

DECLASSIFIED MR 22 SEPT 72

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WAR CABINET TECHNICAL SUB-COMMITTEE ON AXIS OIL.

ENEMY OILS AND FUELS COMMITTEE.

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REPORT ON GERMAN C.3 (GREEN) TYPE OF AVIATION GASOLINE.

PROPERTIES, COMPOSITION AND POSSIBLE METHODS
OF MANUFACTURE.

A SURVEY OF SAMPLES EXAMINED OVER THE PERIOD SUMMER 1940
TO AUTUMN 1943.

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The work recorded in this report was carried out by Imperial Chemical Industries Ltd. (Billingham Division).

GERMAN C3 (GREEN) TYPE AVIATION GASOLINE.

PROPERTIES, COMPOSITION AND POSSIBLE METHODS OF MANUFACTURE OF SAMPLES OBTAINED DURING THE PERIOD SUMMER 1940 TO AUTUMN 1943.

SUMMARY & CONCLUSIONS.

Spread over a period of $3\frac{1}{2}$ years, since the introduction during the Battle of Britain in the late summer of 1940, some 22 authentic samples of the green C3 type of aviation gasoline have been examined, 14 of these by detailed fractionation and analysis.

It is concluded that this gasoline consists of a blend of at least three components :-

- (a) 25-30% of light-cut gasoline (ca. 85°C. end point).
- (b) 60-50% of highly aromatic naphtha of low volatility.
- (c) 15-20% of synthetic octane.

It is further concluded that all three components are produced in conjunction with hydrogenation plants. The aromatic naphtha is highly characteristic and is considered to be the product of high temperature "aromatising" destructive hydrogenation of a bituminous material. The octane is considered to be the product of a low temperature butylene polymerisation process which gives large amounts of 2:2:4 trimethyl pentane (it is not alkylate) which is probably operated in conjunction with the hydrogenation plants.

Composition and specification have shown only minor changes from mid 1940 up to early 1943, when the engine performance was increased from 95 weak 110 rich to 97 weak 125-130 rich by adding 5% more octane, 5-10% more light petrol and most of all by removing 8-10% of higher boiling naphthenes by some further dehydrogenation treatment.

Some speculations as to the possible German fuel position are followed by a discussion of the main points of interest arising out of the analytical work, while the actual analytical methods are described and analytical results tabled in Appendices I to V.

SPECULATION ON GERMAN AVIATION FUEL POSITION.

When the whole position of aviation gasoline production in Germany is considered, it is seen that throughout the war there has been a marked preference for gasoline rich in aromatic hydrocarbons. This preference for aromatics is shown firstly by the green C3 type of aviation fuel which contains 35-40% aromatics, and is considered to be based largely on a highly aromatic hydrogenation product and secondly by the blue B4 aviation fuel which for three years contained 10-15% aromatics and is now up to 20% aromatics and is now considered to contain some of the same aromatic naphtha made by hydrogenation as is present in the green fuel. Motor gasolines also often contain large amounts of added benzole (up to 25% benzene added to Fischer Tropsch material) and it is probable that some benzole is also being added to the aviation fuels (possibly in a hydro-refining process).

The high aromatic contents are well known to be particularly useful for rich mixture performance and the green C3 fuel has been found to have a very high rich mixture rating when examined under British standard test conditions. However, such trials as have been carried out with captured German engines on German green fuel, or a match for it, have indicated that German engines are not taking full advantage of the possibilities of green fuel at the rich end. At the weak mixture end, on the other hand, there is a deficiency in fuel performance as judged by the U.K. methods of test for 100 Octane Number fuels.

In view of the large potential production capacity of naphthalene fuels and synthetic octanes in hydrogenation plants which the Germans have, it is surprising to find an apparently unbalanced fuel of this nature, but the explanation seems to be that official policy at or before the outbreak of war was to concentrate on aromatics as high octane blending agents rather than synthetic octanes. The hydrogenation plants are, of course, as capable of making an aromatic blending agent as a paraffinic.

It would appear that practically the only hydrogenation products which are going into aviation or motor gasoline are those made by such 'aromatising' processes which consume relatively little hydrogen. It is fairly certain in view of the marked shortage of iso-pentane that no plants are being operated in Germany using sensitive-catalyst vapour phase hydrogenation process such as that used in the U.K., which produces a volatile aviation gasoline and much iso-pentane, but which also consumes more hydrogen.

The synthetic octane found in German green fuel is characterised by a high proportion of 224 trimethyl pentane. It may be that this particular iso-octane is valued for its high weak mixture rating. It is considered that the octane is being made from butane produced by hydrogenation processes, using a low temperature high throughput phosphoric acid polymerisation process, probably operated with partial polymerisation so as to increase the yield of 224 trimethyl pentane.

At the end of 1942 there was an appreciable change in the composition of the green fuel, the octane content rising by 5 per cent and the high boiling naphthenes content falling by 8 to 10 per cent due to further dehydrogenation treatment. These changes had the effect of raising the C.F.R. motor method octane rating by 2 points, and the 3C rich mixture rating by 15 points. The change at both the weak and the rich end has been largely due to the removal of the high boiling naphthenes. Both main engine and single cylinder aero engine tests carried out on the green fuel have indicated very clearly that, at least by our standards, the German main engines are not taking advantage of this increased rich mixture performance. The solution to the puzzle of why the Germans have an aviation fuel specification apparently far better than their engines would seem to need can only come from further work with German engines.

It is also difficult to find a reason why, when at the end of 1942 the Germans decided to improve the quality of this type of gasoline that they should introduce an additional aromatising or hydroforming type of dehydrogenation process which had the effect of increasing still further the (apparently surplus) rich rating and still further unbalancing the fuel at the weak end rather than to expand on octane production and increase the (apparently deficient) weak rating unless there are some unknown factors limiting octane production or which make this course preferable from the German point of view. Meanwhile the following are possible explanations:-

1. That the policy of using aromatics as the main high performance additive inevitably leads to a surplus of quality at the rich end.
2. That our test work on German fuels is not rating them as they are rated by the Germans. In this connection it is understood that the Germans plot the B.M.E.P., not against a specific consumption, but against a per cent of theoretical air consumption based on the hydrogen carbon ratio of the fuel. One set of data has been plotted in this way and shows that the German green fuel is displaced in a manner relative to British 100 octane grade so that the weak mixture performance of the German fuel is rated as better than the British.
3. That this improved green gasoline was introduced at the beginning of 1943 in anticipation of a new service engine which would make full use of it, but that this engine has been delayed by development troubles.

DISCUSSION.

1) Samples Obtained.

Green (C3) aviation gasoline first appeared in aircraft destroyed during the Battle of Britain in the late summer of 1940. The total number of authentic samples obtained to date is small; so that it is unwise to draw conclusions as to the extent of use of this type of fuel, although from total actual samples received the indication is that less than a fifth of the total operational planes use this type of material.

Some twenty-one samples of green C3 aviation gasoline have been recorded (Appendix I) and to date fourteen have been analysed in detail by fractionation (Appendix II-IV).

There was a period towards the end of 1942 when so few samples of this type of aviation gasoline were encountered that the suggestion arose that the use of this gasoline was being discontinued; a number of recent samples have shown, however, that this fuel is still being used.

2) Use of C3. Aviation Gasoline

Captured documents infer that this type of aviation gasoline must be used in at least two types of motors :- Daimler Benz D.B. 601 N., and the B.M.W. 801. C & D. There are cases of its use in Junkers machines, although practically all recent samples are from F.W.190 fighters.

The indication was that this fuel (initially of 94-95 C.F.R. motor rating) was a special fighter-grade fuel as distinct from the bomber and general purpose fuel - the B4. blue-coloured aviation gasoline of 90 C.F.R. motor octane number. Some fairly recent Mc.109 F. fighters with D.B. 601 E engines have been operating on the B4 gasoline and the contention that present aero-engines used by the G.I.F. are not being operated to take advantage of the rich mixture potentialities of the C3 type of gasoline render the reasons for the introduction and use of this fuel somewhat puzzling.

A number of samples of this fuel have been obtained from the Middle East and some from the Russian front (table I Appendix I).

3) General Description of Green C3 Type Aviation Gasoline - Specification
(see also Appendix I)

The lead content of the green C3 gasoline is the same as that of the lower grade B4 blue gasoline.

The average properties have been :-

Colour	C.3.		B.4.
	(a)	(b)	
Knock Ratings:-			
C.F.R. Motor	94-95	96-97	90-91
3-C Rich mixture rating	110	125-130	
Base spirit, lead-free C.F.R. motor	83	83	72-74
" " lead & aromatic-free C.F.R. motor	77	78	67-70
tetra ethyl lead mls/U.S. gal.	4.6	4.6	4.6
density 15/15	0.782	0.770	0.733-0.748
Volatility % to 75°	7	15	20
" " " 100°	40	50	55-60
" " " 140°	77	85	95
End point °C.	185-175	175	160
" " °F	365-345	345	320
Butanes + pentanes % vol.	6	10	8 - 13
Reid vapour pressure lbs./sq.in.	3-4	5	5 - 6
Aromatics % vol.	37	37	9 - 20

The C3. type of gasoline is readily recognised by such tests.

Early in 1943 changes occurred in the C3. gasoline towards a more volatile fuel of increased performance as shown at (a) and (b) in the above table. This change is discussed more fully below.

4) Hydrocarbon composition - Interpretation

The C3 type of gasoline is of low volatility for an aviation fuel and contains nearly 40% of aromatic hydrocarbon. It has also been shown to contain 15-20% of synthetic octanes. About 14 samples have been examined in detail by super-fractionation and also in several cases by spectroscopic analysis.

The composition and distribution of the aromatic hydrocarbons are highly characteristic, as also are the amount and distribution of naphthalene hydrocarbons.

The interpretation of such analyses involves comparison with as wide a field as possible of products from known sources. It has always been emphasised that conclusions based on such comparisons are much stronger when based on wide dissimilarities in composition. Thus it is possible to conclude positively that an unknown hydrocarbon mixture has not been obtained from a certain source, but where composition is similar to that of a known product it can only be concluded that the source "could be" the one in question.

The composition of C3. type fuels obtained by the above methods have been compared with a fairly wide field of products of known origin, including :-

- (1) alkylates, hydrocodiners (hot and cold acid, of various types)
- (2) aromatics from coal carbonisation; hydroreformed petroleum and creosote-hydrogenation naphthas; products from selective dehydrogenation (hydrofining) of petroleum and various hydrogenation naphthas from coal or petroleum; highly aromatic naphthas made by high temperature "aromatization" destructive hydrogenation of bituminous materials.
- (3) About 20 virgin petroleum gasolines and naphthas from a variety of sources; a variety of high pressure sensitive-catalyst "vapour phase" hydrogenation gasolines from bituminous coal creosote and also from petroleum gas oils; certain Fischer Tropsch gasolines; a single sample of catalytically cracked gasoline.

By comparison of the highly characteristic hydrocarbon composition of the C3 type of gasoline with such a necessarily limited field of products of known origin it is concluded that the C3. type of aviation gasoline is a blend of at least three components.

A possible composition which would agree with the analytical evidence is :-

- I. 25-30% of light cut gasoline (providing pentanes, hexanes, and C₆ naphthalenes) and probably of boiling range up to about 85°C.
- II. 60-50% of a highly aromatic naphtha of low volatility and probably boiling over the range 85-175°C. The aromatic content of this naphtha may be as high as 70%.
- III. 15-20% of synthetic octane of which the major component is 2:2:4 trimethyl pentane with 2:3:4 trimethyl pentane as the second main component.

Recently, certain changes have occurred in composition which are discussed below, but it is still considered that the C3. gasoline is made up from the above three components with the possible addition of hydro-refined benzene (or coke-oven aromatics mainly benzene), and possibly some added pentane.

5) Source and Method of Manufacture of Above Components

- I. Light gasoline cut. It is considered that this could be produced in the hydrogenation plants (e.g. by high temperature operation or with less active catalysts than those which we associate with "vapour-phase" destructive hydrogenation), although the composition is nearer to that usually associated with straight petroleum products. The conclusion that a light gasoline fraction has been added as a separate component of the final blend is based on the amounts of naphthalenes boiling in the range above 85°C, which are very much less than in normal hydrogenation products, whereas the C.3 gasoline contains the normal amount of cyclohexane found in virgin petroleum gasolines. The comparative absence of any material distilling at 90°C. suggests that the end point of the light cut is below 90°C.

II. Highly Aromatic Naphtha. In view of the highly characteristic composition of the aromatics (ethyl benzene, n-propyl and n-butyl benzene) which is discussed in detail in Appendix II, it is considered that this material is derived by high temperature hydrogenation treatment of bituminous raw material containing condensed polynuclear aromatics such as naphthalene. It is fairly certain that this material is produced in those high temperature high pressure hydrogenation plants such as Welheim.

Recent C.3. gasoline samples of improved rating have shown a change in aromatic composition in conjunction with a marked decrease in the amount of higher boiling naphthenes. It is concluded that the highly aromatic naphtha made by the above process is now being given a further treatment whereby naphthenes are converted into aromatics (possibly hydroforming or hydrofining). This further treatment is considered to be largely responsible for the rise in engine performance. It may be that hydroforming the aromatic naphtha would produce the extra low boiling paraffins found in such recent samples of C3 gasoline.

An alternative possibility is that the process for production of the previous type of highly aromatic naphtha (hydrogenation at high temperature and possibly high pressure in possibly relatively few plants) is now not adequate to meet present fighter requirements of aromatics (possibly not now available), and an alternative means of providing a highly aromatic naphtha (to maintain this type of composition) is to hydroform a suitable naphtha (possibly a hydro-naphtha of another type).

It is known that hydroformed products from treatment of petroleum naphthas will yield products containing up to 70% aromatics with less than 10% of naphthenes. A more naphthenic or less paraffinic type of material would be available for treatment from the hydrogenation processes. It is more in keeping with the known recent increase in engine performance to conclude that the previous type of aromatic naphtha is now being given a further dehydrogenation treatment rather than to conclude that the change in aromatic composition is due to addition of another aromatic naphtha made by dehydrogenation of a hydro-naphtha. It is possible that coal tar aromatics are now being added but there is no evidence of increase in sulphur content.

III Synthetic octane (see also Appendix III)

The main components are 2:2:4 trimethyl pentane and 2:3:4 trimethyl pentane in the ratio of about 3:1. The absence of more than traces of dimethyl hexanes and of 2:3:3 trimethyl pentane and the absence of 2:2:5 trimethyl hexane are considered to be sufficient evidence to exclude C₄ alkylates of the types examined. The presence of 2:3:4 trimethyl pentane and such tracer compounds as 2:3 dimethyl pentane is considered as evidence for the presence of hydrogenated co-polymer.

The relatively high proportion of 2:2:4 trimethyl pentane differentiates this octane from that normally produced by the hot phosphoric acid polymerisation of isobutylene and is closer to octane produced by the cold sulphuric acid process.

It is most probable that the synthetic octane is produced by dehydrogenation of C₄ gases produced in the hydrogenation plants with a subsequent polymerisation process operated at a low temperature.

It has been suggested that the composition could be met by postulating a mixture of cold acid octane with some other type of octane. It is still considered that the evidence excludes alkylates and the remarkably constant composition maintained over three years production suggests that only one type of process is involved.

Speculation as to the method of production of the octane is bound up with the suggested scheme for production of the rest of the blend, and the suggested methods of operation of the hydrogenation plants and a general survey of the availability of C₄ and C₅ hydrocarbons for aviation fuel purposes. High temperature 'aromatising' hydrogenation processes would tend to make much hydrocarbon gas and yet viewing the whole German aviation gasoline position (blue and green types) there appears to be a marked shortage of iso-pentane. This is in agreement with the view that relatively little of the total aviation gasoline is produced by the medium temperature sensitive-catalyst vapour phase process as used in U.K. which produces large amounts of iso-pentane.

The earlier samples of green gasoline were estimated to contain 15% of synthetic octane. Early in 1943 coincident with the rise in engine rating there was an increase in octane content to about 20%. Composition of the octane added has remained unchanged.

6) Changes in specification and Composition

Definite changes in composition have occurred as follow:- (see also table I)

- (a) during 1940 increase in aromatic content from 35% to 37% vol.
- (b) end of 1940 aromatic naphtha was cut back to a lower end point, but aromatic content maintained.
- (c) " " " octane content raised from 13% to 15%
- (d) end of 1942 increase in octane content up to 18%, also increase in content of light petrol and pentane, general rise in volatility and fall in aromatic content (by dilution). Marked increase in C.F.R.-M. rating to 97 and in 3-C Rich rating to 120.
- (e) summer 1943 still further increase in rating with octane content up to 20% and aromatics increased back to 37%, and decrease of 9% in content of higher boiling naphthenes.

The average analysis of green fuel can be taken as some indication of specification

	<u>1940</u>	<u>1941</u>	<u>1942</u>	<u>1943</u>
density 15/15	0.782	0.782	0.782	0.772
F.B.P. °C	185	175	175	175
Volatility at 75°C vol.%	7	7	7	15
" " 100°C " "	41	41	41	51
" " 140°C " "	77	85	85	86
Vapour Pressure lbs.	2-4	2-4	2-4	5
Wt.% C ₄ + C ₅	5½	5½	5½	8½
Vol.% <u>aromatics</u>	34-35	37	37	34 → 37
% of aromatics >166°C	30	10	10	10
Vol.% <u>octanes</u>	13	15-16	15-16	18 → 20
Vol.% naphthenes boiling above 95°C	16	16	16	13 → 7
T.E.L. content mls/Imp. Gal.	5.5	5.5	5.5	5.5
= mls/U.S. Gal.	4.6	4.6	4.6	4.6
= mls/litre	1.2	1.2	1.2	1.2
<u>Knock Rating</u>				
Weak C.F.R. motor	94	94	95	97
Rich 3-C % grade 130		110		120 → 125

The significance of this recent change is great. It may mean that the Germans have introduced an additional process in order to reduce the amount of high boiling naphthenes in order to gain considerable improvement in rich performance, which as yet they have shown no evidence of being able to use in their existing aero-engines. Alternatively, the improved rating may be incidental and the change in aromatic composition may mean that the Germans have been forced to change to another process (i.e. by bombing of plants working the previous process). The latter explanation would seem unlikely, although it may be that hydroreforming (or other dehydrogenation process) applied to a naphtha already essentially boiling within the range of the finished product (and hence not requiring "splitting") coupled with a normal hydrogenation-splitting process to produce the naphtha, would be a more flexible tie-up applicable to more plants than the alternative process of high-temperature high-pressure "aromatising-splitting" postulated for the earlier types of aromatic naphtha production. In the latter the 'aromatising' and 'splitting' are done together in one stage and require high temperatures to give an aromatic product and high pressures to maintain catalyst life, while in the other method two separate stages only require medium or comparatively low pressures.

In alternative view is that this recent change in composition is evidence of an effort to overcome a limitation in weak mixture performance.

The remarkably close similarity in hydrocarbon composition of samples of C.3 type of aviation gasoline obtained from such widely scattered sources as Britain (shot down), Russian front and middle East (Tripoli and Tunis) suggest that this fuel is a synthetic blend made in comparatively few plants, all working under very similar conditions, and all probably using the same type of raw materials.

Other anti-knock blending additives.

Lead content has remained constant at 5.5 cc/Imp. Gal = 4.6 cc/U.S. Gal = 1.2 cc/litre. There has been no evidence in any sample for the presence of

Cumene or tertiary butyl benzene.

Aromatic amines, aniline, methyl aniline or xylylides.

Iron carbonyl.

Alcohols, ethers or any water soluble component.

GENERAL INSPECTION

(numbers refer to large folding table page)

- (1) Colour. The characteristic fluorescent yellow green colour has been maintained throughout (probably fluorescein dye).
- (2) Density The average density used to be 0.782 up to about summer of 1942. (samples of higher density were probably weathered e.g. AIR 118). All samples obtained during 1943 are of lower density averaging 0.772 (except weathered samples AIR 289, and 312 jettisoned from fighters). It is possible that this change occurred as early as autumn 1942 (AIR 195, 240).
- (3) I.P.T. boiling range. A change occurred at the end of 1940 when the F.B.P. fell from 185°C to 175°C and 95% from 178°C to 165°C. This change at the end of 1940 had little effect on the volatility to 75°C or 100°C or on the vapour pressure. It is reflected markedly in the volatility to 140°C and in the percentage of material distilling above 165°C in a T.B.P. column (see line 5).
- (4) Volatility two changes occur :-
- at end of 1940 the end point was reduced and volatility at 140°C raised, but volatilities at 75°C and 100°C remained at about 7% and 41% respectively.
 - at the end of 1942 the 'front end' volatility was raised (as described below by adding more octane and more light petrol), pentane content was increased as was Reid vapour pressure, and volatilities to 75°C and 100°C were raised to 15% and 50-52% respectively. This caused little or no change in the volatility to 140°C or the T.B.P.% above 165°C.

(5) T.B.P. Vol.% above 165°C Up to the end of 1940 this was 17-19% in keeping with the high F.B.P. of 185°C. Reduction of the F.B.P. to 175°C. at the end of 1940 brings the T.B.P.% distilling above 165°C down to 7-8%. The later increase in 'front end' volatility at the end of 1942 has not affected this appreciably.

(6) Butane content. All the green fuels examined have contained 1-2% wt. of butane. In all cases this has been practically entirely normal butane.

(7) Pentane content All fuels up to the end of 1942 contained only 3½-4% wt. of pentane. In 1943 this has been increased to about 6% wt. while such recent samples as AIR 317, 318 and 328 contain 8% of pentane and practically no butane. It should be noted that although more iso-pentane than normal pentane is present these fuels all contain much less iso-pentane and a much lower iso/N-pentane ratio than would be obtained by normal vapour phase hydrogenation treatment. Green fuel AIR 317 is of interest since more iso-pentane is present, but this higher ratio is not maintained in the most recent samples.

	WEIGHT %		
	Iso-pentane	N-pentane	% iso-pentane in total pentane
Green fuel 1940	2.5	1.8	58
" " 1941	2.3	1.7	58
" " 1942	2.4	2.2	50
" " 1943	3.7	2.5	60
" " AIR 317	5.6	2.9	65
" " AIR 318-330 av.	4.5	3.1	60
V.P. Hydrogenation fuel (creosote) 17	3		85

(8) Vapour Pressure. All samples have had a low vapour pressure of $2\frac{1}{2}$ -5 lbs., the extra pentane added has only brought the V.P. up to 5-lbs.

(9) Bromine Number. With possible exception of samples obtained during 1941 (AIR 141, 144 and 176) the bromine number has been less than 1, showing that unsaturates are practically absent. (V.P. hydro petrols have bromine numbers less than 0.2).

(10) Aniline Point. Initial aniline point (I) is largely indicative of the aromatic content. The 1940 fuel had I.P. of about 19°C ., which fell to 16°C . in 1941 when the aromatic content was increased from 34-55% to 57-58% vol. The aniline point has risen again in 1943 fuels (AIR 285, 305 and 311) to 23 - 24°C due to the addition of more octane and light petrol and the falling aromatic content. The latest sample AIR 317 etc. have a lower aniline point of about 20°C ., since aromatic content has again been increased.

(11) Aromatic-free aniline point. This figure in the green fuels is a guide to octane content. The aromatic-free an.pt. has remained fairly constant at about 57.5°C . up to the end of 1942. Figures of over 60°C (62 and 63°C) now recorded are due to increased octane content and increase in pentane and light petrol fractions.

(12) & (25) Aromatic content. Is determined directly on the uncut fuel (12) and by summation of analyses of fractions (25) shows that for 1941 there was an increase in aromatic content from 34% to 37% vol. which was maintained through 1941 and 1942 until it was reduced to 33% vol. in 1943 due to the dilution effect of adding more octane and light petrol. It would now appear (AIR 317) that the aromatic content has again been restored to 37% while keeping the higher content of octane and light petrol, largely at the expense of the higher boiling naphthenes.

(13) & (14) Naphthenes & Paraffins. These figures determined without fractionation are not very reliable. They serve to show that right up to the end of 1942 the non-aromatic portion of the fuel remained fairly constant with about 30% of naphthenes and 30% of paraffins and with an aniline point of 57.5°C (11) and density 0.732 (15), but in 1943 the extra octane and light paraffinic petrol cut added have caused a marked change to 15-20% naphthenes and over 40% paraffins with aniline point up to 62 - 63°C . and density down to 0.725 (AIR 285, 305) and later to 0.715 (AIR 311, 317 etc.).

(17) Lead Content. Apart from fuels which have weathered and thereby increased in lead (AIR 289, 312) the lead content has remained constant at 5.5 mls. TEL/Imp. Gal (= 4.6 mls T.E.L./U.S. gal. or probably 1.2 mls. T.E.L./litre of fuel).

Even in the recent fuel of much increased ratings there has been no increase in lead content.

(16) (18) (19) Knock Ratings. The C.F.R. motor octane number up to the end of 1941 remained at 94. Samples obtained in 1942 may have been higher at 95-96, while 1943 samples show figures up to 97. The C.F.R. motor rating of the fuel freed from lead shows no similar changes. An average figure of 82-83 is due to the high aromatic content and the presence of octane.

The C.F.R. motor ratings of the fuel freed from both lead and aromatics are again variable. Up to end of 1942 the 'base fuel' was probably about 76.5-77, whereas 1943 fuel is 78 or over. In both cases this O.N. is high due to the presence of octane. Assuming 10% of octane in the earlier fuels and 20% in 1943 fuels the lead, aromatic and octane-free base fuel probably has an octane number of about 70-71. Although this residual paraffin/naphthene mixture is fairly rich in normal paraffins it would be expected to have such a rating since the greater part consists of low-boiling components. (more than 75% boiling below 100°C).

Some 3-C rich mixture ratings are given below. Recent 1943 type green fuels have risen to over 125% grade 130. This increase could be accounted for in terms of the changes in composition found, since the appreciable reduction in the amount of higher boiling naphthenes which has occurred in the most recent samples would be expected to cause an appreciable increase in the rich mixture rating while this change and the addition of more aromatic and light petrol are considered to account for the increase of two units in weak mixture rating.

	1940 - 1942 of green fuel	AIR 285	AIR 305	AIR 311	AIR 317	AIR 318-327	AIR 328-330
<u>Knock Ratings</u>							
C.F.R. Motor as received	94	96	96½	97	97	97	97
T.E.L. mls/Imp.Gal. Research O.N. mls	5.5	5.6	5.5	5.5	5.6	5.65	5.65
TEL/US gall on octane 3-C Rich mixture rating % of grade 130	110	118		124	125	>125	>125
<u>Composition (Billingham Analysis)</u>							
Aromatics % by volume	37	33	32½	34	36½	37½	37½
Butanes + Pentanes % by volume	7	9½	10	10	10½	10½	12
Trimethyl pentanes 2,2,4; " 2,5,4	11) 16	13) 18	13) 20	15) 20	15) 20	15) 20	13½) 20½
Naphthalenes boiling above 95°C % vol.	16	13	11	7½	6½	6½	6½

(20)-(25) Distribution of Aromatics (Billingham fractionation)

The aromatic distribution is determined quite reliably by the fractionation method. This distribution expressed as a volume percentage of the total fuel is detailed in the large table while below figures are given expressed as a percentage of the total aromatics and as a percentage of the C₆ + C₇ + C₈ aromatics boiling below 145°C.

It will be seen from both sets of figures that changes have been made as follows:

1940 fuel (GF 28 & 40/41) 34% aromatics 30% of which boil above 166°C.

1940 " (GF 31 & GF 32) 37% " " " " " "

1941 " " " only 10% of which boil above 166°C.

1942 " " " " " " " "

1943 " 33½ " " " " " " "

Later

1943 " (AIR 317 etc) 37½ " " " " " " "

One major change occurred at the end of 1940 when two thirds of the high boiling (>166°C) aromatics were removed by cutting the fuel to a lower end-point. At the same time the total aromatic content was maintained.

Considering only the distribution of C₆, C₇ & C₈ aromatics the table below shows that this has remained surprisingly constant up to sample AIR 305, but from sample AIR 311 onwards the samples have contained proportionately less benzene and more toluene and C₈ aromatics. Even in these fuels, however, the ratio of C₇/C₈ aromatics is much the same as in the previous fuels.

Distribution of Aromatic Hydrocarbons

Fuel No.	TOTAL Vol.% on Fuel.	% of total aromatics				% of Arom. up to 145°C.		
		0 - 90°C	90-118	118-145	145-166	166	0-90°C	90 - 118
G.F. 28	35.35	18½	23½	20	9½	28½	30	38
40/41	32.6	19½	23	19½	8	30	31½	31
G.F. 31	37.35	17	23	20	11½	28½	28½	39
G.F. 32	35.35	18½	22	19½	10	30	30½	32½
AIR 141	37.7	21½	32	24½	11	11	27½	41
AIR 144	37.5	26½	31	23	8½	11	33½	38
AIR 176	37.4	23	33	26	11	7	28	40
AIR 189	38.6	23	32	24	11	10	29	41
AIR 285	32.9	23	30½	26	8	12½	28½	38½
AIR 305	32.45	22½	32	24½	12	9	28½	40½
AIR 311	33.95	17	32½	27	11½	11	22	42
AIR 317	36.25	18	34½	27½	9½	10½	22½	43
AIR 318	36.55	19½	33½	28½	10	8½	24	41
AIR 328	35.75	18½	33	29½	9	10	23	40½

Further information obtained by ultra violet spectroscopic analysis shows that recent changes in distribution are accompanied by marked changes in composition of individual aromatics (see Appendix II)

It should be noted that these fuels average 6% and in some cases up to 9.7% wt. of benzene (AIR 189) and still show no signs of freezing out at -60°C.

(31) & (32) Aromatic Composition (Spectroscopic Results)

The important figures here are the high content (in relation to xylenes) of ethyl benzene which averages 6% for samples prior to 1943 (and thus represents about 66% of the total C₈ aromatics), and hydrindene which generally amounts to 1.5-2% of the fuel.

There are indications that the more recent fuels of 1943 contain less ethyl benzene and more ortho xylene, as well as less propyl and butyl benzenes and more ethyl terpenes (see Appendix II)

(26) & (27) Methyl Cyclopentane & Cyclohexane

The average contents compared with other fuels are :-

	<u>Green Fucl.</u>	<u>Str. Run Petroleum.</u>	<u>Vap. Phase</u>
	(Roumanian etc.)		<u>Gasosote</u>
			<u>Hydrogenation</u>
Methyl cyclopentane	5.5	5	12
Cyclohexane	4.5	4.5	2

There is no indication of any marked change in the more recent fuels, although the ratio is slightly more in the direction of hydro-petrol.

(28)-(30) & (33)-(35) Octanes

The Billingham fractionation method shows the presence of octanes, but only gives an approximate measure of the ratio of 2:2:4 / higher boiling trimethyl pentanes and the amounts present. These rough estimates show that the 1940 fuel contained about 13% octanes which was increased to 16% for 1941-1942 and has later been increased again to 20% in 1943.

The boiling range of the paraffins has indicated 73-75% 2:2:4 trimethyl pentane in most cases, (the sole exception has been fuel AIR 189 in which 2:2:4 T.M.P. was down to 50%). The recent 1943 fuel has shown a somewhat higher proportion of the higher boiling trimethyl pentanes with about 65% 2:2:4. trimethyl pentane.

Spectroscopic examination has generally confirmed the figure for 2:2:4 T.M.P. and has shown that 2:3:4 T.M.P. is the main component of the higher boiling trimethyl pentanes.

The spectroscopic analyses in uncut or roughly cut samples are somewhat uncertain. Detailed analyses of more finely cut material are discussed in Appendix III.

Presence of other anti-knock additives.

No evidence has been found for the presence of any of the following anti-knock agents in any sample of the green aviation gasoline examined :-

Cumene or tertiary butyl benzene.

Aromatic amines or xylylides

Iron carbonyl

Alcohols ethers or any water soluble components, other than small traces of phenols.

APPENDIX I.

TABLE I.

SUMMARY OF RELEVANT ANALYSES OF ALL AUTHENTIC SAMPLES OF GERMAN GREEN AVIATION FUEL

REF.	DATE OF CRASH OR CAPTURE OF SAMPLE SAMPLE NUMBER	1940				1941				1942			
		Summer	27th Sept.	Autumn		8th May	9th June	10th July	17th April	23rd June	Spring	Winter	
		GF. 20	44/41	GF. 31	GF. 32	AIR 113	AIR 141	AIR 144	AIR 176	AIR 189	AIR 195	AIR 240	
	TYPE OF PLANE ENGINE	Ju.38	Me.110	Me.110	Me.110	Me.109 E7 (cath- erized)	Mc.109 DB.601	Mc.109 F DB.601	Middle East	FW.190 BMW 801 D	C3 ex Russia via M.E.W.	Egypt T.D. 533	
1.	Colour												
2.	Density d.15/15	.782	.779	.785	.781	.790	.785	.784	.788	.784	.778	.777	
3.	I.P.T. distillation 95% °C. F.B.P. °C.	173		177	177	163	165	163	163	155			
4.	I.P.T. % dist. + loss at 70°C.	183		184	182	193	176	173	181	170	175		
	" " " 75°C.	5		4	7	3	3	3	3	5			
	" " " 100°C.	8		7 $\frac{1}{2}$	11	4	5	6 $\frac{1}{2}$	4	8 $\frac{1}{2}$			
	" " " 140°C.	38		40 $\frac{1}{2}$	42	35	35	43	58	44	33	44	
5.	T.B.P. vol. % boiling above 165°C.	77		76	77	74	82	85	81	87 $\frac{1}{2}$			
		19	16	17 $\frac{1}{2}$	17	8 $\frac{1}{2}$	7 $\frac{1}{2}$	3	3	7			
6.	Wt. % iso-butane	0	0	0	0	0	0	0	0.2	0			
	" " N-butane	0.85	1.6	0.9	1.4	1.75	1.65	0.55	1.2				
7.	" " iso-pentane	2.4	4.0	2.2	2.85	2.05	2.4	1.85	2.65				
	" " N-pentane	1.85	2.3	1.25	1.85	1.95	1.4	2.6	1.9				
	" " Total C ₄ + C ₅	5.1	7.9	4.35	6.1	5.7	5.45	5.2	5.95				
8.	Reid vap. pressure lbs. sq. in.					2.1			4.7				4.5
9.	Bromine number	0.9		0.8	0.8	3.5	2	1.7	1.2	1.7	1.0		
10.	Aniline point I °C.	20.3		17.7	19.5	16.7	15.4	15.4	16.2				
11.	" " IV °C.	57.3		57.7	57.8	wt. (%) 57.8	57.4	58.1	57.0	wt.(v)	wt.(v)		
12a.	Aromatics % wt.	(37.3)		(40.2)	(38.8)	40	41.3	42.4	41.6	41.6	42.5	35.5	
12b.	Aromatics % vol. (T.C.I.)	33.6		36.3	34.9	37.3	38.2	37.7	37.5				
13.	Naphthenes % "	35.5		32.6	32.3	32.5	32.3	31.2	30.9	33.5			
		30.1		31.1	32.3	27.5	30.1	30.6	31.1	29.2			

15. Aromatic free density c.15/15		.732	.731	.732	.732	.737	.732		
<u>Knock Rating</u>									
16. C.F.R. motor, as received	94.0	94.2	94.2	93	93.0	94.4	95	95.0	96
17. T.E.L. content mls/Imp. Gall.	5.7	5.45	5.4	5.7	5.5	5.5	5.5	5.55	4.6
18. C.F.R. Motor, lead free	81.3	65.6	63.6	61	82	35.1			
19. " " lead & arom. free		76.7	77.2	74	76	77.7	74.5	75.2	
<u>I.C.I. Distillation (Billingham)</u>									
20. Benzene % vol. (0-50°C)	6.2	6.35	6.35	6.55	7	8.05	10.1	8.5	8.8
21. Toluene % (0-113)	7.0	7.55	8.6	7.9	9.5	12.2	17.5	12.5	12.3
22. C ₈ aromatics% (118-145)	6.65	6.3	7.55	6.95	7.5	9.25	8.55	9.8	9.2
23. C ₉ " " (145-166)	3.2	2.5	4.35	3.5	4.15	3.2	4.05	4.4	available
24. C ₁₀₊ " " (> 166)	9.55	9.2	10.5	10.5	4.05	4.2	2.6	3.9	available
25. Total aromatics	23.35	32.0	37.55	35.55	37.7	37.5	37.4	38.3	
26. Methyl cyclopentane	5.1	5.95	5.0	5.5	3.5	5.45	3.9	4.1	
27. Cyclohexane	5.3	4.05	4.0	4.5	5.35	4.55	5.3	5.35	
28. 2,2,4 Trimethyl pentane (est.)	9	9	10½	10	12½	12	11	7	
29. Higher " pentane (est.)	3	3	3½	3½	4½	5	4	8	
30. Total T.M.P.	12	12	14	13½	17	17	15	15	
<u>Spectro-on fractions (Oxford & Cam.)</u>									
31. Ethyl benzene					6.1	5.	6.0	5.6	
32. Hydrindenes			1.1		1.4	2.1	1.4	1.44	
33. 2,2,4 Trimethyl pentane (+ 2,2 D.M. Hex)					11	12	11-12	8	
34. Higher T.M.P. (2,3,4 etc.)					5	5	3.7	8	
35. Total T.M.P.					15	17	15	16	
I.C.I. Report number	G40/1	G40/2	G40/2	G40/2	-	G41/25 G41/29 G42/57	G42/56	-	-

S = Analysis by Shell

V = Analysis at Vauxhall Lab.

Other samples generally by I.C.I.

APPENDIX I.

TABLE 1 (contd.)

SUMMARY OF RELEVANT ANALYSES OF ALL INTERCEPTED SAMPLES OF GERMAN GREEN AVIATION FUEL

REF.	DATE OF CRASH OR CAPTURE OF SAMPLE	1943									
		9th May			4th June	21st June	15th June				
	SAMPLE NUMBER	AIR 265	AIR 287B	AIR 289	AIR 291	AIR 305	AIR 311	AIR 312	AIR 317	AIR 318- 321	AIR 328- 330
	TYPE OF PLANE	Ju.88		FW.190 tank jetti- soned (weath- ered)	FW.190	FW.190	FW.190 tank jetti- soned (weath- ered)	Barrel Middle East	Barrels ex Middle East	Barrels ex Middle East	Middle East
	ENGINE										S.298 T.D.739 (Suez Report)
1.	Colour			FLUORESCENT GREEN							
2.	Density d.15/15	.773		.783		.772	.768	.787	.771	.773	.773
3.	I.P.T. distillation 95, °C. F.B.P. °C.	163.5			167	165.5			160.5	160.5	162.5
4.	I.P.T. % dist. + loss at 70°C. " " " 75°C. " " " 100°C. " " " 140°C.	175		178	175	175	179	170.5	173	173	171
5.	T.B.P. vol.% boiling above 165°C.	8			10 $\frac{1}{2}$	11		12	8 $\frac{1}{2}$	8 $\frac{1}{2}$	
		12		5	15		1	17 $\frac{1}{2}$	15 $\frac{1}{2}$	13	
		43		39	49 $\frac{1}{2}$	51	32	5 $\frac{1}{2}$	47	47	
		84			86	86		86 $\frac{1}{2}$	85	87	
		84			86	86		86 $\frac{1}{2}$	85	87	
		9			7	8 $\frac{1}{2}$		6	7	8	
6.	Wt.% iso-butane	0			0.05	0.9		0	0	0	
	" N-butane	1.5			2.0	2.7		0	0.7	0.35	
7.	" iso-pentane	3.5			3.9	2.45		5.6	4.25	4.8	
	" N-pentane	2.85			2.25	2.0		2.95	3.3	2.9	
	" Total C ₄ + C ₅	7.65			8.2	8.05		8.55	8.25	8.05	
8.	Reid vap. pressure lbs. sq.in.	4.3		2.9	5.0	5.0	2.3	4.9	4.5	4.1	4.0
9.	Bromine Number	1.1		1.4	0.5	0.7	1.7	0.8	0.6	0.7	2
10.	Aniline point I °C.	22.8			23.7	24.4		20.5	19.6	20.1	
11.	" " IV °C.	58.8		wt.-%(V)	60.3	62.4	wt.-%(V)	63.2	62.5	62.3	wt.
12a.	Aromatics % wt.	36.8		41.0	37.3	38.5	45	43.0	42.3	42.2	41
12b.	Aromatics % vol. (I.C.I.)	32.7			33.2	34.0		32.2	32.6	32.5	

13.	Naphthenes % vol. (")	29.3		16.5		24.9	19.3	18	15.9	18.4	19.1	17
14.	Paraffins % vol. (")	38.0		42.5		41.9	46.7	37	45.9	44.0	43.4	41
15.	Aromatic free density d.15/15	.727		.725		.715		.	.712	.713	.714	
	<u>Knock Rating</u>											
16.	C.F.R. motor, as received	97.5	Camb.	95	Camb.	96.4	97.0	94 $\frac{1}{2}$	97.3	97	97	96
17.	T.E.L. content, mls/Imp. gall.	5.6	rough	6.3	rough	5.5	5.5	6.75	5.6	5.7	5.75	5.6
18.	C.F.R. Motor, lead free	81	cut	82	cut.	82	82	Camb.	83	83	83 $\frac{1}{2}$	Camb.
19.	" " , lead & arom. free	77.7				77.1	78	rough	78.1	79	79	rough cut
	<u>I.C.I. Distillation (Billingham)</u>			Wt. % (V)								
20.	Benzene % Vol. (0-90°C)	7.5	5.2	5.5	7.50	7.35	5.75	6.3	6.5	7.1	6.65	6.8
21.	Toluene % " (0-118)	10.05	11.5	13	12.3	10.4	11.0		12.5	12.2	11.65	11.3
22.	C ₈ aromatics" (118-145)	8.65	Xy. 6.4	13	Xy. 7.3	8.0	9.6		10.0	10.4	10.5	11.1
23.	C ₉ " " (145-166)	2.55				3.8	3.95		3.5	3.65	3.25	
24.	C ₉ " " (166)	4.1		{ 8.5		2.9	3.55		3.75	3.2	3.7	
25.	Total aromatics.	22.9	36		41.5	32.45	33.95	34.2	36.25	36.55	35.75	
26.	Methyl cyclopentane	5.8				5.9	5.8		5.1	5.05	5.1	
27.	Cyclohexane	4.2				3.75	2.95		3.2	2.75	3.65	
28.	2,2,4 Trimethyl pentane (est.)	15				12 $\frac{1}{2}$	13 $\frac{1}{2}$		13 $\frac{1}{2}$	14	13 $\frac{1}{2}$	
29.	Higher " pentane (est.)	5				7	7		7	6 $\frac{1}{2}$	7	
30.	Total T.M.P.	18				19 $\frac{1}{2}$	20 $\frac{1}{2}$		20 $\frac{1}{2}$	20 $\frac{1}{2}$	20 $\frac{1}{2}$	
	<u>Spectro-on fractions (Oxford & Cam.)</u>			rough		rough		rough				
31.	Ethyl benzene	4.2	cut 5.5		cut 6.0		3.0	cut	3.5		4.5	
32.	Hydronenes	1.7	1.6		1.8		1.2		1.5+		1.6	
33.	2,2,4 Trimethyl pentane (+ 2,2 D.M.Hex)	12.1	12.0		13.3			12	1.3		12	
34.	Higher T.M.P. (2,3,4 etc.)	5.8-6.1	6.1		6.1			5	6		5.5	
35.	Total T.M.P.	18.2	18.1		19.4			17	19		17.5	
	I.C.I. Report number	G43/73	-	-	G43/74	G43/75	-	G43/75,	G43/77	G43/78	-	
								79				

S = Analysis by Shell

V = Analysis at Vauxhall Lab.

Other samples generally by I.C.I.

APPENDIX II

AROMATIC HYDROCARBONS.

ANALYSIS

Considerable information about the amount and distribution of the aromatic hydrocarbons is obtained by fractionation and determination of the aromatic content of individual fractions. This method is part of the general Billingham method of analysis (see Appendix V and Refs. 3 & 4). Aromatic contents in the absence of unsaturated compounds are determined quite satisfactorily and with a fair accuracy by the simple aniline point method (before and after sulphonation) already described (Ref. 3 & 4).

This method only allows an estimate to be made of individual aromatics benzene and toluene, and gives a bulk figure for total C₈ aromatics (116-145°C) and some information about the distribution of higher aromatics. Further information about the nature and amount of individual C₈ and higher aromatics is obtained by ultra violet spectroscopic examination of individual fractions (see also Refs. 5, 6, 11, 12 etc.) It is possible to obtain limited information by direct spectroscopic examination without fractionation (table I and Refs. 5, 6, 7 etc.), but the results are not very reliable.

RESULTS

The aromatic composition and distribution obtained by fractionation and analysis by the aniline point method for fourteen green C₈ type gasolines are collected in Table II, which also includes further information on individual aromatics obtained by spectroscopic methods applied to fractions.

In order to deduce possible methods for production of these aromatics it was necessary to examine products from as wide a variety of known sources as possible. The results of such examinations have been given in detail in a number of separate reports (Ref's. 13 - 55) and also in various summary reports (Ref's. 1, 2, 5, 6 & 7) and will be collected in a complete set of analyses to be issued as a further summary report.

Table III is included here, however, to give the relevant information from fractionation on the amount and distribution of aromatics in most of the samples obtained from known sources, while Table IV records most of the additional information obtained by U.V. spectroscopic analysis.

INTERPRETATION OF RESULTS

The green C₈ type of aviation gasoline has always been characterised by the high content of aromatics. In the earliest samples obtained in 1940 (G.F.28-G.F.32) interest arose in the high content (10%) of high boiling (ca 175°C) aromatics. Examination of these aromatics led to the discovery that 1-2% of hydridene was present. Hydridene had also been found in the small amount of breakdown product obtained in naphthalene hydrogenation at 400°C. for tetralin and decalin manufacture. Further spectroscopic examination of this material showed that the monocyclic aromatics were predominantly of the type of normal mono-alkyl benzenes (*i.e.* *t*-ethyl, ethyl, *n*-propyl and *n*-butyl) (*i.e.* would be expected from cracking of naphthalene via tetralin (Hall J.S.C.I. 1935 etc.). It was then confirmed that ethyl benzene was the main C₈ aromatic in the German green gasoline (65% of the C₈ fraction) and also that appreciable amounts of *n*-propyl benzene (3%) and *n*-butyl benzene (at least 2%) were present (Table II).

Extension of the spectroscopic method of analysis to a variety of other products (Table IV) showed that this type of aromatic composition - presence of hydridene and predominance of normal mono-alkyl benzenes was only found in products obtained by destructive hydrogenation of bituminous raw materials, such as naphthalene and creosote. The larger the number of steps used in the hydrogenation process the more these characteristics tend to disappear, but even in the high volatility aviation petrols made in two stages from creosote the amount of ethyl benzene is greater than that of the xylenes (Table IV, line 24 etc.).

In no other products examined were these characteristics found and in general it was concluded that aromatics from all other sources were characterised by:-

absence of hydrindene

relatively small proportion of ethyl benzene in C₈ aromatics

(20-30, or less - table IV) and marked predominance of meta xylene
(m/p ratio approx. 4/1)

relatively small proportion of n-propyl benzene in C₉ aromatics, with marked predominance of ethyl toluenes (particularly meta) and propylcunene.

practically no n-butyl benzene and large amounts of ethyl xylenes etc.

Calling the two types of aromatic composition :-

A = hydrindene and predominance of normal mono alkyl benzenes

B = no hydrindene and predominance of poly alkyl benzenes (particularly meta)

it will be seen from Tables II & IV that the samples examined can be divided into these classes :-

Type A Hydrindene & predominance of normal mono-alkyl benzenes

- (1) Products from destructive hydrogenation of :
naphthalene (in tetralin manufacture) (table IV line 26)
creosote (in various stages of gasoline manufacture) (table IV, lines 22-25)
- (2) German green C3 type aviation gasolines (table II)

Type B No hydrindene & predominance of meta poly alkyl benzenes

- (1) Probably most natural virgin gasolines and naphthas from petroleum (table IV lines 1-8)
- (2) Products from destructive hydrogenation of petroleum gas oils (table IV lines 19-21)
- (3) Products from direct hydroforming of petroleum naphthas (table IV lines 12-14)
- (4) Products from dehydrogenation (hydrofining) of petroleum naphthas of aviation boiling range.
- (5) Products from dehydrogenation (hydrofining) of hydro-naphthas of aviation boiling range whether these have been produced from petroleum or bituminous raw materials (table IV lines 16-18)
- (6) Aromatic oils from coal carbonisation (table IV lines 9-11)

Table III lists the amount of aromatics and the distribution for 43 materials from various known sources, largely arranged in ascending order of aromatic content.

It will be seen that most natural naphthas are immediately excluded from consideration as possible source of aromatics in green fuel, on the ground that the total aromatic content is too low (table III) and the distribution differs from that in the green fuels (tables III and IV). The above evidence would also exclude any aromatic extract obtained from such sources, while Borneo and Venezuelan 'B' naphthas, which contain more aromatics, have the wrong composition (table IV).

Most normal sensitive-catalyst type of hydrogenation products are also excluded on the ground of the low total aromatic content, although Edelcrude extraction of a low aromatic content hydro-product from a bituminous raw material would possibly fit the analytical evidence.

Apart from Edelcrude extraction other methods of producing a highly aromatic fuel are:-

- (a) Catalytic cracking (e.g. of hydrogenated brown coal tar)
- (b) 'Aromatisation' of Fischer Tropsch products
- (c) Hydrofining or selective dehydrogenation of cyclohexane naphthenes.
- (d) Hydroforming of natural or hydro naphthas.
- (e) Direct addition of aromatics from coal carbonisation (or via hydro-refining)
- (f) Alkylation of coke over benzole
- (g) High temperature aromatising hydro-cracking.

(a) Nothing is known about the composition of the aromatics from catalytic cracking, particularly if this were applied to a suitable hydrogenated fraction of brown coal tar; but it is thought that this process is not being used by the Germans.

(b) Similarly, little is known about the possibility of aromatising Fischer Tropsch products, but it is felt that unless products of high naphthalene contents were available this method would not yield a naphtha rich enough in aromatics and poor enough in paraffins to use for the green fuel.

(c) The hydrofining process of selective dehydrogenation of naphthalenes to aromatics could certainly be used on a suitably naphthenic naphtha to yield material of high enough aromatic content. This process does not entail any noticeable amount of "splitting" and would thus have to deal with a naphtha already boiling in the aviation range (e.g. 80-170°C). If such a naphtha were from a petroleum source it would yield aromatics of the wrong composition and even if it were a product from hydrogenation of a bituminous material our experience shows that aromatic composition would be wrong, since in destructive hydrogenation down to the aviation boiling range the cyclohexane naphthalenes tend to be of the poly-alkyl type and yield xylenes etc. on dehydrogenation. Thus a hydro gasoline from creosote containing 12% aromatics and 3% of C₈ aromatics will have 50-60% of ethyl benzene in the C₈ aromatics. Dehydrogenation will raise the aromatics to 25% and the C₈ aromatics content to 7½%, but the new C₈ aromatics formed are mainly xylenes and the ethyl benzene in C₈ aromatics falls to 30% (cf. table IV lines 24 and 16).

(d) The hydroforming process is similar to the hydrofining process, but is more severe with a small amount of cracking and more aromatisation by some cyclisation and isomerisation. The same arguments apply to this process, namely that treatment of a hydro product already boiling within the gasoline range will give aromatics rich in xylenes.

(e) Examination of several samples of coke oven aromatics have shown these to be of type 'B', (cf. table IV lines 12-15) deficient in ethyl benzene with m-xylene predominating. Coal tar aromatics could not provide for the n-propyl and n-butyl benzene. It is possible that some coal tar benzene is being added to bring the benzene content to about 7%, since it is difficult to account for such a high benzene content by the proposed hydro-aromatisation process proposed below. This would be in keeping with the addition of large amounts (25%) of benzene to motor spirit. The low (0.02%) sulphur content of the green fuel may imply that the benzene is being given a hydro-refining treatment. The remarkably constant ratio of benzene to toluene and other aromatics (table II) rather suggests that these are both formed by the same process and that benzene is not being added separately.

(f) Alkylation of coke oven benzene with olefines derived either from Fischer Tropsch or as 'by products' from dehydrogenation processes designed to produce synthetic octanes or synthetic rubber could be used to produce a higher boiling aromatic mixture. Such a process could be used for the production of ethyl benzene but it is very unlikely that ethyl benzene produced as such would be allowed to go to fuel when this is in demand for styrene. Alkylation would produce isopropyl benzene (cumene) and tertiary and secondary butyl benzenes, but would not yield the normal derivatives. Neither isopropyl benzene nor tertiary butyl benzene have ever been detected in samples of green fuel.

(g) The only process known to produce n-propyl and n-butyl benzenes as well as a preponderance of ethyl benzene and little xylenes is that involving the cracking of material containing polycyclic aromatics such as naphthalene. It is known that high temperature (500°C or more) hydrogenation of creosote oil from bituminous coal can give low volatility highly aromatic naphthas containing aromatics of this type. The hydrindene will be produced from indene present in the creosote.

NOTES ON SUGGESTED PROCESS FOR PRODUCTION OF AROMATICS BY HIGH TEMPERATURE "HYDRO-AROMATISING."

U.K. experience with this type of process is very limited, but it is known that for many years before the war I.G. Farbenindustrie were very keen on so-called "aromatising" processes which all produce highly aromatic material of low volatility. It is also known that the Welheim plant was designed to hydrogenate pitch in the liquid phase at a temperature of 490°C., and a high pressure of 700 ats. and that this process gave a 'liquid phase' petrol which contained as much as 70% of aromatics.

U.K. limited experience some years ago of vapour phase aromatisation of creosote middle oil (170-300°C) at 200 ats. and 530°C. indicated that the process was unsatisfactory on recycle due to loss of catalyst activity. The conversion to a 180°C. end-point naphtha was about 45%. The naphtha contained 38% aromatics and had a very low volatility (5% to 70°C, 22% to 100°C). The difficulty of dealing with the still bottoms on a straight through process in view of the apparent absence of any 'normal' vapour phase operation suggests that a recycle process must be used. This would suggest that much higher pressures are being used to overcome catalyst deterioration. It is known that I.G. were doing much work at pressures up to 800 ats. before the war, and it is known that the plants at Stettin, Celsenkirchen, Scholven, Welheim, Magdeburg & Nordstern were constructed to work at pressures up to 700 ats. on bituminous coal. Such high-pressure high-temperature converters will require special steels.

Since no brown coal hydrogenation products or brown coal tars have been available for treatment and examination it is not known whether brown coal would yield 'aromatised' products with the characteristics described, but it is felt that the probability is very high that products from bituminous coal are being used. The actual raw material may be either bituminous coal or any of its products such as creosote, or pitch.

The essential criterion of the process used is that the aromatics are formed directly by cracking of bicyclic (or polycyclic) aromatics in the presence of some hydrogen to prevent olefine and carbon formation and loss of catalyst activity, but at a temperature high enough to prevent any appreciable hydrogenation to cyclohexane. This process is essentially different from the dehydrogenation of naphthenes which have been formed in another hydrogenation process (hydroforming or selective dehydrogenation) since the latter two-stage process gives the wrong type of aromatics.

EVIDENCE FROM THE NON-AROMATIC HYDROCARBON-NAPHTHENES.

The composition of the non-aromatics is considered in Appendix III (octanes) and IV (naphthenes and other paraffins). It is sufficient to point out here that the green fuels are deficient in naphthenes particularly above 85°C. This is considered to be in keeping with the above view of the method of production of the aromatics. The green fuel contains the normal amount of methyl cyclopentane (5%) and cyclohexane (4%) which would be associated with an average gasoline from petroleum, but is very deficient in higher boiling naphthenes, particularly the dimethyl cyclopentanes boiling at 90°C. This, and other factors are considered to be evidence that the green fuel consists of low volatility highly aromatic naphtha of boiling range 95-180°C. produced as above, blended with a light-cut 0-85°C. from some other source.

RECENT CHANGE IN COMPOSITION OF GREEN FUEL AROMATICS.

At the end of 1942 or early in 1943, progressive changes occurred in the green fuel:-

- (1) Addition of 3% more octane and more light petrol causing a reduction in aromatic content from 37% to 33% by dilution, but actually accompanied by a rise in weak mixture rating.
- (2) Still further increase of 2% in octane content with a return to the previous aromatic content of 37% and further rise in weak and rich mixture ratings.

The second part of this change was also accompanied by a marked change in the composition of the aromatics (samples AIR 285 - AIR 328, table II). There was an increase of 1½-2% in toluene, about 2% increase in C₈ aromatics and small increases in higher aromatics, but if anything a decrease in the benzene content. Spectroscopy brought to light even more marked changes:-

- (a) ethyl benzene fall from 6.2% to 3% or less in spite of overall rise in C₈ aromatics, so that ethyl benzene in C₈ aromatics fell from about 65% to about 30%.
- (b) the increase in C₈ aromatics was partly due to meta xylene and para xylene but more remarkable was the sudden appearance of ortho xylene at up to 1.8% where previously none had been detected.
- (c) marked fall in n-propyl benzene from 2% to as low as 0.6% coupled with a rise in ethyl toluenes (particularly meta).
- (d) apparently also a reduction in amount of n-butyl benzene.

These changes are all away from the mono alkyl benzenes previously considered as characteristic of this type of fuel and towards the type of aromatics produced by many other processes.

These changes have also been accompanied with a marked decrease in the amount of higher boiling naphthenes present in this fuel:-

°C.	Naphthenes		Aromatics	
	AIR 189	AIR 317	AIR 189	AIR 317
C ₅ 40-60	Cy. pent.	0.7	1.0	
C ₆ 60-75	Mo. cy. pent.	4.1	5.1	C ₆ benzene
C ₆ 75-84	Cy. hex	5.35	3.25	C ₇ Toluene
C ₇ 84-95	Di-Me. Cy-pent.	0.9	1.2	(ethyl benzene
C ₇ 95-110	Me Cy. hexane	4.65	1.6	3.0
C ₈ 110-125	Di Me Cy. hex	1.55	1.1	5.35
C ₈ 125-137	Et. Cy. hex	2.95	1.1	{ o. xylene
>137		5.8	2.55	{ n-propyl
Total naphthenes		26.0	16.8	{ ethyl toluenes
>95°	16	6	Total aromatics	1.4
				2.75
				36½

In view of the similarity of composition of aromatics in the most recent green fuels with that of hydroformed products, particularly as regards the ortho xylene and the decrease in naphthenes, it is suggested that the aromatised naphtha as made by the high temperature process described above, is now being given an additional treatment, probably by hydroforming which produces xylenes by conversion of the naphthenes. This additional process is being used largely to remove high boiling naphthenes. The decrease in benzene content may imply that benzene is not coming from the aromatising processes, but is being added as benzole. Dehydrogenation is still not complete since some cyclohexanes are still present in the latest fuels (e.g. 1.65% methyl cyclohexane in sample AIR 317).

% of C ₈ aromatics as ethyl benzene	Green Fuel		Hydroformed Iranian Naphtha
	1942	1943	
" " " m-xylene	65	33	23
" " " p-xylene	29	39	48
" " " o-xylene	6	12	10
	0	16	19

The view that the recent increase in weak and rich mixture ratings has been achieved by removal of a large part of the higher boiling naphthenes by hydroforming received some confirmation from the A.I.O.C. experiment in which a sample of green gasoline of the previous type was subjected to hydroforming and considerable increases in ratings achieved.

Type Sample No.	1941		1943 AIR 317-330 as received
	AIR 141 as recvd.	Hydroformed	
% aromatics	37½		36½
Ethyl benzene in C ₈ arom.	65		35
Total % naphthenes	27		17
<u>Knock ratings:</u>			
weak C.F.R. motor	94	95	97 *
Rich 3-C % grade 130	100-110	140	> 125

* due also to addition of further 5% octane and more light petrol.

TABLE II

DISTRIBUTION & COMPOSITION OF AROMATICS IN GERMAN C.3 (GREEN) AVIATION GASOLINE

GREEN GASOLINE REF. NUMBER.	GF 28	40/41	GF 31	GF 32	AIR 141	AIR 144	AIR 176	AIR 189	AIR 235	AIR 305	AIR 311	AIR 317	AIR 318	AIR 328
DATE		1940			1941	1941	1942	1942			1943			
VOL.% on fuel (An.Pt. Method)														
benzene 0 - 90°C	6.2	6.3	6.35	6.55	8.05	10.1	8.5	8.8	7.5	7.35	5.75	6.5	7.1	6.65
toluene 90-118°	7.8	7.55	8.6	7.9	12.2	11.5	12.5	12.3	10.05	10.4	11.0	12.5	12.2	11.65
C ₈ aromatics 118-145°	6.65	6.3	7.55	6.95	9.25	8.55	9.8	9.2	8.65	8.0	9.6	10.0	10.4	10.5
C ₉ " 145-166	3.2	2.5	4.35	3.5	4.15	4.0	4.0	4.4	2.55	3.8	3.95	3.3	3.65	3.25
C ₁₀ etc. >166°	9.55	9.9	10.5	10.6	4.05	4.15	2.6	3.9	4.1	2.9	3.65	3.8	3.2	3.7
TOTAL	33.4	32.55	37.35	35.5	37.7	37.5	37.4	38.6	32.85	32.45	33.95	36.3	36.55	35.75
DISTRIBUTION (% on total arom.).														
C ₆	18½	19½	17	18½	21½	26½	23	23	23	22½	17	18	19½	18½
C ₇	23½	23	23	22	32	31	33	32	30½	32	32½	34½	33½	33
C ₈	20	19½	20	19½	24½	25	26	24	26	24½	27	27½	28½	29½
C ₉	9½	8	11½	10	11	8½	11	11	8	12	11½	9½	10	9
C ₁₀₊	28½	30	26½	30	11	11	7	10	12½	9	11	10½	8½	10
DISTRIBUTION (, on C ₆ +C ₇ +C ₈)														
C ₆	30	51½	23½	30½	27½	33½	25	23	26½	28½	22	22½	24	23
C ₇	32	37½	30	37	41	38	40	41	38½	40½	42	43	41	40½

C ₈	32	31	33 ₁ 2	32 ₂	31 ₂	28 ₁	32	30	33	31	35	34 ₂	35	36 ₂
<u>ULTRA VIOLET SPECTROSCOPIC ANALYSIS</u>														
ethyl-benzene					6.1	5.6	6.2	6.4	4.2		2.45	3.5		
m-xylene					3.15	2.65	2.9	2.5	2.5		3.35	4.15		
p-xylene					0.35	0.35	0.7	0.7	0.7		1.25	1.2		
o-xylene					0	0	0	0	0.95		1.85	1.7		
% ethylbenzene in C ₈ arom.					63	65	63	69	50		28	33		
n-propyl benzene			2		2.0	2.0	2.4	2.0	0.9		0.9	0.6		
m-ethyl toluene			0.5				1.2	1.0	1.75		1.55	2.1		
p-ethyl toluene			0.3				0.4	0.3	0.5		0.5	0.65		
pseudo-cumene							0.6		0.8		1.05	0.8		
n-butyl benzene			0.8		1.9	2	2	res.						
hydrides			1.1		1.4	2.1	1.4	1.44	1.7		1.4	1.5		
naaphthalene											0.08			

TABLE III

BOIL. & DISTRIBUTION OF VARIOUS DISTILLATION PRODUCTS FROM VARIOUS SOURCES
 (all figures vol. % by Aniline Point Method)

	End Pt. °C.	Total Arom. Vol. %	DISTRIBUTION VOL. % ON FUEL					DISTRIBUTION AS % OF AROM.					% Ethyl Benzene in C ₈ Arom.	Hydrin- dones	% Naphthenes in Fuel	
			0-90	90-115	115-145	145-166	166	C ₆	C ₇	C ₈	C ₉	C ₁₀				
			C ₆	C ₇	C ₈	C ₉	C ₁₀₊									
<u>Natural petroleum gasolines</u>																
Russian Fuel AIR 151	152	1.75	0.25	0.5	0.3	0.2	-	15	29	44 ¹ ₂	11 ¹ ₂	-	50	abs.	64 ¹ ₂	
Midway light cut	103	2.05	1.35	0.7	-	-	-	65	35	-	-	-	-	-	39 ¹ ₂	
Reitbrook (Germany)	149	2.6	0.1	0.85	-	1.65	-	62	32 ¹ ₂	63	-	-	-	43	abs.	48 ¹ ₂
Trinidad high octane	95	3.3	2.4	0.9	-	-	-	72	20	-	-	-	-	-	39 ¹ ₂	
Miri aviation	111	3.3	1.15	1.9	0.25	-	-	55	56	7	-	-	-	-	6 ¹ ₂	
Lagunillas light naphtha	140	3.5	0.75	1.75	-	1.0	-	21 ¹ ₂	50	-	26 ¹ ₂	-	-	30	abs.	45
Venezuelan 'A'	153	4.1	0.5	1.15	1.85	-	0.55	12 ¹ ₂	28	45 ¹ ₂	15 ¹ ₂	-	-	-	47	
Kettlerain light cut	111	4.3	1.55	2.75	-	-	-	36	54	-	-	-	-	-	37	
Californian (8127)	124	5.25	1.2	3.3	0.75	-	-	23	53	14	-	-	-	-	45	
Sumatra (Palempong)	96	5.5	5.2	0.3	-	-	-	95	5	-	-	-	-	-	24	
Venezuelan (8020)	143	5.9	0.7	2.35	2.25	-	0.5	12	40	38	-	10	-	-	43	
Shell light cut (SR.164)	112	5.6	2.15	4.45	-	-	-	53	57	-	-	-	-	-	31 ¹ ₂	
Romanian (8247)	126	6.95	1.4	5.0	-	0.6	0	20	71 ¹ ₂	81 ¹ ₂	-	-	-	33	abs.	48 ¹ ₂
Romanian (P.B.)	150	7.35	1.2	3.05	2.4	0.6	0.1	16	41 ¹ ₂	33	8 ¹ ₂	1	-	-	40 ¹ ₂	
Lagunillas gasoline	214	7.5	0.5	1.2	2.05	1.05	2.75	6	16	27 ¹ ₂	14	36 ¹ ₂	-	-	47 ¹ ₂	
Shell 73 octane	151	10.9	1.5	4.6	3.7	1.1	-	14	42	34	10	-	-	-	44 ¹ ₂	
Venezuelan 'B'	163	21.0	1.4	3.5	8.8	2.3	4.7	6 ¹ ₂	17	42	12	22 ¹ ₂	10	abs.	29 ¹ ₂	
Borneo 'C' grade	178	28.3	3.9	9.4	8.1	3.95	2.95	14	33	29	14	10	17	abs.	35	
<u>"Normal" hydrogenation gasolines</u>																
Creosote 'saturated' product	290	21.6	0.7	1.0	1.85	1.0	17.05	3 ¹ ₂	4 ¹ ₂	8 ¹ ₂	4 ¹ ₂	79	65	0.9	75	
From creosote H.O.	200	6.65	1.25	1.2	1.35	0.5	2.3	16 ¹ ₂	18 ¹ ₂	20 ¹ ₂	8	35	56	0.29	63 ¹ ₂	
" " "	150	2.0	0.75	0.95	0.7	0.25	0.15	26 ¹ ₂	34 ¹ ₂	25	9	5 ¹ ₂	50	0.05	54	
" " "	145	4.25	1.7	1.35	1.1	0.1	-	39	32	26	3	-	-	-	50	
" " "	130	12.9	4.45	5.4	3.05	-	-	34 ¹ ₂	42	23 ¹ ₂	-	-	-	50	(low F.B.P.)	41
" " H.O.	130	15.35	4.7	8.25	2.4	-	-	31	54	15	-	-	-	59	(low F.B.P.)	44 ¹ ₂
From petroleum gas oil	200	10.2	0.7	2.05	2.9	2.1	2.45	7	20	28 ¹ ₂	20 ¹ ₂	24	20	abs.	41 ¹ ₂	
								18	56 ¹ ₂	25 ¹ ₂	-	-	25	abs.	33 ¹ ₂	

150	8.42	1.4	4.4	0.75	-	-	21	67	11	-	-	28	abs.	52 $\frac{1}{2}$
150	6.55	1.4	4.4	0.75	-	-	11 $\frac{1}{2}$	56	45	7 $\frac{1}{2}$	-	-		32
(Hydro-Albenian) (Intern)	11.4	9.1	1.1	3.45	4.35	0.7	11 $\frac{1}{2}$	56	45	7 $\frac{1}{2}$	-	-		42
257	3.2	0.55	1.5	1.3	-	0.05	17	40 $\frac{1}{2}$	40 $\frac{1}{2}$	1 $\frac{1}{2}$	-	-		
<u>Hydro-refined (cat. dehydro).</u>														
Hydro-cracke gasoline	140	20.4	4.5	10.4	7.5	-	20	45 $\frac{1}{2}$	33 $\frac{1}{2}$	-	-	31	abs.	31 $\frac{1}{2}$
Hydro-petroleum gasoline	140	15.8	1.4	3.3	4.1	-	10	60	30	-	-	17	abs.	25
Hydro-petroleum (SO ₂ extract)	160	70	2	23	34.5	10.5	5	52	50	15	-	8	abs.	
<u>Hydroformed</u>														
East Texas naptha	150	51.5	4.2	11.7	11.15	4.2	13	37	35 $\frac{1}{2}$	14	-	20	abs.	25.1
Iraqi naptha	153	58.8	4.9	20.5	25.9	5.9	2.6	6	55	40	6 $\frac{1}{2}$	42		6.2
Iranian naptha No. 1	162	49.3	5.2	12.0	15.8	0.0	6	32	40	-	20	23	abs.	12.5
Iranian naptha No. 2	188	50.4	2.5	14.9	21.6	5.5	4.4	5	30	43	15	19	abs.	7.0
Hydro-cracke 156-200° naptha	210	61.5	6.8	3.4	7.1	9.7	40.5	1 $\frac{1}{2}$	55	11 $\frac{1}{2}$	15 $\frac{1}{2}$	66	5	29
<u>High Temperature Aromatization</u>														
'Aromatised' creosote	180	38.2	4.5	9.8	10.2	9.5	4.2	12	25 $\frac{1}{2}$	26 $\frac{1}{2}$	25	11		52.7
Fores ex tet & dec.	187	36.6	0.3	1.1	9.8	-	27.4	1	5	25	71	87	8.8	61
<u>Aromatics from Coal Carbon.</u>														
Gas spirit	ca95	67.9	0	9.5	51.5	4.5	1.4	0	14	76	6 $\frac{1}{2}$	3 $\frac{1}{2}$	11	abs.
Coke oven spirit	100	0	32	63	5	0	0	32	63	5	0	< 10	abs.	
Coke oven 'Xylanes'					>95									
<u>Catalytically Cracked Petroleum</u>	251	13.0	1.5	5.25	5.1	1.1	tr.	11 $\frac{1}{2}$	40 $\frac{1}{2}$	39	8 $\frac{1}{2}$	-		32 $\frac{1}{2}$

TABLE I

COMPOSITION OF INDIVIDUAL IRGOMITES IN A VARIETY OF CARBOILITES & BURNING AGENTS FROM KNOWN SOURCES

	By fract. & An. Point.			U. V. SPECTROSCOPIC RESULTS											
	Total Aroms.	Benzene	Toluene	C ₈ Aromatics				C ₉ Aromatics				C ₁₀			
		0-90°C	90-118°C	Ethyl benz.	m	p	c	n	Ethyl tol.	trimethyl n-but.	1,2,4	1,3,5	benz.	Hyd. in-% denos	% eth.benz in C ₈ arom.
<u>Straight run petroleum naphthas</u>															
1. Russian fuel N.R. 151	1.8	0.3	0.5	0.4	0.3	0.1	0	0.2	no higher aromatics present				abs.	50	
2. Reitbrook (Germany) gasoline	2.5	0.1	0.85	0.55	0.3	0.3	0	0.36	0.11				abs.	48	
3. Lagunillas light naphtha	3.5	0.75	1.75	0.25	0.45	0.15	0	no higher aromatics present				abs.	30		
4. Romanian 82+7	7.0	1.4	5.0	0.2	0.3	0.1	0	abs.				abs.	33		
5. Reitbrook naphtha	12.2	0	0	0.3	0.15	0.15	0	0.2	1.2	3.6	1.0	abs.	50		
6. Lagunillas heavy naphtha	17.6	0	0.15	0.5	0.65	0.2	0.3	0.4	0.2	0.2	0.7	0.5	abs.	30	
7. Venezuelan 'B'	21.0	1.4	3.5	0.9	5.9	0.8	1.3	tr.	1.4	0.4	0.65	0.35	abs.	10	
8. Borneo 'C' grade	28.3	3.9	9.4	1.3	5.4	0.9	0	0.55	1.6	0.4	1.2		abs.	17	
<u>Aromatic oils from coal</u>															
9. Gas spirit	67.9	0	9.5	5.9	28.3	8.2	8.5	ca	0.1	0.05	0.05		abs.	11	
10. Coke oven spirit	ca 95	0	32	0.3	39.0	9.15	ca	0.2				abs.	<1		
11. Coke oven 'xylenes'	>95			>5	ca 75	ca 23							abs.	<10	
<u>Hydroformed</u>															
12. ex petroleum East Texas naphtha	31.3	4.2	11.7	2.3	6.05	1.3	2.0	0.9	0.5	1.0	0.6	abs.	20		
13. " " Iranian No. 1	40.3	5.2	12.8	3.6	7.4	1.65	2.85	1.5	3.6	0.9	0.8	0.4	abs.	23	
14. " " Iranian No. 2	50.4	2.5	14.9	5.5	11.75	3.05	2.5	res.	1.1	0.65	3.5	1.5	abs.	24	
15. ex hydro-cresote (130-200°C)	61.5	0.8	3.4	2.0	3.75	0.95	0.4	1.4	6.8	2.25	2.3	res.	5.0	26	
<u>Selective dehydrogenation (hydrorefining)</u>															
16. from hydrogenated creosote (130° end pt.)	22.4	4.5	10.4	2.35	4.1	1.05	0	no higher aromatics				abs.	31		
17. from hydrogenated petroleum													abs.	<17	

APPENDIX III

COMPOSITION OF SYNTHETIC OCTANES IN GERMAN GREEN AVIATION GASOLINE:

A. FRACTIONATION & ANALYSIS BY ANILINE POINT:

The results obtained by fractionation in 30-40 plate stills and analysis of fractions by the aniline point method (Ref. 3,4) are collected in Table IX, Appendix IV. This method applied to the first samples of the green fuel received in 1940 showed that some 10% of the fuel consisted of paraffins boiling at about 99°C. These fractions after freezing from small amounts of toluene had high aniline points of above 72°C (see Table XIV Appendix V) and of high octane number.

The presence of 2,2,4 trimethyl pentane was confirmed by infra red spectroscopic analysis.

It was also found that a further 4% of paraffins distilled at about 108-111°C and when freed from toluene these were also found to have a high octane number. Spectroscopic analysis showed this fraction to consist largely of 2,3,4 trimethyl pentane (which apparently distils at a lower temperature in the presence of much toluene.)

Two rough methods for estimation of the amount of trimethyl pentanes from these figures have been used:-

- (a) from octane numbers of aromatic-free fractions by calculation
- (b) by assuming figures for the small amount of normal heptane and dimethyl hexane present in the basic fuel.

In this way it has been possible to arrive at a rough estimate of the amount of 2,2,4 trimethyl pentane and the amount of "higher boiling trimethyl pentanes" present in such fuels. The figures deduced in this way are given in Table I lines 28-30 (Appendix I) and are to be compared in a number of instances with the results obtained by infra red spectroscopy. (Table I lines 33-35). In general the fractionation method gives a useful rough figure for total trimethyl pentanes and an approximate figure for the proportion of 2,2,4 trimethyl pentane. This method of course gives no information about the individual higher boiling trimethyl pentanes or dimethyl hexanes and would be badly in error if there were large changes in the amount of N-heptane present.

These rough figures are:-

	1940				1941			1942			1943			
	GF	No.	GF	GF	AIR	AIR	AIR	AIR	AIR	AIR	AIR	AIR	AIR	AIR
28	40/41	31	31	32	141	144	176	189	235	305	311	317	318	328
2,2,4 tri-mo. pent.	9	9	10 $\frac{1}{2}$	10	12 $\frac{1}{2}$	12	11	7	13	12 $\frac{1}{2}$	13 $\frac{1}{2}$	13 $\frac{1}{2}$	14	13 $\frac{1}{2}$
higher boiling TMP ^a	3	3	3 $\frac{1}{2}$	3 $\frac{1}{2}$	4 $\frac{1}{2}$	5	4	8	5	7	7	7	6 $\frac{1}{2}$	7
Total	12	12	14	13 $\frac{1}{2}$	17	17	16	15	18	19 $\frac{1}{2}$	20 $\frac{1}{2}$	20 $\frac{1}{2}$	20 $\frac{1}{2}$	20 $\frac{1}{2}$
% 2,2,4 in total TMP	75	75	75	74	73	71	74	46	72	64	66	66	67	66

These rough results show that there have been small increases in total trimethyl pentanes on several occasions, the most marked increase being at the end of 1942 or early in 1943. With the sole exception of sample AIR 189 these rough figures would indicate that the same type of octane containing 75% 2,2,4 trimethyl pentane had been used throughout.

B. ANALYSIS BY INFRA RED SPECTROSCOPY:

It was considered that a detailed knowledge of the composition of the octane components might enable a conclusion to be reached as to the type of process being used. The method which has been used mostly has been to use the fractions produced in the 30 plate distillation of 6-8 litres of material done at Billingham for analysis by aniline point method.

Since toluene interferes it is necessary to analyse the toluene free fractions. Generally toluene has been removed by shaking with 98-99% sulphuric

acid. It has been realised that this method may cause decomposition and isomerisation of the trimethyl pentanes and time of contact with acid was consequently reduced to a minimum (5-10 minutes) when it was felt that little decomposition occurred, at least as regards 2:2:4 trimethyl pentane. Recently it has been possible to remove toluene by azeotropic distillation with methanol followed by refractionation. The composition found for the octanes by this method (ref. 81) is practically identical with that found by the much more rapid method of acid washing, so that it is concluded that the rapid acid washing method is fairly satisfactory provided time of contact is kept short.

I. Reference Synthetic Octanes - Characteristics:

In order to identify the method of manufacture it would be desirable to examine a very wide field of alkylates and hot and cold hydrocodimers made under all varieties of conditions, but unfortunately relatively few samples representative of different types of processes have been available, but the samples examined appear to show sufficiently well defined differences in composition for these to be assumed to be characteristic of the processes in question. Table V gives the infra red analyses of only five samples, but the general conclusions appear to be well supported by other analyses reported in the literature.

The main points are:-

(a) C₄ alkylates are characterised by:-

1. A preponderance of 2:3:3 trimethyl pentane as compared with 2:3:4 T.M.P. (1.4/1)
2. Little or no 2:2:3 trimethyl pentane (less than 1%)
3. Relatively little 2:3 dimethyl pentane
4. The presence of appreciable amounts of dimethyl hexanes (10-15%)
5. The presence of an appreciable amount of 2:2:5 trimethyl hexane. (5%)

(b) C₄ hydrocodimers (U.O.P. phosphoric acid type and possibly hot sulphuric acid types) are characterised by:-

1. A preponderance of 2:3:4 trimethyl pentane as compared with 2:3:3 T.M.P.
2. More 2:2:3 trimethyl pentane than alkylates (5-10%)
3. Appreciably more 2:3 dimethyl pentane than alkylates (10%)
4. Much less dimethyl hexanes than in alkylates (Generally less than 2%) and generally present as 2:2 dimethyl hexane, whereas alkylates contain more of the 2:4 and 2:5 isomers.
5. Much less 2:2:5 trimethyl hexane than alkylates (less than 1% or not detected)
6. Sometimes if a sharp cut has not been made some hydro-trimer may be present (such as a pentamethyl heptane B.P. 170-180°C)

C₄ hydrocodimers (cold acid type) characterised by:-

Main component is 2:2:4 trimethyl pentane which generally amounts to 85-95% of the product. Other components probably 2:3:4 T.M.P.

The content of 2:2:4 trimethyl pentane is little guide to identification unless this is above 80% which would indicate a cold-acid type of octane. The amount of 2:2:4 T.M.P. is known to vary from as low as 10% up to as high as 60% or more in hot acid octanes and alkylates, depending very much on temperature of polymerisation etc.

The appreciable content of 2:3 dimethyl pentane in U.O.P. type octane from the Heysham Plant is possibly due to the presence of some propane in the butane and may not be entirely characteristic of this process.

Other alkylates (not reported here) have apparently had a very similar composition and several authors have noted that the presence of dimethyl hexanes and 2:2:5 trimethyl hexane is characteristic of this process.

Nothing is known of the composition of possible cross-polymers such as C₃-C₅ alkylate, C₄-C₅ alkylate, C₄-light petrol alkylate etc. etc. It is

considered that these will have a more complex composition and will probably contain more single branch paraffins such as are beginning to appear in C₄-C₄ alkylates.

TABLE V
REFERENCE SYNTHETIC OCTANES (VOL. 1)

(Characteristic Hydrocarbons which differentiate two types are marked 'C')

	B.P. ^{CC}	Alkylates				Hydrocodimers			
		Aruba I.A.A. 119	Baton Rouge I.A.A. 122	Texas P.R.F. 798	Standard P.P.F. 785	Aruba A204	Heysham HG. 6 45/3/60	Standard Indiana N.A.G.A.	
<u>Trimethyl pentanes</u>									
2:2:4	C 99.2	30.95	22.5	22.4	30.7	12	30.0	26.5	9.9
2:2:3	C 109.8	2.7	1.0	11.5	1.6	18	8.25	8.5	9.2
2:3:4	C 113.5	13.0	9.5	14.8	9.0	28	36.75	34.35	43.9
2:3:3	C 114.7	18.0	14.5	10.4	14.5	28	5.5	4.1	8.6
Total		64.7	47.5	49.1	55.8	86	80.5	73.5	71.6
<u>% Distribution of trimethyl pentanes</u>									
2:3:4	C 48	47½	45½	55	14	37	56	14	
2:2:3	C 4	2	3	3	21	10	11½	13	
2:3:4	C 20	20	30	16	32½	45½	46½	61	
2:3:3	C 28	50½	21½	26	32½	7½	5½	12	
<u>Other characteristic components</u>									
2:2 dimethyl hexane	C 106.8	-	-	-	2	2.0	1.95	1.2	
2:5 " "	C 109.1	4.2	4.0	5.2	1.0	-	-	2.7	
2:4 " "	C 109.4	3.3	2.5	5.1	7.1	-	-	4.0	
5:3 " "	C 111.9	-	-	0.9	0.5	-	-	-	
2:3 " "	C 115.6	0.95	1.4	3.4	3.7	-	-	2.15	5.6
2:3 dimethyl pentane	C 79.2	-	<0.05	-	-	-	1.25	1.2	
C7 2:4 " "	C 80.6	3.65	3.3	6.2	3.6	-	2.2	1.6	1.2
2:3 " "	C 89.7	2.5	2.1	3.4	1.6	-	11.65	7.9	1.1
2:2 dimethyl butane	C 49.8	-	-	0.5	-	-	-	-	
C6 2:5 " "	C 58.0	4.55	5.35	8.1	6.1	-	0.9	0.75	
2:2:5 trimethyl hexane	C 124.1	5.65	5	8.8	12.7	-	v.small	v.small	
C9 2:3:5 " "	C 131.4	-)	1.9	1.9	-	ca 2	ca 2	
C10 2:2:6 trimethyl etc. heptane		ca 2.5) 9			-	small		
other high boiling paraffins		3)	1.7	2.4				
<u>Single Branch</u>									
C6 2 & 3 methyl pentanes	C 60-63	1.45	1.4	3.9	2.7	-	0.1		
C7 2 & 3 methyl hexanes	C 69-91	0.4	0.2	1.7	0.9	-	0.1	0.4	
Butanes and pentanes	C <40	4.4	18.7	18.7	20.0	1		1	

* A.P.I. N.E.S. analyses by Augustus R. Glasgow by fractionation and analysis by refractive index.

All other figures for Aruba and Baton Rouge alkylates, Aruba and Heysham hydrocodimers, determined by fractionation & analysis by infra red spectroscopy

II. German Aviation Gasolines - C3 Green Type:

14 samples have been fractionated and analysed by aniline point method which gives fairly satisfactory figures for total 2,2,4 T.M.P. and total octanes 105-115°C (2,2,3, 2,2,4 and 2,2,5 etc.)

5 samples have been analysed in detail by infra red methods applied to separate aromatic-free fractions and also applied to one sample freed from toluene by azeotropic distillation.

4 samples have been analysed without or with only rough fractionation.

Spectroscopic analysis of individual fractions is the best method, but the other data is included as confirmatory evidence.

TABLE VI

Sample		Fine fractionation & aniline point method			Fine fractionation & infra red analysis			Uncut or rough fracn. & infra red		
NO.	DATE	2,2,4 T.M.P.	Higher T.M.P.'s	Total in T.M.P.	2,2,4 T.M.P.	2,3,4 etc.	Total in T.M.P.	2,2,4 T.M.P.	2,3,4 etc.	Total % T.M.P. in T.M.P.'s
GF28	Summer '40	9	3	12	75					
40/41	Sept. '40	9	3	12	75					
GF31	Autumn '40	10 $\frac{1}{2}$	3 $\frac{1}{2}$	14	75					
GF32	" '40	10	3 $\frac{1}{2}$	13 $\frac{1}{2}$	74					
AIR141	Juno '41	12 $\frac{1}{2}$	4 $\frac{1}{2}$	17	73	11	5	16	69	
AIR144	July '41	12	5	17	71	12	5	17	70	
AIR176	April '42	11	4	15	74	11 $\frac{1}{2}$	3 $\frac{1}{2}$	15	76	
AIR189	Juno '42	7	8	15	46	8	8	16	50	
AIR285	May '43	13	5	18	72	12	6	18	66	
AIR287									12	6.1
AIR291									13.3	6.1
AIR305	June '45	12 $\frac{1}{2}$	7	19 $\frac{1}{2}$	64					18.1
AIR311	" '43	13 $\frac{1}{2}$	7	20 $\frac{1}{2}$	66					68
AIR312	" '43								12	5
AIR317	(Mid. E)	15 $\frac{1}{2}$	7	20 $\frac{1}{2}$	66	13.0	6.0	19.0	68 $\frac{1}{2}$	71
AIR318										
321, 327	(Mid. E)	13 $\frac{1}{2}$ -14	6 $\frac{1}{2}$	20 $\frac{1}{2}$	67					
AIR328										
330	(Mid. E)	13 $\frac{1}{2}$	7	20 $\frac{1}{2}$	66					
AIR331	(Mid. E)								12	5.5
										17.5
										68

^{xx} Includes 2:2 dimethyl hexane (ca 0.9%) with 2,2,4 trimethyl pentane
⁺ Includes 2:2:3 & 2:3:3 trimethyl pentanes with 2:3:4 trimethyl pentane
^x On material freed from toluene by azeotropic distillation

TABLE VII
COMPOSITION OF TRIMETHYL PENTANES (Infra Red Method)

Fuel	AIR 141	AIR 144	AIR 176	AIR 189	AIR 285	AIR 317
<u>Vol. % on Fuel</u>						
2,2,4 T.M.P.	11.0	12.0	11.5	8.0	12.1	13.05
2,2,3 T.M.P.	-	trace?	-	-	0.6	1.2
2,3,4 T.M.P.	5.0	5.0	4.0	8.0	4.6	4.1
2,3,3 T.M.P.	trace?	-	0.5	-	0.6	0.7
2:2 dimethyl hexane						0.25
2:4 " "					0.33	0.10
2:3 " "						0.23
2:3:5 trimethyl hexane					absent	

^x freed from toluene by azeotropic distillation (Ref. 81)

TABLE VIII

DETAILED COMPOSITION OF PARAFFINS OF FUEL A.I.R.285IN COMPARISON WITH KNOWN OCTANES:

(fractionated in 40 plate still and toluene removed by acid washing)

A.I.R. 285

	Vol. % on fuel	Vol. % on added octane (calc.)	C ₄ Alkylate	C ₄ Hot acid (U.O.P.)	C ₄ Cold Acid
<u>C₈</u>					
2,2,4 trimethyl pentane	12.07)	55)	20-30	30	90
2,2,3 " "	0.62)	3)	1	10	
2,3,4 " "	4.60) ¹⁷	21) ⁸¹	10-15	35	5-10
2,3,3 " "	0.56)	2.5)	15-20	5	
2:4 dimethyl hexane	0.33	1½)		
2:2 " "	not det.	0) 8-10	<2	
<u>C₇</u>					
2:3 dimethyl pentane	1.62	8-9	2	10	
2:2 " "	not det.	0) 4	2-3	
2:4 " "	not det.	0)		
3:3 " "	0.14	?	0	0	
2 methyl hexane	0.69	nil (?))		
3 methyl hexane	0.50	nil (?)) 0.5	0	
<u>C₆</u>					
2:3 dimethyl butane	0.95	4 (?)	4-5	1	
2:2 " "	0.1	0.5 (?))		
2 methyl pentane	0.97	nil (?)	2	0	
3 methyl pentane	(0.4 +)	nil (?))		
<u>C₉</u>					
2:2:5 trimethyl hexane	not detected	0	5	<1	
2:2 branched paraffins B.P. 175°(hydro-trimer)	present (say (say 2%)	say 5%		may be present	
	say 22%	100			

DISCUSSION AND CONCLUSIONS:

It is concluded from the small amounts of dimethyl hexanes and the preponderance of 2:3:4 trimethyl pentane with relatively little 2:3:3 trimethyl pentane and the absence of any 2:2:5 trimethyl hexane that the added octanes are not alkylate.

The predominance of 2:3:4 trimethyl pentane, the presence of 2:2:3 trimethyl pentane and 2:2 dimethyl hexane as well as the presence of more 2:3 dimethyl butane and 2:3 dimethyl pentane than would be expected to be in the base fuel, all point to the material being a hydrocodimer. This is also supported by the presence of about 2% of multi-branched paraffins boiling about 175-180°C which is probably a small amount of hydrogenated trimer.

The close similarity with hydrocodimer is brought out in Table VIII above where it would appear that fuel A.I.R.285 contains about 22% of octane material, 81% of which is actually trimethyl pentanes.

The main difference between this material and the Heysham octane is that the German material is richer in 2:2:4 trimethyl pentane and is thus nearer to a cold acid octane.

It is suggested that the process used is actually involving phosphoric acid type catalyst operated at a low temperature and high throughput with incomplete conversion and a high proportion of 2,2,4 T.M.P. and a low make of trimer, so that the whole product can be hydrogenated directly and put into the green fuel together with the 10-15% trimer. The unpolymerised olefines possibly with other olefines and propanes, butanes and pentanes are then passed to alkylation to yield a fairly poor quality alkylate which goes to the B4 blue aviation fuel.

It is possible that this process uses butanes from the hydro-aromatisation process which operated at high temperature would be richer in normal butane.

It is also possible that the addition of a dehydrogenation (hydroforming?) process to the aromatised naphtha (as has been suggested for recent samples of green fuel) would produce more butanes and so increase the availability of octane.

COMPOSITION OF COMBINE FUEL - POSSIBLE MAKE-UPANALYSIS:

Table IX gives details of the distribution of paraffin and naphthalene hydrocarbons in fourteen samples of the green fuel as determined by the method of fractionation in 30-40 plate columns and analysis by the "smooth-curve" aniline point method.

The absolute accuracy of such a method is not high due to deviations of the aniline points of actual paraffins and naphthalenes present in narrow cuts from the smooth curve relating average aniline point and boiling point. The magnitude of the errors introduced by this method and other factors tending to cause incorrect results are discussed in Appendix V. The results are, however, reasonably consistent and reproducible and hence marked differences in composition will have a real meaning.

INTERPRETATION:

To interpret the results in a comparative sense it is necessary to consider the results of similar analyses of a wide variety of products from known sources. These analyses, which include more than 20 natural petroleum gasolines, a wide variety of hydrogenation gasolines, and a number of other products are to be tabulated in detail in a future report.

The outstanding points about the composition of the non-aromatic hydrocarbons in the earlier samples of the green fuel emphasised in Table IX and X are :-

- (1) Large amount of paraffins distilling in the range 97-112°C and shown to include about 15-20% of trimethyl pentanes (Table IX).
- (2) Low content of pentanes and hexanes as compared with most natural gasolines from petroleum or 'normal' hydrogenation petroils (Table X).
- (3) Relatively high proportion of normal paraffins in the pentanes and hexanes (this is really a deficiency in iso-paraffins).
- (4) Relatively small amounts of paraffins boiling in the range 113-155°C (methyl heptanes, n-octanes, nonanes etc.) and an unusually high proportion of paraffins distilling at about 175-180°C (probably hydrogenated trimer).
- (5) Normal content of C₆ naphthalenes as compared with natural petroleum gasolines, and also a similar ratio of methyl cyclopentane to cyclohexane (approx. 1-1.5 to 1), but a deficiency of methyl cyclopentane and excess of cyclohexane when compared with medium temperature 'normal' vapour phase hydrogenation gasolines (ratio 6 : 1 or higher).
- (6) Deficiency of naphthalenes boiling at 90°C (diethyl cyclo-pentane) when compared with 'normal' hydrogenation gasolines or with such straight run petroleum spirits as 75 octane Ronmin (Table X).

Octane content and Composition of octane-free base naphtha

Fractionation and spectroscopic analysis of fractions 90-120°C has shown (Appendix III) that the green fuel has always contained from 13% to 20% of trimethyl pentanes. Detection and estimation of smaller amounts of other paraffins which probably originate in the synthetic octane added to the base fuel suggest that some 16% to 24% by volume of total synthetic octane material has been added (containing about 80% trimethyl pentanes).

There have been progressive changes in composition with small increases in octane content, which are discussed more fully below, but generally roughly four variations in the composition can be distinguished. Combining all the analytical evidence it is possible to allow for the synthetic octane components added and deduce the composition of the base gasoline to which this has been added.

Table X gives figures obtained in this way for the composition of the variations in base material (octane-froe) in comparison with 73 octane virgin Roumanian gasoline and with several types of hydrogenation gasolines.

The obvious points of difference between the base fuel and Roumanian or normal vapour phase hydro-petrol are :-

- a) Much higher aromatic content of green fuel base.
- b) Lower "front-end" volatility.

Table X also shows that whereas the green fuel compares with Roumanian or some of the lower volatility of "vapour phase" type of hydro-petrol as regards amount of C₅ and C₆ naphthalenes it is very deficient in C₇ and C₈ naphthalenes. The small amounts of such naphthalenes as methyl cyclohexane, dimethyl cyclohexane, and ethyl cyclohexane in what is probably a hydro product from a bituminous raw material, are considered to support the view that such naphthalenes have been destroyed by dehydrogenation or were never formed as in an aromatising splitting process which largely produces aromatics. The comparative absence of such naphthalenes is also considered as evidence against the supposition that green fuel consists of a blend of aromatics added to a base fuel of lower aromatic content and more normal naphthalene distribution.

If the composition of the base material is expressed on the basis of absence of both synthetic octane and aromatics, it is apparent that the distribution of the remaining 45-40% of paraffins and naphthalenes is very different from either Roumanian or normal hydro petrois in that the proportion of C₆ paraffins and naphthalenes is much higher (Table XI).

This fact of the presence of a fairly normal amount of C₆ hydrocarbons relative to C₇ and C₈, and the abnormally low content of 90°C flat (isooctanes and dimethyl cyclopentanes) and the presence of an appreciable amount of cyclohexane compared with the low content of methyl cyclohexane all suggest that the lower part of the fuel has not been produced by the same process as that used for the higher boiling range.

These anomalies suggested that a low boiling fraction containing C₅ and C₆ hydrocarbons of end-point about 85°C was being added to a low volatility highly aromatised naphtha containing comparatively little material boiling below 95°C.

On these grounds it was suggested that the earlier type of green gasoline final blend was made up from :-

- 25-30% ... Light cut of C₅ and C₆ hydrocarbons, mainly boiling below 85°C. Possibly with additional pentane.
- 55-50% ... Low volatility, highly aromatised, naphtha made by destructive hydro aromatisation of a bituminous material. Such a naphtha would have a composition of about 60% aromatics, 30% naphthalenes, 10% paraffins and would have a boiling range essentially 90-175°C.
- 5% ... Refined motor benzole.
- 20% ... Synthetic octane of the phosphoric acid type, but rich in 2,2,4 T.M.P.

It was also argued that the light-cut fraction was not made by "normal" * hydrogenation since :-

- a) This would yield more iso-pentane and less normal pentane.
- b) More iso-hexanes and less n-hexane would be present.
- c) More methyl cyclopentane and much less cyclohexane would be present.

The arguments regarding proportions of iso and normal paraffins would certainly exclude the normal medium temperature hydrogenation process from supplying any appreciable portion of this fuel. These analyses are considered to be fairly reliable.

* The word "normal" hydrogenation is used to distinguish the medium temperature (ca. 400°C) destructive hydrogenation carried out in the vapour phase with sensitive catalysts from the liquid phase process or high temperature 'aromatising'.

VOL.% ON OCTANE-FREE BASIS	GERMAN GREEN GASOLINE		HYDROGENATION (BITUMINOUS)						ROUND- L.M. 75 OCTANE	
	1941-1942 1943		MEDIUM TEMP. CETANIC VAPOUR PHASE			LIQUID PHASE	"RIGHT- ISED"			
	End-Point °C	175	175	200	160	145	130	220	180	126
Iso-pentane	4	8	7	9	12½	18	2.5	0.8	4½	
n-pentane	3	5	2	2	2½	4	1.7	1	3½	
% Iso- in pentanes	55	60	75	32	83	82	60	ca.50	55	
Iso-hexane	3	6½	4½	8½	11	11	2.5	1	7½	
n-hexane	3	4½	1½	2	2½	2	1.4	1	3½	
% Iso in hexanes	50	60	90	83	82	85	65	ca.50	70	
Methyl cyclopentane	6	6½	6½	10	13½	12.2	2.8	3	5	
Cyclohexane	6	4½	2	1.8	2	2.5	1.4	5	5½	
% N.C.P. in C ₆ naphthalenes	50	60	80	85	87	85	65	40	47	
% aromatics	45	50	6½	5½	4	15	30	38	7	
% naphthenes	34	20	63	57½	50	40	62	53	46½	
% paraffins	21	30	30½	37	46	47	8	9	44½	

The estimation of methyl cyclopentane is also considered satisfactory (Appendix V), but the aniline point method tends to over-estimate cyclohexane, and this error is increased by anomalous behaviour on distillation in the presence of large amounts of benzene. Even so there is certainly more cyclohexane present than in 'normal' medium temperature hydro-petrols particularly in the earlier samples of the green aviation fuel.

It has already been pointed out (Appendix II) that more benzene is present than would be expected (unless this is formed from phenol in the raw material). A probable explanation is that since benzol is being added to many other types of fuels some will also go into this aviation fuel. Motor benzole may be added to the raw material being treated for hydro-aromatisation in such a way that the benzole is refined and also partially hydrogenated to cyclohexane. This explanation would account for the larger ratio of C₆ naphthenes to C₆ paraffins than is normally the case.

The earlier type of green gasoline contains more naphthenes than paraffins (when corrected for added octane) and if it is also assumed that the fraction up to 95°C is from a different source the aromatised naphtha fraction 95-175°C will have some such composition as 61% aromatics, 31% naphthenes and only 8% paraffins and is thus similar to the low volatility product from high temperature "aromatisation" of creosote. (Hydro gasoline (4) in Table X).

The absence of any appreciable amounts of alkyl cyclopentanes as compared with normal medium temp. hydro-petrols is also considered to support this view of the process used. The naphthenes remaining in the aromatised naphtha will be largely alkyl cyclohexanes formed by direct hydrogenation of aromatics with little or none of the isomerisation to cyclopentanes which is so characteristic of medium temperature splitting hydrogenation processes.

	Green fuel (oct. free)	Typical medium temp. hydro-petrol
Methyl cyclopentane	...	6
Dimethyl cyclopentanes	...	1½
Ethyl cyclopentane	...	½

Little information is available regarding the composition of hexanes and pentanes made from higher temperature high pressure destructive aromatisation, but it is known that such conditions and also operation of liquid phase processes with less selective catalysts would yield products with higher proportions of cyclohexane relative to methyl cyclopentane and normal paraffins relative to iso-paraffins (see table above and Table X). It is thus possible that such high temperature or liquid phase hydrogenation processes would provide the whole of the base material in the green fuel, although it is still considered that light cut material from another source is being added to increase the front end volatility of the aromatised product.

CHANGES IN COMPOSITION OF NON-AROMATICS IN GERMAN GREEN C-3 AVIATION GASOLINES:

Table IX lists all the samples examined and shows that several changes have occurred. These are :-

(1) End of 1940

End-point reduced from 185°C to 175°C by cutting back the aromatised naphtha. This mainly had the effect of reducing the amount of high boiling aromatics without much change in composition of non-aromatics although octane content was raised from about 16% total to about 19%.

(2) 1941-1942

Little change, apart from slight further increase in octane content.

(3) During early part of 1943

A number of progressive changes occurred :-

a) Further increase in octane content by 5% up to 24% vol.

b) Increase in pentane content from 5-6% vol. up to 10% vol., and also an increase in hexane content from about 4% vol. up to about 8% vol.

These changes at first resulted in a reduction in aromatic content due to the dilution effect of adding 10-15% more material, but later during 1943 the aromatic content was restored to the previous figure of about 36% vol. and this last change was accompanied by :-

c) Marked decrease of 8-10% in the amount of higher boiling naphthenes.

and d) Considerable change over in the composition of the aromatics, away from such mono alkyl benzenes as ethyl, n-propyl and n-butyl towards the meta poly-methyl benzenes such as m-xylene and m-ethyl toluene.

These changes are clearly shown in the following table :-

- V -

TABLE XII
CHANGES IN COMPOSITION OF GREEN AVIATION FUELS

DATE	1941-1942	1943					
Sample No.	AIR 176	AIR 285	AIR 305	AIR 311	AIR 317	AIR 318	AIR 328
<u>Knock Ratings:</u>							
Weak	95	96	96½	97	97	97	97
Rich, % grade 130	ca. 110	118½	124	> 125	> 125	> 125	> 125
Vol.% octane material (total)	18	21	22	24	25	25	25
Vol.% pentane (+ butane)	6.55	9.45	10.2	10.0	10.5	10.25	9.95
" hexanes	4.45	5.85	6.2	8.3	8.4	7.85	8.1
Vol.% total aromatics	37.4	32.9	32.45	33.95	36.3	36.55	35.75
Total naphthenes, vol.%	26.9	25.65	23.5	18.8	16.8	16.6	17.6
Boiling below 95°C	11.2	12.6	12.1	11.15	10.4	9.9	10.95
Boiling 95°C-180°C	15.7	13.0	11.3	7.65	6.4	6.7	6.7
Aromatics below 95°C (benzene)	8.5	7.5	7.35	5.75	6.5	7.1	6.65
Cyclohexane	5.3	4.25	3.75	2.95	3.25	2.75	3.65
Methyl cyclopentane	3.9	5.8	5.9	5.8	5.1	5.05	5.1
Cyclopentane	0.85	1.0	0.75	1.0	0.9	1.0	1.0
<u>Aromatics above 95°C</u>	28.9	25.4	25.1	28.2	29.3	29.45	29.1
C ₇	12.5	10.05	10.4	11.0	12.5	12.2	11.65
C ₈	9.8	8.65	8.0	9.6	10.0	10.4	10.5
C ₉ + C ₁₀	6.6	6.7	5.9	7.6	7.3	6.85	6.95
<u>Naphthenes above 95°C</u>	15.7	13.0	11.3	7.65	6.4	6.7	6.7
C ₇	4.4	2.35	2.8	1.8	1.6	1.85	1.8
C ₈	4.9	4.5	3.7	1.75	2.2	2.2	2.3
C ₉ + C ₁₀	6.4	6.15	4.9	3.1	2.6	2.65	2.6
Ethyl benzene	6.2	4.2		2.45	3.5		
m-xylene	2.9	2.5		3.35	4.15		
p-xylene	0.7	0.7		1.25	1.2		
o-xylene	0	0.95		1.85	1.7		
Ethyl benzene % on C ₈ arom.	63	50		28	33		
N-propyl benzene	2.4	0.85		0.9	0.6		
Ethyl toluenes	1.6	2.25		2.05	2.8		

The most interesting changes are those occurring early in 1943 when apparently a further manufacturing step was introduced to dehydrogenate the higher boiling naphthene present in the aromatised naphtha by some such process as hydro forming or possibly recycle of the aromatised naphtha.

Most of this decrease in naphthene content has occurred in the range above 115°C :-

	> 115°C fraction of recent green fuels		
	1942	1943	
Vol.% of fuel > 115° (T.B.P.)	33	50	2.9
Composition % on > 115° fraction			27½
Aromatics	51	52	56½
Naphthenes	32	32	27
Paraffins	17	16	16½
			19

It should be noted that when 5% more octane and 8% more pentanes and hexanes are present in the most recent 1943 fuels there has actually been a decrease in cyclohexane and in benzene contents. This may be a dilution effect or may indicate that less benzole is being added and that cyclohexane is now being dehydrogenated in the last process. The increase in pentanes and hexanes with a decrease in benzene and cyclohexane would appear to confirm the view that the light cut is a separate component of the blend.

(Changes in true boiling point distribution on fractionation are also apparent. These are discussed in Appendix V and Table XIII).

CONCLUSION:

The most recent type of green fuel is now considered to be made up from the following components :-

Vol.%

- (1) 23% ... Light cut, possibly from hydrogenation providing most of the pentanes, hexanes, and methyl cyclopentane and boiling up to 85°C. This cut would have composition 7% benzene, 29% naphthalenes, 64% paraffins.
- (2) 5% ... Hydro-refined benzole, providing 4 parts of benzole and possibly 1 part of the cyclohexane.
- (3) 42% ... Doubly aromatised naphtha. Made in two stage process :
 - a) By high temp. destructive aromatising hydrogenation of a bituminous raw material to give a low volatility highly aromatic naphtha, possibly of some such composition as :

61%	aromatics
31%	naphthalenes
8%	paraffins

and boiling 95-175°C with little below 95°C.
 - b) This aromatised naphtha is then given a second aromatising treatment (probably different conditions) or is hydro-formed (dehydrogenated) whereby the composition becomes :

74%	aromatics
16%	naphthalenes
10%	paraffins

A certain amount of gas and low boiling hydrocarbons made in this process may supplement components (1) and (4) (see Ref. 40).
- (4) 24% ... Synthetic octane material made by low temp. operation of phosphoric acid process. The composition is approx. :

80%	trimethyl pentanes
12%	other paraffins
8%	hydro trimer

2:2:4 trimethyl pentane forms 70% and 2:3:4 trimethyl pentane about 22-25% of the total trimethyl pentanes.

TABLE IX

NON-AROMATIC HYDROCARBON COMPOSITION OF 14 SAMPLES OF C₃ (GREEN) TYPE OF ENEMY AVIATION GASOLINE:

(Analysis by fractionation and aniline point method. Volume %)

Probable Chief Component	Range °C	GF 28	40/41	GF 31	GF 32	AIR 141	AIR 144	AIR 176	AIR 189	AIR 285	AIR 305	AIR 311	AIR 317	AIR 318-27	AIR 328-30
<-- - - - 1940 - - - - > <-- 1941 -- > < - 1942 - - > < - - - - 1943 - - - - >															
<u>Paraffins:</u>															
C ₄ iso butane)	0	0	0	0	0	0	0.25	0	0	0.05	1.1	0	0	0
C ₄ normal butane)	'Pod'	1.1	2.05	1.2	1.8	2.1	2.1	0.7	1.55	1.65	2.55	3.45	0	0.9
C ₅ iso pentane)	analysis	3.0	5.0	2.75	3.6	2.55	3.0	2.35	3.6	4.35	4.8	3.0	6.9	5.3
C ₅ normal pentane)		2.3	2.8	1.6	2.3	2.4	1.75	3.25	2.35	3.5	2.75	2.45	3.6	4.05
C ₆ methyl pentanes	40-65	3.4	3.95	3.2	3.2	1.3	2.15	1.55	2.5	2.9	3.5	5.1	5.1	4.6	4.7
C ₆ normal hexane	65-80(75)	2.6	2.45	2.55	2.55	2.7	2.15	2.9	1.8	2.9	2.7	3.2	3.3	3.25	3.4
C ₇ 2,2 and 2,4 dimethyl pentanes	(75-85)									0.45	0.7	0.6	0.6	1.0	0.6
C ₇ methyl hexanes	80(85)-95	4.1	3.45	3.4	3.55	2.15	2.45	2.6	1.95	3.0	3.75	3.4	3.2	3.4	3.35
C ₇ normal heptane)	9.75	9.9	11.4	10.45	13.35	15.1	11.9	7.95	12.95	11.9	12.9	13.1	13.35	13.45
C ₈ 2,2,4 trimethyl pentane	95-102														
C ₈ dimethyl hexanes (& T.M.P.'s)	102-113	4.1	3.55	4.5	4.55	5.3	6.55	4.75	8.9	4.8	6.3	5.9	5.75	5.45	6.05
C ₈ methyl heptane	113-123	1.25	1.4	1.15	1.4	0.3	1.0	0.75	2.1	0.65	0.7	0.9	0.5	0.4	0.3
C ₈ N-octane (& T.M. hex.)	123-129	0.4	0.45	0.55	0.55	0.15	0.35	0.25	0.4	0.1	0.3	0.5	0.4	0.3	0.4
C ₉	129-137	1.05	0.75	1.0	1.0	0.6	0.55	0.8	0.4	0.8	0.5	0.9	0.65	0.95	1.1
C ₉	137-153	0.4	0.45	0.55	0.35	0.4	0.2	0.35	0.4	0.5	0.5	0.6	0.8	0.8	0.4
C ₁₀ Same hydro trimer)	>153	2.25	2.6	4.15	3.7	1.6	0	3.3	1.45	2.95	3.05	3.25	3.0	3.05	2.9
etc.															
Total paraffins	?	35.7	38.8	38.0	39.0	34.9	35.35	35.7	35.35	41.5	44.05	47.25	46.9	46.85	46.6
<u>Naphthenes:</u>															
C ₅ cyclopentane	40-60	0.65	0.65	0.75	0.7	0.7	0.75	0.85	0.7	1.0	0.75	1.0	0.9	1.0	1.0
C ₆ methyl cyclopentane	60-75	5.1	5.95	5.0	5.5	3.5	5.45	3.9	4.1	5.8	5.9	5.8	5.1	5.05	5.1
C ₆ cyclohexane	75-84	5.3	4.05	4.0	4.5	5.35	4.55	5.3	5.35	4.25	3.75	2.95	3.25	2.75	3.65
C ₇ dimethyl cyclopentanes	84-95	2.4	2.0	1.55	1.75	0.85	0.95	1.15	0.9	1.6	1.7	1.4	1.2	1.1	1.2
C ₇ methyl cyclohexane + etc.	95-110	5.15	4.9	3.3	3.4	4.2	3.65	4.45	4.65	2.35	2.75	1.8	1.6	1.85	1.8
C ₈ dimethyl cyclohexanes etc.	110-125	2.8	2.25	2.3	2.05	1.0	1.9	1.9	1.55	2.4	1.85	1.3	1.1	1.05	1.15
C ₈ ethyl cyclohexane etc.	125-137	3.1	3.25	2.25	2.5	3.65	2.65	3.0	2.95	2.1	1.85	1.45	1.1	1.15	1.15
C ₉	137-153	1.95	1.85	1.5	1.2	1.85	1.45	1.55	1.65	2.0	1.2	0.8	0.4	1.2	0.7
C ₁₀₊	>153	4.45	3.75	4.0	3.0	6.3	5.8	4.85	4.15	4.15	3.75	2.3	2.15	1.45	1.9
Total naphthenes		30.9	28.65	24.65	25.5	27.4	27.15	26.9	26.0	25.65	23.5	18.8	16.8	16.6	17.65

TABLE X

COMPOSITION OF TYPICAL GERMAN GREEN GASOLINES COMPARED WITH NATURAL PETROLEUM AND HYDROGENATION GASOLINES

(figures mainly by aniline point method - supplemented by spectroscopic methods)

PROBABLE COMPONENTS	TYPE	TRUE B.P. °C	B.P. RANGE IN FRACTn.	GERMAN GREEN C-3 GASOLINES		NATURAL ROMANIAN 73 OCT. 130° END POINT	HYDROGENATION					OPEOS. H.O. LIQ. PHASE	PET.G.O. MED. TEMP. V.P.	
				1943			CREOSOTE MIDDLE OIL		HIGH TEMP. V.P.					
				1940	1941-2		MED.TEMP.	NORMAL V.P.						
Estimated octanes added as vol.% of final blend:														
2:3 dimethyl pentane etc.	C ₇	88-95	1	1	1½	2	-	Ref.No.-	(1)	(2)	(3)	(4)	(5)	(6)
2:2:4 trimethyl pentane	C ₈	95-105	9½	12	12½	13½	-		-	-	-	-	-	-
2:3:4 trimethyl pentane etc.	C ₈	105-112	3½	5	5	5½	-		-	-	-	-	-	-
Hydro trimer (dodecanes)	C ₁₂	ca.175	2½	1	2½	2	-		-	-	-	-	-	-
	TOTAL			16½	19	21½	23½	nil	nil	nil	nil	nil	nil	nil
Calculated vol.% composition of octane-free base:														
Iso-butane	C ₄	-11.5)	0	0	0	0	0.6		0	0.85	4.05	0.75	1.55	0
Et-butane	C ₄	- 0.5)	2.0	2.2	2.3	0.65	1.3		0.2	0.8	2.5	0	2.35	0
Iso-pentane	C ₅	28.0)	0- 40	4.25	3.3	5.3	7.9	4.35	18.0	9.05	7.1	0.8	3.5	23.3
Et-pentane	C ₅	36.1)		2.7	2.9	4.0	5.15	3.35	4.5	2.0	2.15	0.95	2.2	3.35
Cyclopentane	C ₅	49.3	40- 57	0.85	0.95	1.15	1.3	0.6	0.9	0.55	0.35	0.7	0.6	0.9
Methyl pentanes	C ₆	58-63	57- 65	4.15	2.1	4.1	6.3	7.65	10.8	8.55	4.45	1.15	2.5	14.95
Et-hexane	C ₆	68.8	65- 75	3.0	3.15	3.55	4.3	3.4	2.1	1.85	1.55	1.05	1.5	2.0
Methyl cyclopentane	C ₆	71.8	65- 75	6.3	5.3	7.45	6.65	4.9	13.2	10.15	6.55	2.85	2.9	8.9
Cyclohexane	C ₆	80.8	75- 84	5.5	6.3	5.05	4.2	5.45	2.5	1.85	2.1	5.55	1.5	1.1
2:2 and 2:4 dimethyl pentanes	C ₇	79-80	75- 84	trace	small	0.4	0.2	?	small	trace	small	trace	small	0.45
Benzene	C ₆	80.1	65- 90	7.65	11.0	9.45	8.8	1.4	4.4	1.65	1.25	4.5	1.8	1.4
Methyl hexanes	C ₇	89-92	84- 95	2.7	1.75	2.2	1.5	8.3	5.4	5.55	3.3	0.6	2.25	8.65
Dimethyl cyclopentanes	C ₇	90-92	84- 95	2.0	1.25	2.1	1.6	6.45	5.4	6.95	4.0	1.65	1.65	6.5
Et-heptane	C ₇	98.4	95-102	0.9	0.8	0.6	0.5	1.4	0.25	0.25	0.3	0.75	0.7	0.6
Methyl cyclohexane (+ ethyl C.P., Dimethyl hexanes, trimethyl C.P.s)	C ₇	101-103	95-110	5.7	5.1	3.25	2.2	18.25	10.15	9.95	7.95	12.55	4.0	9.5
Toluene	C ₈	ca.108	102-111	0.9	0.75	0.75	0.65	3.6	1.75	1.1	0.55	1.05	1.2	3.5
Methyl heptanes	C ₇	110.6	90-113	9.55	14.9	13.0	15.85	5.0	5.5	1.75	1.2	9.3	4.05	4.4
Dimethyl cyclohexanes (etc)	C ₈	117-120	111-123	1.7	1.2	1.0	0.55	8.0	2.15	3.55	2.3	0.8	1.45	3.75
*M-octane etc.	C ₈	120-124	110-125	2.8	1.95	2.7	1.5	11.0	5.75	6.75	5.85	3.9	2.7	4.85
Ethyl cyclohexane (etc)	C ₈	125.6	123-129	0.5	0.4	0.4	0.5	0.9	0.15	0.25	0.25	0.1	0.95	0.3
Ethyl benzene (U.V.)	C ₈	132	125-137	3.15	3.8	2.5	1.5	1.25	3.0	4.55	3.7	5.05	3.45	1.4
M-xylene (U.V.)	C ₈	136.4)			7.1	5.35	4.35	0.2	1.75		0.75		0.2	0.2
P-xylene (U.V.)	C ₈	138.5)	118-145		3.3	3.2	5.25	0.3	0.95		0.5		0.4	0.4
O-xylene (U.V.)	C ₈	139.2)		0.8	0.9	1.55	0.1	0.25	0.25	0.1	0	0.1	0.1	0.05
Total C ₈ aroms. (An.Pt.) }				8.25	11.4	10.6	13.45	0.6	2.95	1.6	1.35	10.2	6.2	0.75
C ₉ naphthenes	C ₉	137-153	1.65	2.0	1.25	1.05	0.7		0.7	6.95	4.85	8.75	3.8	1.35
M-ethyl toluene(U.V.)	C ₉	161.5)		1.35	2.2	2.75	0		0		0.2		0	
P-ethyl toluene(U.V.)	C ₉	162.1)		0.5	0.65	0.85	0		0		0.05		0	
Pseudo cumene (U.V.)	C ₉	169.2)	145-169	0.75	1.0	1.2	0		0		0.1		0	
Et-propyl benzene(U.V.)	C ₉	159.2)		2.6	1.15	0.8	0		0		0.2		0	
Total C ₉ aroms. (An.Pt.) }				4.05	4.7	4.05	4.5	nil	nil	0.45	0.5	9.5	2.7	nil
C ₉ + C ₁₀ and higher paraffins	C ₉ ,C ₁₀ etc.	>137	2.3	1.6	2.15	2.0	1.5		1.1	3.0	1.5	1.2	4.0	nil
C ₁₀ and higher naphthenes	C ₁₀	>153	4.9	6.9	5.05	2.5	trace		nil	9.9	23.1	10.7	23.1	0
M-butyl benzene (U.V.)	C ₁₀	183.1)		2.5		0			0		0.5		0	
Hydrindenes (U.V.)	C ₉ ,C ₁₀	176-186	>166	1.5	1.8	2.1	2.0	0	0		0.3			
Total C ₁₀ & higher aroms. (An.Pt.) }				12.3	4.45	4.45	4.65	nil	nil	0.15	2.3	4.15	16.4	nil
Base Fuel total vol.%	Paraffins			25	20	27	30½	44½	46½	37	30	9	25	61
	Naphthenes			33	33½	30½	22½	48½	40½	57½	63½	53	44	32.5
	Aromatics			42	46½	42½	47	7	13	5½	6½	38	31	6.5

* More detailed analyses by spectroscopy on these gasolines are reported in following pages.

NOTES ON TABLE X:

The composition of the seven gasolines have been calculated from the figures determined by various joint methods to an octane-free basis allowing for the components which have been estimated in various ways. These figures are only approximate, but provide a rough basis for comparison with various gasolines of known origin.

Composition of the individual higher boiling aromatics is only known in a few cases where spectroscopic analyses have been made.

Other properties of the gasolines from known source quoted in Table X are:-

	Petroleum Aviation	(1)	(2)	(3)	Hydrogenation	(4)	(5)	(6)
Final Boiling pt. ^o C	126	130	139	195	122	220	125	
% distillate + loss to 75 ^o C	11 $\frac{1}{2}$	41	21 $\frac{1}{2}$	19	5	13	46	
" " " " " 100 ^o C	60 $\frac{1}{2}$	77	50	34	22	20	82	
" " " " " 140 ^o C	100	100	67	35	66	42	100	
Reid Vapour Pressure	5.5	7.0	5.6	2	(3)	8	7.6	
pt. of C ₂ + C ₃	5	12	11	12	(4)	7 $\frac{1}{2}$	23 $\frac{1}{2}$	
DR. Motor Octane No.	73.5	79	74	68	77	70	77 $\frac{1}{2}$	

The hydrogenation gasolines (1) to (6) can be distinguished as:-

- (1)) all from creosote middle oil by medium temperature sensitive catalyst
- (2)) "vapour phase" operation with full recycle
- (3)) illustrates a range of end-point and operating conditions
- (4) High temperature(500^oC) "cracking" cracking of creosote middle oil at 210 atm. to yield a low volatility aromatic naphtha of 150^o end point.
- (5) "Liquid Phase" hydrogenation of creosote heavy oil to yield a high end-point low volatility aromatic gasoline. This material requires heavy refining treatment and contains unsaturates and some tar acids and tar bases.
- (6) Medium temperature vapour phase sensitive catalyst destructive hydrogenation of a petroleum gas oil to yield an aviation grade gasoline of high volatility.

TABLE XI
DISTRIBUTION OF NON-AROMATIC C₆, C₇ & C₈ HYDROCARBONS

	Groen C ₈ gasolines (octane free)			Nat. Reurn. 1940 1941- 1942	Mod. temp. crecs end point °C Oct.	Hydrocarbonation						
						High		Cresylo Petr.				
						temp.	180°	220°	H.O.P.	G.O.		
									V.P.			
% C ₆ +C ₇ +C ₈ paraffins, on fuel	13.85	10.15	12.8	14.5	35.3	22.6	21.1	12.65	5.5	10.6	53.9	
+ naphthalenes " "	25.45	23.7	23.05	17.65	47.3	39.9	40.2	30.1	27.05	16.4	31.6	
" P + N " "	69.3	33.85	35.85	32.15	60.6	61.6	61.5	42.75	32.55	27.0	65.5	
As % of C ₆ +C ₇ +C ₈ P+N												
Paraffins 40-65° C.	10.6	6.2	11.5	19.6	9.5	17.5	14.0	10.4	3.0	9.3	22.5	
65-84	7.6	9.3	9.9	13.4	4.2	5.5	3.0	3.6	2.8	5.6	3.1	
84-95	6.9	5.2	6.7	5.3	10.3	8.8	9.0	7.7	1.6	8.4	13.8	
95-102	2.3	2.4	1.7	1.5	1.8	0.4	0.4	0.6	1.9	2.5	0.9	
102-111	2.3	2.2	2.1	2.0	4.5	2.8	1.8	1.3	2.8	4.4	5.5	
111-123	4.3	3.5	2.8	1.7	9.9	5.5	5.8	5.4	2.1	5.4	5.7	
123-129	1.3	1.2	1.1	1.6	1.1	0.3	0.4	0.6	0.2	3.7	0.5	
TOTAL	35.3	30.0	35.0	45.1	41.3	36.8	34.4	29.6	14.4	39.5	51.8	
Naphthalenes 60-75° C	16.0	15.7	20.7	20.0	6.1	19.9	16.5	15.3	7.5	10.8	13.6	
75-84	14.0	18.6	14.1	13.1	6.0	3.8	3.0	4.9	14.6	5.6	1.6	
84-95	5.1	3.7	5.9	5.0	6.0	8.8	11.4	9.5	4.3	6.6	9.2	
95-110	14.5	15.1	9.0	6.0	22.7	16.4	16.2	10.6	33.0	14.3	14.5	
110-125	7.1	5.7	7.5	4.7	18.6	9.4	11.0	13.7	10.3	10.0	7.4	
125-137	8.0	11.2	7.0	4.7	1.5	4.9	7.4	8.6	15.9	12.7	1.9	
TOTAL	64.7	70.0	64.2	54.9	50.7	63.2	65.5	70.4	55.6	60.7	40.2	
% Methyl cyclopentanes in C ₈ naphthalenes	54	45	60	61	47	64	65	76	55	66	69	
% iso-paraffins in total									ca			
Pentanes	61	53	59	61	57	61	62	77	50	61	57	
hexanes	58	40	54	59	69	63	62	74	"	63	63	
heptanes (approx.)				75	C5	95	96	91	"	72	9.1	

* i.e. paraffins distilling between 40° C and 139° C, determined by An.pt. method

+ i.e. naphthalenes " " 57° C and 157° C, " " " " "

NOTES ON METHODS OF ANALYSIS - ACCURACY & REPRODUCIBILITYI. GENERAL NOTE

The method of analysis of petrols used at Billingham for some years has been fully described in various reports (see Refs. 3 & 4).

A fairly simple method was designed to enable a large number of samples to be examined in a reasonably short time and with fairly simple methods for analysis. This policy was adopted because it was realised that any attempt at interpretation of the analytical results could only hope to have any real meaning :-

- (a) if a sufficiently large number of samples of enemy aviation gasoline were analysed so as to give a measure of the limits of fluctuation between different samples. This is necessary so that obviously weathered or contaminated samples could be excluded, and so as to be able to arrive at a satisfactorily representative average analysis.
- (b) if a sufficiently wide range of samples were analysed of aviation gasolines or blending components from known sources or produced by known processes to be able to identify an unknown hydrocarbon mixture as being derived from a particular source by reason of some highly characteristic factors in the composition or distribution of the individual hydrocarbons.
- (c) if the differences in composition of aviation blending components and naphthas from different sources as determined by the method of analysis used were considerably greater than possible errors in the method of analysis.

Obviously some compromise had to be made between highly accurate analysis of only a few samples or approximate analysis of as wide a selection of samples as possible.

Since it had been found that a simple fractionation analysis method (refs. 3 & 4) gave reproducible results and demonstrated that hydrogenation gasolines had characteristics in composition which apparently allowed them to be distinguished from natural petroleum gasoline, it was decided to use this method throughout and apply the results in a comparative way to determine whether the unknown material could contain large proportions of any of the known reference materials examined, or whether differences in composition were great enough to exclude such sources.

The comparative simplicity of this method has allowed it to be applied over a period of four years to :-

- 66 samples of Enemy blue B4 aviation gasoline
- 14 " " " green C3 "
- 3 miscellaneous samples of Enemy Diesel oils and motor gasolines
- 8 synthetic octanes from various sources (and many other Hoysham samples)
- 22 natural petroleum gasolines from a wide variety of sources
- 8 aromatic materials, including coko cycn products, hydroformed, aromatised, 'hydrofined' etc.
- over 100 samples of hydrogenation gasolines from various processes and raw materials.

The method has later been extended considerably on the analytical side by using ultra violet spectroscopic techniques to identify and estimate the individual aromatics in separate fractions from the still, while infra red spectroscopic technique has been used successfully to identify and estimate individual paraffins and naphthenes in the fractions freed from aromatics by acid treatment. (see Refs. 5 - 12)

Methods of analysis have developed very considerably over the last two years, both as regards much improved methods of separation by more efficient fractionating columns and special methods for removal of the interfering aromatics, and also by the rapid development in spectroscopic technique for analysis of the fractions. These latest developments have not yet been applied fully to the problems of analysis of a sample of enemy aviation gasoline since the time taken would be considerably longer than with the present method, and the additional and more accurate information

obtained would only become of value if such elaborate methods could also be applied to the reference materials. Some scattered results are collected in Table XVI.

Recommendation

Since the simpler methods now appear to have defined fairly closely the composition of the green aviation fuel and allowed an interpretation to be put forward as to the probable method of manufacture it may now be worth while analysing a typically representative sample of green gasoline alongside products made by the processes suggested for its manufacture.

II. FRACTIONATION

All the samples examined have been distilled in 7ft. x $1\frac{1}{2}$ " glass columns jacketed to be nearly adiabatic and operated with a reflux ratio of 40 to 60/l. In the earlier distillations the columns were packed with 'Digby' best cyclots and were tested as having 27 theoretical plates. More recently, these columns have been used packed with $\frac{1}{8}$ x $\frac{1}{8}$ " gauze rings, when the test shows 40-60 theoretical plates.

In all cases some 6-8 litres of material is used as a charge to the boiler and about 95% is distilled into about 40-50 separate 2% fractions over a continuous period of about 170 hours operation.

It has been pointed out (ref. 4) that distillation at this efficiency is ample to separate individual hydrocarbons or groups of hydrocarbons, whose boiling points differ by about 5-8°C. or more. This separation gives considerable information alone or when coupled with some method of analysis of the fractions. The next step in separation of individual members of such close boiling groups as occur at 90°C. would require stills of at least 200 theoretical plates, and a considerably longer operating time.

True Boiling Point Distillation & Distribution

Typical distillation curves obtained in the 30-40 plate stills are reproduced in figure (1). In all such distillations these curves show clearly defined 'plateaux' separated by regions where the temperature is rising steeply. The mid-points of such steep slopes have often been used as 'cut points' (see ref. 4) for measuring the amount of material distilling over each plateau. Such figures for the volume percentage distilling between such 'cut-points' are reasonably reproducible and afford a direct means of comparing different samples, since this method of comparison only involves reproducibility of fractionation and does not involve any method of hydrocarbon analysis.

Table XIII lists the "true boiling" distribution for the fourteen samples of green aviation gasoline examined :-

- Cut (1) 0-40°C. is a measure of butanes + pentanes.
- Cut (2) 40-65°C. " " " isohexanes + cyclopentane
- Cut (3) 65-75°C. " " " N-hexane + methyl cyclopentane + about 1½% of benzene
- Cut (4) 75-84°C. " " " cyclohexane + the rest of the benzene
(Cuts (2)-(4) thus measure the C₆ hydrocarbons)
- Cut (5) 84-95°C. is a measure of dimethyl cyclopentane + branched heptanes, but may include some of the 2,2,4 trimethyl pentane if much is present.
- Cut (6) 95-114°C. is a measure of 2,2,4 trimethyl pentane + other trimethyl pentanes and dimethyl hexanes + C₇ naphthalenes (such as methyl cyclohexane) + toluene. The main components here are toluene and trimethyl pentanes.
- Cut (7) 114-130°C. includes such C₈ paraffins as methyl heptanes and N-octane and any trimethyl hexanes and such C₈ naphthalenes as dimethyl cyclohexanes.
- Cut (8) 130-150°C. consists mainly of C₈ aromatics, with small amounts of C₈ and C₉ paraffins and naphthalenes.

Cut (9) 150-170°C includes the C₉ aromatics such as n-propyl benzene and ethyl toluenes, as well as some C₉ naphthenes.

Cut (10) 170-180°C includes hydrides and other C₉ and C₁₀ aromatics as well as some hydrogenated trimer (2,2,4,6,6 pentamethyl heptane?)

Cut (11) > 180°C includes some higher boiling aromatics - possibly n-butyl benzene

Comparison of T.B.P. Figures

The figures for boiling point distribution show that certain changes have occurred, while in other cases, groups of samples are very similar. The main points are summarised Table XIV.

The 1940 material is characterised by the large amount boiling above 170°C. All four samples are similar in this respect. Sample 40/41 has a higher volatility and may have had more added pentane since the whole of this difference is in the 0-40°C fraction.

In 1941 the amount of material boiling above 170°C was reduced by 10% presumably by cutting back the aromatised naphtha. But benzene, toluene and C₈ aromatic contents were increased considerably, presumably by increasing the severity of aromatisation. These factors account for the decrease in >170° fraction and the increase in 75-84° (benzene), 95-114°C (toluene) and 130-150°C. (C₈ aromatics). Part of the increase in 95-114°C fraction is due to about 2½% increase in octane added. It would be expected that simple cutting back to a lower end point would increase the front-end volatility whereas actually there has been a decrease of about 4% in the C₆ paraffins and naphthenes, and possibly 2% in the C₇ compounds. This change again supports the view that the lower boiling fractions are produced in a separate process and that the aromatisation produces very little C₆ paraffins.

In 1942 no further changes were apparent apart from possibly a slight reduction in the octane content.

In 1943 the more volatile lower gravity fuels appeared with lower aromatic content of 32-33%, and about 7% more C₅ and C₆ paraffins and naphthenes. The octane content was also higher. Later during 1943, the amounts of C₇ and C₈ aromatics were increased and the amounts of higher boiling naphthenes considerably decreased.

The two extreme types of this fuel are compared in figure (1), which clearly shows the differences in boiling range distribution.

III ANALYSIS

The method of analysing the separate fractions for aromatics, paraffins and naphthenes by determination of the aniline point before and after removal of the aromatics by sulphonation, has already been described and the errors considered which arise from the use of any type of "smooth-curve" relating boiling point and the average physical property of a series of hydrocarbons (Ref. 4).

It was shown (Ref. 4) that little improvement in accuracy is obtained by using methods based on specific refraction or refractivity intercept and often these methods are less sensitive and require considerably more time than the simple aniline point method.

It was also shown in the above report (Ref. 4) that the "smooth curve" aniline point method is liable to quite large errors when applied to fractions rich in hydrocarbons which have aniline points deviating markedly from such smooth curve relationships. Such compounds as cyclohexane, methyl cyclohexane, ethyl cyclohexane all having lower aniline points are over-estimated, and the associated paraffins under-estimated. 2,2,4 trimethyl pentane may also tend to be over-estimated, while dimethyl cyclopentanes will be under-estimated. These errors are obvious from a consideration of figure (2).

Such errors can be overcome by assuming that particular hydrocarbons are present according to boiling point and then using the correct physical constants for calculation of composition. This is certainly an improvement in many cases, but may lead to other errors, if the exact behaviour of the hydrocarbons in the distillation cannot be defined in relation to boiling point.

The best method appears to be to use spectroscopic methods to identify the components present and then calculate composition from accurately measured physical constants. This would certainly be the most reliable method if distillation could limit the cuts to only two components. Several authors have used the method of superfractionation and identified and estimated the components by direct refractive index measurements. It is felt that this method may be unreliable where anomalous vapour pressure relationships exist, or where the physical constants of the pure components are not sufficiently different.

Presentation of results

The method of presentation of the results obtained by aniline point analysis of separate fractions (see table XV) is to express these as a percentage of the material charged to the still, and so by summation to construct three separate T.B.P. curves for paraffins, naphthenes and aromatics (see figs. (3), (4) and (5)). These are then subdivided into plateau and the results expressed as in table IX. (appendix IV)

In comparing gas-lines of different end-point and possibly with varying amounts of added pentane and also possibly with added aromatics, it has been found preferable to consider the distribution of the C₆, C₇ and C₈ paraffins and naphthenes only. These are divided into 15 main groups which are plotted on a diagram as in figures (7), (8) etc. These 'hydrocarbon pictures' give at a glance the main essentials of the distribution of C₆, C₇ and C₈ non-aromatics (usually about 70% of a normal aviation gasoline) and enable a quick decision to be reached as to which gasolines are similar, and which are not.

ERRORS IN ANILINE POINT METHOD AS AFFECTING MAIN ARGUMENTS & CONCLUSIONS

The aniline point method was checked against a synthetic blend made up from pure components and gave remarkably good results (ref. 8).

Cyclopentane, iso-hexane, N-hexane and methyl cyclopentane are all probably estimated fairly truthfully (see Ref. 5)

Cyclohexane

If any paraffins boiling at 80°C (2,2 and 2,4 dimethyl hexane) are present the aniline point method may tend to over-estimate cyclohexane. Actually, most gasolines contain very little of these paraffins (0.2%). If enough benzene is present cyclohexane will distil as an azeotrope with 50% benzene at 77.2°C. The separation from methyl cyclopentane is then not so good as in the absence of benzene. If very much benzene is present, some of the paraffins normally boiling at 90°C. may distil at 73-79°C. and will lead to marked over-estimation of cyclohexane.

Although the green gasolines contain 6-8% benzene it is doubtful whether the errors made in estimating cyclohexane are large enough to vitiate the argument on this point regarding normal hydro-petrols, which is also supported by evidence from iso/normal ratios in the paraffins and several other points.

Many figures are available from independent estimations of cyclohexane by spectroscopic methods (see ref. 5), which show that generally the aniline point method is not in error to such a great extent even with the green gasolines.

Synthetic	Blond.	Legunillas	Roumanian	Venezuelan	Normal Hydro	Green Gasoline AIR 144	Green Gasoline AIR 176
'Smooth curve' an.pt.	5.0	5.9	5.5	4.5	2.5	0.6	4.6
'corrected'	" "	4.9	5.1	4.7	3.8	2.5	0.6
Infra red		4.5	5.1	6.1	3.9	2.2	0.7

Dimethyl cyclopentanes and iso-heptanes

The relatively high aniline point of the trans form of 1:3 and 1:2 dimethyl cyclopentanes (which distil with the heptanes 2:3 dimethyl pentane, 2 methyl hexane - 3 methyl hexane in an inseparable mixture at 90-92°C) cause these naphthenes to be underestimated and the iso-heptanes over-estimated by use of the smooth curve method (see fig. 2 and Ref. 4.)

The amount of '90°C. flat' in the green gasolines is abnormally small and this fact has been used to support the argument that such gasolines consist of a blend of two fractions with a gap in boiling range at about 90°C.

A small amount of the 90° flat paraffins are brought down to 79°C. when distilling in the presence of excess benzene.

These errors are relatively insignificant and do not affect the main argument regarding deficiency of 90°C. naphthenes. This is supported by spectroscopic analyses (table XVI).

More 2:3 dimethyl pentane has been found by spectroscopy than would be expected in comparison with the other heptanes 2 methyl and 3 methyl hexane. It is suggested that this has come from the added synthetic octane.

Methyl cyclohexane, N-heptane and 2,2,- trimethyl pentane

The very high aniline point of 2,2,4 trimethyl pentane and the low A.P. of methyl cyclohexane results in over-estimation of 2,2,4 T.M.P. and under-estimation of the 100°C.'naphthenes' (methyl cyclohexane and ethyl cyclopentane). It is impossible to estimate N-heptane in such mixtures without considerably improved fractionation. N-heptane can be estimated roughly by octane number determinations. Fairly close agreement with independent infra red estimations of the content of 2,2,4 trimethyl pentane are reported in table VI (Appendix III). In making such rough estimations a low figure was taken for N-heptane content, based on O.N. figures and the relatively small amount of iso-heptanes. A single infra red determination (table XVI) gives n-heptane = 0.4%.

The an.pt. method indicates that the amount of methyl cyclohexane is small and that there has been an appreciable decrease during 1943 (table XI). Independant figures by infra red (table XVI) confirm this.

Higher boiling trimethyl pentanes & toluene

The analysis of fractions 106-112°C containing the higher boiling trimethyl pentanes is rendered difficult due to the presence of high concentrations of toluene. Removal of toluene by sulphonatation introduces the risk of decomposing the trimethyl pentanes, although it has been found that with rapid acid treatment decomposition is negligible (Ref. 81). In the presence of much toluene it has been found that such trimethyl pentanes as 2,3,4 distil at about 109°C, which is several degrees below its true boiling point.

Due to the anomalous behaviour of so many non-aromatic hydrocarbons when distilled with aromatics it is obviously preferable to remove the aromatics and fractionate these separately. SO_2 extraction does not give sufficiently complete separation; phenol extractive distillation is not easy to apply to the whole boiling range from 70°C to over 180°C; azeotropic distillation has worked very well for particular problems such as removal of toluene from the octanes (Ref. 81), but is more laborious when applied generally and entails several distillations with difficulties in getting a complete balance; the method of selective adsorption of aromatics on silica gel offers some promise but may be difficult to apply to large volumes of spirit rich in aromatics so as to get quantitative separation and recovery.

Comparison of Analytical Results

The figures obtained for distribution of aromatics have already been discussed in Appendix II (table II), and for paraffins and naphthenes in Appendix IV (table IX).

Progressive changes in composition have been noted (Appendix IV). These are clearly demonstrated by comparing figures (3), (4) and (5), which show the separate T.B.P. curves for aromatics, naphthenes and paraffins for the three samples GF.32 (1940), AIR 285 (early 1943) and AIR 328 (late 1943).

Comparison of these curves show:-

- a) the large amount of high boiling aromatics (B.P. ca 180-185°C) in the 1940 gasoline, which are not present in later types.
- b) the increased amount of toluene and C₈ aromatics in the later samples.
- c) " " " octanes in the later samples.
- d) " " " hexanes " " "
- e) the marked decrease in amount of higher boiling naphthenes, which is very apparent in a comparison of AIR 285 and AIR 328.

The paraffin/naphthenic composition of different fuels can also be expressed by plotting curves of aniline point against boiling point for the non-aromatic hydrocarbons as in fig. (6). By plotting aniline point against B.P. rather than volume %, no direct measure of the amounts of individual components is possible, but since the curves were all obtained by fractionation at the same efficiency they indicate whether large amounts of certain components are present by the closeness with which the curves approach the aniline points for individual hydrocarbons.

It is seen that methyl cyclopentane is separated fairly pure from the hydro-petrol where large quantities are present, but that a purer cyclohexane is obtained from the earlier sample of green gasoline.

The main differences from normal hydro-petrol are that the aniline points are generally higher indicating more paraffins and less naphthenes. Again, there is a difference between the early green gasoline GF.32 and the later sample AIR 328.

The more paraffinic nature of green gasolines is largely due to the presence of added octanes. The presence of high aniline point material is shown markedly in the ranges 95-100°C, 105-112°C and 170-185°C. The first peak is due to 2,2,4 trimethyl pentane of exceptionally high aniline point. This is not isolated pure; even in AIR 328, presumably due to the inability of the still to separate N-heptane and methyl cyclohexane.

The trough in aniline point at 102°C. is due to methyl cyclohexane. Much less is present in the green gasolines and with high aniline point octanes on each side the trough is less marked than in normal hydro-gasoline. Again, AIR 328 contains more octanes and less methyl cyclohexane than GF.32.

The peak at 100-112°C. is due to 2,3,4 trimethyl pentane and other trimethyl pentanes. This peak is not so pronounced since these paraffins have lower aniline points, but it is probable that material in this range is largely 2,3,4 trimethyl pentane, which in the presence of toluene apparently distils below its true boiling point.

The third peak occurs at 170-185°C. and is probably due to the presence of hydrogenated trimer contained in the added octanes.

Hydrocarbon Pictures

Figures (7) - (14) illustrate the value of the method in clearly demonstrating different types of hydrocarbon composition and distribution of C₆, C₇ and C₈ non-aromatics.

Fig. (7) Green CG gasolines
Fig. (8) Blue BI gasoline

Fig. (9) Blue BI gasoline

Fig. (10) Blue BI gasoline

CF 38, 40/41, CF.31, CF.33 (1940 type)
no hydro-petrol, small content of
alkyl aromatics, low aromatic content
(SO/H/2) 7 very similar samples.
no hydro-petrol, small content of
alkyl aromatics with higher aromatic
content (SO/H/1) 3 very similar
samples.
estimated 50% hydro-petrol, no alkyl
cetanes, no alkyl aromatics (SO/H/1)
2 very similar samples.

It is clear that these samples can be divided into a number of groups, members of
which are very similar. Many other examples have been reported (Refs. 1, 2 and
separate reports).

Fig.(11) Lagunitas, and two Venezuelan aviation gasolines

Fig.(12) 130°C. and pt. normal hydro gasoline from petroleum gas oil.

Fig.(13) 150°C. " " " " " " creosote.

Fig.(14) 200°C. " " " " " " creosote.

The above are a few examples of the large number of materials analysed
in this way. The characteristic type of 'picture' for a hydrogenation gasoline
is easily distinguished from petroleum gasolines (Fig. (11)) and it is apparent
that the blue gasolines of Fig. (10) are closer in composition to a real hydrogenation
gasoline, than those of Figs. (3) and (8), whereas the green gasoline (Fig. 7.) is
seen to be very different from normal hydrogenation spirit.

TABLE XIII

"TRUE BOILING POINT" DISTILLATIONS

Volume % distilled in 30-40 Plate
Columns

	1940				1941		1942			1943					
	GF 28	40, 41	GF 31	GF 32	AIR 141	AIR 144	AIR 176	AIR 189	AIR 285	AIR 305	AIR 311	AIR 317	AIR 318	AIR 328	
<u>Vol. %</u>															
Up to 40°C	6.2	9.6	5.9	7.7	7.0	7.0	6.6	7.5	9.6	10.15	10.0	10.65	9.8	9.9	
" 65	10.7	14.3	9.8	12.0	9.0	9.5	9.3	10.4	13.5	14.5	16.2	16.55	15.9	15.7	
" 75	21.1	24.6	18.3	21.3	16.35	18.9	17.0	17.7	23.9	24.85	26.6	26.4	25.8	25.6	
" 84	28.7	33.6	27.5	30.8	28.7	32.2	29.5	31.2	34.1	34.3	34.2	35.15	34.95	35.0	
" 95	35.1	38.7	32.5	36.0	31.7	35.45	33.4	33.7	39.2	40.65	39.5	40.25	39.9	40.2	
" 114	60.9	65.2	60.3	62.3	66.1	70.1	67.0	67.1	69.4	71.1	71.1	72.6	72.0	73.0	
" 130	66.3	70.7	65.9	67.0	70.0	74.9	71.5	72.6	73.3	75.2	74.2	74.9	74.5	75.2	
" 150	79.3	81.0	77.1	78.5	84.3	86.9	85.2	86.1	86.8	86.2	87.3	88.2	89.3	87.7	
" 170°C	82.2	86.2	84.0	83.9	92.9	93.5	93.4	94.0	92.0	93.7	93.0	94.4	94.8	93.9	
<u>Cut No.</u>															
1) 0-40°C.	6.2	9.6	5.9	7.7	7.0	7.0	6.6	7.5	9.6	10.15	10.0	10.65	9.8	9.9	
2) 40-65	4.5	4.5	4.3	4.3	2.0	2.5	2.7	2.9	3.9	4.35	6.2	5.9	6.1	5.8	
3) 65-75	10.4	10.3	10.5	9.3	7.35	9.4	7.3	7.3	10.4	10.35	10.4	9.95	9.2	9.9	
4) 75-84	7.6	9.0	9.2	9.5	12.35	13.3	12.5	13.5	10.2	9.45	7.6	8.75	9.15	9.4	
5) 84-95	6.4	5.1	5.0	5.2	3.0	3.25	3.9	2.5	5.1	6.35	5.35	5.1	4.95	4.8	
6) 95-114	25.8	26.5	27.8	26.3	34.4	34.65	33.6	33.4	30.2	30.45	31.55	32.35	32.1	32.8	
7) 114-130	5.4	5.5	5.6	4.7	3.9	4.8	4.5	5.5	3.9	4.1	3.1	2.3	2.5	2.2	
8) 130-150	12.0	10.3	11.2	11.	14.3	12.0	15.7	13.5	13.5	11.0	13.1	13.5	14.8	12.5	
9) 150-170	3.9	5.2	6.9	5.4	6.6	6.6	8.2	7.9	5.2	7.5	5.7	6.2	5.5	6.2	
10) >170	17.8	14.8	16.0	16.1	7.1	6.5	5.6	6.0	8.0	6.3	7.0	5.6	5.2	6.1	
11) >180°C.	12.1	10.0	8.1	10.9	3	3	3	3			3			3.2	
Vol. ; Arom.					35				57 $\frac{1}{2}$		33			36	

TABLE XIV

SUMMARY OF MAIN DIFFERENCES IN DISTILLATION DISTRIBUTION

	1940	1941, 1942	1943 early later	Comments
<u>C₅</u> 0-40°C	7	7	10	butanes & pentanes, increased during 1943
<u>C₆</u> 40-65°C	4 $\frac{1}{2}$	3	4	iso-hexanes
65-75°C	10	7 $\frac{1}{2}$	10 $\frac{1}{2}$ 10	N-hexane + methyl cyclopentane + benzene
75-84°C	9	12 $\frac{1}{2}$	10	cyclohexane + benzene
Total C ₆	23 $\frac{1}{2}$	23	24 $\frac{1}{2}$	increased during 1943
Benzene	6 $\frac{1}{2}$	8 $\frac{1}{2}$	7 $\frac{1}{2}$	increase in '41', '42
C ₆ paraffins + naphthenes	17	14 $\frac{1}{2}$	17	now down again
C ₇ (& octanes) 84-95°C	5	3	5	increased in 1943
95-114°C	26 $\frac{1}{2}$	34	30	iso heptanes, dimethyl cyclopentanes
Total C ₇ (+ octanes)	31 $\frac{1}{2}$	37	35	trimethyl pentanes,
Toluene	8	12	10	toluene, etc.
Octanes + C ₇ (95-114°)	16 $\frac{1}{2}$	22	20	toluene increased again during 1943
includes methyl cyclohexane & N heptane.				
<u>C₈ (& C₉)</u>				
114-130°C	5	5	4	C ₈ naphthenes
130-150°C	11 $\frac{1}{2}$	13 $\frac{1}{2}$	13 $\frac{1}{2}$	decreased during 1943
C ₈ aromatics	6 $\frac{1}{2}$	9	10 $\frac{1}{2}$	increased during 1943
130-150°(P+N)	5	4 $\frac{1}{2}$	5	naphthenes decreased during 1943
<u>C₉</u>				
150-170°C	5 $\frac{1}{2}$	8	6	
aromatics (150-170°)	5 $\frac{1}{2}$	4	5 $\frac{1}{2}$	increased during 1943
P + N (150-170°)	2	4	2 $\frac{1}{2}$	decreased " "
<u>C₁₀ & higher</u>				
>170°C	16	6 $\frac{1}{2}$	8	
Aromatics(>170°C)	10	4	3 $\frac{1}{2}$	decreased for 1941
P + N(>170°C)	6	2 $\frac{1}{2}$	4 $\frac{1}{2}$	naphthenes decreased during 1943.

TABLE XV

PROPERTIES OF FRACTIONS OF ENEMY AVIATION GASOLINE (GREEN C.3 TYPE)
BULKED SAMPLE NO. AIR. 320, 229, 320

(6,000 mls. distilled. No.4 Still. Ref.43/9/71)

B.P. °C (CORR.)	TOTAL DIST. VOL. %	ORIGINAL FRACTIONS					IRON-FREE FRACTIONS		TOTAL H.C.s AS VOL. % ON TOTAL		
		D 15	A.P. °C n D	H.C.s (VOL. %)			D 15	A.P. °C	A + U	N	P
0-30	5.53		1.3510	0	0	100			0	0	5.530
30-40	9.90		1.3570	0	0	100			0	0	9.900
40-57.0	11.90		1.3892	0	51.0	49.0			0	1.020	10.880
61.1	15.90		1.3750	0.4	0	99.6			0.008	1.020	12.872
65.0	15.70		1.3770	2.1	0	97.9	.659	71.0	0.046	1.020	14.634
69.1	17.70			6.1	8.4	85.5	.670	65.4	0.168	1.188	16.344
70.4	19.70	.711	46.9)							
71.6	21.75	.750	29.4)	9.7	53.7	36.6	.718	48.1	0.561	3.363
72.3	23.75	.768	19.2)							
75.0	25.55	.775	11.9)	21.5	72.5	6.0	.747	37.9	1.378	6.118
77.2	27.55	.808	<5)							
78.3	29.55	.824	<5)	49.3	49.4	1.3	.758	37.3	3.550	8.094
79.0	31.55	.830	<5)	58.2	32.0	5.8	.745	41.4	4.514	8.734
79.6	33.55	.833	<5)							
84.0	34.95	.807	<5)	58.8	30.6	10.6	.735	46.0	6.514	9.774
90.7	36.95	.724	55.2)	6.3	24.4	69.3	.716	51.8	6.640	10.262
92.9	38.95	.720	60.3)							
95.0	40.18	.714	65.0)	1.6	20.6	77.8	.715	53.9	6.692	10.927
98.6	42.18	.708	69.9)	2.9	0	97.1	.705	72.9	6.750	10.927
99.0	64.18	.705	74.2)							
99.1	46.18	.702	74.6)	2.4	0	97.6	.681	76.9	6.846	10.927
99.2	48.25	.708	72.3)							
99.3	50.25	.714	69.5)	4.1	0	95.9	.689	75.5	7.013	10.927
99.6	52.25	.719	66.4)	4.3	0	95.7	.710	71.0	7.099	10.927
102.9	54.25	.741	52.2)	9.0	30.0	61.0	.731	61.6	7.279	11.527
107.8	56.25	.779	22.2)							
108.5	58.25	.794	9.1)	41.4	17.4	41.2	.733	63.0	8.935	12.223
108.7	60.25	.801	<5)							
109.0	62.25	.808	<5)	56.9	5.8	37.3	.723	67.3	11.211	12.455
109.1	64.25	.809	<5)							
109.4	66.25	.818	<5)	63.5	3.7	32.8	.717	68.2	13.751	12.603
109.9	68.25	.833	<5)							
110.0	70.25	.837	<5)							
110.0	71.75	.839	<5)	72.7	2.3	25.0	.755	67.6	17.749	12.730
122.4	73.75	.820	24.0)							
125.0	74.28		50.4)	26.2	45.8	28.0	.781	56.5	18.112	15.889
133.9	76.28	.790	25.0)	31.4	38.8	29.8	.755	59.7	19.040	14.665
135.8	78.28	.840	<5)	72.1	11.2	16.7	.752	64.5	20.482	14.889
136.8	80.28	.855	1.4660)							
137.9	82.28	.861	1.4900)	84.5	4.7	10.8	.749	66.8	23.862	15.077
138.2	84.28	.862	1.4920)							
143.4	85.28	.864	1.4902)	91.5	5.5	3.0	.770	60.1	27.522	15.297
139.4											
145.0	87.06	.861	<5)							
155.1	88.20	.840	<5)							
160.3	89.09	.838	<5)	64.2	27.8	8.0	.786	58.3	29.326	16.078
161.4	89.98	.850	<5)							
162.2	90.87	.852	<5)							
164.3	91.76	.852	<5)							
166.0	92.74	.852	<5)	74.1	16.3	9.6	.792	55.2	32.031	16.673
167.7	93.63	.849	<5)							
172.3	94.52	.850	<5)							
172.3	95.41	.846	<5)	60.8	10.7	28.5	.785	71.1	33.654	16.959
175.3	96.30	.844	<5)							
181.6	97.19	.852	<5)	50.3	2.8	46.9	.771	76.1	34.549	17.009
184.0	98.15	.838									
184 Res	100.0	.842			43.2	22.1	34.7	.803	70.2	35.763	17.530

SPECTROSCOPIC ANALYSES OF HIGH-AROMATIC HYDROCARBONS

In no case have a complete set of fractions of a German green gasoline been examined spectroscopically since interest has mainly centred on the two problems of octanes and higher aromatics. A few figures have been obtained, however, which are of interest in comparison with other fuels and to compare with other methods such as the melting point (Billingham) or refractive index methods (U.S.I.).

TABLE XVI

TRUE B.P. [°] C	HYDROCARBON	GERMAN GREEN CS GASOLINES				BLUE B4 GASOLINE				RUMM 73 OCT.	HYDR.G. (normal) Cross Pot. G.P.		
		AIR	AIR	AIR	AIR	AIR	AIR	AIR	AIR				
		144	173	199	215	317	177	206	209				
49.3	Cyclopentane									1.4	9.6	1.0	0.9
49.7	2,2 dimethyl butane				0.1					-	-	0.15	0.5
56.0	* 2,5 " "				0.55					-	0.9	1.2	2.1
60.25	2, methyl pentane		0.4	0.5	0.97	3.7	3.05	3.1	7.6	5.6	7.0		
63.3	3, " "		0.7	0.5	0.47	2.1	2.6	3.1		3.0	4.6		
68.75	N-hexane	2.5	2.4	2.0		3.6	3.65	3.6	3.6	1.6	2.6		
71.05	Methyl cyclopentane	5.5	4.1			5.6	6.45	5.75	4.95	12.5	9.0		
76.6	Cyclohexane	3.9	5.1			5.0	4.9	4.15	0.15	3.5	1.2		
80.1	benzene	12.1	6.6	6.6	7.5	0.5	4.1	7.6	5.7	1.4	4.4	1.4	
79-80.6	2,2 & 2,4 di.no.pont.	-	-			-	-	-			0.25	0.5	
86.1	3,3 dimethyl pent.	-	-	0.14		-					-	-	
88.6	1,1 dimethyl cy.pont	-	-	0.15		-					-	-	
89.7	* 2,3 dimethyl pentane	0.4		1.02		-					0.5	0.5	
89.9	2 methyl hexane	0.4	0.6	0.09	1.0	1.3	1.6				1.5	3.5	
91.0	1,3 dimethyl cy.pont.	0.4		1.4		-					5.0	4.7	
91.0	2 methyl hexane		0.4	0.5	1.2	2	2.0				3.1	4.2	
93.4	3 ethyl pentane	-	-	-	-	-	-	-			-	-	
96.4	N-heptane				tr	0.25					0.4	0.9	
99.2	* 2,2,4 tri.no.pont.	12	11.5	8.1	12.1	13.1	2.5	Tr			-	-	
91.0, 99.4	1,2 dimethyl cy.pent.										3.0	2.5	
100.3	Methyl cyclohexane			3.4	2.8	1.05	0.5				6.6	5.1	
103.4	Methyl cyclopentane					0.4					1.5	1.9	
106.0	* 2,2 di.no.hexane					0.25	-				-	tr	
109.1	* 2,4				0.32	0.32					0.7	0.6	
115.0	* 2,3 " "				0.35	-					0.4	0.7	
116.6	Toluene	11.5	12.5	13.5	14.1	14.4	7.3	6.7	5.6	4.95	5.5	4.4	
129.0	* 2,2,5 trimethyl pent.	tr.	-	-	0.6	1.2	-				-	-	
115.5	* 2,5,6 " "	5	4.4	6.6	4.6	4.1	2.6				-	-	
114.0	* 2,3,3, " "		0.5	-	0.6	0.7	1.0				-	-	
109-115	tri.no. cy.pont. (1,2,4)				0.3						1.6	2.6	

* Components due to added synthetic octane.

The detailed analyses of the two 'normal' hydrogenation gasolines (Nos. 1 & 4 of Table X) can be expressed to show the type of non-aromatic hydrocarbons. The following figures clearly show that the bulk of the paraffins are single branch of the 2 methyl type and about two-thirds of the total naphthalenes are cyclopentanes. The proportionate composition is very similar for two widely different raw materials.

ex creosote middle oil ex petroleum gas oil

Paraffins:

	<u>ex creosote middle oil</u>	<u>ex petroleum gas oil</u>
N-butane	0.3	0
N-pentane	4.6	4.0
N-hexane	1.8	2.0
N-heptane	0.4	0.9
N-octane	0.2	0.3
Total	7.2	7.2
2 methyl butane	17.9	22.9
" pentane	5.6	7.9
" hexane	1.5	3.3
" heptane	0.75	0.7
3 methyl pentane	3.8	4.6
" hexane	3.1	4.2
" heptane	1.5	2.0
4 methyl heptane	0.1	0.5
3 ethyl pentane	absent	absent
" hexane	absent	absent
Total	34.2	46.1
2:2 dimethyl propane	absent	absent
2:2 " butane	0.15	0.3
2:3 " "	1.2	2.4
2:2 " pentane	0.05	0.1
2:4 " "	0.2	0.4
3:3 " "	absent	absent
2:5 " "	0.3	0.5
2:2 " hexane	absent	trace
2:5 " ") 0.66
2:4 " "	0.7)
2:5 " "))
3:3 " ") 0.4) 0.7
3:1 " "))
dimethyl heptanes	ca 0.5	ca 1.1
methyl ethyl pentanes	absent	absent
Total	3.5	5.15
Total paraffins	47%	61%

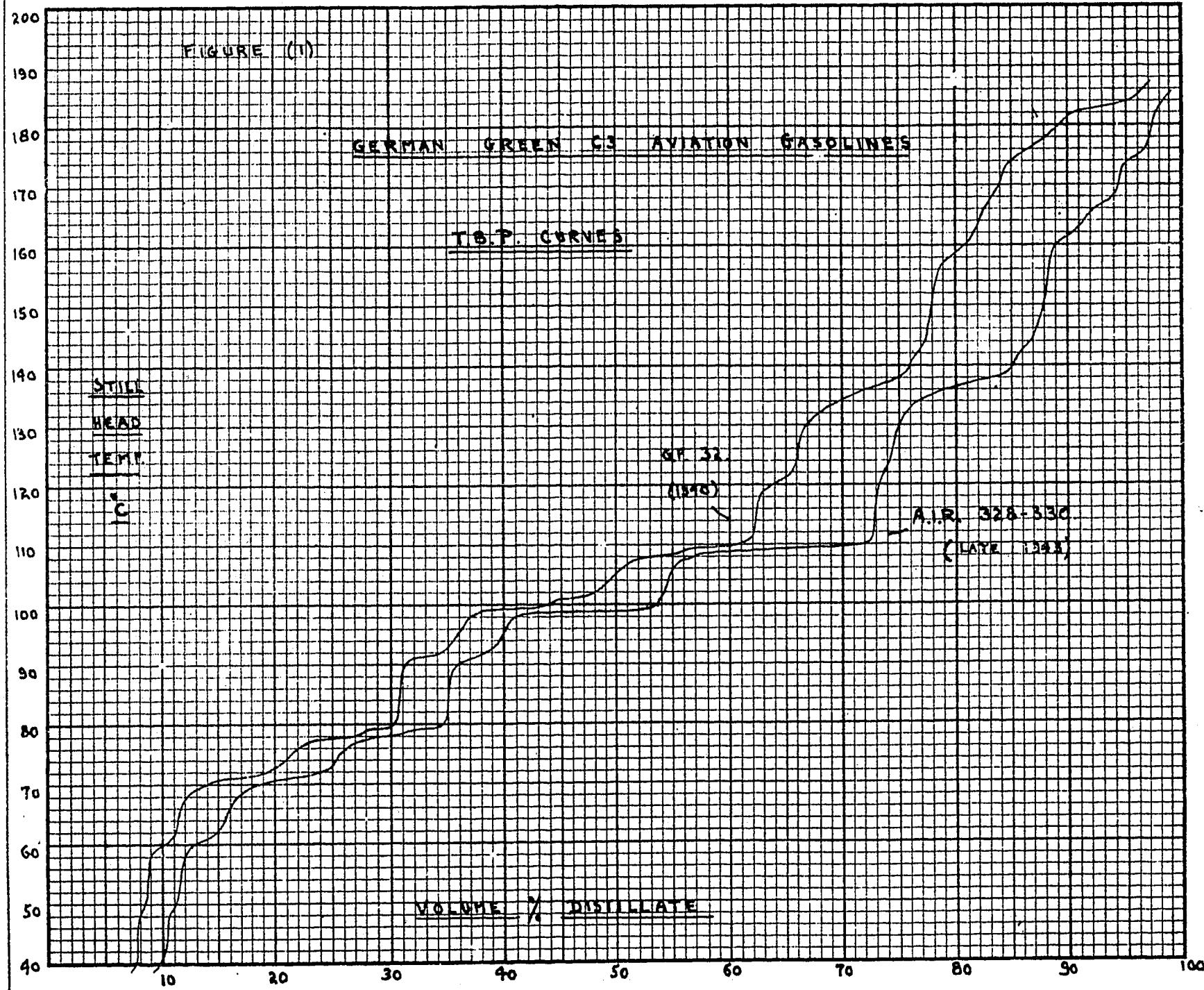
approx. % of total paraffins as:-

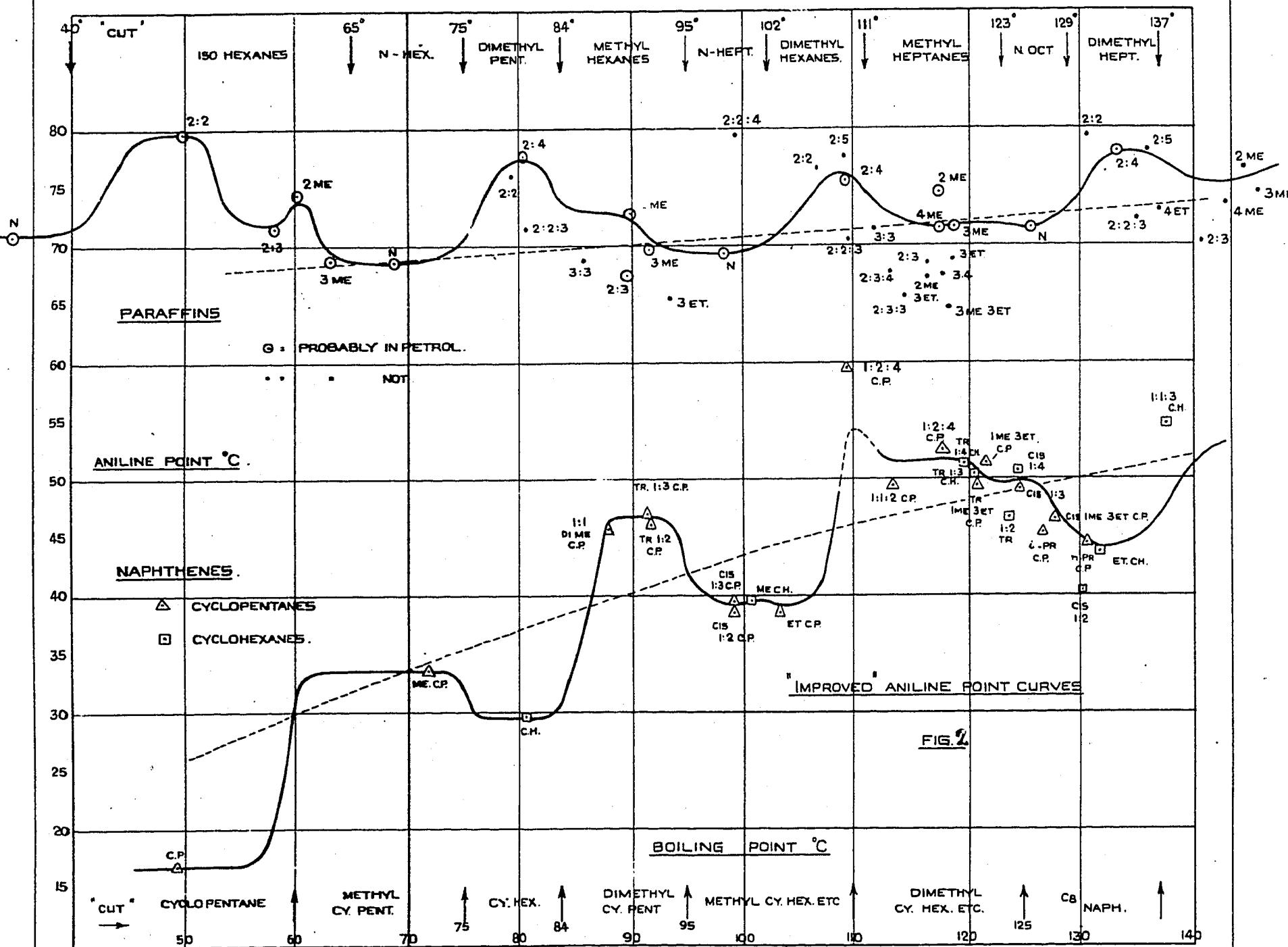
straight chain	16	12
single branch	76	79
double branch	8	9
triple branch	0	0

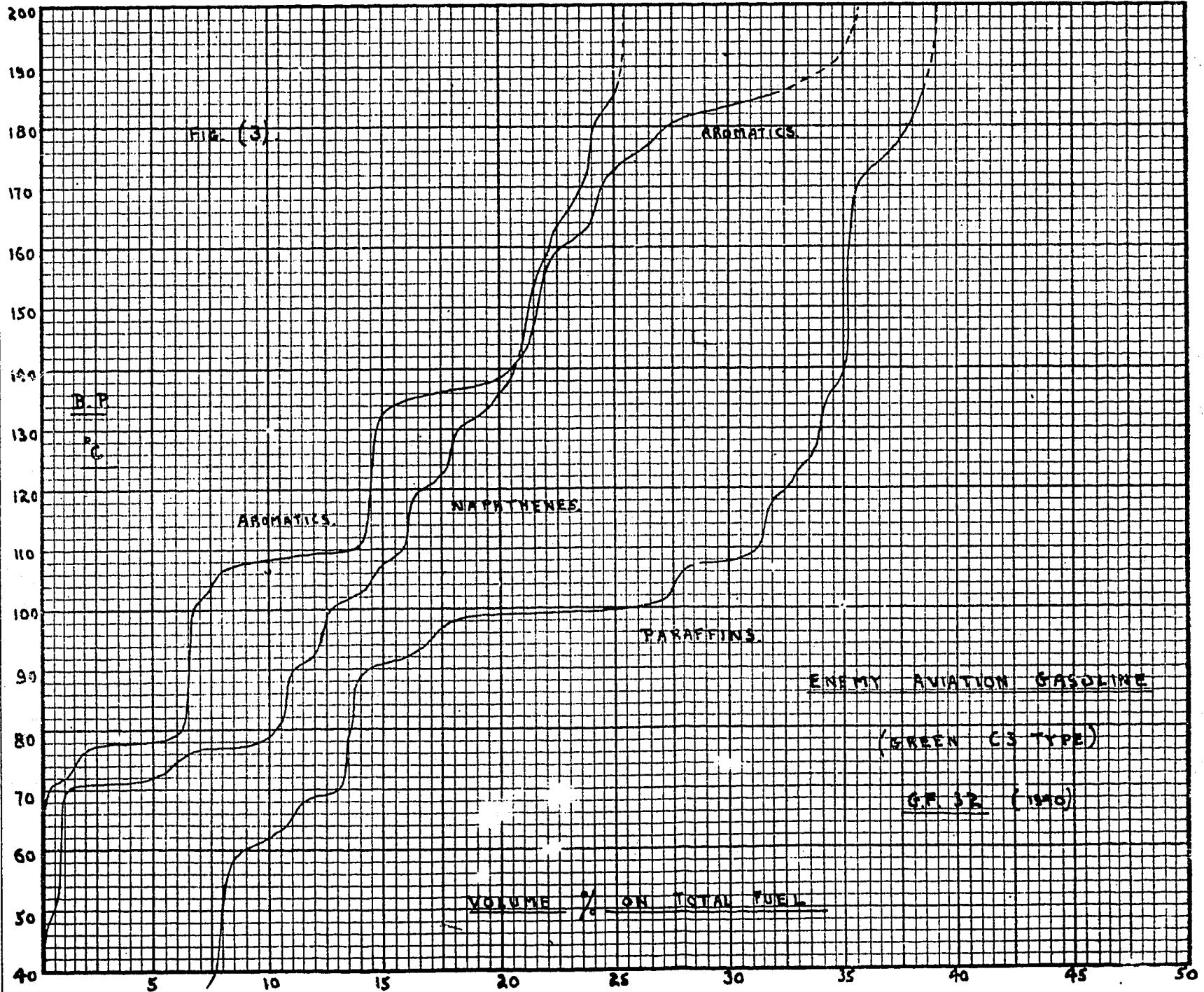
Naphthalenes:

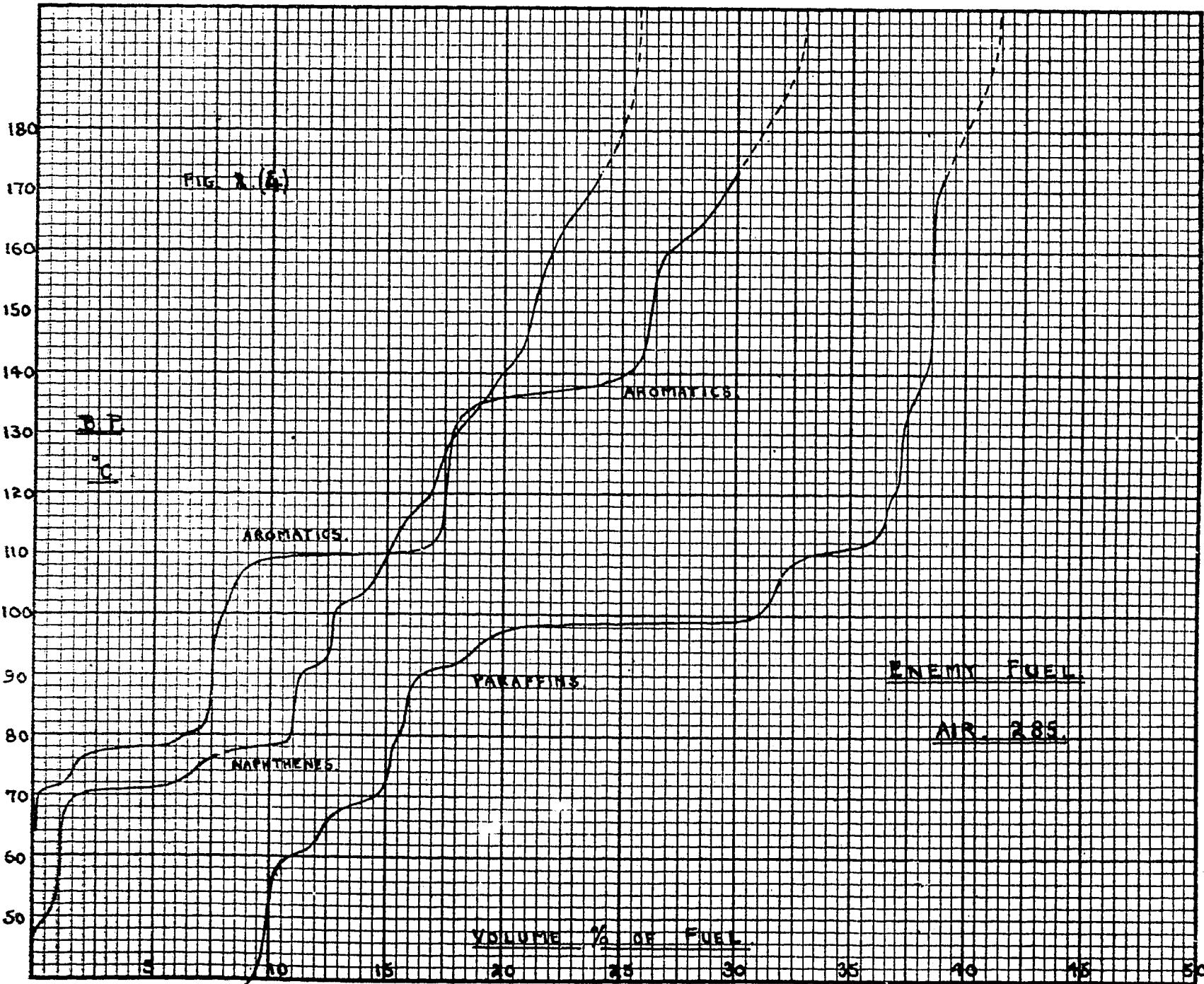
cyclopentane	0.8)	0.9)
methyl "	12.0)	9.0)
ethyl "	1.5)	1.9)
n-propyl "	traces?)	traces?)
cyclhexane	2.5)	1.2)
methyl "	6.5)	5.2)
ethyl "	0.8)	0.6)
n-propyl "	traces)	traces)

1:1 dimethyl cyclopentane		abs.	abs.
1:3 " " trans		5.2	4.5
1:3 " " cis (?)		0.6	0.5
1:2 " " trans		2.6	2.4
1:2 " " cis		0.35	0.2
1 methyl 3 ethyl ")		2.4	2.0
1 " 2 " ")			
	Total	11.15	9.6
1:1 dimethyl cyclohexane		abs.	abs.
1:2 " " trans)	-	
1:2 " " cis)	traces) 0.2
1:3 " " trans		2.7	2.0
1:3 " " cis		1.4	0.9
1:4 " " trans		0.35	0.1
1:4 " " cis		0.35	0.2
isopropyl " "		abs.	abs.
	Total	5.1	3.7
trimethyl cyclopentanes (1:2:4?)	ca	1.8	ca 2.0
	Total naphthenes		
% of total naphthenes as:-		40%	32 $\frac{1}{2}$ %
cyclopentanones		65	60
cyclohexanones		35	31
non-substituted		8	6
mono-alkyl		49	49
di-alkyl		39	39
tri-alkyl		4	6









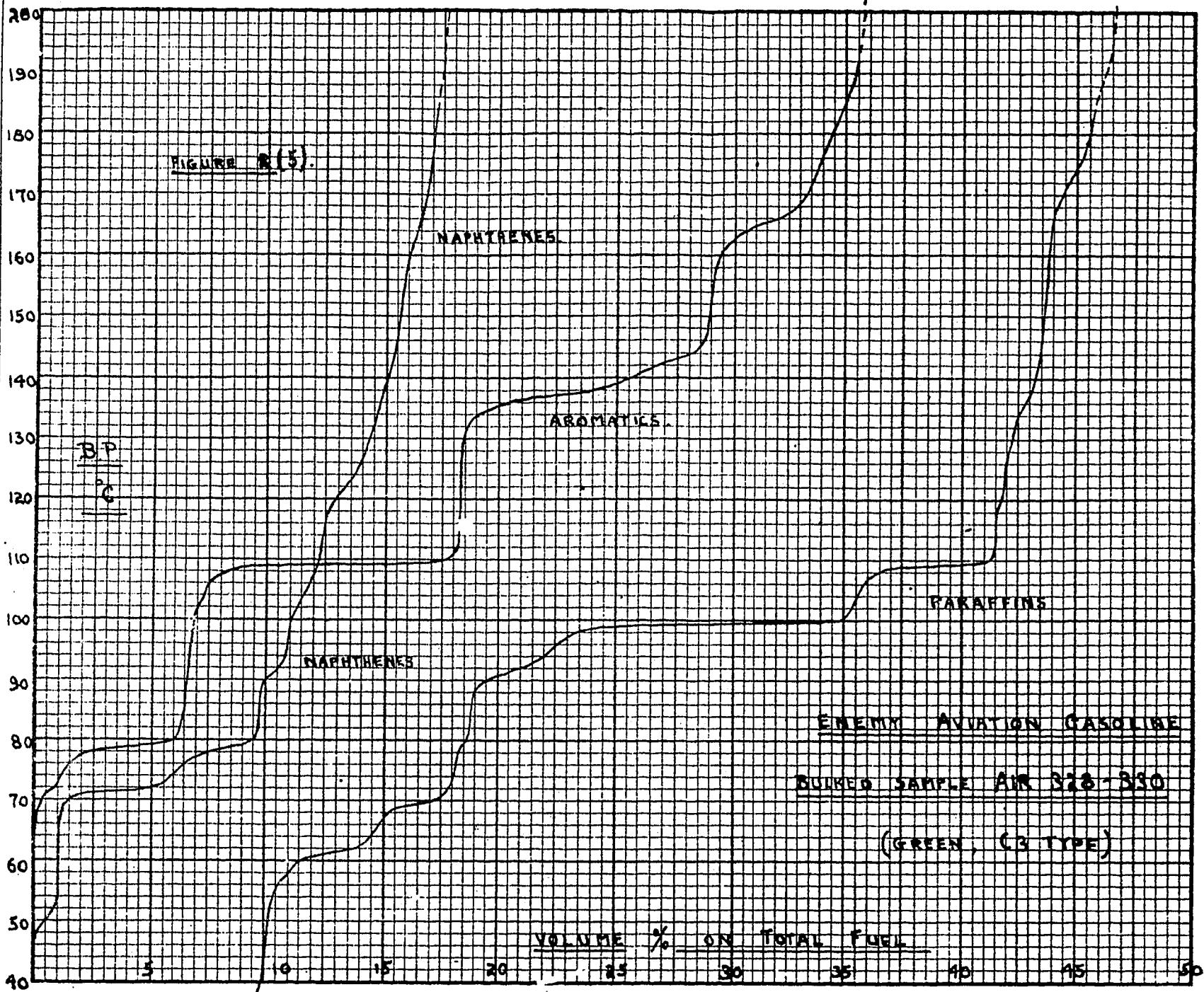
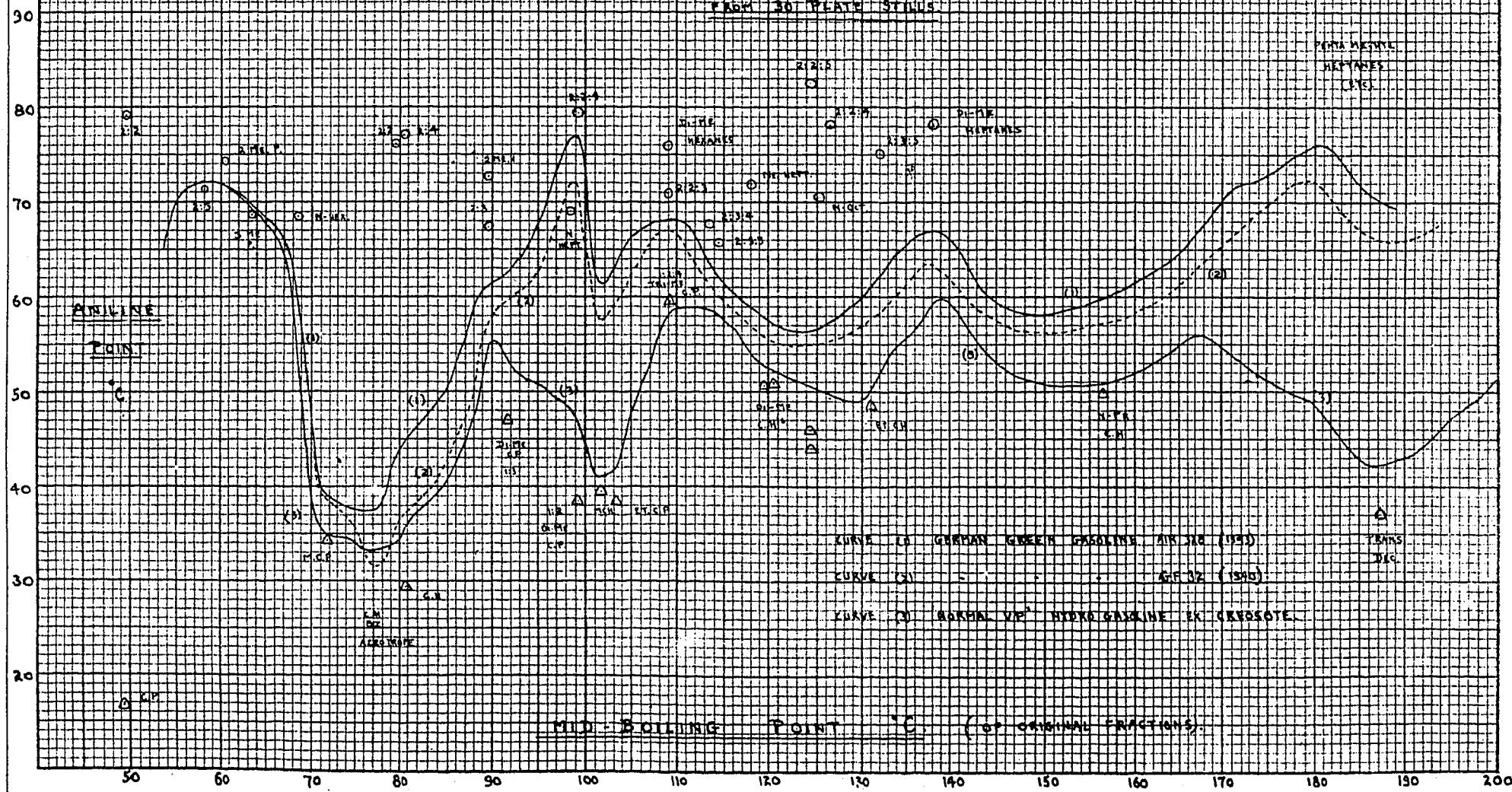
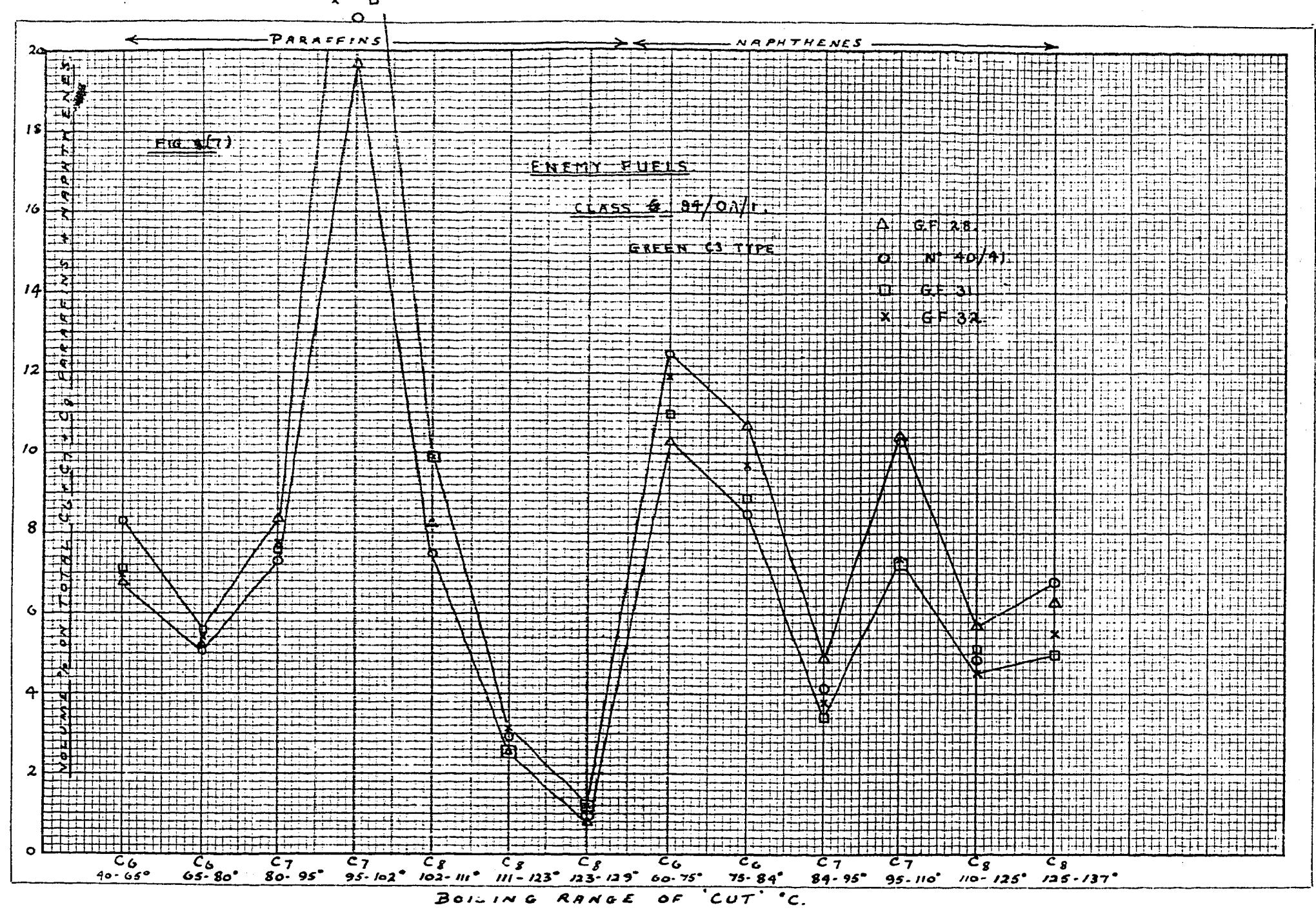


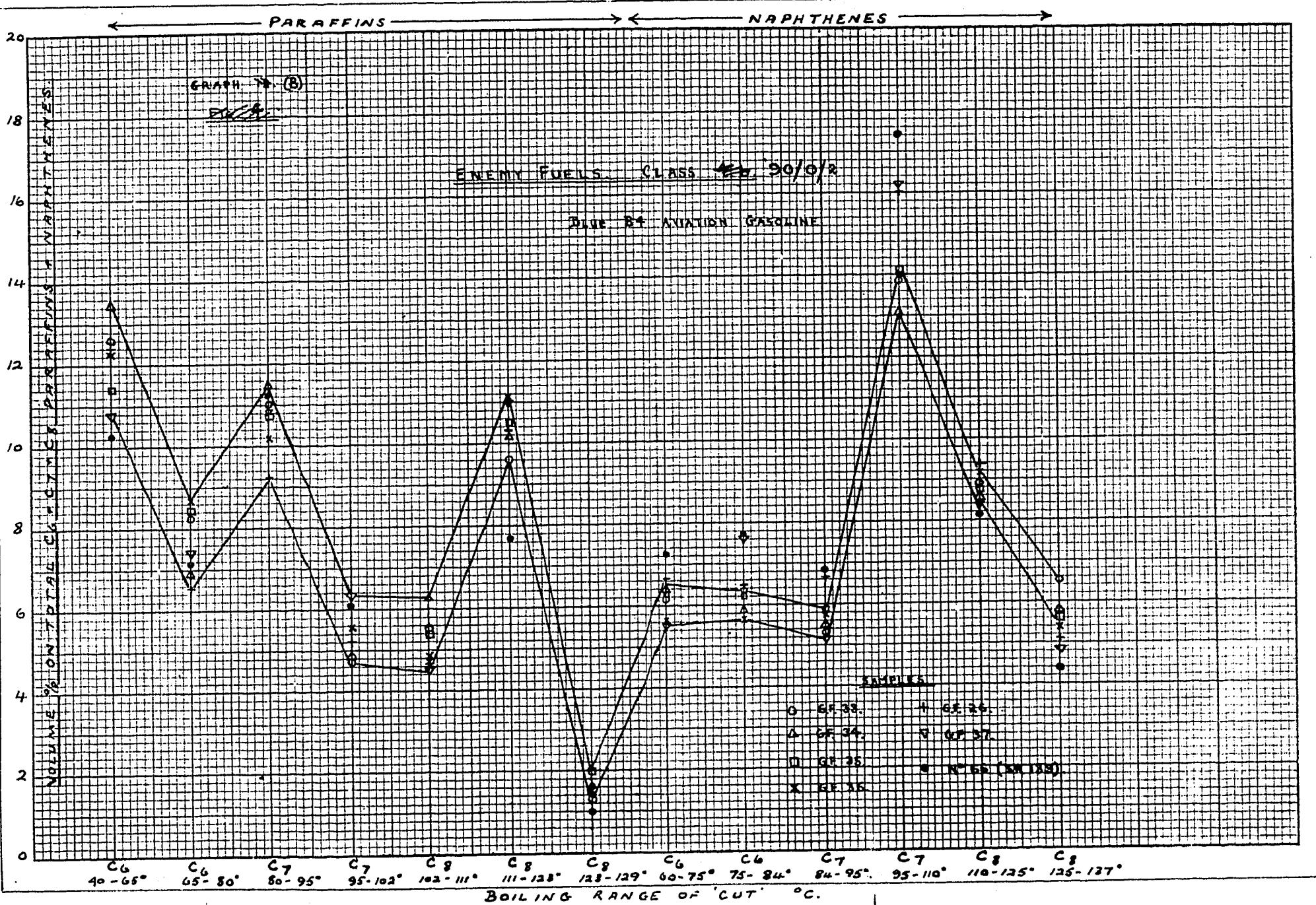
FIGURE (6)

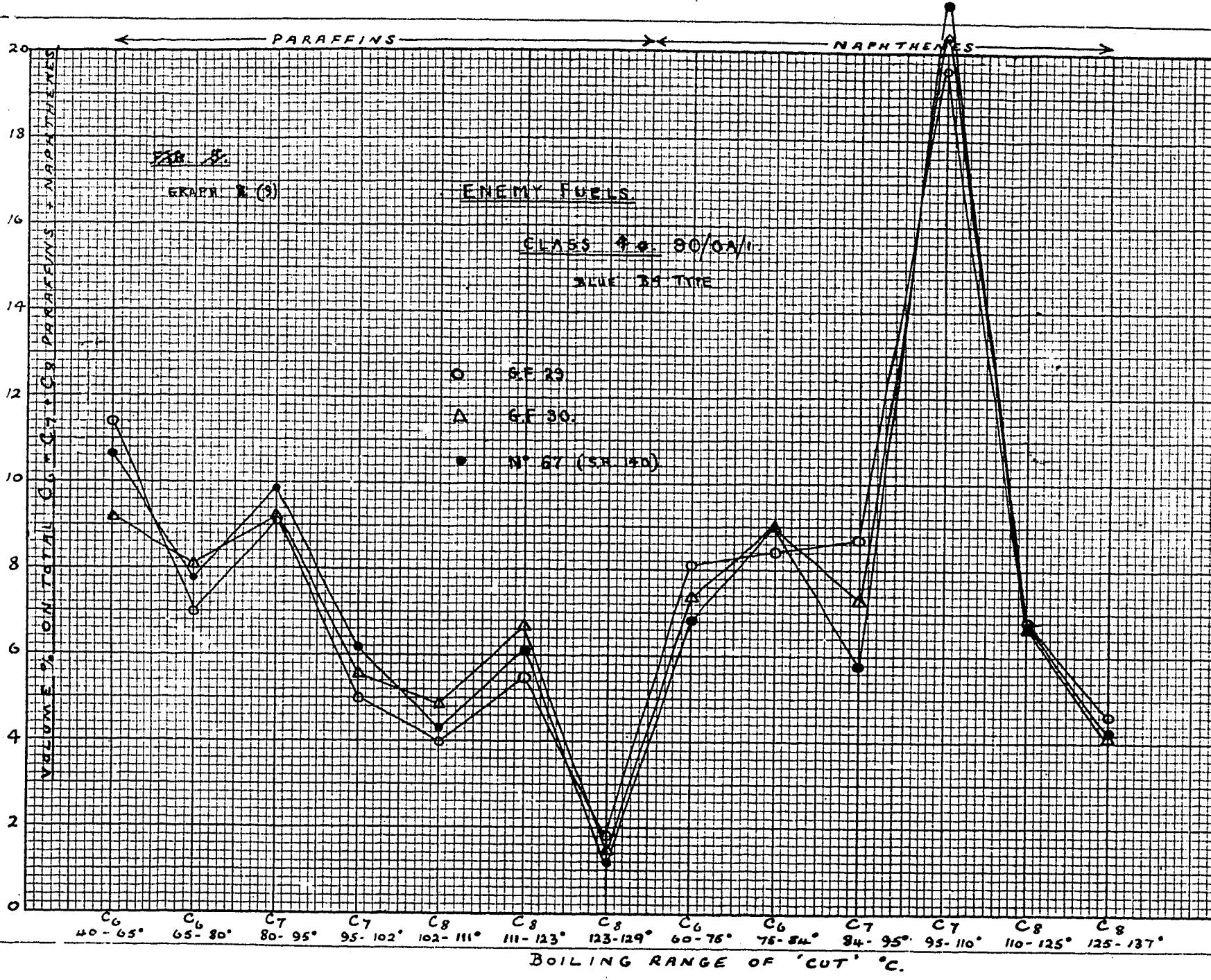
AVILINE POINT - BOURNE COUNTY - COUNTRY

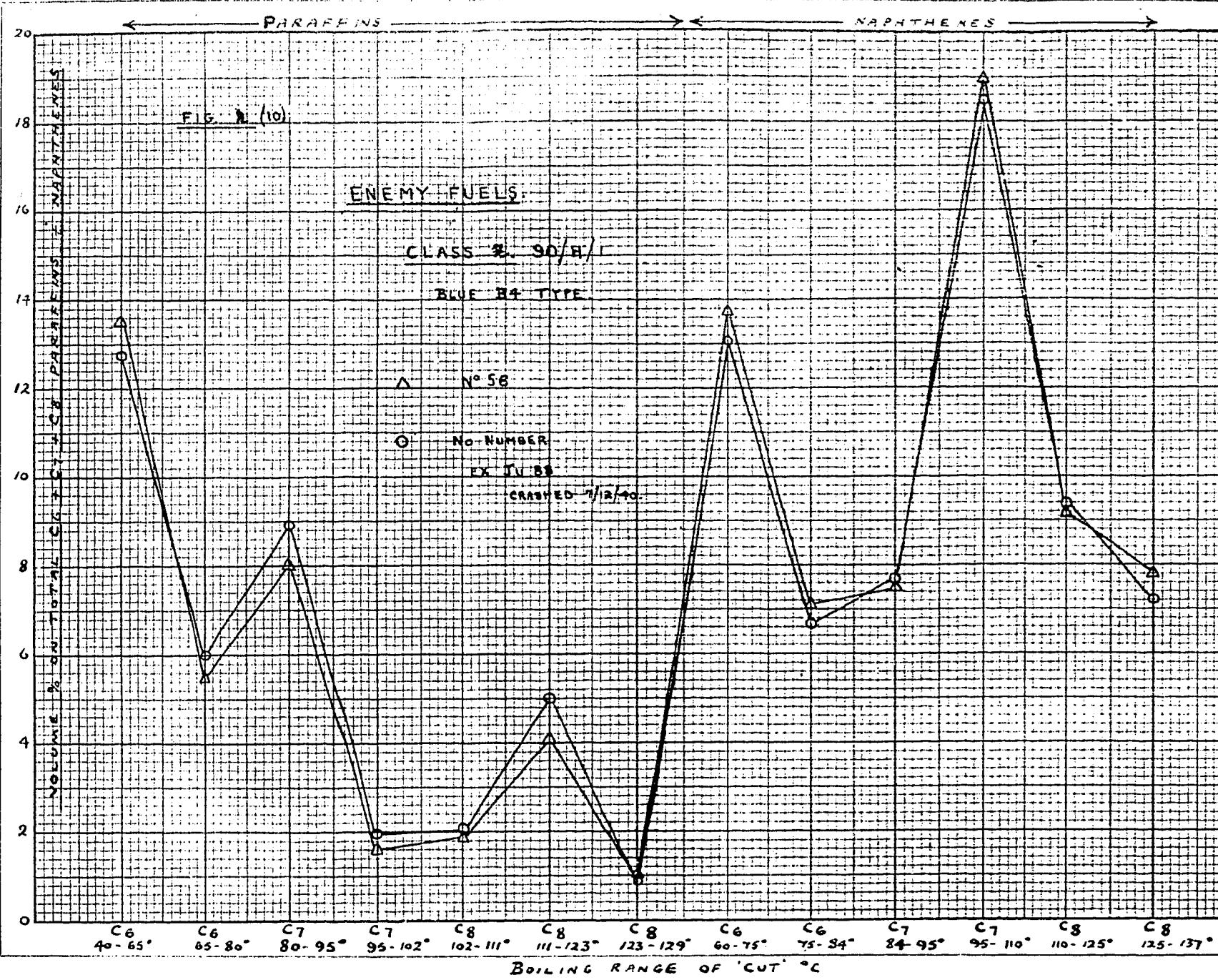
FOR AROMATIC-FREE FRACTIONS (SULPHONATES)
FROM 30 PLATE STILL

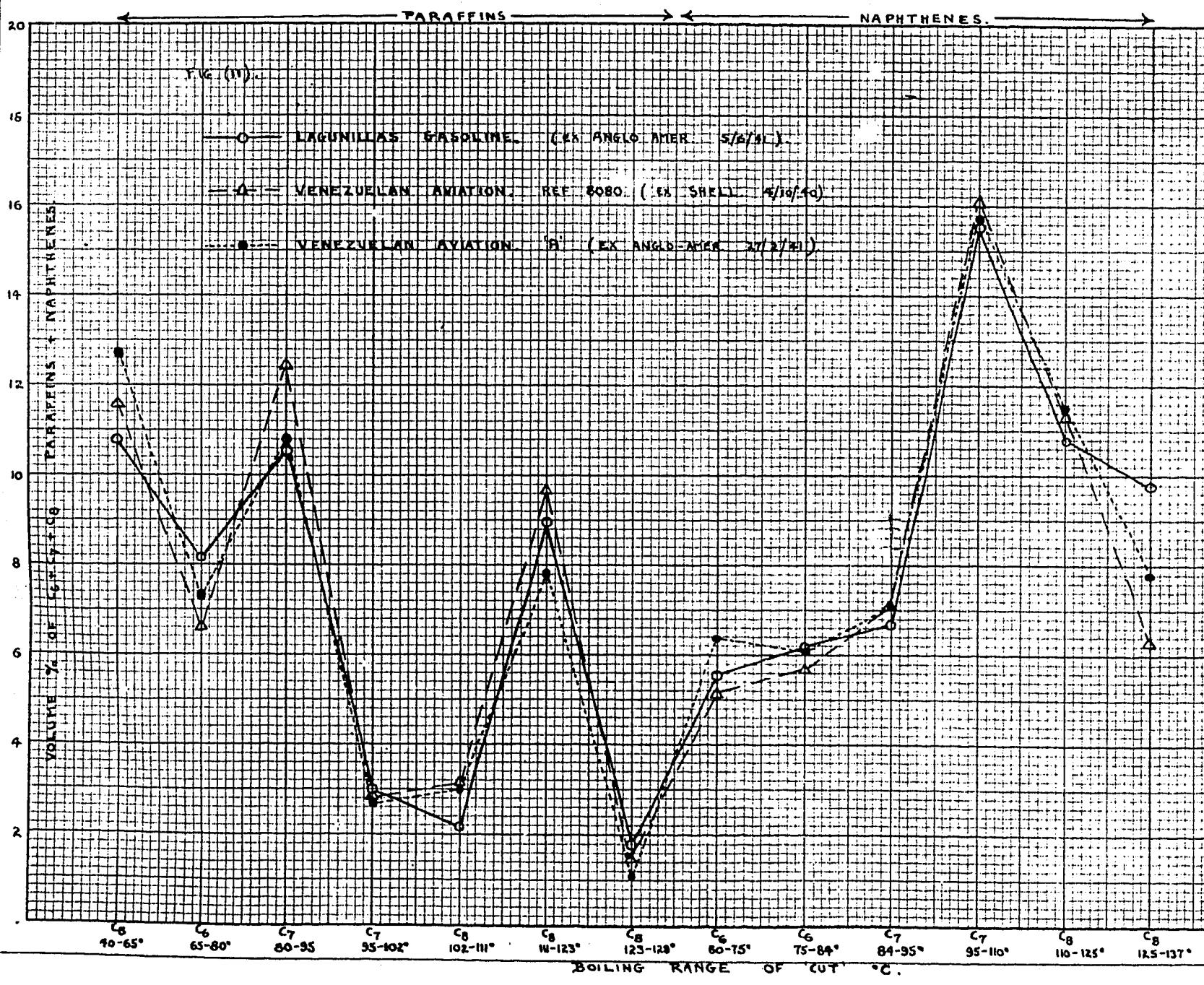






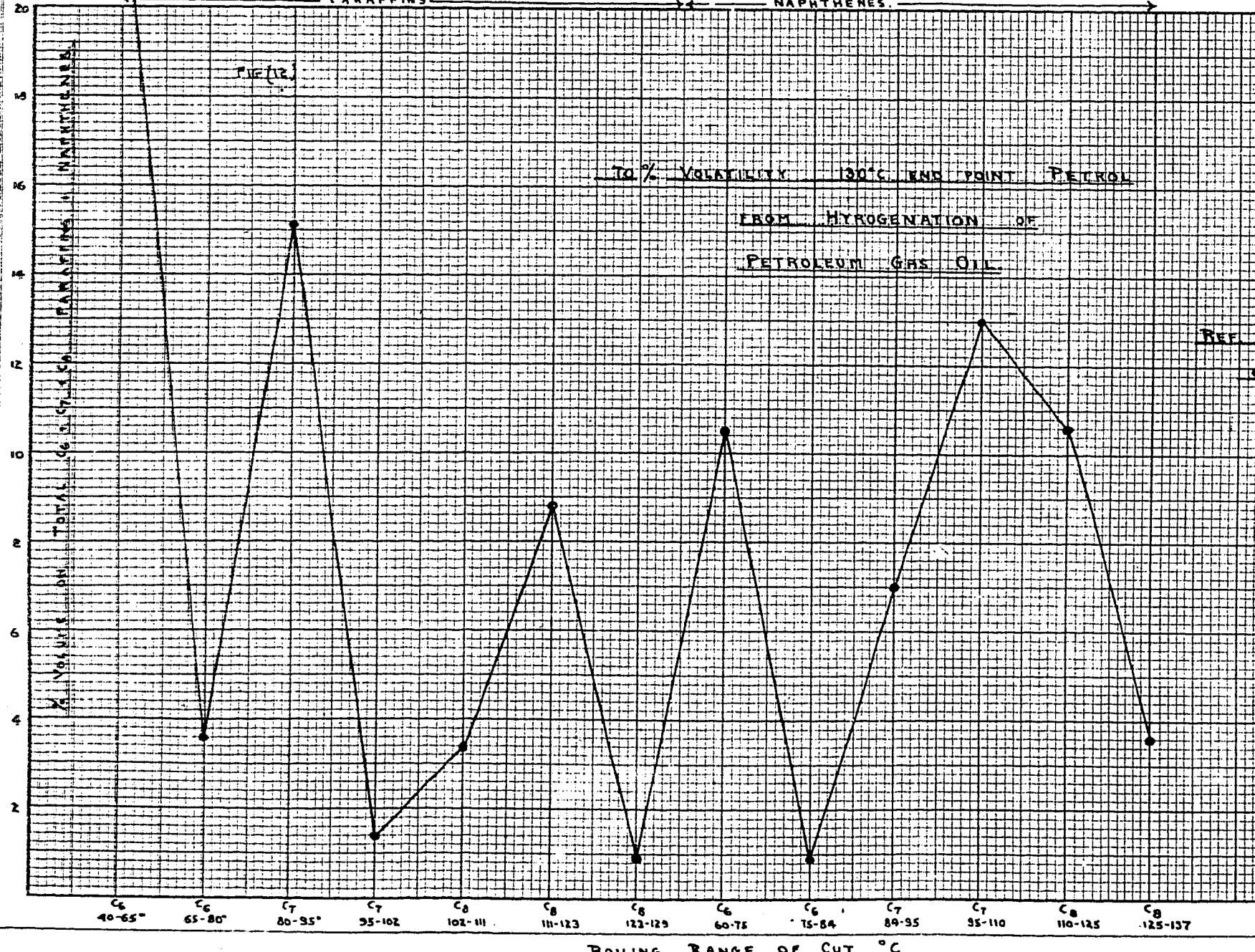






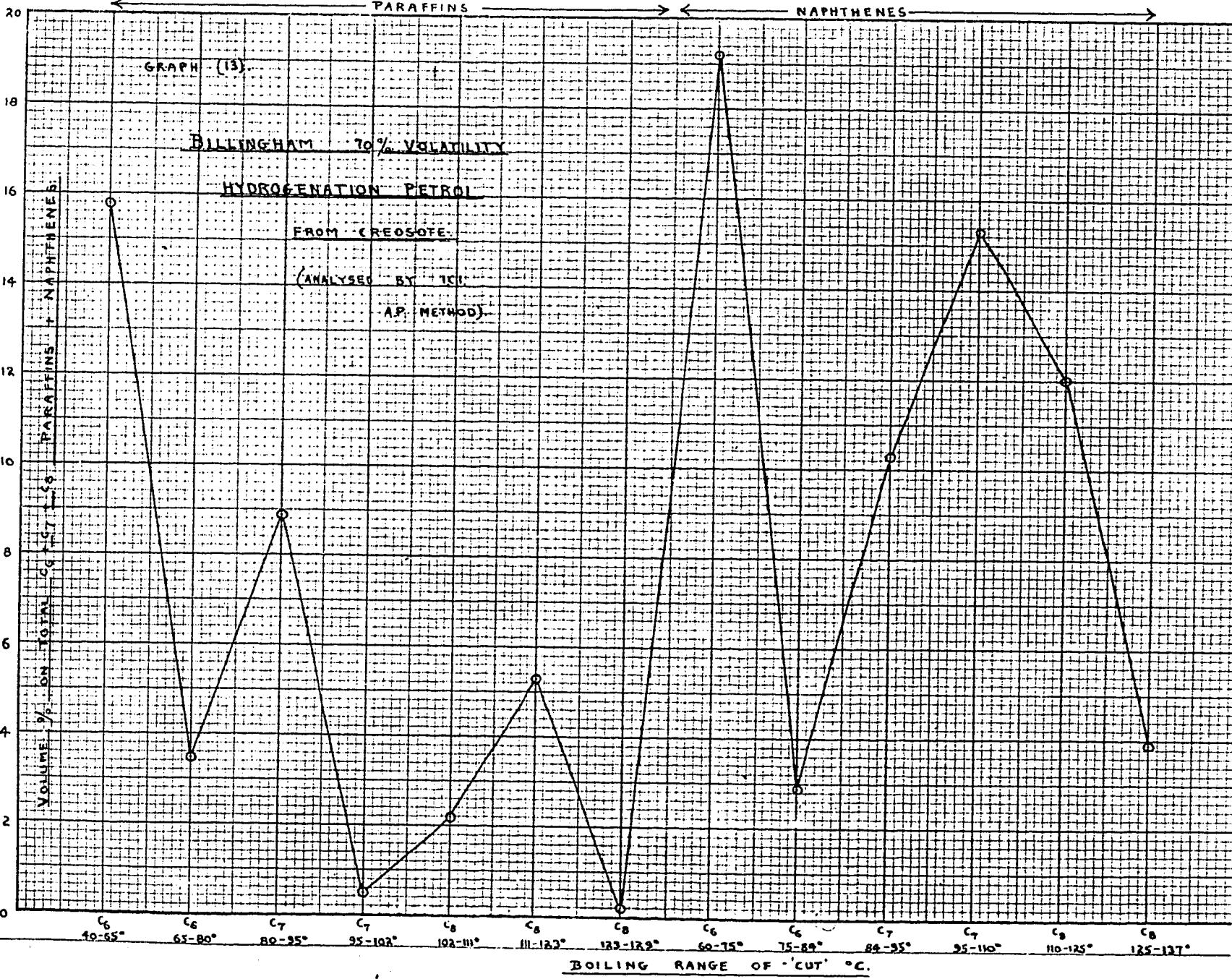
PARAFFINS

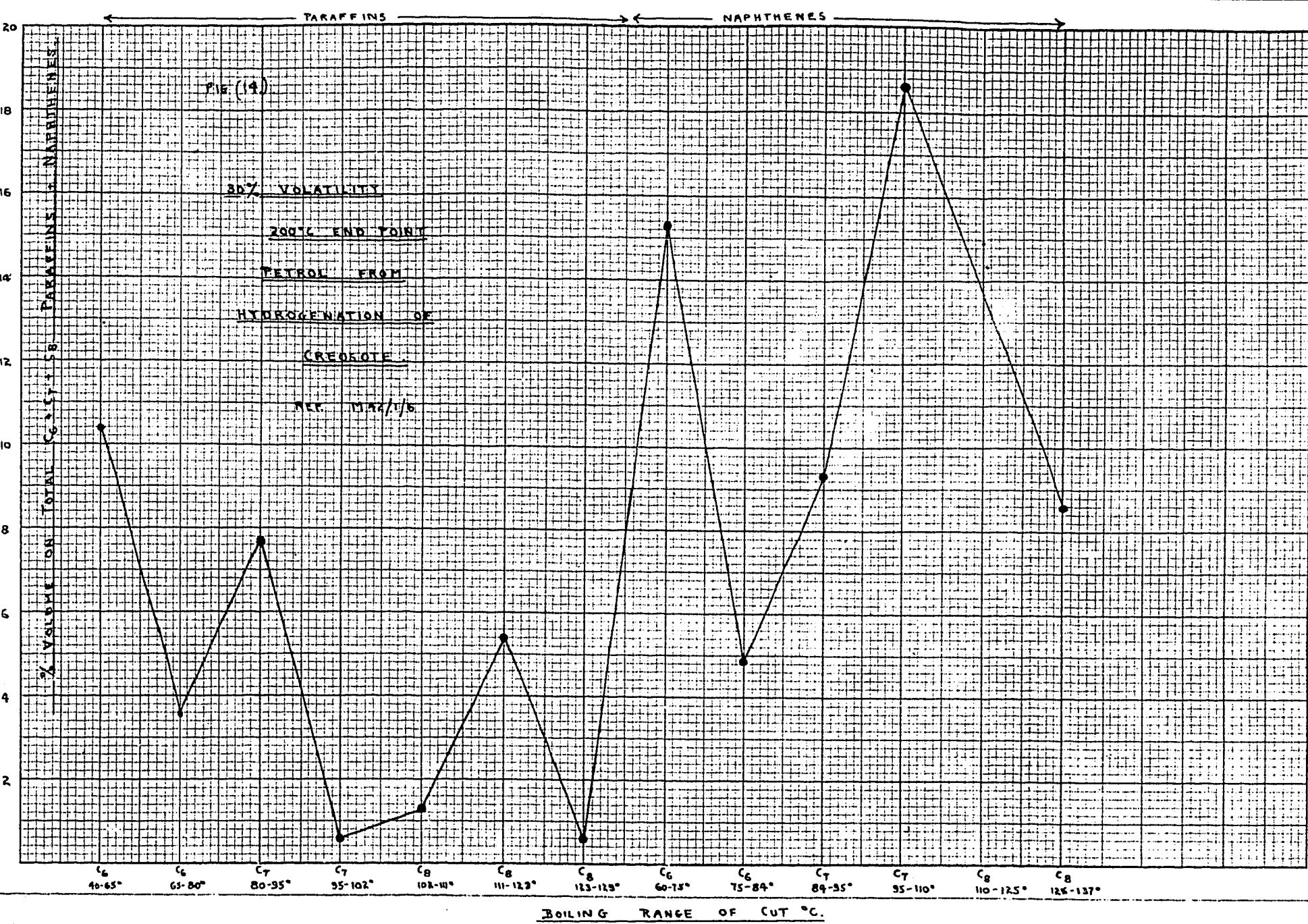
NAPHTHENES



PARAFFINS

NAPHTHENES





REF E R E N C E S

<u>Ref. No.</u>	<u>General Analytical Reports</u>	<u>Author</u>	<u>Date issue</u>
1.	Report G.40/2 Report on Examination of Enemy Aviation Fuels (summary to end of Nov. 1940)	R. Holroyd D. Peel	7/12/40
2.	Report G.40/2 Examination of Enemy Aviation Fuels. Second Report.	R. Holroyd D. Peel	12/3/41
3.	Detailed Examination of Enemy Fuels Discussion of Analytical Methods	R. Holroyd D. Peel	11/2/41
4.	Report VI. "The Billingham Method of Analysis of Petrols"	D. H. Peel	31/5/43
5.	"Examination of Fuels by Infra Red & Ultra Violet Spectroscopic Methods. Summary of results obtained up to July 1st, 1942."	D. Peel	10/8/42
6.	"Report on Examination of fuels by Infra Red & Ultra Violet Spectroscopic Methods. Second Summary covering period 1st July - 1st December, 1942."	D. Peel.	29/12/42
7.	Summary of Work of Infra Red Panel.		Dec. 1942.
8.	Report II Analysis of Synthetic Octanes by Spectroscopic Methods.	G. B. Sutherland	June, 1943
9.	Report III, Pt. I. Analysis of Aviation Fuels by Spectroscopic Methods. Pt. I. range 20° to 100°C.	H. W. Thompson	"
10.	Report III, Pt. II. Analysis of Aviation fuels by Spectroscopic Methods. Pt. II. range above 95°C.	G. B. Sutherland	"
11.	Report IV. Detection & Estimation of Aromatics in Hydrocarbon Mixtures.	W. C. Price, G. B. Sutherland, H. W. Thompson.	"
12.	Report V. Analysis of Mixtures containing Ethyl Benzene & the Three Xylenes by U.V. Method	A. I. O. C. No. 2196	"

Individual Fractionation Analysis Reports
I. Reference Samples of Known Origin.

(a) Virgin - straight run

<u>Report No.</u>	<u>Sample Description</u>	<u>Source/Notes</u>
13.	G.40/1 Roumanian aviation gasoline	(see ref.1)
14.	G.40/1 Roumanian aviation " (8247)	(see ref.1)
15.	R.41/44 Roumanian aviation " (8247)	D. Peel 20/12/41
16.	G.40/1 Venezuelan aviation " (8080)	(see ref.1)
17.	R.41/10 Venezuelan 'A'	D. Peel 19/5/41
18.	R.41/11 Venezuelan 'B'	D. Peel 19/5/41
19.	R.41/32 Lagunillas gasoline	D. Peel 29/8/41
20.	R.41/43 Lagunillas light naphtha	D. Peel 18/12/41
21.	R.42/49 Lagunillas heavy naphtha	D. Peel 8/9/42
22.	R.41/12 Trinidad high octane light cut	D. Peel 27/6/41
23.	G.40/1 Californian aviation (8127)	(see ref.1)
24.	R.41/15 Midway light blending stock	D. Peel 30/6/41
25.	R.41/14 Kettleman " " "	D. Peel 30/6/41
26.	G.40/1 Shell Aviation 73 octane	(see ref.1)
27.	- Shell light blending cut S.R.164	
28.	R.41/31 Miri aviation petrol	28/8/41
29.	R.41/35 Borneo aviation	1/9/41
30.	- Product from Sumatra (Palembang)	(not reported)
31.	R.41/28 Reitbrook gasoline (Hamburg, Germany)	20/8/41
32.	R.42/50 Reitbrook naphtha (" ")	8/9/42
33.	R.41/41 Russian fuel AIR 151	D. Peel 12/11/41

<u>Ref. No.</u>	<u>Report No.</u>		<u>Author.</u>	<u>Date issue</u>
<u>(b) Miscellaneous</u>				
34.	R.43/71	Catalytically cracked I.A.A. 110 (Intava)	D.Peel	4/2/43
35.	R.41/40	Fischer Tropsch	D.Peel	13/10/41
<u>(c) Aromatised & other aromatic products</u>				
36.	R.41/36	Hydroformed East Texas naphtha	D.Peel	10/10/41
37.	R.41/37	" Iraqi naphtha	D.Peel	10/10/41
38.	R.41/38	" Iranian No. 1 naphtha	D.Peel	10/10/41
39.	R.41/39	" Iranian No. 2 naphtha	D.Peel	10/10/41
40.	R.42/54	" hydrocreosote 130-200°C. naphtha	D.Peel	6/11/42
41.	R.42/62	Forcrunnings from naphthalene hydrogenation	(not yet issued)	
42.	R.42/63	High temp. hydro-aromatic prod. from creosote	D.Peel	5/10/42
43.	R.42/51	Gas spirit from bit.coal carbonisation	D.Peel	8/9/42
44.	R.42/52	Coke oven spirit from bit.coal carbonisation	D.Peel	8/9/42
<u>(d) Hydrogenation gasolines & naphthas from coal & creosote</u>				
45.	R.42/58	30% volatility 200°C. end point	D.H.Peel	15/9/42
46.	G.40/1	50% " 160°C. " "	(see Ref. 1)	
47.	G.40/1	70% " 140°C. " "	(see Ref. 1)	
48.		75% " 130°C. " " (42/11/10)	(see Refs. 4, 9 & 10)	
49.	R.42/61	Total saturated product	D.Peel	24/9/42
<u>from petroleum gas oil</u>				
50.	R.42/59	40% volatility 200°C. end point	D.Peel	5/10/42
51.	G.40/1	70% " 130°C. " "	(see Ref. 1)	
52.	R.42/60	70% " 120°C. " "	D.H.Peel	16/9/42
53.		70% " 130°C. " " (42/1/37)	(see refs. 4, 9 & 10)	
54.	G.40/1	67% " (ex Intava)	(see Ref. 1)	
55.	R.41/13	56% " (ex hydrog. Albanian oil)	D.H.Peel	
<u>(e) Synthetic Octanes</u>				
56.	R.42/64	Aruba Alkylate (also see Refs. & 70)	D.Peel	5/10/42
58.	R.42/67	Baton Rouge Alkylate (also see refs. 6, 7.)	D.Peel	2/11/42
59.		Baton Rouge Hydrocodimer (see refs. 6, 7)	(see Ref. 6)	
60.		U.K. Phosphoric acid Hydrocodimer (H.G.C.)	(see Refs. 6, 7)	
61.		U.K. Phosphoric acid Hydrocodimer (43/3/69)	(see Ref. 7)	
84.	R.42/48	Synthetic Phenol, issued 25/1/42 Enemy Aviation Gasolines (Green) C3 type		
<u>Billingham Fractn. Analysis Report</u>				
<u>Sample No.</u>	<u>No.</u>	<u>Date of Issue</u>	<u>Spectroscopic Analyses</u> (see refs. 5, 6, 7 etc.)	
			<u>Oxford. Cambridge. Billingham.</u>	
62.	GF.28	G.40/1	(see Ref. 1)	
63.	No.40/41	G.40/2	(see Ref. 2)	
64.	GF.31	G.40/2	" "	
65.	GF.32	G.40/2	" "	
66.	AIR 118			
67.	AIR 141	G.41/25	31/7/41	x x
68.	AIR 144	G.41/29	25/8/41	x x
69.	AIR 176	G.42/57	26/8/42	x x
70.	AIR 189	G.42/56	14/8/42	x x
71.	AIR 195			
72.	AIR 240			
73.	AIR 285	G.43/73	27/8/43	x x
74.	AIR 287			x
75.	AIR 289			x
76.	AIR 291			x
77.	AIR 305	G.43/74	30/8/42	x
78.	AIR 311	G.43/76	8/10/43	x
79.	AIR 312			x
80.	AIR 317	G.43/75 &		x
81.	" "	G.43/79	(removal of toluene, azeotropic distillation)	x
82.	AIR 318-327	G.43/77	29/10/43	
83.	AIR 328-330	G.43/78	30/10/43	

x Separate Reports & letters have been written on Spectroscopic Analyses of these materials.