blade 32" long rotating at 120 r.p.m. The rate of feed is 50 bbls. of hydrocarbon and 50 bbls. of acid per hour. The feed is cooled by heat exchange to 46°F and the temperature of the reaction mixture is maintained at 32°F by evaporation of butane and maintaining the pressure in the reactor at 7 psig. About 230,000-250,000 cu.ft./hr. of butane are circulated for refrigeration. Sulphuric acid containing 96% H_2SO_4 is used and the concentration of the spent acid is maintained at 90% H_2SO_4 by periodic withdrawal (every 3 hours) of spent acid. The acid consumption amounts to 1.2 lbs. 96% acid per gallon of alkylate. The isobutane-olefin ratio is maintained at about 6:1. The residence time in the reactor is 40 minutes.

The composition of the reactor effluent is as follows:

42.8%	by wt.	iso-butane
41.0%	" "	n-butane
15.0%	" "	alkylate
1.2%	" "	propane

The acid-hydrocarbon emulsion is allowed to settle for 2 hours in a settler of a total capacity of 188 bbls. and a capacity up to the overflow of about 157 bbls. The hydrocarbon effluent then passes through a heat exchanger where its temperature is raised to 59°F by exchange where the alkylation feed enters a final settler (capacity 630 bbls). Subsequently, the hydrocarbon mixture is washed with caustic (10% NaOH solution) and fractionated in the usual manner. The debutanizer consists of a tower of about 9' diameter packed with Raschig rings to a height of about 65'. The tower is operated at a pressure of 59-99psi and a bottom temperature of 356°F obtained with indirect steam. The reflux ratio is maintained at 0.4:1. The separation of n-butane and iso-butane takes place in an 80 plate tower of 9' diameter and 130' height. ~~The distance between the plates is about 20". This tower is operated under a~~ pressure of 118 psi and a reflux ratio of 4.5:1. The bottom product represents 96% n-butane. The overhead is passed into the depropanizer which is a packed tower of 4' diameter and 20' of packed height. The packing consists ~~in the upper section of Raschig rings of 1/2" diameter and in the lower sec-~~tion of rings of 1" diameter. The operating pressure is 265 psi. The bottom product has the following composition:-

85%	by vol.	iso-butane
12%	" "	n-butane
3%	" "	propane

The alkylate is distilled under vacuum in order to make it possible to use steam (175-220 psig) as heating medium. The distillation is carried out at a pressure of 11.6 psia and bottom temperature about 350°F in a tower of about 5'6" diameter and a height of about 65'; the tower is packed with Raschig rings.

A flowsheet of the alkylation process is shown in Fig. XIX. A photograph of an alkylation reactor is presented in Fig. XXII.

Alkylate Quality:

The alkylate produced has the following properties:

IBP	185°F
80-85%	248°F
E.P.	392°F

Reid vapour pressure below 7.4 lbs.
Octane No. 93-94
(Research)

Alkylate production in Germany:

The Leuna alkylation plant was designed for an annual production of

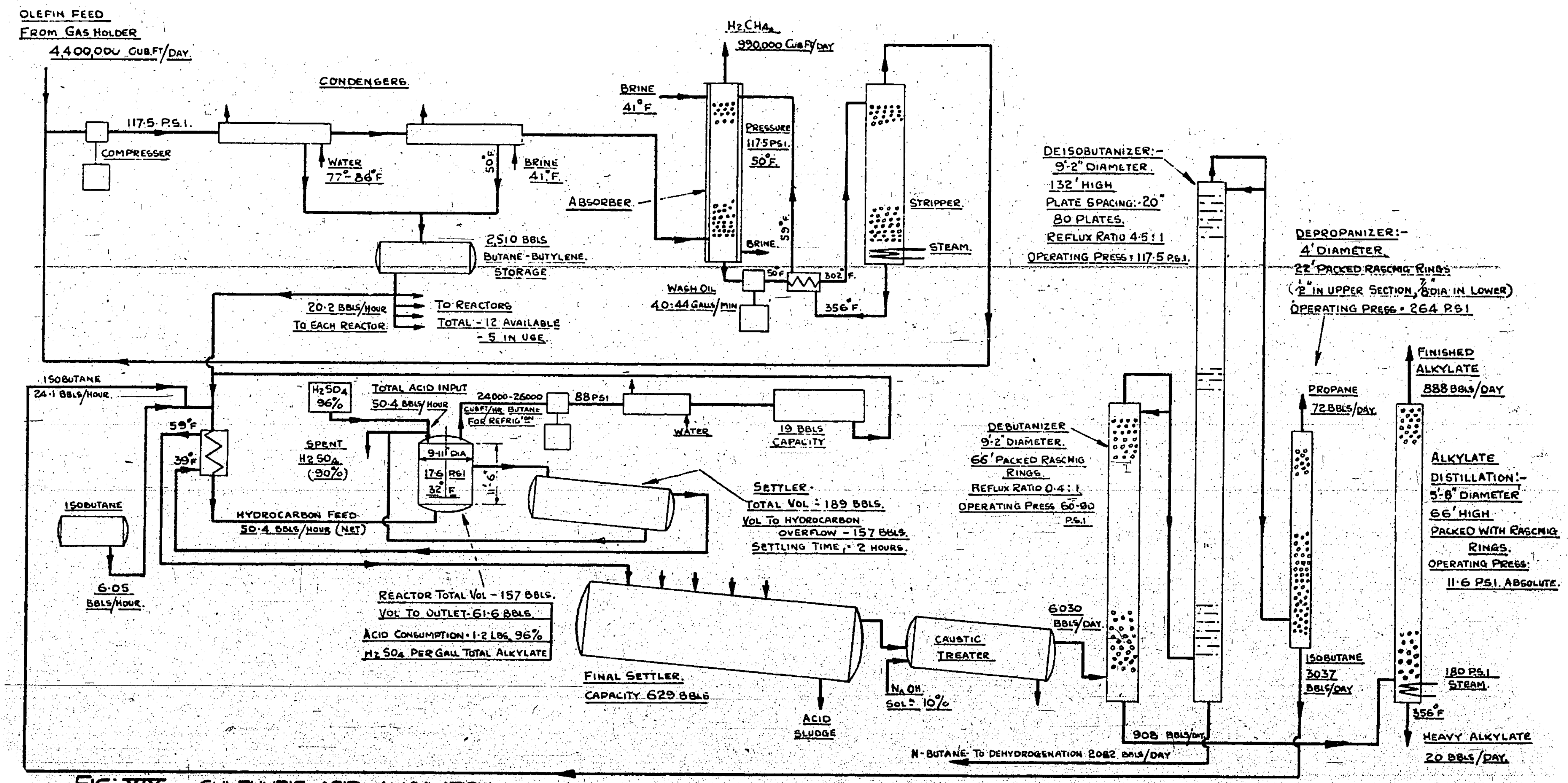


FIG: XIX SULPHURIC ACID ALKYLATION AMMONIAKWERK MERSEBURG LEUNA WORKS.

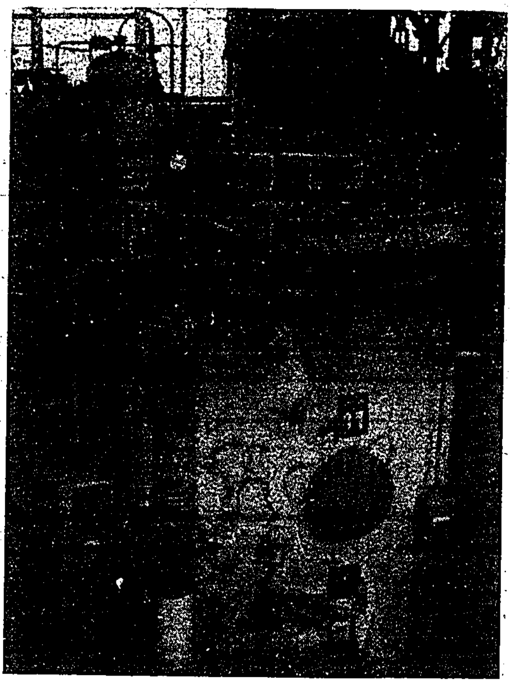


FIGURE XXII

50-60,000 tons (445,000 to 533,000 bbls) but the actual production averaged only 36,000 tons per year (320,000 bbls.)

The only other German alkylation plant which was completed and in operation was at Scholven. This unit operated only for 6 months in 1944 and during this time its rate of production was the same as the actual rate of production at Leuna (2-3,000 tons/month, 17,800 - 26,800 bbls./month).

The Leuna plant started operations in Spring, 1942, and ceased operation in December 1944. The butane dehydrogenation equipment has not been extensively damaged. Half of the alkylation reactors, and auxiliary equipment, has been completely destroyed together with most of the tankage serving the entire unit. The fractionation section appears to be intact.

Economics of Leuna operation:

Data on energy and labour requirements for butane dehydrogenation and alkylation were provided by the foreman of the plant, Dr. Strätz, and are given in Table VIII. The photographs were taken by J. P. Jones.

TABLE VIII

Operation	High pressure steam (176-220 psi), lbs/barrel of Alkylate.	Low pressure steam (37 psi) lbs/barrel of Alkylate.	Power high voltage KWH/barrel of Alkylate	Low voltage KWH/barrel of Alkylate	Circulating water gals/barrel of Alkylate	Make up water gals/barrel of Alkylate.	Fuel Gas BTU/barrel of Alkylate	Labour		
								Fore-men	Lab. Tech-nician	Process Workers
Dehydrogenation	-	320	-	11.1	646	-	937,000)			
Compression of de-hydrogenated gas and absorption unit	35	-	23.2	1.4	2,530	-	-)	4		35
Alkylation, including Refrigeration.	1,225**	-	-	8.2	3,840	-	-	3		20
Butane-isobutane separation, Depropanizer	-	1,100	-	2.7	3,840	27	-)			
Debutanizing of Alkylate, distillation of alkylate	302	382	18.5*	2.7	3,840	27 147*	)	4	1	28
TOTAL	1,562	1,802	41.7	26.1	14,696	201	937,000	11 +3 machinists 14	1	83

** for butane refrigeration
* for water circulation

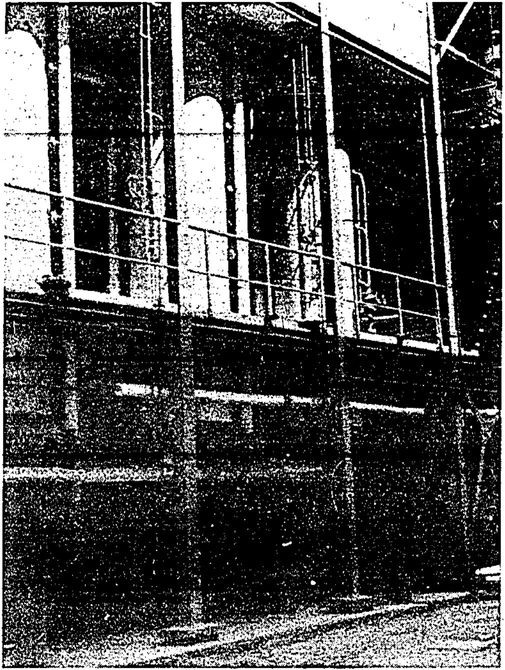


FIGURE XXIV

X. ISOMERIZATION OF NORMAL-BUTANE

The isomerization of normal butane is carried out using aluminium chloride catalyst activated with HCl. This is the only plant in Germany for the isomerization of butane. The process, as used in Germany, is similar to one variation used in the United States. A simplified flow diagram of the process is attached as Fig. XXIII and a photograph of the three isomerization reactors is shewn in Fig. XXIV.

Each reaction vessel consists of a 1 metre diameter cylindrical vessel having a cone bottom. The straight section of the reactor is approximately 6 m. in length. Liquid normal butane of 95-96% purity is first dried by washing with 96% sulphuric acid. The dried feed is pumped under 18 atms. pressure through a preheater where it is heated to 95°C and then mixed with 100-150 cu.m. of recycle HCl gas for 1.6 cu.m. of liquid feed to give a 10% concentration of HCl in the reactor charge. The charge enters the base of the reactor near the cone, flows upward through a 2 m. depth of Raschig rings, then through a 1 m. bed of lump aluminium chloride occupying a volume of approximately 700 litres. Above the aluminium chloride, the material passes through an empty zone of 1-1½ m. in height to prevent aluminium chloride carry-over. The effluent from the top of the reactor is cooled to 25°C by indirect water cooling, and passes to a receiver from which some sludge is removed. The hydrocarbon-HCl mixture from the receiver is pumped through a preheater where the temperature is raised to 60°C and introduced near the top of a HCl stripping tower. The bottom temperature of the stripping tower is maintained at about 118°C to remove the butanes and any propane formed so that propane does not build up in the recycle HCl stream. Reflux is supplied to the top of the column by means of a water-cooled condenser in the ratio of 2.5 parts of reflux to one of overhead product. The recycle gas contains 80% HCl, 15% propane, and 5% isobutane. Make-up HCl is added to this recycle stream and it is mixed with the feed to the reactor.

The catalyst employed in the process is technical aluminium chloride containing a small amount of ferric chloride as an impurity. The ferric chloride is said to be essential for the reaction. The conversion of normal butane to isobutane per pass is 25-30% with an ultimate yield of 95-97%. Each reactor produces 250-300 kgs. of isobutane per hour. The consumption of aluminium chloride is 1% by weight of the isobutane produced. The consumption of HCl is 0.1 - 0.3% by weight of the isobutane produced.

According to the personnel interrogated, ordinary carbon steel is used in the construction of the reactor. It was reported that no corrosion trouble had been encountered with the use of carbon steel, although this appears very unlikely since the aluminium chloride sludge has been found to be very corrosive in a similar type unit. Difficulty was encountered, however, with deposition of aluminium chloride in the cooler at the outlet of the reactor. Apparently no effort was made to remedy this trouble.

This process has not reached the stage of development obtained elsewhere and it is doubtful whether anything new is to be learned from the Germans in the field of isomerization using aluminium chloride. The isomerization of pentane and hexane has not progressed beyond the laboratory stage.

XI. SYNTHETIC LUBRICATING OIL MANUFACTURE - LEUNA.

Information on this subject was secured at Leuna by inspection of the plant and by interviews with the following I.G. personnel (May 8 -15, 1945):

- Dr. Giessen - in charge of organic chemicals manufacture.
- Dr. Gericke - in charge of operation of the lubricating oil plant and some smaller chemical plants.
- Dr. Zorn - in charge of lubricating oil research for the past 15 years.

SUMMARY OF PROCESS:

Ethylene of 95% purity is obtained by thermal cracking of ethane in admixture with oxygen. The ethylene is polymerized batchwise in the presence of a special aluminium chloride catalyst. The ploymerized oil is separated from the aluminium chloride complex, steam distilled to remove light ends, and given a final clay treatment before use.

The plant was designed for the production of 200 B/CD (850 metric tons/month) finished lubricating oil from 1650 MCF/D (60°F - 760 mm.) of ethane. Actual production in continuous operation was about 85% of this figure. Yield of finished lube oil from original ethane was about 48.5 weight per cent.

PROCESS DETAILS:

The overall material balance for the plant is given in Fig. XXV based on 170 B/CD (700 T/Mo) lubricating oil production. Details of processes are given in Figs. XXVI - XXIX, based on design stream day operation where available.

1) Thermal Cracking of Ethane

The ethane cracking equipment consists of four parallel units, each with an ethane charge capacity of 617 MCF/D. Ethane (three volumes) and oxygen (one volume) are preheated separately at atmospheric pressure in gas-fired tubular heaters to 1100 - 1200°F and 750°F, respectively. The heaters are constructed of Sicromal (8-12% Cr). The hot gases are mixed during passage through a refractory assembly ("tulip") in the bottom of the subsequent ethane cracking furnace. The mixture passes upward through the cracking chamber, which is filled with 1-1/4" dia. ceramic spheres. Cracking conditions are approximately 1616°F and 300-400 mm. mercury absolute pressure. The cracked gases are quenched by a water cooled heat exchanger and then by direct injection of water. Vacuum is held on the cracking furnace by a water sealed vacuum pump which discharges the cooled gases to the next stage of the process.

It is interesting to note that the design capacity of four cracking furnaces is 2470 MCF/D ethane, producing 4,200 MCF/D water-free cracked gas; actual requirement (once through) for the 200 B/D lubricating oil production is 1,825 MCF/D, indicating a 75% stream time efficiency. The factor determining stream time efficiency is coking of the lower section of the ethane

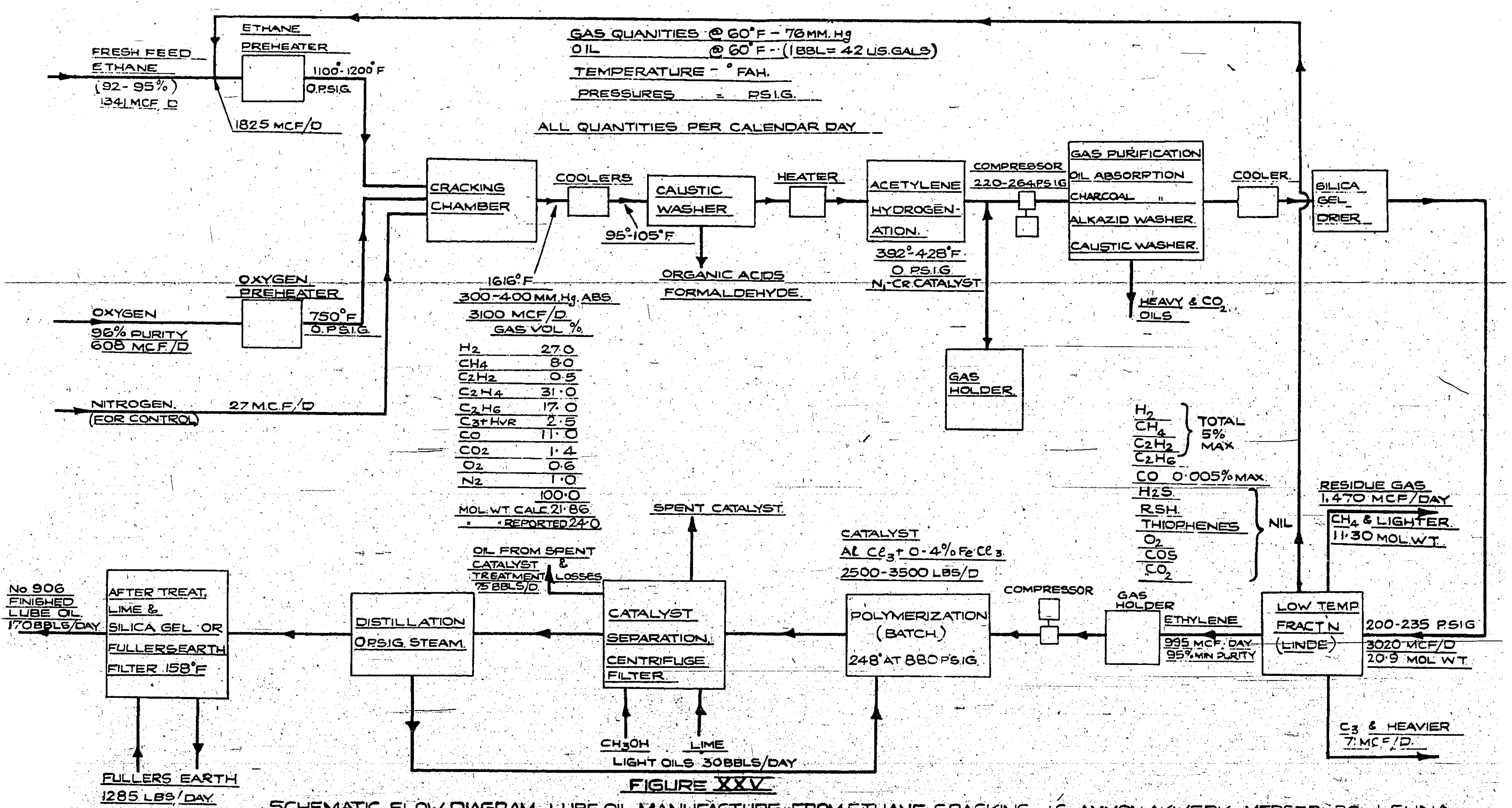
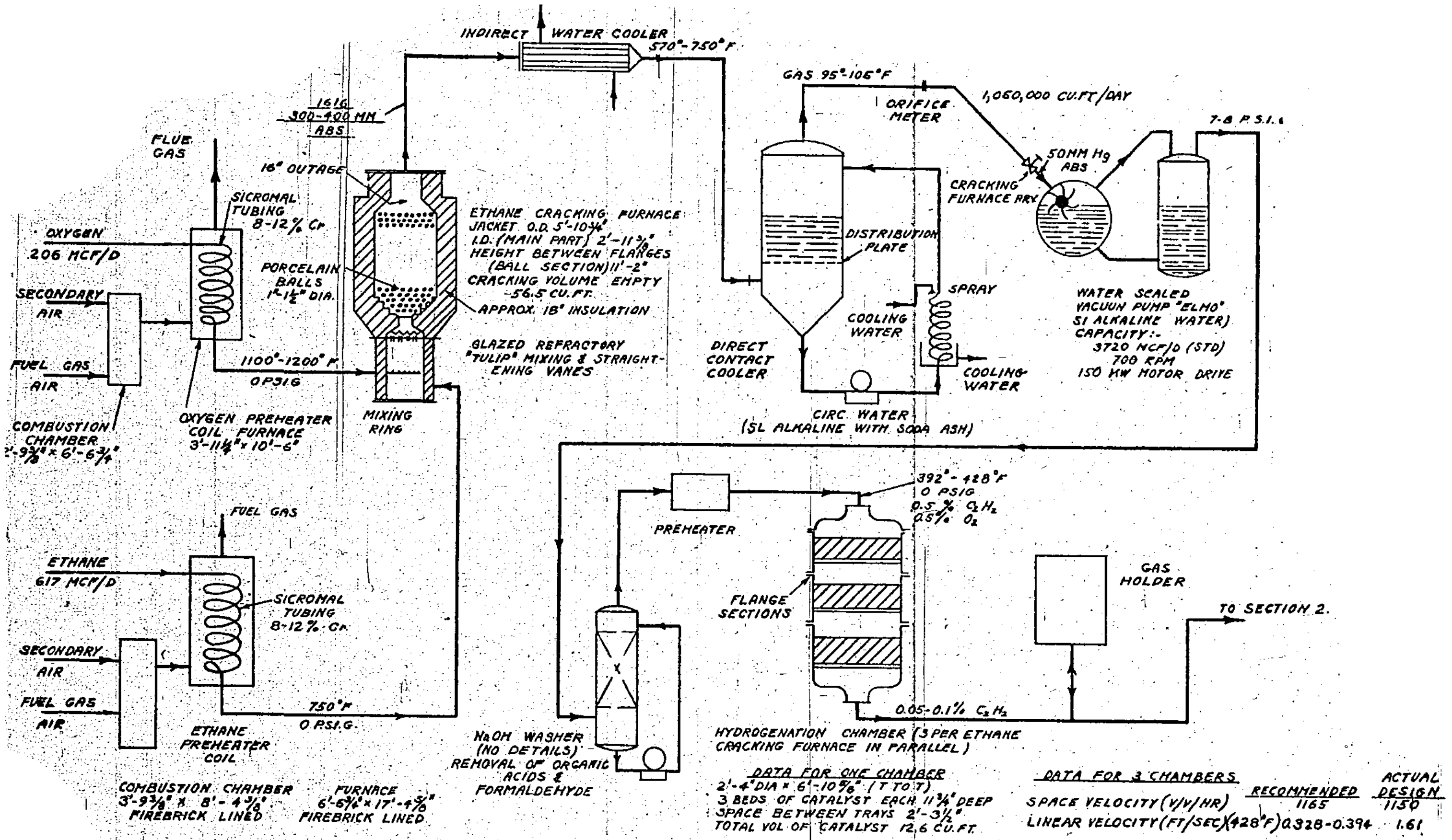


FIGURE XXV

SCHEMATIC FLOW DIAGRAM. LUBE OIL MANUFACTURE FROM ETHANE CRACKING I.G. AMMONIAKWERK MERSEBURG, LEUNA.



DATA FOR ONE CHAMBER
2'-4" DIA x 6'-10⅝" (T TO T)
3 BEDS OF CATALYST EACH 11¾" DEEP
SPACE BETWEEN TRAYS 2'-3½"
TOTAL VOL OF CATALYST 12.6 CU. FT.

DATA FOR 3 CHAMBERS	RECOMMENDED	ACTUAL DESIGN
SPACE VELOCITY (V/V/HR)	1165	1150
LINEAR VELOCITY (FT/SEC)(428° F)	0.328-0.394	1.61

FIGURE XXVI - FLOW DIAGRAM SECTION I. LEUNA WORKS. LUBRICATING OIL FROM ETHYLENE. ETHANE CRACKING DESIGN DATA FOR ONE UNIT FOUR UNITS PARALLEL.

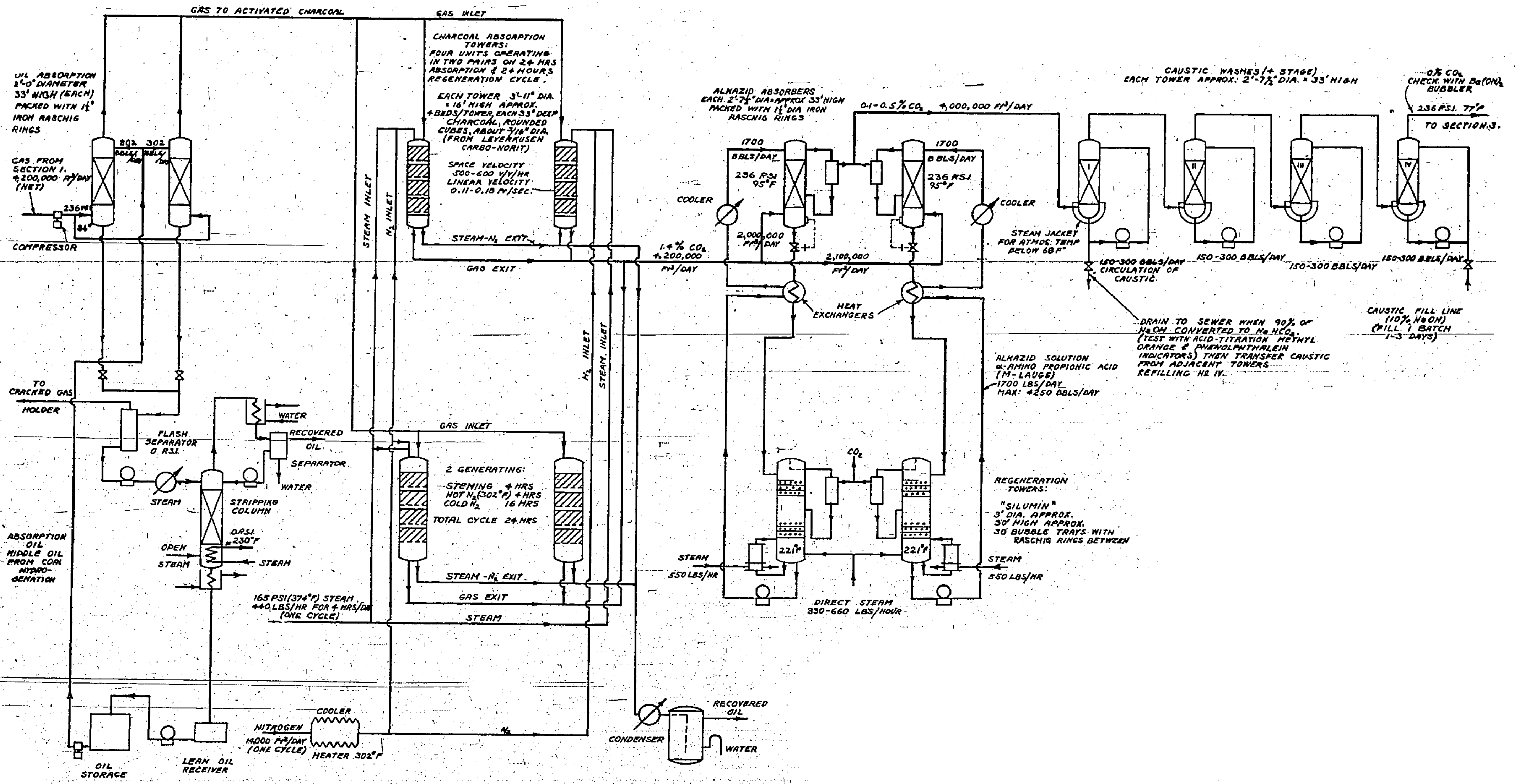
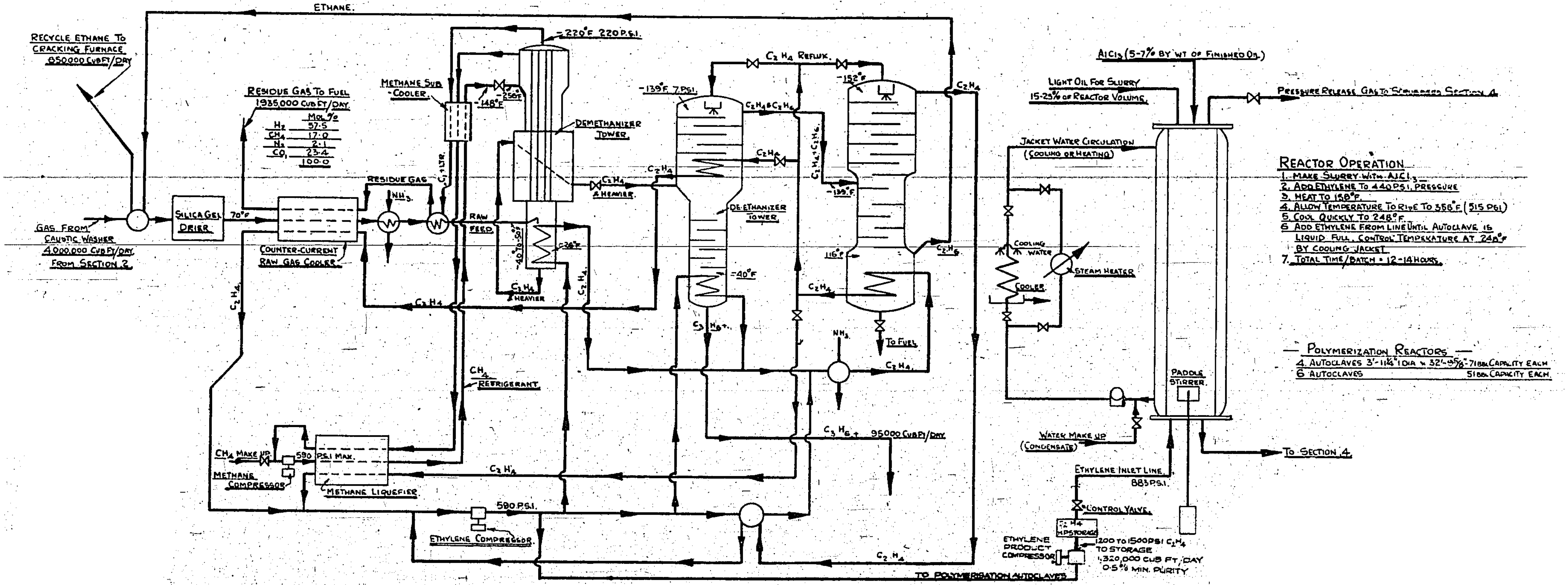


FIGURE XXVII.- LEUNA WORKS FLOW DIAGRAM-LUBRICATING OIL FROM ETHYLENE (SECTION 2) ETHYLENE PURIFICATION.



REACTOR OPERATION

1. MAKE SLURRY WITH $AlCl_3$
2. ADD ETHYLENE TO 440 P.S.I. PRESSURE
3. HEAT TO 158°F.
4. ALLOW TEMPERATURE TO RISE TO 356°F (515 PSI)
5. COOL QUICKLY TO 248°F.
6 ADD ETHYLENE FROM LINE UNTIL AUTOCLAVE IS LIQUID FULL. CONTROL TEMPERATURE AT 248°F BY COOLING JACKET.
7. TOTAL TIME/BATCH = 12-14 HOURS.

— POLYMERIZATION REACTORS —

4. AUTOCLAVES 3'-11¼" I.DIA × 32'-9⅝" - 718 GAL. CAPACITY EACH
6 AUTOCLAVES 518 GAL. CAPACITY EACH.

FIGURE XXVIII

FLOW DIAGRAM SECTION 3. LINDE LOW TEMP. FRACTIONATING PLANT - LEUNA WORKS.
2 PARALLEL PLANTS OPERATED FOR THRU' PUT SHOWN. HEAT EXCHANGE SYSTEM IS APPROXIMATE. POLYMERISATION REACTORS.

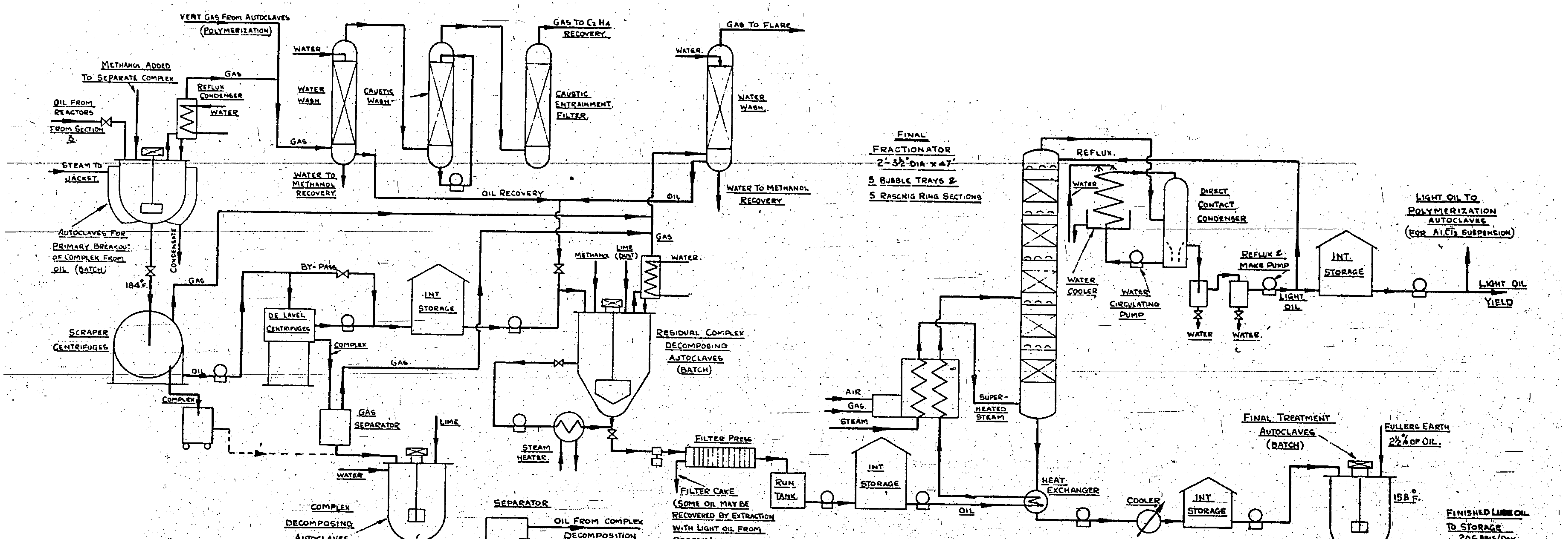


FIGURE XXIX

FLOW DIAGRAM SECTION 4. LUBRICATING OIL FROM ETHYLENE. (LEUNA WORKS)
CATALYST SEPARATION & FINAL OIL TREATING.

cracking furnace where oxidation occurs. A small amount of nitrogen (up to 2% of the ethane) is added to the ethane cracking furnace as a control of cracking.

The products of cracking are next washed with caustic soda in order to remove organic acids and formaldehyde.

2) Acetylene removal:

Acetylene is removed by hydrogenation over a nickel-chromium catalyst at a temperature of about 400°F, atmospheric pressure and a gas space velocity of 1,165 volumes gas (at standard condition)/volume catalyst/hour. Linear velocity was stated to be 0.33 - 0.39 ft/sec. but vessel dimensions indicated a greater linear velocity at the above space velocity. The hydrogen required for hydrogenation is already present in the cracked gas. Any oxygen present in this gas is hydrogenated to water.

After hydrogenation, the four gas streams are conbined in one gas holder. From this point the gas is compressed to 220-264 psig. and undergoes four further purification processes at this pressure.

3) Oil Absorption:

The gas is passed counter-current to a middle oil (from coal hydrogenation) for absorption of benzene and higher hydrocarbons. The rich oil is stripped with stem in the usual way.

4) Activated Charcoal Absorption:

The gas is next passed through towers containing activated charcoal (rounded cubical pellets 13/64" diameter from Carbo-Norit Union, Leverkusen) in order to remove the last traces of benzene. These towers are operated on a 24-hour absorption/24-hour regeneration cycle. Regeneration is accomplished by steaming at 374°F followed by drying and cooling with nitrogen. The effectiveness of the absorption is checked by cooling a gas sample down to -76°F and noting whether there is any condensation.

5) Alkazid Washer:

The bulk of the CO_2 is removed by counter-current washing with an alkazid solution ("M-lauge", α-amino-propionic acid). The alkazid solution is regenerated by heating and steam stripping at atmospheric pressure. The exit gas contains 0.1 to 0.5% carbon dioxide.

6) Caustic Washer:

Four counter-current towers in series are used, each circulating individually. The last tower in the series is filled with new 10% caustic soda (15° Be), and the caustic solution is transferred stepwise to the preceding tower in the system. The caustic in the first tower is dumped when 90% of the available sodium hydroxide has been converted to the bicarbonate. The caustic soda is not regenerated.

To ensure complete removal of carbon dioxide, a sample of exit gas is continuously bubbled through a barium hydroxide solution.

7) Linde Low Temperature Fractionation:

This plant was designed by the Linde Company for the separation of the washed gas into four fractions. The gas is dried over silica gel, precooled and fed into the first tower under pressure. The first tower produces methane and permanent gases as overhead product and ethylene and heavier as bottoms product. Reflux is secured by a methane compression refrigeration cycle. The overhead product is put to fuel gas.

The bottoms from the first tower expand into the second tower at about 7 psig. This tower yields ethylene and ethane overhead and propylene and heavier hydrocarbons are passed from the kettle to fuel gas. Reflux is provided by expanding ethylene directly into the top of the tower.

~~The ethylene + ethane overhead fraction passes to the third tower, which~~ gives ethylene as an overhead product and ethane as a bottoms product. Reflux is provided in the same manner as in the second tower. The ethylene is compressed to 1200-1500 psi for storage and the ethane fraction is recycled to the ethane cracking furnace. This recycle constitutes about 26.5% of the total feed to the furnace.

Reboil heat is supplied indirectly to all three towers by relatively warm ethylene from the discharge of the ethylene refrigeration compressors. The general heat exchange arrangement is shown in the attached flow sheet, Fig. XXVIII.

The three towers are copper lined and all equipment inside the towers is made of copper. The three towers and part of the heat exchanger system are enclosed in an insulated box. Two parallel plants are used for this fractionation at full load.

8) Polymerization of Ethylene to Lubricating Oil:

The reaction is carried out in batch autoclaves. The Leuna plant has ten reactors, four of 400 cu.ft. capacity each and six of 290 cu.ft. capacity each. A batch can be run through a reactor in 12-14 hours.

The procedure for polymerizing a batch of ethylene comprises the following steps:

(a) A slurry is made in the reactor by mixing aluminium chloride (5-7% by weight on the finished lubricating oil) with light oil from the process. This slurry occupies 15-25% of the volume of the reactor and is kept in suspension by the mixer at the bottom of the autoclave. The aluminium chloride contains 4-6% ferric chloride.

(b) The reactor is purged of air with ethylene and then closed in.

(c) Ethylene is added to give 440 psi pressure.

(d) The autoclave is heated to 158°F by circulation of hot water in the jacket. Reaction immediately sets in, the temperature rises to about 356°F and the pressure to about 515 psi. The compound thus formed represents the catalyst for the subsequent polymerization of ethylene.

(e) The reaction is quenched at the above maximum point by circulating cold water in the jacket. This procedure, from the first addition of ethylene, requires about fifteen minutes.

(f) When the temperature is reduced to 230°- 248°F., ethylene (at 882 psi) is introduced and the temperature is held constant in this range by jacket cooling. The polymerization causes a pressure drop in the reactor until the reactor is liquid full. At this point the temperature at the top and bottom of the autoclave are the same and the pressure in the autoclave is the same as the ethylene line pressure.

(g) When the autoclave is liquid full, the ethylene supply line is closed, the pressure on the reactor is vented down by gas release at the top of the reactor (to be described later), and the contents are ready for further processing.

The above procedure refers to the preparation of an oil to a final viscosity at 220 S.S.U. at 210°F (6° Engler at 100°C). To produce an oil of viscosity 105 S.S.U. at 210°F. (3° Engler at 100°C), the polymerization temperature is controlled at 356°F. The yield of oil from ethylene is reduced at the higher temperature.

The first Leuna autoclaves were made from steel containing 12-16% Cr and the oil manufactured was of the desired high viscosity. Subsequently more reactors were added, and these were manufactured from ordinary carbon steel. With a 95% purity ethylene from Leuna, these latter reactors gave a low viscosity oil (3-4° Engler) for 3 to 4 months, but subsequently gave a high viscosity oil. The plant at Schkopau (see following section), operating on a higher-purity ethylene, had no difficulty making a high viscosity oil in carbon steel reactors from the first. Gericke believes that, from this and other evidence, a high-purity ethylene is essential and that impurities in the ethylene, as well as reactor wall material, may influence polymerization. No corrosion difficulties have been experienced at Leuna as long as the equipment is kept absolutely dry.

9) Catalyst Separation and Disposal:

The contents of a reactor are pressured into a batch separation vessel. If the oil and catalyst complex layers do not readily separate, a small amount of methanol is added. The total mixture then passes through a scraper-type (schal) centrifuge, in which the heavier complex is continuously scraped from the outer drum and retained for further processing. The oil may then pass through a DeLaval centrifuge for further catalyst separation. The optimum temperature for catalyst separation is about 194°F.

The oil, still containing a small amount of complex, next goes into an autoclave in which methanol (2% on oil) and lime dust are added. This treatment breaks down the catalyst complex and neutralises the acid formed. The entire contents of this autoclave are put through a filter press and the filtered oil is stored prior to distillation.

The $AlCl_3$ complex recovered by centrifuging is decomposed in batches by the addition of water. Any oil separating in this process can be either treated and fractionated with the main oil stream or recovered separately.

The filter cake from the filter presses can be extracted with the light oil fraction from the process for additional heavy oil recovery, either by washing in situ or subsequently in batch autoclaves. The total extract oil can be recombined with the main oil stream before the filter presses.

The gas liberated from the purging and venting of the polymerization autoclaves and from the centrifuges and adjacent receivers is water washed, caustic washed and its ethylene content recovered.

All vessels using methanol are provided with methanol reflux systems, after which the gases still vented are water washed before being discarded. The wash water is saved for methanol recovery.

10) Oil Fractionation:

The combined oil from the filter presses is steam distilled at atmospheric pressure to remove about fifteen per cent light ends. These light oils are used in making up catalyst slurry in the polymerization reactors.

The product from the base of the still is batch treated with about 2.5% of a natural Fuller's earth (from near Munich) at 158°F, filtered through presses to give the finished oil.

In some cases lime and silica gel are used in the final treatment instead of Fuller's earth.

OPERATING REQUIREMENTS

Utilities: The following utility requirements for the Leuna plant were given, based on one barrel of finished lubricating oil:

	Ethane Cracking & Ethylene Purification	Polymerization & Refining
H.P. Steam (220 psi), pounds	1080	430
L.P. Steam (22 psi), pounds	650	1950
Water (from River- Once-through)		
Winter (40-50°F), gallons	11200	3700
Summer (86°F), gallons	22400	3700
Nitrogen, Cubic Feet	----------1,350----------	
Electricity, KWH	450	160
Fuel Gas (250 BTU/CF, lower heating value), BTU.	1.51×10^6	0.10×10^6

Operators: The following operating personnel was required for the plant. These figures are based on a 56-hour week, or 3 men per job for 24-hour operation. They do not include any maintenance labour.

	Total		Per Shift	
	Operators	Foremen	Operators	Foremen
Ethane Cracking	18	3	6	1
Ethylene Purification	87	3	29	1
Polymerization & catalyst separation	68)	6	23)	2
Distillation	12)		4)	
Final refining of lubricating oil	10		10 (Days only)	-
General Plant Foreman (Gericke)	-	1	-	1 (Days only)
Laboratory	7	1	2	1
Day Shift:			74	6
Total:	202	14		
Night Shift:			64	4

The total of 105 operators in the ethane cracking and purification plant might be reduced to 80 if more skilled operators were available.

Normally the plant is shut down for inspection for a 3-day period every 60 - 120 days. To come on stream from a complete shut-down requires about two weeks.

TESTS ON PRODUCTS

As indicated above, the plant could be operated to produce either a 6° or a 3° Engler viscosity oil (at 100°C). These products from Leuna were referred to as SS (Schmierstoff) 906 and 903 respectively and specifications for the products were as follows:

	SS.906	SS.903
Specific Gravity at 20°C Max.	0.862	0.860
(API at 60°F. Min.)	31.9	32.3
Viscosity at 50°C (Engler	44-46	14-15
" " 100°C (Engler)	5.63(Min)	3.0(Max)
(SSU at 130°F)	1200-1250	400-440
(SSU at 210°F)	205(Min)	105(Max)
Viscosity Index. Min.	107	115
Slope constant "M" in Pole Height Calc., Max.	3.05	3.20
Pole Height, Max.	1.73	1.60
Pour Point °F, Max.	-13	-31
Flash Point, °F, Min.	435	392
Neutralization No. (mg KOH/g), Max.	0.06	-
Saponification No., Max.	0.30	-
Noack Evaporation Test (482° F) Max.%	8	-
Conradson Carbon Residue, Max.	0.2	0.2
Ash, Asphalt, Water	0	-

The SS 906 product was usually blended with an equal quantity of bright-stock derived from petroluem oil, the blend being used as an aviation lubricating oil (denoted S-3).

The natural lubricating oils used in the blend were from three sources, all from refining Austrian crudes, and were denoted as follows:

607	From Rhenania, Harburg. Vacuum distilled oil, refined with sulphuric acid.
707	From Vacuum Oil Co., near Bremen. Duo-Sol refined.
807	From Nerag, near Hanover, Furfural refined.

Alternate stocks to the SS 906 (Leuna) product in this S-3 blend were the following:

SS 1106	6°Engler (100°C) oil by polymerization at Pölitz of olefines obtained by cracking paraffin.
SS 1006	6°Engler (100°C) oil by polymerization at Rhenania, Harburg, of olefines obtained by cracking paraffin.
SS 906	6°Engler (100°C) oil by polymerization at Schkopau of ethylene produced, via acetylene, from calcium carbide.

The specification for the S-3 blended aviation lubricating oil is given below:

Viscosity, Min. 2.8° Engler at 100°C (98 SSU at 210°F).	
Viscosity Index, Min.	95
Flash, °F., Minimum	428
Pour Point, Maximum	-4
Conradson Carbon Residue, Max.	0.3

A 3° Engler (100°C) oil from Pölitz (SS 1103 was sometimes used directly. Maximum production of this grade was 200 To/yr (4 B/D).

A standard engine test was used for the determination of the ring-sticking tendencies of aviation lubricating oils. As a reference oil, a refined petroleum lubricant (Vacuum Oil Co. "Rotring") was used, and results were reported in terms of hours operation before ring-sticking. The various oils described above compared as follows:

Reference oil (Rotring)	8 hours
Synthetic oil (Leuna) 100 SSU/210 (SS 903)	32 hours
" " (Pölitz) " (SS 1103)	20-22 hours
Finished Blend (S-3)	12 hours
" " " plus 0.2% Inhibitor "R"	16 hours

PRODUCTION DATA

Total German production of synthetic aviation lubricating oil was as follows:

	Design		Actual Production	
	Metric Tons/Mo	B/D	Metric Tons/Mo	B/D
Leuna	850	206	700	170
Schkopau	350-500	85-121	350-500	85-121
Pölitz	1200	290	1000	242
Rhenania, Harburg	700	170	500	121
Total (Max.)	3250	787	2700	654

This production had been reduced by bombing as follows:

Leuna - No production after July-August 1944 because of lack of ethane after bombing of hydrogenation plant.

In later raids the lubricating oil plant itself was damaged. The vessels and pipe line of the cracking section were badly pierced by bomb splinters but the cracked gas purification plant was not too badly damaged. The Linde refrigeration plant compressor house was wrecked but possibly 50% of the compressor capacity could be salvaged. The polymerisation and distillation sections appeared more or less intact but storage tanks and general service piping in the area were very badly damaged.

Pölitz - Production reduced to 500-600 T/Mo. in last 6 months' operation.

~~Rhenania - No production after July 1944 bombing. Plant was~~ planned to be moved to Harz Mountains but was not completed there.

An ultimate total production capacity of 70,000-80,000 Tons/yr (1410-1610 B/D) synthetic lubricating oil was planned and plants had been erected at Moosbierbaum and Blechhammer, but never operated.

NOTES ON CATALYSTS AND REACTION CONDITIONS

1) Acetylene Removal Catalyst

The catalyst (Kontakt 4738) is manufactured as follows:

Fifty kg. (110 lbs) chromic acid, 9.24 kg. (20.6 lbs) nickel nitrate, and 20 litres (5.3 U.S. gal.) water are mixed in a stainless steel vessel. The vessel is gas-fired, and the mixture is hand-stirred for several hours until it gives a thick black mixture with no more evolution of nitrogen-gases. This mixture is heated 12 hours at 572°F in an electric-heated furnace. After cooling, the resultant hard cake is broken by hand into 3/8" (8-10mm) granules.

The granulated mass is placed in an electrically-heated reduction oven, heated in an atmosphere of nitrogen to 842°F and held at this temperature for eight hours in the presence of hydrogen. The catalyst is cooled in a stream of hydrogen and stored in containers in a nitrogen atmosphere.

The composition of the finished catalyst is approximately 95% chromic oxide and 5% nickel.

2) Ethylene Purity Required

For ethylene polymerization, the following limitations on ethylene purity must be observed:

Carbon dioxide - Complete absence, no trace with barium hydroxide test.

Oxygen - Complete absence, reactor must be purged with ethylene before starting operations.
Hydrogen Sulphide - Complete absence.
Carbonyl Sulphide - Complete absence.
Mercaptans - Complete absence
Thiophenes - Complete absence.
Carbon Monoxide - Maximum 0.005%. Check with standard haemoglobin solution, followed by spectroscopic determination of the width of the absorption band.
Hydrogen, methane, ethane, acetylene - Total must not exceed 5%

3) Polymerization Catalyst

Pure alumium chloride is unsuitable as a polymerization catalyst because it is too active and permits too many side reactions, including isomerization and cracking. It is modified to a suitable form by the addition of about 4% by weight of ferric chloride. The catalyst is prepared at Ludwigshafen and Schkipau by treatment with carbon monoxide and chlorine of a natural bauxite which contains about the correct amount of iron oxide. Any traces of titanium, silicon, or magnesium chlorides present in the finished catalyst do not seem to affect its polymerizing qualities.

The maximum temperature reached during formation of the catalyst complex with ethylene in the presence of light oil controls the activity of the catalyst and the type of oil subsequently produced. The higher this maximum temperature the higher both the VI and the pour point of the product. A good compromise on these two tests calls for a maximum temperature of 356°F.

As previously mentioned, the polymerization temperature governs the viscosity of the final product. According to Zorn, an oil of 6° Engler at 100°C (220 SSU at 210°F) is produced at 212-230°F and an oil of 3° Engler at 100°C (105 SSU at 210°F) at 266-284°F. These temperatures are lower than those already reported for Leuna plant operation, probably because of a difference in ethylene purity between laboratory and plant operations.

Other catalysts have been tried for ethylene polymerization properties, but without much success. Aluminium chloride plus metallic aluminium is too strong a catalyst for the reaction and hydrofluoric acid tends to form ethyl fluoride instead of a polymer.

Boron trifluoride in HF can be used as a polymerization catalyst but produces an inferior quality of oil.

THEORY OF LUBRICATION

This subject was discussed in detail with Dr. Zorn at Leuna. His work in this field has been continuous since about 1927, and he is credited with the development of the commercial synthetic lubricating oil manufacture.

Preliminary research showed that an olefine to be used for polymerization to a high V.I. lubricating oil must have a double bond at the end of a straight chain molecule, with the exception that an iso-structure at the opposide end of the molecule from the double bond may give some advantage, as discussed later. No substitution may appear at the double bond.

For instance, the following examples of isomeric octene polymerizati bring out the effect of differences of structure:

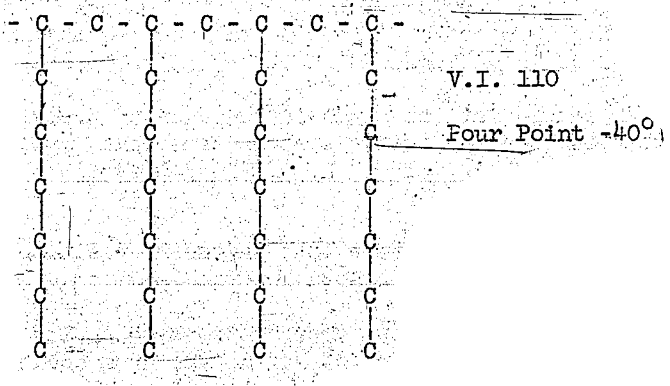
	Polymerized Product				
		Viscosity			
Olefine Feed	Mol.wt. (Approx.)	Engler at 100°C	SSU at 210°F	V.I.	Yield wt.%
n-octene-1	800	2.8	98	100	80
2-methylheptene-1	350	1.2	32	20	20
n-octene-4	200	0.8	28	-10	5-10
6-methylheptene-1	1500-1700	7.9	290	100	85-90

The theory based on these observations and some organic syntheses is as follows:

The ability of an oil to function as a lubricant involves a molecular structure which permits close approach of the chain carbon atoms and the metal surface so that dispersion forces between the atoms of the metal and the lubricant can become effective. For good viscosity characteristics, likewise, it is necessary that the molecules should have a structure which gives close contact of the individual molecules in order to utilize the dispersion forces active between molecules of the oil. As the magnitude of the dispersion forces increases, the viscosity index of the oil increases also, and more energy (heat) has to be added to overcome those forces and decrease the resistance to flow of the oil. This is a disadvantage insofar as the pour point of the oil increases when the viscosity index of the polymerized oil is increased. A compromise between these two properties must be made in practice by preparing an oil with a V.I. somewhat higher than that of petroleum oils and with a reasonably low pour point.

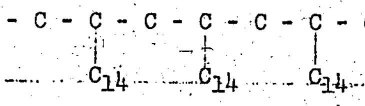
The relation between V.I. and pour point is demonstrated by the following examples:

(1) Octene - 1 polymerized to this type of structure:



This is approximately the structure which is obtained by ethylene polymerization at Leuna.

(2) Hexadecene - 1 polymerizes to this type of structure:

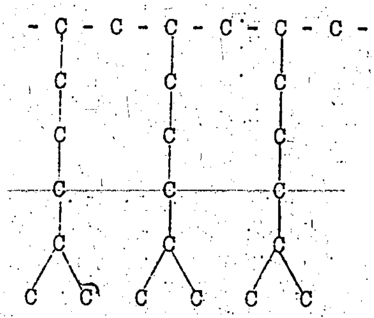


$$-C-\underset{\underset{C_{14}}{|}}{C}-C-\underset{\underset{C_{14}}{|}}{C}-C-\underset{\underset{C_{14}}{|}}{C}-C-$$

V.I. = 140

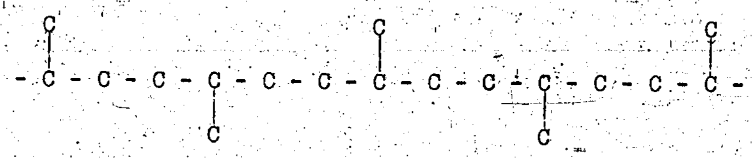
Pour Point = +10°F

Polymerization of a branched chain olefine like 6-Methylehptene-1 yields a product of the following structure:



In this case the viscosity of the oil is increased because additional forces become effective between the terminal methyl groups.

Isobutylene polymerizes to give a polymer of the following structure:



$$-\overset{\overset{C}{|}}{C}-C-C-\underset{\underset{C}{|}}{C}-C-C-\overset{\overset{C}{|}}{C}-C-C-\underset{\underset{C}{|}}{C}-C-C-\overset{\overset{C}{|}}{C}-$$

The location of carbon atoms on alternate sides of the straight chain prevents close contact between the carbon atoms in the main chain and the atoms of the metal to be lubricated. Consequently the isobutylene polymer cannot be used as a lubricant, in spite of its high V.I. (110-120) and satisfactory physical properties. Bearing failure results after a few hours when this oil is used in an engine.

Similar considerations apply in the case of propylene, which apparently forms chains through the centre carbon atom, thus giving side chains on both sides of the main chain. The V.I. of the polymer is about 85 and the polymer is unusually heat stable.

N-butylene with the double bond in the 1- position gives a good lubricating oil but butene -2 does not.

The change in dispersion forces between molecules is further illustrated by the change in melting point of hexadecane upon addition of methyl groups.

	Melting Point °F
Hexadecane	+48
+ 1 CH_3 group	-47
+ 2 CH_3 groups	-126

Sources of Olefines:

Olefinic material suitable for polymerization has been obtained by cracking several types of wax. The wax must be of a straight-chain structure and must be cracked in the vapour phase with no liquid present. To obtain structures with the double bond at the end of the molecule, the cracking time must be short at high temperatures, forming at least 95% olefine, followed by a quench to prevent isomerization of the olefine and migration of the double bond.

Wax from the atmospheric pressure Fischer-Tropsch process without the heaviest ends (controlled by maximum melting point of 176°F) is a suitable cracking stock. Wax from the 20-atmosphere (300 psi) Fischer-Tropsch synthesis is unsuitable because of branched chain paraffins. Wax from brown coal tar distillation is suitable for production of the required type of olefine.

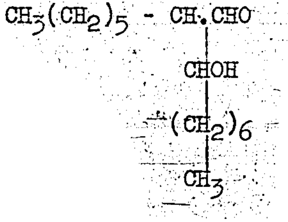
Petroleum wax as such cannot be easily handled by the above process, but can be converted to suitable wax by a combination cracking-hydrogenation step which yields a mixture of 50 per cent Diesel oil and 50 per cent straight chain paraffin wax. Hydrogenation is carried out at 3000 psi and 750°F with a tungsten sulphide catalyst and this process is in use at Ludwigshafen where 1000 tons per month slack wax from Hanover crude containing 60 per cent paraffin is processed.

The plant at Pölitz cracks a mixed wax containing Fischer-Tropsch wax, brown coal tar wax, and the special petroleum wax prepared at Ludwigshafen. A special process has been developed by Rhenania for direct utilization of petroleum wax.

Hydrocarbon Synthesis:

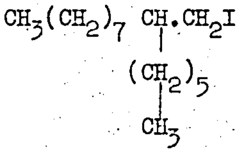
In the course of the study of the structure of lubricating oils, certain hydrocarbons were synthesised. The general method of synthesis is outlined as follows:

1. n-octyl alcohol was oxidized to the aldehyde.
2. An aldol condensation was carried out on the aldehyde to yield the following product:



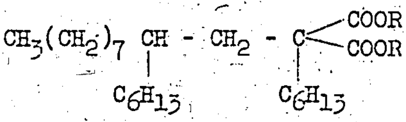
$$\begin{array}{l} CH_3(CH_2)_5 - CH.CHO \\ \qquad\qquad\quad | \\ \qquad\qquad CHOH \\ \qquad\qquad\quad | \\ \qquad\qquad (CH_2)_6 \\ \qquad\qquad\quad | \\ \qquad\qquad CH_3 \end{array}$$

~~3. This product was reduced to the alcohol and converted into~~ the iodide:



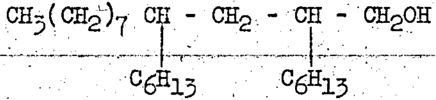
$$CH_3(CH_2)_7\ \underset{\substack{|\\(CH_2)_5\\|\\CH_3}}{CH}.CH_2I$$

4. This compound was condensed with a suitably substituted malonic ester to give:



$$CH_3(CH_2)_7\ \underset{\substack{|\\C_6H_{13}}}{CH} - CH_2 - \underset{\substack{|\\C_6H_{13}}}{C}\Big\langle\begin{matrix}COOR\\COOR\end{matrix}$$

5. This product was reduced to give:



$$CH_3(CH_2)_7\ \underset{\substack{|\\C_6H_{13}}}{CH} - CH_2 - \underset{\substack{|\\C_6H_{13}}}{CH} - CH_2OH$$

6. Steps 3 to 5 were repeated to add side chains and build compounds up to about 600 molecular weight.

LUBRICATING OIL ADDITIVES & SPECIAL PRODUCTS.

As the war progressed, it became necessary to develop lubricants, sometimes to augment dwindling supplies of otherwise satisfactory materials, but usually, as in the case of Machine Gun Oil, Recoil Oil, R.R. Axle Oil, and others, to secure improved products, usually with rust preventive properties. The development and manufacture of many of these new special materials was assigned to Dr. Zorn's laboratory at Leuna, on account of the wide experience available there on synthetic lubricating oil.

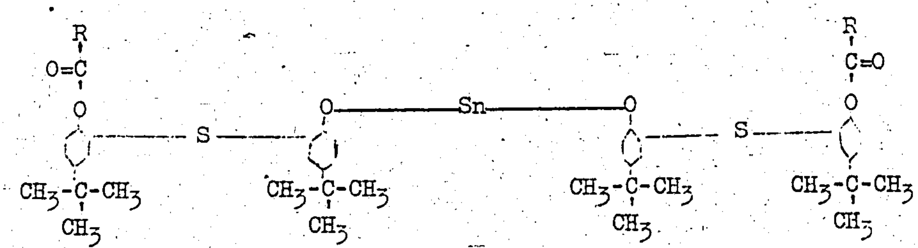
Special attention was given to compounds which could be made readily from materials already available at Leuna and two outstanding developments were Mesulfol 2, an extreme-pressure additive, and KSE, a rust preventive. Other important blending agents of the ester type were being manufactured for inclusion in special oils used by theGerman armed forces. Detailed information on the blending agents made at Leuna, the methods of preparation, properties and utilisation was obtained from Dr. Rössig and samples of the various products were obtained for assessment.

The individual additives are first dealt with and then the specialised lubricants incorporating these additives.

I Additives

(1) Inhibitor "R" (also known as "ZS-1") This inhibitor does not prevent oxidation of the oil, but guides the course of oxidation so that harmful ring-sticking products are not formed. The inhibitor has no effect on pour point, bearing corrosion, wear, or lubricating properties (Schmierfähigkeit)

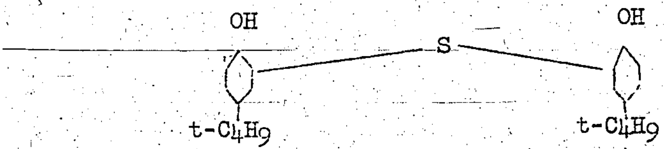
The inhibitor has the following chemical formula:



where R represents branched-chain hexyl, heptyl or octyl groups.

The steps in the synthesis of this inhibitor are as follows:-

1) Phenol is alkylated with isobutyl alcohol to give p-tert-butyl phenol.
2) P-tert-butyl phenol is treated with S_2Cl_2 to give the following compound:



3) This compound is treated with metallic sodium to make the corresponding sodium salt.
4) The acid chloride of the carboxylic acid to be used later in the esterification step is prepared by treating the acid with sulphuryl chloride. The carboxylic acids are manufactured from higher alcohols obtained as by-products during synthesis of isobutyl alcohol.
5) One mole of the product from step (3) is combined with one mole of the product from step 4 to esterify one phenolate group only.
6) This product is treated with stannous chloride in methanol to give the inhibitor as final product.

(2) E.455. A mixture of the adipic esters of 140-180°C alcohols obtained as by-products from isobutanol synthesis is prepared by heating, to 160°C, a mixture of 1.6 g. alcohols, 0.48 g. adipic acid, and 0.0015 g. β-naphthalene sulphonic acid. The reaction mixture is washed with a 20% NaOH solution and distilled under 0.2 mm. Hg. pressure until the still bottom temperature reaches 100°C. The material remaining in the still is then refined with CaO and Fullers Earth.

(3) E.504. A mixture of adipic esters of 160-200°C alcohols (C_8 - C_{12}) from isobutanol synthesis. Three methods of preparation were obtained:

(a) 1.7 g. alcohol mixture, 0.64 g. adipic acid and 0.0017 g. β-naphthalene sulphonic acid are heated to 180°C.

(b) Direct esterification of pure adipic acid, using 15% excess alcohols and 1.0 - 1.5% benzene sulphonic acid as catalyst at 150 - 160°C. (N.B. in both (a) and (b) water distils off at 150 - 160°C and equilibrium is shifted towards completion of the desired reaction).

(c) If pure adipic acid is not available, the methyl ester of adipic acid is first prepared. After purification, the methyl ester is reacted with the alcohol fraction under similar conditions to (b). The last method was in general use at Leuna.

The reaction product is washed with 20% NaOH solution and the washed ester distilled at 0.2 mm. Hg. pressure until the overheads temperature reached 110°C. The liquid remaining in the still is refined with CaO and Fullers' Earth.

Physical properties of the ester are:

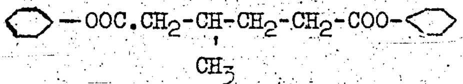
Pour Point	- 94°F
Viscosity Index	135 - 155

Production of this ester at Leuna was about 20 tons/month. It was noted that straight chain alcohols did not give as satisfactory a product as the branched chain alcohols.

(4) E.515 Mixed adipic esters of 140-180° alcohols from isobutanol synthesis.

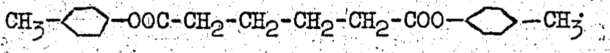
1.7 g. alcohol mixture, 0.42 g. adipic acid, 0.0017 g. β-naphthalene sulphonic acid are heated to 220-230°C and the reaction product washed with 20% NaOH solution. The washed ester is distilled at 0.2 mm. Hg. pressure until the overheads temperature reaches 135°C. The liquid remaining in the still is refined with Fullers' Earth.

(5) E.3022 The ester formed between cyclohexanol and 2-methyladipic acid



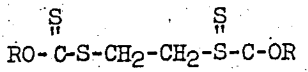
1.5 g. cyclohexanol, 0.82 g. 2-methyladipic acid and 0.002 g. β-naphthalene sulphonic acid are heated to 170°C. The reaction product is washed with caustic soda and then water. Excess cyclohexanol is distilled off and the ester distilled at 0.2 mm. Hg. The distillate is stirred with 2% CaO plus 3% Fullers' Earth for 1 hour at 70°C to remove acid.

(6) E.3023 The adipic ester of p-methylcyclohexanol



prepared in a similar way to E.3022, from 1.5 g. p-methylcyclohexanol, 0.75 g. adipic acid and 0.002 g. β-naphthalene sulphonic acid.

(7) Mesulfol 2.

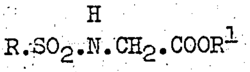


$$RO-\overset{S}{\overset{\|}{C}}-S-CH_2-CH_2-S-\overset{S}{\overset{\|}{C}}-OR$$

where R is C_5 or C_6.

The particular xanthate (dissolved in ketones, alcohol or water) is reacted with ethylene dichloride at 70°C. The product is washed with water and distilled.

(8) K.S.E.



$$R.SO_2.\overset{H}{N}.CH_2.COOR^1$$

where R_1= C_{15} radicle
R is derived from 180-250°C alcohols from isobutanol synthesis.

0.46 g. of a C_{15} hydrocarbon fraction, treated with SO_2 and Cl_2 to give a sulphonyl chloride is reacted with 2.2 g. mesamidoacetic acid and 0.69 g. of the alcohol fraction at 150°C in the presence of 0.002 g. β-naphthalene sulphonic acid as catalyst and propyl ether or ester distillate as azeotrope-forming agent to effect removal of the water produced during esterification. The reaction mixture is neutralised with carbonate solution, washed with 5% NaCl solution or distilled at 120°C (base temperature) at 10 mm. Hg., diluted with 50% middle oil and washed with a mixture of 2 parts methanol and 1 part water. The washed crude ester is distilled at 2-5 mm Hg until the still bottom temperature reaches 140°C and the liquid remaining in the still is refined with Fullers' Earth.

Other compounds not yet used in fuels or lubricating oils, which were being studied, included

(1) Ester 1321 - a mixture of adipic esters of C_9 alcohols.
(2) Ester 1473 - the reaction product of C_9 branched-chain alcohols with one mole of ethylene oxide and adipic acid.
(3) Mellit L-85 - a reaction product of trimethylol ethane with carboxylic acid and 160-180°C alcohols.
(4) Paladinol - a plasticisor made from phthalic acid and n-butanol or 140.-180°C alcohols.

II. Special Lubricants.

(a) Waffenol Blau 44, a rust preventive gun oil containing Mesulfol 2 in an amount corresponding to 3% sulphur in the final product. The other components are ester E-455 and a light distillate from synthetic lubricating oil known as VT-120. No production figures were available.

Compositon:	VT-120	45%
	E.455	45%
	Mesulfol 2	10%

Properties:	Viscosity	1.9°E at 20°C.
	Flash Point	125°C.

(b) Torpedo Oil T-1 was developed as a replacement for neatsfoot oil. It was made only at Leuna and was tested at Gdynia. Total production for 1944 was 100 Tons, and the last shipment from Leuna was 40 Tons of finished product.

Composition:	SS.903	35%
	E.515	63%
	KSE	2%
Properties:	Viscosity	11.5-12.5°E at 20°C.
	Pour Point	below - 50°C

(c) V-weapon Oil SS-1631 was developed at Leuna after about nine months of research. A monthly production of 100-200 tons was planned, but total production amounted to only 100 Tons. The last shipment of this material had been to Göttingen.

Composition:	SS.903	25%
	E.515	72%
	KSE	3%
Properties:	Viscosity	2°E at 50°C
	Pour Point	below -45°C
	Flash Point	145°C

(d) Low Pour-point oils, K.10 and K.19. were developed for use in Russia and had been reported as satisfactory in service.

		K.10	K.19
Composition:	SS.903	50%	75%
	E.515	50%	25%
Properties:	Viscosity	1.65°E at 99°C	2.0°E at 99°C
	Pour Point	below -50°C	below -45°C
	Viscosity Index	135	130

(e) "Y" railroad axle oil was developed for use in extremely cold weather after the experiences of the first winter of the Russian campaign. Tests have shown that an additional 100% loading can be put on railroad cars using this lubricant and all equipment failures due to lubricants are eliminated. A test has been run using the oil as an automotive lubricant in one German army' corps in Russia and all the Leuna vehicles use it. These tests showed no ring-sticking or corrosion difficulties.

Composition:	"R" Oil	80%
	E.504	20%
	Dye	0.1%

"R" Oil is the oil obtained on neutralising the $AlCl_3$ catalyst complex in synthetic lubricating oil manufacture.

Properties:	Pour Point.	-45 to -50°C.
	Viscosity Index.	118-122

(f) Aviation hydraulic Oil was developed to pass tentative specification Do 2000, put into effect in late 1943. The oil has excellent corrosion-resistant properties and low rubber-swelling properties (less than 2% increase in volume after 24 hours immersion). A fluorescent dye was added to the oil to meet the Luftwaffe colour specification.

Composition:	V-120	84%
	E.3022 or E.3023	12%
	KSE	4%
	Dye	.006%
Properties:	Viscosity	1.75°E at 20°C 650°E at -60°C
	Pour Point	-70°C
	Flash Point	120°C.

Conclusions and recommendation.

The use of esters in order to obtain low pour-point lubricants merits further close study. The excellent extreme-pressure properties of Mesulfol 2 and the outstanding properties of KSE as a corrosion preventive should also be investigated further.

XII. SYNTHETIC LUBRICATING OIL - SCHKÖPAU.

Introduction:

Construction of Buna Werke, A.G. Schkopau, the first and largest synthetic rubber plant in Germany, was started in 1937 and completed in 1939. It is owned and operated by I.G. Farbenindustrie. The lubricating oil plant at Schkopau was built by I.G. as a semi-works plant to utilise the excess acetylene from the large synthetic rubber plant, Buna Werke A.G. In the latter plant, acetylene, manufactured from calcium carbide and water, is converted to butadiene by the aldol process, and then polymerized with styrene made from ethyl-benzene for the preparation of Buna S. The normal Buna S production is 6,000 T/month when operating at capacity. In the Buna S plant, part of the acetylene is hydrogenated to ethylene, and the ethylene reacted with purchased benzene to make ethyl benzene. Excess acetylene can be converted to ethylene in the same manner and diverted to the manufacture of synthetic lubricating oil, where the ethylene is subsequently polymerized with aluminium chloride, neutralized, reduced to the desired viscosity and contacted with fine clay for the manufacture of SS-903 and SS-906, synthetic lubricating oils Normal average production is 500 T/month, or slightly more than 100 B/D (42 U.S. Gal.)

Description of the Process:

Excess acetylene from the rubber plant is hydrogenated to ethylene using 0.01% palladium oxide catalyst supported on silica gel. Hydrogen is obtained by pipe line from Leuna. The reaction takes place at 200-250°C and atmospheric pressure. Each oven contains approximately 4 cubic metres of catalyst arranged in three beds with direct water spray between stages to control the reaction temperature. At the end of 6-8 months, the catalyst is reactivated with air at 500-600°C. The yield of ethylene was reported to be 72% of theoretical. After water washing, the gas is fractionated in the Linde plant to yield 99% pure ethylene.

From the Linde plant, the ethylene passes to the polymerization step. The six reaction vessels, for polymerizing the ethylene, are made of stainless steel (V_4A), 12 m. high and 800 mm. or 1200 mm. i.d., pressure tested at 200 atmospheres, nominal working capacity, 6-8 cu. metres. The reactors are water and steam jacketed with bolted, flange heads, with provisions for admitting the aluminium chloride and the light recycle material through the top flange. A small stirrer, with stainless steel blades, is driven through a liquid seal stuffing box in the bottom flange. A 5 HP electric motor with reduction gears drives the stirrer at 120 RPM. Ethylene is also admitted through a suitable connection in the bottom flange.

The reactors are operated batchwise. 1.5 cu.m. of the "Vorlauf-öl" (low boiling hydrocarbon recycle stock) is charged to the reactor along with a quantity of aluminium chloride equivalent to approximately 7% by weight of the finished polymer. Ethylene is then bubbled through the aluminium chloride-hydrocarbon mixture at 60-100 ats pressure and with the temperature maintained at 120-140°C. The initial reaction is exothermic and cooling water must be circulated through the jacket to absorb the excess heat evolved. As the reaction proceeds, heat must be supplied to maintain the temperature at

120-140 C. The reaction is completed in 8-10 hours. The sour oil (polymer-aluminium chloride sludge mixture), now at atmospheric pressure, is transferred to small intermediate tanks, equipped with stirrers to keep the sludge in suspension, 10-12% by volume of methanol is added, and the resultant mixture centrifuged.

Six basket-type centrifuges (baskets rotating at 900 RPM on a horizontal axis and driven by 35 HP electric motors) built by Escher Wyss, Ravensburg, are used. The supernatant oil is pumped to a neutralizing vessel, equipped with stirrers, and enough lime is added to neutralize any free HCl. Normally, 2% by weight of lime is needed, but this varies with the amount of HCl evolved during the polymerizing step. The neutralized oil is pumped to plate-and-frame filter presses to remove the calcium chloride. Six presses have been installed, only three are normally used. The neutralized oil is then reduced to the desired viscosity, using vacuum and steam at a maximum temperature of 250°C. The methanol vapours from the reducing still, along with the methanol vapours from the centrifuges and the intermediate handling tanks, pass to the methanol recovery system where 97.0 - 98.0% of the methanol is recovered by rectification. The "Vorlauf-öl" (light hydrocarbon recycle oil) is returned to the reaction vessel for re-use.

The bottoms from the vacuum reducing still are pumped to the clay contact units and contacted with 5% by wt. of fine clay or silica gel. Two contactors are in use, each with a capacity of 10 cubic metres, equipped with stirrers operating at 50 RPM., clay treatment is carried out at 100-120°C for 30 minutes. The oil-clay mixture is pumped to a plate-and-frame filter press where the fine clay is removed. The filtered oil is next pumped to a plate-and-frame filter press where the fine clay is removed. The filtered oil is next pumped to a de Laval centrifuge to remove any traces of fine clay leaking through the filter press. The filter cake is blown with nitrogen to recover the oil soakage.

The finished lubricating oil, usually 8-10° Engler at 100°C., is blended with oil of lower viscosity for 5.8 - 6.2° Engler, and shipped to various blending stations where it is blended with an equal volume of natural mineral oil for use in aircraft engines. Synthetic lubricating oil from Schkopau was used only in the production of aviation lubricating oil because of its excellent non-ring sticking properties. Typical tests of Schkopau synthetic lubricating oil are as follows:-

Description:	SS-903 Oil	SS-906 Oil
Inspection:		
Specific Gravity	0.80-0.83	0.805-0.835
Viscosity, Engler° 100°C	2.9 - 3.0	5.8 - 6.0
Viscosity Index	105 - 115	105 - 115
Flash: °C	205	225
Pour: °C	-35	-30
Carbon Residue: %	0.02	0.03
Neutralization No.	nil	nil
Ash %	nil	nil
Chlorides: %	nil	nil

Typical quantities of raw materials and utilities needed per ton of synthetic lubricating oil, are as follows:

Acetylene	1700 kg.
Methanol	2.7 kg.
Vorlauf-ol	1.2 "
Aluminium Chloride	70.0 "
Lime	30.0 "
Fuller's Earth	10.0 "
High Pressure Steam	1.7 tons
Low Pressure Steam	6.0 "
Fuel Gas (2000 kg. Cal/M^3)	250 M^3
Electricity	150 KWH
Water	150 M^3

Miscellaneous:

The German technicians interrogated maintain that little corrosion difficulties have been encountered; stainless steel is used in the reaction vessels, while intermediate sour oil tanks have synthetic rubber liners faced with brick. Some corrosion was noticed in the vapour condensers of the vacuum reducing-still but this was eliminated by adding caustic soda to the reflux to the vapour fractionator.

Aluminium chloride is obtained from the I.G. Farbenindustrie A.G., Ludwigshafen-am-Rhein, in special metal drums. The drums are dumped into the reactor by hand using a funnel that fits the end of the drum. A gate valve controls the rate of admittance, when charging the reactor. The effect of impurities in the aluminium chloride was not known.

The rubber plant employs 15,000 men when operating at normal capacity. The lubricating oil plant normally employs 65 men. Operation is intermittent, depending upon the supply of acetylene from the rubber plant. The plant has not been damaged to any extent and operations can be resumed as soon as a supply of ethylene can be obtained.

Conclusions:

While the production of lubricating oil from acetylene is of interest, the cost of the finished product is high. Assuming that acetylene can be made for 25-30 pfg. per kg. from natural gas (methane) by the electric arc process used at Huls, the large capital expenditure for equipment and the number of men required for operation, make the cost of the synthetic lubricating oil too high to compete with lubricating oils from selected American crude oils, unless an examination of the samples obtained, indicates that these oils have some valuable properties for special uses.

XIIA. SYNTHETIC LUBRICATING OIL MANUFACTURE AT STETTIN-PÖLITZ

Source of Information:

Information on this plant was secured in the course of an interview with Dr. Zorn at Leuna on 15th May 1945.

Summary:

A mixture of Fischer-Tropsch wax (maximum melting point 176°F), and a special wax from brown coal tar distillation (made by a combination cracking/hydrogenation process at Ludwigshafen) is cracked under closely controlled conditions to give 95-97% olefines. These are polymerised at law pressure in the presence of aluminium chloride. The oil is separated, neutralised and vacuum distilled with steam to remove light ends.

Ultimate yields from the paraffin wax charged are:-

	Weight %
Gas	27-30
Lubricating Oil ...	49-52
Diesel Oil (light ends)	6-7
Steam cylinder oil (from decomposition of catalyst complex).	8-11
Total accounted for	90-100

Production capacity of this plant was rated as 1000-1200 metric tons/month (242-290 B/D). In the final 6 months' operation, production was about one-half this figure.

Description of Process:

Wax Cracking:

The wax is preheated in a pipe still at low pressure to 842-896°F and completely vaporised. It then flows upward in a parallel tube bank heated by circulating flue gas. The outlet temperature is controlled at 968-977°F at atmospheric pressure. This cracking tube bank is made of 18-8 stainless steel (V2A) to avoid coking and dehydrogenation. Residence time in the preheater is 1-2 minutes, and in the cracking coil about 0,1 second. No steam is used in the furnaces.

The effluent is quenched in a steam heat exchanger to 500°F. All condensate at this temperature is recycled to the furnace. The vapours (about one-third of total) are cooled indirectly with 68°F water and the gas is vented from this condensation.

Gas composition is:

	%
Hydrogen	1-2 (analysis used for plant control).
Ethylene	30
Propylene	15
n-Butylenes	15
Paraffins	40

Ultimate yield of gas on fresh feed is about 30 weight per cent, with a minimum of 27-28 weight per cent. This gas was not used for polymerisation.

The liquid product is 95-97% unsaturated. Determination of the iodine number is used as one control in the cracking step. This liquid is used directly in the polymerisation step.

Polymerisation:

Polymerisation is carried out at atmospheric pressure in reactors of 125 barrel capacity, water-jacketed, and equipped with straight blade stirrers revolving at 100 RPM. The aluminium chloride used in polymerisation is first suspended in light oil from the process. A part of the olefine feed is added, the kettle is heated to 158-176°F to start the polymerisation and then controlled at the desired polymerisation temperature by the rate of addition of cold feed. The total olefine feed is added in about 22 hours and the reaction is completed by heating the batch to 212-230°F and stirring at that temperature for two hours to further polymerise lower polymers formed in the early part of the reaction. Two grades of lubricating oil have been manufactured in this equipment:

SS 1103 nominally 3° Engler Viscosity at 100°C
SS 1106 " 6 " " " "

Their respective characteristics are discussed later. Operating conditions for the reactors for these products are as follows:

	SS 1103	SS 1106
Al Cl_3 catalyst consumption (% of finished oil)	7-8	14-16
Reaction temperature °F	158	(Low as possible. (Winter - 104 (Summer - 122

Refining of Polymerised Oil.

The total product from the polymerisation reactors is separated into oil and aluminium chloride addition compounds by ordinary centrifuges. No methanol is needed for this separation. Centrifuging is done at 176°-212°F without any additional heat being supplied. The aluminium chloride addition product so separated is in a liquid form.

The lubricating oil portion is treated with water at room temperature to decompose traces of aluminium chloride, then treated with lime and Fuller's earth, filtered and distilled under vacuum with steam. The light ends are partially recirculated for suspension of aluminium chloride in the polymerisation reactors and partially yielded as Diesel oil. This oil can also be hydrogenated and then treated with sulphur dioxide and chlorine in the Mersol synthesis.

The aluminium chloride addition product from the centrifuges is decomposed with water, treated with lime and Fuller's earth and used as steam cylinder oil after stripping of low boiling hydrocarbons for flash point specifications. This steam cylinder oil is considered better than the corresponding product from ethylene, because it is obtained at a lower polymerisation temperature and is less unsaturated.

Tests on Products:

	Lubricating Oil		Diesel Oil	Steam Cylinder Oil
	SS-1103	SS-1106		
Viscosity °Engler at 100°C.	3.0	5.5-5.6		6.0
SSU at 210°F	105	200-205		220
Viscosity Index	115-124	108-112		115-116
Flash Point °F	428 min.	482-500		572-590
Pour Point °F	-22 max.	13 max.	32±2	-4 max.
Conradson C.Res.	0.2 max.	0.2 max.		0.4-0.5
Iodine No.				20
Cetane No.			72-73	
IBP			302 min.	
Sulphur %			0	

Yields:

The ultimate yields from the original paraffin are summarised as follows:

	Type of Operation	
Weight per cent	SS-1103	SS-1106
Gas from Cracking	27.0 - 30.0	27.0 - 30.0
Finished Lubricating Oil	49.0 - 52.5	49.0 - 52.5
Diesel Oil	7.0	5.6
Steam Cylinder Oil	8.4	11.2
Unaccounted for	8.6 - 2.1	7.2 - 0.7
Total:	100.0	100.0

XIII. AVIATION FUEL MANUFACTURE AND ENGINE TESTING.

Introduction:

The following information was obtained by interrogation of Dr. Ester, Mr. Scholz and Mr. Honicker.

The test engines originally installed at Leuna have now been evacuated to Wethau and Stossen. These locations were visited.

Octane Number Determination and Specification:

For day-to-day control of aviation gasoline component quality, Octane Number tests were carried out on C.F.R. Motor Method engines and on the I.G. Prüfmotors; the latter being used almost exclusively as spare parts for the C.F.R. engines became impossible to obtain. In 1944 there were 170 of these engines in use in Germany.

The Octane Number specifications in force in early 1945 were as follows:

D.H.D. Gasoline	78 Octane No. clear
Hydro Gasoline	70 " " "
	87 " " with 0.09% vol. T.E.L.

I.G. Prüfmotor

Swept volume	342 ccs.
Compression Ratio	Variable up to a max. of 14:1
R.p.m.	900 for Motor Method 600 for Research Method
Spark Advance	26° for Motor and Research Method
Jacket Temperature	100°C for Motor Method 100°C for Research Method
Mixture Temperature	165°C for Motor Method Room temperature for Research Method

This engine is used with a multi-bowl carburetter in the usual way and all Octane Number determinations are made at max. knock mixture strength. Bouncing pins and knock meters made by Siemens are employed. The normal method of carrying out Octane Number determinations is to adjust the mixture strength to max. knock; increase the compression ratio until a standard rating on the knock meter is obtained; measure this compression ratio by a conventional micrometer and determine Octane Number directly from a standard chart in which Octane Number is plotted against compression ratio. The Octane Number can also be directly read from a scale attached to a mechanism geared to the movable cylinder head.

This engine has also been used for supercharged tests and 5 to 10 supercharged engines were stated to be in use in various parts of Germany. This development followed initial tests in 1941 in Oppau, and Leuna first carried out supercharged tests of this nature at the end of 1941. In these tests pressure fuel tanks and a pressure carburettor are employed together with an air meter and the standard boost pressure ~~is 1,000 mm. absolute. Test results~~ ~~are expressed in the form of a graph relating air/fuel ratio to compression~~ ratio for constant knock, but a direct octane scale can be used in this case also.

B.M.W. 3-litre Single-cylinder Aero Engine:

This engine was employed at Leuna for official acceptance tests. Due, however, to air raids, this engine had been dismantled and crated for erection at some other location. The tests were only carried out to obtain acceptance of the aviation fuel components since blending of the finished fuel was carried out at the WIFO blending stations. Laboratory blends conforming to the official formula were prepared and tested. The engine operates at a constant compression ratio of 6.5 : 1 with variable supercharge. Other operating conditions are 1600 r.p.m., ignition 30° B.T.D.C., inlet air temperature 130°C., air cooled and direct injection. Tests are carried out in a normal manner by plotting air/fuel ratio against M.E.P. Acceptance was granted when the M.E.P. air fuel ratio curve approached the standard acceptance curve.

Aviation Gasoline:

The following information on the development of aviation gasoline was obtained from Dr. Ester, chemist in charge of gasoline quality control by engine testing.

The necessity for manufacturing a fuel with high aromatic content was due to the development by BMW and Daimler-Benz of engines which had a mean effective pressure of 294 psi at an air/fuel ratio of 0.75 for starting and combat and m.e.p. of 147 psi at air/fuel ratio of 1.2 for cruising. The Junkers engine, however, was said to operate on 90 octane fuel which was prepared from hydrogenation gasoline with 4.5 cc of TEL per gallon and represents the normal grade aviation fuel (B_4). Inspection of the lean and rich mixture curves indicated that iso-octane would have been the ideal fuel for the German engines. Since a fuel of this kind could not be obtained, it was necessary to incorporate 35-45% vol. of aromatics into the aviation fuel. No isopentane blending was practiced and the components themselves were stabilised to give ~~a~~ Reid vapour pressure below 7.4 for the final blend.

The source of the blending component with a high concentration of aromatics was the hydroforming of the hydrogenation gasoline (DHD process) Alkylate was obtained by dehydrogenation of n-butane and conventional alkylation of the resulting n-butylenes with iso-butane, using concentrated sulphuric acid as the catalyst. Iso-octane is obtained by hydrogenation of diisobutylene.

The fighter grade aviation fuel (C_3) was blended as follows:

80% DHD gasoline
20% alkylate or ET 120 or mixture of both
4.5 cc TEL/gallon

~~The DHD gasoline contains 0.1% by volume of mixed cresols as gum inhibitor. This fuel was slightly better than engine requirements but it~~ was expected that engine design would very shortly make full use of it.

All German aviation engines are of the direct injection type, and it is claimed that this arrangement results, among other things, in good mixture distribution to all cylinders and the absence of difficulties by ice formation. In order to increase the quantity of aviation fuel, tests have been carried out to prepare a fuel which would dispense with the DHD process which operates with high gas make. Addition of 2% methylaniline and 7.5 cc TEL/gallon to hydrogenation gasoline and use of this fuel in conjunction with methanol/water injection as well as change of the injection cycle appeared to give the desired result. The tests were carried out by Junkers on the regular BMW test engine. Daimler-Benz and BMW, however, claimed that they could not get their maximum output (2400 HP) with this type of fuel. It seems desirable to mention that the Junker's motor JuMo 213A had an output of 2800 HP with the fighter grade aviation fuel.

Nomenclature of Aviation Fuels:

~~The following nomenclature was used in Germany for the various grades of~~ aviation fuel components and finished blends. This list does not include identifications for all German plants but only the code numbers obtained during the interview with Dr. Ester.

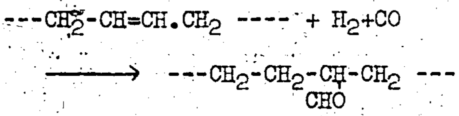
B Fuels	hydrogenation gasoline, leaded
C Fuels	high efficiency fuel
ET 110	technical iso-octane (96 octane no.)
ET 120	alkylate (94 " ")
VT 702	hydrogenation gasoline from Leuna + 4.5 cc TEL/gal. (90 octane no.)
VT 705	hydrogenation gasoline from Scholven, leaded as above.
VT 706	hydrogenation gasoline from Pölitz, leaded as above.
VT 708	hydrogenation gasoline from Gelsenberg, leaded as above.
VT 810	hydrogenation gasoline from Böhlen, leaded as above.
VT 812	" " " Brüx " " "
VT 342	hydro-formed hydrogenation gasoline (DHD gasoline)
D 1000	pure iso-octane reference fuel.

The sulphur content for all aviation fuels and components was specified to be 0.005%. A stability test was included in the specification according to which 200 cc. of gasoline were kept at 103 lbs. (7 atm) oxygen pressure and 212°F for 2 hours; the gasoline was passed without further testing if no pressure drop took place during this period. In case of a pressure drop the gum formed was determined and the permissible gum content was set at 5 mg/100 cc of gasoline.

XIV. OXO PROCESS.

Introduction:

The OXO Process consists of the reaction of olefines with water gas in the presence of Fischer Tropsch catalyst to give aldehydes according to the general equation



$$\text{---}CH_2\text{-}CH{=}CH.CH_2\text{----} + H_2{+}CO \longrightarrow \text{---}CH_2\text{-}CH_2\text{-}\underset{CHO}{CH}\text{-}CH_2\text{ ---}$$

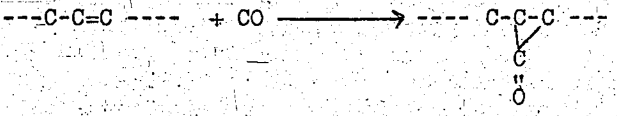
The aldehydes are hydrogenated to alcohols in a subsequent step.

The basic reaction was discovered by Ruhrchemie but the large-scale development of a continuous process resulted from a co-operative effort by Ruhrchemie and the I.G. The Chemo-Gesellschaft was a development organisation formed by these two companies on a 50/50 participation basis. The process was later licensed to the operating company - the OXO Gesselschaft.

Extensive research on the process was carried out at Leuna where a plant of 100 T/month design capacity operated for 1½-2 years. The actual production was, however, only 40/50 T/month because of shortage of the preferred raw material - Kogasin. Leuna processed a certain amount of "Gelböl", an olefinic by-product of the higher alcohols process to supplement their Kogasin supplies but it was stated that it was an inferior raw material. The present report is limited to information obtained at Leuna. Details of Ruhrchemie work are given in other reports, notably that on the Ruhrbenzin A.G. Target No. 30/5.01.

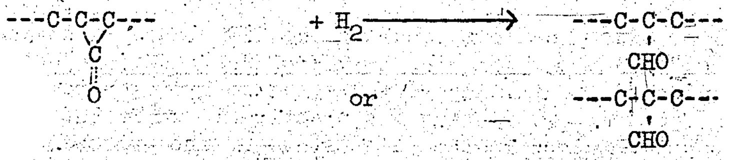
Chemistry of the OXO Process:

The first step in the process appears to consist of the addition of CO to the olefine according to the equation -



$$\text{---}C\text{-}C{=}C\text{ ----} + CO \longrightarrow \text{----}C\text{-}\underset{\substack{C\\ \|\\ O}}{C}\text{-}C\text{ ---}$$

This intermediate product cannot be isolated because it is hydrogenated immediately to give aldehydes as follows:

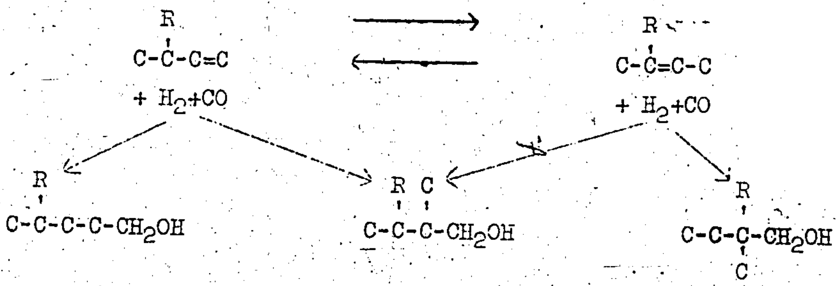


$$\text{---}C\text{-}\underset{\substack{C\\ \|\\ O}}{C}\text{-}C\text{---} + H_2 \longrightarrow \text{---}C\text{-}\underset{CHO}{C}\text{-}C\text{---} \quad \text{or} \quad \text{---}\underset{CHO}{C}\text{-}C\text{-}C\text{---}$$

dependent on the point at which hydrogen enters the molecule.

Further hydrogenation, mainly carried out in a separate reaction stage, yields the corresponding primary alcohols.

It will be seen that even in the simplest case, the OXO Process gives a mixture of aldehydes or alcohols. This tendency towards a mixed product is further increased by isomerisation of the olefine under the OXO Process conditions, thus:



The reaction involving the least steric hindrance predominates. Thus, using isobutylene as the olefine

$C\text{-}\overset{C}{C}\text{-}C\text{-}CH_2OH$ is obtained in greater quantity than $C\text{-}\overset{C}{\underset{C}{C}}\text{-}CH_2OH$.

Similarly, when using trimethylpentenes obtained from polymerisation of isobutylene, the main OXO products are those derived from the $C\text{-}\overset{C}{\underset{C}{C}}\text{-}C\text{-}\overset{C}{C}\text{=}C$ isomer as distinct from $C\text{-}\overset{C}{\underset{C}{C}}\text{-}C\text{=}\overset{C}{C}\text{-}C$.

The mixed alcohols obtained from the OXO Process are mainly used after sulphonation for detergent manufacture. For this purpose the mixed alcohols are said to be better raw materials than single compounds.

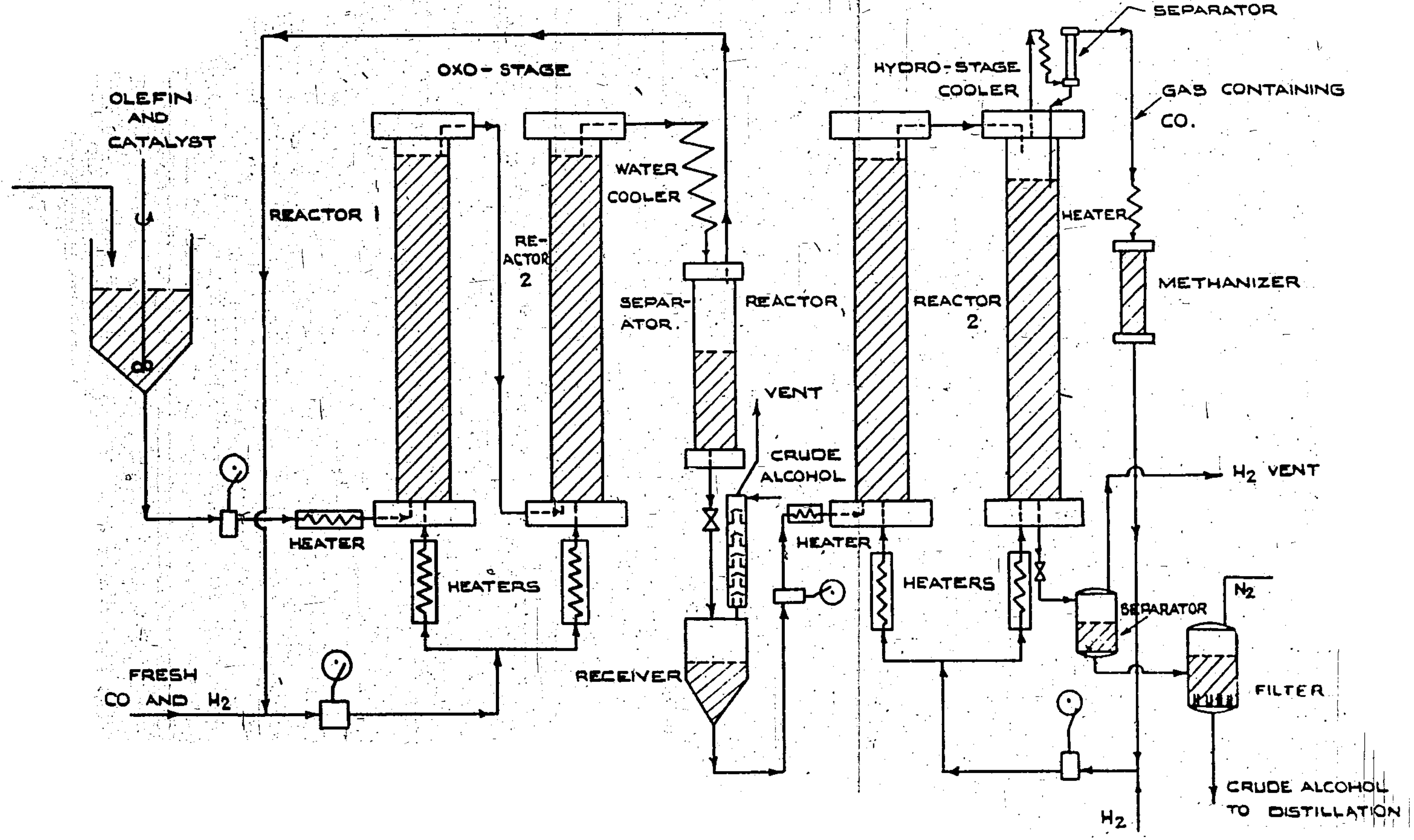
Process Conditions:

The first stage of the process is carried out at about 200 ats. pressure and 150° - 160°C in the liquid phase. Finely divided Fischer Tropsch catalyst is suspended in the liquid feed in a concentration of 3-5% by weight. Most of the catalyst is recycled and the make up requirement is said to be very small. Normally, when using Kogasin as the olefinic feed, the reaction time required is of the order of 20 minutes. Lower olefins reacted very readily. In the case of low molecular weight olefines, they have to be used in solution in a liquid medium.

A number of side reactions occur in the OXO stage. Aldehydes polymerise to give "Dickol" which comprises up to 20% of the crude product. About one third of the aldehydes initially formed are also hydrogenated to the corresponding alcohol. It is thus not practicable to isolate aldehydes from the crude product obtained in the first stage of the process. If these products are required, it is considered preferable to complete the hydrogenation in the second step, separate the alcohols and oxidise them to the corresponding aldehydes.

FIGURE XXX

OXO PLANT



This second step of hydrogenation, in addition to converting the aldehydes in the alcohols, breaks down about 50% of the Dickol to alcohols of the same composition as are derived from the corresponding aldehydes. The hydrogenation is hindered by the presence of CO. It is therefore necessary to let down to atmospheric pressure the crude product from the first OXO stage and to carry out the hydrogenation in a separate step. This stage is carried out at about 200 ats and at a temperature of 170-195° C. The same catalyst as used in the first stage can be employed, or, alternatively, this catalyst can be filtered out of the first stage crude and it can be replaced by the more readily available copper chromite. When Fisher Tropsch catalyst is employed, some carbon monoxide is formed in the hydrogenation reaction as a result of reduction of cobalt carbonyl. In order to keep down the concentration of carbon monoxide in the circulating hydrogen, the exit gas is treated over an iron catalyst to convert carbon monoxide to methane. The methane content of recycle gas can be as high as 10% without adverse effect on the reaction. This concentration is maintained by bleeding off the requisite amount of gas from the circulating system.

The first step of the OXO Process is not affected by the presence of sulphur compounds in the raw materials but these impurities do hinder the subsequent hydrogenation step if carried out with Fischer Tropsch or copper chromite catalyst. When dealing with sulphur-containing olefine raw material, therefore, it is necessary to filter off the first-stage catalyst and to carry out the hydrogenation over fixed nickel tungsten sulphide catalyst. It is necessary to carry out a partial hydrogenation of the crude first-stage product prior to filtration in order to convert any cobalt carbonyl into cobalt.

Leuna Operation:

The process, as originally worked out by Ruhrchemie, was a batch process and the pilot plant at Holten consisted of 18 units originally intended for batch operation. Work at Leuna showed that considerably higher throughputs were obtained from continuous operations.

The following description of the latest method of operation of the Leuna plant was obtained by W. A. Horne from Dr. Gemassmer, who was the chemist directly in charge of these operations. It should be read in conjunction with Fig. XXX.

The olefine or olefine-containing charge is mixed with 3-5% by weight of catalyst, most of which is recycled material. This suspension is pumped at the rate of 300 - 700 litres/hour and at a pressure of 220-240 ats. through a heater which raises its temperature to approximately 150° C. The preheated feed enters the bottom of the first reactor and passes upward concurrently with a steam of 60 M^3/hour of carbon monoxide and hydrogen which has been separately preheated to 150-190° C (maximum: 200° C). This synthesis gas is partly recycle gas from the process (40-50 M^3/hour) and partly make up gas which consists of equal molecular proportions of hydrogen and carbon monoxide. The first reactor, which is constructed of carbon steel, has an internal diameter of 200 mm. and a length of 8 M. It contains 6 vertical 21 mm. OD, 17 mm. ID, steel cooling tubes which are connected to a water jacket surrounding the reactor. Cooling by these tubes is used only when very reactive olefines are charged and the heat release is high. A thermocouple well extends the length of the reactor and the temperature of the exit products is normally controlled at 150°C. The temperature and feed rate depend on the concentration and molecular weight of the olefines in the charge stock. As previously stated, lower molecular weight olefines are more reactive. Low concentration of olefines in the feed necessitates the use of lower feed rates and higher temperatures in order to ensure that reaction proceeds to the required extent. Normally, roughly 70% of the olefines charged are converted in the first reactor.

The exit products from the top of this first reactor pass to the bottom of the second reaction vessel where they come into contact with an additional 60 M^3/hour of synthesis gas. The second reactor has the same dimensions as the first but is fitted with baffles to increase the efficiency of contact. No cooling tubes are required. The normal operating temperature is 170°C. Essentially all the remaining olefines are converted and some 20% of the aldehydes made are hydrogenated to alcohols.

The exit products from the top of the second OXO reactor now flow through a water cooler to a separator from which synthesis gas is recycled to the preheater. The liquid product is let down to atmospheric pressure and the released dissolved gases are purged after scrubbing with crude second-stage product to prevent loss of liquid by entrainment. The crude first-stage product is now pumped under a pressure of 200-250 ats. to the second-stage preheater from which it passes to the bottom of the first reactor of the hydrogenation stage. 60 M^3/hour of a mixture of preheated fresh hydrogen and methanised recycle gas is also introduced at the bottom of the reactor. The reactor is identical with the first reactor of the OXO stage but operates at an exit temperature of 180°C. The exit product from the top of this reactor passes to the top of the second hydrogenation reaction vessel and is passed downwards counter-current to an additional 60 M^3/hour of reaction gas. The exit temperature of this second reactor is roughly 200°C. The draw-off of liquid product from the bottom of this converter is regulated so as to keep the reactor full of liquid. The top of the second reactor serves as a high pressure separator vessel for hydrogen and liquid products. The hydrogen containing some carbon monoxide is water-cooled and passes to a catch-pot for separation of condensed liquid which is returned to the hydrogenation reactor. Before being recycled to the hydrogenation reactors, the gas is reacted at 250°C over an iron catalyst (similar to that used in the Synol Process) in order to convert carbon monoxide to methane.

The liquid product is let down to a pressure of 10 ats. to a separator from which dissolved gases are vented. The liquid from this separator is charged under its own pressure to the filter system illustrated in Fig. XXXI. The liquid, in batches of 700 litres, enters the filter vessel (which is pressured with nitrogen through Valve 1) and is filtered through the porous ceramic tubes situated at the bottom of the vessel. This operation requires about 10 minutes with a new filter but can take up to 30 minutes when the filters are old. When filtration is complete, fresh olefine charge is introduced through Valve 3 and passes in the reverse direction through the filter thereby washing off the catalyst material. The whole vessel is rotated at 60 revs/minute for 2-3 minutes. It is stopped in the inverted

FIG XXXI

OXO PLANT BATCH FILTER (FILLING POSITION)

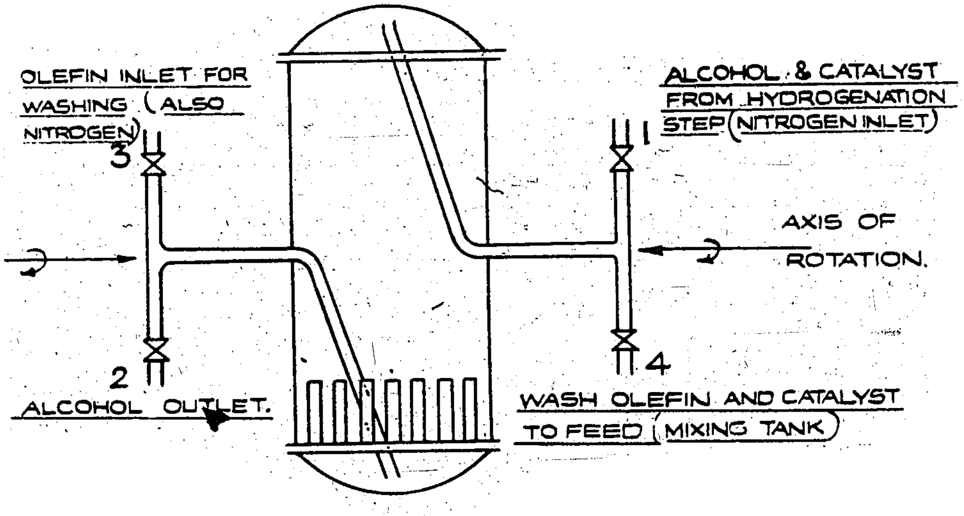
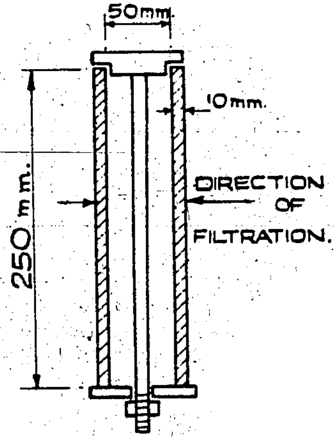


FIG. XXXI A

DETAILS OF OXO PLANT CERAMIC FILTER TUBES



position and the olefine catalyst suspension is forced out through Valve 4 by nitrogen pressure, nitrogen being introduced through Valve 3. This suspension is then transferred to the feed mixer of the OXO Process. The cycle time for a complete operation of the filter is one hour per batch of 700 litres of crude product.

The treatment of the filtrated crude product depends on the type of olefinic raw material used. If this raw material has initially a boiling range not exceeding 30°C, the alcohols can be separated from hydrocarbons by simple distillation. If, on the other hand, a raw material of wider boiling range is employed, alcohols have to be separated by the boric acid method as described in Section XV dealing with the Synol Process.

A number of variations of the above process had been tried out at Leuna. The effect of introduction of liquid feed at the top of one or both of the OXO reactors was tried, as was also the operation of the OXO Process with liquid and gas flowing counter-currently. The process was also operated with only one reactor in the OXO and hydrogenation stages. According to Dr. Gemassmer, however, the method described in detail above was found to be the most satisfactory.

An essential of any scheme for operating the OXO Process is that the synthesis gas rate in both the OXO and hydrogenation stage must be sufficiently high to ensure efficient stirring and complete suspension of the catalyst. A large excess of synthesis gas is not necessary from the purely chemical standpoint. Research carried out by the I.G. suggests that the OXO stage might be operated at 40 - 50 ats. pressure but under these conditions the throughput would be lower and the temperature somewhat higher. One of the difficulties sometimes encountered was that unless the conditions in the OXO stage are carefully controlled, olefine polymerisation takes place. The polymers so formed, after hydrogenation in the second step, are difficult to separate from the higher boiling alcohol products.

Catalyst Preparation:

The Fischer Tropsch catalyst used in the OXO Process was obtained from the catalyst plant of Ruhrchemie at Oberhausen-Holten. It was reported to have the following approximate composition:

30%	Cobalt
2%	Thorium Oxide
2%	Magnesium Oxide
66%	Kieselguhr

Due to the scarcity of cobalt, the content of this component of the catalyst has latterly been decreased. The last shipment contained only about 25% of cobalt. This apparently had little effect on the process operation.

The catalyst in powder form is reduced with pure sulphur-free hydrogen. The hydrogen flow is contolled at a rate high enough to prevent settling of the catalyst powder, i.e. the catalyst is fluidised by the hydrogen stream. The period of reduction is 2-4 hours.

OXO Processing of Cracked Middle Oil:

In addition to Kogasin and Gelböl, Leuna had investigated the treatment of cracked petroleum oil by the OXO Process. Dr. Gemassmer provided the following data from a run, the conditions of which were not considered to be optimum.

The olefinic feed material had the following properties:

Density	0.848
Pour Point	-18°C
Av. Molecular Wt.	195
Iodine No. (Hanus)	46-48
Sulphur Content	.24% by wt.
Boiling Range	230°-350°C
Volume % soluble Kattwinkel solution	51.

The charge was mixed with 3% by weight of catalyst and reacted with water gas at 240 ats. Total reaction time in the OXO stage was approximately 1 hour. The temperature at the inlet to the first reactor was 150 C and that at the exit of the second reactor 190 C. The hydrogenation of the crude product was carried out at 220 ats with hydrogen of 97% purity. The temperature was 195 - 200 C and the total reaction time approximately 1 hour. The product had the following properties:-

Density	.862
Iodine No. (Hanus)	19.6
OH No.	36-40 mgm KOH/gm.
CO No.	3.5
Saponification No.	5 mgm KOH/gm.

The OH number is determined by acetylation with acetic anhydride followed by titration with KOH solution. The CO number is a measure of the aldehyde and ketone content and is determined by forming the oximes of aldehydes and detones followed by titration with KOH solution.

The crude product contains 16-17% alcohols which may be separated from the hydrocarbons by forming boric esters. It is not possible to separate the alcohols by simple distillation because of the wide boiling range of the charge stock.

Only about 60% of the olefines was converted and of this, approximately 80% was recovered as alcohol.

Fig. XXXI (B) is a photograph of the OXO converters.

In addition to the authors, Major A. V. J. Underwood contributed notes and these were of very great assistance in compiling the above report.

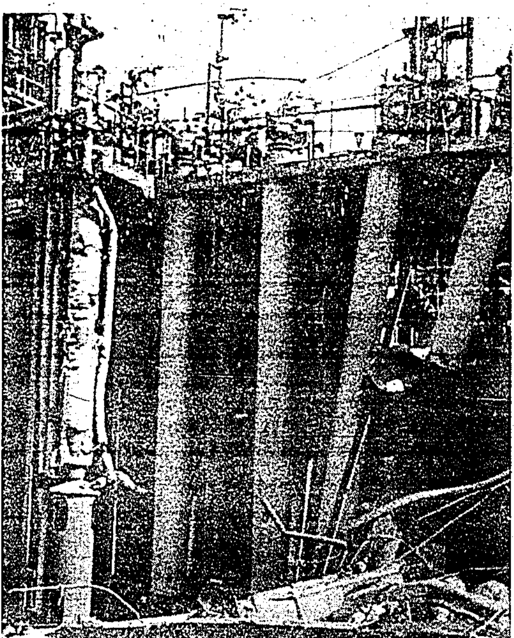
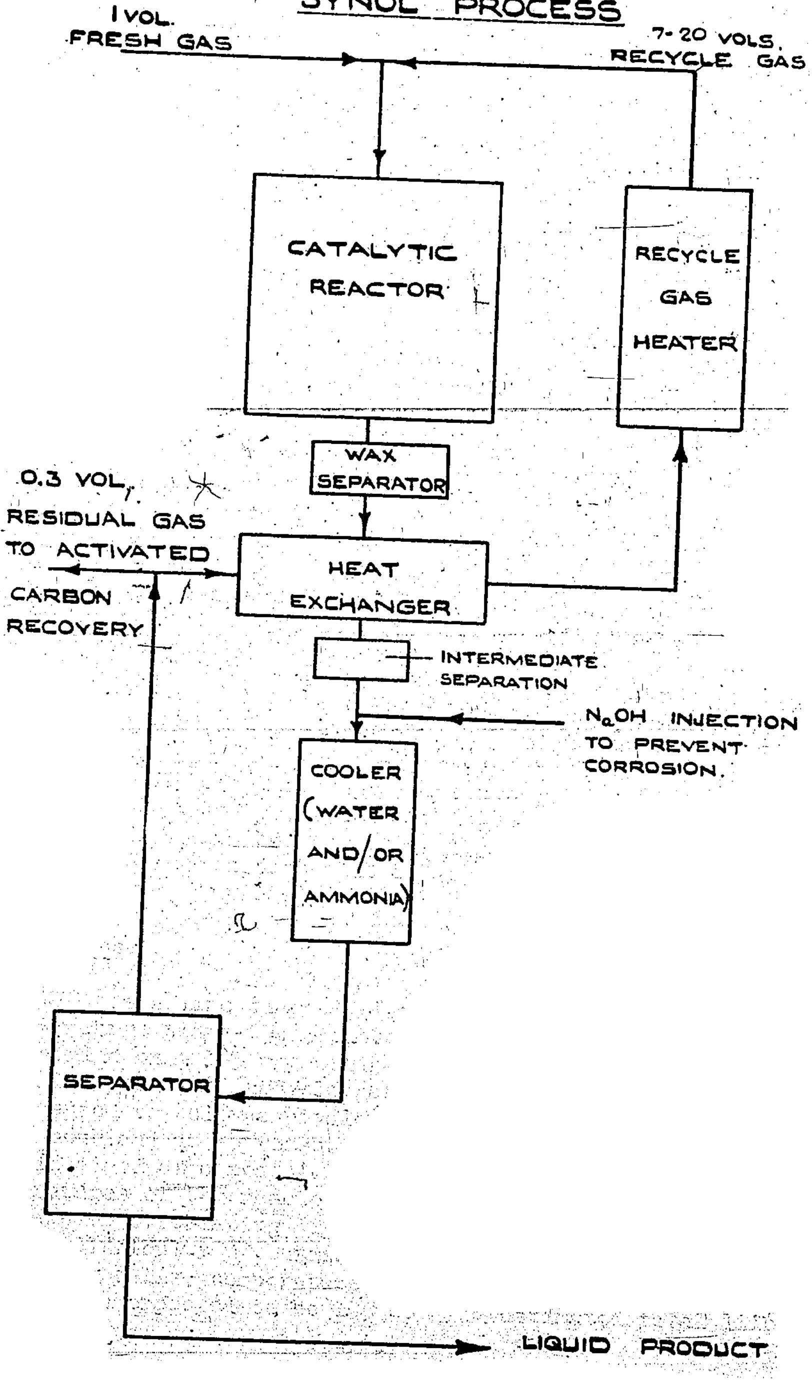


FIGURE XXXI B

FIGURE XXXII

SYNOL PROCESS



XV. SYNOL PROCESS

The I.G. have always held the view that Fischer Tropsch synthesis is more likely to be of value for the production of liquid products for use as chemical intermediates than as a source of fuels. Mainly from this standpoint they have been working on the Fischer Tropsch process and modifications of it since 1925. The particular modification designated "The Synol Process" is a development made by Dr. Wenzel in which the I.G. have been interested since 1940. The process consists essentially of the reaction of a carbon monoxide hydrogen mixture (ratio of 1 CO : 0.7/0.8 hydrogen) at 18 -25 ats and a temperature of 190 - 200 C over a sintered iron catalyst such as is used for ammonia synthesis. The liquid product consists principally of alcohols and hydrocarbons, the former being thought to consist entirely of straight chain primary alcohols.

Synthesis Gas:

The synthesis gas used in the Synol Process is made at Leuna by the addition to water gas of carbon monoxide obtained from the copper liquor carbon monoxide removal plant which operates in conjunction with the main ammonia and hydrogenation systems. In the absence of this source of carbon monoxide, it was intended to produce a synthesis gas of the required composition by gasification of coke with carbon dioxide and oxygen.

Scale of Operations:

The full commercial-scale development of the Synol Process was not complete. Some 25 small laboratories and pilot plant units, ranging in size from .2 - 36 litres catalyst capacity, had been operated to study the relative merits of multi-stage versus single-stage and gas recycle versus straight through operating conditions. A four-stage unit consisting of 100-litre tubular reactors and with a capacity of 3-5 tons/month of liquid product had been erected and operated for 9 months in order to give pilot plant-scale data of various possible multi-stage processes. A second pilot plant consisting of a single plate-type reactor with a capacity of 10-15 tons/month of liquid product had also been erected for a further study of recycle operation. This plant had been shut down because of bomb damage before any serious work had been completed.

Process Conditions:

Fig. XXXII is a line diagram of the process which it was proposed to operate in the large plate-type reactor. Feed gas, completely free from H_2S and containing only 1-3 mg. organic sulphur per cu.metre, together with 7 - 20 times its volume of recycle gas, is passed down-flow through the reactor at a space velocity equivalent to 110-120 vols. make up gas/vol. of catalyst per hour and at a pressure of 18 - 20 ats. When the catalyst is new it is maintained at a reaction temperature of 185°C and the inlet and outlet temperatures of the reactor are controlled to within 1°C of this figure by means of circulating diphenyl. Diphenyl is used in place of water because of the difficulty of obtaining steel for pressure operation. As the catalyst activity falls, temperature is gradually raised so that at the end of three months it is expected to be 195 C. The estimated total life of a

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catalyst is 9 months and at the end of this period the reaction temperature will probably have to be 210-225°C. The exit product from the reactor passes first to a wax separator in order to prevent plugging of the cooler parts of the plant with soft wax and thence to a heat exchanger where it gives up heat to the recycle gas. The heat exchanger exit temperature is carefully controlled so that no water is condensed or separated at this stage. Otherwise, excessive acid corrosion results. From the heat exchanger it passes to an intermediate separator where higher boiling liquid products are collected and then, via a cooler to a cold separator where C_6 and heavier hydrocarbons and alcohols are collected. Just before the products enter the cooler a caustic soda solution is injected into the stream in order to guard against acid corrosion. The exit gas from the separator, apart from a small purge equivalent to 30% of the fresh make up gas, is recycled via the heat exchanger and a gas heater to the reactor. The vent gas, which provides a purge for CO_2 from the system, is passed through an ammonia cooler and an activated carbon absorber in order to recover light hydrocarbons.

An alternative method of operation, which, according to Dr. Gemassmer, was latterly considered to be the most likely scheme to be adopted for large-scale operation, is shown in Fig. XXXIII. This is a two-stage process with gas recycle and, like the single-stage process described above, does not involve CO_2 removal between the stages. In this method of operation, very high gas velocities are employed. Fresh gas is introduced at the rate of 100-150 vols./vol. of catalyst and the recycle rate is 50:1 in both first and second stages. Approximately 65% of the fresh gas is converted in the first stage and 25% in the second, giving an overall conversion of 90%.

When working under straight-through gas conditions and with multi-stage conversion, it appears necesssry to remove CO^2 between the stages. This introduces the difficulty that alcohols are lost by water solution in the CO_2 removal step. It was stated that a two-stage process, as described above, gives approximately the same yields as a four-stage process operated without recycle but with CO_2 removal.

Yields.

The optimum yield is estimated to be 155-165 gm. of primary liquid product per M^3 of hydrogen + CO. Very variable data was produced on the composition of this liquid product but it would appear to be of the following order:

Alcohols	35 - 50%
Olefines	25 - 40%
Paraffins	20 - 35%

30 - 40% of the crude product boils in the range 50 - 100°C, 35 - 40% in the range 100° - 200°C, and 25 - 30% in the range 200 - 350°C. The alcohol content appears to be greatest in the range 150 - 200°C as shown by the following yields supplied by memory by Dr. Gemassmer:-

SYNOL PROCESS - FIG: XXXIII

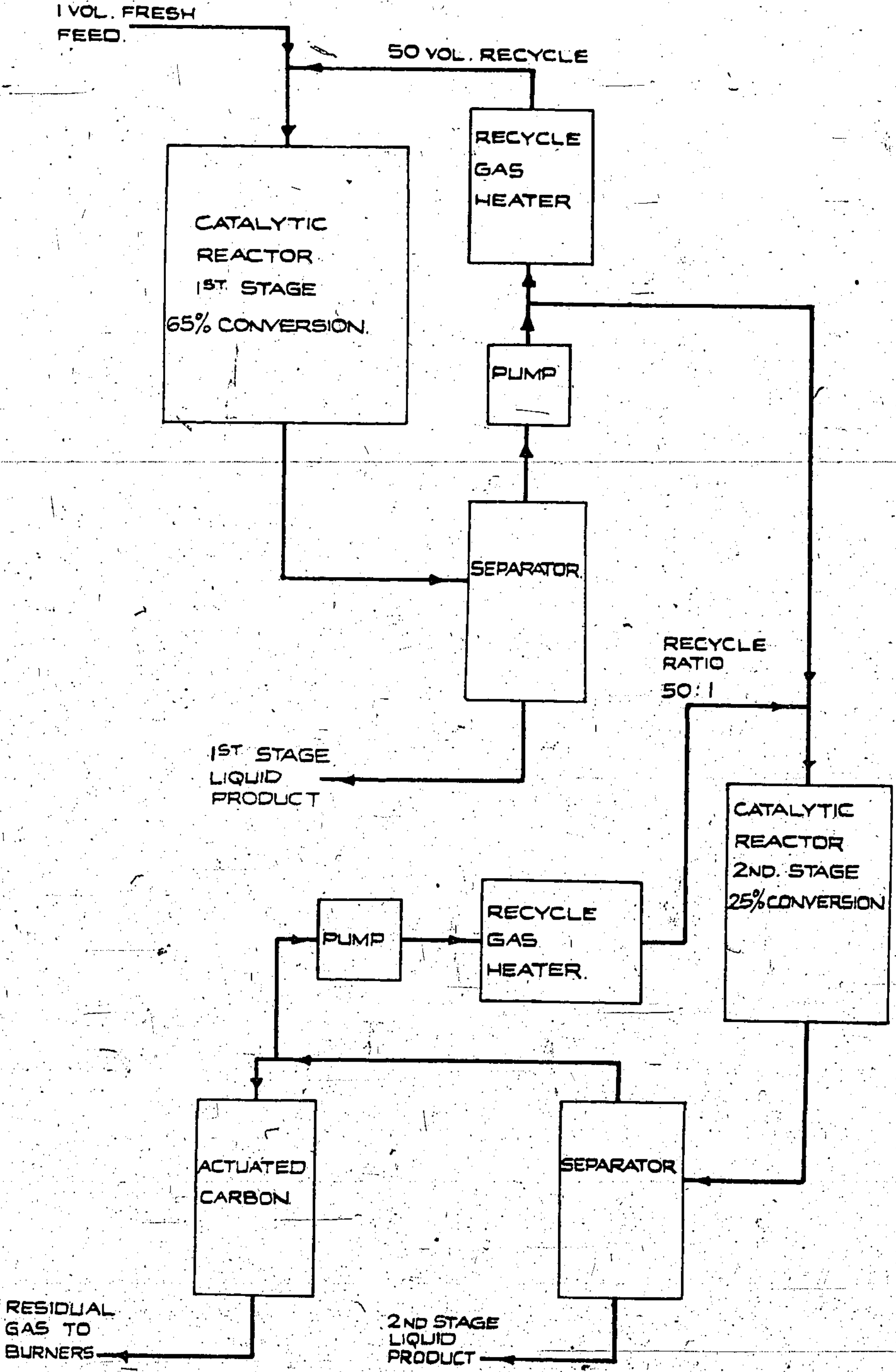
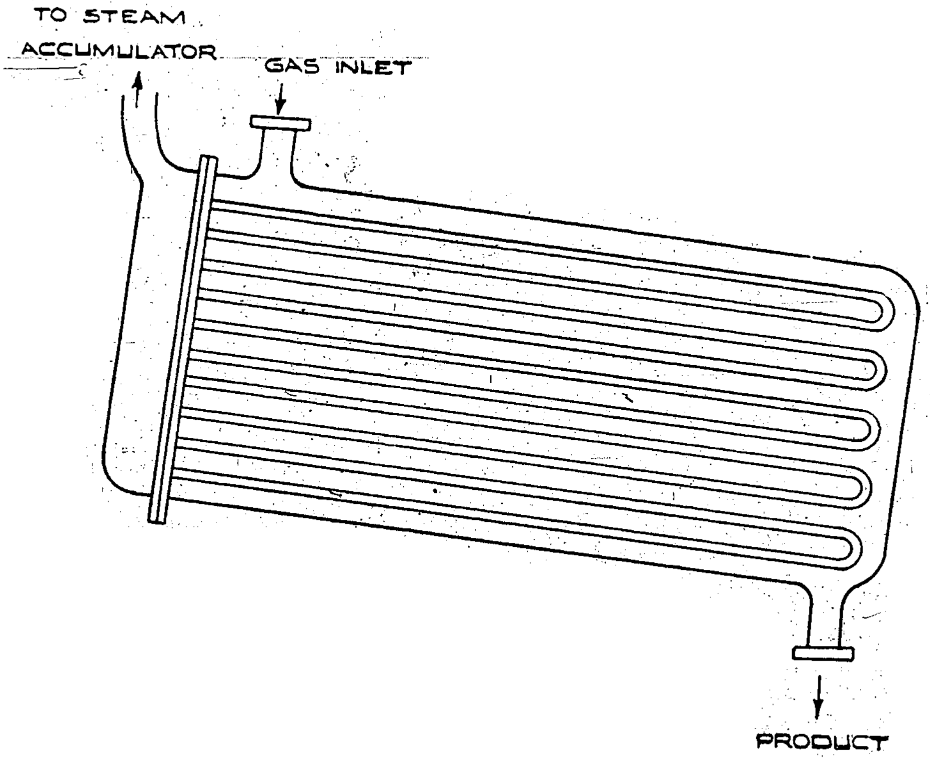


FIGURE XXXIV

PROPOSED DESIGN FOR SYNOL REACTOR



Temp. Range °C.	Alcohol	Sat. Hcs.	Olefine Hcs.
to 150	20	40	40
150-200	70	15	15
200-300	50	20	30
over 300	30	42	28

The main essential for maintenance of a good yield appears to be high space velocity involving a low conversion per pass and a low reaction temperature. Low space velocities lead to the reaction of carbon monoxide and water formed in the reaction, and high temperatures produce iron carbonyl and also appear to lead to carbon deposition due to reaction of hydrogen and carbon monoxide.

Design of Reactors.

Neither tubular not plate reactors used in the latest Leuna pilot plants were considered to be entirely satisfactory. The principal disadvantage of both was that during operation the catalyst caked badly and was very difficult to remove. In the case of the tubular reactor which was made up of 14 mm. I.D. tubes spaced 26 mm. centre to centre, it was found necessary to use an electric drill to remove the catalyst. Similarly, the plate reactor, which was essentially similar in design to the Fischer Tropsch atmospheric pressure convertor, had to be dismantled and the catalyst drilled and chiselled from between the plates. It had been decided to construct a reactor of the type shown in Fig. XXXIV. The catalyst was to be packed between the cooling tubes which were to contain water under pressure. It was considered that when it was necessary to remove spent catalyst, the flange could be unbolted, the inlet and outlet connections dismantled, and the whole case removed, thereby exposing the catalyst which could be relatively easily knocked from between the cooling tubes.

Catalyst Preparation:

The catalyst is prepared by placing 19 kgs. of iron from a wood charcoal preparation in a shallow water-cooled iron pan 50 cm. in diameter and 15 cm. high. Pure oxygen, supplied by two nozzles, is directed toward the mass which melts in 10 minutes. 16 kgs. of aluminium nitrate, 4 kgs. of potassium nitrate and 2 litres 66° Be nitric acid is added along with 2-4 litres of water. The mixture is boiled until solid, and melting is continued from there on for 30 minutes. The melt is poured out on an iron pan and allowed to cool slowly. It is then broken up into granules (1-3 mm) while the dust is remelted electrically.

The following is the final analysis of the catalyst:

2.5%	Al_2O_3
0.2-0.6%	K_2O
0.16%	S
0.03%	C
97%	Fe_3O_4

The apparent catalyst density is 2.0.

The catalyst is reduced batchwise with pure hydrogen (less than 0.02 mg. of sulphur per M^3) as shown in the simplified diagram, Fig. XXXV. The pressure is substantially atmospheric and the reduction temperature usually about 450°C. The reduction temperature does not appear to be critical; a range 380° - 650°C was stated to be satisfactory. The essential features of the catalyst reduction were said to be (a) a maintenance of a high hydrogen rate corresponding to a minimum linear velocity of 20 cms/second and a minimum space velocity of 2,000 l/hour per litre of catalyst, and (b) efficient drying of the recycle and make up hydrogen.

The recycle hydrogen leaving the reduction oven contains 1-2 gms water/M^3. It passes through a water cooler at 20°C, an ammonia cooler at 4°C and after mixing with fresh hydrogen, goes through a silica gel dryer.

The time required for reduction of a batch of catalyst is about 50 hours. Absence of water in the exit gas is used as a criterion of completion of reduction.

After reduction and cooling to 50°C the catalyst was blanketed with CO_2 and transferred to smaller steel containers. From these the catalyst, in a CO_2 atmosphere, was measured into glass tubes which were used to charge the reaction rubes individually, so that exactly the same amount of catalyst was present in each tube, especially since the tubes were often only partially filled. This was to ensure equal pressure drop through each tube and therefore provide equivalent gas flow in each.

The used catalyst could be regenerated only by remelting and rereducing, after which it operated at a higher reaction temperature (225 to 250°C) and the product contained a smaller percentage of alcohols.

Except for the reduction part of the catalyst preparation, the catalyst employed for the Synol process is exactly the same as that used for the ammonia synthesis at Leuna.

Work up of Crude Synol Product:

The method proposed for the separation of alcohols from the crude Synol product depended on the formation of boric acid esters. A flow diagram of this process is shown in Fig. XXXVI. The crude product is fractionated into 50-60° boiling range cuts which are worked up separately.

The esterification is carried out with solid boric acid present in slight excess of the theoretical requirement. The mixture is heated to 95-120°C at atmospheric pressure. The water formed, together with some of the lower boiling hydrocarbons has to be continuously removed as overhead. The secret of the esterification process was stated to be the complete removal of water as formed. The residual mixture of esters and hydrocarbons is then distilled at atmospheric pressure or under vacuum if this is necessary, in order to avoid ester decomposition. This separation of hydrocarbons and esters by distillation is a simple matter as will be seen from the following boiling range figures for charge and esters:

FIG: XXXV

SYNOL PROCESS – CATALYST REDUCTION.

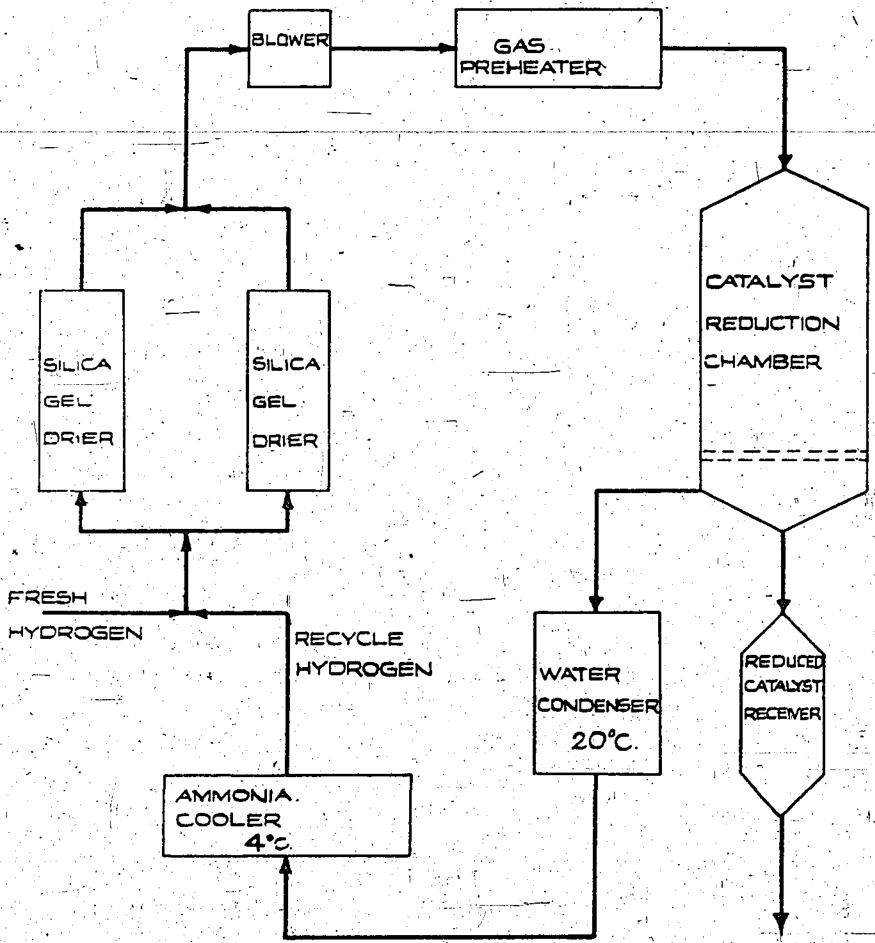
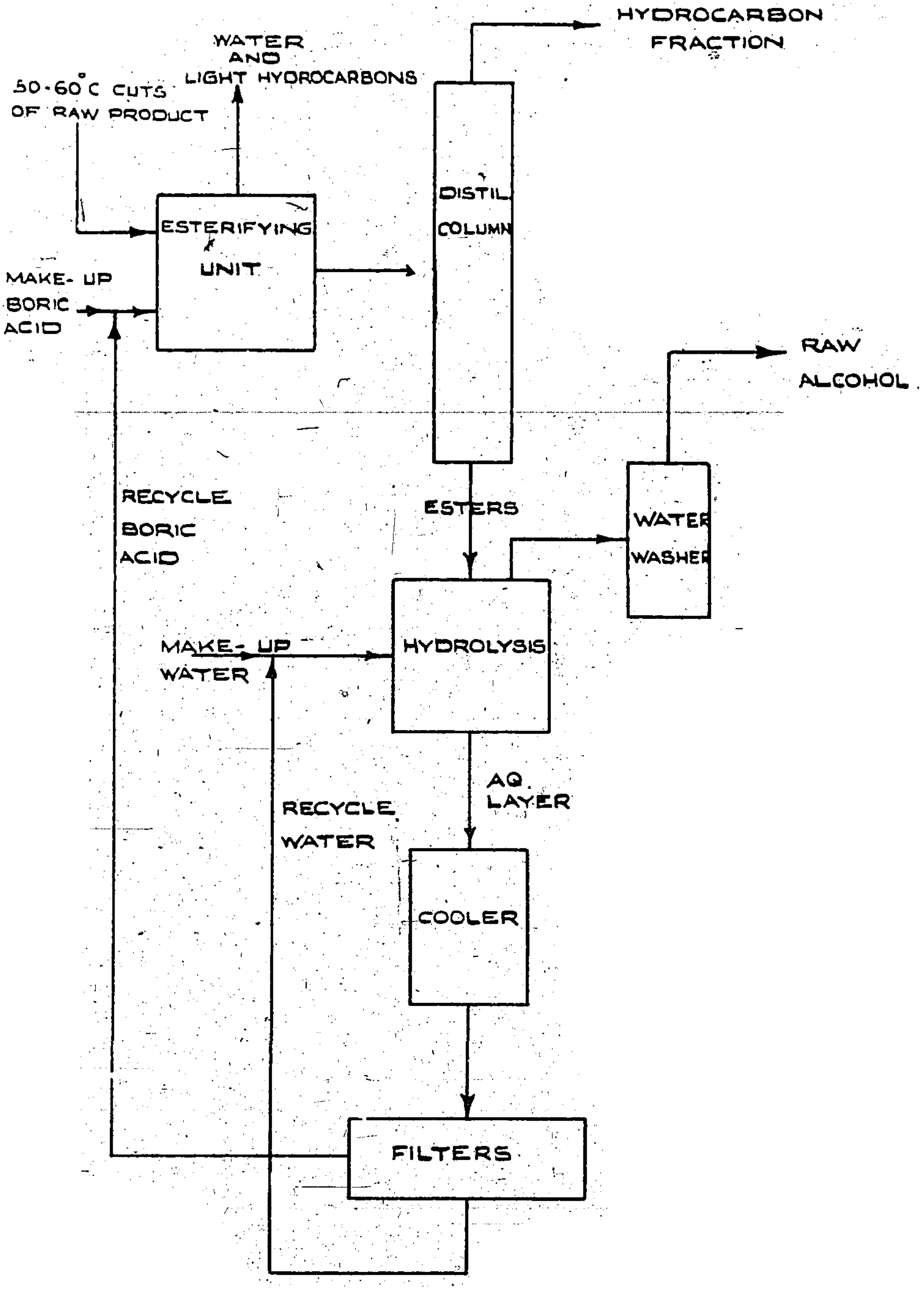


FIGURE XXXVI
SYNOL PROCESS - BORIC ACID PLANT



Boiling Range of Charge	Boiling Range of Esters
160 - 220°C	280 - 340°C
270 - 274°C	490 - 494°C

The esters are stable up to about 300°C at atmospheric pressure.

The separated esters are mixed with recycle dilute boric acid solutio and hydrolysed by heating to 95 - 120°C. The hot mixture of alcohols and boric acid (16 - 17% H_3BO_3) separate into two layers and the upper alcohol layer is water washed and re-distilled. The boric acid solution is cooled to 5°C and the boric acid crystals filtered off for recirculation to the esterification stage. The filtrate is recycled to the hydrolysis stage.

In addition to the authors, Major A. J. V. Underwood contributed notes and these were of very great assistance in compiling the above report.

XVI. MERSOL PROCESS

The Mersol reaction consists in treating paraffin hydrocarbons with SO_2 and chlorine to produce sulphonyl chlorides.

$$R.H + SO_2 + Cl_2 = R.SO_2Cl + HCl$$

These are subsequently saponified to give the sodium sulphonates.

Scale of Operation:

The Mersol plant at Leuna had a capacity of 50,000 tons per year of products using about 35,000 tons per year of kogasin.

Process Conditions:

The starting material was a kogasin fraction boiling between 220 and 320°C. I.G. would have liked to have included material up to 340°C but this was required for oxidation to fatty acids. The olefin content of the kogasin varied between 5 and 12%, according to the works of origin and the age of the catalyst used in producing it.

The kogasin was subjected to a preliminary hydrogenation at 200-230 atm. pressure to convert the olefins to saturated compounds. Otherwise the olefins absorb chlorine. A nickel tungsten sulphur ~~catalyst~~ was used.

The Mersol reaction was carried out at ordinary temperature and atmospheric pressure using ultra violet light to catalyse the reaction. The reaction was carried out batchwise until the necessary absorption had taken place. SO_2 and Cl_2 were blown through the reaction mixture using a small excess of SO_2.

The reaction towers were 6-7 m. high and 1.8-2 m. diameter. They were filled to a depth of 4-5 m. with an initial charge of 10-12 tons of material. An increase in volume takes place during the reaction, even though the density increases. Completion of the reaction required about 12-16 hours. The reaction towers were made of steel lined with Igelite (hard PVC).

Ultra violet light was provided by small quartz lamps mounted on a shaft inserted into hard glass tubes of about 120 mm diameter passing through the reaction vessels. Absorption of the shortest wave lengths by the glass tubes is considered desirable as they tend to cause decomposition. These small quarts lamps were about 70 watts each. The power consumption was said to be very small, less than 0.002 KWH per kilo of product.

After the reaction was completed, the product was blown with air or nitrogen to remove HCl. This product, which was known as Mersol D, contained about 82% sulphonyl chlorides and 18% unreacted hydrocarbons. Beyond this stage the reaction becomes very much slower owing to absorption of ultra violet light by the products. There is also a possibility of forming higher sulphonyl chlorides which give inferior products on saponification.

The Mersol D was sent to the soapmakers for saponification. Herold said the soaps made from it were not as good as natural soaps as they lacked colloidal material to maintain the dirt in suspension. For this reason it was usual to add water glass or "Tylosa" (made from sodium cellulose and acetyl chloride). The product was principally used for soap powders. The Mersol soaps, also known as "Mersolates" had been used with kaolin for tablet soap but their high solubility resulted in high consumption. The general practice seems to have been to use the "Mersolates" for soap powders and the fatty acids made by oxidising paraffins for tablet soaps.

Herold said that the synthetic soaps are very good for removing dirt but not so good for removing stains. Repeated washing with them results in a greyish colour and it is difficult to get the pure white colour which is obtained when using pyrophosphate and oxidising materials. Such materials can be used with Mersolate soaps. Herold said that better quality soaps would be obtained by using the longer chain hydrocarbons, which they were not permitted to use owing to the requirements for oxidation to fatty acids. Herold thought that it would be difficult for these synthetic soaps to compete in general with natural soaps but he thought they had a considerable future for special industrial uses, e.g. wool washing. Their advantage was that they were not alkaline and could be used at a low temperature. For removing grease he thought they were better than natural soaps.

Herold said that the Mersol soaps were excellent for emulsion polymerisation and had been widely used in this way for PVC. They were also very effective for Buna, but the rubber manufacturers who had been using "Nekal" (isopropyl sodium sulphonate) for some years were unwilling to risk making a change.

A product known as Mersol 30 was also made at Leuna. For this production, the reaction with SO_2 and Cl_2 was only carried to the extent of 30-33%. The product was then esterified with alkali and the separated neutral oil washed and returned to the process. The Mersolate solution was evaporated to give a water-free product and finally cooled in the form of flakes. This product is a thin liquid above 130-150°C. In the evaporation, steam at 15 atm. was used. An advantage of this method of operation is that the lower degree of conversion compared with Mersol D avoids the risk of forming disulphonyl chlorides.

Mersol D can only be made from kogasin but Mersol 30 can also be made from other materials. Kogasin has the advantage that it is more transparent to ultra violet light. If other oils are used, the olefins and aromatics must be hydrogenated to prevent an excessive chlorine consumption. When chlorination takes place, this results in the formation of hydroxyl groups after the saponification and the oil returned to the Mersol reaction must be hydrogenated again to remove them as they interfere with the reaction. The Mersol plant at Leuna was started with oil from the hydrogenation plant, but they preferred the paraffinic Fischer-Tropsch material as it requires a smaller hydrogenation plant and a smaller consumption of chlorine. This applies even more strongly to natural petroleum fractions. Herold said that with kogasin at 30 pf. per kilo and petroleum oil at 18 pf. per kilo, there is not much difference in the cost of the final product.

XVII. METHYLAMINE

The following information was obtained from Dr. Helmut Hanisch on 12th and 14th May. Reference should be made to Figure XXXVII.

About 80 T/month of mono- and di-methylamine were made. A batch mixture was made up, presumably at pressure above atmospheric, containing 4 to 5 mols NH_3 to 1 mol CH_3OH, and the mixture was pumped at the rate of about 1000 l/hr. to a converter. This was run at any pressure from 60 to 200 ats, but the effect of pressure was not ascertained. The convertor and interchanger were both made of S1 steel (low carbon steel) with copper lining and the electrical preheater was copper-covered. The converter was 500 mms I.D. and 8000 mms long, containing about 900 l. of catalyst. There was said to be little difference in performance between catalyst 6069 (90% Al_2O_3 and 10% kaolin) and catalyst 6067 (50% Al_2O_3 and 50% kaolin), samples of which were obtained.

The make was let-down into a reservoir kept at 25 ats. The de-watering still was copper-lined and filled with 18 m of porcelain Raschig rings, run at a pressure of 20 ats.

Trimethylamine (TMA) and excess NH_3 were then separated from the mono- and di- (MMA and DMA) in a continuous double still run at 15 ats. The top column contained bubble-plates, with a TMA-NH_3 azeotrope taken overhead and NH_3 taken from the bottom. The bottom column was filled with Raschig rings, with crude MMA and DMA mixture taken off the bottom.

The TMA-NH_3 azeotrope was fed back continuously into a similar converter, for partial reconversion to MMA and DMA. The product was fed into the same de-watering still as the main stream.

Final purification of the crude MMA and DMA mixture was carried out in a batch still. A batch consisted of 30 M^3 of the crude mixture, with 5 M^3 NH_3 added to provide NH_3 for TMA separation. The still had an I.D. of 700 mm and was packed with 18 m of Raschig rings. With the top temperature kept at 40°C and the bottom temperature at 55° to 60°C, the TMA-NH_3 azeotrope was taken off as the pressure was dropped from 15 to 10 ats, then MMA as the pressure was dropped further to 8 ats. and then DMA as the pressure was dropped to 5 ats, with water left behind. The MMA and DMA fractions were then given a further final purification.

Dr. Hanisch said that copper could be used in this process if care was taken to exclude oxygen.

ISOBUTYLAMINE MANUFACTURE

Dr. Hanisch said that 20 to 25 T/month of higher alkyl amines were made and gave the following details of the manufacture of isobutylamine as typical.

In contrast to methylamines, which were made from methanol and ammonia over a dehydrating catalyst, isobutylamine was made from the aldehyde and ammonia in the presence of hydrogen.

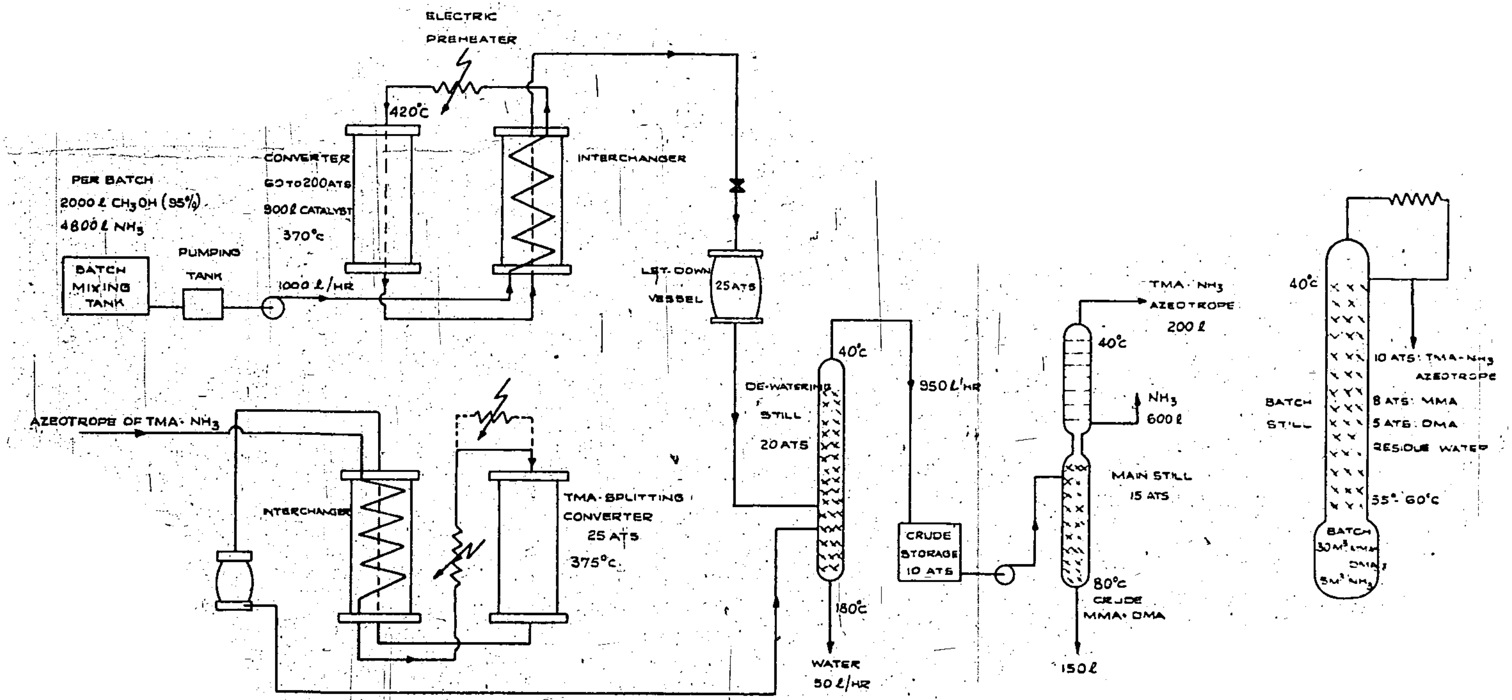
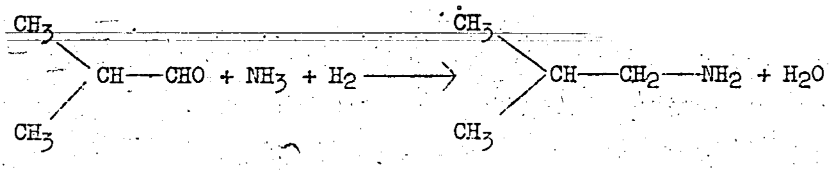


FIG XXXVII METHYLAMINE MANUFACTURE



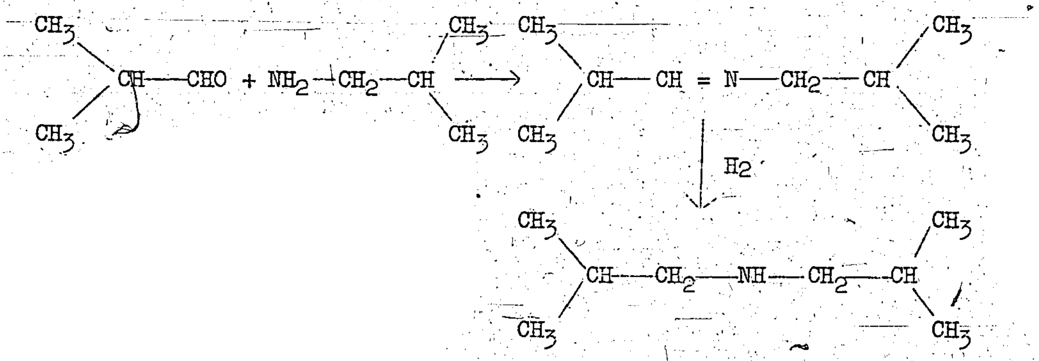
The only details obtained of the manufacture of isobutyraldehyde were that, whereas formerly this had been made by passing isobutanol at 1 at. and 370°C over 2493 (zinc sulphide on pumice, a sample of which was obtained), the method now preferred was to pass isobutanol with air over a silver gauze.

The synthesis of isobutylamine was carried out at 220 ats. over catalyst 3076, $NiS.WS_2$, a sample of which was obtained, at a temperature of 300°C. 1800 to 2000 M^3/hr. H_2 and 600 to 800 l/hr. NH_3 were circulated with a feed of 60 l/hr. isobutyraldehyde over 90 to 100 l catalyst. The product was separated after cooling and the surplus H_2 recirculated. The crude was stored at 50 ats. and distilled for purification, releasing surplus NH_3, which was recirculated.

Amines of other higher alcohols were made in a similar way.

SCHIFF'S BASE

Dr. Hanisch said this was made by reacting isobutylamine and isobutyraldehyde at 1 at (the catalyst, if any, was not specified) and hydrogenating the product at 200-220 ats.



The hydrogenation was carried out in apparatus similar to that used for the manufacture of isobutylamine, using the same catalyst, $NiS.WS_2$. The feed rate at Schiff's base was 40 l/hr. and the make-up H_2 rate was 40 to 50 M^3/hr, the temperature being 220 to 310°C; the catalyst volume was only 40 l

XVIII. MANUFACTURE OF CARBOXYLIC ACIDS.

Information on this process was obtained from Dr. Goricke, the pl foreman, with whom the installation was inspected.

The process is based on the following reaction:

$$R\ CH_2\ \ CH + NaOH \longrightarrow RCOONa + 2H_2$$

It is carried out by vaporising the alcohol and passing the alcohol vapours into a mixture of NaOH and alcohol maintained at 446 - 518°F; the violent mixing obtained in this way is important for successful operation. An excess of 17% NaOH beyond the amount required for complete conversion of the total quantity of alcohol is used in the reaction. The resulting sodium salt of the carboxylic acid is subsequently converted into the free acid. N-butyl, iso-butyl, hexyl and heptyl alcohols have been successfully processed but the C_8-C_{12} alcohols were most frequently used because the resulting acids were utilised in the preparation of the lubricating oil inhibitor "R". Another use of these acids consisted in the preparation of metal salts (Zn, Ca, Mg) to be used as substitute protective coatings. The alcohols were obtained in the course of the isobutyl-alcohol synthesis.

The production of this plant amounted to 60 -70 tons/month (132,000 154,000 lbs/month). Capacity was 150 tons/month.

XIX. POLYMERISATION OF C_6 AND C_7 OLEFINES.

The information on this process was obtained by plant inspection and interrogation of Dr. Gericke, the foreman in charge of the plant.

The process consists of the polymerisation of C_6 and C_7 olefines to C_{12} and C_{14} olefines which were used in the alkylation of phenol in the course of the manufacturing process for a detergent. This part of the synthesis was carried out at Höchst and only the C_{12}, C_{14} polymers were prepared at Leuna.

The feed stock was made by dehydration of the alcohols boiling in the iso-hexyl and iso-heptyl alcohol range and obtained in the isobutylalcohol synthesis. The olefine fraction of maximum boiling point of 203°F was used as feed stock.

Olefine and sulphuric acid (85%) were mixed at a rate of 105 gals. of olefine to 663 gals. of acid per hour. The mixture was preheated in a 2-1/2" diameter lead coil (steam heating of a water bath) to about 120°F and introduced into a lead-lined tower of 3 ft. diameter and about 80 ft. height packed with iron Raschig rings. The mixture passed from the bottom of the tower into a settler from where it was recycled. Circulation was continued until a hydrocarbon sample withdrawn from the settler indicated that the desired polymerisation had taken place as shewn by the results of a laboratory fractional distillation. The product was then caustic washed, water washed and distilled. The yield of desired polymer, boiling between 324 and 446°F, amounted to 50% by wt. of the olefine feed. The distillation range of the total reaction product and its utilisation are given as follows:

% by wt. of feed stock	Boiling Range °F	Utilisation
5 - 10	140 - 203	Recycled
5 - 10	203 - 324	Blended with heavy polymer
50	324 - 446	Sp.g. product at 20°C = 0.730.
20 - 30	Above 446	Heavy polymer to hydrogenation plant.

The design capacity of the plant was 440,000 lbs. of product/month but the actual output of C_{12}, C_{14} polymers was only 66,000 - 88,000 lbs/month. Samples of the olefine feed stock and polymers product were obtained for detailed examination.

XX. FERTILISERS AND NITRIC ACID

This Division covers the manufacture of Ammonium Sulphate, Nitric Acid, Calcium Nitrate (Kalksalpeter), Ammonium Nitrate and Calcium Carbonate mixture (Kalkammonsalpeter, equivalent to Nitro Chalk), Leuna Salpeter, and Phosphate Fertilisers. Dr. Ernst Willfroth was interrogated on May 12th; he was the Manager of the Nitrogen Division. There appeared to have been no major developments in what were old-established processes.

Ammonium Sulphate

This was made by the reaction of Anhydrite with NH_3 and CO_2. The capacity of the plant up to 1935 was 500 T/D N; in 1935 a part of the building was taken over to produce Leuna Salpeter, so that the capacity of Sulphate dropped to 300 T/D N.

Carbonated liquor was manufactured by the Ammonia Division by scrubbing out CO_2 from catalysed gas at 1 at. This liquor contained 14% as $(NH_4)_2CO_3$. These scrubbers were followed by a Sulphuric Acid wash to recover Ammonia.

The reaction with Anhydrite was carried out in the presence of excess NH_3, and after filtering the liquor could either be decomposed by heating to recover NH_3 or else it could be neutralised with 60% H_2SO_4 (Sulphuric Acid was made on site, the source of Sulphur being H_2S in water gas recovered in an Alkacid Plant and converted to Sulphur in a Claus Plant).

The filtered mud contained 0.5% Nitrogen (≡ 2% Ammonium Sulphate) on a dry basis. Rotary filters were installed but Dr. Willfroth preferred the old wooden plate type, which was still in use; these had plates suspended inside large wooden troughs.

The evaporation of the liquor was done in double-effect evaporators. The first effect was merely a concentrator, without salting; the steam pressure was 7 lbs. g, the temperature of the solution 106°C and the internal pressure 100-200 mm.Hg. The second evaporator ran with steam vapours at 0.2 ats. abs. with a steam temperature of 56-62°C and a liquid temperature of 46-52°C, the final vapour pressure being 65 mm.Hg. Each evaporator had a heating surface of 124 M^2, and the combined output was 170 T/D Ammonium Sulphate. Steam consumption was about 0.9 T/T Sulphate.

The solution prior to evaporation at density of 1.24, contained 530-540 g/l Ammonium Sulphate and about 0.2 g/l H_2SO_4, with a p_H of about 5.

The evaporators were lead covered throughout, but it was not stated whether any alloying metal was included. The evaporator tubes were 50 mm. I. D. and 78 mm. O. D.

The anhydrite used came from a quarry in the Harz about 130 km. away. Fuller mills were originally used, and some of these were still there, but others had been replaced by Löscher mills, which occupied far less space but had the same energy consumption. These mills worked on the principle of one roll working on a vertical axis, with two inclined rolls running on the top, the ground material being removed by hot air.

The plant itself was very old and there had been no advances made in recent years; the double-effect evaporation has been in use for many years. The plant has been shut down since May of 1944, owing to non-availability of NH_3. Direct air raid damage was not very great, and the plant personnel estimated that they could make 100 T/D N after 4-6 weeks and 300 T/D N after 10 months.

Nitric Acid

The plant was built in 1927 and was said to be the only plant in Germany working at 5 ats. The original capacity was 150 T/D N, but it had been enlarged (during the war?) to 260 T/D. Most, if not all the other I. G. plants erected elsewhere operated at 1 at. The main advantage of using a pressure process was stated to be the saving of space for the absorption system, and the process was economic if energy was not too expensive.

Power was recovered from the hot let down gases by passing them through a turbine working on the same axis as the air compressor.

The catalyst favoured was platinum with 5% rhodium. This catalyst was much better than 1% rhodium, but in a pressure process 10% rhodium was stated to give no better results. NH_3 conversion efficiency was stated to be 96% on the gauze and 92-94% after absorption. Final scrubbing of the gases was done with a lime solution. The final acid contained 48% HNO_3 and was all used for making Nitrate of Lime and Ammonium Nitrate mixtures.

It had been found that if welding took place in the neighbourhood of the air compressors, poisoning of the catalyst resulted, and this was put down to the presence of poisons such as PH_3 in the acetylene.

The plant was not inspected closely but from a distance it appeared to be relatively undamaged.

Concentrated Nitric Acid

This was not made by working up 48% HNO_3, but was made directly from the nitric acid oxidation gases. Gases after the waste heat boiler were further cooled and then oxidation of NO to NO_2 allowed to take place. The gases were then indirectly cooled with water to remove H_2O as weak HNO_3. The gases were then further cooled to -10°C to give liquid NO_2. This NO_2 was then treated in an autoclave at 80-100 ats. and 70°C with dilute Nitric Acid and Oxygen, yielding pure HNO_3 plus N_2O_4. On distillation this mixture evolved NO_2, which was returned to the process and gave 99% HNO_3 at the bottom of the still.

Ammonium Nitrate

Only a small quantity of the pure material was made; the bulk was made into Kalkammonsalpeter. This latter plant was not investigated but the process was said to be very similar to that used in making Nitro-Chalk. The spray tower was at the end of the building.

Calcium Nitrate (Kalksalpeter)

This plant was very heavily-damaged but the material could be produced in the Nitro-Chalk plant, although not at the same time as Nitro-Chalk.

Phosphate Fertilisers

This was contained in the same building as Ammonium Sulphate, but none had been made during the war, owing to shortage of phosphates.

Leuna Salpeter (Amm. Sulphate & Nitrate)

This plant also formed part of the Ammonium Sulphate plant, but was not inspected in detail; it had suffered little air raid damage.

Ammonium Chloride Fertilisers

No work had been done on developing Ammonium Chloride fertilisers, which were said to be unsuitable for German soils.

XXI. SYNTHESIS OF TOLUENE FROM BENZENE AND METHANOL

Introduction:

The process for synthesis of toluene by reaction of an excess of Benzene with Methanol at medium pressure over an acid zinc silico-phosphate catalyst was originally developed at Leuna. A commercial plant with a ?design capacity of 5,000 T/month of Toluene was erected at Waldenberg in Silesia where the I. G. have a factory which includes a Methanol plant. O. U. D. A. erected the plant, W. I. F. O. financed it and it was operated by the I. G. on a management-fee basis.

The Waldenberg plant started operations in mid-1942. The maximum achieved production was 3,800 T/month of Toluene but latterly only 2,500-3,000 T/month were made on account of transport difficulties and consequent shortage of raw materials.

A description of the process and of the Waldenberg plant was provided in the first place at Leuna by Dr. Herold, the head of the Development Department. His information was later confirmed and some additional data produced, also at Leuna, by Dr. Klopfer who was in charge of catalyst testing. A process description was also found in an I.G/W.I.F.O. Agreement, a copy of which was removed from Leuna.

General Process Data

Methanol and Benzene used for the process must be as free as possible from impurities, particularly nitrogen compounds. Methanol is specially purified from amines, by means of an organic cation exchanger, down to a maximum nitrogen content equivalent to 2 mgms. NH_3/litre. Nitriles are the chief impurities in the benzene and no satisfactory method has been developed for their removal; formation of zinc chloride addition compounds is not successful. In the end, the I. G. have resorted to careful analytical control of all batches of benzene so that these can be blended to give a feed to the plant which never contains more than 0.5 mgms. NH_3/litre.

Benzene and Methanol are reacted in the molecular ratio 4:1. Reaction temperature is 340-380°C and pressure 30-35 ats. Feed rate is 0.25 M3/M3 catalyst volume/hour with fresh catalyst. In order to maintain the catalyst in an active form steam must be added to the reactants. Substantially all the Methanol is converted in a single pass.

The catalyst, which has a life of 4-6 weeks, was stated by Dr. Klopfer to have the following composition:

ZnO	6%
P_2O_5	60%
Kieselguhr	25%
Acid treated Bleaching Earth	3%
Water	6%

Dr. Hanish stated that the catalyst was made by mixing orthophosphoric acid, Kieselguhr and zinc oxide, and drying a 2 cm-deep layer of the resultant paste at a temperature below 250°C. The cake obtained is broken up and sieved, pieces of about 20 mm size being used as catalyst. Fine materi amounting to about 30% of the charge, is recycled to the pasting stage.

Loss of activity of the catalyst is caused by carbon formation during reaction; after 4-6 weeks the catalyst contains about 40% carbon. Attempts to revivify catalyst by burning off this carbon were unsuccessful because of conversion of orthophosphoric into the inactive metaphosphoric acid.

Plant Operation

The Waldenberg plant consisted of 14 units, each consisting of 1 converter 1700 mm. external diameter and 16 M long. Each converter contained 15 M^3 of catalyst. Fig. XXXVIII shows the general layout of a unit. Benzene and Methanol in the weight ratio 9:1 are injected at 35 ats. and pass through a heat exchanger and gas-fired preheater where they are vaporised and heated to 280°C (Dr. Klopfer) or 350°C (Dr. Herold). They then enter the top of the reaction vessel which is divided into four or five catalyst beds separated by layers of Raschig rings. Cold benzol is injected in controlled quantity at the entry to the converter and to each of the Raschig ring beds in order to maintain a reaction temperature of about 370°C with a maximum of 380°C. The reaction is extremely exothermic, the heat evolution per converter being 100,000 Kg. cals/hour. There is a layer of calcined lime about 80 cms. thick at both the top and bottom of each converter. Lining of the converter is acid-resistant refractory brick. A 5% caustic soda solution is injected into the products immediately on leaving the converter in order to prevent corrosion by phosphoric esters. The products then pass via the interchanger and a water-cooled condenser to a separator vessel. Gas, consisting of methane, CO_2, CO dimethylether and benzene vapour, is removed from the top of this vessel and is compressed and cooled to recover benzol (800 grms/M^3). The liquid product separates into water and hydrocarbon layers, the latter having the average composition:

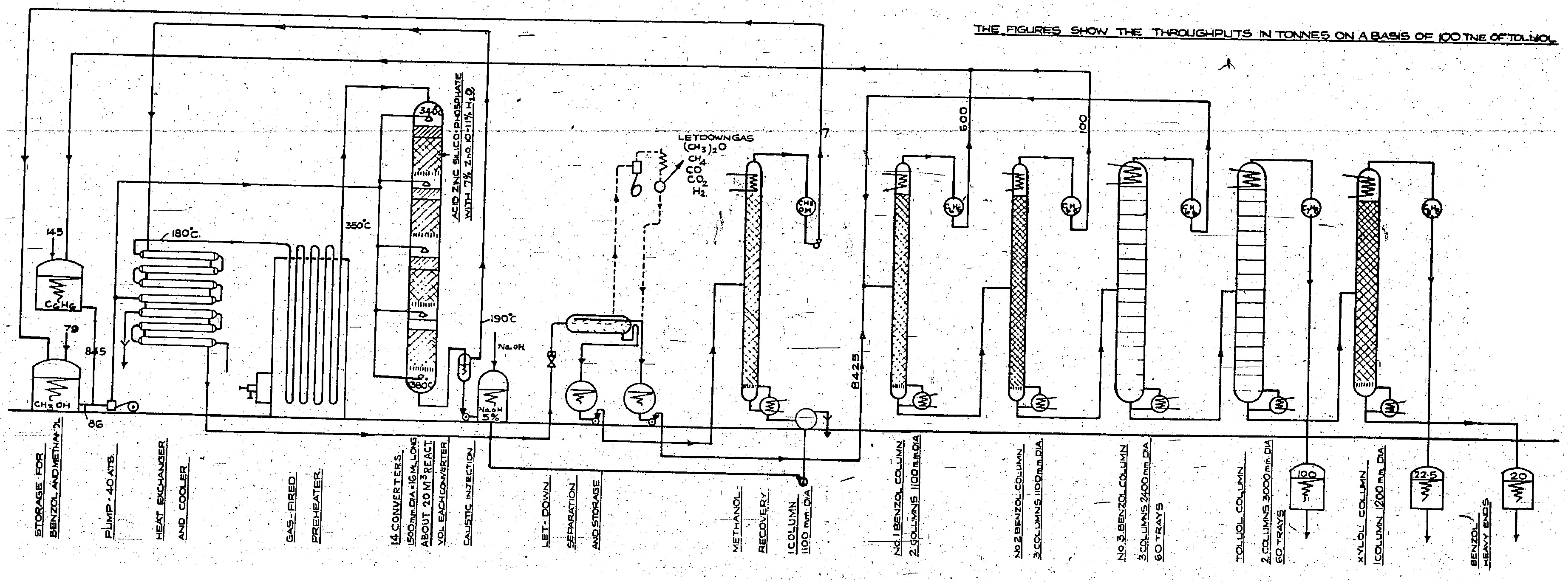
71 - 80% vol.	Benzene
12 - 17% "	Toluene
4 - 6% "	Xylene
4 - 6% "	Higher methyl benzenes.

The production of 1 Ton Toluene requires 1.45 T. Benzene and 0.85 T. Methanol.

The water layer is distilled for recovery of a small amount of unreacted Methanol which is returned to feed. The hydrocarbon product is first fractionated (2 packed columns of 1100 mm. diam.) to remove benzol and dimethylether as overheads. The bottoms pass to a second distillation stage (3 packed columns also of 1100 mm. diam.) in which most of the benzol and only a trace of Toluene is distilled over. The next distillation ~~is for~~ complete stripping of Benzene from the product. This is carried out in 3 to 60 plate columns of 2,400 mm. diameter and the overhead contains some 15% Toluene. These overheads are returned to the feed of the first benzene-removal column.

FIGURE XXXVIII

TOLUOL SYNTHESIS - CAPACITY 5000 TNE/MONTH - WALDENBURG - SCHLESIEN.


THE FIGURES SHOW THE THROUGHPUTS IN TONNES ON A BASIS OF 100 TNE OF TOLUOL.

The benzene-free bottoms of the third distillation stage are next fed to two 3,000 mm. diameter 60 plate stills from which a nitration grade Toluene is taken overhead. The fifth stage of distillation consists of the separation of the fourth stage bottoms into Xylene and heavier alkyl benzenes.

Development work on Related Processes

Leuna have experimented with the reaction of Benzene with alcohols containing upwards of 5 carbon atoms, available as by-products of the higher alcohols synthesis. The same catalyst and general conditions as used for Toluene synthesis have been employed.

Long chain alkylates are not formed. Instead, splitting of the alcohol occurs giving simpler alkyl benzenes and some olefines which can be recycled.

Isopropyl benzene was the main product obtained. The above experiments reached the semitechnical stage and a large-scale plant was being considered for Heydebrech.

XXII. CATALYST PREPARATION

The compositions and method of preparations were obtained for all catalysts that had been manufactured or used at Leuna for the preparation of fuels, oils, etc. Since many of the senior officials had left the district, most of the personnel interrogated were of the second or lower ratings, and were not familiar with all the details of the processes in question. In particular, Dr. Emil Schich had replaced Dr. S. Schneider as Works Manager. In addition, the time available, before the Russians moved into the area, was insufficient for a thorough analysis of the methods of manufacture of catalysts and there was no opportunity to make a study of the catalyst plant and its equipment. It is believe, however, that the information on composition and preparation of catalysts is adequate and that the catalysts could be prepared after only the usual amount of experimentation. The information on the methods of manufacture was obtained from Dr. Kurt Hill.

Purchase of chemicals for catalyst manufacture was not made on the basis of specifications, as is the general rule. The principal metal oxides and salts were purchased by "mark", and were in all instances the technically pure grade. Distilled water or condensate was used throughout for making solutions and for washing. Condensate was usually freed from oil by use of charcoal filter.

The numbering of catalysts at Leuna has not been systematic; the only certain information conveyed by the numbering is the chronological order in which they were produced commercially. For the principal catalysts, estimated productions at the peak of manufacture have been given.

Catalyst 616

Use: Methanol synthesis, from carbon monoxide and hydrogen.

Composition:

Cr_2O_3	33%
ZnO	60%
Graphite	1%
Water and impurities	6%

Preparation: Sixty kilograms of chromic acid anhydride is run in a chaser for thirty minutes; 100 kg. of zinc white is added and the mixing continued for 20 minutes. Thirty litres of water is next added, and ten minutes later 1 kg. of graphite (natural). Mixing is continued until all components are well blended. The chaser is then emptied, the charge is passed through a drum sifter (coarse pieces are returned to the chaser), and the mixture is pressed into 9 mm. pellets.

Quantity: 30 tons per month.

Catalyst 1132

Use: Isobutanol synthesis, from carbon monoxide and hydrogen.

Composition:

Cr_2O_3	33%
ZnO	60%
Graphite (natural)	1%
K_2O	1%
Water and impurities	5%

Preparation: Procedure is the same as for catalyst 616, except that K_2O is introduced by adding potassium hydroxide or potassium carbonate along with the zinc white. Good mixing and fine grinding are again important factors.

Quantity: 60 tons per month.

Samples: Nos. 17 and 18.

Catalyst 1750 A mild hydrogenation catalyst.

Use: After-hydrogenation of higher alcohols (same as No. 1930).

Composition:

Cu	1.25 mol.
Cr_2O_3	0.50
ZnO	1.00

Preparation: 125 kgs. of copper sulphate ($CuSO_4.5H_2O$) is dissolved in 1400 litres of water. 50 kgs. of Chromic acid anhydride is dissolved in 300 litres of water and reduced with SO_2. After mixing the two solutions, a solution of 200 kg. of sodium carbonate in 500 litres of water is added with constant stirring. When the precipitation is finished, 15.1 kg. of zinc white is added while stirring. The whole is heated to 78°C and held at this temperature for 24 hours (alcohol bath). The contents are withdrawn into a filter, washed, dried and pressed into pellets.

The time spent in mixing, heating, etc. was said not to be critical.

Sample: No. 73.

Catalyst 2493

Use: Dehydrogenation of alcohols to aldehydes.

Composition:

ZnS	25%
Pumice (Italian)	75%

Preparation: The pumice is broken into 4-7 mm. granules, sifted and washed. Ten kg. of wet pumice is run in a pill-coating apparatus until the pieces are uniformly coated with the 3 kg. of zinc sulphide (Merck) that is added. The grains are put in shallow metal pans, dried for 12 hours at 80-90°C and sifted to remove fines.

(Not made for last 4 years.)

Catalyst 2730

Use: Polymerisation of isobutylene to iso-octylene (used for relatively pure isobutylene).

Composition:

H_3PO_4	35%
Activated carbon	60%
Water	5%

Preparation: Eight kgs. of activated carbon, 4 litres of water and 5.12 kg. of phosphoric acid are run in the mixer until all the liquid is absorbed. The mass is then dried for 24 hours at 80-100°C.

Catalyst 3076

Use: Hydrogenation of di-isobutylene to iso-octane. Also hydrogenation of Kogasin.

Composition:

NiS	2 mols.
WS_2	1 mol.

Preparation: Fifty kgs. of nickel powder is dissolved in 250 litres of 60% HNO_3. The nickel is then precipitated by adding a solution containing 90 kg. of sodium carbonate (volume said not to be highly important). The precipitate is filtered, washed free from nitrates and dried. The dried material is ground and analysed. For each 25 kg. of nickel found by analysis, there is added to the metal precipitate in a kettle, 50 kg. of $WO_3.H_2O$ in 25 litres of water. The contents are mixed continuously and evaporated to a thick paste. The mass is then put into shallow metal pans, dried for 12 hours, recovered from the pans, treated at 400°C with H_2S, ground, mixed with 1% of graphite and pelleted. These pellets are ground and reformed into 10 mm. pellets.

Quantity: 1 ton per month.

Sample: No. 9.

Catalyst 3390

Use: Strong hydrogenation catalyst, for example, hydrogenation of phenol to cyclohexanol.

Composition:

Ni	3 mols
Al_2O_3	1 mol

Preparation: Nickel powder (70.6 kg.) is dissolved in the stoichiometric amount of strong nitric acid in a small agitator: 21.56 kg. of sheet aluminium is dissolved in a second small agitator with caustic soda solution (stoichiometric quantity of NaOH, concentration not important). The small agitators are then filled up with water, and the two solutions simultaneously run into a large agitator which originally contains about 1 M^3 of water. The filling operation takes about half an hour, but time is not critical. Caustic soda solution is added for precipitation. The precipitate is separated in a filter press and washed well with water. The filter cake is removed and dried for about 8 hours at 200°C in a drying oven, then ground and pressed into 5 mm. pellets.

Quantity: 1 ton per month.

Sample: No. 70.

Catalyst 3510 (Not made since 1935/1936; replaced by catalyst 5058).

Use: Vapour phase hydrogenation of middle oil to gasoline.

Composition:

MoO_3	1 mol
ZnO	1 mol
MgO	1 mol

Preparation: The three materials are pasted with water, spread on a metal plate, cut into cubes and dried.

Catalyst 4577

Use: Preparation of stearylamine from stearic acid and methylamine.

Composition:

NiS	1 mol
MoS_2	1 mol

Preparation: Two solutions are prepared separately:

(a) 45.36 kg. molybdic acid anhydride (MoO_3) in 100 litres of 50% caustic soda, and

(b) 91.67 kg. nickel nitrate ($Ni(NO_3)_2.6H_2O$) in 100 litres of water. The solutions are run simultaneously and slowly (24 hours) into an agitator. The precipitate is removed and washed on a filter press. The filter cake is then dried at 100°C and is formed into tablets in a hydraulic press. The tablets are broken by hand into 4-6 mm. granules, and converted into the sulphide as described above under catalyst 3076.

(Note: There is a large loss of MoO_3 due to incomplete precipitation).

Quantity: 100 kgs. per year.

Catalyst 4788

Use: Hydrogenation of acetylene to ethylene (ethylene purification for lubricating oil manufacture).

Composition:

Cr_2O_3	approx. 95%
Ni	" 5%

Preparation: 50 kg. of chromic acid anhydride (CrO_3) in 20 litres water are mixed with 9.24 kg. of nickel nitrate ($Ni(NO_3)_2.6H_2O$) in a stainless steel (V2A) mixer. The slurry is evaporated with continuous stirring (by hand, with special spades) until no more nitrogen oxides are given off. The material is then heated in a muffle furnace for 12 hours at 300°C before breaking into 8-10 mm. granules. The granules are reduced by heating for 12 hours at 400°C in a stream of hydrogen (high space velocity no recycle of H_2). The product is cooled under a stream of nitrogen and stored under nitrogen.

Sample: No. 20.

Catalyst 4821

Use: Polymerisation of isobutylene to iso-octylene. (For gases low in isobutylene concentration (20-30%).)

Composition:

Asbestos (serpentine, long fibre Canadian, unwashed; later Russian or Finnish).	Approx. 25%
P_2O_5	Approx. 75%
Water	4-5%

Preparation: 16 litres of phosphoric acid is heated at 260°C for 3 hours and then mixed with 8 kg. of asbestos. The mixture is hand-formed into 1-cm. cubes, which are dried for 60 hours at 150°C. The resulting catalyst is very hard.

Samples: Nos. 34 and 35.

Catalyst 5058

Use: Vapour-phase hydrogenation of middle oil to gasoline.

Composition:

WS_2

Preparation: Tungstic acid ($WO_3.H_2O$) is dissolved in the mother liquor from a previous preparation by gassing with NH_3 at a temperature below 60°C. The solution is precipitated with H_2S, cooled, and the $(NH_4)_2WS_4$ filtered under vacuum. The crystals are dried in a nitrogen stream on the filter at room temperature, and then converted to WS_2, NH_3 and H_2S by heating at 450°C in a stream of hydrogen in a scroll-type furnace. The resulting WS_2 is ground in a mill and pressed into 10 mm. pellets under a nitrogen atmosphere.

<u>Quantity</u>: Made up to May 1, 1944 - 25 tons per month.

<u>Samples</u>: Nos. 30, 31, 32, and 33.

<u>Catalyst 5436</u> (Identical with Catalyst 5931 except that caustic is from a different source. No. 5939 uses the same Al_2O_3 as 5436 with only 5% MoO_3).

<u>Use</u>: Conversion of paraffinic gasoline into aromatic and isoparaffinic hydrocarbons - HF or DHD processes.

<u>Composition</u>:

Al_2O_3	90%
MoO_3	10%

<u>Preparation</u>: Catalyst 5780 (see below) in cubical form is soaked once with ammonium molybdate solution, then dried. The solution is so prepared that the above composition of catalyst results.

(Note: For 5436 or 5931, use about 20% MoO_3 in 25% NH_4OH. For 5939, dilute with water.)

<u>Quantity</u>: 10 tons per month.

<u>Sample</u>: No. 44 - Catalyst 5931.

<u>Catalyst 5623</u>

<u>Use</u>: Toluence synthesis from benzene and methanol.

<u>Composition</u>:

P_2O_5	60%
ZnO	6%
Acid-treated clay (Montmorillonite type)	3%
Kieselguhr (Hanover No. 120R fused with NaCl and washed with HCl).	25%
Water	Balance

(any ignited kieselguhr can be used)

<u>Preparation</u>: 44.1 kg. of kieselguhr, 9.0 kg. ZnO, 4.5 kg. clay and about 130 litres of 85% phosphoric acid are mixed in a kneader for about 40 minutes, placed on trays, dried for about 10 hours at 300°C, broken up and finally screened.

~~Quantity: 150 tons per month.~~

Sample: No. 19.

Catalyst 5633

Use: Conversion of paraffinic hydrocarbons to aromatics and isoparaffins (HF and DHD Processes).

Composition:

Al_2O_3	95%
MoO_3	5%
Na_2O	up to 0.7%

Preparation: Technical alumina is plasticised in a kneader with a little nitric acid and water, then extruded and rolled into balls. These are dried and later ignited at 450°C. The balls are then soaked in an ammonium molybdate solution, controlled so as to give 5% MoO_3 in the catalyst on subsequent drying.

Catalyst 5780 (also prepared at Ludwigshafen as No. 695A).

Use: Dehydration of alcohols. Intermediate product in the production of other catalysts.

Composition:

Al_2O_3 Gamma-form.
Na_2O (usual 0.03-0.04%) - less than 0.1%
Water - 4%

Preparation: 400 kg. of technical alumina (65% (Al_2O_3) is dissolved in 410 litres of 50% caustic soda at 110-120°C and diluted with 600 litres of water to 1.35 sp. gr. The solution is cooled and precipitated with nitric acid at a pH of 6.5, then filtered, washed, resuspended, brought back to a pH of 6.5 with NH_3, washed and dried at 100°C. (This intermediate product is known as 5780 Z 100). This product is ground, peptized with 1% nitric acid in a kneader, spread on a sheet, cut into cubes and dried stepwise at temperatures from 60 to 180°C (slow drying, 2-3 days. It is finally ignited at 450°C in air until nitrate-free.

Laboratory tests of catalyst activity are based on (1) absorption of propane, (2) dehydration of isobutyl alcohol at 350°C.

Quantity: 100 tons per month.

Catalyst 6067

Use: Amine synthesis (very small amounts used). Catalyst 6069 is preferred.

Composition:

Al_2O_3	50%
Kaolin	50%

Preparation: See No. 6069.

Catalyst 6069

Use: Preparation of methylamine from methanol and ammonia.

Composition:

Al_2O_3	90%
Kaolin (flotation to remove excess SiO_2 by a Siemens electro-osmosis machine)	10%

Preparation: 150 kg. catalyst 5780 Z 100 (ground) are mixed with about 140 litres of water and 225 cc. of 52% HNO_3 and 11 kg. of kaolin then added. The mixture is kneaded for 2 hours, spread on trays, cut into cubes, air dried for 24 hours, dried 12-15 hours at 120°C and finally ignited for 4-6 hours at 450°C.

Quantity: 10 tons per month.

Catalyst 6448

Use: Dehydrogenation of n-butane to butenes.

Composition:

Al_2O_3 (use ordinary alumina for iso-butane dehydrogenation)	90%
K_2O	2%
Cr_2O_3	8%

Preparation: 22.5 kg. catalyst 5780 (finely ground), 2 kg. catalyst 5780 Z 100 (as peptizer-binder), 1.53 kg. KOH, 1.63 kg. CrO_3, 2.7 litres HNO_3 (62%) and about 7-9 litres water are mixed for about 40 minutes in a kneader, then formed into balls or cubes, dried at 150°C for about 16 hours, and finally ignited at 450°C for 4 hours.

Quantity: 100 tons per month.

Samples: Nos. 68 and 69.

Catalyst 6523

Use: Hydrogenation of phenol to cyclohexanol.

Preparation: Catalyst No. 3390 is reduced for 8 hours at 300°C with hydrogen (in situ; high space velocity, 400-600 cu.m./hr/500 litres catalyst) and purged with nitrogen.

Catalyst 6853 (Arobin Catalyst)

Use: Conversion of high boiling aromatic middle oil into lower boiling aromatic hydrocarbons. Conversion of higher alkyl benzenes to lower homologues.

Composition: Catalyst 7187 plus 1% MoO_3.

Preparation: Catalyst 7187 is soaked in dilute ammonium molybdate solution so made that the product after drying contains 1% of MoO_3

Sample: No. 11.

Catalyst 7187

Use: Catalytic cracking (atmospheric pressure conversion of middle oils into isoparaffinic gasoline.)

Composition:

SiO_2	85.1%
Al_2O_3	14.9%

Preparation: Kieselguhr (with 70% SiO_2) and activated alumina (70% Al_2O_3, catalyst 5780 Z 100) are mixed to a stiff paste in a kneader with a little water and the addition of a small amount of nitric acid (sufficient stoichiometrically to convert 1% of the Al_2O_3 to $Al(NO_3)_3$. This mass is allowed to stand 24 hours at 60-70°C to "ripen". It is then further kneaded, extruded and formed into 6 mm. balls, dried at 100°C and ignited at 400° until nitrate-free. There is no humidity control during the drying.

Quantity: Planned to make 100 tons per month.

Samples: Nos. 36 and 37.

Catalyst 10927:

Use: Liquid-phase hydrogenation of tars.

Composition: 5% Fe on Winkler generator coke.

Preparation: Winkler generator fines are soaked with iron sulphate solution and then with an equivalent amount of caustic soda solution, the concentrations being adjusted so that the final dried product contains 5% of Fe.

Ammonia-Catalyst (No number)

Use: Ammonia synthesis from hydrogen and nitrogen. Synol catalyst (manufacture of alcohols from CO and H_2).

Composition:

Fe_2O_3	75%
FeO	20%
Al_2O_3	1.9%
K_2O	1.1%

Preparation: Five tons of pig iron is melted by a direct blast of oxygen. A cake containing a mixture of 200 kg. of crude alumina, 50 kg. of aluminium nitrate and 25 kg. of concentrated nitric acid is introduced into the molten iron with continued blowing with O_2. The melt is allowed to cool and is broken up and screened to the desired size. Oxygen consumption: 7,000 cubic metres.

Sample: No. 23 - Synol Catalyst.

XXIII. METALLURGY

I. G. Experiences with Hydrogen-Resistant Steels

The following information was obtained at Leuna from Dr. Wyszomirski and Dir. Strombeck. For the early 250 ats. hydrogenation stalls a 6% chromium steel (N6) was normally used. This had satisfactory hydrogen-resistance properties but its creep strength limited its use to pressures not exceeding 200 ats. at 560°C. For 350 ats. stalls 1% molybdenum and 1% tungsten was added to N6 to give a steel which was designated N7. These additions improved the creep properties but resulted in difficulties in fabrication and in heat treatment. Molybdenum and tungsten contents were accordingly reduced to 1/2% (N8) and the resulting steel was found to be perfectly satisfactory as regards heat treatment which simply consisted of quenching from 700°C. No annealing was necessary and no heat treatment was required after welding. The steel was suitable for vessels operating at 350 ats. pressure and at temperatures up to 550°C. It could also be used for the cooler parts of 700 ats. stalls.

An improved material was nevertheless required for 700 ats. operation, particularly in the preheater elements. V2A could not be obtained because of the short supply of nickel and a new steel (N10) was developed which had the following analysis:-

Carbon	0.18 - 0.22%
Chromium	3.0 - 3.6%
Molybdenum	0.5 - 1.2%
Tungsten	>0.3%
Vanadium	>0.75%

Dr. Wyszomirski explained the theory behind the development of this steel. Pure iron-chromium alloys have a very poor creep resistance but this can be overcome if the steel contains finely divided carbides. In order to obtain a suitable chromium/carbon steel the chromium content must be limited. Too much of this component tends to absorb the carbides and also to increase the grain size of disseminated carbides thereby reducing creep resistance.

The composition of N10 is very critical. A minimum of 0.18% carbon is required to give the creep quality but a content of 0.22% must not be exceeded if welding difficulties are to be avoided. At least 3% of chromium is needed to give the necessary hydrogen resistance; more than 3.6 of this component has an adverse effect on creep properties. At least 0.5% molybdenum is required to give a workable steel but the 1.2% has the same effect as excess chromium in reducing creep resistance. Vanadium is necessary from creep considerations but this component appears to be responsible for much of the difficulty which has been experienced in getting an even distribution of fine carbide grains in the steel.

In addition to careful control of the composition of N10 the I. G. pay great care to its heat treatment. It is first heated to 1,050°C and when it has assumed an even temperature, it is cooled through the range

800-600°C at a minimum rate of 25°C/minute. This is to avoid the complete transformation of austenite via martensite to pearlite. If this treatment does not result in even properties of the steel it is reheated to 1,150°C and the process is repeated.

A special heat treatment bench was developed dealing with preheater elements. A complete element was laid horizontally on a brick bench which was so designed that each leg of the preheater was immediately above a long 25 mm. wide slot which extended the full length of the element. Compressed air could be injected through the slots by means of a series of jets. The element was heated electrically by passage of a direct current and even heating was ensured by providing a removable insulated cover fitted with auxiliary electric heating elements.

When the preheater element had attained a temperature of 1,050°C the top cover was removed and replaced by an arrangement by which air could be impinged on the preheater tube from above. During this change of covers the preheater element usually cooled to 850-900°C. Rapid control cooling down to 600°C was then carried out by means of the air jets.

Trials had been made with water for rapid cooling but this method was found to be less reliable than the air cooling method particularly in the case of fin tubes which scaled badly under water treatment.

Finally the steel was given a secondary heat treatment consisting of reheating to 680°C followed by slow cooling in air.

The I. G. claim that the above method of heat treatment results in at least a 33% higher creep strength at 560°C than is obtainable by oil quenching.

Enamelling of Preheater Bends

It has been mentioned in an earlier section of this report that troubles had been experienced at Leuna with the erosion of preheater bends when working at high paste rates. In an attempt to overcome this erosion, experiments have been made with enamelled preheater bends. Difficulty was experienced in getting an even distribution of enamel powder over the inner surface of the tube and in cooling the bends sufficiently rapidly to avoid an uneven enamel layer resulting from the flow of molten enamel. Enamel is in any case useless for pressures above 325 ats. because differences in expansion in enamel and steel led to cracking of the enamel layer.

Chromium-Plated Injector Rams

Normal deliveries of hard plated chromium rams were found to be very satisfactory for pressures up to 50 ats., reasonably good for working up to 250 ats. but useless for 700 ats. pressure. The makers tried to improve the chromium surface by high frequency electric treatment but little success was achieved.

Material for Butane Dehydrogenation Reactor Tubes

FF30, a 30% chromium steel with about 40% nickel and about 0.10% of carbon, was found to be satisfactory mechanically but it catalysed carbon formation in the reaction, particularly at low space velocity.

Material for Catalytic Cracking Regenerators

For the regenerator of the catalytic cracking unit which was to be erected in the Kuchuk plant at Niedersachswerfen the I. G. proposed to use a steel of the following composition:

Chromium	0.8 - 1.0%
Silicon	0.5%
Carbon	0.12%

This steel was stated to have excellent resistance to oxidation.

XXIV. BLECHHAMMER

Introduction

Practically the entire Blechhammer staff left the plant at the end of January, one or two days before the Russians entered the area. Following a pre-arranged plan, they congregated at Naumberg about 20 miles from Leuna where an office was set up to arrange for their distribution to other German hydrogenation plants. By the end of February, Naumberg was so full of evacuees that the authorities insisted on the removal of the Blechhammer people and a large proportion of them went to Vorhum, near Peine (Brunswick). The movement of these people was surrounded with a good deal of secrecy due, it was disclosed, to their fear of being handed over to the Russians for restart of the Blechhammer factory. The managing director of Blechhammer, Dr. Josenhans, was interviewed in Naumberg and Dr. Kronig, the chief chemist, was interrogated at Vorhum.

700 ats. pressure hydrogenation of selected Upper Silesian coal provided the main source of liquid products at Blechhammer. Hydrogen production was based on gasification of medium temperature coke made by carbonisation of bituminous coal briquettes. The tar produced as a by-product to coke manufacture was obtained in two fractions by controlled condensation. The lighter fraction was sold as Navy fuel oil after topping off light petrol and the heavy tar was used as a pasting oil component in the coal hydrogenation process.

The original plan was to hydrogenate coal in the ordinary way, i.e. recycling to the liquid phase stage all products heavier than middle oil. Before the erection of the plant was completed, however, it was decided to increase the production of Navy fuel oil by operating the liquid phase hydrogenation stalls in such a way that the production of distillate heavy oil exceeded pasting oil requirements. Blechhammer data on this method of operation are of particular interest because they provide a basis for assessment of a three-stage coal hydrogenation process, i.e. 700 ats. liquid phase hydrogenation of coal to give heavy oil, middle oil and petrol, liquid phase hydrogenation of distillate heavy oil to give middle oil and petrol, and vapour phase hydrogenation of middle oils to petrol products.

Another change which was made to the original Blechhammer plan was that as the shortage of aviation fuel became more acute, it was decided to make aviation fuel instead of motor petrol. D. H. D., butane dehydrogenation and alkylation units were therefore erected.

Ten medium temperature carbonisation units were installed, each with a design capacity of 275 tons/day of coal. These units behaved very satisfactorily and a throughput of up to 325 tons/day was achieved. The coal was briquetted using sodium sulphite lye from paper manufacture as a binding agent and the finished briquettes contained 2% of moisture and 12% of ash. The coal had a carbon content on the ash-and-moisture-free basis of 83.5%. The tar yield on carbonisation was 9% by weight on the coal, the heavier tar fraction amounted to 35% of the total tar.

The carbonisation units were started up in October 1943. Before the hydrogenation plant was ready, the tar middle oil, topped to 120°C in order to reduce the flash point below 85°C, was sold as fuel oil and the heavy tar was disposed of to other companies for use as road tar, etc.

The hydrogenation plant actually installed at Blechhammer included four liquid phase stalls for 700 ats. operation. Each stall had four converters similar to those used at Gelsenberg. The internal diameter was 1,000 mm. and height 18 M. The internal diameter of the reaction basket was 850 mm. and the reaction volume provided by four converters was roughly 37 M^3.

Two vapour phase pre-saturation stalls were installed. Each had three converters and was designed for 300-350 ats. operation. The plant was equipped with two vapour phase splitting stalls fitted with two converters each and designed to operate at 300-350 ats.

The coal used for hydrogenation was specially selected Upper-Silesian coal with an ash content of 5% and a carbon content on the ash-and-moisture-free basis of 80-82%.

It was originally planned to add two further sections to the hydrogenation plant, each comprising two 700 ats. liquid phase units, one pres aturation and one vapour phase splitting stall. With these additions, the total output of Blechhammer was to have been 450,000 tons/year of motor spirit and 500,000 tons/year of fuel oil.

It was considered likely that the demand for fuel oil would decrease and accordingly, consideration had been given to the erection of one or more additional 700 ats. stalls designed for the catalytic hydrogenation of distillate coal heavy oil to middle oil. The idea was to re-distil distillate coal heavy oil leaving a 10% heavy residue which would be returned as pasting oil to coal hydrogenation. The distillate was to be hydrogenated over 8376 catalyst at 700 ats. and at a temperature of about 450°C.

The hydrogenation plant started up in April 1944 but by July, bomb damage to other hydrogenation plants had resulted in such a large surplus availability of brown coal tar that it was decided to import this material for hydrogenation at Blechhammer. During the three months in which the coal hydrogenation plant operated, it was stated that operation was extremely satisfactory.

It was found that for the hydrogenation of brown coal tar it was necessary to increase the number of converters in each of the vapour phase stalls to four. It was found impossible to operate liquid phase hydrogenation of brown coal tar at 700 ats. because the rate of hydrogenation of asphalts was so high that catalysts could not be kept in suspension in the reaction vessels. Pressure was accordingly reduced to 400 ats.

Details of Coal Hydrogenation to give Excess Heavy Oil

The flowsheet shown in Fig. XXXIX was supplied by Dr. Kronig. For simplicity, it refers to operation with coal as the only raw material. Actually, the amount of heavy tar which it was proposed to introduce into the coal paste at Blechhammer was comparatively small and would not greatly influence the flowsheet figures. All figures are tons/hour and refer to the operation of the total plant installed at Blechhammer, i.e. 4 liquid phase and 4 vapour phase stalls.

The coal was crushed and the first catalyst, iron sulphate, was added before drying. Dr. Kronig considered that better results would be obtained if the iron sulphate was added as a solution in order to obtain more even distribution. The mixture was then dried and it was stated that during this process, neutralisation of alkaline constituents of the coal ash was effected. The dry coal, with 2% of moisture was next mixed with approximately 1.5% of its weight of Bayermasse, a residue from aluminium preparation. This Bayermasse was previously dried to a moisture content of 15%. A third catalyst, 0.3% on the original coal of sodium sulphide, was next added, immediately prior to the pasting stage.

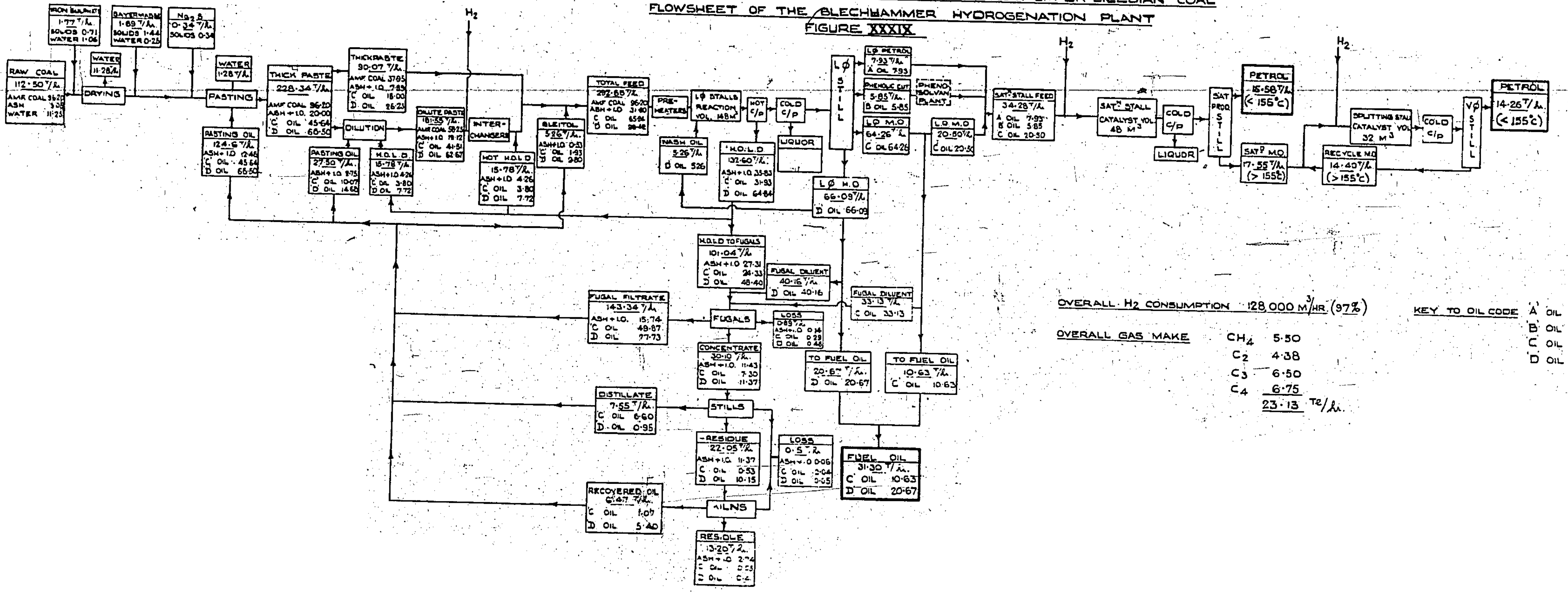
In order to produce heavy oil as one of the new-formed products of coal hydrogenation, it is necessary to reduce to a minimum the amount of recycle heavy oil in the coal paste. This necessitates the use of paste with a maximum coal content and the use of middle oil as a pasting oil component. Special difficulties are thereby introduced. For example, heat exchange between ingoing paste and exit products is not satisfactory with very thick pastes. Again, pastes made up of light oils and containing a low concentration of asphalts tend to settle when hot. These difficulties were overcome at Blechhammer in the following way: All the coal was first made up into a thick paste containing approximately 51% of total solids. About 40% of this thick paste was injected directly to the preheater, bypassing the paste interchanger. The remaining 60% was diluted down to approximately 43% total solids, i.e. maximum solid content for satisfactory paste interchange, and injected to the hydrogenation stall via the paste interchanger. In order to guard against settling of solids in the preheater, as much as possible of the diluent oil was supplied as high asphalt content heavy oil let down from the hot catchpot. Settling in the preheater was further guarded against by circulating a quantity of heavy oil let down from the catchpot to the preheater, without cooling or letting down to atmospheric pressure. This recycle was carried out with the same type of remote control hot-recycle pump as used in the tar hydrogenation stalls at Leuna.

A small amount of pasting oil (5% on the coal treated) was continuously injected direct to the preheater. The object of this was, firstly, to prevent plugging of the preheater in the event of a breakdown of the paste injectors and secondly, to provide a lubricant film between the paste and the inner wall of the preheater tubes.

PRODUCTION OF AVIATION PETROL & FUEL OIL FROM UPPER SILESIAN COAL

FLOWSHEET OF THE BLECHHAMMER HYDROGENATION PLANT

FIGURE XXXIX



OVERALL H_2 CONSUMPTION 128,000 M³/HR. (97%)

OVERALL GAS MAKE

CH_4	5·50
C_2	4·38
C_3	6·50
C_4	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

The total liquid injection to the stall was equivalent to a rate of 1.9 tons per M^3 of reaction volume per hour. This corresponds to the treatment of 0.65 tons of ash-and-moisture-free coal per M^3 of reaction volume per hour. The figure supplied at Ludwigshafen for complete 700 ats. hydrogenation of bituminous coal to middle oil plus petrol was 0.45 tons per M^3 of reaction volume per hour.

The paste temperature at the exit of the interchanger was not allowed to exceed 310°C. The exit temperature of the preheater was usually controlled to 415°C and was never allowed to exceed 425°C. The reaction temperature in the converters was kept as uniform as possible at about 485°C.

The circulating gas rate was equivalent to 3.5 M^3 per kg. of ash-and-moisture-free coal. The hydrogen partial pressure of the inlet of the converter system was 585 ats.

The whole of the products from the hydrogenation reactors passed to a hot catchpot which separated heavy liquid and solid products to the extent of 45-50% of the ingoing paste. Some 12% of this product was recycled hot to the preheaters as already described. The remaining 88% was cooled and let down to atmospheric pressure, after which a further 12% was returned direct to pasting as diluent for "thin" paste. The residual 76% was mixed with roughly 70% of its weight of diluent heavy oil obtained by topping off petrol and middle oil from the cold catchpot product and the mixture was fugalled. The fugalled filtrate was used as pasting oil and the residue was carbonised for recovery of oil.

The feed to the carbonisation ovens was given a preliminary flash distillation treatment to remove part of the oil. Recovered oil from the flash distillation and carbonisation ovens was used as a pasting oil constituent. The coke from the carbonisation ovens contained all the ash constituents of the original coal plus the catalyst plus the coke equivalent to the coal which had resisted liquefaction by the hydrogenation treatment. The latter amounted to roughly 4% on the a.m.f. coal fed.

The efficiency of recovery of oil in the two-stage sludge carbonisation plant was of the order of 75% and the oil lost at this stage amounted to 4.5 - 5% on the a.m.f. coal treated.

The vapors from the hot catchpot were cooled and the condensed liquid separated from recycle hydrogen in the cold catchpot. The liquid product was let down, separated from aqueous liquor and distilled to give 0-160°C, 160-210°C, 210-325°C and > 325°C fractions. Roughly half the 210-325°C and two-thirds of the > 325°C cuts were recycled as pasting oil components. The yields of new-formed oils, expressed as weight % on the a.m.f. coal treated, were approximately -

0° - 160°C	8.2%
160° - 210°C	6.1%
210° - 325°C	32.4%
> 325°C	21.5%
Total	68.2%

210-325°C middle oil and 325°C distillate heavy oil were blended in the ratio of 1:2 to give fuel oil, the yield of which amounted to 32.5% by weight on the a.m.f. coal treated.

The remaining middle oil blended with the lighter boiling fractions was subjected to vapour phase hydrogenation in two stages. Pre-saturation was carried out over 8376 and 5058 catalyst, followed by splitting hydrogenation over 6434.

The pre-saturation was carried out in two stalls, each with three converters of 8 M^3 catalyst volume. The first two converters were packed with 8376 and the third with 5058. The pressure was 300 ats., mean reduction temperature 410°C and the maximum throughput 0.8 kg. per litre of catalyst per hour. The yield of saturated product was 97% by weight on the feed. This product was distilled to give a petrol fraction which was blended in a final petrol product and middle oil was fed to splitting hydrogenation. The cutting temperature depended on whether aviation or motor fuel was required. In the former case a 0-155°C fraction amounting to roughly 45% of the saturated product, was blended direct into the final petrol.

The residual middle oil was hydrogenated in two stalls, each with two converters of 8 M^3 catalyst volume, packed with 6434 catalyst. Pressure was 300 ats., average mean reaction temperature 390°C and maximum throughput - 1 kg. per litre per hour. The conversion per pass was 50-55% when making aviation fuel and 65-70% when making motor petrol. Yields were 81-82% by weight of the feed of 0-155°C aviation fuel, or alternatively, 91-92% of 0-185°C motor gasoline. The former had a volatility of 55% at 100°C and a clear octane number of 74 which could be increased to 88 by addition of 0.09% by weight of TEL. The volatility of motor petrol was 35% at 100°C and the clear octane number was 70. The final blend of splitting stage motor petrol with the light distillate from the saturated product had a clear octane number of only 64. It was intended that, when making aviation fuel, the light distillate from the saturation product should be treated by the D.H.D. Process. A D.H.D. plant with a capacity of 26 tons/hour of feed had been installed. An alkylate plant for the production of 6.3 tons/hour of final product had also been built.

Phenol Extraction

Phenols in the liquors from both coal carbonisation and coal hydrogenation were extracted with phenosolvan (isobutyl acetate). This was a development made jointly by Lurgi and the I. G. The two liquors were treated separately and there were three plants; two operating and one spare.

It was intended to increase the output of phenolic products by washing the 160-210°C petrol fraction with recycle hydrogenation plant liquor from the phenosolvan extraction plant. This washing was to be carried out counter-current at a temperature of 75°C.

The spent liquor from the phenosolvan plant contained rather less than 200 mgs. of tar acid per litre. There were serious restrictions on effluent disposal at Blechhammer and the spent liquor had to be treated in the following way:

it was first diluted with recycle cooling water to reduce tar acid content to 20 mgs/litre and to raise the temperature to 25°C. It was then treated with diplococcus-type bacteria which reduced the tar acid content to 2 mgs/litre. Effluent from this treatment was finally pumped over waste ashes from the power station, when phenols were oxidised down to less than 0.5 mgs/litre.

Treatment of Hydrocarbon Gases

A Linde plant had been erected at Blechhammer in order to provide methane, ethane, propane and butanes from the mixed hydrocarbons produced in the hydrogenation process. These separated gases, apart from those required at Blechhammer for alkylate production, were to be sent to Heidebrech for use as chemical raw materials. A pipeline, 8 km. long, had been installed for this purpose.

Costs

Very little data on costs were available. The delivered cost of coal was 10-11 marks/ton, skilled workers were paid 80 pfgs - 1 mark/hour and unskilled workers 55-70 pfgs/hour. The middle German brown coal tar which was supplied subsequent to July 1944 cost 80 marks/ton.

According to Dr. Kronig, the estimated costs of production of heavy oil and aviation petrol at Blechhammer were 250 marks/ton and 450 marks/ton respectively. 65% of these costs were capital charges which included interest on capital at the rate of 4-1/2% and amortisation of the plant over a period of 11 years.

XXV. BRÜX

Introduction

Several bus-loads of staff and workmen from the Hermann Goering Works at Brüx arrived at Leuna on the night of 12/13th May. They had left Brüx on the night of 7th/8th May just before the Russian entry. The party included Dr. Damm, the managing director and Dr. Amon, the chief engineer. Dr. Ottens, the chief chemist of the plant had been separated from the main party en route and was expected later. Dr. Damm had no papers and was in no condition to give a detailed account of the plant and its operations. He disclosed that arrangements had been made in March to evacuate to Schwarzenfeld, near Amberg, Bavaria, in the event that a Russian occupation of Brüx appeared likely. When the Western advance developed, this plan was dropped but a considerable number of documents were evacuated to the Porceline Fabrik Buchtal A. G. at Schwarzenfeld. A further batch of documents had been sent to the Kohlen Chemische Institut at Claustal in the Hartz Mountains. Others had been hidden in the central shaft of the brown coal mine at Brux.

It was the intention of the Brüx staff to proceed to the Hermann Goering Works at Walenstadt, near Brunswick, where they hoped to work out a plan for distribution of people to other works.

General Outline of the Brüx Factory.

The plant, erection of which was commenced in 1939, consisted of the following sections:

(a) Brown Coal Carbonisation

This consisted of four groups of 20 carbonisation units designed by Lurgi to operate with recycle gas. The coal carbonised was the local hard brown coal containing 30% water. Each unit had a throughput of 250-300 tons/day of wet coal. Parts of this plant commenced operation in 1942 and by May 1944 when the programme began to be interrupted by air raids, 60 units had been erected and 55 were working. Tar yield was 10-12% by weight on the coal carbonised and middle oil and heavy tar were produced separately by fractional condensation of the tar vapours. It was proposed to sell the middle oil as heating oil after topping it to increase the flash point to >85°C. The heavy tar was to be the feed to the hydrogenation plant.

(b) Hydrogen Production

Six large Winkler Generators, each with a capacity of 20,000 M^3/hour water gas, were installed, together with Linde units for oxygen manufacture. The hydrogen plant for completion of the reaction $CO + H_2O = CO_2 + H_2$ operated at 12 ats. pressure. Nine hydrogen plant units were installed at Brüx. They were all Bamag design.

The anticipated steam savings were not achieved and initially trouble was experienced by salting up and corrosion of parts of the plant. Trouble was also experienced with the life of catalyst which had to be removed every 4-6 weeks for cleaning by rumbling and sieving. At times, the operation of the hydrogen units definitely limited plant operation and Dr. Damm was firmly of the opinion that atmospheric pressure hydrogen sets are to be preferred.

(c) Hydrogenation Plant

The hydrogenation plant was in two sections, each consisting of two liquid phase stalls, two pre-saturation and two splitting hydrogenation stalls. Each stall had four converters operating at 325 ats. The anticipated output of final liquid products from this plant, i.e. fuel oil from carbonisation + petrol and diesel oil from the hydrogenation units, was 600,000 tons/year. The plant began operations in May 1943 and by May 1944 output had been brought up to 45,000 tons/month. Bombing commenced in May 1944 and continued at regular intervals. The output of the plant was greatly reduced as a result and in the last 6 months of 1944 was only 20,000 tons of liquid product. Output during 1944 was 100-120,000 tons. It was considered that, apart from air raid damage, the output of the complete plant could have been easily increased from 600,000 to 1,000,000 tons/year liquid product by the addition of two more liquid phase stalls and by increasing the capacity of the carbonisation plant.

(d) Phenol Extractions

The brown coal tar was very rich in phenols. Aqueous liquors produced in the carbonisation and hydrogenation plants were extracted with phenosolvan as at Blechhammer. Phenols from the crude cold catchpot product of the hydrogenation plant were recovered by a method developed by Koppers. The product was subjected to steam distillation and the distillate passed through caustic soda solution and maintained at about 100°C, the resulting phenate being worked up in the ordinary way. A third source of phenol was the light oil from the carbonisation units, which was extracted with caustic soda.

The phenosolvan extract was very rich in catechol. The crude extract was purchased by the I. G. and was worked up at Leuna. The rest of the caustic soda extracted phenols were worked up at Brux and sold through the Phenols Sales Board in Berlin. Refining was not carried beyond the crude carbolic acid and crude cresols stages although it was intended later to install plant for the production of pure phenolic products.

Operation of the Hydrogenation Units

The heavy brown coal tar was hydrogenated in much the same way as employed at Leuna. The heavy tar was mixed with the cold catchpot product and fractionated into middle oil boiling up to 325°C and heavy oil, the latter being fed to the liquid phase hydrogenation stalls and hydrogenated, using a suspended iron on Grude catalyst.

The Brüx tar was quite difference from Middle German brown coal tar. In addition to its higher content of phenols, including catachol, it had a considerably higher asphalt content. It was also apt to contain arsenic compounds which gave rise to considerable trouble in the plant. Arsenic compounds were found in deposits in the pre-saturation hydrogenation stall interchangers and on the catalyst. The source of the arsenic was thin bands of high arsenic content Pyrites in the coal. As a temporary measure, trouble was minimised by careful selection of the coal but it was intended to install a coal washery, operating the flotation process in order to remove Pyrites from the coal carbonised.

Dr. Amon stated that ordinary gas-fired preheaters were used for the liquid phase and the splitting hydrogenation stalls but the preheaters for the pre-saturation stalls were electrically heated.

Costs

At the full output of 600,000 tons/year liquid products, it had been calculated that motor gasoline would cost 260 marks/ton at Brüx. This assumes that crude wet coal costs 12 marks/ton delivered, and is made up as follows:

Raw materials	120	marks/ton	
Operating costs	80	"	"
Capital charges	60	"	"

The corresponding cost of heating oil was estimated to be 220 marks/ton.

Present Condition of Brüx Plant

When the staff left Brüx, 16 carbonisation units were capable of operating and another six could have been put on line very quickly. Dr Damm considered that within 12 weeks, 30 carbonisation units could be in operation. Three Winkler gas Generators were in operating condition and it was estimated that the Linde plant could be made to operate at half capacity in 1-2 months' time, given freedom from air raids. The same was considered to apply for the hydrogen sets CO_2 and CO removal and compression.

As far as the hydrogenation plant was concerned, one liquid phase unit was in running order and a second could be put on line in four weeks. Two saturation and two splitting hydrogenation stalls were in working order.

Storage tanks had suffered badly in air raids but Dr. Damm considered that sufficient tanks were available for operation of the plant at roughly half its flowsheet output. Most of the storage tanks were sunk about one-third of their height below ground and were surrounded with 18" concrete walls

Underground Hydrogenation Plant

The Hermann Goering Works at Brüx hed started work on an underground hydrogenation plant at Bad-Schandau in Polenstal. This plant was intended to make 5,000 tons/month of petrol from tar. It consisted of two liquid phase and two vapour phase stalls and was known as Schwalbe III.

TABLE IX.

	Motor Spirit	Aviation Base VT. 702	DHD Aviation Base.VT.342	Diesel Oil 1	Diesel Oil 2	Marine Fuel Oil
Density at 15°C	0.735-0.765	0.715-0.730	0.760-0.810	0.845-0.865	0.820-0.840	0.845-0.865
Boiling Range	35°-200°C	40°-145°C	40°-175°C	200°-330°C	115°-285°C	200°-330°C
Flash Point	-	-	-	>55°C	>21°C	>65°C
Aniline Point	-	max.52°C	max.10°C	-	-	-
Vapour Pressure, ats at 40°C	0.6 - 0.8	max.0.5	max.0.5	-	-	-
Residue on distillation	10 mgs.max.	5 mgs.max.	5 mgs.max.	-	-	-
Sulphur Content % by wt.	max. 0.1	max.0.05	max.0.05	max.0.5	max.0.5	max.0.5
Freezing Point	below -25°C	below -60°C	below - 60°C	-	-	-
Aromatic Content % by vol.	-	max. 15	40 - 55	-	-	-
Min. temperature for filtrability	-	-	-	at least -5°C	at least -30°C	at least 0°C
Pour Point °C.	-	-	-	at least -10	at least -40	at least -5
Viscosity at 20°C(Engler)	-	-	-	1.5 min.	1.2 min.	1.5 min.
Ash & Hard Asphalt Content	-	-	-	-	-	-
Octane No.	min.65	min.70	min.78	-	-	-
Octane No. with 0.09% by vol. of lead	-	min. 87	min. 87	-	-	-
Cetane No.	-	-	-	45	40	45

TABLE X. - GERMAN OIL PRODUCTION DATA.

Hydrogenation Plants	Capacity in 1000 Tonnes/year				Actual normal monthly production in late 1943 and early 1944						
	Total Petrol	Aviation base	Alkylate & Octane	DHD petrol in Aviation Base	Aviation base inc DHD	Motor Spirit	Diesel Oil	Fuel Oil	Lube Oil	Misc.	Alkylate & Octane
Leuna 1)	600	350	60	(300) 100	20	10	20				
Böhlen 1)	240	180	(30)	(200)	15	12 x	11				
Magdeburg 1)	220	120				9	9				
Zeitz 1)	280					5	12		2.5	3.5	
Scholven 1)	216	216	60	(200) 100	16						
Gelsenberg 1)	350	350			29						
Pölitz 1)	600	540	64	(300) 100	45			5	1.0		
Wesseling 1)	200	144	(20		10		7				
Welheim 2)	160	50			4			9			
Brüx 1)	(400)	250	(24)	(300)	20		8	4			
Blechhammer 1)	(425)	(205)	(40)	(200)		1		1			
Lützkendorf 1)	50					2	1				
Oppau 5)	50	50	4	50	4						
Heydebreck 7)				(50) 12	1	0.3					
Aushwitz 7)			(24)								
Moosbierbaum 5)	106	106		(140) 106	7						
Hüls 6)	12	12		(20) 12	0.7						
Schkopau 6)	9	9		9	0.6						
Total	3,918				172.3	27.3	57	19	3.5	3.5	16.0
Fischer Tropsch Plants											
Ruhrchemie 3+4)	72					2.1	0.8		1.2	1.4	
Victor Rauxel 3)	40					1.5	1.0			0.8	
Rehinpreussen 3)	70					2.8	2.1		0.2	1.1	
Krupp Benzin 3+4)	69					2.2	1.1			1.7	
Essener Benzin 3)	80					4.1	1.8			0.8	
Hoesch Benzin 4)	47					0.5	1.2		0.2	2.0	
Schwarzheide 3)	170					8.4	2.5			3.1	
Schafgotsch 4)	40					0.7	0.8			1.8	
Lützkendorf 3)	(70) 12					0.2	0.1			0.7	
	591					22.5	11.4		1.6	13.4	
Brown coal for distillation	50					3.0	9.5	27		4.3	
Total Hydrogenation + Fischer + Carbonisation					172.3	52.8	77.9	46	5.1	21.2	
German Petroleum	1920					13	56	10	65	3.5	
Bit. Coal Tar Distu.								32			
Benzol etc.					4	27					
Bit.Coal Carbonisation	36							3			
Grand Total German Production:					176.3	92.8	133.9	91	70.1	24.7	

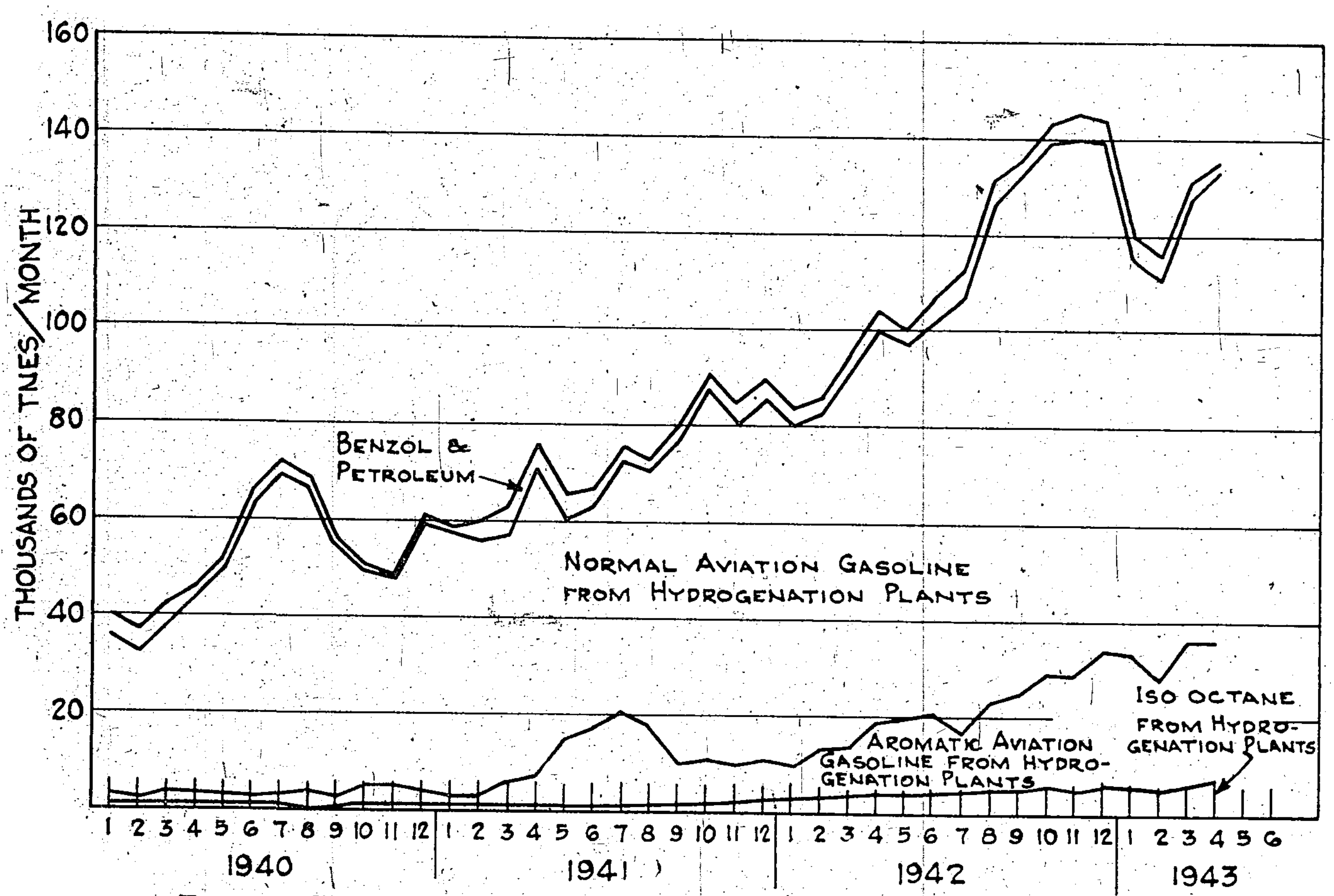


FIGURE XI.- AVIATION GASOLINE PRODUCTION.

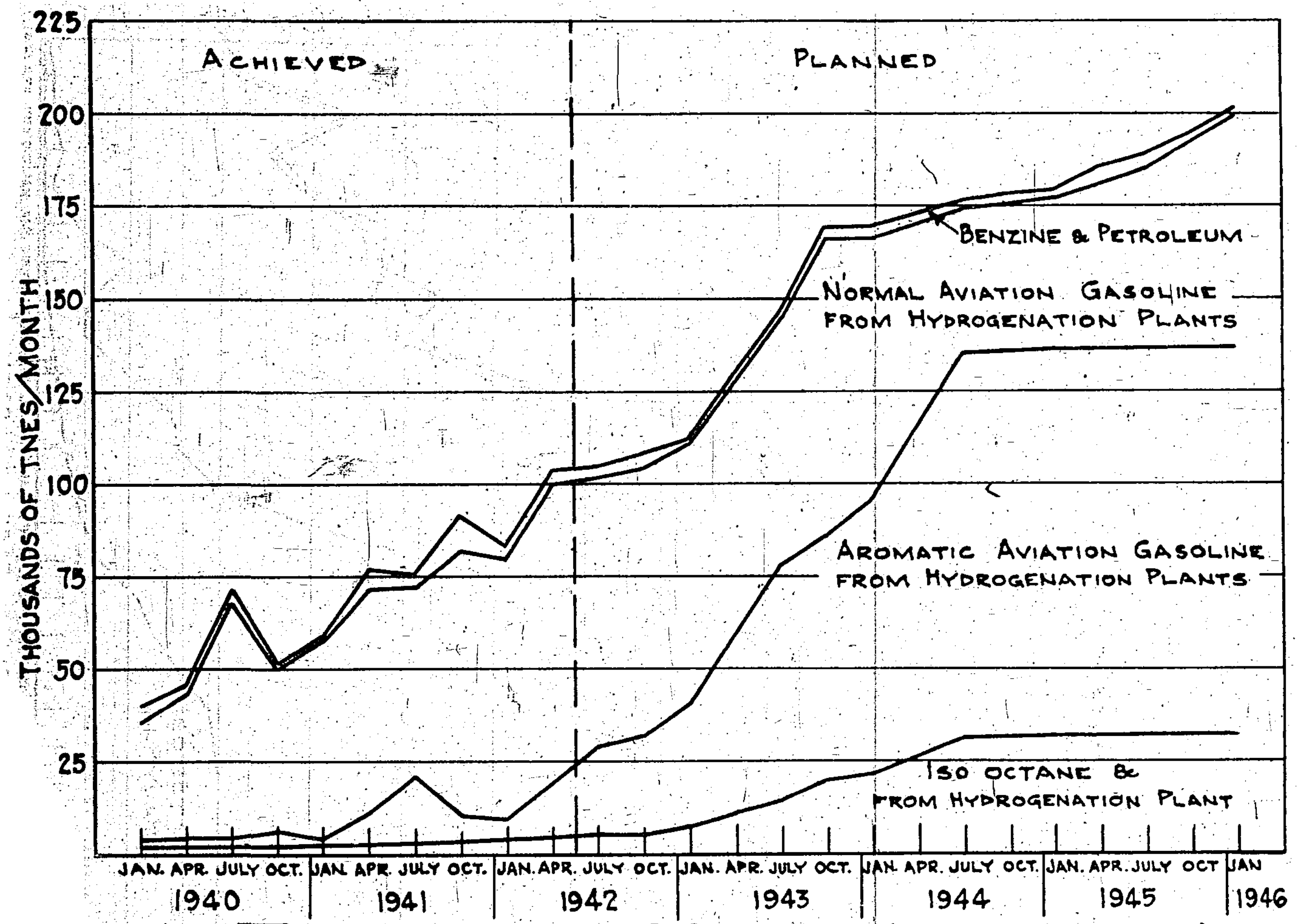


FIGURE XLI.- AVIATION GASOLINE PRODUCTION (NORMAL PROGRAMME)

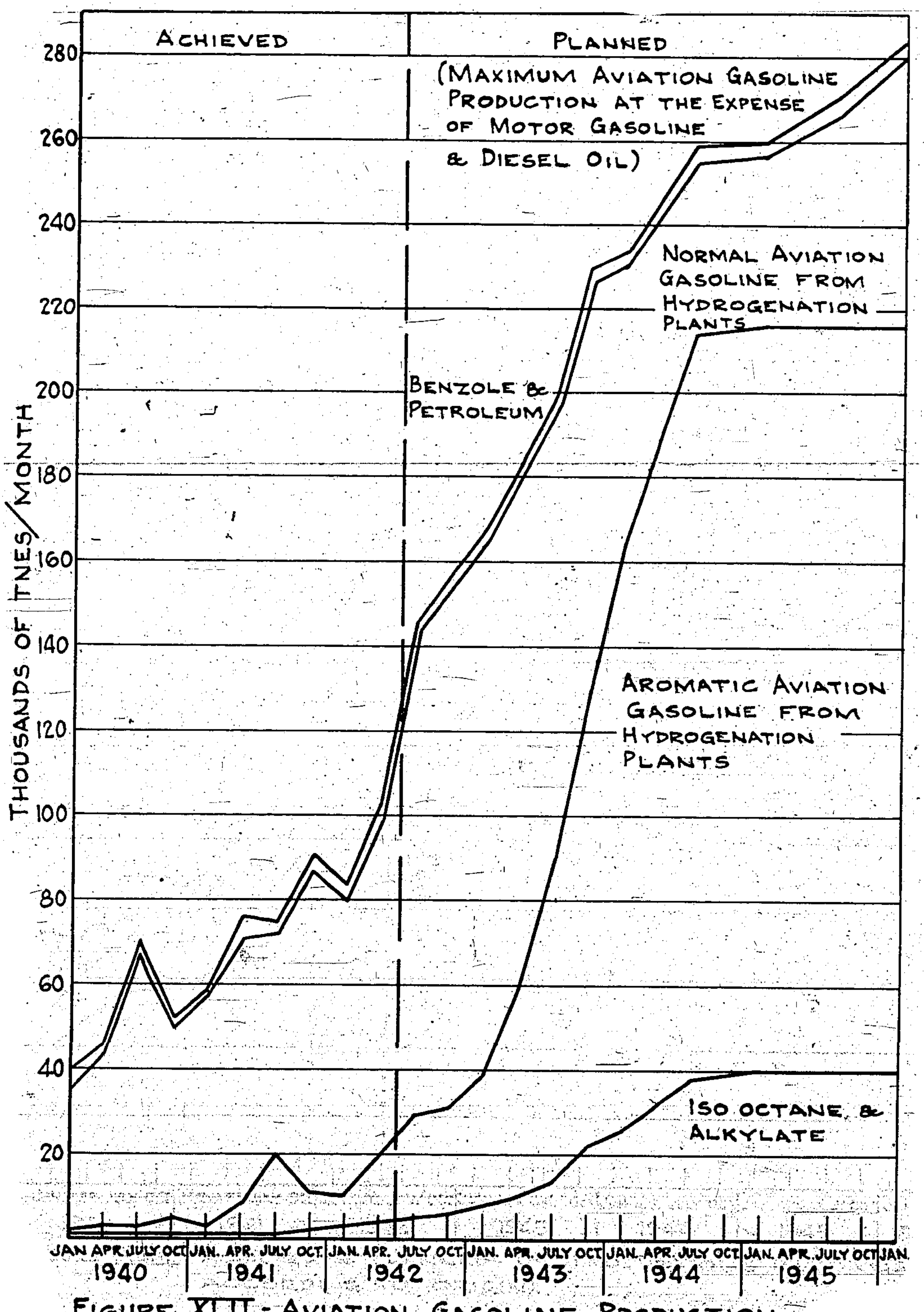


FIGURE XLII. - AVIATION GASOLINE PRODUCTION (MAXIMUM PROGRAMME)

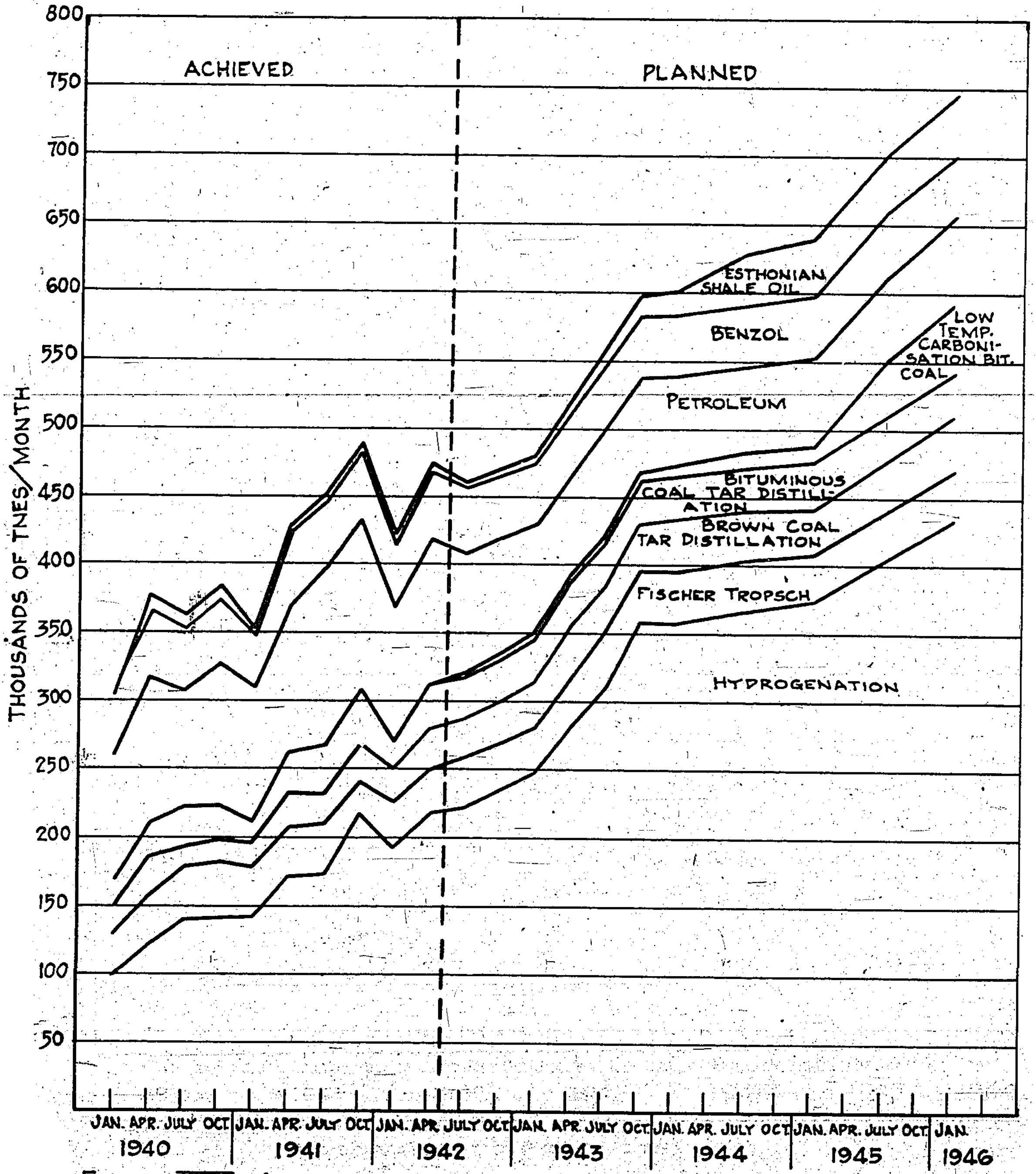


FIGURE XLIII - ACHIEVED & PLANNED OIL PRODUCTIONS (SUB-DIVIDED ACCORDING TO ORIGIN).

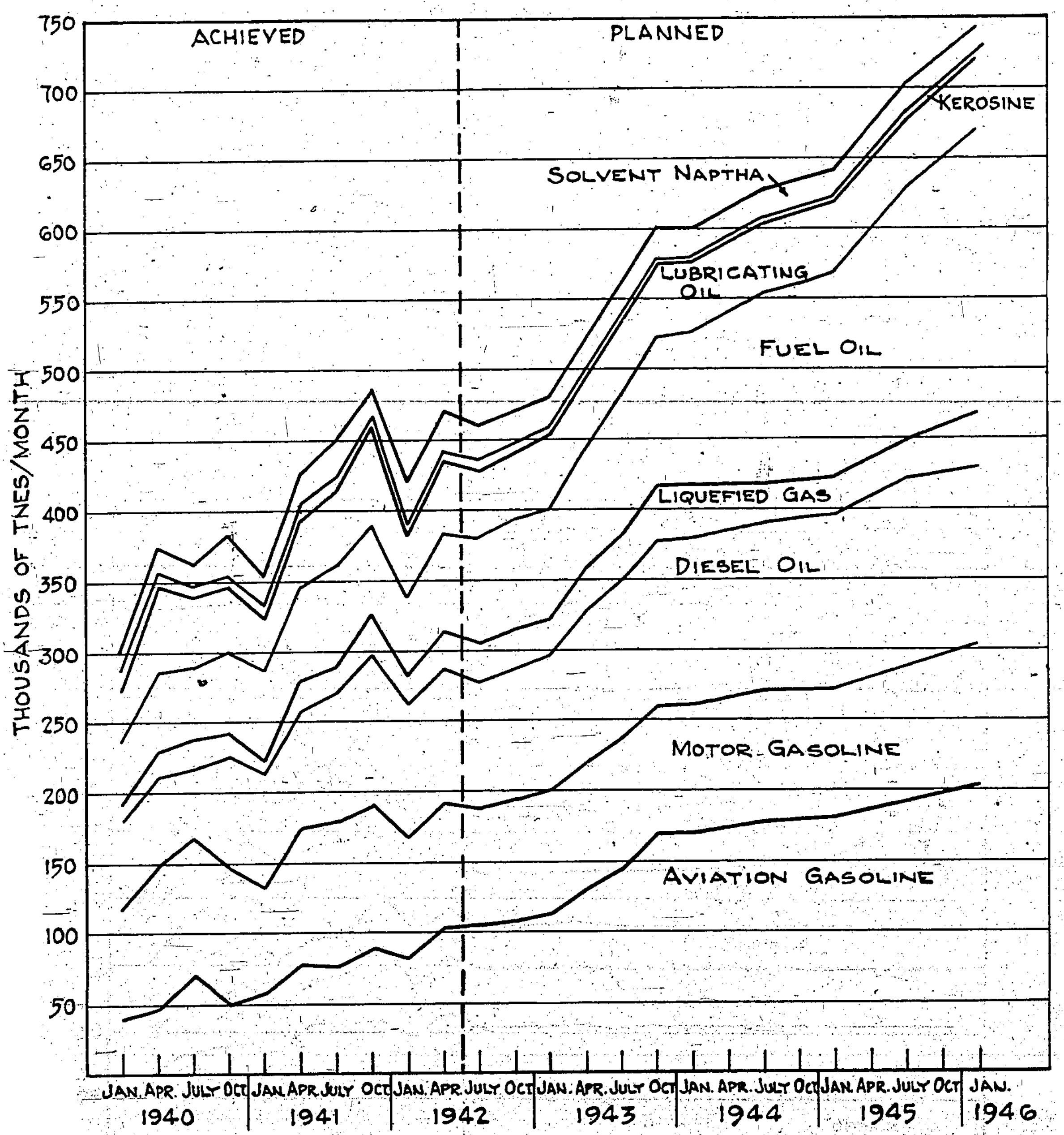


FIGURE XLIV.- ACHIEVED & PLANNED OIL PRODUCTIONS (SUB-DIVIDED ACCORDING TO PRODUCTS).

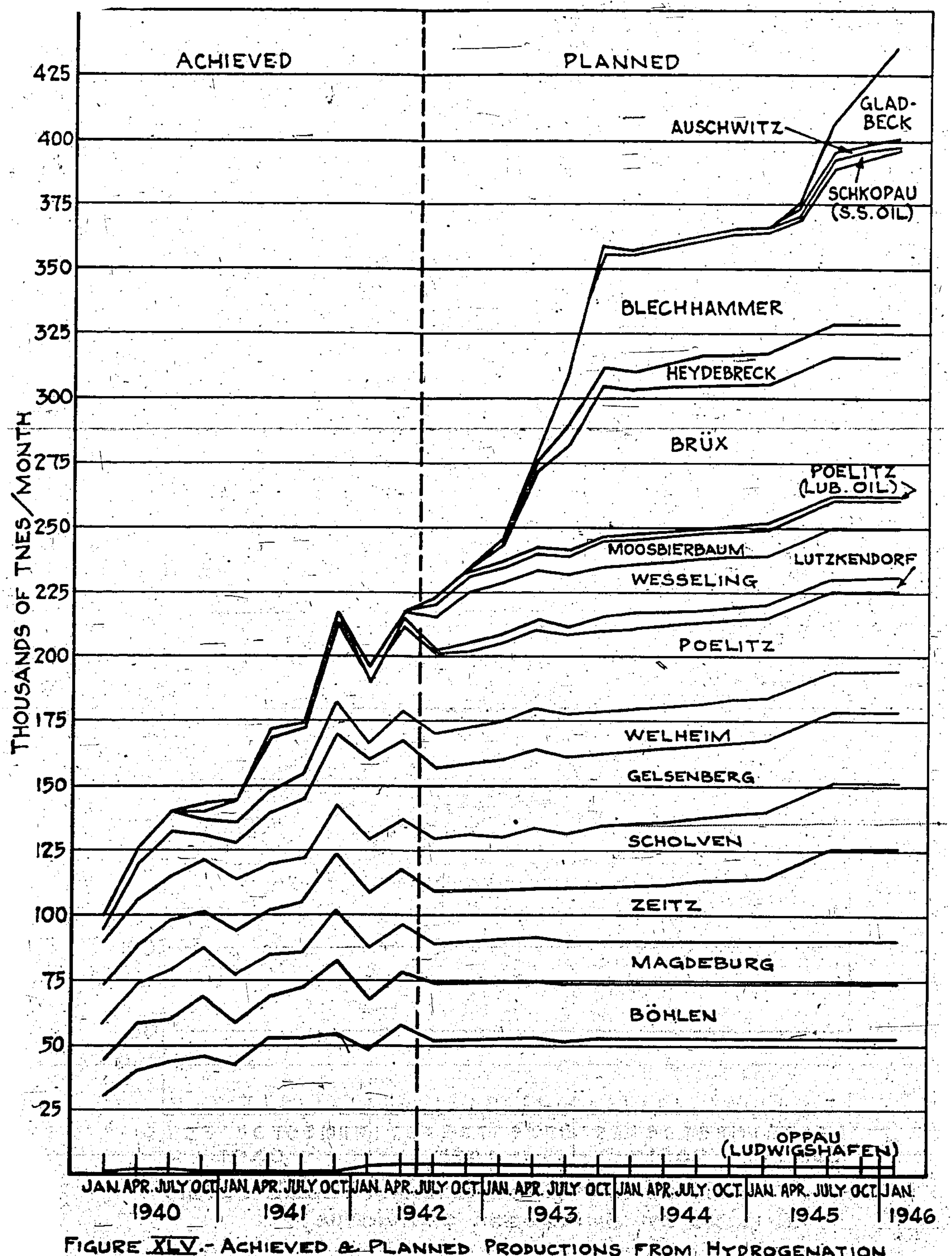


FIGURE XLV.- ACHIEVED & PLANNED PRODUCTIONS FROM HYDROGENATION PLANTS (INCLUDING HYDRO FORMING DHD, Di 1000 & S.S. OIL).

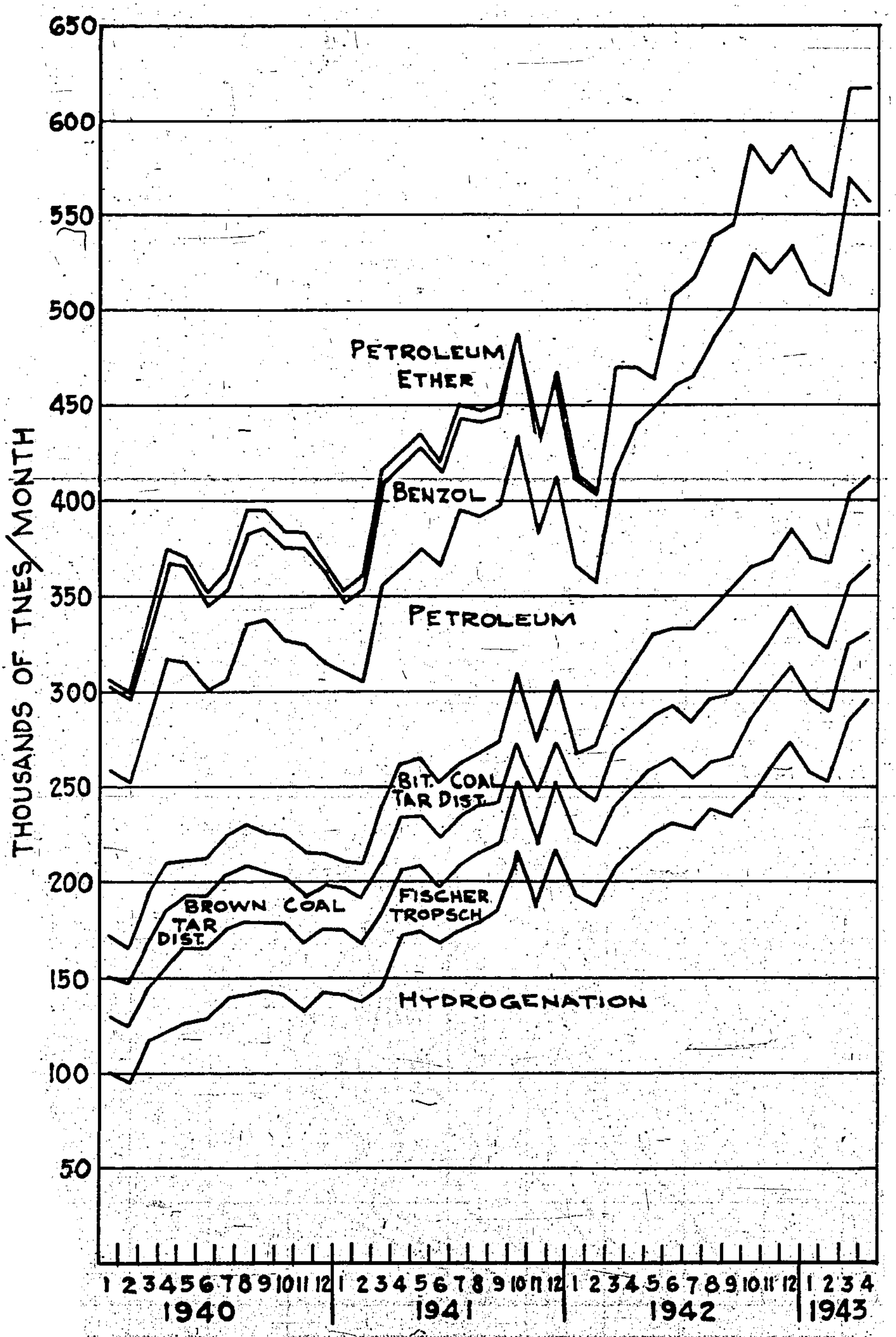


FIGURE XLVI.- ACHIEVED OIL PRODUCTION (SUBDIVIDED ACCORDING TO ORIGIN).

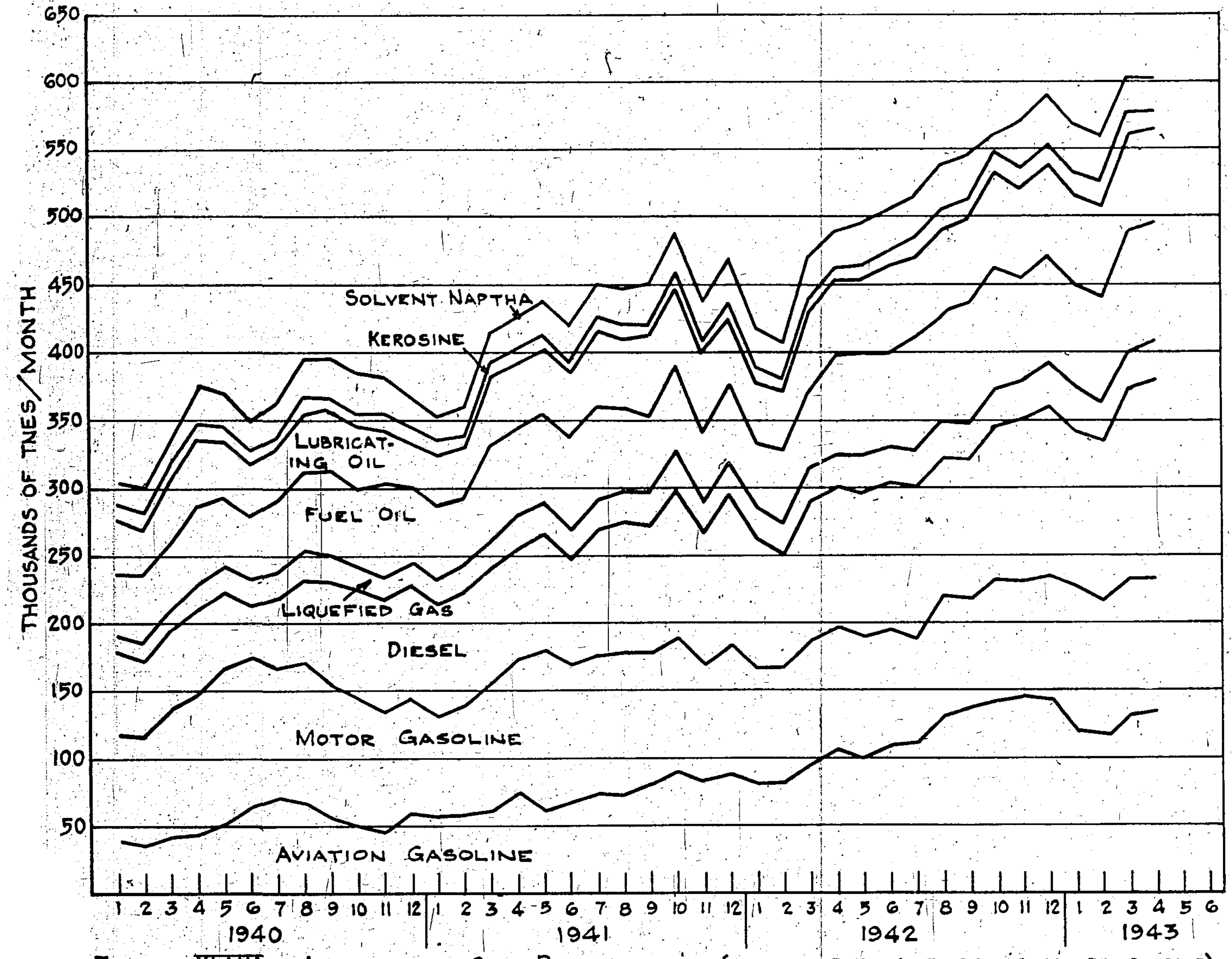


FIGURE XLVII.- ACHIEVED OIL PRODUCTION (SUB-DIVIDED ACCORDING TO PRODUCTS)

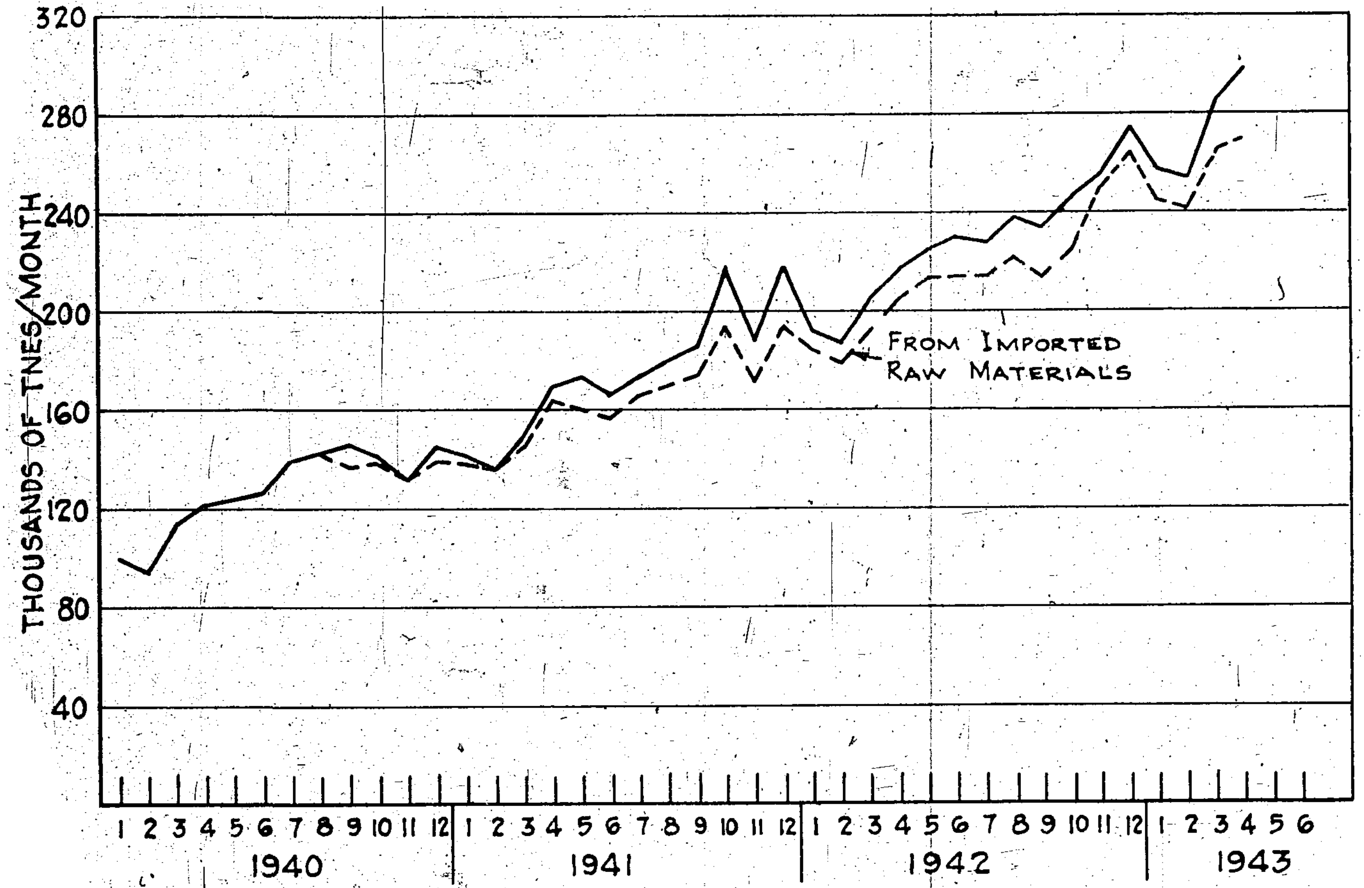


FIGURE XLVIII.- ACHIEVED OIL PRODUCTION FROM HYDROGENATION PLANTS.

XXVI. GERMAN OIL PRODUCTION

Dr. Bütefisch of Leuna was Chairman of the Wirtschaftgruppe for fuel production and of A.R.S.Y.N., the organisation which co-ordinated the production programmes of the various German refineries. He was questioned regarding the overall German oil position and supplied the figures given in Table IX.

The capacity figures in brackets refer to plant in course of construction. Lubricating oil figures refer to production by direct refining of oil products and do not include synthetic lube oils such as those made by polymerisation of ethylene. Production of liquefied butane and propane is not shown in the table but was normally 25-30,000 tons/month. Most of the Rumanian and Hungarian oil products were supplied direct to the armed forces in the Eastern areas and these supplies are not included in the table. The total Rumanian crude production was said to be roughly 6,000,000 tons/year.

Of the German crude oil production of 1,920,000 tons/year, some 8-900,000 tons/year came from the Austrian fields, 6-700,000 tons/year from the Hanover district, 200,000 tons/year from Heide and the remainder from Baden and the Polish frontier area. The German crudes, particularly those from Austria which contained only 5-7% petrol, were particularly good for lubricating oil production.

Examination of the table shows the overwhelming contribution of the hydrogenation plants to German aviation fuel production. It is also interesting to note the negligible extent to which Fischer-Tropsch activities were in process of extension.

Further data on German achieved and planned production of oil products were obtained in the form of graphs which were found in Dr. Bütefisch's Leuna office. These data are reasonably in line with those supplied personally by Dr. Bütefisch. Nine of the graphs are reproduced in this report as Figs. XL to XLVIII.

Dr. Bütefisch and Dr. Ottens supplied the data in Table X on the latest specification for German oil products.

XXVII. USE OF BOTTLED PROPANE AND BUTANE FOR ROAD VEHICLES

According to Dr. Butefisch, it was aimed to turn 60-65% of all German cars and commercial vehicles to bottled gas fuel. Shortage of steel and labour interfered with this plan and priority had to be given to conversion of trucks and vans. Actually only about 35% conversion was achieved. The monthly consumption of liquid gas was 25-30,000 tons. This compared with total consumption of petrol and diesel oil apart from that used by the armed services of 50,000 tons a month.

Pure butane was never used in Germany as bottled gas for road vehicles. Pure propane was used for household heating and lighting and it was also considered desirable to use propane in the winter months for road vehicles. In summer a mixture containing up to 85% butane was considered satisfactory. In actual practice, a blend of butane and propane in the proportions which corresponded to availability was employed during the war.

Dr. Scholtz of Leuna was the inventor of much of the equipment used in connection with liquid gas vehicles. He supplied the following information on I. G. development of liquid gas vaporisers.

In the first gasifier to be produced in commercial quantity, liquid gas was vaporised by means of a hot water preheater and the resultant vapour let down in two stages, firstly to a pressure of 0.4 ats. and finally to -20 m.m. water pressure. The sub-atmospheric second-stage pressure ensured efficient closing of the second-stage let down valve when the engine was shut off, but it led to difficulty because of a variable air/fuel ratio at different throttle openings. Air leakages backwards into the second stage let down chamber were prevented by fitting a non-return valve (actually a gas mask valve was used) between this vessel and the jet chamber.

The second type of gasifier was similar to the first except that the second-stage let down pressure was atmospheric. In order to ensure that no leakage occurred when shutting off the engine, a stop valve was incorporated in the liquid feed line. This was connected so that as long as there was a positive engine oil pressure it remained open. This model was extremely satisfactory and Dr. Scholtz considered it to be the best gasifier which has been produced. It is, however, fairly expensive; a pre-war production cost of 200 marks was mentioned.

A cheaper type has been developed during the war costing only 25-30 marks to make. Some 100-150,000 of this type of gasifier have been manufactured by the German Solex Carburetter firm. The preliminary vaporisation of the liquid gas is carried out in a coil heated by exhaust gases. The resulting vapour at a pressure of 1.2 ats. is let down first to 0.4 ats. and secondly to -5 m.m. water gauge. This assures satisfactory closing of the second stage let down valve and eliminates the rather expensive oil operated stop valve. At the same time it is sufficiently near atmospheric to avoid wide fuel air ratio variations with speed.

A third type was being developed in which vaporisation was brought about between the first and second let down stages.

Samples of these various types of gasifiers were procured at Leuna, together with detailed drawings. They were despatched to London through the usual channels but so far they have not materialised.

Dr. Scholtz said that a liquid gas had been used for running-in all aero engines during the war. A report giving a detailed description of the set up employed is amongst the documents removed from Leuna.

Some experimental work had been carried out at Leuna with a car running on neat methanol and also on a mixture of methyl ether and methanol.