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CNO ltr. Op-23-PT
Serial no. 327P23
dated 22 October 1945

80385

TECHNICAL REPORT No. 115-15

THE MANUFACTURE OF AVIATION GASOLINE IN GERMANY

July 1945

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File: A9-16(3)(10/Ms)

80386

Serial: 0721

28 July 1945.

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Subject: U. S. Naval Technical Mission in Europe Technical
Report No. 145-45, The Manufacture of Aviation
Gasoline in Germany - Forwarding of.

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TECHNICAL REPORT No. 145-45

THE MANUFACTURE OF AVIATION GASOLINE IN GERMANY

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SUMMARY

This report records information obtained by technical investigators on the quantity, quality, composition, and manufacture of German aviation gasolines during the past war years.

Figures for the quantities of components and finished gasolines produced are presented and analyzed. The qualities and compositions of the different grades are shown and discussed.

The methods and plants used in Germany for synthesizing isoparaffins, for manufacturing base stocks, and for synthesizing aromatics are described. Process and operating data are given for these operations, particularly where the practice is new or different from that used in the United States.

The synthesis of nitration grade toluene is described in an appendix.

There are attached to the original copy of this report several German documents which will serve to elaborate some of the subjects covered herein.

July 1945

U. S. NAVAL TECHNICAL MISSION IN EUROPE

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THE MANUFACTURE OF AVIATION GASOLINE IN GERMANY

1. Introduction.

It was well known that Germany had always depended largely on synthetic operations for her liquid fuel supply. As the air force of that nation grew and developed, and its fuel requirements increased both in quantity and quality, it was correctly concluded that synthetic oil plants had kept pace with the aircraft development and continued to be the main source of fuel supply.

The ever increasing quality of aviation gasoline used by the Allies was paralleled by that of the German supply. The many new processes applied in America for manufacturing high quality gasolines were well understood by the Germans. They obtained information through Allied technical publications, through analysis of gasoline from captured planes, and otherwise. At the same time, German research in great force was supplying new processes, many the same as those being developed by the Allies, to their own operations. Toward the end of the war the quality of fuel being used by the German fighter planes was quite similar to that being used by the Allies.

In entering Germany to study their manufacture of aviation gasoline, it was to be expected therefore that many processes and developments would be found that were the same as those in use in America. Also, from examination of the gasoline in captured enemy planes, it was believed that no radically new compounds were being synthesized by the enemy. It could be anticipated, however, that new manufacturing techniques and technology might be found, that new designs in engineering might be seen, or that new or better catalysts might be in use in the various synthetic processes.

In the course of the technical survey being reported herein, most of the plants that manufactured aviation gasoline components were visited. Many industrial and government technical people were interrogated. A great variety and volume of technical and operating documents were obtained and studied.

In the following sections are discussed the overall German position on supply of aviation gasoline, and there are described the plants and processes producing the isoparaffin, base stock, and

1. Introduction (Cont'd.)

aromatic components. Some of the newer research work is described. The manufacture of nitration grade toluene is also reported, because its production was rather closely related to the aviation gasoline systems.

2. Supply and Composition of Aviation Gasolines.

(a) Supply and Sources.

The German aviation gasoline volume came very largely from the synthetic oil plants that hydrogenated coals and coal tars. A very small volume only came from petroleum, while essentially none came from the Fischer-Tropsch plants. Some components in small volume came from various chemical plants.

Parallel to the situation in the United States, great efforts were put forth continually in Germany to increase the supply of aviation gasoline. Much of the new construction was never completed due firstly to Allied bombing and then to termination of the war.

In Table I is given a partial breakdown of the sources and volumes of supply of aviation gasolines and their components.

TABLE I.

Sources and Supply of German Aviation Gasoline. (All figures are barrels per day)

<u>Company and Location</u>	<u>Total Aviation Components</u>	<u>Base Stocks & Aromatics</u>	<u>Synthetic Isoparaffins</u>
I.G. - Leuna	6,900	5,500	1,400
Brabag - Böhlen	4,100	4,100	-----
Brabag - Magdeburg	2,750	2,750	-----
Hibernia - Scholven	5,800	4,400	1,400
Gelsenberg - Gelsenkirchen	8,000	8,000	-----
Pöhlitz A.G. - Pöhlitz	13,900	12,400	1,500
Rheinbraun - Wesseling	2,750	2,750	-----
Ruhröl - Welheim	1,100	1,100	-----
Sudetendeutsche - Erdz	5,500	5,500	-----

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2. Supply and Composition of Aviation Gasolines (a) (Cont'd.)

TABLE I (Continued)

<u>Company and Location</u>	<u>Total Aviation Components</u>	<u>Base Stocks & Aromatics</u>	<u>Synthetic Isoparaffins</u>
I.G. - Oppau	1,200	1,100	100
I.G. - Heydebrek	600	300	300
I.G. - Moosbierbaum	2,000	2,000	---
I.G. - Hüls	200	200	---
I.G. - Schopau	200	200	---
Total from above-listed Plants.	55,000	50,300	4,700
Aromatic Oils from Coal Tar	1,100	1,100	---
Grand Total	56,100	51,400	4,700

The volume figures given in Table I represent the highest production level in 1943 before bomb damage interfered greatly with production. (The highest production for an entire month was in 1943, and the average daily volume during that month was 52,200 barrels.) At that time, when the maximum daily production of total aviation gasoline was about 56,000 barrels, there was under construction, or being developed, extensions to increase that figure to nearly 100,000 barrels. (It is interesting to note that at the time the aviation gasoline production reached the figure of 56,000 barrels per day, the total German motor gasoline production was 55,000 barrels per day.)

(b) Composition and Specifications.

There were two (2) grades of aviation gasoline produced in volume in Germany, one the B-4 or blue grade, and the other the C-3 or green grade. Both grades were leaded with the equivalent of 4.35 cubic centimeters tetraethyl lead per gallon. The B-4 grade was simply a fraction of the gasoline product from coal and coal tar hydrogenation. It contained normally 10 to 15 percent volume aromatics, 45 percent volume naphthenes, and the remainder paraffins. The octane number was 89 by a measurement corresponding to the C.F.R.

2. Supply and Composition of Aviation Gasolines (b) (Cont'd.)

motor method. The C-3 grade was a mixture of 10 to 15 percent volume of synthetic isoparaffins (alkylates and isooctanes) and 85 percent of an aromatized base stock produced by hydroforming types of operation on coal and coal tar hydrogenation gasolines. The C-3 grade was permitted to contain not more than 45 percent volume aromatics. This aromatic limitation sometimes required that the base stock component include some diluent other than the aromatic fraction, which could then be balanced if necessary by the inclusion of slightly more isoparaffin. (The C-3 grade corresponded roughly to the U. S. grade 130 gasoline, although the octane number of C-3 was specified to be only 95 and its lean mixture performance was somewhat poorer.)

The components of the two grades were therefore simple and few in number. The isoparaffins were produced by standard, well known methods and there was nothing abnormal found in their compositions. The base stocks were fractionated to end points of 300 to 320 degrees fahrenheit. No normal isopentane separation was carried out, and the pentane and butane contents were adjusted simply for vapor pressure control. Small amounts of specially synthesized aromatic compounds were included from time to time, but no regular large scale use of such materials was practiced. No aromatic amines or other special additives were used.

Oxidation inhibitors were not used in the regular blended aviation gasolines. It will be seen that the components were in general of such nature that oxidation inhibition should not have been necessary. Lead deposition from fuels was an operating problem, however, but no inhibitors were used for its prevention. This "lead instability" was believed to be related to aromatic content, and fear of lead deposits was a reason for the limitation of the aromatic contents of the two grades.

The relative volumes of production of the two grades cannot be accurately given, but in the last war years the major volume, perhaps two-thirds (2/3) of the total, was the C-3 grade. Every effort was being made toward the end of the war to increase isoparaffin production so that C-3 volume could be increased for fighter plane use. The isoparaffin usage in that grade had already been cut to a minimum.

In Table II are given the important RLM (Reichs Luftfahrtministerium) specifications for aviation gasolines supplied to the Air

2. Supply and Composition of Aviation Gaslines (b)(Cont'd.)

Ministry. The complete specification sheet is appended. On that RLM sheet are also given specifications for aircraft diesel fuel. (The subject of diesel fuel manufacture in Germany is being covered by a U. S. Naval Technical Mission in Europe Report entitled, "German Diesel Fuel".)

TABLE II.

RLM Specifications for B-4 and C-3 Gasolines.

	<u>Blue Grade</u> <u>B-4</u>	<u>Green Grade</u> <u>C-3</u>
Density at 59°F.	0.710 - 0.760	0.760 - 0.795
Distillation °F., IBP	104 min.	104 min.
10 percent	167 max.	176 max.
50 percent	221 max.	230 max.
90 percent	320 max.	320 max.
E.P.	338 max.	356 max.
Recovery, percent volume	98 min.	98 min.
Reid Vapor Pressure lbs.	7.0 max.	6.3 max.
Aromatic Content, percent volume	25 max.	45 max.
Tetraethyl Lead Content, percent volume	0.115 - 0.120	0.115 - 0.120
Ethylene Dibromide Content, percent volume	0.050 - 0.053	0.050 - 0.053
Melting Point, °F	-76 max.	-76 max.
Leaded Octane Number (Motor Method)	89 min.	95 min.

Note--The mixture response curve for each gasoline shall at least equal that of a standard reference fuel, supplied by the R.L.M., at all air-fuel ratios between 0.75 and 1.3/ The following document transmitted to the Bureau of Ships relates to specifications:

- I. Technische Lieferbedingungen für die Flugmotoren-Frontkraftstoffe. (RLM specifications for aviation gasolines).

2. Supply and Composition of Aviation Gasolines (Cont'd.)

(c) Engine Testing.

The anti-knock performance of aircraft fuels was evaluated in two (2) different manners: by the octane number, using a test very similar to the C.F.R. Motor Method, and by a mixture response curve. The specifications of B-4 and C-3 fuels include both octane number and the mixture response curves.

Octane number was measured on the one-cylinder "I.G. Prüfmotor". The technical data for this engine are as follows:

Bore	65 mm.
Stroke	100 mm.
Volume	332 cc.
Power Output at 900 rpm.	0.7 kw.
Consumption at 900 rpm.	600 cc. per hour
Compression Ratio	4.0 to 15.0
Inlet valve clearance (cold)	0.20
Inlet valve opens	11° after top center
Inlet valve closes	173° " " "
Outlet valve clearance (cold)	0.25
Outlet valve opens	173° after top center
Outlet valve closes	3° before top center

The values obtained with this I.G. test engine agree quite closely with those obtained on the C.F.R. engine. All values given herein for octane numbers, motor method, were determined on I.G. engines. The test conditions for measurement of aviation fuels were as follows:

Speed	900 rpm.
Cooling Medium	Glycol and Water
Cooling Medium Temperature	300°F.
Inlet Temperature of Fuel-air mixture	300°F.
Ignition	22° before top center
Compression Ratio	Start of "medium heavy" knocking

The mixture-response curves of aircraft fuels were measured on a B.M.W. (Bayerische Motorenwerke) 132-F single cylinder engine. Liquid injection was employed and the following test conditions were used:

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2. Supply and Composition of Aviation Gasolines (c) (Cont'd.)

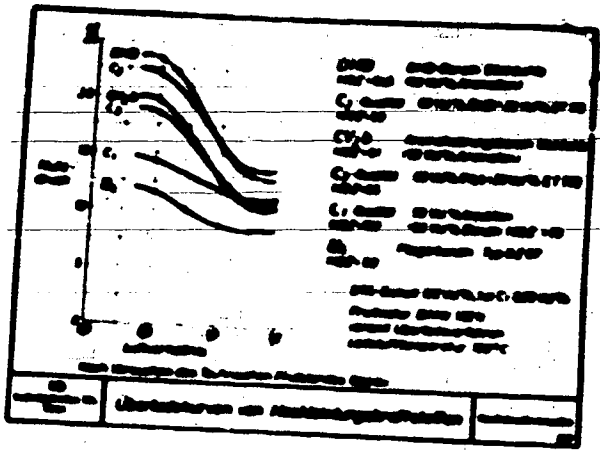
Speed	1600 rpm.
Compression Ratio	6.5
Cooling air temperature	77°F.
Cooling air pressure	200 mm H ₂ O
Begin Liquid Injection	26° to 30° after top center.
Injection Pressure	60 atmospheres
Inlet air temperature	175° and 265°F.
Ignition	Highest power output at air to fuel ratios of 0.7, 0.9, 1.3 without knocking.
Air to Fuel Ratio	0.7 to 1.3
Measurement of knock	Audible

There are attached on the following pages two (2) small photographs which give several comparable mixture response values and plots for different components and fuels.

The first is a plot of air-fuel ratio (abscissa) against "useful" pressure in atmospheres. The B-4 and C-3 fuels are shown thereon (MOZ is motor method octane number).

The second is a table with a title meaning "Mixture-Response Power Outputs for Aromatic Fuels" showing relative power outputs of several components at air-fuel ratios of 0.9 and 1.1, and also their motor method and research method octane numbers. The top group is for mixtures of 50 percent volume of 73 octane number (unleaded) coal hydrogenation gasoline, leaded with 4.35 cc. tetraethyl lead per gallon, and 50 percent volume of each of the components listed, also leaded. The lower group is of well known materials for comparison. (Fliegerbenzol is aircraft fuel; Dehydrier means "from dehydrogenation process"; Aromatisierungs means "produced by a process yielding high aromatic contents.")

The composition of C-3, with a high aromatic content, resulted in that gasoline having a good rich mixture (less than 1.0) performance. Its performance, i.e., allowable power output, at lean mixture was not entirely satisfactory, however. If more isoparaffin had been included, the lean mixture performance would have been



Durch Überladung erzielbare Leistung bei Aromaten-Kraftstoffen.

Leistung mit Äthyl-propylbenzol bei $\lambda = 0,9$
 gleich 100° a. gesteuert

20 Vol.-% Gemisch aus Benzolbenzol mit Äthyl-Propylbenzol 0,27 + 0,12 Vol.-% Pb mit:	% Leistung bei Luftüberschuss		Ölverbrauch	
	$\lambda = 0,9$	$\lambda = 1,1$	Motor Methode	Rechner Methode
Äthyl-propylbenzol	100	71	99	110
Dibenzol	95	67	97	107
Fluorbenzol	81	64	94	104
Dibenzol-Aromaten 120-175°C	80	59	93	103
Dibenzol-Aromaten 175-220°C	77	55	92	101
Luftbenzol	60	52	100	101
Zum Vergleich: bekannte Kraftstoffgemische				
Ö. Z. 67 Fluorbenzol aus Benzolbenzol 0,27 Vol.-% Pb	44	33	88	91
Ö. Z. 100 Kraftstoff aus an 20 Vol.-% Benzolbenzol 0,12 Vol.-% Pb	35	40	101	104
Aromatengemische aus Benzolbenzol 0,17 Vol.-% Pb	64	30	90	110
Aromatengemische aus Pb 700 0,17 Vol.-% Pb	80	39	93	103
Luftbenzol 0,09 Vol.-% Pb	77	67	114	115

1-5-1
 1-8-1
 1-9-1
 1-10-1

2. Supply and Composition of Aviation Gasolines (c)(Cont'd.)

improved. This was recognized as the outstanding shortcoming in the German aviation fuel quality position. Had raw materials and equipment been available, more isoparaffins would have been included in the C-3 blend. As isoparaffin content increased, the aromatic content could simultaneously have been decreased (by use of base stocks with octane numbers equal to those of the aromatic base stocks) and a gasoline with increased heat content would have resulted. However, because of the relatively greater ease of manufacturing aromatics, they were used in large quantity to help gain a satisfactory lean mixture performance, with the result that rich mixture performance was not limiting.

(d) Safety Aviation Fuels.

A note should be made regarding the development of safety aviation fuels. The Germans were quite aware of the desirability of safety fuels. Tests had been made with 390 to 660 degrees fahrenheit fractions of coal and coal tar hydrogenation products, but no full scale use of such materials was being made.

Some tests had been made to relate flash point and boiling range of a safety fuel to its resistance to ignition by incendiary bullets. It was concluded from this work that for a safety fuel to be effective, the flash point must exceed 200 degrees fahrenheit and should be in the region of 300 degrees fahrenheit.

3. Specifications and Supply of Jet Fuels.

The requirements for jet fuels in Germany were increasing rapidly at the end of the war. The 1944 consumption was 650 barrels per day, and it was planned to increase that figure to 3,250 barrels per day in 1945. While that consumption apparently never was reached, the demands had become appreciable in terms of Germany's available supply of liquid fuels.

Mixtures of gasoline and diesel oil fractions were used as fuel in 1944, but with increasing requirements efforts were being made to use higher boiling fractions only in order to release all gasoline for other critical uses. Tests were in progress using materials from the sump phase and pre-hydrogenation steps in coal hydrogenation.

3. Specifications and Supply of Jet Fuels (Cont'd.)

The tests had shown that only a low aromatic content could be tolerated if clean burning was to be obtained, and it was also concluded that some gasoline was necessary in order to obtain satisfactory ignition.

The status toward the end of the war was that gasoline-rich mixtures were still being used with the higher boiling diluents being any available material such that the blend met the following specifications:

(1) Viscosity maximum 12 centistokes at -31 degrees fahrenheit (or maximum 22 centistokes at -4 degrees fahrenheit). The viscosity specification was to insure flow through the fuel pump and good distribution in the fuel jets.

(2) Pour point maximum -31 degrees fahrenheit. (It was stated in another instance that in practice the maximum pour point was -40 degrees fahrenheit and that no crystal appearance could occur above -13 degrees fahrenheit). In a flight of one (1) to one and one-half (1½) hours, such as is experienced with jet fighters, the contents of the fuel tank can reach a temperature as low as -31 degrees fahrenheit. For long distance flights it was believed that the pour point specification would have to be lowered to -56 degrees fahrenheit.

(3) The fuel shall burn without carbon formation. Aromatic oils deposit carbon in the combustion chamber and the turbine. Paraffinic oils are clean burning and therefore desired for jet fuels. It was the opinion in Germany that the chemical character (and hence burning quality) of the fuel was of more importance than such properties as boiling range.

(4) Heating value minimum 18,000 BTU per pound.

(5) Sulfur content maximum 1.0 percent weight.

4. Synthesis of Isoparaffins.

Isoparaffins were synthesized commercially in Germany by two (2) processes; isobutylene polymerization followed by hydrogenation of the polymer, and by alkylation of butylenes and isobutane. Of the two processes, alkylation was much the more important from the stand-

4. Synthesis of Isoparaffins (Cont'd.)

point of volume produced. Both of the above processes have been highly developed in America, and the German applications were not more highly developed than present practice elsewhere. They are described below, however, together with the methods by which their raw materials are produced.

The production of isoparaffins other than those obtained from the two commercial processes was given extensive study. The synthesis of triptane was studied and a process was designed from this work, although triptane itself is not the end product. This development is described below.

The isomerisation of normal butane was being carried out commercially to supply isobutane to alkylation. The commercial process used is described in this section together with some new research on the isomerisation of normal C₆ and C₇ paraffins.

(a) Isobutylene Polymerization and Polymer Hydrogenation.

This process for isooctane manufacture was employed at Leuna, Ludwigshafen-Oppau, and Heydebrek.

Isobutyl alcohol was synthesized directly from CO and H₂ by the "Isobutyl Synthese" (described in U. S. Naval Technical Mission in Europe Report titled "Synthesis of Hydrocarbons and Chemicals from Mixtures of CO and H₂"). The alcohol was dehydrated to isobutylene over precipitated alumina at 630 to 680 degrees fahrenheit and normal pressure. In this temperature interval a 95 percent conversion of alcohol to olefin was obtained, with a small accompanying yield of isobutyraldehyde. A one pass operation was therefore employed. Isobutyraldehyde and water were separated from the isobutylene by simple distillation. The aldehyde was hydrogenated to alcohol and recycled back to dehydration feed.

Isobutylene from the alcohol dehydration was compressed to 20 atmospheres, heated to 300 to 350 degrees fahrenheit and polymerized over a catalyst of 25 percent phosphoric acid on activated carbon. Unpolymerized isobutylene was separated and recycled, and combined dimers and trimers were taken overhead in a second column, leaving only a small amount of high boiling polymers as bottoms. The dimer-trimer mixture was then hydrogenated under 200 atmospheres of

4. Synthesis of Isoparaffins (a)(Cont'd.)

hydrogen pressure at 660 degrees fahrenheit, using a tungsten nickel-sulfide catalyst. A hydrogen recycle of four (4) to one (1) based on fresh hydrogen was employed.

The hydrogenated fraction, known as ET 110 or Di 1000, had the following properties:

Density at 59° F.	0.710
Distillation, ° F, IBP	176
Distillation 10 percent	214
Distillation 50 percent	217
Distillation 90 percent	230
Distillation EP	385
Octane Number (Motor Method)	
Unleaded	98
Octane Number with 4.35 cc. Tetraethyl Lead/gallon 115.	

Before the advent of the alkylation process, isobutylene was being produced by isobutane dehydrogenation at Leuna, Politz, and Scholven. Polymerization and polymer hydrogenation systems were used to convert this isobutylene to T-52, a product nearly identical to ET 110. The processing of the isobutylene to T-52 differed from the ET 110 system only in that, due to slightly different feed composition, the polymerization catalyst in the T 52 process was 50 percent phosphoric acid on asbestos instead of the 25 percent phosphoric acid on active carbon catalyst in the ET 110 system.

The following document, transmitted to the Bureau of Ships, relates to this process:

II. Herstellung von Di. 1000.
(Flow diagram of the Di 1000
or ET 110 process)

(b) Alkylation.

Although research and development work on alkylation was started in Germany prior to 1940, the commercial production of alkylate did not begin until 1943. Prior to that time, Leuna, Politz, and Scholven had

4. Synthesis of Isoparaffins (b)(Cont'd.)

been producing isobutylene by isobutane dehydrogenation, and those dehydrogenation plants were then shifted to normal butane feed.

In early 1944, these three plants were still the only operating alkylation units, but plants were being constructed in Wesseling, Brux, Bohlen, and Elechhammer. Had these plants all been completed and put into operation, Germany's alkylate outturn would have risen about 50 percent above her actual attained production.

Normal butane dehydrogenation and isomerisation processes were both in use in Germany. Appendix I to this report describes dehydrogenation, and the general subject of isomerisation is discussed later.

Only butylene alkylation was practiced in Germany. By the application of the processes of dehydrogenation, isomerisation, and alkylation, C_4 components from the large coal and coal tar hydrogenation plants could be totally converted to butylene alkylate. (Some C_4 fraction was still being used as liquefied gas, but nearly all of the large hydrogenation plant C_4 outturn was to have gone ultimately into alkylates).

No propylene or amylene alkylation was carried out commercially. While these operations had been completely explored in the laboratory, it was not considered worthwhile to dehydrogenate propane, for example, to supply an additional olefin to alkylation and thereby increase the volume of alkylate at a sacrifice in quality. In calculating the optimum position on isoparaffin production, the most stress was placed on lean mixture performance rating. Rich mixture performance was at a lower premium apparently because of the relatively greater availability of aromatics and aromatizing capacity.

The alkylation plants varied in a few respects only from those in common use in America. (Complete plant descriptions are attached). Refrigeration of the reactor was accomplished by evaporating C_4 from the surface, compressing and liquefying, and returning the liquid to feed. The reactor itself was sometimes a stirred autoclave with no external recycle of reactor hydrocarbon phase being practiced. Only pure isobutane, prepared from reactor product through a series of columns, was then used for recycle to build up the isobutane to olefin ratio.

4. Synthesis of Isoparaffins (b)(Cont'd.)

In other plants, however, a reactor system was used which consisted of a mixing and cooling vessel, where vapor was withdrawn to the refrigerating cycle, a circulating pump, and a time tank. Emulsion was recycled, and a portion of the emulsion was withdrawn to a settling vessel, from which acid was recycled back to the mixing vessel.

The important operating variables and yield figures for a butylene plant employing the last described reactor system are summarized in Table III. Triisobutylene from EI 110 plants was used for alkylation feed when available, and the alkylate yield and quality were about equal to those obtained when using the equivalent amount of isobutylene.

Regeneration of spent sulfuric acid from alkylation was practiced in at least one location (Leuna). In that plant, alkylation acid was diluted to ca. 50 percent concentration, the liberated oil (tar) layer was separated off, and the acid was reconcentrated in a "Pauling Kessel" to 93 or 94 percent acid. It was then fortified with SO_3 to 98 percent concentration.

The following documents, transmitted to the Bureau of Ships, relate to alkylation:

III. Herstellung hochklopfester
isoparaffinischer Treibstoffe durch
Alkylierung aliphatischer Kohlenwasserstoffe.

(I.G. Leuna - Dr. Pohl II report of 6 Jan. 1943)

IV. Alkylierung - Anlage-Leuna

(I.G. Leuna - flow diagram of Alkylation Plant)

V. Alkylierung und Destillation

(I.G. Leuna - report by Dr. Strätz of about
April 1944)

TABLE III

Characteristic Operating and Yield Data for ButyleneAlkylation PlantsReactor Feed Composition

Isobutane, percent wt.	54.8
n-Butane, percent wt.	34.0
n-Butylene, percent wt. *	4.3
Propane, percent wt.	6.9
Ratio Isobutane to Olefin in Feed	13

Reactor Operating Variables

Pressure, atms.	1.5
Temperature, °F	32
Fresh H ₂ SO ₄ Feed, percent wt. acid	98
H ₂ SO ₄ in Reactor Acid Phase, percent wt.	90-92
Acid to Hydrocarbon Volume Ratio	0.8 to 1.1
Acid Consumption, lbs. H ₂ SO ₄ /gallon of Aviation Alkylate	0.80
Ratio Isobutane to Olefin in Reactor	ca. 95

Yields and Product Quality

Volumes Isobutane consumed per volume Olefin Feed	1.32
Volumes Aviation Alkylate produced per volume Olefin Feed	1.75
Octane Number (Motor Method) of Aviation Alkylate, Unleaded	94
Octane Number, Leaded with 4.35 cc Tetraethyl Lead/gallon	110
Aviation Alkylate, percent volume of total Debutanized Alkylate	93.5
Composition of Aviation Alkylate, percent volume	
2,3 Dimethyl Butane	6
2,4 Dimethyl Pentane	6
2,2,4 Trimethyl Pentane	21
2,3,4 " "	29
2,3,3 " "	28
Nonanes	10

*Of which alpha butylene is 43 percent and beta butylene is 57 percent.

4. Synthesis of Isoparaffins (Cont'd.)

(c) The Peroptan Synthesis.

The premium value of triptane as an aviation gasoline component was recognized in Germany and much effort was put forth to develop a method for its synthesis. The most extensive study was made by a research group from I.G. - Ludwigshafen-Oppau.

Some triptane was first made by a Grignard reaction for testing to establish its anti-knock properties. In contemplating then what reaction could be used for its commercial production, the combination of isopropyl chloride (chloropropane-2) with isobutane was considered. Also, by the use of the same type of reaction, it was considered that tertiary butyl chloride and isobutane might yield 2,2,3,3 tetramethyl butane, another octane with outstanding anti-knock properties.

In 1943 a program of study of the above type of reaction was undertaken. Propyl chloride was first made by direct reaction of propane and chlorine, using ultraviolet light as a catalyst. An 8:1 mol ratio of propane to chlorine was fed into a vertical iron tube, down the center of which was a mercury arc tube. The feed inlet temperature was 70 degrees fahrenheit and the heat of reaction was adequate to raise the temperature of the system to 140 degrees fahrenheit. A pressure of 20 atmospheres was maintained to keep the system totally liquid. Under these conditions complete reaction of the chlorine was obtained. The product was fractionated, removing first hydrogen chloride, then propane, and then separating the two monochlor isomers. A very small yield of residue remained.

The isopropyl chloride was reacted with isobutane at 32 degrees fahrenheit, using both ultraviolet light and a slurry of aluminum chloride as catalysts. One part of isopropyl chloride, five parts of isobutane, and one part of $AlCl_3$ were agitated under ultraviolet light until HCl liberation subsided. The HCl was removed, then isobutane was separated, and the higher boiling materials were examined. No triptane was ever found in the product, but essentially the entire yield was a mixture of isoparaffins boiling in the 190 to 370 degrees fahrenheit range. About 50 percent of the yield was 2,2,3 trimethyl pentane, and most of the product boiled between 210 and 230 degrees fahrenheit. The octane number of the total mixture was 96 to 98 and the rich mixture rating exceeded that of 2,2,4 trimethyl pentane.

4. Synthesis of Isoparaffins (c)(Cont'd.)

It was found that chloropropane-1 was equally as effective as isopropyl chloride for this reaction and the separation of the two isomers was discontinued. It was found also that all material boiling below 190 degrees fahrenheit formed in the reaction could be recycled back into the system without build-up. Based on propane and isobutane feeds, an 80 percent weight yield of product could be obtained.

The above operation was proposed as a process and the product was named "Peroptan". A plant to produce about 100 barrels per day was being designed for construction at Ludwigshafen-Oppau, but by early 1945 it had not progressed beyond the design stage. The plant was to take propyl chloride available at Oppau from the synthetic glycerin plant. The reactor for propyl chloride - isobutane was to be a 40 barrel autoclave. The 190 to 370 degrees fahrenheit fraction was to be separated and given a purifying hydrogenation over Raney nickel catalyst to remove about one percent weight of chlorine that remained combined in that fraction.

Isobutyl chloride and tertiary butyl chloride were also reacted with isobutane, following the same general procedure as given above for propyl chlorides. No 2,2,3,3 tetramethyl butane was ever detected in the products. It was found that the products from the two butyl chlorides were the same and, surprisingly, they were very similar to the products from propyl chloride. The compositions and qualities were not significantly different.

Ethyl chloride-isobutane reaction was attempted but HCl liberation could not be obtained.

Other efforts to synthesize highly branched paraffins were made in Germany but none had resulted in a practical process. For technical interest the following documents, transmitted to the Bureau of Ships, relate to the chemistry of these studies:

VI. Die Herstellung von Trimethylbutan.
(I.G. - Ludwigshafen - review by
Dr. Baeren of 22 October 1943).

VII. 2,2,3 Trimethylbutan und andere
verzweigte Kohlenwasserstoffe durch
Hydrierung von Trialkylelessigsäure.

4. Synthesis of Isoparaffins (c)(VII.)(Cont'd.)

(I.G.-Ludwigshafen - report by Dr. Bueren of 15 February 1944)

VIII. Die Wichtigsten Daten und Herstellungsgeweisen einiger Isoparaffin unter besonderer Berücksichtigung ihrer Verwendung als Motortreibstoffe. (I.G.-Ludwigshafen-tabulation of 16 March 1944).

(d) Isomerization of Normal Paraffins.

Normal butane isomerization plants producing isobutane for alkylation had been built in Blechhammer, Böhlen, Leuna, and Scholven.

The plants employed a vapor phase process over aluminum chloride as contact. The installations were not greatly different from the vapor phase plants in wide use in America.

The German reactors were operated at 200 to 210 degrees fahrenheit under 16 atmospheres pressure. The normal butane feed to the reactor contained 10 percent weight HCl. The $AlCl_3$ catalyst (technical grade) was put into the reactors in crude lump form. At 200 degrees fahrenheit and a liquid hourly space velocity of 3.0 (volumes liquid normal butane per volume of catalyst per hour), a conversion of ca. 30 percent was obtained and a 96 percent weight recovery of total C_4 was obtained. The aluminum chloride consumption was not above 1.2 percent weight, based on isobutane produced, and the corresponding figure for anhydrous HCl was 0.6 percent weight.

The conversion of normal to isobutane could be increased to 40 percent by raising the operating temperature to 210 degrees fahrenheit, but the C_4 recovery dropped to 95 percent weight and catalyst consumption increased somewhat.

There are attached quite complete descriptions and a flow diagram of the process. The reactor design described is interesting. The lump aluminum chloride catalyst was put in on top of a section of Raschig rings, and both below the rings and above the catalyst layers there were large free spaces (volumes) in the vertical reactor. The feed butane-HCl mixture entered the bottom of the reactor and flowed upward. As the catalyst formed hydrocarbon complexes, it began to fluidize and

4. Synthesis of Isoparaffins (d)(Cont'd.)

run down over the surface of the Raschig rings. By supplying an adequate height of ring layer, the fluid reaching the bottom and running off into the reactor free space was completely spent. The spent liquid collected in the bottom head of the reactor and was withdrawn. The free space above the layer of catalyst was to serve as a zone of "after reaction" in which sublimed catalyst would react with the butane mixture, form a liquid and return to the catalyst bed rather than be carried out as sublimed AlCl_3 . (In practice this was not quite realized and AlCl_3 did carry over, causing condenser tube plugging.)

Although chrome-nickel steels were preferred for use in the reactor, condenser, piping, etc., only low carbon steels were available. Some corrosion difficulties were originally experienced in the plants, but with good drying of the feed, corrosion was no serious operating problem.

There was no commercial isomerization of pentane in Germany, but the process had been extensively studied in the laboratory.

Of technical interest was some research conducted by I.G.-Leuna and by the Kaiser Wilhelm Institute in Mülheim on the isomerization of C_6 paraffins.

Hexane isomerization was carried out on a normal hexane fraction (from Fischer-Tropsch) at I.G.-Leuna. A 50 atmosphere pressure of hydrogen was applied, and the temperature was 160 to 175 degrees Fahrenheit. The catalyst was aluminum chloride with added HCl equal to ca. 30 percent weight of the AlCl_3 in the system. (The AlCl_3 was mixed with SbCl_3 or chlorinated hydrocarbons or phosgene to obtain a liquid phase catalyst at the operating temperature). A particular experiment with a contact time of 5 hours gave a 70 percent conversion, and the approximate yield structure was 15 percent weight of 2,2 dimethyl butane, 10 percent weight of 2,3 dimethyl butane, 10 percent weight of 3 methyl pentane, 15 percent weight of 2 methyl pentane, 30 percent weight unconverted normal hexane, and 20 percent weight of C_4 , C_5 and other components. (Ethane and propane were usually absent in the products produced by cracking, and isobutane was the main product of disproportionation reactions).

Less cracking is obtained in paraffin isomerization when hydrogen pressure is high and temperature is low. Of course, as temperature is lowered a longer contact time is required in order to attain a given

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4. Synthesis of Isoparaffins (d)(Cont'd.)

conversion.

In a K.W.I. experiment at 100 atmospheres of hydrogen, 160 to 175 degrees fahrenheit, 0.2 mols of $AlCl_3$ and 2 mols of HCl per mol of normal hexane, and a contact time of about 18 hours, a 90 percent conversion of normal hexane was obtained and very little cracking or disproportionation occurred. Based on total hexanes, the yield was 57 percent of 2,2 dimethyl butane, 9 percent of 2,3 dimethyl butane, 31 percent of a mixture of the two methyl pentanes, and 3 percent of unconverted normal hexane.

I.G. consider that the practical application of normal hexane isomerisation would be under conditions to obtain perhaps a 30 percent conversion, and they estimated that at such a conversion the dimethyl butane isomers would be more than half of the total isomer yield.

Isomerization of normal heptane was studied under hydrogen pressures up to several hundred atmospheres. It was found impossible even under these conditions to avoid substantial cracking of heptane in contact with $AlCl_3$.

The production of branched hexanes by the isomerization of cyclohexane was studied. Cyclohexane was contacted with 15 percent weight of $AlCl_3$ and 7 percent weight of anhydrous HCl in the presence of 150 atmospheres of hydrogen. At a temperature of 210 degrees fahrenheit and a contact time of 6 hours, the product obtained was a mixture of one percent weight isobutane, 20 percent of 2,2 dimethyl butane, 6 percent of 2,3 dimethyl butane, 18 percent of a mixture of 2 and 3 methyl pentanes, a small amount of normal hexane, a small amount of methyl cyclopentane, and the rest was unconverted cyclohexane. It was stated in a patent application that the $AlCl_3$ can be recovered essentially unchanged from the operation.

The following documents transmitted to the Bureau of Ships, relate to paraffin isomerization:

IX. Die Isomerisierung von n-Butan mit $AlCl_3$.

(I.G. - Leuna - report by Dr.

Pohl II, etc. of 22 February 1943)

4. Synthesis of Isoparaffins (8)

X. Schema der Isomerisierung.

(I.G.-Leuna - flow diagram of butane isomerisation plant).

XI. Isomerisation.

(I.G.-Leuna - report by Dr. Strätz of early 1944).

XII. Über Isomerisierung von Paraffinen.

(KWI - Mulheim copy of speech by Dr. Koch on 24 June 1943).

5. Synthesis of Aromatics and Production of Base Stocks.

Since isoparaffins constituted only 10 to 15 percent volume of C-3 gasoline and none of B-4, and since components other than synthetic isoparaffins and base stocks were used only in small quantities in these aviation fuels, the base stocks themselves then consisted at least 85 percent of Germany's total aviation gasoline volume.

Most of these base stocks originated in coal and coal tar hydrogenation plants. Only a very small volume of carefully selected petroleum fractions was blended directly into aviation gasolines. The large high pressure hydrogenation plants at Leuna, Scholven, Pölitz, Brux, Gelsenkirchen, Böhlen, Magdeburg, Blechhammer, and Wesseling all produced aviation base stocks. These plants consist of three stages of hydrogenation, the first (sump) phase being the bulk destruction operation to produce an intermediate boiling distillate from the coal or heavy tar, the second being a purifying treatment of the distillate, and the third being a fine hydrogenation step producing directly (as the only product) a gasoline of the required end point. All material boiling above the gasoline end point is recycled back to the third stage feed.

The B-4 aviation gasoline of Germany was this hydrogenated gasoline, stabilized to the specified vapor pressure (refer Table II). The quality varied somewhat, depending upon the raw material to hydrogenation, and individual gasolines needed some quality correction, either with small amounts of isoparaffin or outside base stocks. In general, however, the straight hydrogenation gasolines constituted the total supply of B-4 quality. In Table IV are given a few average data

5. Synthesis of Aromatics and Production of Base Stocks (Cont'd.)

for these gasolines obtained from four (4) different hydrogenation plant feeds, all of which were used in Germany during the war.

TABLE IV

Properties of B-4 Base Stocks from
High Pressure Hydrogenation Plants

<u>Feed to Hydrogenation</u>	<u>Brown Coal</u>	<u>Stein Coal</u>	<u>Brown Coal Tar</u>	<u>Stein Coal Tar</u>
<u>B-4 Base Stock</u>				
Density at 59°F.	0.723	0.730	0.725	0.725
Volume percent Distilled at 212°F.	65	57	58	65
End Point, °F.	270	308	302	320
Paraffin Content, percent volume	53	40	60	37
Naphthene " " "	42	52	30	55
Aromatic and Olefin Content, percent volume	5	8	10	8
Octane Number, Motor Method, Unleaded	71	73	69	76
Octane Number, Motor Method, with 4.35 cc Tetraethyl Lead/Gallon	90	91	89	94

The supply of the high quality 85 percent base stock component to C-3 grade aviation gasoline involved additional processing of the hydrogenated gasolines. In order to obtain gasolines that were high in anti-knock performance throughout the whole range of air-fuel ratios, aromatizing processes were invoked.

By applying a particular set of operating conditions to the second stage of hydrogenation, the Ruhröl - Welheim installation produced a high aromatic content base stock directly. Distillate from the sump phase hydrogenation of coal tar pitch was fed to a second stage operating at 700 atmospheres pressure over a new catalyst containing molybdenum, chromium, and lead on an inert carrier. At 930 degrees fahrenheit and in one step, a 350 degrees fahrenheit end point gasoline was produced which contained 40 to 45 percent volume aromatics and which was used directly as the base stock ingredient of C-3 gasoline. This base

5. Synthesis of Aromatics and Production of Base Stocks (Cont'd.)

stock had an unleaded octane number of 80, and with 4.35 cc. tetra-ethyl lead per gallon it was 92. This process of producing directly in hydrogenation plants a highly aromatic aviation gasoline base stock was a new development in Germany and was being widely discussed. It is likely that applications to locations other than Welheim would have been made had earlier conditions continued to prevail in Germany.

Perhaps the most important aromatizing operation was the "DHD Process", an operation used on hydrogenated gasoline to increase their aromatic contents. Hydroforming was also used, but on a small scale only. Catalytic cracking was studied but no plant was in operation. Also, several processes were in operation synthesizing individual aromatics, but they made a small contribution only to the total gasoline volume. There are discussed below these processes and their contributions to the German aviation gasoline supply.

(a) The DHD Process.

The DHD process (Dehydrierung unter Druck or dehydrogenation under pressure) was developed by I.G. in Ludwigshafen. It was a catalytic process for increasing the aromatic content of a gasoline, through both naphthene dehydrogenation and paraffin cyclization.

At the end of the war there were four (4) DHD plants in operation; Ludwigshafen, Ienna, Scholven and Politz. The combined intake capacity of these four plants was about 20,000 barrels per day. These plants were fed gasolines produced from both coals and coal tars. There were about ten (10) other DHD plants and plant extensions planned which were never completed. It was planned that ultimately nearly all of the hydrogenation plant gasolines, and certain crude oil factions as well, would have been processed through DHD plants.

Because of their high naphthene contents, gasolines from stein coal and stein coal tars were preferred feeds to DHD. By altering operating conditions to encourage paraffin cyclization as well as naphthene dehydrogenation, gasolines from brown coal and brown coal tars were also greatly increased in aromatic content by this operation.

The feed gasolines to the process had end points of about 360 degrees fahrenheit. These feeds were first stabilized to remove ca. 15 percent volume overhead which was the non-naphthene containing

5. Synthesis of Aromatics and Production of Base Stocks (a)(Cont'd.)

fraction boiling to about 160 degrees fahrenheit. The stabilized gasoline was then pumped together with recycled hydrogen gas through a feed-product heat exchanger and a preheater which raised the temperature to 930 degrees fahrenheit. The vapor mixture entered the top of the first of a series of five (5) reactors. The operating pressure was 25 atmospheres total, of which 10 atmospheres was the hydrogen partial pressure, when the feed gasoline originated from brown coal (or its tar). For stein coal gasolines, the total pressure was 50 atmospheres, of which 35 was hydrogen. (The lower pressure with brown coal materials was used to encourage paraffin cyclization).

The reactors were filled with a catalyst consisting of 10 percent weight MoO_3 on Al_2O_3 . The alumina was precipitated and impregnated with molybdenum oxide and formed into cubes of about $\frac{1}{2}$ inch on a side. (Catalyst was made from "Tonerde" (hydrated alumina earth). The earth was first dissolved in caustic and then precipitated at 120°F ., with HNO_3 at a pH of 5.5 to 6.5. The precipitate was filtered, washed and dried up to an 80 percent Al_2O_3 concentration, pilled into $\frac{1}{2}$ inch cubes, and calcined at 840°F .. The catalyst cubes were then washed with an ammonium molybdate solution of such concentration that the final dried catalyst contained 10 percent wt. of MoO_3 . The catalyst was dried at 400°F .. for a short period and then at 750°F ., until all ammonia liberation ceased. The apparent density of the finished catalyst was about 0.8.) Each reactor contained about 280 cubic feet of catalyst. The reactors had steel shells lined with fire brick and an internal liner of N8 steel. The space velocity employed was about 0.5 volumes of liquid feed per volume of total catalyst in the system per hour.

The endothermic heat of reaction caused the temperature to drop from 930 degrees fahrenheit at the top of the first reactor to 840 degrees fahrenheit at the bottom exit. A heater was therefore supplied after each of the first four reactors, raising the temperature back to 930 degrees fahrenheit at the top of the second and third reactors. With the extent of reaction subsiding, the entering temperature in the fourth reactor was raised to 950 degrees fahrenheit, its exit temperature was ca. 930 degrees fahrenheit, and the fifth reactor feed was 970 degrees fahrenheit with very little temperature drop occurring through it.

A sixth reactor was used for saturation of olefins. After leaving the fifth reactor, the temperature was lowered to about 650 degrees

5. Synthesis of Aromatics and Production of Base Stocks (a)(Cont'd.)

fahrenheit. The sixth reactor was filled with DHD catalyst except for the bottom fifth which was filled with Florida earth.

After 40 hours of operation on brown coal gasoline, or 250 hours with stein coal products, a regeneration for carbon removal was necessary. A 20 to 24 hour period was required for the complete regeneration. In regeneration, exit gas was recycled to control burning rate and limit the temperature to a maximum of 1,030 degrees fahrenheit. The carbon deposition on catalyst was equivalent to about one percent weight of brown coal gasoline and 0.1 percent weight of stein coal gasoline, which corresponded to a coke content on spent catalyst of about 3 percent weight.

The life of the catalyst was at least a year and perhaps would become considerably longer with more operating experience. Sulfur was a definite catalyst poison, but this was a problem in Germany only when operating on crude oil fractions. In general, stocks with the lowest possible sulfur content should be chosen as feeds.

Operating under the above described conditions, the yield of redistilled, stabilized gasoline was 75 to 85 percent by weight of the stabilized gasoline fed to the DHD unit proper. (The higher yield was obtained from stein coal gasolines).

The DHD outturn contained 65 percent volume of aromatics, so that when the original 15 percent of low boiling fraction was reblended, the final gasoline contained about 50 percent volume of aromatics. The overall weight yield, based on the original hydrogenated gasoline, was therefore 78 to 87 percent, and the corresponding volume yield figures were 75 to 83 percent.

The final product from this DHD operation had the following average properties:

Density at 59° F.	0.780
Volume percent distilling at 212° F.	48
End Point, ° F.	340
Paraffins, percent volume	30
Naphthenes, percent volume	20
Aromatics, percent volume	50

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5. Synthesis of Aromatics and Production of Base Stocks (a)(Cont'd.)

Olefins, percent volume less than 0.5	
Octane Number, Motor Method, unleaded	80
Octane Number, Motor Method, with 4.35 cc. Tetraethyl Lead/Gallon	92
Octane Number, Motor Method, unleaded, of Residual Oil after Aromatic Extraction	70

There appears on the following page a photostat of an I.G. tabulation showing the properties of DHD gasolines made from various raw materials.

A copy of a speech by Dr. Pier of I.G. in 1941 was transmitted to the Bureau of Ships. This paper gives some of the background of German aviation gasoline developments leading up to the manufacturing position existing at the end of the war:

XIII. Über Fliegerbenzine und ihre
Herstellung.
(I.G.-Ludwigshafen-speech by
Dr. Pier on 21 November 1941)

There was also transmitted the following document describing the DHD process:

XIV. Technische Entwicklung des DHD-
Verfahrens.
(I.G.-Ludwigshafen-Report of
15 October 1942)

(b) Hydroforming.

There were two (2) hydroforming plants in operation in German territory. Both were located in the Moosbierbaum refinery near Vienna. A straight run petroleum gasoline boiling from 140 to 330 degrees Fahrenheit was hydroformed in conventional discontinuous units. (The process and design data were obtained from America.) Both Roumanian and Austrian crudes were processed at this refinery.

Kategorie	Hydrocarbon					
	Benzene		Naphthalene		Anthracene	
Gasoline	0.05	0.05	0.05	0.05	0.05	0.05
Jet Fuel	0.05	0.05	0.05	0.05	0.05	0.05
Aviation Turbine Fuel	0.05	0.05	0.05	0.05	0.05	0.05
Motor Oil	0.05	0.05	0.05	0.05	0.05	0.05
Transformer Oil	0.05	0.05	0.05	0.05	0.05	0.05
Industrial Solvent	0.05	0.05	0.05	0.05	0.05	0.05
Paints	0.05	0.05	0.05	0.05	0.05	0.05
Adhesives	0.05	0.05	0.05	0.05	0.05	0.05
Plastics	0.05	0.05	0.05	0.05	0.05	0.05
Other	0.05	0.05	0.05	0.05	0.05	0.05

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5. Synthesis of Aromatics and Production of Base Stocks (b)(Cont'd.)

The operation was carried out at 15 to 30 atmospheres pressure, of which the hydrogen partial pressure was 65 to 70 percent. The reaction temperature was 930 degrees fahrenheit and the space velocity was 0.5 volumes of oil per volume of catalyst per hour. The catalyst was 5 to 10 percent weight MoO₃ on alumina.

The operating cycle was from 17 to 30 hours with 9 hours required for regeneration.

The hydroformed product was used in the same manner as was DHD gasoline; i.e., as the base stock for C-3 grade aviation gasoline.

In Table V are given some yield and analytical data for the average Moosbierbaum operation.

TABLE V.

Yield and Analytical Data on Moosbierbaum Hydroforming of Straight Run Gasoline.

<u>Yield Data</u>	<u>Feed</u>	<u>Product</u>
Gasoline, percent wt.	100.0	79.0
Redistillation Residue, percent wt.	---	3.5
Coke, percent wt.	---	1.1
Hydrogen, percent wt.	---	1.4
C ₁ plus C ₂ plus C ₃ , percent wt.	---	11.0
Isobutane, percent wt.	---	1.3
Normal Butane, percent wt.	---	2.7
Total	100.0	100.0
<u>Analytical Data</u>		
Density at 68° F.	0.750	0.776
Distillation, ° F., I.B.P.	114	112
Distillation, ° F., End Point	330	330
Distilled at 212° F., percent Volume	18	36
Distilled at 320° F., percent Volume	95	94
Olefin Content, percent Volume	0.5	1.5
Aromatic Content, percent Volume	14	54
Naphthene Content, percent volume	44	8

5. Synthesis of Aromatics and Production of Base Stocks (b)(Cont'd.)

TABLE V. (Continued)

Yield and Analytical Data on Moosbierbaum Hydroforming of Straight Run Gasoline.

<u>Analytical Data</u>	<u>Feed</u>	<u>Product</u>
Reid Vapor Pressure, lbs.	5.3	5.1
Octane Number, Motor Method, unleaded	58	80
Octane Number, Motor Method, with 4.35 cc. Tetraethyl Lead/Gallon	79	91

The following documents transmitted to the Bureau of Ships, relate to hydroforming:

XV. HF-Verfahren und Anlage Moosbierbaum.
(I.G. - Leuna - report by Dr. Kaufmann of 9 December 1941).

XVI. Das HF-Verfahren.
(I.G.-Leuna-report by Dr. Wels of 12 February 1943).

(c) Synthetic Alkyl Aromatics.

The only important commercial synthesis of alkyl aromatics in Germany was of diethyl benzene. The chemical plants of I.G. at Huls and Schopau produced together about 300 barrels per day of this material, named "Kybol", as a by-product in the manufacture of styrene. Benzene was alkylated with ethylene and the product, containing some diethyl benzene, was fractionated to separate into one fraction all of the diethyl compound together with a small amount of higher boiling alkylated benzenes. This fraction boiled from 325 to 350 degrees Fahrenheit.

No cumene (isopropyl benzene) was being made, but one installation was being considered for producing a mixture of alkyl benzenes which would have contained cumene. Propane was to have been cracked thermally, yielding ethylene and propylene, and the olefins would then have been selectively absorbed with a copper nitrate-ethanol amine solution. The mixed olefins were to be used to alkylate benzene,

5. Synthesis of Aromatics and Production of Base Stocks (c)(Cont'd.)

obtaining thereby a mixture of mono- and di-ethyl and isopropyl benzenes.

Of technical interest is a new German process, developed but never applied on large commercial scale, to dealkylate high boiling aromatics and reduce their boiling points down into the gasoline range. The process, known as the "Arobin Verfahren", was considered for application on high aromatic content hydroforming and DHD residues boiling from 340 to perhaps 600 degrees fahrenheit (50 percent points of ca. 380 degrees fahrenheit). A catalyst of synthetic aluminum silicate containing one percent weight of MnO_2 was used at a temperature of 750 to 780 degrees fahrenheit and under a hydrogen pressure of 200 atmospheres. At a space velocity of one volume total liquid feed (of which 50 percent is recycle) per volume catalyst per hour, an 85 to 87 percent weight yield of 330 degrees fahrenheit end point product containing 70 percent volume aromatics was obtained. A hydrogen consumption equal to 3 percent weight of the product gasoline was incurred. Through the use of the high hydrogen pressure, coke deposition on the catalyst was very low and long operating cycles (i.e., several hundred hours) were predicted. In Table VI are given some typical yield and analytical data for this operation.

The following documents, transmitted to the Bureau of Ships, relate to this subject:

XVII. Das Arobin - Verfahren.

(I.G. - Leuna - report by Dr. Wels of 22 October 1943).

XVIII. Arobin-Anlage.

(I.G.-Leuna-material flow diagram of 13 July 1943).

XIX. Bericht über die erste

Fahrperiode des Arobinofens.

(I.G.-Leuna-memorandum of 27 March 1944).

5. Synthesis of Aromatics and Production of Base Stocks (c)(Cont'd.)

TABLE VI.

Yield and Analytical Data on Feed and Products of Arobin Process.

<u>Yield, Percent Wt.</u>	<u>Feed</u>	<u>Product</u>
Gasoline	100.0	85.7 to 87
Methane	---	0.2 to 0.3
Ethane	---	1.7 to 2.0
Propane	---	4.8 to 5.2
Isobutane	---	3.8 to 4.2
Normal Butane	---	2.4 to 2.6

<u>Analytical Data</u>	<u>Feed</u>	<u>Product</u>
Density at 68° F.	0.91	0.807
Distillation, °F., I.B.P.	340	120
" " 50 percent	380	260
" " E.P.	600	330
Aromatic Content, percent volume	95	65
Naphthene Content, percent volume	--	27
Paraffin Content, percent volume	--	8
Bromine Number	ca.8	0.8
Octane Number, Motor Method, unleaded	--	86
Octane Number, Motor Method, with 4.35 cc. Tetraethyl Lead/Gallon	--	93.5

(d) Catalytic Cracking.

There were no commercial scale catalytic cracking units in operation in German areas. One was being planned for operation at Moosbierbaum in Austria, a plant to carry out an operation referred to as catalytic cracking was being processed for Rucrchemie at Holten, and a large underground refinery planned for Niedersachswerfen (near Nordhausen) was to have a catalytic unit.

The Moosbierbaum and Niedersachswerfen units were to process crude oil fractions to produce aviation gasoline base stocks. The development work on the process was done by I.G. at Leuna, and a large pilot plant had been built at Deuben (south of Leuna).

5. Synthesis of Aromatics and Production of Base Stocks (d)(Cont'd.)

The catalytic cracking process that was developed for plant application was quite similar to the TCC process in use in America. A silica-alumina catalyst, in the form of small spheres, was to be used at a temperature of 840 degrees fahrenheit and atmospheric pressure to crack straight run gas oil boiling up to about 750 degrees fahrenheit. The silica-alumina catalyst was made as follows: (A caustic aluminate solution was acidified at 220° F., with nitric acid to a pH of 6.5. The Al₂O₃ precipitate was washed free of sodium ion and dried at 210° F., to a water content of 25 to 30 percent wt. The dried Al₂O₃ was then mixed with 15 percent of its weight of SiO₂ (Kieselguhr). The mixed oxides were then ground until 90 percent passed through a screen containing 10,000 openings per meter. The powder was moistened with water acidified with nitric acid, well mixed, and then heated to 150° F., for 24 hours. It was extruded into cylindrical pellets, and put between two counter revolving plates which rolled the cylinders into small spheres of ca. 0.2 inches diameter. The spheres then were heated at 750 to 840° F., for 8 to 12 hours.) The main yield was to be a 340 degrees fahrenheit end point distillate for use directly, without repassing or other treatment, in C-3 quality aviation gasoline. A 30 percent weight yield of this fraction, a 3 percent weight yield of hydrogen plus methane plus ethane-ethylene, and a coke yield of 4 percent wt., all based on feed, were anticipated. A conversion of 50 percent volume; i.e., a disappearance of one-half ($\frac{1}{2}$) of the feed from its initial boiling range, was expected while employing a space velocity of 0.6 volumes of liquid feed per volume of catalyst (in reactor) per hour.

Catalyst regeneration was to be carried out at a temperature not exceeding 1020 degrees fahrenheit.

The plant design was to employ one catalyst elevator only. The regenerator would be mounted directly above the reactor, and regenerated catalyst would be dropped directly through control valves into the top of the reactor. Spent catalyst from the bottom of the reactor would then be elevated to the top of the regenerator.

A set of test data was reported for the catalytic cracking of 355 to 670 degrees fahrenheit fraction from a mixed base crude, using a 0.5 space velocity and 790 degrees fahrenheit reactor temperature. A 36 percent weight yield of 330 degrees fahrenheit end point gasoline was obtained which contained 20 percent weight aromatics and 4 percent weight olefins. The unleaded octane number was 75, and with 4.35 cubic

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5. Synthesis of Aromatics and Production of Base Stocks (d)(Cont'd.)

centimeters tetraethyl lead per gallon it was 94. The yield of low boiling components through butanes was 6.7 percent weight of which 3.1 percent was isobutane.

It was the opinion of most German technical people interrogated that catalytic cracking of the above type or of the other types employed in America, could have only limited applications in Europe. The process was being considered during the war only because it represented a method of making aviation gasoline directly from crude oil fractions. (The hydrogenation of such fractions of crude oil does not give high quality gasolines). Catalytic cracking is not considered applicable to coal tars directly because of high carbon deposition on catalyst, and the process has no obvious application in high pressure hydrogenation systems.

The following documents transmitted to the Bureau of Ships, pertain to this process of catalytic cracking:

XX. Flugbenzin durch Katalytisches Kracken.
(I.G.-Leuna-report by Dr. Kaufmann of
July 1942).

XXI. Flow Diagram of I.G. Experimental
Catalytic Cracking Unit.

The Ruhrchemie process referred to as catalytic cracking was an operation designed initially to crack the normal paraffin residues of intermediate Fischer-Tropsch fractions used for various olefin-consuming chemical syntheses. A plant was being constructed at Holten on the basis of development work carried out there.

The reaction was designed to obtain the maximum yield of low boiling olefins for synthesis of high octane aviation gasoline ingredients. It had been concluded that the normal paraffins did not respond adequately to conventional catalytic cracking, that their isomerization was not a promising possibility, and hence that destruction to low boiling molecules (synthesis raw materials) over a catalyst was the most attractive method of converting them to high performance fuels.

The operation was to be at low (atmospheric) pressure and 930 degrees Fahrenheit over a synthetic silica-alumina catalyst of 0.7 apparent density. A liquid space velocity of ca. 0.1 was to be employed in

5. Synthesis of Aromatics and Production of Base Stocks (d)(Cont'd.)

order to obtain a 40 percent conversion per pass (disappearance from the original boiling range) of a 340 to 660 degrees fahrenheit Fischer-Tropsch fraction. Of the converted feed material, 75 percent appeared as C₃, C₄ and C₅ fractions, of which about 90 percent were olefins. Gasoline was only 15 percent of the converted yield.

By employing a recycle, a 75 percent weight ultimate yield of usable materials could be realized.

The process was to be discontinuous, with catalyst regeneration after operating cycles of 20 to 25 minutes. The carbon yield was estimated to be 1.5 percent weight of reactor feed.

In Table VII is given a set of yield and product composition data characteristic of this operation. A copy of a report by Ruhrchemie, which describes quite completely the development of the process and its planned application, was forwarded to the Bureau of Ships:

XXII. Herstellung von Isogasolen und Flugbenzin aus Syntheseprodukten.

(Ruhrchemie report by Dr. Kolling in January 1943).

TABLE VII

Yield and Product Composition Data - Ruhrchemie Catalytic Cracking.

Feed to process is Fischer-Tropsch fraction of 340 to 660 degrees fahrenheit boiling range.

Yields of Components, Percent wt. of Feed

Total Conversion	40 percent wt. of feed
Gasoline (C ₆ to ca. 320° F.)	6-8
C ₅ Fraction	7.6-9.6
C ₄ Fraction	10-12
C ₃ Fraction	8-10
C ₂ Fraction	2-2.8
Methane & Hydrogen	0.4-0.8
Coke	1.2-1.6

5. Synthesis of Aromatics and Production of Base Stocks (d)(Cont'd.)

TABLE VII. (Continued)

Yield and Product Composition Data - Ruhrechemie Catalytic Cracking.Olefin Contents, percent volume

C ₅ Fraction	85-90
C ₄ "	90-95
C ₃ "	90-95
C ₂ "	60-65

Iso-Contents, percent volume

C ₅ Paraffins	60-65
C ₅ Olefins	45-50
C ₄ Paraffins	60-65
C ₄ Olefins	38-43

6. Conclusions.

(a) The maximum rate of production of total aviation gasolines achieved by Germany during the war was roughly 50,000 barrels per day, of which essentially the entire volume came from coal and coal tar hydrogenation plants. Of this total volume of liquid, about 10 percent was synthetic isoparaffins, 40 percent was high aromatic content base stocks produced by processing of hydrogenation plant gasolines, and the remaining 50 percent was almost entirely hydrogenation plant gasolines of aviation gasoline endpoint and volatility.

(b) Two grades of aviation gasoline were produced, one with a motor method octane number of 91, and the other of 95. The former, labeled B-4 (blue) contained about 10 percent volume aromatics, while the latter, known as C-3 (green), contained about 40 percent volume aromatics and would thus allow much higher power output under rich mixture conditions. Both grades contained 4.35 cc. tetra-ethyl lead per gallon (American). The 50 percent distilled specifications were 221 and 230 degrees fahrenheit, for B-4 and C-3, respectively.

(c) The B-4 grade was produced directly by the addition of tetra-ethyl lead to the entire liquid product from the large coal and coal tar hydrogenation plants. The volatility was adjusted to about 7 pounds Reid vapor pressure by stabilizing and no further refining or blending

6. Conclusions (c)(Cont'd.)

was done.

(d) The C-3 grade was a leaded blend of about 15 percent volume of synthetic isoparaffins and 85 percent volume of a base stock containing 45 to 50 percent volume aromatics, produced by further processing of a hydrogenated gasoline almost identical to unleaded B-4. The C-3 grade represented at least two-thirds (2/3) of the combined volume of the two grades.

(e) Small amounts of synthetic aromatic compounds such as diethyl benzene, were used as components, but with unimportant exceptions, no additives or components other than those mentioned above were included in the commercial blends. No inhibitors of any kind were normally used.

(f) Had raw materials and manufacturing facilities been available, more isoparaffins would have been produced to improve the lean mixture performance of both grades and, ultimately, to allow a decrease in the aromatic content of the C-3 grade. The rich mixture performance of the gasolines was satisfactory for the engines being built and used.

(g) Synthetic isoparaffins were manufactured primarily by the alkylation of butylenes and isobutane. Some isobutylene polymerization and polymer hydrogenation was being carried out. No propylene or amylene alkylation was being done. No triptane synthesis had been developed, and no isoparaffin syntheses other than those mentioned above were being used.

(h) Isobutylene for polymerization was made by dehydrogenation of isobutyl alcohol which was synthesized directly from carbon monoxide and hydrogen. Normal butylene for alkylation was produced by catalytic dehydrogenation of normal butane produced by the coal and tar hydrogenation plants. Isobutane for alkylation came in part directly from the hydrogenation plants and in part by catalytic isomerization of some of the normal butane.

(i) To produce the bulk of high aromatic content base stock used in C-3, a process known as DHD was employed. This process produced aromatics both by dehydrogenation of naphthenes and by cyclization of paraffins. Hydroforming was used at one refinery to produce base stock, of quality eligible for use in C-3 grade, from Austrian and Roumanian crude oil fractions.

6. Conclusions (Cont'd.)

(j) No catalytic cracking units existed in the German area, but the process had been studied and two plants installations were being planned. It is generally agreed that catalytic cracking of the type employed today in America will not find wide application in the synthetic oil industry. It was of interest to Germany only as a wartime means of producing aviation gasoline. The units being planned were similar in general design to a TCC unit and were to use a synthetic silica-alumina catalyst.

(k) Some new processes developed in Germany during the war years but which were not in commercial operation included:

(1) A specific and efficient catalytic process for dealkylating aromatics;

(2) A catalytic cracking process for normal paraffins boiling in the kerosene range, producing primarily C₃, C₄ and C₅ olefins;

(3) A catalytic process for producing an ultimate weight yield of 70 to 78 percent of toluene from normal heptane, and

(4) A process for producing high quality gasoline isoparaffins by combining propane and isobutane via chlorination.

(1) Jet fuels were being produced in Germany at a rate of ca. 1,000 barrels per day in 1944. The fuel was a mixture of gasoline and diesel oil fractions. The specifications for jet fuel were lenient; no unusual quality was demanded and no unusual specifications were forthcoming.

Prepared by:

M. E. SPAGHT,
Technician.

APPENDIX ITHE DEHYDROGENATION OF BUTANE TO BUTYLENE.

Two (2) methods for the dehydrogenation of butane to produce feed for polymerization and alkylation plants were studied in Germany. One involved the direct release of hydrogen over a catalyst, and the other was via chlorination and HCl splitting. The catalytic dehydrogenation process was developed by I.G. and plants were built at three locations. The chlorination process was also developed by I.G. but no commercial installation was made or planned. For general information, however, there is attached a process flow diagram of a hypothetical plant employing the chlorination process.

The catalytic dehydrogenation process was carried out at 1020 to 1100 degrees fahrenheit at practically atmospheric pressure, using a catalyst consisting of 2 percent weight K_2O , 8 percent weight Cr_2O_3 , and 90 percent weight Al_2O_3 . The conversion to olefins was ca. 18 percent per pass when a space velocity of 8 volumes of liquid butane per volume of catalyst per hour was used.

The catalyst was made by first precipitating alumina from an aluminum sulfate solution, then drying and grinding the precipitate. The ground alumina was then soaked in a chrome solution, pilled, dried, and put into the reactor. The finished catalyst had an apparent density of 1.0.

The reactor was a vertical bundle of $2\frac{1}{2}$ inch tubes with flue gas circulated around the tubes. The tubes were made of 17 percent chrome, 17 percent nickel, "high" molybdenum content steel. The flue gas circulated around the tubes was at a temperature about 200 degrees fahrenheit above that of the inside catalyst.

Catalyst was continually added at the top of the bundle and continually withdrawn at the bottom. The time required for the catalyst to pass through the tube was about 200 hours. Catalyst deactivation occurred primarily through carbon formation and deposition. The spent catalyst contained 2.5 percent weight carbon and in regeneration with air it was reduced to 1.5 percent weight and returned to the system. In the regeneration, care was taken that the temperature did not exceed the operating level of 1020 to 1100 degrees fahrenheit.

The same space velocity and conversion were used for both normal

Appendix I (Cont'd.)

and isobutane, but with normal butane the operating temperature was 1100 degrees fahrenheit compared with 1020 degrees fahrenheit for isobutane.

The exit stream from the dehydrogenation furnace was first cooled and then hydrogen, methane and other low boiling materials were separated. The butane-butylene mixture then was fed directly to alkylation. Acid life in alkylation was markedly influenced by the quality of dehydrogenation product. Small amounts of butadiene adversely affected acid life. Butadiene formation was minimized by carefully controlled dehydrogenation furnace operation, particularly avoiding tube plugging with resulting catalyst overheating.

In obtaining a product containing 18 percent olefins, a total weight loss of about 5 percent is incurred. That is, a 95 percent weight recovery of total C_4 fraction is obtained. On this basis, an ultimate weight conversion of 78 percent butane to butylene is realized. Losses through fractionation and alkylation plants will of course reduce this figure.

Dehydrogenation under hydrogen pressure was studied, and the low pressure system was chosen in preference. (This decision was influenced by the difficulty of obtaining high pressure equipment in Europe during the war).

The following documents, transmitted to the Bureau of Ships, relate to this subject:

- XXIII. Dehydrierung
(I.G. - Leuna - report of Dr. Herbert)
- XXIV. Materialfragen in der Dehydrierung.
(Poltz - report of Dr. Hüttner)
- XXV. Mengenschema zur AT Anlage mit
katalytischer Dehydrierung.
(I.G.-Leuna - flow diagram and
material balance of system in-
cluding catalytic dehydrogenation
of normal butane)

Appendix I (Cont'd.)

- XXVI. Die Katalytische Dehydrierung
von Propan zu Propen.
(I.G. - Leuna - report by Dr.
Nowotny of 16 March 1944)
- XXVII. Chlor-Dehydrierung nach Bährⁿ
(I.G. - Leuna - process flow
diagram of butane dehydrogena-
tion plant)

APPENDIX IITHE MANUFACTURE OF NITRATION GRADE TOLUENE.

The German supply of nitration grade toluene came from several sources. In addition to coal tar fractionation and refining of DHD fractions, there were employed the Witol process, the Leutol process, and aromatization of heptanes.

The DHD process is fundamentally a device for producing aromatics, and it was logically seen to be a potential source of toluene. Some nitration grade toluene was made directly from the normal DHD product by separation of a C7 fraction and application of methanol in an azeotropic distillation process. In another instance, a C7 fraction was separated from the DHD product and repassed again through the same process. The repassed product was then fractionated directly without the aid of added agents to produce toluene of nitration grade. In both cases, sulfuric acid treatment and redistillation were employed as a finishing operation.

The Witol process was a synthesis of toluene by the combination of methanol and benzene. A four to one ratio of benzene to methanol was reacted, and the alkylated benzenes consisted of 70 percent toluene and 30 percent higher homologues.

To produce toluene from the poly-methylated benzenes, the Leutol process, which was quite similar to the Arabin process (discussed in this report), was employed. In the Leutol process, an aluminum silicate-molybdenum oxide catalyst is used, with a hydrogen pressure of ca. 200 atmospheres, to dealkylate the higher boiling compounds.

Perhaps of widest technical interest, however, is the heptane aromatizing process developed by Ruhrchemie. A plant was being built at Helten but it had not been completed by the end of the war.

The Ruhrchemie cyclizing process is specially designed for heptane - heptene fractions from the Fischer-Tropsch synthesis. These fractions would consist largely of normal heptane, with perhaps 10 percent of heptene-1 and 5 percent of other heptenes. This mixture was to be carefully fractionated from C6 and C8 components; i.e. to 99.5 percent purity. It was then to be passed over a chrome-alumina catalyst at atmospheric pressure and a temperature of 860 degrees Fahrenheit. The chrome-alumina catalyst was made as follows:

Appendix II (Cont'd.)

(Al₂O₃ was precipitated, washed, dried, and ground in conventional manner, but careful washing was considered important. The ground alumina was then mixed with pure chromic nitrate salt with adequate water to make a viscous mixture. This mass was extruded into small cylinders, dried and finally roasted at a temperature of 1200 degrees fahrenheit. Small amounts of cobalt, nickel, manganese, and thorium had been used in individual tests as activators.) By using a liquid hourly space velocity of 0.1, a 50 percent conversion to toluene was anticipated. By the recycle of unconverted heptane - heptene, an ultimate yield of toluene equal to 78 percent weight of the feed was obtained in a pilot plant; this figure was expected to decrease to 70 percent in the commercial plant.

In the pilot plant, in obtaining a 50 percent weight yield of toluene in one pass, the total loss to other materials was ca. 1.2 percent weight hydrogen, percent weight methane and other low boiling materials, and 3 to 4 percent weight of light gasoline, high boiling residues, etc.

The reaction cycle in this process was one-half ($\frac{1}{2}$) hour on production, about one-quarter hour oxidizing off carbon, and one-quarter hour reducing the catalyst after oxidation. In the reduction step, hydrogen produced in the operation is used.

The toluene is separated from the reactor product liquid by simple fractionation, and after acid treating and redistillation it meets nitration grade specifications.

The use of a low pressure operation without hydrogen recycle is possible because of the absence of cyclopentanes in the feed. At low pressure cyclopentanes would decompose extensively to carbon and result in very rapid catalyst fouling.

Ruhrchemie was planning the application of this process to a wide boiling (190 to 390° F.) Fischer-Tropsch fraction to improve it as a motor gasoline component. Such a fraction could be reformed by this method to give a 93 percent weight yield of material of the same boiling range as the feed. With a 47 percent volume aromatic content, the octane number of the product would be 68 compared with 18 for the feed.

The catalyst life was estimated to be about one year, which would be equivalent to a catalyst consumption of roughly one pound per barrel

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Appendix II (Cont'd.)

of liquid throughput.

A general description of the process as announced by Ruhrchemie in 1943 was transmitted to the Bureau of Ships:

XXVIII. Die Aromatisierung von gradkettigen
aliphatischen Kohlenwasserstoffen
aus der Fischer-Tropsch - Synthese.
(Ruhrchemie - report by Dr. Rottig
in January 1943).