300 ats process, but in spite of this, because of the lower reactivity of
the feed oil, the amount of gasoline obtainable from a given reaction vol-
ume is little more than half that obtained in the normal splitting process.
For a petrol product of the same volatility, the gas make in the 700 ats
process is some 5-6% greater than that obtained by the normal method. The
chief advantage is the elimination of the saturation step and the production
of a much more aromatic gasoline and therefore one having a higher octane
number. The aromatic content of the final gasoline is very dependent on the
nature of the feed stock. Middle oil obtained by the liquid phase hydrogena-
tion of pitch or bituminous coal or from the fractionation of bituminous coal
tar gives rise to a gasoline containing around 45% aromatics and having an
octane number of at least 78 without lead. Middle oils from brown coal or
from petroleum oil give rise to gasolines of much lower aromatic content.

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

h) D.H.D. Process.

For the highest quality aviation gasoline, the Luftwaffe insist-
ed on a high aromatic content. The 700 ats hydrogenation method described
above met this requirement, but only as far as very high aromatic middle oil
feed stocks were concerned. Another method was therefore adopted for the
main production of first quality aviation gasoline which consisted of the
dehydrogenation of the 80 - 185% cut of gasolines obtained from petroleum
distillation or by 300 ats splitting hydrogenation of coal and tar products.
In particular, this process was applied to the comparatively low quality
gasoline distilled from the crude saturation stage product. Usually, the
naphtha cut was 80-85% by weight of the original petrol. The process is dis-
continuous, reaction periods of rather more than 100-150 hours for bitumin-
ous coal naphthas and about 60-80 hours for brown coal and petroleum feeds
alternating with 20-24 hour catalyst reactivation periods. The usual reac-
tion conditions were -

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

Average Reaction Temp: 510 - 520°C.

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

Circulating hydrogen to oil feed ratio: Approx. 1,000 m^3 per
ton.

Yield data were given as follows:

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

The hydrocarbon gas made in the reaction is roughly made up of equal proportions of C_1, C_2, C_3 and C_4 hydrocarbons. Heavy polymer is formed during the reaction and re-distillation of the crude product to an end point of 180° C left a residue of approximately 4% by weight.

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

Fresh feed and recycle gas (containing 50-65% by volume of hydrogen) is heated by interchange with the out-going product and with a gas-fired preheater to a temperature of 500°C. It then enters the first of a series of converters, usually four or five in number. The reaction volume of each converter is 9-10 m³. Each converter contains a single bed of catalyst, which is active alumina on which has been deposited 10% of molybdic oxide. The reaction being strongly endothermic, it is necessary to re-heat reactants before passing them from one converter to the next. This intermediate heating is done in the same furnace as the main preheating step. On leaving the last reaction converter, the products are interchanged with incoming feed and the temperature reduced to 300°C, after which they pass to a final refining converter for removal of unsaturated products by hydrogenation. The catalyst in this refining stage is usually the same as is used in the D.H.D. reaction, but it is possible to work with 80% D.H.D. catalyst and 20% activated Terrana with no metal addition. The product is finally cooled by further interchange with the feed and by water coolers, let down to atmospheric pressure, stabilized and redistilled. The final distillate is blended back with the light $0 - 85^{\circ}$C fraction of original gasoline.
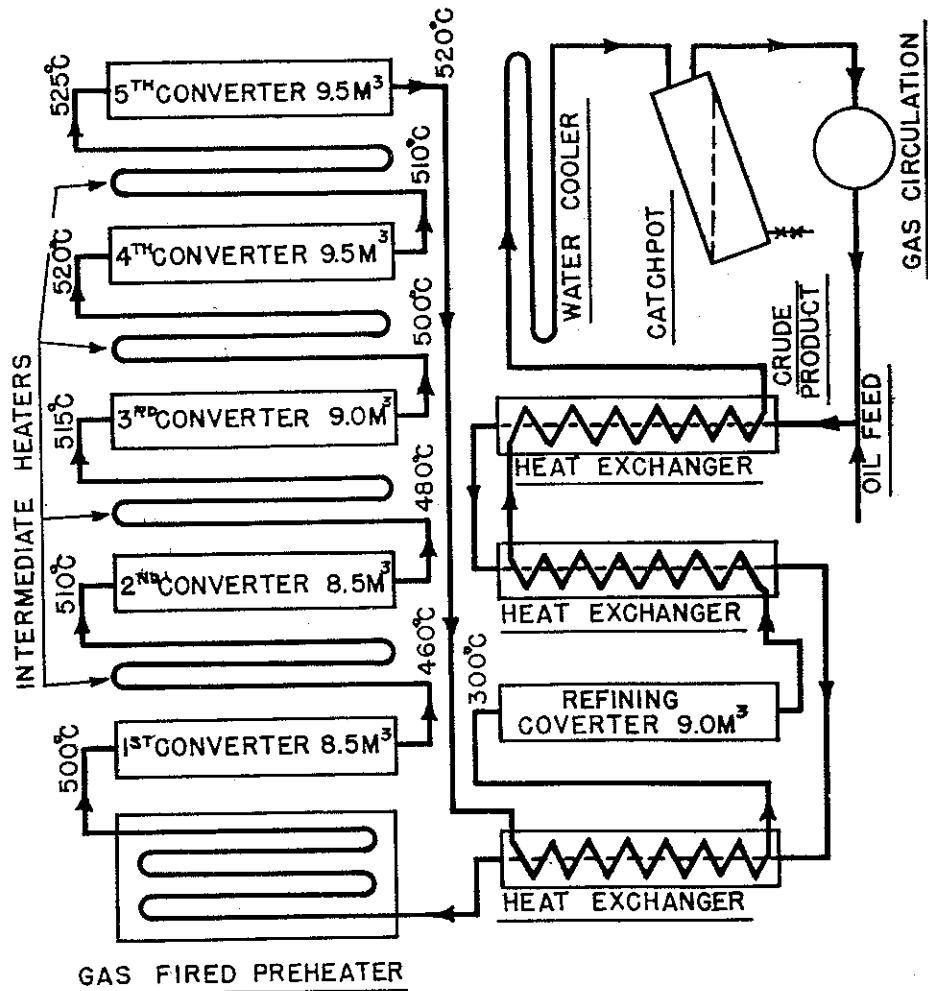
Gaseous products produced in the process are purged, (a) as dissolved gas released on letting down the crude product and (b) as a purge from the recycle gas system.

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

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FIG. XVI

FLOW DIAGRAM   D.H.D. PROCESS.

INTERMEDIATE HEATERS

525°C 5THCONVERTER 9.5M^3 520°C
510°C
520°C 4THCONVERTER 9.5M^3
500°C
515°C 3RDCONVERTER 9.0M^3
480°C
510°C 2NDCONVERTER 8.5M^3
460°C
500°C 1STCONVERTER 8.5M^3

GAS FIRED PREHEATER

300°C

REFINING COVERTER 9.0M^3

HEAT EXCHANGER

HEAT EXCHANGER

HEAT EXCHANGER

WATER COOLER

CATCHPOT

CRUDE PRODUCT

OIL FEED

GAS CIRCULATION

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

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

It has already been pointed out that, when aromatic middle oils are available, direct 700 ats gas phase splitting hydrogenation can produce a gasoline of practically the same quality as that obtainable by the 3-stage saturation/300 ats splitting/D.H.D. method. It is therefore interesting to compare the yield efficiencies of these two processes. The single-stage process gives a yield of about 83% of final gasoline. The first two steps of the multi-stage process produce from the same raw material 89% by weight of the normal hydro gasoline. This, on distillation, gives 73.5% of naphtha and 15.5% of light gasoline, both expressed as % by weight on the original feed stock. Treatment of the naphtha by D.H.D. process gives 60% by weight on the original middle oil of redistilled naptha which, when blended back with the light gasoline, gives a total of 75.5% by weight of final aromatic petrol. Thus, in addition to the multi-stage process being much more complicated to operate, it would appear to give 9% less final product than the direct 700 ats hydrogenation process. It is also interesting to note that the yield of finished D.H.D. gasoline from brown coal tar or petroleum middle oil calculated in the same way as above, is only 71-72%. This compares with an 89-90% yield of ordinary 6434 hydro-gasoline, showing that the Luftwaffe were prepared to sacrifice up to 20% output in order to obtain a highly aromatic fuel. In assessing this cost of the improvement in aromatic content, it must, of course, be borne in mind that the hydrocarbon gases, particularly the butane produced in the D.H.D. process, could be used for increasing the output of other aviation components, such as iso-octane or alkylate.

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

Naphtha dehydrogenation is also carried out on a scale of about 40,000 tons/year at Moosbierbaum. The D.H.D. process is not employed. A slightly modified version of the normal American "hydroforming" method is used.

i) Iso-Octane and Alkylate Production

The first method adopted in Germany for the production of iso-octane consisted of the dehydration of iso-butanol (made by the higher alcohol synthesis from carbon monoxide and hydrogen) to give iso-butylene, the polymerisation of this iso-butylene to di and tri iso-butylene, and the hydrogenation

of the dimer and trimer. This process was operated at Ludwigshafen/ Oppau and at Leuna in the early days of the war and is still the process employed at the new plants, Heydebrech and Auschwitz.

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

By 1940, the I.G. had developed a process for dehydrogenation of butane available from the hydrogenation plants and this opened up the second phase of branched paraffin production in Germany. Butane from the hydrogenation plants was fractionated into iso and normal isomers, the normal butane was used for liquid gas and the iso-butane dehydrogenated. The resulting iso-butylene was worked up to iso-octane as before. The butane dehydrogenation process, which was developed at Leuna, is a continuous process operating at 550-570°C and at substantially atmospheric pressure with a chromium on alumina catalyst (10-15% chromium). The process was made continuous by adopting the moving catalyst bed principle. The catalyst, which was made in the form of spheres, passed downward through externally heated reactor tubes cocurrently with the butane feed. The residence time of catalyst in the tubes is approximately 4 hours, after which it is removed to an external reactivation vessel. Reactivation is carried out by burning off deposited carbon with diluted air. The rate of butane feed is about 700 m^3 per m^3 of catalyst per hour and 20-25% of the inlet butane is converted per pass. About 85% of the butane converted goes to butylene. Carbon content of catalyst leaving the converter is 4% and this is reduced to about 1.5% in the reactivation step. No attempt is made to burn of all the carbon in the inner core of the catalyst and there is a theory that the presence of a certain amount of carbon in regenerated catalyst helps to keep down carbon formation. The process was first operated on a large scale at Leuna, Pölitz and Scholven.

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

j) Fuel for Jet Planes

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

3o Engler at -20°C. The fuel had also to be substantially free from phenols in order to avoid acid corrosion.

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

k)   Summary Table of German Hydrogenation Activities.

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

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

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

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

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

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

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

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

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

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

1199   - 29 -

It is also clear that the use of 700 ats pressure does not alter the position that the liquid phase stage is the really expensive part of the synthesis of petrol from high molecular weight raw materials. It may be calculated from the figures supplied at Heidelberg that, starting with bituminous coal at 21.5 RM per ton, the cost of production of 1 ton of crude liquid phase product is 155 RM. Similarly, starting with H.T. tar at 40 RM a ton, it costs 124 RM for each ton of crude liquid phase product. Compared with the above, the total cost of producing a ton of petrol from liquid phase product, including hydrogen but excluding the cost of the oil feed, is not more than 75 RM per ton. Expressed in another way, the value of liquid phase product from bituminous coal or bituminous coal tar hydrogenation compared with bituminous coal at 21.5 RM per ton is roughly 150 RM per ton. The comparative value, on the same basis, of liquid phase product from petroleum residue (which requires less hydrogen in the gas phase treatment than does bituminous coal product) is as high as 170 RM a ton.

(D) Research

A large proportion of the effort and equipment of the Ludwigshafen Oil Research Section has been devoted during the war to the development of the D.H.D, T.T.H and the 700 ats vapour phase splitting hydrogenation processes and to routine evaluation of raw materials and catalysts. A mass of reports and documents relating to this work has been evacuated and awaits detailed study. In the writer's opinion it is questionable whether the effort entailed can be justified and it is suggested that the easiest way to obtain a full account of these researches would be to bring a selected team of German workers to this country and have them write up summary reports of their work using the captured documents for reference.
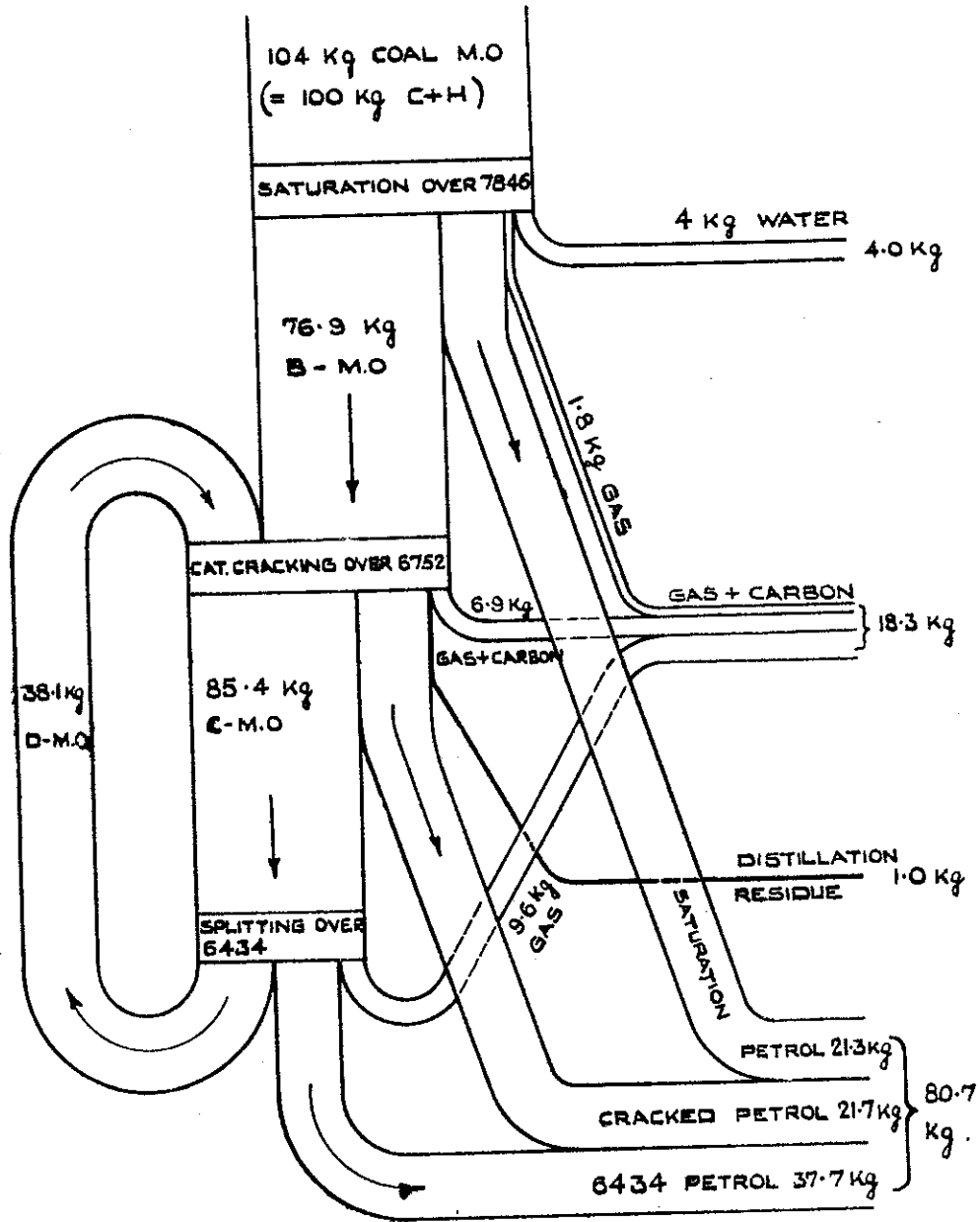
In addition to work on processes which are now in use on the large scale, considerable research was carried out on catalytic cracking, isomerisation, synthesis of branched chain hydrocarbons, etc. The following brief notes give an idea of the type of work in hand on these subjects.

Catalytic cracking.

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

FIG. XVII

COMBINATION OF HYDROGENATION & CAT. CRACKING

104 Kg COAL M.O
(= 100 Kg C+H)

SATURATION OVER 7846

4 Kg WATER — 4.0 Kg

76.9 Kg
B - M.O

1.8 Kg GAS

CAT. CRACKING OVER 6752

6.9 Kg — GAS + CARBON
GAS + CARBON — 18.3 Kg

38.1 Kg
D - M.O

85.4 Kg
C - M.O

9.6 Kg GAS

SATURATION

DISTILLATION
RESIDUE — 1.0 Kg

SPLITTING OVER
6434

PETROL 21.3 Kg
CRACKED PETROL 21.7 Kg
6434 PETROL 37.7 Kg
80.7 Kg.

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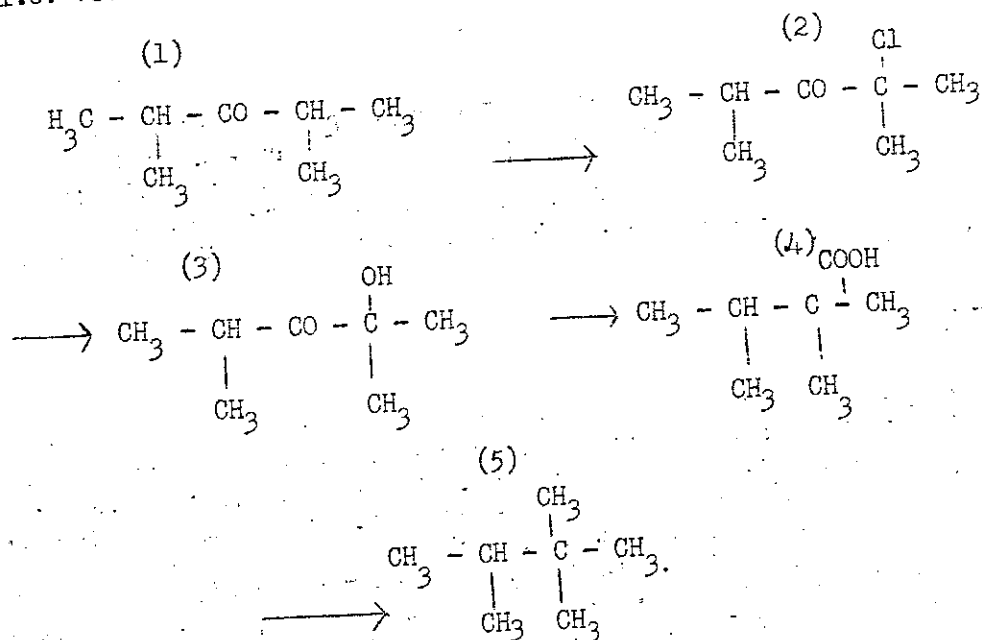
Isomerisation

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

Synthesis of branched chain hydrocarbons.

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

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

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

(1)

$$H_3C - CH - CO - CH - CH_3$$
$$\qquad\; |\qquad\qquad\; |$$
$$\qquad\; CH_3\qquad\quad CH_3$$

$\longrightarrow$

(2)

$$\qquad\qquad\qquad\qquad Cl$$
$$\qquad\qquad\qquad\qquad\; |$$
$$CH_3 - CH - CO - C - CH_3$$
$$\qquad\quad |\qquad\qquad\; |$$
$$\qquad\quad CH_3\qquad\quad CH_3$$

(3)

$$\qquad\qquad\qquad\qquad OH$$
$$\qquad\qquad\qquad\qquad\; |$$
$$\longrightarrow\; CH_3 - CH - CO - C - CH_3$$
$$\qquad\qquad\quad\; |\qquad\qquad\; |$$
$$\qquad\qquad\quad\; CH_3\qquad\quad CH_3$$

(4) COOH

$$\qquad\qquad\qquad\qquad\qquad\; |$$
$$\longrightarrow\; CH_3 - CH - C - CH_3$$
$$\qquad\qquad\qquad |\quad\; |$$
$$\qquad\qquad\qquad CH_3\; CH_3$$

(5)

$$\qquad\qquad\qquad CH_3$$
$$\qquad\qquad\qquad\; |$$
$$\qquad\quad CH_3 - CH - C - CH_3.$$
$$\longrightarrow\qquad\qquad |\quad\; |$$
$$\qquad\qquad\qquad CH_3\; CH_3$$

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

(1)

$$\qquad\quad OH\qquad\qquad\; OH$$
$$\qquad\quad |\qquad\qquad\qquad |$$
$$CH_3 - C - CH - CH - C - CH_3$$
$$\qquad\quad |\qquad\qquad\qquad |$$
$$\qquad\quad CH_3\qquad\qquad\; CH_3$$

(2)

$$\qquad\qquad\qquad CH_3\qquad OH$$
$$\qquad\qquad\qquad\; |\qquad\quad\; |$$
$$\longrightarrow\qquad CH_3 - C - CO - C - CH_3$$
$$\qquad\qquad\qquad\; |\qquad\qquad\; |$$
$$\qquad\qquad\qquad CH_3\qquad\quad CH_3$$

(3)

$$\qquad\qquad\qquad CH_3\; COOH$$
$$\qquad\qquad\qquad\; |\qquad\; |$$
$$\longrightarrow CH_3 - C - C - CH_3$$
$$\qquad\qquad\qquad\; |\qquad\; |$$
$$\qquad\qquad\qquad CH_3\quad CH_3$$