EXAMINATION OF SOME LIQUID PRODUCTS DERIVED FROM CANNEL COAL

by

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SUMMARY.

1. The following equipment has been designed and constructed for the requirements of this research:-
    - a. complete carbonization unit of a capacity of about 42 lb. of cannel coal per carbonization,
    - b. continuous distillation unit,
    - c. batch distillation unit,
    - d. automatic fractionating column of maximum efficiency equivalent to 141 theoretical plates, at total reflux, and ancillary equipment.
2. A substantial quantity of Newbattle cannel has been carbonized at low temperature.
3. The crude oil obtained has been subjected to continuous and batch distillations, whereby suitable material has been separated for high-efficiency fractionations.
4. All material boiling in the range 26.9°-158.5°C. has been fractionated and separated into 137 narrow- or constant-boiling hydrocarbon concentrates, the properties of which have been determined.
5. Selected fractions have been analyzed with respect to their constituents by silica gel adsorption methods. Simple properties of the

separated hydrocarbons have been determined and the composition of the analyzed fractions evaluated.

6. 18 hydrocarbons (5 paraffins, 4 alkane mono-olefins, 3 cyclic mono-olefins and 6 aromatics), present in substantial quantities, have been separated from the concentrate fractions, purified and identified by measurement of physical constants. The identity of aromatic hydrocarbons has been confirmed by absorption spectra in the ultra-violet.
7. The approximate hydrocarbon composition of the material examined (representing approximately 7.9% wt. on total crude oil) has been evaluated and presented.
8. Tar acids and tar bases extracted from the continuous distillation overheads have been partly examined.

CONCLUSIONS

As a result of the work carried out, the following conclusions have been drawn with regard to the chemical composition of cannel naphtha boiling in the range 26.9°-158.5°C.:-

1. Unsaturated hydrocarbons are the principal constituents of the naphtha (amounting to about 46% wt. on total material examined). Saturated and aromatic hydrocarbons are present in lower concentrations (33% and 21%, respectively).
2. So far as the paraffins and olefins are concerned, n-paraffins and olefins-1 are the predominant compounds in each hydrocarbon group, while toluene is the major aromatic constituent.
3. The unsaturated constituents of cannel naphtha are composed of straight-chain, branched-chain and cyclic mono-olefins only (23%, 13% and 10% wt. on naphtha, respectively). Compounds containing two or three double bonds in the molecule have not been detected in the material examined.
4. The saturated constituents of the naphtha consist of straight-chain and branched-chain paraffins, and naphthenes (amounting to 22%, 7% and 4%, respectively).

5. The aromatic constituents consist of benzene and simple substituted benzenes only.
6. From the standpoint of hydrocarbon-type composition, cannel naphtha resembles shale naphthas and cracked petroleum stocks of similar boiling range, while the actual hydrocarbon composition of the material shows closest resemblance to Scottish shale naphtha.

PART I.

INTRODUCTION.

OCCURRENCE AND NATURE OF SCOTTISH CANNELS.

In view of the constantly growing demand for more specific gaseous and liquid fuels, greatly increased effort has been applied to the examination of organic constituents of crude and refined oils, derived from naturally occurring and synthetic materials. A further and equally significant stimulus for this extensive study has been provided by the relative lack of knowledge of the ultimate nature of such oils. Full credit for the initiation of these investigations must inevitably go to the petroleum industries of this country and the United States, which, in the past twenty years, have spared no effort or expense in the quantitative and qualitative examinations of petroleums and their products. As a direct result of this, tremendous improvements have taken place in the processes of manufacture of the various petroleum products and entirely new processes have been developed. Furthermore, the studies of the composition of gaseous and liquid fuels have resulted in the accumulation of a considerable amount of knowledge on the physical and chemical characteristics of hydrocarbons of all classes.

Within recent years, the hydrocarbon composition of the lower boiling fractions of bituminous coal tars and shale oils has been investigated by means similar to those applied to the examination of petroleum. The results thus obtained provide a very useful basis for comparison between the various oils and for their characterization according to the type of hydrocarbons present.

Owing to the relative lack of data on the properties and composition of cannel coal tars, the work described in this report takes the form of a preliminary examination of the lower hydrocarbon constituents of an oil produced by the destructive distillation of a typical Scottish cannel coal.

Although cannel coal and its carbonization products have been the subject of numerous studies in the past, there is very little available information on the composition of cannel oils. The majority of published work deals with the possible utilization of cannel coal as a source of marketable products, such as motor spirit, diesel oil, wax etc., and their production by a variety of methods, while very little attention is paid to the composition of the crude and refined oils.

This lack of information may perhaps be most justifiably explained by the facts that the once flourishing cannel industry is at present almost entirely extinct and that, at the period when great interest was shown in cannel, analytical techniques were not adequately developed to permit investigations of the constituents of oils. Further, the knowledge of the ultimate composition of oils was not essential to their successful commercial utilization.

Nevertheless, cannel coal is a mineral of very interesting properties and may be regarded as a potential source of tar or oil, rich gas and coke. The reserves in Scotland of good quality cannel, of low ash and yielding over 40 galls. of crude oil per ton, are considerable (vide infra) and, in most cases, easily accessible. There is, therefore, no doubt that the present state of abeyance of the industry will not continue and a revival of commercial interest is bound to return.

Scottish cannel coals are most frequently found in association with bituminous coal seams, where they appear as relatively thin lenticles or bands of limited area, forming the roof or the base of the seam, or a layer within the coal seam. They also occur as separate beds of an area seldom exceeding a few square miles. As pointed out by MacGregor (61) cannel coals are found in the Lower Limestone Group, in the Limestone Coal Group, in the Upper Limestone Group and in the Productive Coal Measures. As a rule they are impersistent and lenticular in their mode of occurrence and seldom constant enough to be regarded as other than local index-horizons. Though closely associated with bituminous coal, cannel coals differ from it not only in structure and composition, but also in mode of occurrence and origin.

The nature of cannels varies considerably with the locality of the seams, and several varieties of the mineral are known, and referred to by numerous names, derived either from the locality or some characteristic property. Names such as torbanite, boghead, parrot, gas coal and cannel are freely and loosely used. The term "cannel", originally derived from "candle" because the mineral produced long, luminous flames when burning, is most commonly applied to these materials, irrespective of their more or less marked differences in properties. Several attempts have been made to produce a systematic classification of canneloid materials, based either on their proximate or ultimate analyses, but so far these attempts have met with little recognition. A classification based on specific gravity has recently been advanced by Mott (71), and is claimed to show, better than any other, the interconnection between the various canneloid materials.

In the hand specimen, typical cannel coals are characterized by their homogeneity and absence of lamination. They vary in colour from a dull brownish tone to black with a pronounced satiny lustre. They have a compact grain and smooth texture, and emit a rather "wood-like" sound when struck. They have a higher elasticity and lower density than normal coals, and exhibit a conchoidal fracture.

Most valuable information, however, concerning the composition and origin of cannel coals is obtained by their examination under the microscope. They may be thus characterized by the highly disintegrated condition of the vegetable debris, of which a high proportion is translucent in thin section. Surrounded by this matrix are varying quantities of round or flattened "yellow bodies", together with fragments of cuticles, spore exines, resin bodies and, occasionally, fish remains. The nature of the "yellow bodies" has caused considerable controversy in the past and numerous theories have been advanced to account for their presence and composition. Originally considered to be plant tissues or globules of bitumen or oil, these "yellow bodies" have been definitely shown, by Temperley (91), to be of algal origin, not differing in any material respect from the living algae Botryococcus Braunii, and it is to these algae that the oil-yielding ability of cannels is chiefly ascribed. The appearance of algal bodies in an otherwise typical cannel marks the transition to the algal cannels, and their further concentration leads to bogheads and torbanites, which differ little from typical cannels, except that they are browner and tougher. Similar algae have been reported, by Conacher (16) and Mawson (70), to be found in Coorongite, a substance found on the shores of lakes of fresh or brackish water in South Australia, and regarded as the mother-substance of boghead coals and, possibly, petroleum.

The nature of Scottish cannels has been fully discussed by Skilling (88) who concludes:- "Microscopic examination has shown that the material known in Scotland by the name of cannel contains algal remains in varying proportions, the other organic matter consisting of macerated plant debris, microspores, and frequently fish remains. Those varieties in which the algal content is high are brown in colour, have a dull, woody ring when struck and are extremely tough to break. They are commonly referred to as "torbanite", "boghead" or "parrot". Those with much plant detritus are black, with a satiny lustre and conchoidal fracture.

A study of the microstructure of these materials, in conjunction with the yield of oil obtained from them, indicates that the source of the large quantity of oil must be the algal bodies, as those deposits in which the algae are relatively few produce quantities of oil only slightly higher than the average from a bituminous coal."

The present, widely held theory of cannel formation and origin, advanced by several workers, has been summarized by MacGregor (61) who points out that the lenticular mode of occurrence of cannels, their association with ordinary coals and their well defined boundaries, their content of fossil colonial algae and the presence in them of scales, teeth and spines of fresh-water fish indicate formation in lakes or pools among the swamp forests of Carboniferous times. These lakes or pools are considered to have been surrounded by swamp vegetation or lain close to rivers, so that in times of flood, the waters brought down considerable quantities of plant debris of every kind, along with algae, spores and mud. It was this drifted plant debris which, after undergoing subaqueous decomposition, formed the structureless mass present in cannels. Further, the drift of mud or clay accounted for the high ash content of the cannel as compared with the bituminous coal of the same seam. Mott (71) considers that special conditions promoted the flourishing of algal colonies on the surface of the lakes, thereby giving rise to the different types of material. If the algae sank and mixed with the coal debris boghead cannels resulted, while the comparative lack of vegetable debris and the excess of mud resulted in oil shale. If there was no mud or coal base, the algae formed torbanite.

The history of cannel coal industry has been frequently reviewed in the past (17, 21, 71, 109) and several estimates of the possible cannel resources in Scotland have been made, of which those published by the Scottish Development Council's "Oil from Coal Committee" appear to be most reliable and most recent.

The first report, published in 1935, dealt with the low-temperature carbonization and hydrogenation of coal (84), while the second(85),compiled on the basis of a questionnaire issued to every colliery company in the areas mentioned below, dealt with the reserves of cannel and canneloid materials. A geologist appointed by the Committee investigated cannel seams, and obtained and assayed samples of the various minerals likely to yield oil. The areas investigated were Ayrshire, Fife, East and Midlothian, Douglas, Lanarkshire, Campbeltown and Brora. The results of these findings are given in Table 1, which shows the deposition of the main cannel reserves in Scotland.

TABLE 1.

Area	Cannels yielding over 40 galls. of crude oil per ton and containing:-		Total, tons.
	Less than 8% ash, tons.	Over 8% ash, tons.	
Lothians	21,124,600	6,443,000	27,567,600
Fife	467,000	74,073,000	74,540,000
Ayrshire	4,000,000	-	4,000,000
Lanarkshire	500,000	1,235,210	1,735,210
Other areas	22,800	56,000	78,800
Total	26,114,400	81,807,210	107,921,610

In addition, there are several substantial reserves of cannels, of low ash content yielding 20-40 galls./ton, in the Lothians, while in Fife deposits exist of 30" thickness yielding over 50 galls./ton, but of high ash content (13-35%). Though some seams appear to be difficult and expensive to work, most cannel seams appear in existing workings or in thicknesses sufficient to justify fresh workings.

The conclusions reached as a result of this survey are summarized by Wilson (109) as follows:-

1. There are present in Scotland reserves of cannel and canneloid material totalling well over a hundred million tons, and yielding more than 40 gallons of crude oil per ton.
2. The greater part of this material is available in two or three seams of large extent and of reasonable thickness.

Despite this favourable picture, many people of wide experience in the coal industry consider the above estimates optimistic, and there appears to be some controversy regarding the extent of existing cannel deposits.

There is no doubt, however, that the crucial factors upon which the extent of future cannel exploitation will ultimately depend are the reserves, availability and accessibility of good quality, high-oil-yielding cannel coals.

SURVEY OF LITERATURE ON CANNEL TARS AND THEIR PROPERTIES.

Owing to the present lack of interest in cannel coal and its carbonization products, the literature on the subject is somewhat limited. The literature published during the early stages of cannel coal industry (mid and late 19th century) is mostly of historical interest and very little precise information can be obtained from it.

In the present century, the fluctuating interest directed towards the exploitation and utilization of cannels has resulted in a certain amount of work being carried out, dealing mostly with the possibilities of production of marketable fuels and oils, while the more fundamental aspects of cannel oils have been little studied.

The following brief, and by no means exhaustive survey of existing literature is, therefore, primarily intended to indicate the type of work carried out in recent years on the retorting of cannel coals and on the properties and nature of cannel oils, with emphasis on those aspects of the published work which bear a direct relation to the problem in hand.

One of the earliest references to the production of a variety of fuels from cannel is made by Craig (19) and Berry and Dunstan (8), while the great majority, if not all, of the existing modern knowledge on cannel coal and its carbonization products has been included or summarized in several papers presented at the two Oil Shale and Cannel Coal Conferences, held in Scotland in the years 1938 and 1950, and organized by the Institute of Petroleum.

Carbonization of cannel coal at high and low temperatures and on varying scales, and subsequent utilization of the tars for the manufacture of fuels form the subject-matter of most papers. Straight distillation as well as cracking and hydrogenation-cracking are considered suitable for the production of motor spirit, diesel oil, fuel oil etc.

Apart from the commercial aspects, work has been done on the assessment of oil yields and properties of a large variety of cannels. Wilson (109) assayed eighteen different cannels in a mild steel, horizontal retort of 4 lb. capacity, at a maximum temperature of 650°C., and reports the following variation in crude oil yields and properties over the range of cannels carbonized:-

Specific Gravity	0.87 - 0.96
Crude oil yield, galls./ton	40 - 82
Distillate to 180°C., %	11 - 21
Residue over 300°C. at 3-6 mm. Hg. pressure, %	3 - 10
Wax content, %	3 - 23

Similar, only more recent, work is reported by Wood (110), who gives the analyses and the results of assays in a modified Grey-King apparatus at 600°C., for eight cannels obtained from the major known cannel seams. Analyses of coke and gases produced during the assay are also given.

The properties of cannel tars produced on pilot-plant or semi-commercial scale have been determined by a number of workers, though little information is given regarding their composition. Jamieson and King (50) carbonized Newbattle cannel (Parrot seam) in Woodall-Duckham continuous-vertical retorts of over 8 tons capacity, under gas-making conditions and at a low temperature (650°C.) The properties of the tars obtained under the two sets of conditions are given in Table 2, while the distillation of the crude oils yields products in the proportions given in Table 3.(p.13).

TABLE 2.

Properties of cannel tars.

	Vertical retort tar	Low-temperature tar
Specific Gravity	0.997	0.967
Free carbon, %	0.35	-
Tar acids, %	10.3	9.8
Tar bases, %	0.9	1.9
Neutral oil, %	43.0	53.1
Paraffin wax, %	5.8	5.1

Table 2.(contd.)

	Vertical retort tar	Low-temperature tar
Carbon, %	83.9	83.9
Hydrogen, %	9.5	9.8
Nitrogen, %	0.7	0.9
Sulphur, %	0.6	0.5
Oxygen, %	5.3	4.9

TABLE 3.

Distillation yields from cannel tars.
(Calculated per ton of cannel carbonized.)

	Vertical Retort tar.	Low-temp. tar.
Refined spirit from gas, galls.	3.8	2.6
Refined spirit from tar, galls.	1.1	0.6
Octane no. of average spirit	68	-
Neutral oil, 170-300°C., galls.	10	14
Neutral oil, 300°C-pitch, galls.	11	15
Tar acids, galls.	4	4
Pitch, lbs.	161	134
Paraffin wax, lbs.	24	23
M. pt. of wax, °C.	55	67

It appears from the results quoted that carbonization at low temperatures does not lead to greatly increased yields of oils, whereas the yield of gas is greatly decreased. The yield of coke, on the other hand, is increased and the coke is more combustible. However, Jamieson and King favour carbonization at high temperatures and confine most of their work to the examination of the possibilities of utilizing high-temperature tar for the production of gas, motor spirit, diesel and fuel oils. They make an interesting comparison of average yields and cost estimates between Scottish gas coal and the cannel, both carbonized under similar conditions. The authors state that the comparison of yields is in favour of cannel as regards:-

a. increase in gas yield of 30 therms per ton,
b. increase in gas output of 248 therms per retort per day at the same calorific value,
c. increase in spirit yield of 2.7 galls. per ton,
d. increase in tar yield of 40 galls. per ton,

and unfavourable as regards:-

e. decrease in coke yield of 3.5 cwt. per ton.

The results of an examination of the distillates of high-temperature tar, with special reference to their commercial applicability, are included in the paper.

Refined spirit, shown to be suitable as Grade I motor spirit, has the following properties:-

Specific Gravity	0.76
Distillate to 100°C., %	38
Octane number	68
Saturated hydrocarbons, %	32
Unsaturated hydrocarbons,%	40
Aromatic hydrocarbons, %	28

A neutral oil fraction boiling between 170° and 300° C. has properties which make it suitable for use as diesel-engine fuel, though the cetene number of 46 prevents its use in high-speed engines.

The fraction boiling above 300°C. may be used as fuel oil for boiler-firing.

Jamieson and King do not consider the higher boiling fractions as having lubricating qualities, which is also pointed out by Wilson (109), and are of the opinion that only further treatment, such as cracking and polymerization, might produce lubricating oils.

The results of cracking and hydrogenation-cracking of cannel tars and direct hydrogenation of Newbattle cannel are also given.

The conclusions reached by these authors as a result of the examinations indicate that the exploitation of cannel coal, in existing gas-works equipment, for the production of town's gas and saleable fuels offers definite advantages, as compared with bituminous coal, and justifies the separation of cannel during mining and separate treatment in continuous-vertical retorts. The tar may be converted into marketable oils and other products by a. distillation, b. cracking and distillation, or c. hydrogenation-cracking. Comparative yields calculated per 100 gallons of tar would be:-

	a.	b.	c.	
Motor spirit, incl. gas spirit, galls.	12	21	36	or 105
Diesel oil, galls.	24	11	67	-
Fuel oil, galls.	27	5	-	-
Paraffin wax, lb.	58	-	57	57
Pitch, lb.	390	390	-	-

Direct hydrogenation of cannel would give higher yields of oil, but it offers no appreciable advantages over bituminous coal for this process.

Work of similar nature, only on smaller scale, has been carried out by Wilson (loc.cit), but is mainly concerned with low-temperature cannel tar. The carbonization of the cannel (Lower Dysart seam, Francis Pit, Dysart Colliery, Fife) was carried out at the Fuel Research Station (36), in a horizontal, mild steel retort of 100 lb. capacity at a temperature of 550°C. The point of interest in this instance is the considerable variation in yields and properties of the products obtained on this scale as compared with those from the 4 lb. capacity retort (mentioned on p.11). The author assumes that this variation is due to cracking taking place in the large retort, while, in the case of the small retort, great care was exercized to reduce cracking to a minimum. The possibilities of production of motor spirit, diesel and spindle oils are discussed fully and conclusions similar to those of Jamieson and King (loc.cit.) are drawn.

The results of hydrogenation-cracking in the vapour phase indicate that the tar is an excellent raw material for this process.

Vapour-phase cracking of the tar in straight and packed tubes is also discussed and comparisons of results with those of other workers are made.

In a paper on assessing the value of oil shales and cannels, Mott and Spooner (72) discuss the relation of oil yield as obtained by the Grey-King low-temperature assay to the hydrogen content of the dry, ash-free materials, and present formulae for evaluating oil yields by the hydrogen content or by volatile matter in conjunction with either calorific value or oxygen content. The authors list oil yields of several coals, oil shales and cannels obtained both by experiment and calculation. The experimental results appear to be somewhat lower than theory, the discrepancy being due to thermal decomposition (cracking) of the primary oil taking place inside the retort and, in this connection, Mott and Spooner emphasize the importance of withdrawing the oil vapours rapidly from the retort, thereby reducing the time of contact with hot parts of equipment.

The first report of the "Oil from Coal Committee"(84) describes the low-temperature carbonization process for the production of fuels in the event of national emergency. The utilization of a large variety of retortable, oil-yielding materials, including cannels, is considered, but the report is mainly concerned with the carbonization of bituminous coal.

In recent years Wood (110) examined a series of coals from the major known cannel seams with a view to the production of olefins for chemical manufacture. The first part of the work consisted of low-temperature assays in a modified Grey-King apparatus, followed by detailed analyses of the oils and gases produced, special attention being given to the hydrocarbon composition of the latter. The neutral oils were examined with respect to their hydrocarbon-type composition only.

The second part of the paper is concerned with the carbonization of cannels from the Great Seam, Newbattle Colliery, Midlothian, and Lower Dysart Seam, Randolph Colliery, Fife. The retorting was carried out in semi-commercial, rotary Davidson retorts (22) at a maximum temperature of 600°C. The results of retorting and the properties of the products are shown in Table 4.

TABLE 4.

	Lower Dysart		Great Seam	
	Light oil	Tar	Light oil	Tar
Yield, galls./ton	18.0	40.6	4.4	29.2
Specific Gravity	0.83	0.95	0.79	0.98
Tar acids, % wt.	9	20	5.5	36.5
Neutral oil fractionation,%				
0° - 200°C.	-	12.3	-	8.6
200° - 300°C.	-	23.5	-	22.5
300° - 350°C.	-	14.0	-	18.4
Residue	-	50.2	-	50.5
Composition of neutral oil boiling to 350°C., %				
Paraffins	17		15	
Naphthenes	3		1	
Unsaturateds	49		38	
Aromatics	31		46	

As compared with results quoted by Wilson (p. 16), the oils produced on retorting were, within close limits, the same in yield and composition as those obtained on the assay.

The light and crude oils from these two cannels were subjected to vapour-phase cracking in the presence of steam, in order to determine the yield of gaseous olefins in particular. Experimental conditions and full analyses of the gaseous products are given, though little attention is paid to liquid products.

Wood concludes that the low-oil-yielding cannels cannot possibly be a source of gaseous olefins for chemical manufacture, and that those cannels giving high oil yields would find it very difficult to compete with olefins derived from petroleum cracking in Great Britain.

The possibilities of combining the carbonization of oil shales and cannel coals with processes for the production of synthetic oils by the Bergius or Fischer-Tropsch processes are fully discussed by Underwood (96). The discussion is based entirely on theoretical considerations and the wide experience of the author, and, where necessary, values reported by other workers are used.

Conclusion.

As a result of the study of existing literature on the subject of composition of crude and refined oils derived from various naturally occurring and synthetic substances, it may be concluded that extremely little is known about the composition of cannel oils and about the nature of the compounds present therein. The results of type analyses of cannel distillates in the motor spirit range given in literature indicate a predominance of unsaturated hydrocarbons, and in this respect these oils may be best compared with shale oil distillates of similar boiling range, as shown in Table 5.

TABLE 5.

Material	Hydrocarbon-type analysis			Ref.
	Satds.,%	Unsatds.,%	Aromats.,%	
Newbattle Parrot seam cannel	32	40	28	50
Newbattle Great seam cannel	16	38	46	110
Lower Dysart seam cannel	20	49	31	110
Lower Dysart seam cannel	-	36	-	109
Scottish oil shale	46	43	11	45

METHODS OF SEPARATION AND DETERMINATION OF NORMALLY LIQUID HYDROCARBONS.

Hydrocarbons present in petroleum and other similar materials may be broadly classified as:-

a. paraffins,
b. naphthenes,
c. olefins, and
d. aromatics.

In the first three classes, all members below C_5 are gases, from C_5 to C_{15} they are liquids and the rest are waxy solids. This classification is satisfactory for gaseous and most liquid members, since these are characterized by the presence of a double bond, or a naphthene or aromatic ring in the molecule. On the other hand, the higher members of the series may consist of naphthenic or aromatic rings with long paraffin side-chains, in which case they exhibit naphthenic, aromatic or paraffinic properties to an extent depending on the proportion of these structures within the molecule.

The examinations of crude and refined oils with respect to their hydrocarbon constituents are naturally based on either or a combination of the two following methods:-

a. separation of individual hydrocarbons or hydrocarbon classes according to their physical or chemical characteristics, and

b. determination of the constituents on the basis of a certain physical or chemical property, which is either a linear function of the composition or is determinable for each constituent independently of the others.

Investigations concerned with the composition of gaseous and low-boiling liquid hydrocarbon mixtures are relatively straight-forward, as the numbers of possible isomers are not excessively high and their physical properties are known. As the temperature scale is ascended, however, the complexity of the hydrocarbons increases considerably and the problem of examination becomes extremely difficult, if not altogether impossible, not only because very little is known about the higher members of the series, but also the numbers of possible isomers become very large. (It is estimated that C_{13} paraffins have 802, C_{20} 366,319 and C_{40} up to 62×10^{12} possible isomers.) Material boiling in the naphtha or gasoline ranges (end pt. about 200°C.) has been examined in detail and a great amount of knowledge has been accumulated on the relative concentration and nature of the various constituent hydrocarbons, while analyses of higher-boiling material have been mostly confined to hydrocarbon-type estimations and determinations of average structures of the hydrocarbons, expressed in terms of the percentage of aromatic, naphthenic rings, or paraffinic side-chains.

It is impossible, within the limits of this thesis, to present an exhaustive and detailed survey of the various methods and techniques applicable to the resolution of hydrocarbon mixtures of varying complexity. It is, therefore, proposed to include in the following pages a brief discussion of the principal methods only, and to consider their applicability to the examination of the cannel oils under investigation.

A. Methods of separation of liquid hydrocarbons.

Methods applicable to the separation of hydrocarbon mixtures may be classified as:-

(i) Physical methods of separation.
(ii) Chemical methods of separation.

The first group comprises methods such as distillation, extraction, adsorption, which separate individual hydrocarbons according to their properties, while to the second group belong methods by which separations are accomplished on the basis of some specific chemical reaction, such as sulphonation, halogenation, etc. Accordingly, the latter methods find application mainly in separations between hydrocarbon classes exhibiting different chemical properties.

(i) Physical methods of separation.

The separation of a mixture of hydrocarbons into its individual components or simple mixtures containing hydrocarbons of similar physical or chemical properties may be most conveniently accomplished by one or more of the following techniques:-

a. Fractional distillation,
b. Distillation under varied pressure,
c. Azeotropic distillation,
d. Extractive distillation,
e. Solvent extraction,
f. Adsorption.

The separation of hydrocarbons is usually performed by the appropriate interlocking or combination of two or more of the above techniques and the scheme of separation can be described as consisting of three operations:-

a. separation of original mixture (containing paraffinic, naphthenic, olefinic and aromatic hydrocarbons) according to size of molecules,
b. separation of molecules of the same size according to type or group,
c. isolation of individual components.

<u>Fractional distillation.</u>

The most direct and simplest method of separating a complex mixture containing all types of hydrocarbons into a series of fractions of lesser complexity is by means of fractional distillation. The fact that relatively few of the lower hydrocarbons form azeotropic mixtures greatly facilitates their separation by distillation alone, though a given separation can rarely be accomplished by one operation; the number of operations required being dictated by the properties of the original mixture. For example, repeated distillation of a mixture of isomeric hexanes (b.pt. 49°-68°C.) will ultimately yield pure components, whereas it is very doubtful whether it is possible to resolve completely a mixture of C_{10} paraffins containing members, the boiling points of which frequently differ by a fraction of a degree C. It is, nevertheless, feasible, on account of a non-uniform distribution of boiling points and their appearance in clusters, to achieve a certain amount of separation and obtain fractions containing relatively high concentrations of one particular hydrocarbon.

During the past two decades the practice and theory of fractional distillation have undergone tremendous progress; this being best reflected by the constantly growing amount of literature on the subject. Perhaps the greatest advance has been made in all the practical aspects of distillation, with the result that to-day fractionating columns of an efficiency equivalent to 400 theoretical plates have been constructed and used in the concentration of oxygen isotopes. This is readily appreciated when it is considered that only a few years ago the separation of two compounds of 10°C. boiling point difference was hardly possible, unless very large charges and numerous distillations were employed.

The very extensive literature dealing with all theoretical and practical aspects of fractionation has been included in several excellent books (3,53,74,78,101) and has been frequently reviewed in the past. Reviews by Griffiths et al. (40), Fay (29) and Ward (103) cover most of the literature published before 1943 and deal with the whole subject of distillation. More recent, are the annual reviews by Rose (80), which again are concerned with all the aspects of distillation, while a short summary by the same author (79) deals with the present state of distillation. Similar reviews appear regularly in the "Industrial and Engineering Chemistry" (102) and the C.T.R.A. Reviews (77). The design and testing of fractionating columns have been discussed at length by Underwood (97) and French et al. (35), while in a series of papers, Dixon (26) describes the erection and operation of very efficient, automatic columns. A purely theoretical treatment of the design of packed columns in general has recently been presented by Pratt (76), and includes several worked examples of the application of theory to actual design problems. The theory and practice of distillation as applied to the refining of petroleum have been described by Brown and Souders (14), to mention only one.

The literature dealing with the application of fractional distillation to the separation of hydrocarbons and other substances from petroleum, coal tars and shale oils is too voluminous to be reviewed here, and only brief reference will be made to work bearing a direct relation to the problem at hand.

The most significant and important work on the separation of hydrocarbons is that carried on at the National Bureau of Standards by the A.P.I. Research Project 6, under the direction of F. D. Rossini. The work has been in progress since 1927 and has involved, till 1947, over 200 man-years of research. It has been reviewed by Washburn (105), Leslie and White (58), and more recently by Mair and Rossini (63) and Rossini (81). It is concerned with the separation and purification of hydrocarbons present in the midcontinent (South Ponca, Okla.) petroleum under investigation, and is based almost entirely on fractional distillations, conducted on varying scales and in columns having up to 200 theoretical plates. Methods other than distillation, are mostly applied to concentrates containing components of nearly identical properties or forming azeotropic mixtures. After separation, the components are usually re-distilled to yield a given hydrocarbon in a high state of purity (99.8% mole) as required for inclusion in the N.B.S. standard series of hydrocarbons (66).

Work on the chemical composition of petroleum of varying origin has been carried out by numerous other workers all over the world, using procedures similar to those outlined above. The problem of separating petroleum hydrocarbons by fractional distillation has been somewhat simplified by the absence of unsaturated hydrocarbons such as open-chain and cyclic mono-olefins, di-olefins and cyclic hydrocarbons with olefinic side-chains. Recently, however, unsaturateds present in concentrations exceeding 50%, in cracked gasoline and similar stocks, have been equally successfully separated by distillation, though the process is more laborious and requires frequent use of other techniques of separation; this being due to the great azeotrope-forming tendency between the olefins and other hydrocarbons, particularly aromatics (5,75).

The chemical composition of oils derived from naturally occurring materials and containing large proportions of unsaturateds has also been determined. Examinations of Scottish and American shale oils have been carried out using essentially the same methods as those applied to petroleum fractions (4,45,90,92).

In the present work, the investigation of the composition of light cannel naphtha was considered to be most successfully performed by means of high-efficiency fractionations followed by further separation of the concentrates by other suitable techniques, the choice of which would naturally be dictated by the properties and expected composition of the material and the quantities available.

As already shown, cannel naphtha was expected to contain a high proportion of unsaturated hydrocarbons (30-50%) and, therefore, the formation of azeotropic mixtures during distillation was anticipated. Methods capable of separating such mixtures were considered, and are briefly discussed below.

Distillation under varied pressure.

The separation of two or more hydrocarbons of nearly identical boiling points, which do not form an azeotropic mixture, may frequently be performed by distillation under varied pressure, either higher or lower than atmospheric, as the effect of pressure on boiling point varies for different classes of hydrocarbons. According to Sachanen (83) the decrease in the boiling point of aromatic hydrocarbons with decreasing pressure is more rapid than that of naphthenes, and that of naphthenes is more rapid than that of paraffins. Thus, two hydrocarbons, for instance a paraffin and an aromatic, boiling at the same temperature at 760 mm. Hg will have a spread in their boiling temperatures as the pressure is decreased, and proportional to that reduction. Rossini et al. (82) state that the spread in the boiling points for a paraffin and an aromatic of the same boiling point at one atmosphere is about 5°C. when the pressure is reduced to 0.075 atm. Under the same conditions, the spread of a naphthenic and an aromatic hydrocarbon of the same b. pt. is only 2°C. Thus separation of two hydrocarbons at 0.075

atm. may be quite feasible, provided the efficiency of the column is high; of the order of 100 theoretical plates, or more.

Azeotropic distillation.

Though highly efficient fractionating columns have been developed, it is often impossible to separate the components of a hydrocarbon mixture by normal distillation either because of the presence of several components of nearly identical boiling points or the formation of constant-boiling mixtures.

Azeotropic distillation has been used extensively for a number of years in such processes as the dehydration of aqueous alcohol, but it is only comparatively recently that it has been applied to the isolation of pure hydrocarbons or hydrocarbon classes from complex mixtures thereof. The method consists of an addition of an entrainer to the mixture to be separated, which affects the relative volatilities of the components, thereby altering their boiling points in such a way as to permit fractionation of the formed azeotropes. Mair et al. (62) state that, with some exceptions, nearly all polar molecules of the proper volatility form with paraffinic, naphthenic, olefinic and aromatic hydrocarbons, mixtures that have a total vapour pressure greater than that of the more volatile pure components, yielding minimum boiling azeotropic mixtures. The organic compounds that behave in this way include those containing hydroxyl, carboxyl, cyanide, amino, nitro and other structural groups that tend to produce polarity in organic molecules. Further, the azeotrope – forming substance should have the following properties (28):-

- a. boil within a limited range (0-30°) of the hydrocarbon which it is desired to separate,
- b. form, on mixing with the hydrocarbon, a large positive deviation from Raoult's Law to give a minimum azeotrope with one or more of the hydrocarbon types in the mixture,
- c. be soluble in the hydrocarbon at the distillation temperature and for some degrees below it,
- d. be easily separated from the hydrocarbons with which it forms an azeotrope,
- e. be readily obtainable and inexpensive,
- f. be stable at the distillation temperature,
- g. be non-reactive with the hydrocarbon or the column material.

Irrespective of the requirements ennumerated above, the choice of a suitable entrainer is still a rather difficult matter, and to a great extent, is based on practical experience and trial-and-error methods. Ewell et al. (28) report a means of eliminating this difficulty. Their method of selection of entrainers is based on the division of liquids into five classes, according to their hydrogen bond tendencies, from which a systematic summary of deviations from Raoult's Law may be derived and azeotrope-formation tendency predicted.

The application of azeotropic distillation to the separation of hydrocarbons has been extensively described in literature. Mair et al. (62) deal thoroughly with the principles and applications of azeotropic distillation and give data on azeotrope-forming substances, efficiencies of separation, and present a general procedure for the separation of hydrocarbons by the various types of distillations. Robinson and Gilliland (78) present the theoretical aspects of azeotropic distillation, while Sachanen (83) summarizes its applications both on laboratory and commercial scales. The patent literature on the subject is considerable, indicating the wide field of application to a great variety of separating problems. The separation of the lower aromatic hydrocarbons from gasoline cuts by azeotropic distillation has been described by Foster (34), Marschner and Cropper (69), Griswold and Bowden (41), and Mair and Rossini (63), to mention only a few. The formation of azeotropic mixtures between acetonitrile and thiols and hydrocarbons have been recently described by Bishop and Denton (9) and Denyer et al. (24) respectively, while Horsley (47) has published lists of azeotropes and non-azeotropes of binary and ternary systems. The application of azeotropic distillation to the problem in hand was considered and found to be of little value on account of the following:-

a. the cannel naphtha fractions to be investigated with respect to their composition were approximately one litre each with a b.pt. spread (i.e. difference in initial and final b.pts.) varying between 15° and 21°C. Consequently, the maximum volume of fractions taken-off during the distillations should not exceed 25 ml. if simple mixtures were to be separated. The separation of these mixtures by azeotropic distillation, should this be necessary, would involve the erection and operation of separate small-scale, highly efficient columns,

b. the large variety of hydrocarbons present in the cannel distillates would require a wide range of entrainers. Paraffinic, naphthenic and aromatic hydrocarbons have been studied and suitable entrainers are known for very many of these compounds, but comparatively little is known about substances forming azeotropes with olefins. As these predominate in cannel distillates, it would be necessary to develop a series of suitable entrainers for their separation, which would inevitably involve a considerable loss of time,

c. the separation of hydrocarbons according to their class or type could be successfully performed by means of azeotropic distillation in the existing equipment. However, the same type of separation may be performed with similar efficiency and lower expenditure in time and materials by adsorption on silica gel, and this technique of separation was preferred.

The first instance where azeotropic distillation was considered to be of especial value was in the separation of paraffin-naphthene mixtures, but owing to difficulties mentioned in a. above, the method was not used. The second instance was in the separation of pure aromatics from the concentrate (D-) fractions. The method considered here was as follows:- to combine all fractions (about 25 ml. each) containing one particular aromatic hydrocarbon and separate it by azeotropic distillation, followed by normal distillation of the aromatic-free portion. However, the presence of all types of hydrocarbons in the aromatic fractions complicated the selection of a suitable entrainer, whereas the separation could be accomplished by adsorption.

It must be emphasized, nevertheless, that the main reason for not using azeotropic distillation lay in the quantities of cannel naphtha available, and there is no doubt in the author's mind, that its use would considerably facilitate the separations and lead to a larger number of identifiable hydrocarbons.

Extractive distillation.

Extractive distillation is similar to azeotropic distillation in the fact that it is based, through the addition of another compound, on

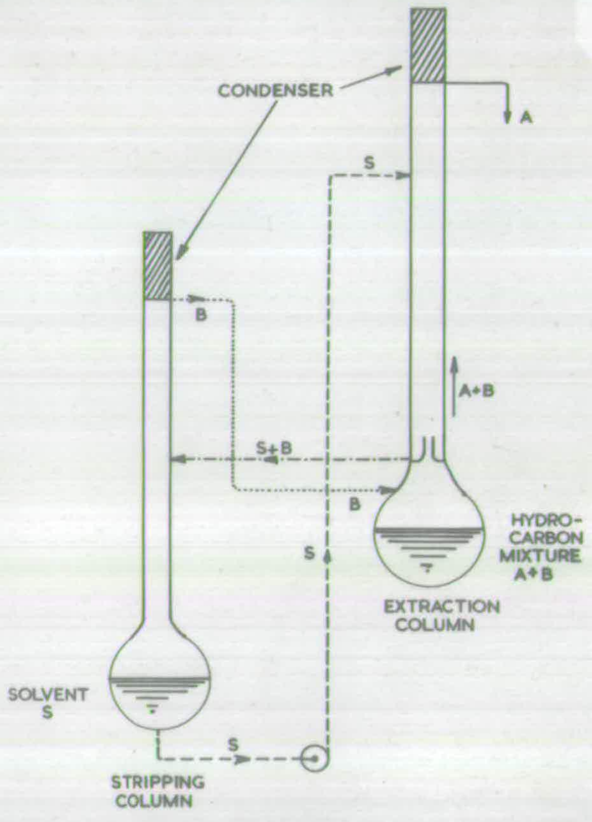

CONDENSER
A
S
B
A+B
S+B
B
HYDRO-
CARBON
MIXTURE
A+B
S
EXTRACTION
COLUMN
SOLVENT
S
S
STRIPPING
COLUMN

FIGURE I.

the modification of relative volatilities of two or more constituents of a mixture, inseparable by normal distillation.

The process requires somewhat modified fractionation equipment, as it is necessary to provide two columns - an extraction and stripping column - and other accessories. A non-hydrocarbon solvent, of considerably higher boiling point than the mixture, is added near the top of the extraction column and in its passage downwards effects a scrubbing action of the ascending vapours, of which one component is preferentially absorbed in the solvent. The solvent-hydrocarbon mixture passes then to the scrubbing column, where it is fractionated; the absorbed hydrocarbon being separated from the solvent and led back to the still of the extraction column, while the solvent is recycled. Material, the volatility of which has been increased by the addition of the solvent, is taken-off, with the result that a complete separation of the original mixture may be achieved. The principle of batch extractive distillation is illustrated diagrammatically in fig. 1.

The underlying principles of extractive distillation have been discussed at length in a number of papers and books. Garner (37) has published an excellent summary of the process and includes an interesting comparison of this method of separation with azeotropic distillation, while Benedict and Rubin (6) present a mathematical and fuller treatment of the process. Robinson and Gilliland (78) devote a chapter of their book to extractive distillation, and again treat the subject on a mathematical basis. The applications of the process and data on design and operation of extractive distillation equipment are also given. Several other papers, too numerous to mention, have appeared in recent literature, most of these have been referred to by the above authors. Typical examples of large scale application of extractive distillation are the separation and purification of C_4 hydrocarbons for the production of butadiene (15,44) and the refining of lubricating oils and diesel fuels (52), to mention only two.

On laboratory scale, the use of the method has been limited by the facts that it presents certain constructional and operational difficulties and separations produced do not justify the additional equipment and labour. The principal advantage of extractive distillation, as compared with azeotropic distillation, is that the selection of suitable solvents is easier and more solvents are available, since the nature of phase relationships in mixtures of solvent and components is not critical to the success of separation. Thus the various hydrocarbon types present in mixtures similar to those under investigation, i.e. of high olefinic content, have been separated (45), though separations were not as good as those produced by other means, such as azeotropic distillation or adsorption.

The application of extractive distillation to the present problem, and particularly to the lower fractions of cannel naphtha, was considered of little value owing to its relatively low efficiency of separation, large material requirements, and the need of erection of suitable equipment. However, as extractive distillation constitutes a very efficient means of separating hydrocarbons belonging to one particular type or group occurring in higher boiling material, such as Kerosene or "wax-free cuts", the fractionating column used in this work was designed so as to be easily converted to an extraction column and provision was made for the erection of a stripping column.

Solvent extraction.

Although of great industrial importance, liquid-liquid or solvent extraction has found limited application in laboratory scale separations of hydrocarbons, especially of those boiling below 200°C.

The Edeleanu and other processes have been applied to the separation of aromatics from relatively low-boiling material (over 120°C.) and the results indicate that, though the separations are moderately efficient, the method is not superior to azeotropic distillation or adsorption (64,65,107). Further, solvent extraction methods usually require large quantities of material and rather stringent operating conditions.

Adsorption.

The extremely wide field of chromatographic adsorption has, within recent years, been extended to cover the separation and quantitative determination of the main classes of hydrocarbons present in complex mixtures thereof. The method, a development of the original Tswett technique of analysis, consists of percolating a sample containing paraffinic, naphthenic, olefinic and aromatic hydrocarbons through a column of suitable adsorbent, such as silica gel, which selectively adsorbs the various types of compounds. A desorbing liquid, added after the sample has fully entered the adsorbent, forces the sample through the column, during which passage fractionation takes place and the various hydrocarbon types present are arranged in the order of decreasing adsorbabilities. The liquid issuing from the column is collected in small fractions and analyzed by refractometric methods. The sum volume and refractive indices of the fractions are plotted, from which graph the percentage composition of the sample is deduced. The method is capable of performing quantitative separations of saturated, olefinic and aromatic hydrocarbons. Mixtures of straight, branched-chain and cyclic paraffins, however, cannot be separated by this means. Straight- or branched-chain and cyclic olefins may be separated to some extent, though separations are not quantitative.

Analysis by adsorption on silica gel has been initially developed for the separation and purification of petroleum hydrocarbons by the National Bureau of Standards and the method has been fully described by Mair in a series of publications (68). The theoretical aspects of the process have been investigated by Mair et al. (67), who base their study on concepts used in theoretical analysis of fractionating processes in general, as for example, the process of distillation, and use the analogy to examine the separation of a binary mixture.

Although the method has been used extensively by numerous workers, relatively few modifications of the original Mair's technique have been proposed. One modification worthy of note, however, is the visual estimation of hydrocarbon classes adsorbed on silica gel, made possible by the addition of fluorescent dyes or other materials to the sample or adsorbent (18,20,38).

The application of adsorption analysis to hydrocarbon mixtures containing olefins has been studied in detail and the results obtained by Fink et al. (31), Dineen et al (25), Haresnape and Lowry (45) and Thorne et al. (92) working with cracked gasoline stocks and shale naphthas, indicate that the method is accurate and gives reliable results. In view of these considerations and the fact that very small quantities of material are required, it was decided to use adsorption analysis in the present investigation.

As will be discussed later, the method was tested with known hydrocarbon mixtures and found to fulfil the claims made by Mair and other workers, and was, consequently, used in determinations of the composition of wide- and narrow-boiling fractions and in the preparation of pure samples of hydrocarbons.

(ii) Chemical methods of separation.

Of the many reactions that hydrocarbons, and olefins and aromatics in particular, undergo, few have found application in the actual small-scale separation of mixtures of hydrocarbons into their individual components. The reasons for this lie mainly in the following facts:-

a. by the suitable combination of the various physical methods, almost any individual hydrocarbon may be separated in a high state of purity,

b. chemical methods are rarely applicable to the separation of individual hydrocarbons, and usually perform separations of one class of hydrocarbons from another, as for example olefins from paraffins,

c. separations by chemical means are infrequently quantitative, thereby resulting in loss of material and introducing error, especially if a given separation is used repeatedly,

d. as chemical separations are based on the formation of compounds between hydrocarbons of the same molecular configuration and a specific reagent, followed by the removal of the formed compound, the regeneration of the reacted hydrocarbons is often difficult, requires special procedures and, again, is seldom quantitative,

e. relatively large quantities of both reactants are usually necessary if experimental error is to be kept within reasonable limits.

The reaction between sulphuric acid of varying concentrations and olefinic or aromatic hydrocarbons is perhaps the best known and most widely used method of separating these hydrocarbons and has found important applications in industry, both in the refining of oils and in the production of raw material for the manufacture of a large variety of surface-active agents. The method has been used extensively in small-scale separations of hydrocarbons twenty to thirty years ago, but more recently it has been almost entirely superseded by the more efficient physical methods.

Another method which has found wide applications is the hydrogenation of unsaturated and, to a lesser extent, aromatic hydrocarbons. Hydrogenations of olefins are usually carried out at low pressures and/or low temperatures in the presence of catalysts such as nickel on kieselguhr

(49,100), Raney nickel (45), palladium (54,106), molybdenum (99) and platinum (23). The hydrogenation of aromatics, on the other hand, requires much more severe conditions, thus enabling selective hydrogenation of olefins without prior separation (83).

Several other feasible methods exist, being discussed at length by Sachanen (83), but in view of the considerations summarized above, it was decided to limit the present work to physical separations only, especially since an attempt was made at a quantitative examination of the cannel oil distillates.

B. Methods of determination of hydrocarbons.

As already pointed out, the methods of determining the constituents of liquid hydrocarbon mixtures of varying complexity, comprise all those methods which do not involve an actual separation of the hydrocarbons, but are based on some physical, or to a lesser degree, chemical property of the mixture, which is assumed to be a linear function of the composition. The properties most commonly used in this connection are:-

molecular weight
ultimate composition
boiling point
density
refractive index
bromine number
aniline point
viscosity

By the appropriate combination of two or more of these properties, the presence and quantity of an individual hydrocarbon, or more frequently, of a group of hydrocarbons of similar molecular structure may be detected and estimated.

Because of the similarity of properties of hydrocarbons belonging to one particular homologous series, it is usually impossible to identify individual constituents of a mixture, and consequently, the majority of the methods described under the present heading are intended for the examination of such mixtures only with respect to their hydrocarbon-type composition. Methods capable of quantitative and qualitative estimation of individual constituents independently of the others have been recently developed, and comprise the highly specialized techniques of mass, ultra-violet, infra-red or Raman spectroscopy.

The determinations of hydrocarbons or hydrocarbon classes utilizing the above properties are based on the facts that a. the simple physical properties of all hydrocarbons within one homologous series are, to a large extent, a function of the boiling point and hence of the molecular weight of the members of the series, and b. the ranges of variation of two or more properties with the boiling point are characteristic of the given series. This is shown in Table 6,(p.44), where the ranges of variation of the four most commonly used properties are shown for the different homologous series of hydrocarbons boiling in the range 40°-150°C., containing from five to nine carbon atoms in the molecule. Each range is given in the direction of increasing boiling point.

TABLE 6.

C_5-C_9 H'carbons b.pt. 40°-150°C.	d_4^{20}	n_D^{20}	Aniline pt., °C.	Br_2 No.
Straight-chain paraffins	0.64-0.75	1.37-1.43	80-65	0
Cyclic paraffins	0.74-0.80	1.40-1.44	50-30	0
Straight-chain mono-olefins	0.63-0.76	1.37-1.43	20-45	190-120
Cyclic mono-olefins	0.77-0.84	1.43-1.46	Ca.-10	230-130
Aromatics	0.86-0.88	1.49-1.51	Below-30	0

Occasionally it is possible to differentiate between normal and branched-chain compounds of the same molecular weight and belonging to the same homologous series, since such properties as density and refractive index are frequently lowest for the former and increase with the number of chain substituents, as shown:-

Hydrocarbon	d_4^{20}	n_D^{20}
n-nonane	0.7176	1.4054
3-methyloctane	0.7207	1.4062
3:4-dimethylheptane	0.7314	1.4111
3:3:4-trimethylhexane	0.7452	1.4178
2:2:3:3-tetramethylpentane	0.7567	1.4236

However, such determinations are not always possible and often require knowledge of boiling points and other properties.

The interrelationship of physical properties of hydrocarbons and the relation of these properties to their structure have been very extensively studied and a considerable amount of data on this subject is now available, some of which has been discussed by Boord (10), Lipkin et al. (59) and Ward and Fulweiler (104).

The methods of determining hydrocarbons present in straight-run or cracked fractions boiling below 160°C. and based on the considerations given above are briefly discussed in the following pages and their application to the cannel distillates under investigation is considered.

Determination of hydrocarbons by refractometric methods.

a. As pointed out by Sachanen (83) the density and refractive index of narrow, straight-run fractions may be used for determining the percentage of aromatics, naphthenes and paraffins. The methods described are based on the great difference of these two properties for aromatic and aromatic-free fractions of the same boiling range. The procedure for determining the percentage of aromatic hydrocarbons in the fraction consists of the removal of aromatics by sulphonation and of the measurement of density and refractive indices of the original and aromatic-free samples. Since it is assumed that the density and refractive indices of a hydrocarbon mixture containing paraffins, naphthenes and aromatics are a linear function of the composition, the percentage aromatics present in the sample is equal to the difference in densities or refractive indices before and after treatment, divided by an appropriate factor. An average deviation of 10% with reference to the aromatics is claimed for the method.

The determination of paraffins and naphthenes may be made by similar methods, though in this case the results are less reliable. Neither method, however, is applicable to material containing olefinic hydrocarbons.

b. Kurtz and Ward (56) showed that the refractivity intercept

$$\text{R.I.} = n_D^{20} - \frac{d_4^{20}}{2}$$

is nearly constant for hydrocarbons belonging to the same class and has the following values for the sodium D-line:-

Paraffins	1.0461
Naphthenes	1.0400
Aromatics	1.0627
Cyclic mono-olefins	1.0461
Non-cyclic mono-olefins	1.0521
Cyclic conjugated di-olefins	1.0643
Non-cyclic conjugated di-olefins	1.0877
Non-cyclic non-conjugated di-olefins	1.0592

The refractivity intercept of hydrocarbons boiling in the gasoline range is approximately a linear function of the composition and, consequently, has been applied to the calculation of composition of narrow gasoline cuts by Kurtz and Headington (55) and, more recently by Gooding et al. (39). Results of the latter workers indicate that the method is sound and gives reliable results, but was not found practicable in the present work as it involves the determination of refractive indices at different wavelengths and is only applicable to straight-run fractions.

c. A method of determining aromatic hydrocarbons in the presence of saturated and unsaturated hydrocarbons and based on measurements of specific dispersion has been introduced by Grosse and Wackher (43) and improved by Groennings (42). The method was used in the present investigation and will be fully discussed in connection with the determination of aromatics in light cannel naphtha fractions (B-fractions).

d. The differentiation between paraffins and naphthenes and their relative concentrations can be deduced from the knowledge of specific refraction R, calculated by the formula

$$R = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{1}{d}$$

where n and d are the refractive index and density respectively, both measured at the same temperature. The method was developed by Waterman and his co-workers (100) for the examination of saturated constituents of higher boiling oils, but may be equally well used for low-boiling fractions, provided the molecular weight is known. Further, since specific refraction of paraffins and five- and six-membered naphthenes equals the sum of atomic refractions divided by molecular weight, the H:C ratio of an oil may also be calculated.

During the present research, paraffins and naphthenes present in the concentrate or D-fractions were frequently determined by this method, their molecular weights being estimated with reasonable accuracy on consideration of boiling point.

Determination of hydrocarbons by aniline points.

The aniline point of an oil is the lowest temperature at which the oil is completely miscible with an equal volume of aniline, (I.P.-2/47), and thus is a quantitative measure of the solubility of the oil (hydrocarbon or fraction) in aniline. The values for aniline points vary considerably with the various classes of hydrocarbons, being highest for paraffins and lowest for aromatics and this variation has been utilized in the determinations of composition of relatively narrow-boiling fractions of straight-run distillates.

The method of determination of aromatics in fractions containing paraffins and naphthenes is based on the depression of aniline points effected by aromatics present in the fraction, the percentage aromatics being obtained by:-

$$\%\text{-ge} = K(T_2 - T_1)$$

where T_1 and T_2 represent, respectively, the aniline points of the fraction before and after removal of aromatics, and K is the coefficient or percentage aromatics (by wt.) effecting 1°C. of depression.

The determination of K and its variation with individual hydrocarbons as well as the methods in general are discussed by Sachanen (83).

The same principle may be applied to the determination of naphthenes in presence of paraffins only, provided the aniline coefficients of naphthenes are known. This determination, however, is not as reliable as the former, owing to the small difference in aniline points between the two hydrocarbon classes.

The aniline point method has been further extended to cover fractions containing olefins, and is now used as a standard method for determining aromatics in the presence of all other types of hydrocarbons (I.P.-3/49). The procedure is similar to the one described above; a correction, based on the bromine number of the fraction being applied for the olefins. This method was used in the present work in connection with the determination of composition of B-fractions and is described later.

Determination of hydrocarbons by bromine numbers.

The determination of unsaturated hydrocarbons by halogenation, and in particular bromination, has been very extensively investigated and numerous methods for the determination of bromine numbers, and hence, of the degree of unsaturation of a given sample, have been developed (83).

Theoretically, any of the methods may be used for the determination of the percentage of olefins in a fraction, though in practice the limitations of some of the methods are considerable. The percentage of olefins is calculated by the simple proportion:-

$$\text{\%-ge wt.} = \frac{100 \cdot X}{B}$$

where X and B are the actual and theoretical bromine numbers, respectively. The method, therefore, may only be applied to very narrow-boiling fractions, the molecular weight of which can be predicted with reasonable accuracy.

In the present work, bromine number determinations were carried out repeatedly on all types of material, the method used being the modified McIlhiney method (I.P.-9/42). No actual estimation of the olefin content by this method was undertaken, though the results of the determinations were used as an indication of the type and degree of unsaturation of the hydrocarbons, and for identifications of individual olefins.

Ring and ultimate analysis.

A method of expressing the ultimate constitution of an oil fraction has been developed by Vlugter, Waterman and van Westen (100). The analysis supposes the oil to be composed of paraffin chains, naphthene and aromatic rings only, and defines composition in terms of the percentage of each of these groups. The method is based on the difference of these classes of compounds in respect of density, specific refraction and aniline point before and after hydrogenation.

The method and its modifications and extensions, described fully by the authors cited, and by Sachanen (83), apply primarily to fractions boiling above 200°C. and containing no unsaturated hydrocarbons.

The approximate structure of hydrocarbons present in a given narrow-boiling fraction may be determined from its empirical formula, obtained by ultimate analysis of the fraction, and the determination of its molecular weight. Both these estimations require rather specialized techniques and, though providing very useful indication as to the type of hydrocarbons, the information thus obtained did not seem to justify the time and labour inevitably involved, especially since well over one hundred fractions were to be examined.

Spectrographic analysis.

The spectrographic methods of analysis of individual hydrocarbons or hydrocarbon mixtures comprise the following techniques:- ultra-violet, infra-red and mass spectroscopy and the Raman effect. The analyses are based on the fact that the absorption of radiation by organic molecules is selective, resulting in the absorption of certain well defined ranges of radiation depending upon the molecular structure. The absorption bands of each hydrocarbon are characteristic of the given structure and independent of other hydrocarbons, thus enabling quantitative and qualitative determinations of constituents of a hydrocarbon mixture. Absorption bands indicate the presence of a compound, while their intensity serves as a measure of its concentration.

A tremendous amount of literature has been published within recent years on the application of the various spectrographic techniques to the examination of hydrocarbons and their mixtures. These methods appear to be extremely sensitive and accurate, and from that standpoint, supersede all other existing methods, especially for the identification of individual compounds. Of the many excellent reviews covering all aspects of the subject, those by Lecomte (57), Lothian (60), Sheppard et al. (86,87) and Twyman and Allsopp (95) may be mentioned.

During the course of the present investigation a number of aromatic hydrocarbons were identified by ultra-violet spectra, but lack of the necessary equipment prevented the extension of this method to the analysis of aliphatic constituents of the cannel naphtha.

Miscellaneous methods of determination.

A number of methods involving the concepts of correlation index, parachor, viscosity index, viscosity-gravity constant, and others, have been described frequently in literature (104). These methods were studied at various stages of the present work and found to be of little value, either because the results thereby obtained would provide little information, or the methods were not directly applicable to the cannel distillates under investigation.

THE OBJECTS AND NATURE OF PRESENT INVESTIGATION.

As already pointed out, very little information is available concerning the ultimate chemical nature, apart from a rough indication as to the hydrocarbon-type composition, of Scottish cannel coal distillates and, consequently, the research described in this thesis had as its principal objects the following:-

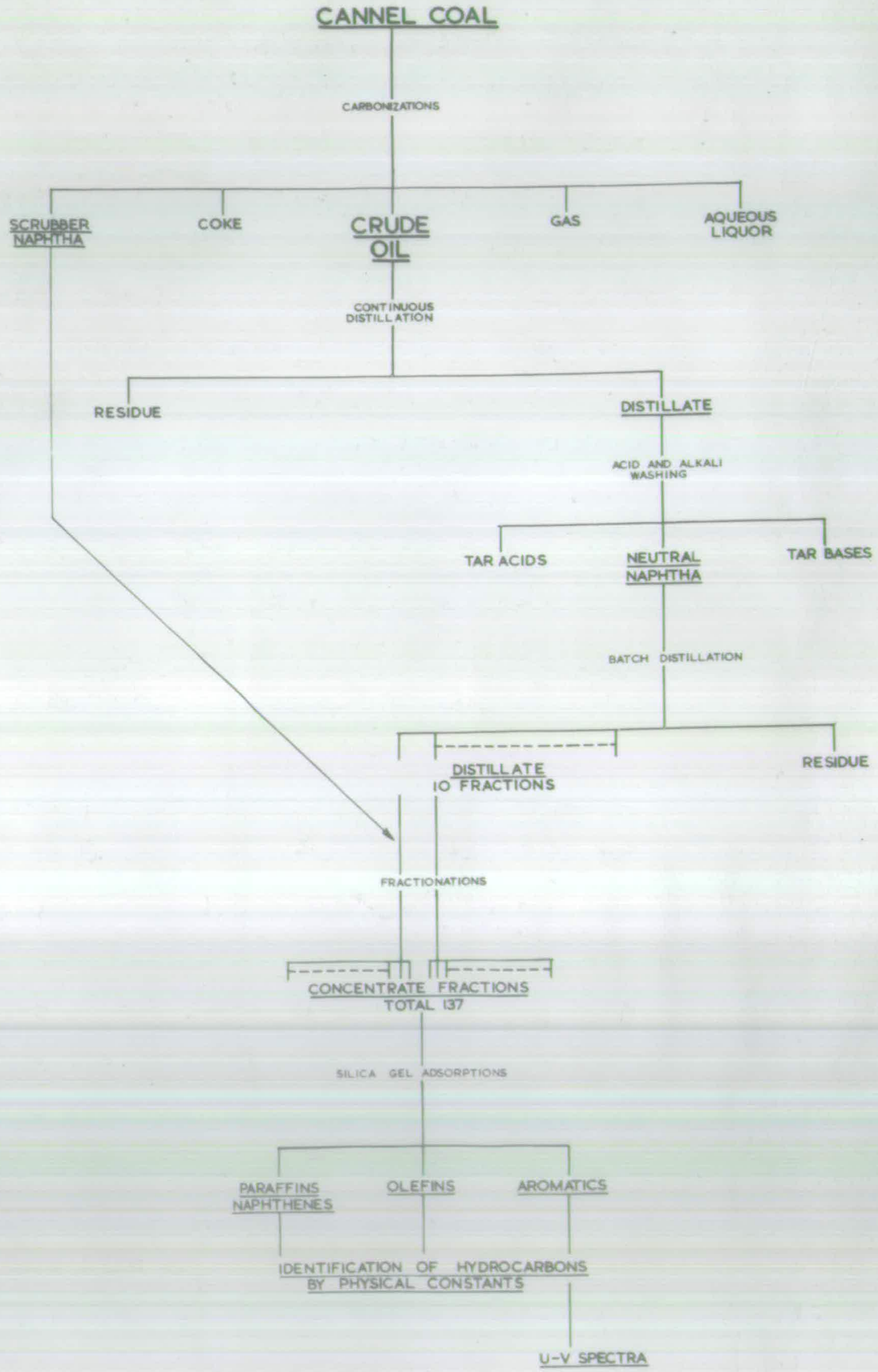
a. examination, conducted as far as possible on a quantitative basis, of the general character of hydrocarbons present in a small fraction (corresponding roughly to straight-run naphtha or gasoline cuts) of crude cannel oil,

b. the identification and estimation of concentration of some of the major constituents of the fraction, and

c. comparison of the cannel naphtha, on the basis of the results obtained, with similar materials from other sources, such as petroleum, shale oil and bituminous coal tar.

Owing to the present state of cannel coal industry in Scotland, the experimental work necessarily included the production of crude cannel

FIGURE 2.


CANNEL COAL
CARBONIZATIONS
SCRUBBER NAPHTHA
COKE
CRUDE OIL
GAS
AQUEOUS LIQUOR
CONTINUOUS DISTILLATION
RESIDUE
DISTILLATE
ACID AND ALKALI WASHING
TAR ACIDS
NEUTRAL NAPHTHA
TAR BASES
BATCH DISTILLATION
DISTILLATE
10 FRACTIONS
RESIDUE
FRACTIONATIONS
CONCENTRATE FRACTIONS
TOTAL 137
SILICA GEL ADSORPTIONS
PARAFFINS NAPHTHENES
OLEFINS
AROMATICS
IDENTIFICATION OF HYDROCARBONS BY PHYSICAL CONSTANTS
U-V SPECTRA

oil, and in all consisted of the following five stages:-

1. low-temperature carbonization of cannel coal, carried out on laboratory scale,
2. preliminary distillations of the crude oil and separation of a series of fractions boiling within the range of normal straight-run naphtha or gasoline cuts,
3. separation of the relatively wide-boiling fractions, by precise high-efficiency fractionation, into hydrocarbon concentrates of narrow-or constant-boiling range,
4. further separation of the concentrates, by adsorption on silica gel, into individual hydrocarbons or simple mixtures,
5. determination of physical constants and identification of the major constituents of the concentrates.

The condensed flow diagram (fig. 2) outlines the general scheme followed, by which a fraction of the crude oil was broken down into a number of identifiable constituents.

The conditions under which the cannel coal was to be carbonized and the type of retorts used were carefully considered and, following the views put forward by previous workers regarding the most satisfactory and favourable exploitation of cannel, it was decided to carbonize the coal in mild steel horizontal retorts, special care being exercized to avoid cracking of the tar vapours.

The major part of the work was centred round stages 3. and 4., the first of which also comprised the design, erection and testing of the fractionating equipment.

The choice of methods most directly applicable to the analysis of hydrocarbon concentrates was largely dictated by the quantities of material available and the type and degree of separation achieved. Chemical methods of separation, as already mentioned, were of little practical value, and of the physical methods considered, percolative adsorption on silica gel appeared to be the most suitable on account of low material requirements, high separating efficiency and relatively simple procedure and apparatus. This method was fully tested with known hydrocarbon mixtures and was so modified as to permit quantitative examinations of 5 ml. samples, without increasing the experimental error involved.

Approximately 75% of the concentrate fractions were analyzed by this means and the results of the adsorptograms obtained allowed a quantitative estimation of the hydrocarbon-type composition of total material investigated.

Concentrate fractions containing substantial quantities of material of constant refractive index (as indicated by adsorptograms) and corresponding to a plateau on the boiling point-% distillate curve were bulked and subjected to a succession of adsorptions until material of absolutely constant

n_D was obtained. The physical constants were then determined and the hydrocarbon was finally identified by comparison of the data obtained with those reported in literature.

Owing to limited quantities of material, identification of the minor constituents of the naphtha was impossible, though usually the information obtained from adsorptions on silica gel, together with the results of determinations of physical constants, provided adequate clues as to the type of material present in a given cut.

Further examination of such material and the confirmation of identity of the major constituents by spectroscopic analysis in the infra-red was, unfortunately, impossible owing to lack of the necessary equipment. However, analyses carried out in the ultra-violet were applied to the examination of the aromatic constituents.

The time expended in the erection of carbonization, distillation and other equipment necessarily curtailed the time available for a more detailed examination of the close-cut fractions and, unfortunately, prevented the extension of the work to cover higher-boiling fractions. For the same reason, several other projected separating techniques, such as azeotropic distillation or hydrogenation, could not be applied to the naphtha or higher-boiling fractions.

PART II.

EXPERIMENTAL WORK.

CARBONIZATION OF CANNEL COAL.

Reference has already been made to the fact that at the present time no cannel coal is being used alone in either the oil- or gas-making industries of this country, and consequently, the production of crude cannel oil constituted a very necessary preliminary to the research described in this thesis. The lack of suitable pilot-plant or large scale carbonizing equipment necessitated the erection of a carbonizing unit in the laboratory; the principal factors considered in this connection being, briefly, as follows:-

a. since the object of this work was the investigation of the composition of a small fraction of crude cannel oil, the quantity of the starting material had to be sufficient to allow examinations of constituent hydrocarbons, expected to occur in concentrations as low as 0.05% of the crude,

b. as a result of this, the carbonizing unit had to be of as large a capacity as laboratory space and materials would permit, so as to be capable of producing the required quantity of crude oil in a reasonable number of carbonizations,

c. all carbonizations had to be conducted under fully standardized conditions in order to yield products of constant properties,

d. the conditions under which the cannel was to be carbonized, viz. at low temperature, were based on opinions put forward by the majority of previous workers in this field (21,109,110).

The carbonization unit was, therefore, designed for operation at a maximum temperature of about 550°C., special attention being exercized to avoid as far as possible the cracking of tar vapours.

Nature of cannel coal used.

The cannel coal used in this investigation was obtained, through the kindness of the National Coal Board, from the Parrot seam, Lady Victoria Pit, Newbattle Colliery, Midlothian. Results of analyses on a representative sample of the coal are given in Table 7.

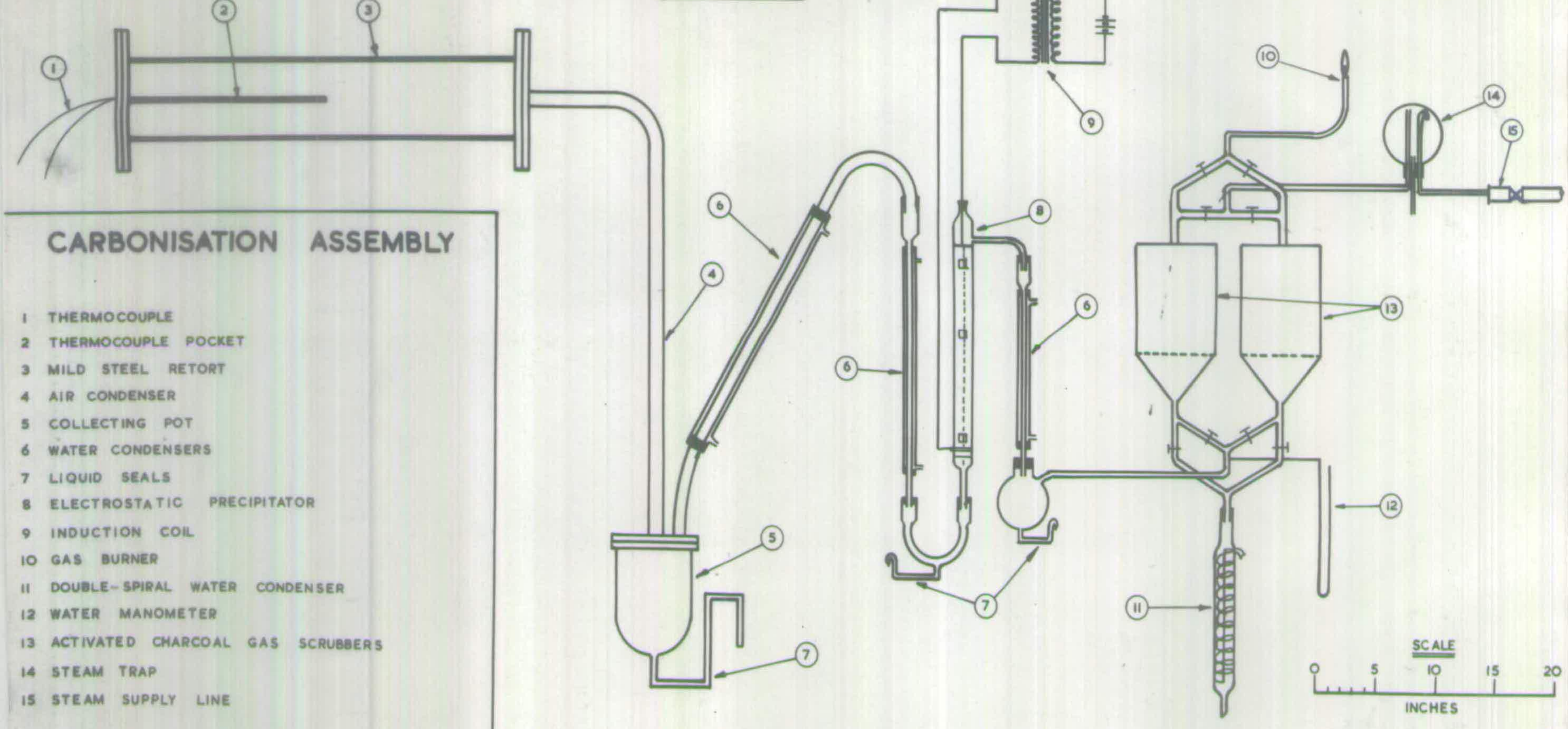
TABLE.7.

Analysis of Newbattle Cannel.

Proximate analysis (% wt.):-	
Moisture	3.3
Ash	5.9
Volatile matter	50.2
"Fixed" carbon	40.6

Calorific value, B.Th.U./lb. 14,560

FIGURE 3.



CARBONISATION ASSEMBLY

1 THERMOCOUPLE
2 THERMOCOUPLE POCKET
3 MILD STEEL RETORT
4 AIR CONDENSER
5 COLLECTING POT
6 WATER CONDENSERS
7 LIQUID SEALS
8 ELECTROSTATIC PRECIPITATOR
9 INDUCTION COIL
10 GAS BURNER
11 DOUBLE-SPIRAL WATER CONDENSER
12 WATER MANOMETER
13 ACTIVATED CHARCOAL GAS SCRUBBERS
14 STEAM TRAP
15 STEAM SUPPLY LINE

Table 7.(contd.)

Grey-King Assay at 600°C.	%wt.	lb./ton
Crude oil	24.1	540
Aqueous liquor	10.2	228
Coke	57.3	1284
Gas and losses	8.4	188
	100	2240
Potential crude oil, gall./ton	59.8	
Ultimate analysis (% wt. a.-f.d.)		
C	85.6	
H	7.1	
N	1.2	
S	0.9	
O (by diff.)	5.2	

Carbonization unit.

The carbonizing unit consisted essentially of the following:-

a. three horizontal, gas-heated retorts,

b. primary condensing system comprising air and water-cooled condensers and a condensate catch-pot,

c. secondary condensing system comprising two water-cooled condensers and an electrostatic precipitator,

d. activated charcoal scrubbers and a gas burner.

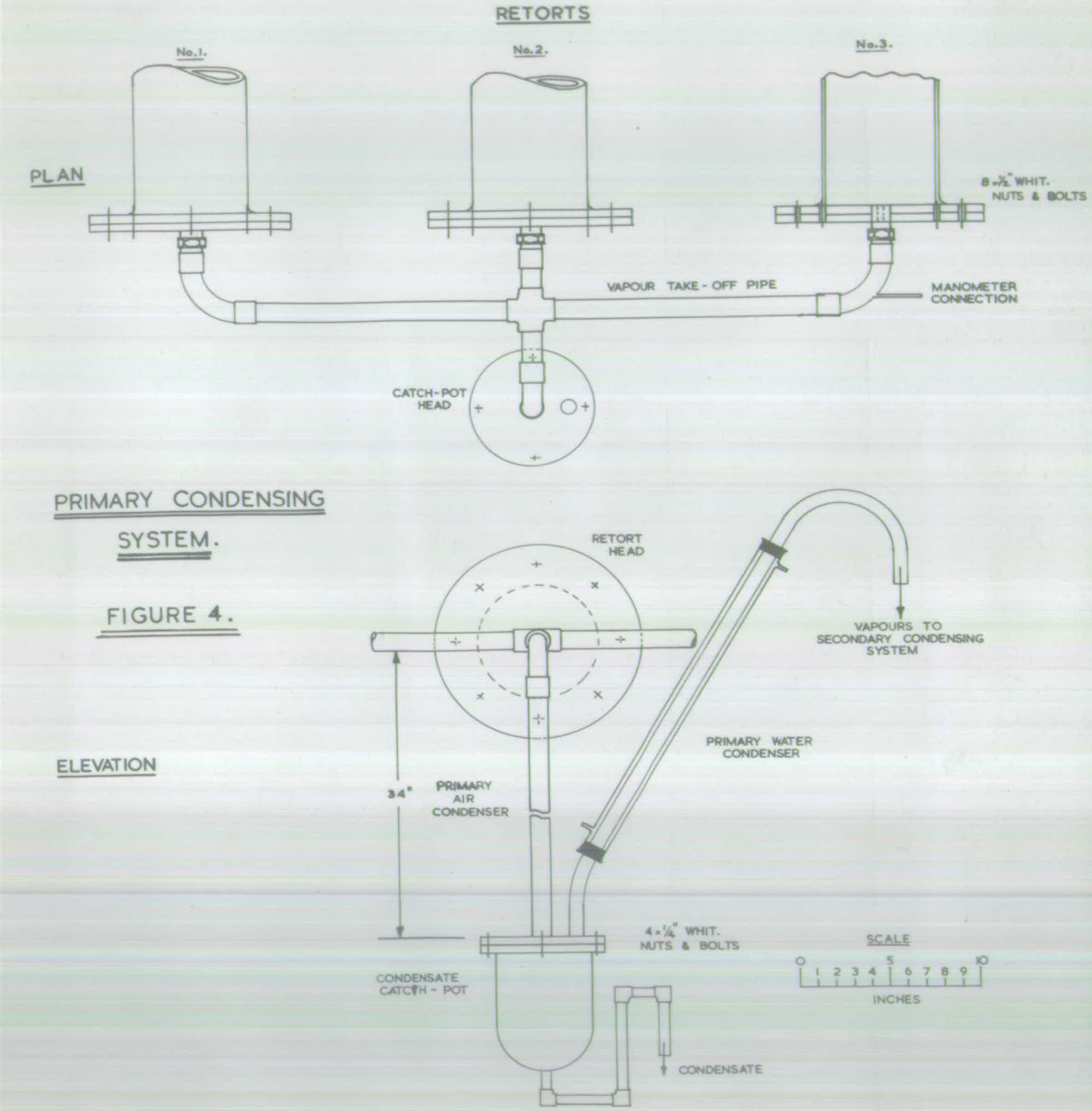
The complete assembly is shown diagrammatically in fig. 3.

The cannel coal was carbonized in three

horizontal, mild steel retorts connected in parallel to a common vapour take-off pipe. The hot vapours leaving the retorts were passed into a vertical air-cooled condenser, where most of the vapour condensation took place, the condensate collecting in a cast iron catch-pot. Provision was made, by means of a U-shaped, liquid-sealed tube mounted in the base of the catch-pot, for continuous discharge of the condensate into an external receiver. On leaving the catch-pot, the vapours entered a water-cooled condenser, where further condensation took place accompanied by the formation of a tar mist. The condensate drained back into the catch-pot, while the mist-laden vapours entered the secondary condensing system. The removal of the tar mist and the final cooling of the gases were accomplished by means of a water-cooled glass condenser, an electrostatic precipitator and a final water condenser. Condensate obtained at this stage was collected and run-off through liquid-sealed U-tubes. After passage through this system, the gases were led to either one of two activated charcoal scrubbers, for final removal of light hydrocarbons, and were burned in a jet burner. Two water manometers were introduced into the system; one at the top of the primary air condenser and the other at the base of charcoal scrubbers.

Retorts.

The retorts consisted of three mild steel pipes, each 6" I.D. and 32" long, flanged at both



PRIMARY CONDENSING SYSTEM.

FIGURE 4.

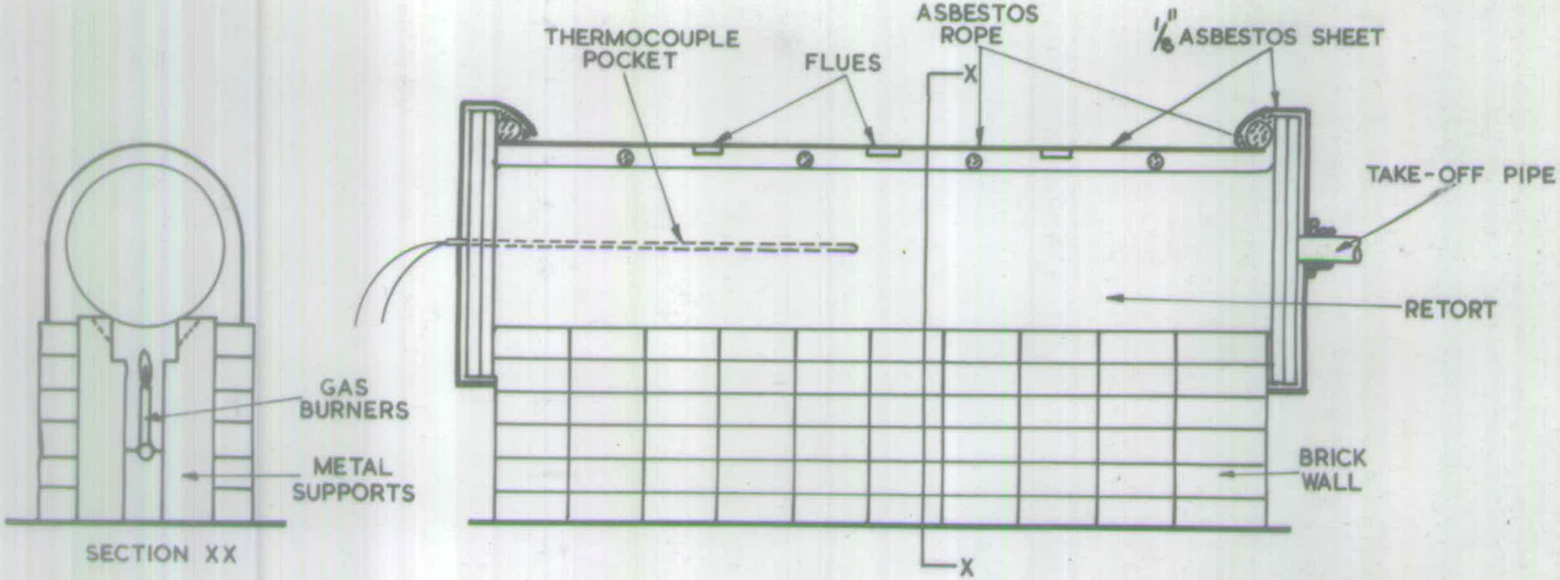


FIGURE 5.

METHOD OF LAGGING RETORTS.

ends and carrying blank end plates. One end of each retort was permanently connected to the common vapour take-off pipe, as shown in fig. 4., while the other end could be opened for the purpose of charging and discharging the coal. Asbestos gaskets were used on all joints. The temperature inside the retorts was measured by iron-constantan thermocouples, connected to a Cambridge direct-reading millivoltmeter, calibrated to read in degrees C. The thermocouples rested in metal sheaths, ¼" I.D. and 17" long, closed at one end, and mounted in the centre of each removable end plate, so as to measure the temperature at the centre of the coal charge.

Heaters.

The heaters were modified gas-fired combustion furnaces, each consisting of 18 individual Bunsen burners mounted on a common base. The body of each retort rested horizontally on the furnace and at such a distance above the burners as to prevent direct impingement of flames on the retorts. The retorts were fully lagged by means of thick asbestos sheets and fireclay bricks. Details of the lagging method are shown in fig. 5. This system of lagging proved quite satisfactory and temperatures of the charge up to 600°C. could be attained. A water manometer connected to the gas supply to each furnace enabled heating conditions to be reproduced successfully.

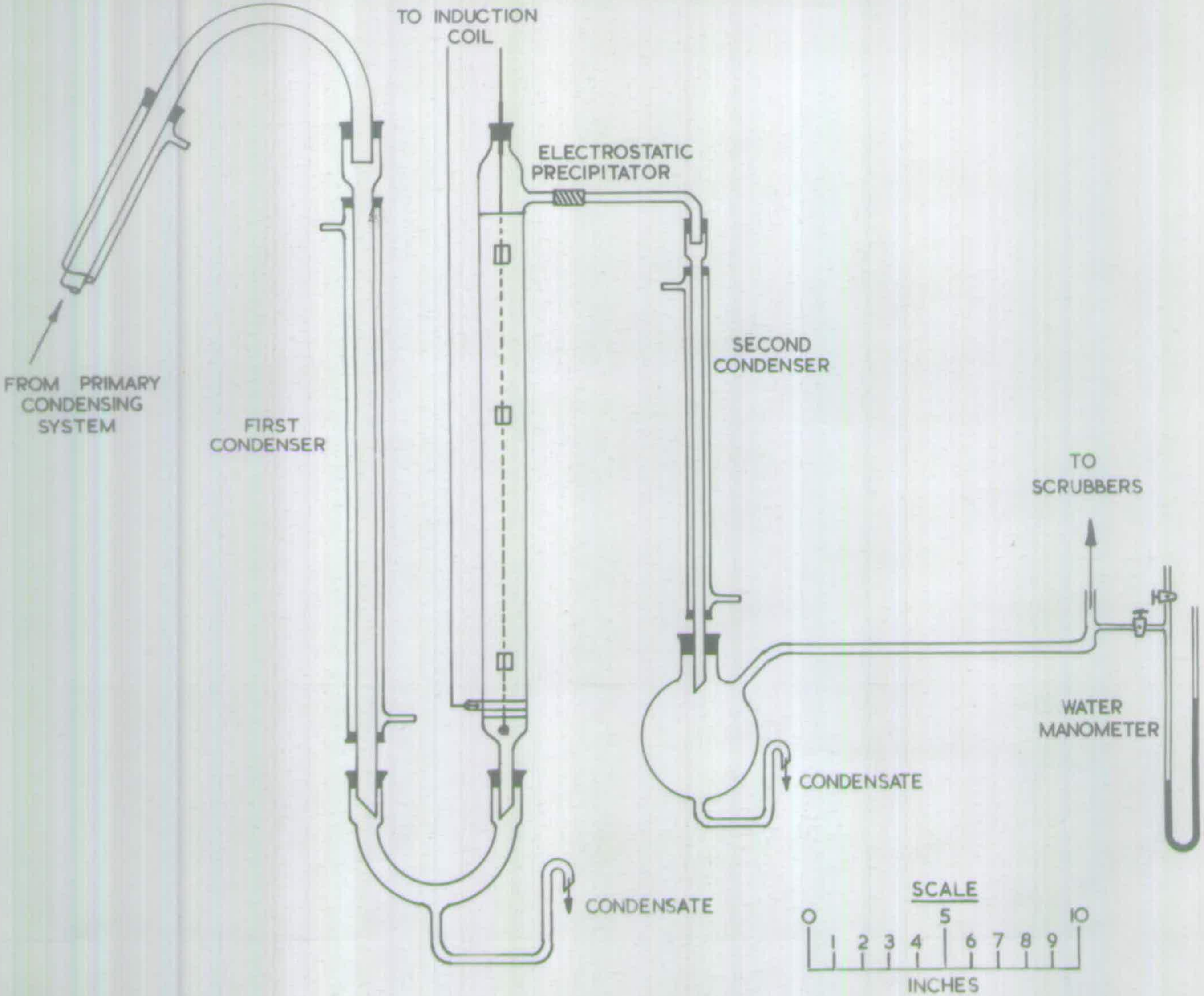


FIGURE 6.

SECONDARY CONDENSING SYSTEM.

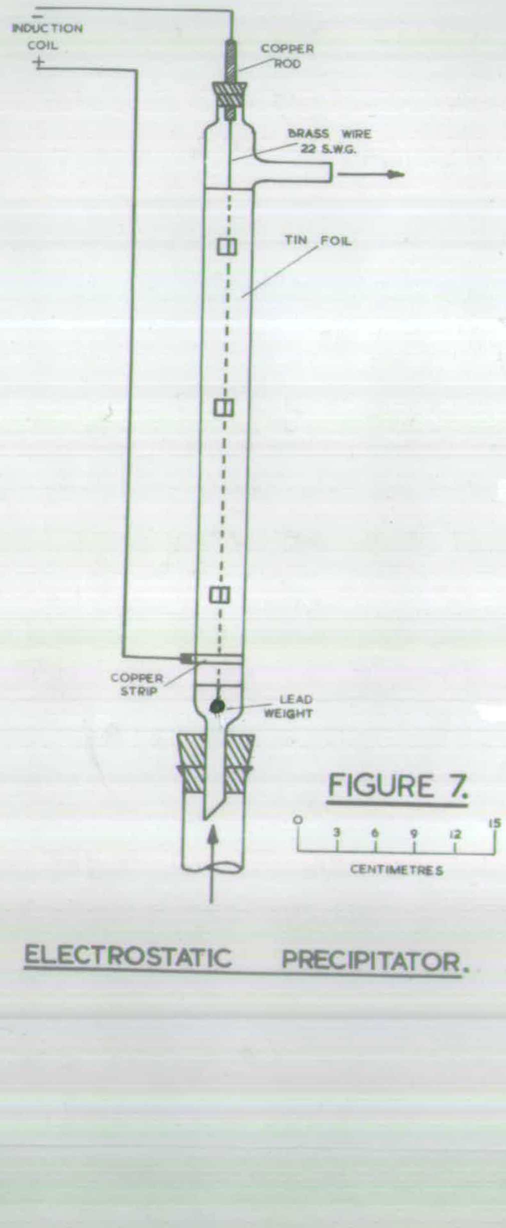


FIGURE 7.

ELECTROSTATIC PRECIPITATOR.

Primary condensing system.

The primary condensing system shown in fig. 4 (facing p. 62) comprised a mild steel air-cooled condenser, 1" I.D. and 34" long, connected at one end to the vapour take-off pipe leading from the retorts, and at the other to a cast iron catch-pot, equipped with a U-shaped pipe for continuous discharge of condensate. A second water-cooled mild steel condenser was mounted on the catch-pot in the manner shown in fig. 4 (facing p.62).

Secondary condensing system.

This system, shown in fig.6, consisted of two water-cooled glass condensers and an electrostatic precipitator, all mounted vertically and in series to the flow of vapours.

Electrostatic precipitator.

The inclusion in the secondary condensing system of an efficient means of tar mist dispersal was found to be very necessary as tar mist deposited on the charcoal of the scrubbers rendering them inactive in a short time. The simple form of electrostatic precipitator used is illustrated in fig. 7. It consisted of a glass tube, 1½" I.D. and 19" long, covered on the outside with tin foil cemented on with shellac varnish. A strip of brass wound tightly round the tin foil formed one connection to a H.T. terminal of an induction coil, while the other electrode was situated inside the glass tube. This central electrode consisted of

18" of 36 S.W.G. wire suspended from a short piece of copper rod passing through a rubber bung inserted in the top opening of the glass tube. The copper rod was connected to the other H.T. terminal of the induction coil. A small lead sphere was attached to the central wire to keep it hanging in a vertical position and parallel to the sides of the tube.

The performance of the precipitator was found to be very satisfactory and complete removal of the mist was attained in the first 6" - 8" of the tube, the tar droplets collecting on the sides of the tube and draining into the U-shaped receiver, while the gas passed on to the second water-condenser.

Gas scrubbers.

Two gas scrubbers were incorporated in the system, in parallel to the gas flow, consisting of two cylindrical vessels of conical base, 6" dia. and overall length 12". A circular piece of wire gauze 5½" dia. was placed in the conical part of each vessel to provide a support for the activated charcoal. The gases entered the scrubbers through an opening in the base and travelled upwards, leaving the scrubbers through an opening at the top. Only one scrubber was being used at a time.

Steaming out and recovery of the adsorbed material was carried out either during or at the conclusion of each carbonization. Steam was passed through the scrubbers in the direction opposite to the gas flow and condensed, along with the recovered hydrocarbons, in a condenser placed underneath the scrubbers.

The gas, after passage through the scrubbers, was burned in a burner of the Bunsen type.

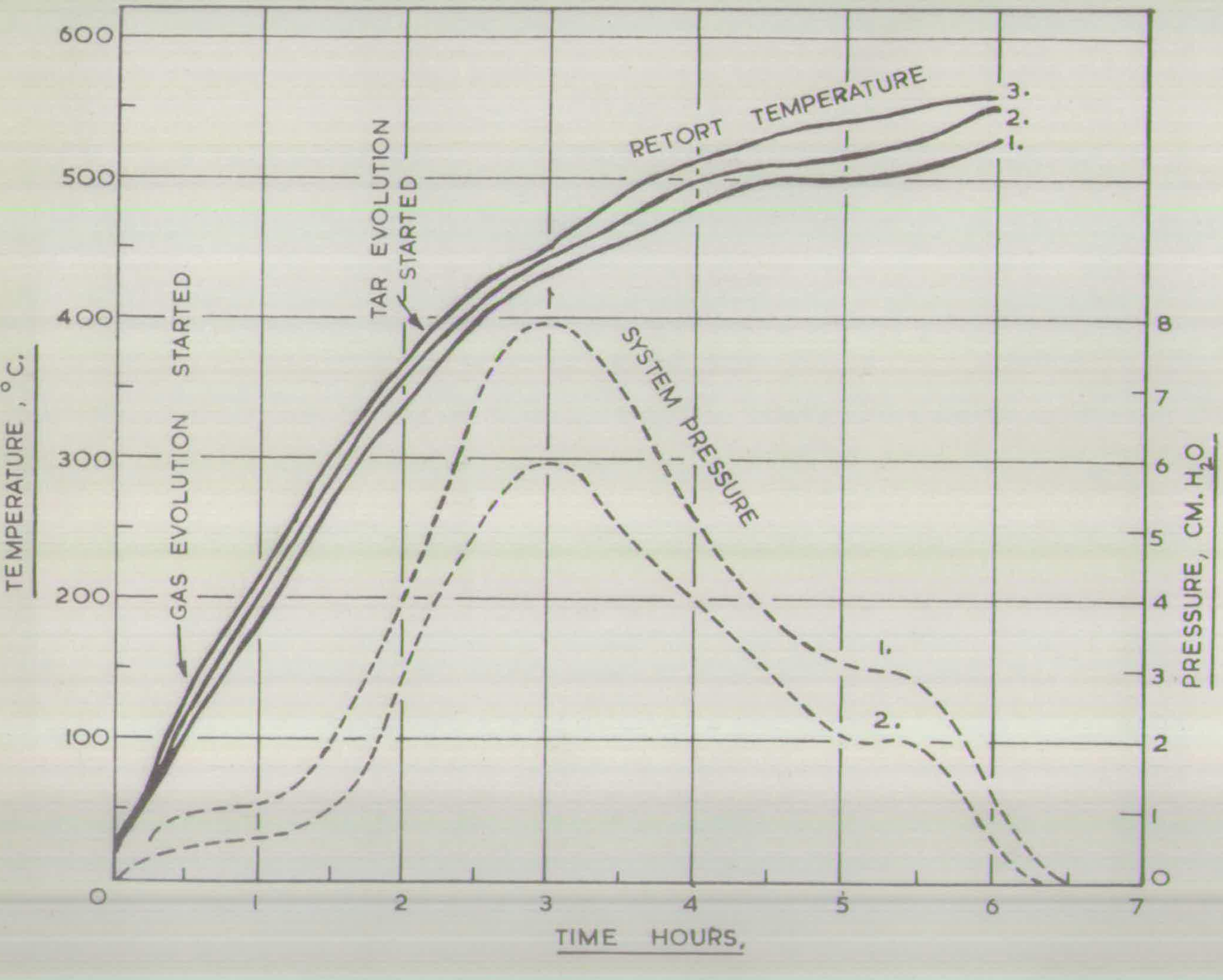
Carbonizing procedure.

The carbonizing procedure followed throughout the series of runs was the same in each case, so that variations in the actual carbonizing conditions were minimized and products could be regarded as being of similar properties.

The end cover plates of the retorts were removed and a weighed quantity of coal, previously ground in a jaw crusher to a size of 1"-2", was charged by hand. The retorts were then closed and heaters turned on. The rate of temperature rise during the initial stages of carbonization was maintained at 100°C. per half hour. Water to all condensers was turned full on and, as soon as tar evolution was noticed, the electrostatic precipitator was switched on. The progress of carbonization was followed by noting the pressure inside the system. A sudden increase in pressure was indicative of undue cracking taking place and was corrected. The size of flame from the gas burner was also used as an indication of conditions within the system, but was found to be less reliable than the two manometers. Readings of temperature of charge, gas and system pressures were taken every half-hour. The condensed tar collecting in the catch-pot and

FIGURE 8.

CONDITIONS DURING A TYPICAL CARBONIZATION.
RUN No. 12.



N.B.

MANOMETER No. 1 - ON PRIMARY AIR CONDENSER
" No. 2 - AT BASE OF CHARCOAL SCRUBBERS

two glass receivers was run off continuously into measuring vessels. The scrubbers were operated one at a time; the change-over being made after 2½ hours of operation.

A sample log of the readings taken during a typical carbonization is given in Table 8. Temperature and pressure conditions during the run are shown in fig. 8.

TABLE 8.

Sample Log.

Carbonization No. 12.

Wt. of coal charge	45 lb.
Wt. of coke obtained	31 lb.
Wt. of liquor obtained	2.64 lb.
Yield of crude oil	7.92 lb.
Yield of scrubber naphtha	110 ml.
Total yield of oil	44.9 gall./ton
Density of crude at 15°C.	0.902

Time, hrs.	Temp. in retorts, °C.			System pressure, cm. H_2O	
	1	2	3	1	2
0	15	15	15	0	0
½	100	110	100	1	½
1	180	190	200	1	½
1½	270	280	310	2	1
2	340	350	360	4	3
2½	400	410	420	7	5
3	430	440	450	8	6
3½	450	470	490	7	5
4	480	500	510	5	4
4½	500	510	530	4	3
5	500	520	540	3	2
5½	510	530	550	3	2
6	530	550	560	1	½

The heating of retorts was continued until tar evolution ceased altogether and gas evolution decreased considerably, producing a flame less than

½" high.

The time required to carbonize a charge varied between 5½ and 6½ hrs.

At the conclusion of each carbonization the tar collected was allowed to settle overnight, after which the aqueous layer was removed and the weight and density of the crude oil determined.

The material adsorbed in the scrubbers was recovered by steaming and, after separation of water, was measured and stored.

The retorts were allowed to cool overnight and the coke or residue was discharged and weighed.

Summary of results.

In all, sixteen carbonizations were carried out, in which 660 lb. of cannel coal were carbonized yielding a total of 11.5 gall. of dry crude oil.

The average charge to retorts was 41-42 lb. of coal, crushed to the required size, yielding an average of 3.8 to 4 litres of crude oil and 80 to 100 ml. of scrubber naphtha.

The overall results of the series of runs performed and a mass balance are shown below.

Total cannel coal carbonized = 300 kg.

	% wt.	Kg.
Dry crude oil	15.7	47.0
Coke	70.0	210
Scrubber naphtha	0.4	1.3
Aqueous liquor	5.6	16.8
Gas and losses (by diff.)	8.3	24.9

TABLE. 9.

Properties of crude oil and scrubber naphtha.

	Crude oil	Scrubber naphtha
Specific gravity at 20°C.	0.8990	0.7254
A.P.I. Gravity, °	25.0	62.5
Distillation:-		
I.B.P., °C.	74	36
2% vol. distilled at °C.	92	44
5% "	110	50
10% "	134	55
20% "	180	64
30% "	210	70
40% "	237	74
50% "	264	84
60% "	293	89
70% "	300	95
80% "	-	102
90% "	-	111
F.B.P., °C.	-	131
Total distillate, %	78	95
Residue, %	22	3.5
Loss, %	Nil	1.5
Lab. temp., °C.	17	18.5
Bar. pressure, mm. Hg.	751.0	754.3
Distilled at 70°C., % vol.	-	30
" 100°C. "	4	78
" 140°C. "	11	-
" 175°C. "	19	-
" 200°C. "	27	-
" 225°C. "	37	-
" 250°C. "	45	-
" 275°C. "	54	-
" 300°C. "	70	-
" 325°C. "	-	-
" 350°C. "	-	-
Viscosity, Redwood No. 1.		
at 70°F., secs.	43.4	-
at 100°F., secs.	35.7	-
at 122°F., secs.	33.1	-
Pour point, °F.	60	-
Flash point, Abel, °F.	71.5	-
Wax content, % wt.	13	-
Water content, % vol.	8.2	Nil
Bromine no.	-	100
Aniline point, °C.	-	20.3
Refractive index, n_D^{20}	-	1.4110
Composition (SiO_2 adsorption), % vol:-		
Paraffins and naphthenes	-	26
Olefins	-	61
Aromatics	-	13
Ultimate analysis, (% wt.):-		
C	82.7	-
H	10.1	-
N	0.9	-
S	0.5	-
O (by diff.)	5.8	-

Since the conditions of carbonization, and in particular the rate of heating of retorts, were standardized, it was assumed that the products of each run had the same physical and chemical properties and all tests were, therefore, carried out on the bulked crude.

The crude oil was of dark greenish-brown colour and had a pleasant paraffinic smell. Owing to a high wax content it tended to solidify at temperatures in the region of 15°C. On standing over prolonged periods of time the crude threw down an insoluble black deposit considered to be a polymerization product of the unstable unsaturated constituents.

The crude light naphtha recovered from the scrubbers was a water-white, evil smelling liquid, slowly darkening to pale amber on standing. The unpleasant smell was attributed to a small quantity of sulphur compounds present as dissolved gases in the liquid. This assumption was later confirmed by the facts that, on distillation, a considerable evolution of non-condensable, evil smelling gases took place. Attempts to separate liquid samples of sulphur compounds, notably mercaptans, proved unsuccessful.

The remaining carbonization products, viz. coke and aqueous liquor were not examined, while the gas was burned during the course of carbonization.

The properties of dry crude oil and scrubber naphtha were determined by standard Institute of Petroleum methods (89) and are given in Table 9.

PRELIMINARY DISTILLATIONS OF CANNEL OILS.

The refining of crude oil obtained on retorting cannel coal, and its separation into a number of fractions suitable for high-efficiency laboratory fractionations, were carried out by means of the following operations:-

a. primary separation of the crude oil into a light wax-free distillate (A-fraction) and a high-boiling waxy residuum,

b. extraction of acid- and alkali-soluble materials present in the distillate,

c. redistillation of the neutral oil to yield a number of fractions of approximately constant volume and relatively narrow-boiling range.

Of these, the first stage was of particular importance since the general character of the distillate, was, to a large extent, dependent on the method employed in carrying out the initial separation. The operation, most commonly used on account of its efficiency and performance, in the initial stages of crude petroleum and shale oil refining is that of continuous distillation, designed to separate from the crude oils a number of fractions suitable for further processing. For the sake of comparison, these are shown below, along with approximate boiling ranges.

Petroleum		Shale Oil	
Cut	B.pt., °C.	Cut	B.pt., °C.
Gasoline	20-200	Light naphtha	50-150
Kerosene	175-275	Heavy naphtha	150-200
Gas oil	200-400	"Wax-free cut"	200-320
Lubricating oil	Above 300	Pressable wax distillate	300-400
Fuel oil	-		
Pitch or coke	-	Residue	Above 400

As the present investigation was concerned mainly with the lower-boiling material, the primary distillation was performed in such a way as to yield only two fractions, the lower one (A-fraction) corresponding roughly to a gasoline or naphtha cut.

A. Continuous distillation of crude oil and washing of distillate.

Apart from its general similarity to large scale crude oil processing, continuous distillation was considered to be the most suitable means of performing the initial separation of crude cannel oil. Its main advantage is that the oil does not remain in contact with hot parts of equipment over prolonged periods of time, as is the case in batch distillations, and therefore, the risk of thermal decomposition or cracking is minimized.

Preliminary examination of the crude oil indicated that 20% boiled below 180°C. which taken off as overheads, would result in material corresponding roughly to a gasoline cut and, at the same time, be of sufficient quantity to permit further

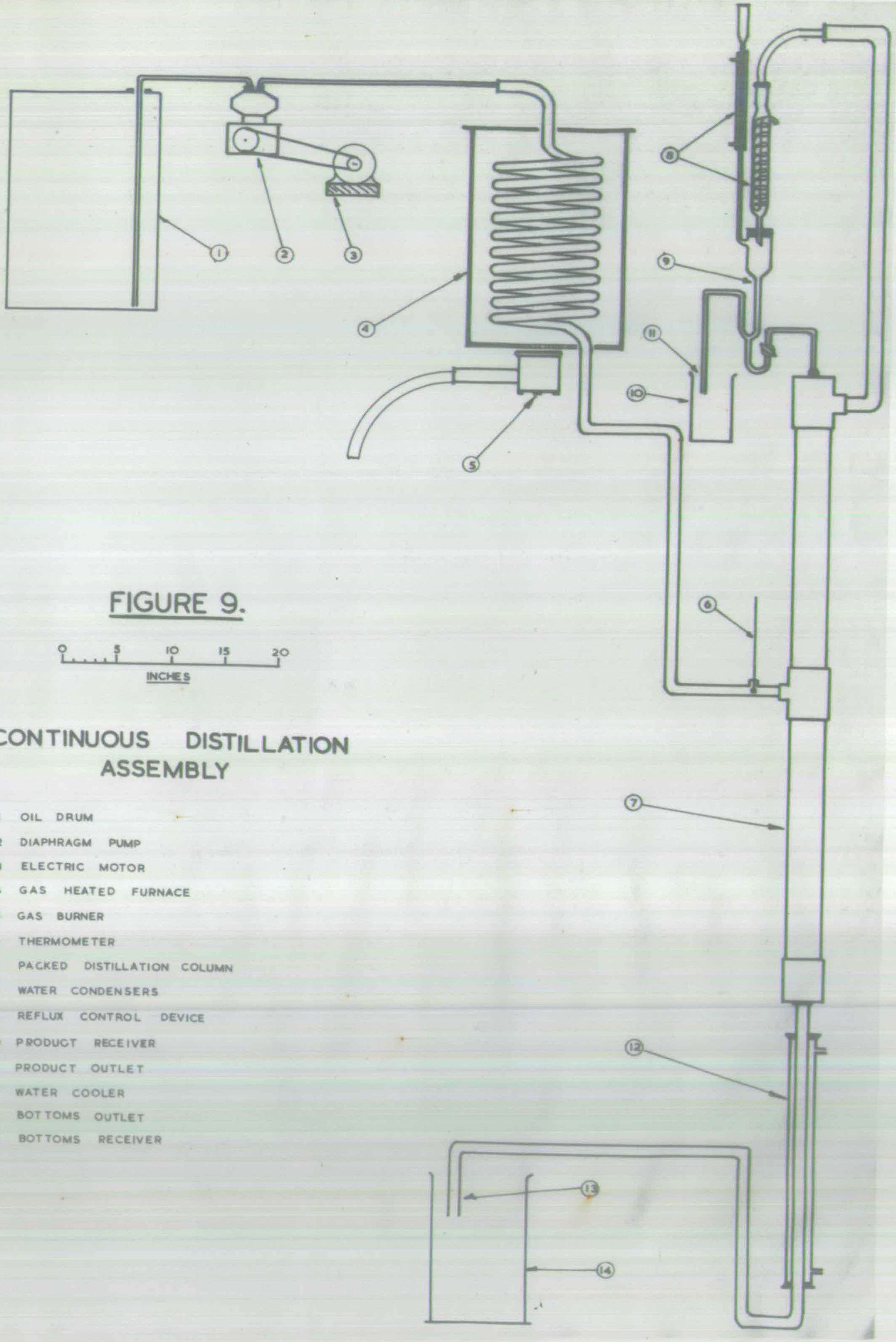


FIGURE 9.

CONTINUOUS DISTILLATION ASSEMBLY

1 OIL DRUM
2 DIAPHRAGM PUMP
3 ELECTRIC MOTOR
4 GAS HEATED FURNACE
5 GAS BURNER
6 THERMOMETER
7 PACKED DISTILLATION COLUMN
8 WATER CONDENSERS
9 REFLUX CONTROL DEVICE
10 PRODUCT RECEIVER
11 PRODUCT OUTLET
12 WATER COOLER
13 BOTTOMS OUTLET
14 BOTTOMS RECEIVER

separations. The absence in the distillate of compounds of high molecular weight would enable batch distillations to be carried out with less possibility of decomposition taking place in the reboiler.

Distillation unit.

The continuous distillation assembly consisted of the following:-

a. crude oil storage tank and feed pump,

b. gas-heated furnace,

c. distillation column, column-head and distillate receiver,

d. bottoms cooler and receiver.

The full assembly is shown diagrammatically in fig. 9.

The crude oil, previously heated to about 25°C. to reduce viscosity, was stored in a drum and pumped into a gas-fired furnace, consisting of a metal coil enclosed in a lagged cylindrical casing. The oil was partially vaporized during its passage through the spiral and entered a packed distillation column as a mixture of liquid and vapour, at a point half-way up the column. The overhead distillate leaving the column was condensed and collected. Although provision was made for returning to the column part of the condensate as reflux, it was decided to operate the column at no reflux, because accurate control of the reflux was impossible, and, small quantities of water present in the distillate collected in the reflux-control device and seriously interfered with the normal rate of distillation. The lack of external reflux, however, was not considered to be of great significance, since the object of this distillation was to achieve an overall separation of low-boiling material from the crude and no attempt at accurate fractionation was made. The heavy bottoms or residue leaving the column were partly cooled and collected in a storage drum.

Feed.

A small diaphragm pump of the type normally used for pumping fuel in aircraft, driven by a 1/20 H.P. motor, was used to convey the preheated oil from the storage drum into the furnace. The inlet or suction side of the pump was connected to a length of glass tubing dipping almost to the bottom of the drum, from which the oil was withdrawn and delivered to the furnace at a constant rate. Due to the presence of small quantities of suspended matter in the oil, which tended to block up the small pump valves, glass non-return valves were fitted on both sides of the pump.

Distillation column.

The column was constructed from two lengths of 2" I.D. iron pipe and packed with ½" iron Lessing rings, supported on perforated aluminium plates. The thermal insulation of the column consisted of "Fibreglass" (compressed glass wool) lagging, while pipe bends and parts of varying diameter were covered with asbestos rope and magnesia-asbestos cement.

On leaving the furnace, the partially vaporized oil was led into the column through a T-piece joining the two sections of the column. The oil temperature was measured at this point. Vapours leaving the rectifying section of the column were condensed in a glass double-spiral condenser, the condensate running into a reflux-control device. For reasons already mentioned, no reflux was fed back into the column, the total condensate being collected and measured. The high boiling residue was withdrawn continuously from the stripping section, brought to about 30°C. in a water-jacketed cooler and collected in a drum.

Distillation procedure.

Before the distillation proper, a number of trial runs were carried out in order to find the operating conditions under which the required percentage of crude oil could be taken off as overheads, and to examine the general performance and separating efficiency of the column.

The method of determining the required conditions consisted of operating the column at a constant rate of feed of oil into the furnace, maintained at a steady temperature throughout the test run. The temperature of the hot feed into the column was noted and the volume of both overheads and bottoms, collected in a given time, measured. Thus, the percentage overheads under a given set of conditions could be obtained. The method of operating the unit during all test runs and the distillation was identical in each case and is given below.

After priming the pump, the pre-heated crude oil was pumped into a cold column until it appeared at the bottoms delivery pipe, at which stage the burner was turned on and the temperature of the furnace gradually brought to the required value. The column was then run for one hour to reach steady operating conditions, during which time the collected overheads and bottoms were returned to the crude oil storage drum. During distillation proper, readings of oil feed temperature were constantly taken, while the amounts of condensate and residue were measured and percentage separations worked out. Any deviation from the specified operating conditions could thus be noted and corrected by altering the heat supply to the furnace.

Distillation results.

Total duration of distillation	6¼ hrs.
Rate of feed of crude oil to furnace	12.8 l./hr.
Temperature of feed entering column	270°C.-273°C.
Mass balance (dry basis):-	
Wt. of crude oil distilled	46.0 Kg.
Wt. of overheads obtained	15.5 Kg.
Wt. %-ge of overheads on crude oil	33.7
Wt. of bottoms obtained	30.1 Kg.
Distillation loss	0.4 Kg.

The overhead product or naphtha was a pale yellow, pleasant-smelling liquid, slowly darkening to amber on standing. The residue was a dark brown solid mass, of smell similar to the original crude. The properties of both products are given in Table 10.

TABLE 10.

Properties of distillate and residue.

	Distillate.	Residue.
Density at 20°C.	0.8592	0.912
Refractive index, n_D^{20}	1.4546	-
Bromine number	48	-
Aniline point, °C.	26.3	-
Wax content,%	-	19
Distillation:-		
I.B.P., °C.	49	252
2% vol. dist. at, °C.	75	286
5% "	94	301
10% "	112	310
20% "	140	325
30% "	159	337
40% "	176	348
50% "	192	-
60% "	207	-
70% "	221	-
80% "	234	-
90% "	250	-
F.B.P., °C.	262	352
Total distillate,%	97	52
Residue, %	2	44
Loss, %	1	4

Acid and alkali washing of naphtha.

The acidic and basic materials present in the naphtha or distillate were extracted by 20% sodium hydroxide and 20% sulphuric acid, respectively. The extraction or washing of the distillate was performed in four batches of approximately 3.5 litres each, each batch being treated in the following manner:- a measured quantity of the washing solution was added to the distillate and the mixture agitated for 10 minutes. It was then allowed to stand for 2 hours during which time the aqueous layer separated out and was withdrawn, while the oil was subjected to further treatment. The washing operation was carried out in this order:-

a. two washes with 500 ml. of 20% H_2SO_4 each,

b. two washes with 500 ml. of 20% NaOH each,

c. three washes with 1000 ml. of water each.

The washing solutions from each batch were bulked and stored. The regeneration of the acids and bases dissolved in the washing medium and their examination are described in Appendix II.

The resulting neutral naphtha was dried over calcium chloride for 24 hours, filtered and weighed. The crude scrubber naphtha obtained on retorting cannel coal was subjected to a similar treatment and found to contain no alkali- or acid-soluble material.

Results.

	Kg.	%wt.on crude
Distillate subjected to washing	15.5	33.7
Neutral, dry naphtha	13.4	29.1
Acid- and alkali-soluble material (by diff.)	2.1	4.6

B. Batch distillation of neutral naphtha.

The final separation of the neutral naphtha into a number of fractions suitable for high-efficiency fractionations was accomplished by means of

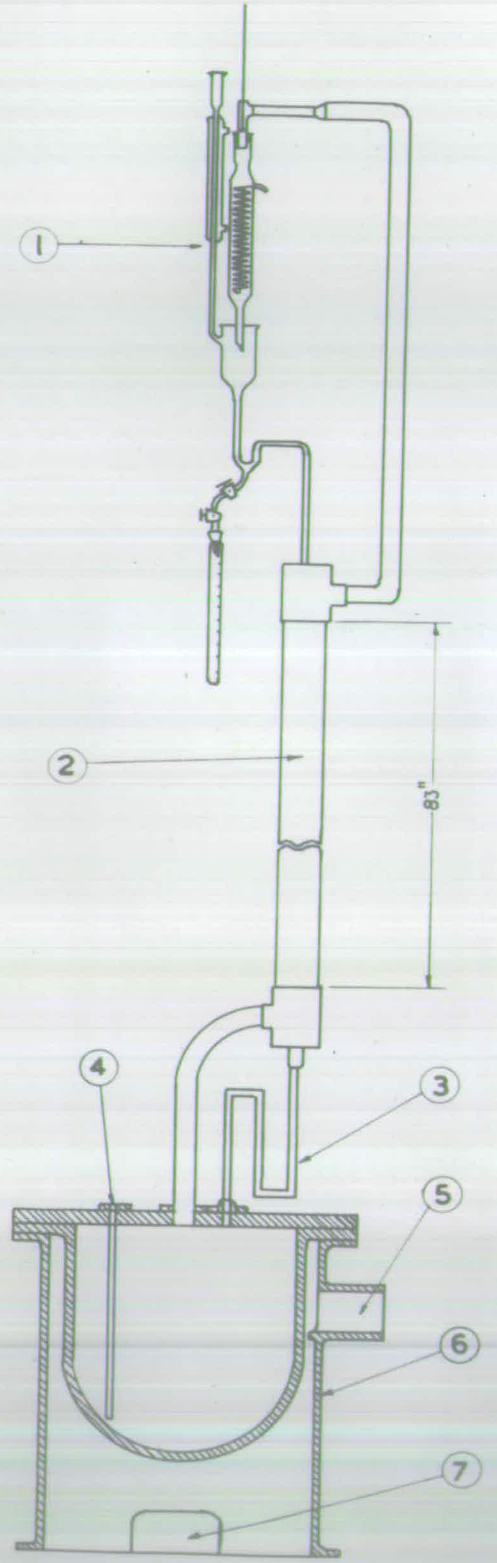


FIGURE 10.

SCALE

0 5 10 15 20

INCHES

BATCH DISTILLATION ASSEMBLY.

1 Reflux control device
2 2" I.D. packed column
3 Seal
4 Thermometer pocket
5 Flue
6 Cast iron reboiler
7 Position of gas burner

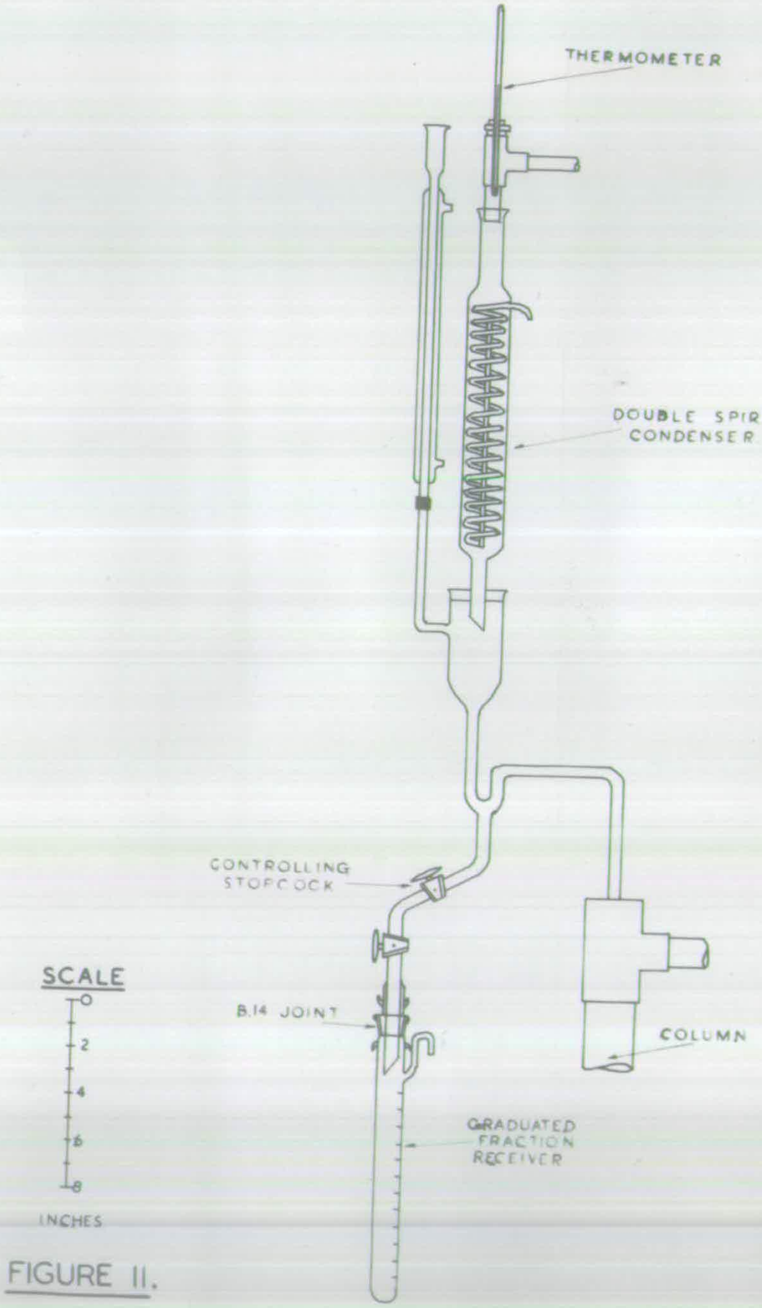


FIGURE II.

DETAILED VIEW OF THE REFLUX CONTROL DEVICE.

Figure 12.
Batch distillation still.

batch distillation at atmospheric pressure. Owing to the comparatively large quantity of naphtha to be distilled, it was necessary to design and construct specially for this purpose, an apparatus capable of performing a satisfactory separation in one operation.

Preliminary examination of the naphtha showed that by this procedure a number of one litre fractions of boiling range not exceeding 20°C. could be taken off and these could constitute suitable charges for subsequent high-efficiency fractionations.

Distillation apparatus.

The distillation unit, shown in figs.10,11 and 12, consisted essentially of a gas-heated reboiler and a packed distillation column, equipped with the usual accessories.

Reboiler.

The reboiler, (fig. 12) a cast iron pot of 5 gall. capacity, was set in a cylindrical casing 6" above ground level with a gas burner placed underneath its base. The top of the reboiler was lagged with asbestos wool held in place by a thin layer of magnesia-asbestos cement. In addition to a vapour upriser leading to the column and a liquid return line, the reboiler was equipped with a thermometer pocket extending to the bottom of the pot and a connection to a water manometer (not shown in diagrams). The base of the column was attached to the vapour upriser and to a U-shaped pipe, through which reflux could be returned continuously into the reboiler without coming in contact with the ingoing vapours.

Column.

The column, 7'6" long and 2" I.D., was packed with ½" iron Lessing rings supported on a perforated aluminium plate, fixed in the base of the column and 3" above vapour entry. The column top carried a T-piece, one end of which was connected to a pipe leading to the still-head, while the other served as a reflux inlet into the column. The lagging of the whole assembly was similar to that described in connection with the continuous distillation unit.

Still-head.

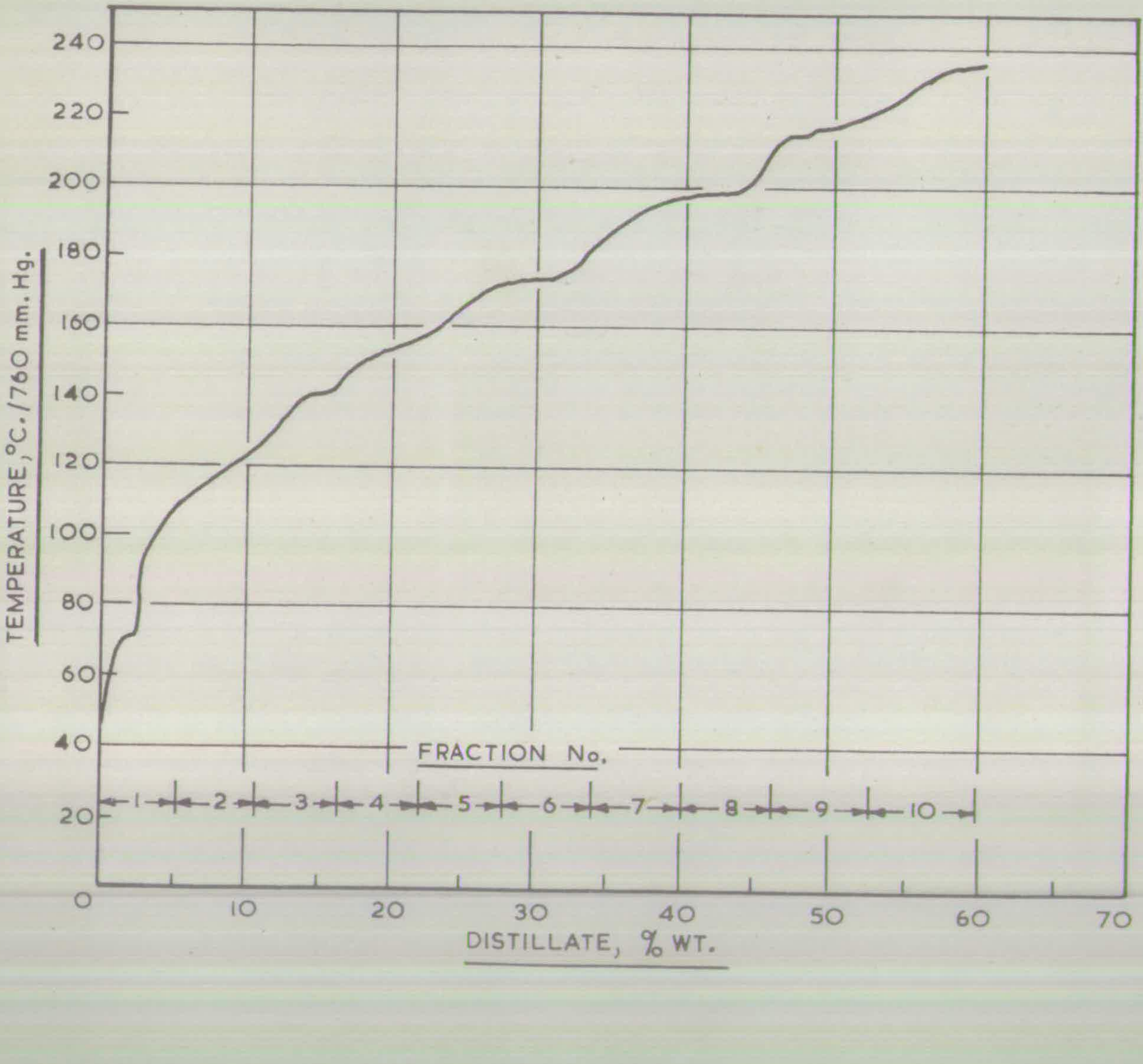
The still-head, shown in fig. 11 (facing p.77), was constructed from glass and consisted of a double-spiral vertical condenser, condensate divider and distillate receivers. A thermometer inserted above the condenser measured the temperature of vapours entering the still-head. The reflux divider operated in the following manner:- the condensate leaving the condenser entered a U-tube, where it either collected and flowed back into the column or could be taken off, depending on the position of the upper, controlling stopcock. At the beginning of a distillation the upper stopcock was set in one particular position depending on rate of take-off required, and remained in that position throughout the run, while the lower stopcock was fully opened, except during change-over of distillate receivers. Thus it was possible to maintain a moderately steady reflux ratio, although no accurate measurements of the reflux could be made. The performance of the still-head was found to be quite satisfactory for the present requirements and a constant rate of take-off could be maintained.

Distillation procedure.

After the usual preliminary runs, during which the column performance was tested and most suitable operating conditions established, the distillation proper was started and continued until the required amount of distillate was collected. The still was, at first, gently heated until the liquid was at boiling point, when the rate of heating was slightly increased, care being exercized to avoid flooding of the column. The distillation was allowed to proceed at total reflux for 6 hours to attain equilibrium conditions. The distillate take-off was then started by opening fully the lower stopcock and adjusting the upper stopcock to give the required rate of distillate removal. The distillate was collected in graduated receivers of 100 ml. capacity and combined to form 1 litre fractions. The following readings were taken every 15 minutes:-

FIGURE 13.

RESULTS OF BATCH DISTILLATION.



a. temperature of overheads,

b. temperature of liquid in reboiler,

c. pressure in reboiler,

d. pressure of gas to burner,

e. volume of distillate collected,

f. rate of take-off of distillate.

The determination of reflux ratio by any of the usual methods was impossible owing to the unknown nature of the mixture and the lack of a boil-up meter. A very rough indication of the reflux ratio was provided by running the column for a short period of time at no reflux and comparing the quantity of distillate obtained with that collected in the same time during normal operating conditions.

Results.

Wt. of naphtha charged	13.4 Kg.
Total wt. of distillate collected	8.0 Kg.
≡	59.7% wt. on naphtha
≡	17.4% wt. on crude
No. of one litre fractions taken	10
Total duration of distillation	27 hours.
Duration of take-off	19 hours
Rate of distillate take-off	525 ± 10 ml./hr.
Approximate reflux ratio	10:1

The boiling point curve for the distillation is shown in fig. 13.

Examination of fractions.

The properties of the ten fractions collected (B-fractions) and of the residue are given in

TABLE 11.

Properties of B-fractions and residue.

No.	Wt., gms.	Wt. % on crude.	Engler b.pt. range, °C. at 760 mm.	d_4^{20}	n_D^{20}	Br_2 No.	Aniline pt., °C.
B-1	700	1.52	41-108	0.7314	1.4119	97	19.9
B-2	740	1.61	108-126	.7667	1.4324	71	14.9
B-3	760	1.65	124-145	.7787	1.4362	61	21.0
B-4	767	1.67	136-157	.7787	1.4361	58	30.3
B-5	790	1.72	159-173	.8041	1.4483	50	27.7
B-6	805	1.75	165-184	.8098	1.4532	45	30.6
B-7	820	1.78	181-197	.8271	1.4581	43	32.4
B-8	830	1.80	194-213	.8549	1.4718	36	25.3
B-9	840	1.83	205-221	.8565	1.4731	33	28.2
B-10	935	2.03	217-235	.8684	1.4788	32	27.1
Residue	-	-	228-274	.8890	1.4820	24	-

Table 11.

The hydrocarbon-type composition of the lower B-fractions was determined by percolative adsorptions on silica gel, using the experimental procedure discussed fully on p.126. The results of the analyses are given in Table 12.

TABLE 12.

Fraction No.:-	B-1	B-2	B-3	B-4
Composition, % vol.:-				
Paraffins & Naphthenes	26	26	30	18
Olefins	62	54	45	61
Aromatics	12	20	25	21

Determination of aromatic content.

In addition to the silica gel analyses, the aromatic content of the four fractions and scrubber naphtha was estimated by the standard Institute of Petroleum method (I.P.-3/49) and by specific dispersion measurements.

Specific dispersion, defined as the difference between refractive indices for the red and blue lines of the hydrogen spectrum (6563 A° and 4861 A°, respectively) divided by density, at 20°C. is fairly constant at 95 to 100 for paraffins and naphthenes, while for the aromatics, benzene is 190, toluene 185 and the xylenes 181 to 174. Thus, the aromatic content of fully saturated samples of specific dispersion intermediate between 100 and 190 can be estimated by direct proportion. The presence of olefins, however, renders this method impossible, since the specific dispersion of mono-olefins varies from 140 to 110 and corrections must be applied. Grosse and Wackher (43), who originally developed this method, use the following equation for estimation of aromatics in cracked gasoline stocks containing olefins:-

$$\% \text{ wt. Aromatics} = \frac{\delta_m - 0.16 \cdot \text{Br}_2 \text{ No.} - 99}{\delta_a - 99} \cdot 100$$

where δ_m = specific dispersion of sample x 10^4

δ_a = specific dispersion of aromatics present x 10^4.

The values of δ_a are:-

Cut, °C.	Compound	δ_a
70- 95	Benzene	190.2
95-122	Toluene	184.9
122-150	Ethylbenzene and xylenes	179.2
150-175	$C_9 - C_{10}$ aromatics	175.0
175-200	$C_{10} - C_{11}$ aromatics	171.0

More recently, Groennings (42) has proposed a correction for the olefin content based on the class, structure and boiling point of olefins present in the sample. The factor by which the bromine number is multiplied to correct for specific dispersion due to non-cyclic and cyclic mono-olefins varies between 0.10 and 0.20, compared to 0.16 proposed by Grosse and Wackher (loc.cit). Another correction is necessary if conjugated diolefins are present, but as these were found to be absent in cannel naphtha, this correction was not applied.

The method of measuring specific dispersion consisted of determining the refractive index for the sodium D-line of the sample at 20°C. by the Hilger Abbe refractometer and, at the same time, setting the Abbe compensator so as to make the dividing edge of the field achromatic and reading the scale of the compensator drum. Several settings of the compensator drum were made and an average value obtained. The dispersion of the sample was then calculated from tables supplied with the instrument, and the specific dispersion obtained by dividing the dispersion by density of the sample at 20°C.

The aromatic contents of the lower-boiling B-fractions and scrubber naphtha determined by the various methods are given below.

Aromatic Content, % wt.

Fraction No:-	B-1	B-2	B-3	B-4	Scrubber naphtha
Silica gel method	14.2	22.5	27.8	23.4	15.5
Specific Dispersion method					
Grosse's equation	13.2	20.5	25.0	15.0	11.6
Groennings's equation	14.8	22.3	26.2	21.7	13.2
I.P. Method.	23.5	32.0	29.9	24.5	22.1

The agreement between the silica gel and specific dispersion results using Groennings's correction is satisfactory and within the limits of experimental error, whereas the I.P. method shows much wider discrepancy of results. The high values for aromatic content obtained by the latter method, based on the change of aniline point of the sample when aromatics and olefins have been removed by 99% H_2SO_4, and corrected for olefins, are considered to be due to:-

a. the high olefin content (up to 63%) of cannel distillates as compared with 0% for straight-run and up to 30% for cracked petroleum distillates, for which this method has been primarily developed,

b. the difficulty of complete removal of benzene by sulphonation, resulting in the lowering of aniline point of the acid-treated sample. (This is supported by the fact that the discrepancy of results is highest for lowest-boiling fractions),

c. a reaction between olefins and conc. H_2SO_4 resulting, apart from acid-soluble alcohols and esters, in the formation of polymers, which by virtue of their complete solubility in the hydrocarbon phase, are not removed by the acid, thereby affecting the aniline point of the treated sample.

(The latter fact has been confirmed experimentally by carrying out the I.P. aromatic content determination followed by Engler distillation of the acid-treated oil. A brown resinous mass (representing 4% of the distillation charge) was obtained, which boiled above 250°C. and showed signs of decomposition on further heating).

THE DESIGN, ERECTION AND TESTING OF FRACTIONATING COLUMN.

The fractionating column was designed to perform efficient separations of relatively low-boiling fractions of neutral cannel naphtha, as obtained from batch distillations, and to operate continuously, day and night, over prolonged periods of time. Emphasis was, therefore, laid on high fractionating efficiency and on provision of automatic and safe means of operation, particularly in the case of constant rates of take-off and fraction collection, and constant boil-up rate.

A. Apparatus.

The unit consisted basically of an electrically heated still, a ⅝" I.D. column made up of two sections 36" each, and containing a total of 68" of packing, and an automatically operated column-head. The whole assembly was mounted on an "Ecofix" framework, fixed rigidly to the floor and adjacent wall. The column itself was provided with heated jackets, the heat input to which could be controlled, so as to maintain adiabatic conditions within the column. The still-head was of the tipping bucket type, developed originally by The Anglo-Iranian Oil Co. (11), enabling constant

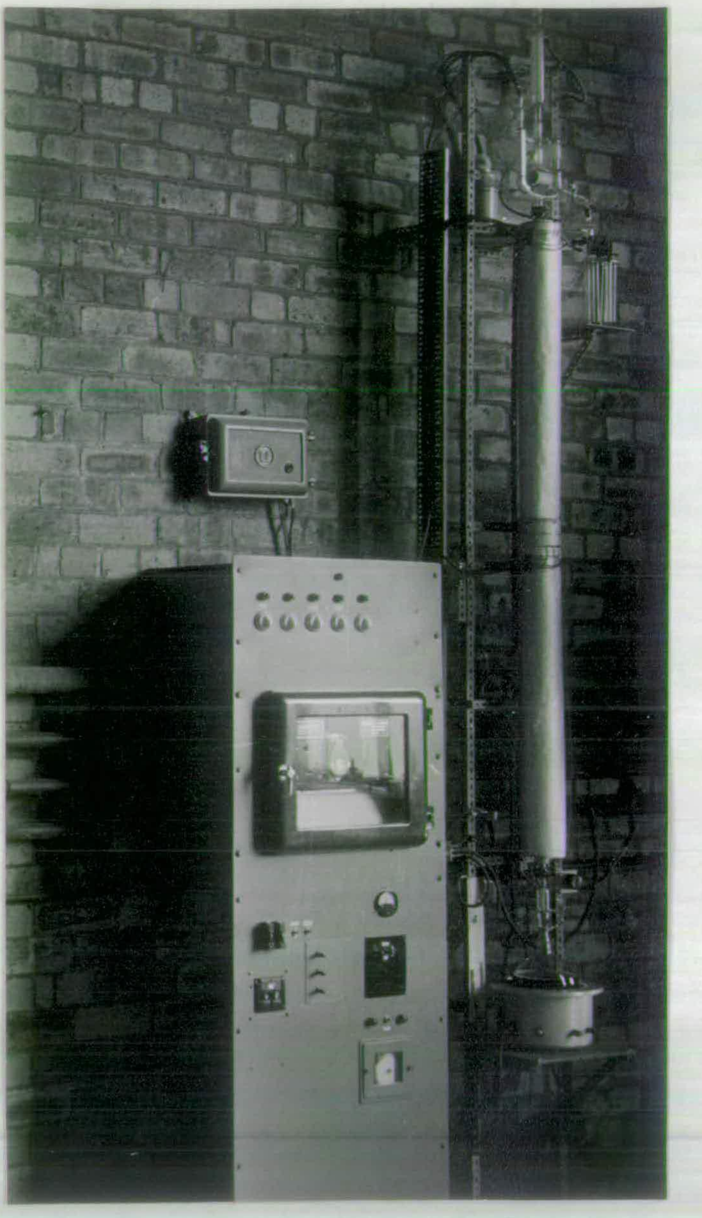


Figure 14.

Fractionating unit.

rates of distillate take-off, when distilling at high reflux ratios. An automatic receiver-changer was operated in conjunction with the still-head, resulting in the collection of fixed and constant volumes of distillate fractions. The temperature of the overheads was measured by copper-constantan thermocouples connected to a Kent "Multelec" temperature recorder.

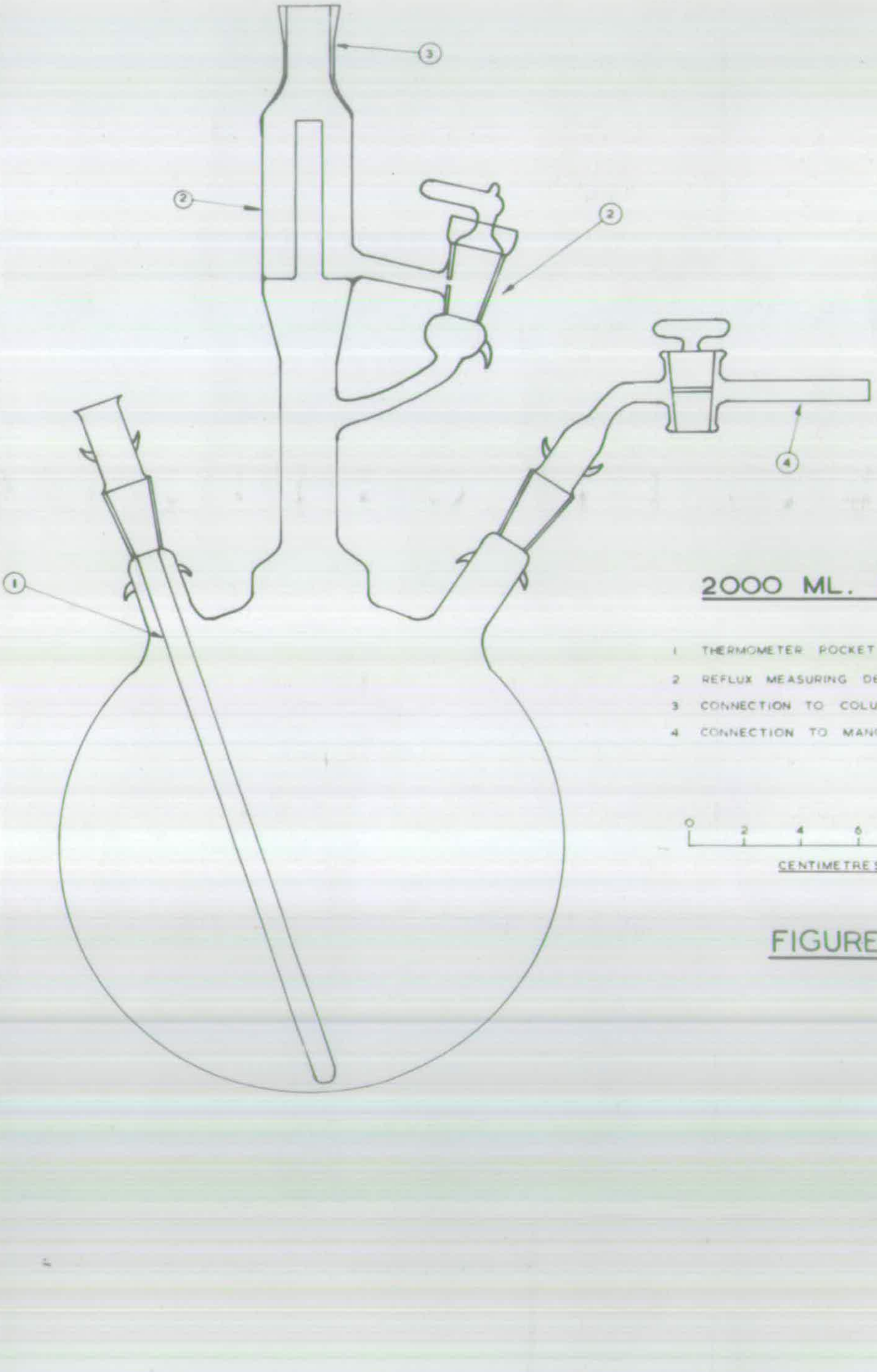
The column was operated at atmospheric pressure and without means of correcting day to day pressure fluctuations. Provision was made for operation at reduced pressures, though such distillations were not performed during the course of this work.

The whole unit was operated from a control panel, which also included the temperature recorder and take-off and receiver-changer mechanisms. The entire unit is shown in fig. 14.

The following is a description of all the items and electrical circuits comprised in the fractionating unit.

Still.

The still or boiler normally used was a 2 litre round-bottom flask equipped with two additional openings carrying B.14 sockets; one for a thermometer pocket and the other for connection to a manometer or insertion of a liquid sampler. In the neck of the flask was incorporated a reflux meter having a central vapour upriser and an external liquid bypass, controlled by a stopcock.



2000 ML. REBOILER

1 THERMOMETER POCKET
2 REFLUX MEASURING DEVICE
3 CONNECTION TO COLUMN
4 CONNECTION TO MANOMETERS

FIGURE 15.

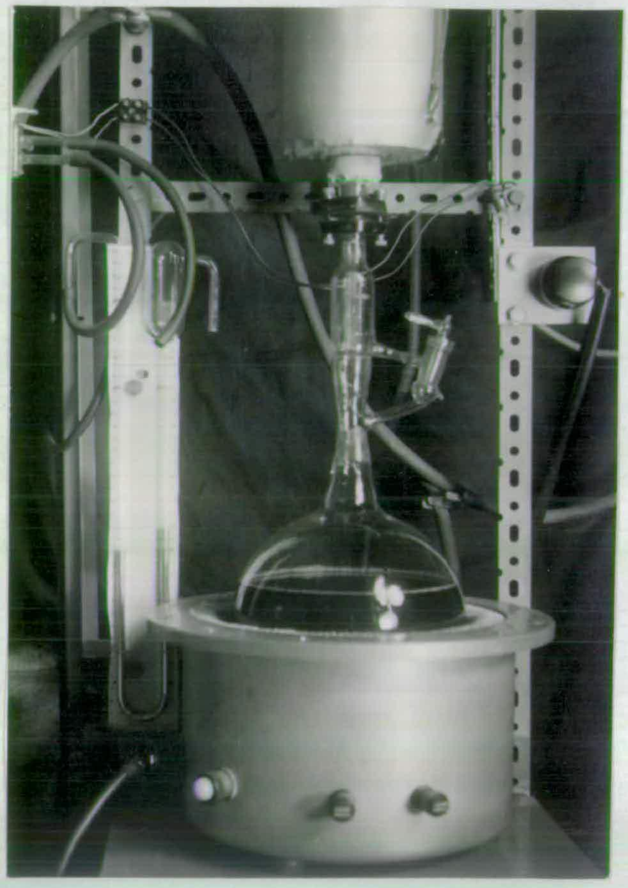


Figure 15 b.
Auxiliary 2 l. still in
position under column.

The operation of the meter consisted of shutting the stopcock and measuring the time taken for reflux to reach a graduation mark on the upper compartment of the meter. During normal operation the stopcock remained open so that liquid could be continuously drained into the still. The top of the meter carried a ⅝" pipeline joint which was connected to the lower section of the column. The flanged-end type of joint was particularly useful in this instance as it completely eliminated the difficulties of perfect alignment and fit associated with cone and socket joints and allowed the withdrawal of the still from the column without lowering it or raising the column to disconnect the joint.

The still is shown in fig. 15.

The still was electrically heated by means of a 450 watt Electrothermal heating mantle, resting on a sliding platform attached to the "Ecofix" framework. The heat input to the mantle was controlled by a Sunvic Simmerstat operated by 230 v. A.C. The portion of the still projecting above the mantle was enclosed by an aluminium casing filled completely with asbestos wool and covered. The remainder of the still, the reflux meter and the joint were insulated with asbestos rope and "Fibreglass" lagging.

Two auxiliary stills of 500 ml. and 2 litre capacity were also available; the latter being shown in fig. 15b.

Column.

The column itself consisted of two sections, ⅝" I.D. and 36" long each, joined together by flanged joints. Each section, a heavy-walled glass tube, was provided with three indentations near one end to act as support for the packing. The sections were normally packed over a length of 34" with stainless steel, 100-mesh, square-weave gauze, 1/16"x 1/16" Dixon rings (12,26) in the following fashion:- three or four ¼" gauze rings were placed on the indentations, followed by 1" of ⅛" gauze rings and the remainder of the section was filled to within 1½" off the top joint with 1/16" rings. Another 1" of ⅛" rings was placed on top and the whole packing was secured by a flat steel spring. In all, about 29,000 1/16" rings and 200 ⅛" rings were used.

Thermal insulation of column.

Each section of the column was provided with electrically heated jackets to compensate for heat losses from the column and ensure adiabatic operation. A Wheatstone network arrangement was used to control the adiabaticity of the column and consisted of winding on each section two identical coils of nickel wire; one on the column itself and one outside a layer of lagging, thus forming two arms of the network, while two standard coils formed the other two arms. An electric heater was wound on another layer of lagging outside the second resistance coil. The heat input to the heater was controlled by a Simmerstat operating at 230 v. A.C. A galvanometer in the bridge circuit indicated the thermal conditions within the column. If there was no temperature gradient inside the lagging, i.e. there was no heat flow to or from the column, the temperatures, and therefore resistances, of the two coils were the same and the bridge was balanced. Any departure from adiabatic conditions, indicated by the galvanometer needle deflection, could then be corrected by adjusting the heat input to the heater.

The lagging and windings on each section were as follows, starting from the column wall:-

a. 1st resistance coil consisting of 60' of 36 S.W.G. pure nickel wire, double-silk-covered, wound non-inductively and giving a total resistance of 53 ohms. The ends of the wire were insulated by sleeving and connected to a connector strip mounted on the outside of each section,

b. two layers of asbestos rope, ⅛" dia.,

c. two layers of asbestos paper,

d. 2nd resistance coil of same length as the first, wound non-inductively,

e. two protecting layers of asbestos paper,

f. 16 S.W.G., 1½" I.D. copper tube, 33" long, to provide equal heat distribution over the section and lessen fluctuations arising from intermittent heat supply to heater,

g. two layers of asbestos paper,

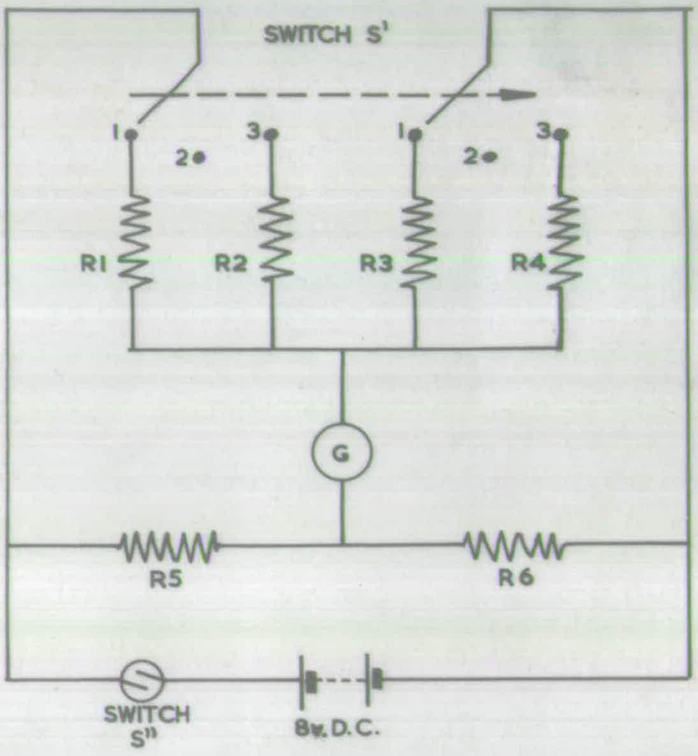


FIGURE 16.

WHEATSTONE BRIDGE CIRCUIT.

h. 125 watt heater, consisting of 30 S.W.G. "Brightray" wire. Both ends of the heater were connected to a connector strip on the outside of each section,

i. one layer of asbestos rope, ⅛" dia.,

j. "Fibreglass" pipe lagging, 2" I.D., 4" O.D.,

k. aluminium painted paper shield to reduce heat losses by radiation.

Each section heater was controlled by a separate Simmerstat, operated by 230 v. A.C. from the control panel. It was found during actual operation of the column that the heaters were of an adequate size to balance any heat losses from the column, and were rarely on for more than 80% of the time, even when the temperature of the column was about 160°C.

Jacket heater controls.

As already mentioned, the temperature of the column jackets was controlled by a Wheatstone network, two arms of which were wound on the column (R1 R3 and R2 R4) while the other two consisted of 50 ohm standard resistance coils (R5 and R6), mounted along with the necessary switches on a detachable section of the control panel (fig. 16).

The network was connected, through a switch (S") to a 8 v. D.C. supply (4 x 2 v. accumulators) and a centre zero microammeter as galvanometer (G). One twelve-contact switch (S') was used to make and break the various circuits, four of the contacts

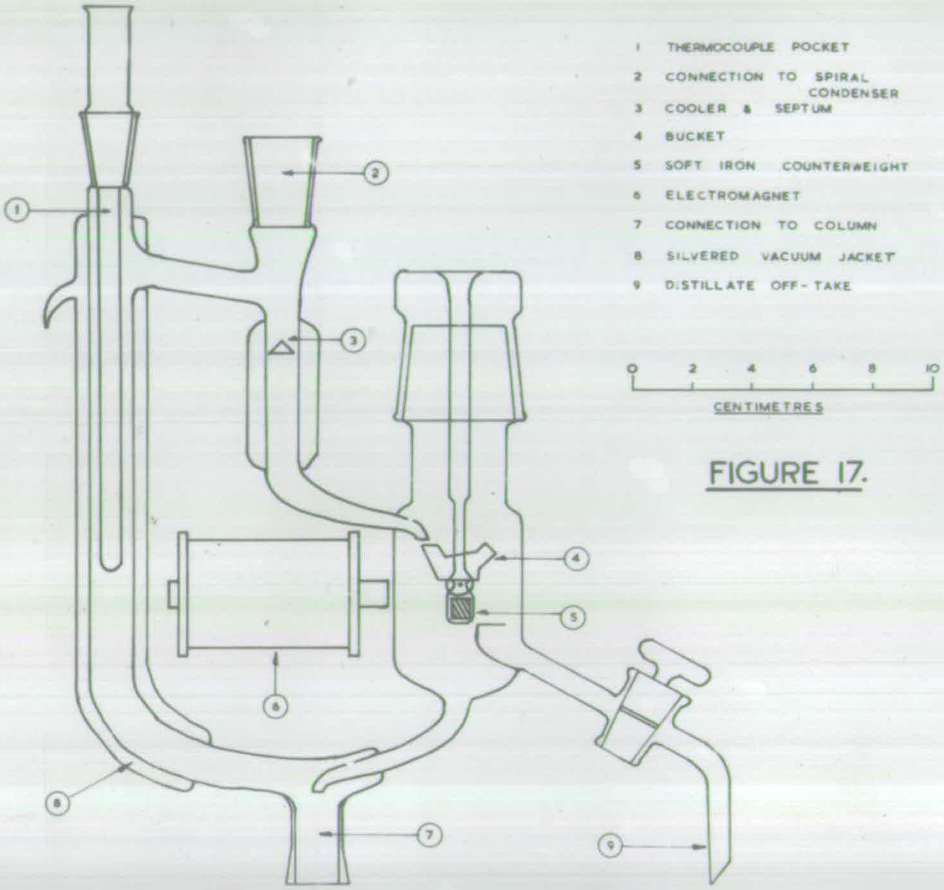


FIGURE 17.

AUTOMATIC COLUMN HEAD

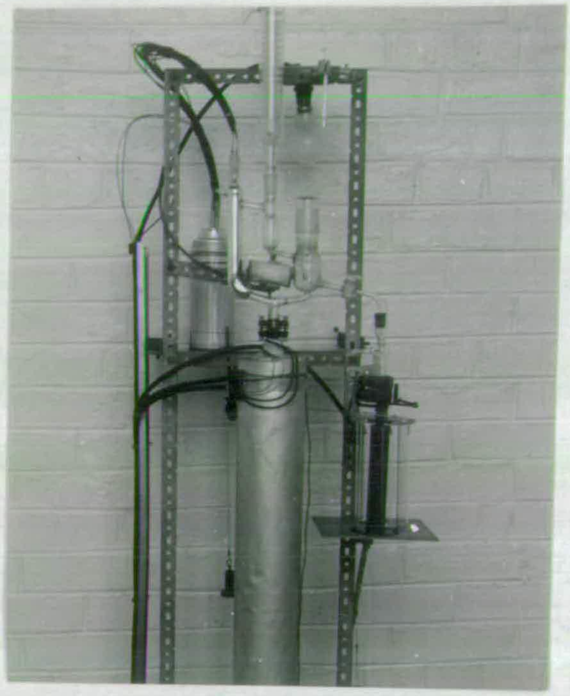


Figure 18.

Still-head.

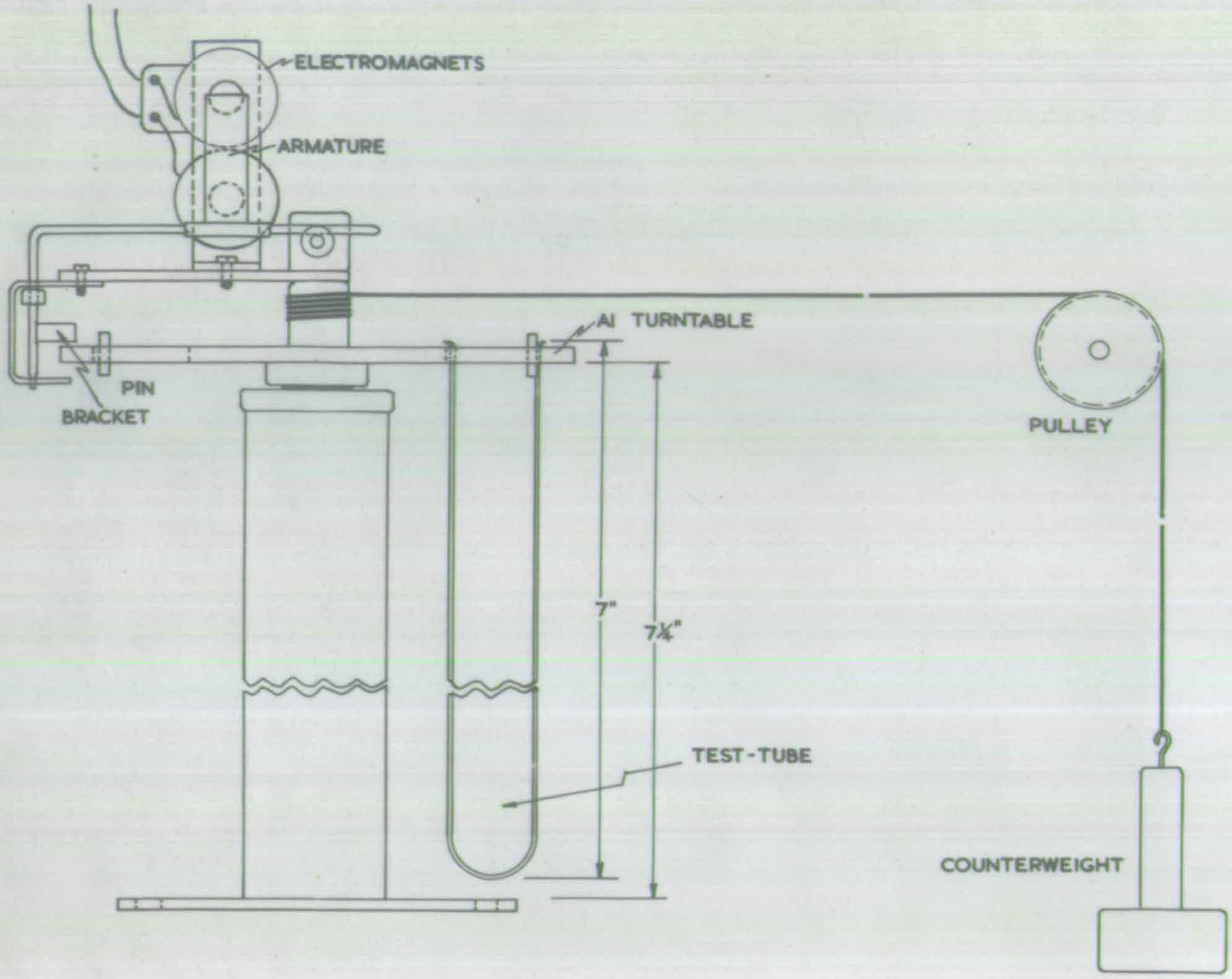
being used for each section. By one throw of the switch the circuit on one section could be broken in two places, and, though the batteries were on, no current flowed through the galvanometer. When the network on a section was switched on, current flowed only through the coils on that particular section (R1 and R3 or R2 and R4). All connections were made through connector strips mounted on each column section and behind the control panel.

Column-head.

The column- or still-head, shown in figs. 17 and 18, was of the tipping bucket, reflux-dividing type, provided with a double-spiral condenser, thermocouple pocket and an additional distillate cooler. This type of head was considered as the most suitable for the present purpose as it allows the column to be operated over a wide range of reflux ratios, is fully automatic, has a low hold-up and, once a given reflux ratio has been fixed, the operation of the head will remain constant. Further, should any fault develop in the solenoid of its energizing mechanism, the column is put under total reflux.

The operation of the still-head is fully described in (11).

The bucket was tipped by means of a solenoid, operated by 8 v. D.C., placed in contact with the bucket chamber. The solenoid consisted of two coils of 1600 turns each, of 28 S.W.G. enamelled copper wire, wound on a single soft-iron



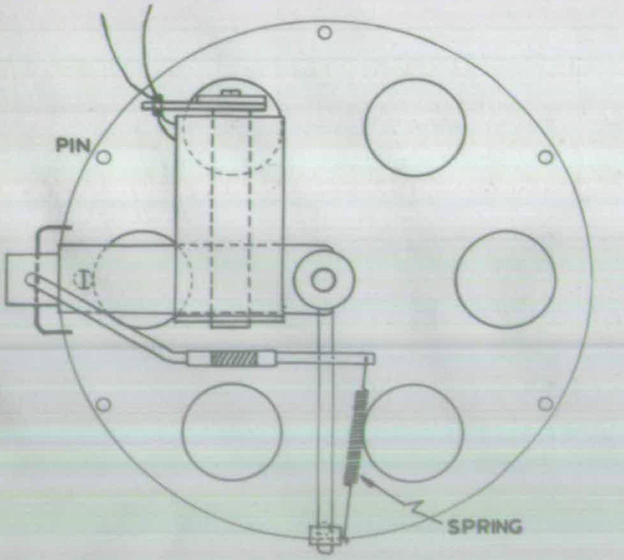


FIGURE 19.

RECEIVER - CHANGER.

core and connected in parallel.

The still-head was attached to the column by means of a ⅝" flanged joint.

Temperature recording.

The temperature of the vapours was measured by seven copper-constantan thermocouples connected in series in order to give the voltage required to operate the recorder. The thermocouples were made from 30 S.W.G. enamelled copper and 26 S.W.G. constantan wires, soldered at each junction with silver solder. They were placed in the thermometer pocket of the still-head (hot junction) and in a Dewar flask containing crushed ice (cold junction). The voltage produced was continuously recorded on a Kent "Multelec" single point moving chart recorder, calibrated to read in millivolts in the range of 0 to 70 mv.

Distillate receivers and changer.

The distillate receivers, consisting of tared and numbered test-tubes of adequate capacity to collect the predetermined volume of distillate per fraction, were suspended from a revolving turntable (4½" dia.) directly underneath the discharge tube of a small glass spiral cooler.

The receiver-changer, shown in fig. 19, was operated by an electromagnet, which, on being energized, attracted a soft-iron armature of the spring-loaded brass angle, thereby altering the position of the bracket of the escapement mechanism in such a way as to allow the turntable to move by

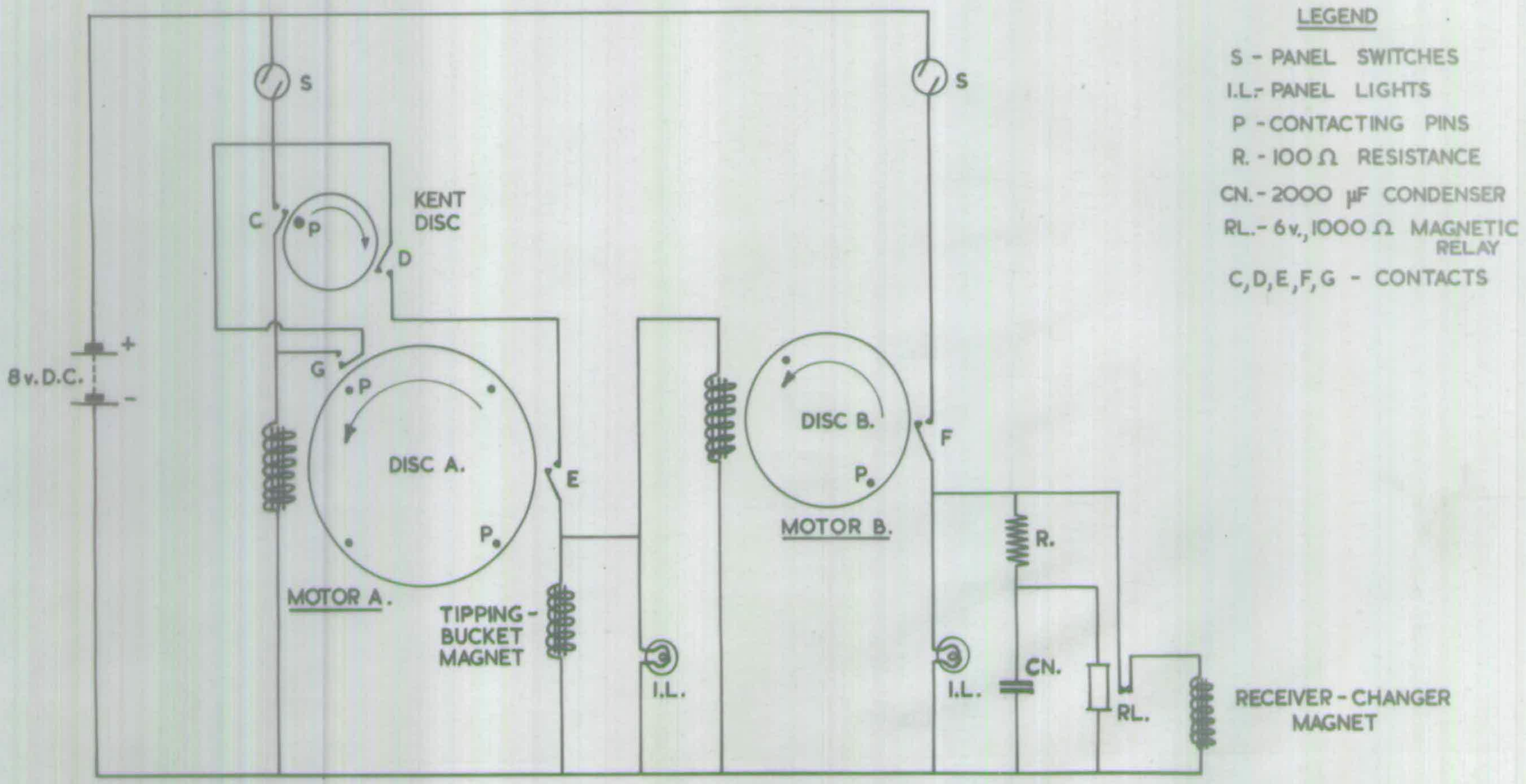


FIGURE 20 b.

D.C. CIRCUIT DIAGRAM.

1/12th of a revolution. On breaking the electromagnet circuit, the angle was sprung back to its original position, the turntable moved a further 1/12th of a revolution and an empty receiver was brought underneath the distillate discharge tube.

The turntable carried six test-tubes, thus permitting operation up to 20 hours without renewal of receivers.

Still-head and receiver-changer timing mechanisms.

The still-head solenoid was energized at regular intervals, variable at will, by a timing mechanism driven by the 110 v. synchronous motor operating the Kent recorder. A projecting part of the motor shaft was provided with a small toothed wheel and coupled, through a suitable gear reduction train giving a spindle speed of $3^1/_3$ r.p.m., to a small disc containing eight holes near its periphery, into which studs could be fitted. The disc usually carried only one stud.

Two contacts (C and D in fig. 20b) were fixed tangentially near the periphery of the disc so that, on revolving, the stud could close each set of contacts, thereby making the appropriate circuits.

The reduction gearing and the contacts were mounted on a brass plate, bolted to the outer casing of the recorder motor.

Two small impulse motors were mounted in an aluminium box behind the control panel. The motors (A and B) were of the standard type, operated by an electromagnet and each carrying a notched wheel containing 104 notches. The first motor (A) was modified, by the insertion of contacts G, so that every twenty-fifth impulse it moved by two notches, thus giving a total of 100. The motor also carried a brass disc drilled to accommodate symmetrically 1, 2, 3, 4, 5, 6, 8 or 10 steel pins. A set of contacts (E) was again placed tangentially near the periphery of the disc, so that a pin coming opposite it would make a circuit. The second motor (B) was provided with a similar, smaller disc carrying one, two or four pins and a set of contacts (F) positioned in the same manner.

The circuit, shown in fig. 20b (facing p.93) was as follows:- motor A was connected to the 8 v. D.C. supply through a switch S and contacts C on the Kent recorder, so that on closing these contacts circuit was made and the motor moved one notch. With one pin (P) on the Kent disc, an impulse was sent to motor A every 18 secs. A pin (P) on disc A coming opposite contacts E brought these together for 18 secs., thereby closing the bucket solenoid circuit in one place. The circuit was made and the solenoid energized when the stud on the recorder disc came opposite contacts D. By that means the bucket remained in a tilted position for only 1 sec. (the time taken for the stud to pass contacts D).

Every time the bucket was tipped motor B moved one notch. A pin on disc B coming opposite contacts F made the circuit of the receiver-changer solenoid and the turntable moved 1/12th of a revolution. On de-energizing the solenoid the turntable moved a further 1/12th of a revolution. As the disc on motor B was considerably smaller than that on motor A, the distance travelled by the pin, as the motor moved by one notch, was not sufficient, and three movements of the disc were necessary to close and release contacts F. Under these conditions, the distillate would discharge on to the turntable, since the solenoid still remained energized. Apart from the loss of material, the drain on the batteries would be high, and therefore, a time-delay circuit which broke the current supply to the receiver-changer solenoid after 2-3 secs. was included.

The required rate of take-off could be obtained by inserting symmetrically the appropriate number of pins on disc A. The frequency of bucket tilting could thus be varied from 2 to 20 tips per hour, though higher frequencies (up to 80 per hour) could be obtained by inserting additional studs on the recorder disc.

Since the movement of motor B, and hence the frequency of energizing the distillate receiver solenoid, was entirely controlled by the tilts of the bucket, the size of the fractions taken remained constant, though it could be varied at will by inserting one, two or four pins on disc B. Motor B carried a wheel of 104 notches, so that a fraction consisted of liquid discharged by the bucket 104, 52 or 26 times or, the capacity of

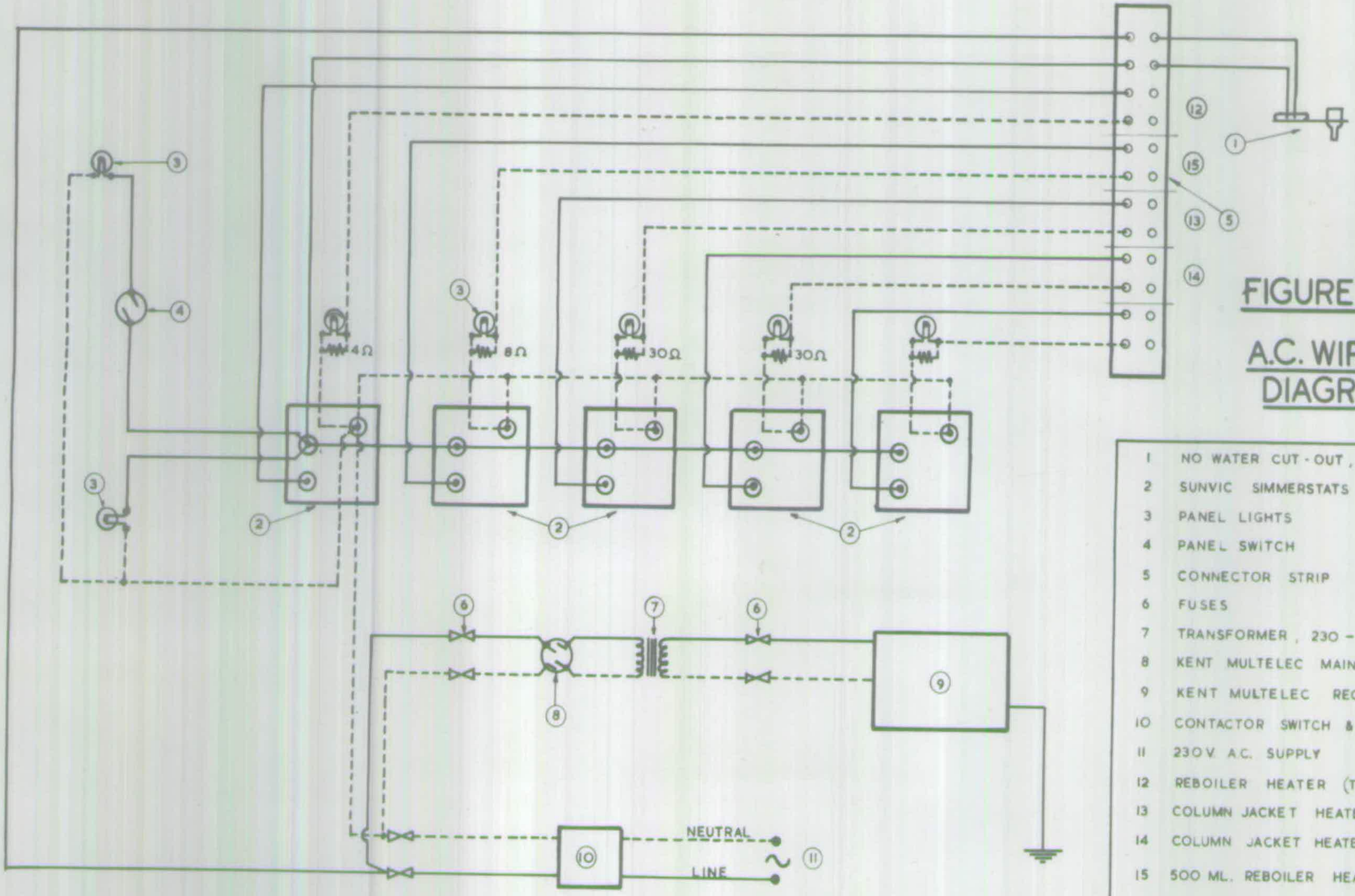


FIGURE 20 a.

A.C. WIRING DIAGRAM.

1	NO WATER CUT-OUT, Hg SWITCH
2	SUNVIC SIMMERSTATS, TYPE TYC
3	PANEL LIGHTS
4	PANEL SWITCH
5	CONNECTOR STRIP
6	FUSES
7	TRANSFORMER, 230 - 110 V
8	KENT MULTELEC MAIN SWITCH
9	KENT MULTELEC RECORDER
10	CONTACTOR SWITCH & PUSH-BUTTON CONTROL
11	230 V. A.C. SUPPLY
12	REBOILER HEATER (THERMOMANTLE)
13	COLUMN JACKET HEATER - TOP SECTN.
14	COLUMN JACKET HEATER - BOTTOM SECTN.
15	500 ML. REBOILER HEATER

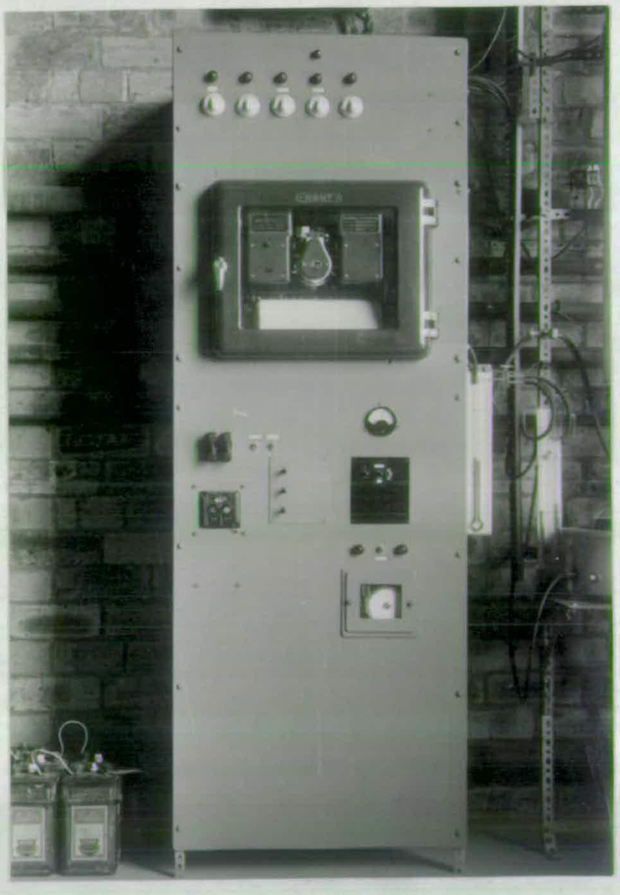


Figure 21.

Control panel.

the bucket being 0.5 ml., approximately 52, 26 or 13 ml., respectively.

Control panel.

The control panel (26" x 73") shown in fig. 21, was constructed from "Hardboard" supported on an "Ecofix" framework. All the electrical circuits, as well as the Kent recorder and timing mechanisms, were centralized on the panel.

The panel was operated direct from the 230 v. A.C. mains supply and the 8 v. D.C. supply provided by four 2 v. accumulators, connected in series. The A.C. wiring diagram is given in fig. 20a. and the D.C. circuits are shown in figs. 16 and 20b. (facing pp. 90 and 93, respectively).

A push-button switch was fitted in the A.C. circuit, so that no current could be provided on the panel until the push-button was pressed. This energized the magnetic relay of the contactor and made the circuit. If the current failed, the magnetic relay broke the circuit and the panel remained dead until the push-button was pressed again. Thus, if the mains supply was restored after a failure, the column did not operate until it was restarted under proper control. A further safeguard was provided by running all the condenser water into a self-draining, glass bucket, before running to waste. The bucket was supported on a counter-balanced, spring-loaded beam, carrying a mercury switch. If the water supply failed, the bucket drained, and the beam and mercury switch were tilted, thereby breaking the A.C. circuit and putting all heaters out of action. A further advantage of this device was that the column could not be operated until the condenser water was turned on and the beam put into the proper position by hand. The Kent recorder circuit was not broken by the no-water cut-out, so that the temperature of the overheads and the time at which water failure occurred could be read from the chart.

The power for the column and the recorder was drawn from a 5 amp. fuse-box, a neon indicating lamp being provided on the panel, and a 70 watt bulb was fitted above the still-head. Separate Simmerstats were used to control the heat input to the still and the two column sections. Each Simmerstat carried a panel light to indicate if current was flowing and to time the on and off periods.

All connections were centralized on a connector strip behind the panel, whence the current was drawn to the heaters etc.

The D.C. supply was drawn from another connector strip from which it was distributed to the timing mechanisms and bridge circuits; each provided with single-pole switches and panel lights indicating bucket tips and distillate receiver changes.

Column supports.

The column itself was supported permanently on the "Ecofix" framework by means of the copper tubes forming part of thermal insulation, and into which the column, wound with resistance wire, and asbestos rope, fitted tightly. The tubes were provided with angles brazed on at both ends in such a way as to permit bolting to horizontal girders on the framework. Thus, each column section was held independently in a perfectly vertical position and could be easily detached for inspection, cleaning or replacement of packing. The still-head surmounting the column was held in position by the joint on the column only, and was not clamped in any way to the framework, thus allowing for movement due to thermal expansion, without introducing strains.

B. Testing of fractionating column.

Prior to analytical fractionations of cannel naphtha, the column was thoroughly tested with regard to its general operating performance and fractionating efficiency. The tests carried out were divided into two groups:-

a. performance and operation tests, and
b. efficiency tests.

Performance and operation tests.

Although some of the tests were carried out during the actual erection and as part of the design of the column, theyare included under the present heading for the sake of continuity.

Since the column was intended for separations of hydrocarbons boiling below 160°C. a mixture of isomeric xylenes (b.pt. 139 - 144°C.) was considered suitable for testing the column performance and operation, while methylcyclohexane was used in tests where the exact knowledge of simple physical and thermal properties of the test liquid was necessary.

The tests consisted of operating the column at total reflux for periods varying from 6 to 72 hours, and noting the temperature of overheads and of liquid inside the boiler, the pressure in boiler, the heat inputs to the still mantle and jacket heaters (Simmerstat positions) and the galvanometer needle deflection when circuits on the Wheatstone bridge were made. Where possible, readings were taken every 15 - 30 mins. and logs kept. To observe the temperatures inside the lagging iron-constantan thermocouples were inserted between the first layer of lagging and the copper tube at both ends of each section, and connected to a direct reading "Integra" potentiometer having a compensating cold junction. By this means it was possible to obtain a quantitative picture of conditions inside the column lagging and, at the same time, test the performance of the heat input controllers.

By adjusting the heat input to the jacket heaters until the galvanometer needle showed no deflection from its zero position (i.e. the bridge was in balance) adiabatic conditions were assumed to have been reached. This was tested by noting the temperature of the jackets and of the overheads. It was found that, once steady operating conditions were reached, the temperature inside the jackets did not vary by more than ±0.2°C. and could be maintained constant over prolonged periods of time, in spite of intermittent heat supply to the heaters. When the bridge was balanced, the jackets' temperature showed a maximum deviation of ±0.3°C. from the overheads' temperature, while differences of 1°C. produced noticeable deflections of the galvanometer needle.

A further indication of the efficiency of thermal insulation was provided by operating at total reflux and measuring both the quantity of reflux flowing down the column (the boil-up rate) at the base of the column, and the quantity of cold reflux entering the column from the still-head. As the still-head operated as a vapour-liquid cycle, it was possible to measure, by counting drops leaving the bucket, the amount of liquid entering the column. It was assumed that no condensation took place in the vacuum-jacketed and lagged part of the still-head. The test liquid used was methylcyclohexane. All operating conditions were maintained steady and the column was allowed 24 hours to attain equilibrium conditions. The liquid entering the column was measured by counting drops leaving the bucket (the size of drops being determined beforehand) and correcting for internal reflux, due to heat exchange between cold reflux and vapours. The quantity of internal reflux was calculated by a simple heat balance:-

$$SR(T - t) = mL$$

where:- S = mean specific heat of liquid,
R = wt. of liquid entering column,
T = temperature of vapour,
t = temperature of liquid,
m = wt. of vapour condensed,
L = latent heat of vaporization,

hence, internal reflux $= m$

$$= \frac{SR(T - t)}{L}$$

and, total reflux $= R + m$

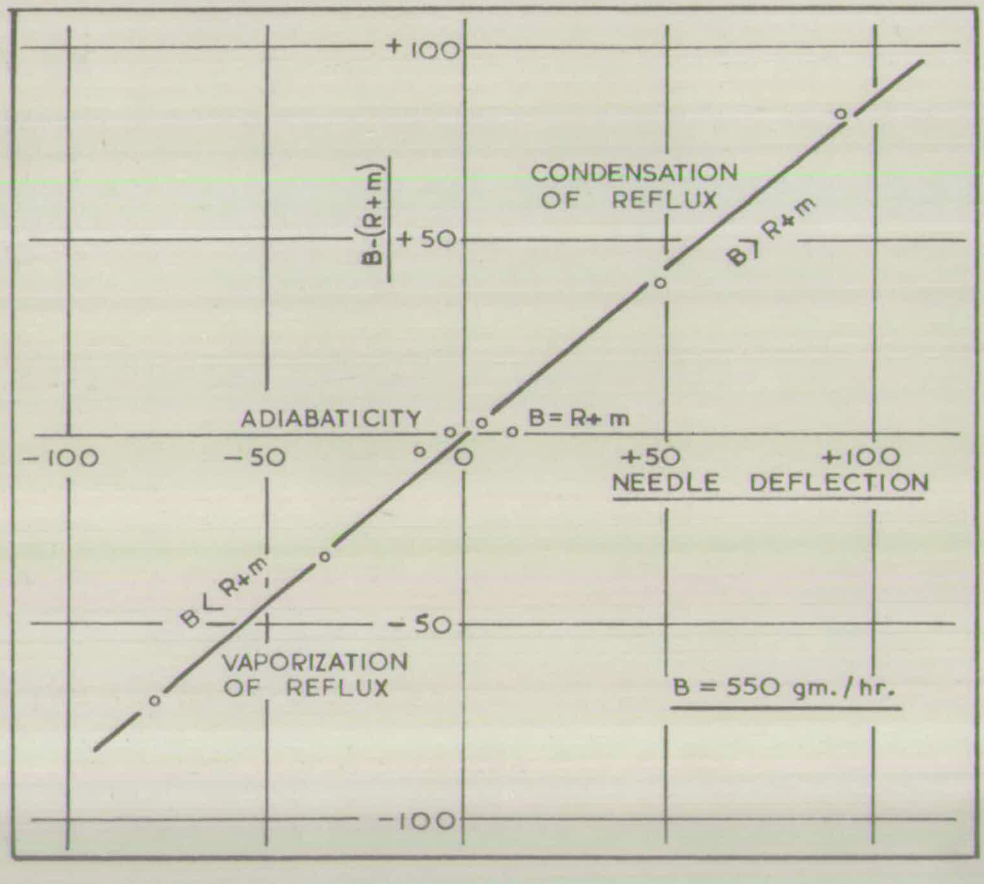
The error associated with the estimation of R and t was calculated to be ± 6%.

By comparing the quantity of reflux $(R + m)$ with the actual boil-up rate (B) it was possible to test the adiabaticity of the column. It was found that, when the bridge was balanced, the difference between B and $(R + m)$ did not exceed 15 gms./hr. when operating at boil-up rates of 500 - 600 gms./hr.

When the bridge galvanometer needle was deflected towards the left of its zero position $(R + m) > B$, i.e. too much heat was supplied to the heaters and partial vaporization of reflux was taking place inside the column, whereas, if the needle was deflected to the right $(R + m) < B$, i.e. vapour condensation was taking place and the

FIGURE 22.

PERFORMANCE OF COLUMN JACKETS.



heat input to the heaters was not sufficient. The results of this test are shown in fig. 22.

A series of test runs lasting up to 140 hours were carried out in order to test the performance of the Simmerstat controllers on the still mantle and column jackets' circuits. Boil-up rates varying from 400 to 900 ml./hr. were used and were found to remain constant, to within ± 10 ml./hr., over long periods of time. The jacket temperature and the adiabaticity of the column were investigated as described above and were also found to vary within narrow limits, though the response of the bridge to any sudden change in conditions was relatively slow.

The performance of take-off and receiver-changer mechanisms was investigated and found to be quite satisfactory, after a number of minor alterations had been made. At a reflux ratio of 120:1 and a rate of take-off of 4.2 gm./hr. the average take-off showed a variation of ±0.25 gms. per 12 hrs., while the difference in weight of fractions consisting of 52 bucket tips each, total 26 ml., (i.e. two pins on disc B) was of the order of 0.30-0.40 gm.

Considerable difficulty was experienced in the early stages of operation with vapour leaks through the flanged and ground glass joints. In the former case, particularly at high boil-up rates or during flooding, vapour leaks were considerable, irrespective of the tightness of the joints.

Materials such as Klingerit, cork sheet, asbestos sheet impregnated with shellac or sodium silicate, and polythene were tried as gaskets and found to be inefficient. The problem was solved, however, by using neoprene gaskets; fresh gaskets being inserted before each distillation.

Similar trouble was experienced in the case of ground glass joints and stopcock lubricants, this being eventually overcome by using Audco greases no. 356 and 657 on movable and permanent joints, respectively.

Determination of the number of theoretical plates.

The determination of the number of theoretical plates was carried out at total reflux, using n-heptane-methylcyclohexane as the binary test mixture. The physical properties of the two components are:-

	B.pt., °C. 760 mm.Hg.	Mol. latent heat (cal.)	d_4^{20}	n_D^{20}
n-heptane	98.43	7624	0.6837	1.3876
me.cyclohexane	100.93	7550	0.7694	1.4232

The vapour-liquid equilibrium and refractive index data for this mixture, given by Bromiley and Quiggle (13) and the National Bureau of Standards (108) values for α, were used throughout in the calculations. The reported values for α are:- 1.0738 at the normal b.pt. of n-heptane and 1.0758 at the normal b.pt. of methylcyclohexane. The refractive index for the sodium D-line at 20°C. was measured by a Hilger Abbe refractometer to the nearest 0.0001. Both the Fenske equation (30) and the N.B.S. equation (108) for the mixture in question were used.

(Under total reflux conditions, and assuming that Raoult's Law holds and α is constant over the operating range, the Fenske equation takes the form:-

$$n = \log \frac{x_n(1 - x_o)}{x_o(1 - x_n)} \Bigg/ \log \alpha_{av.}$$

where n = number of theoretical plates,

x_n = composition of liquid at top of n plates,

x_o = composition of liquid in the still,

$\alpha_{av.}$ = average value for $\frac{P_{o_1}}{P_{o_2}}$

P_{o_1} and P_{o_2} = vapour pressure of the more volatile and the less volatile component respectively at the temperature of the mixture.

The N.B.S. equation, based on the above, is:-

$$n + 1 = \left[32.15 - 0.34\ (t - 99)\right] \log \left[\frac{x_n}{1 - x_n} \Bigg/ \frac{x_o}{1 - x_o} \right]$$

where t = mean temperature.)

Both components of the binary mixture were obtained from The British Drug Houses Ltd. and purified before use. While methylcyclohexane could be purified without difficulty by fractionation at a reflux ratio of 120:1 in a column packed with ⅛" Dixon rings, to give a distillate of constant refractive index (1.4232) and density (0.7690 - .7696), the purification of commercial n-heptane was a more serious problem. Repeated fractionations at high reflux ratios and silica gel adsorptions failed to remove the impurities present, believed to consist mainly of 2:2:4-trimethylpentane, (b.pt. 99.24°C., n_D^{20}= 1.3915). Eventually, however, n-heptane sample of 100% purity was kindly presented to the author by Dr. A. Pryde of Heriot -Watt College, Edinburgh.

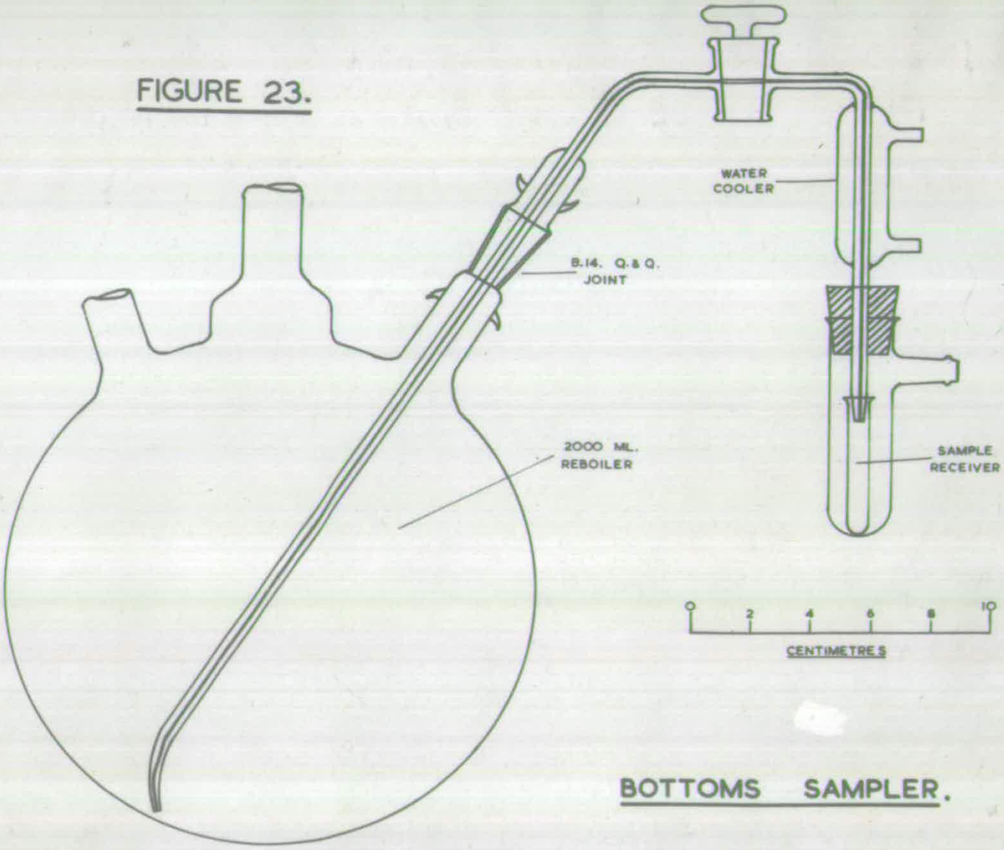
Two main test runs were carried out to determine the column efficiency when packed with:-

a. ⅛" Dixon rings,

b. 1/16" Dixon rings.

The procedure in all tests was identical and consisted of the following:- the test mixture, the composition of which was previously calculated and accurately known, was charged to the still and the still placed in position. All ground glass and flanged joints were then adjusted and tightened and the electric current to the still mantle and column heaters switched on. A very slow rate of heating was maintained till the vapours reached the still-head, after which the heating was slightly increased to give the desired boil-up rate. A period of 30 hours was allowed for the establishment of equilibrium conditions. Since the mathematical derivation of the number of theoretical plates assumes adiabatic conditions, care was exercized to maintain these conditions as far as possible. The overheads were sampled by switching on temporarily the take-off mechanism and tipping the

FIGURE 23.



BOTTOMS SAMPLER.

bucket once, whereby approx. 0.30 gm. of distillate were collected. The bottoms were sampled by the sampler shown in fig. 23, by means of which a similar amount of liquid was withdrawn from the still. The refractive indices of the samples at 20°C. were measured, the composition of the liquids determined from n_D data and the number of theoretical plates calculated. Samples were taken at different boil-up rates, expressed in ml./hr. and measured as reflux at the bottom of the column, a period of 4 - 6 hrs. being allowed before each sampling. A number of determinations were duplicated in order to investigate the reproducibility of results. The pressure drop across the column was measured by a water manometer connected directly to the still, pressures being expressed in mm. Hg.

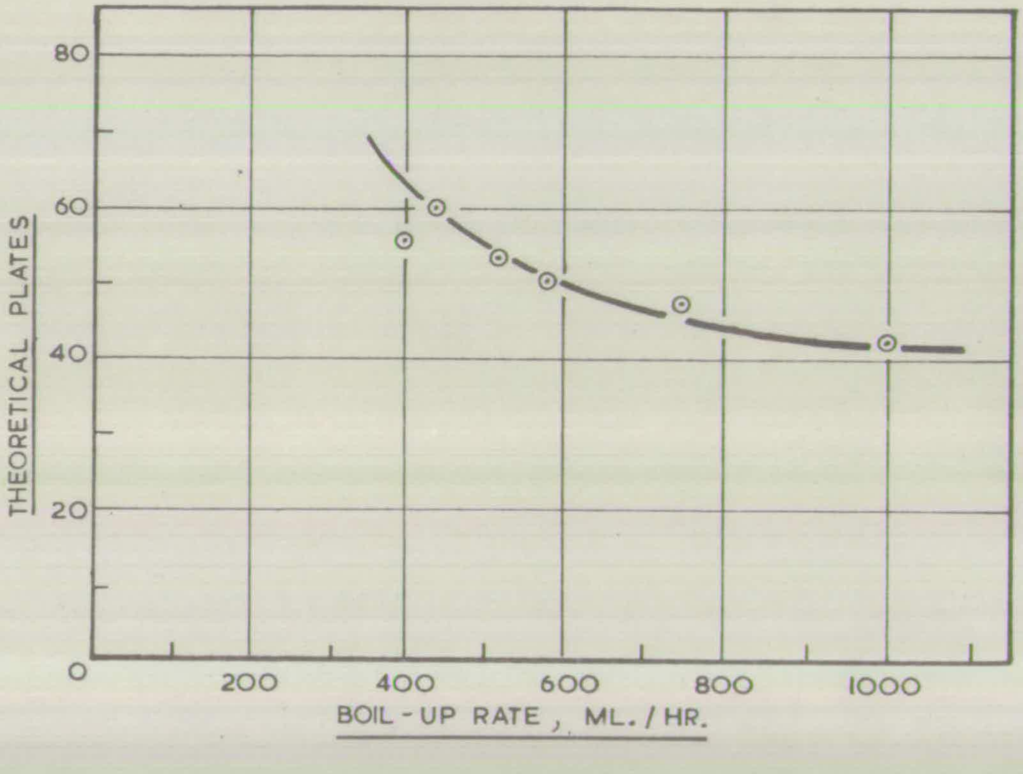
Run No. 1.

The column packing consisted of stainless steel, square-weave gauze, ⅛" x ⅛" Dixon rings. After reaching operating conditions, the column was flooded by adding sufficient heat to the still to force the liquid to the top of the column, after which the column was drained and allowed to reach equilibrium conditions.

The composition of the test mixture charge was 8.84 mol % n-heptane in methylcyclohexane; a figure decided upon after consideration of factors discussed by French et al. (35) and the Anglo-Iranian Oil Co. (1). The results of the test

FIGURE 24.

EFFICIENCY OF COLUMN PACKED WITH 1/8" DIXON RINGS.



are given in Table 13.

TABLE 13.

Boil-up rate, ml./hr.	No. of plates	H.E.T.P., cms.	Pressure drop, mm. Hg.
400 ± 10	56	3.03	1.5
440 ± 10	60	2.84	2.0
520 ± 5	54	3.15	2.3
400 ± 5	56	3.03	1.5
520 ± 5	54	3.15	2.3
570 ± 5	51	3.33	2.9
750 ± 10	47	3.62	3.7
1000 ± 10	43	3.95	6.8
1000 ± 10	42	4.05	6.9

The results indicate that the efficiency of the column expressed as the number of theoretical plates, is very much lower than that claimed by Dixon (26) for a similar column. The plot of variation of the number of theoretical plates with boil-up rate, shown in fig. 24, is similar in shape to that reported by Dixon, but varies considerably in magnitude. The high values for the number of plates quoted by Dixon, which appear to have been obtained by proportion from experiments on shorter columns, could not be reproduced under the conditions outlined above and no satisfactory reason could be found for this. It is quite probable, however, that the ratio of column diameter to packing diameter was too low to give the desired number of theoretical plates.

Run No. 2.

The column packing, in this instance, con-

FIGURE 25. EFFICIENCY OF COLUMN PACKED WITH 1/16" DIXON RINGS.

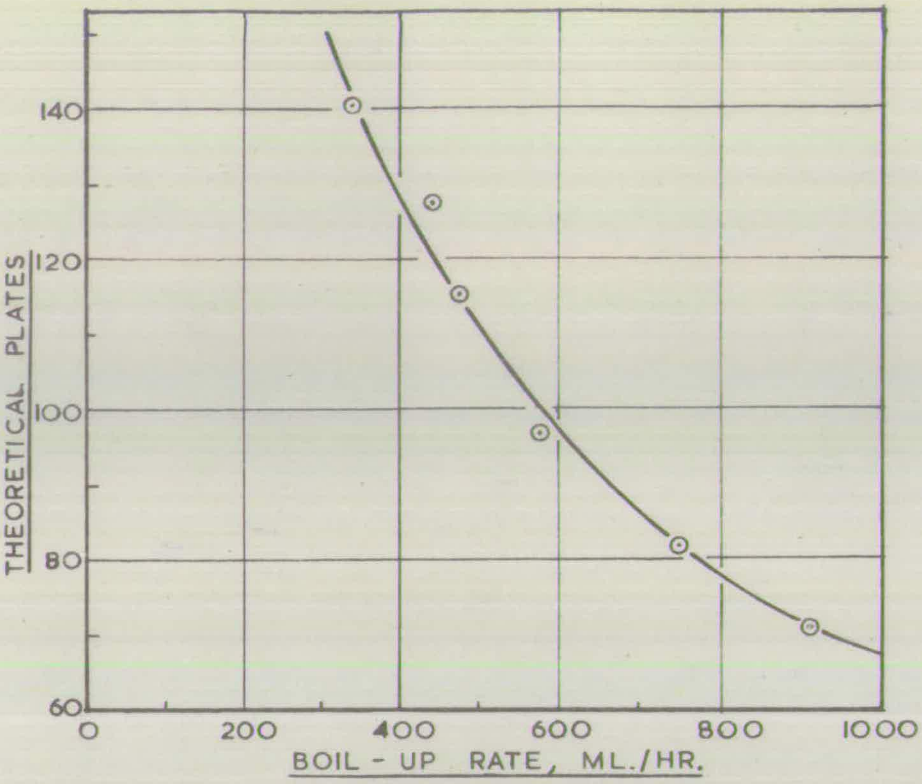
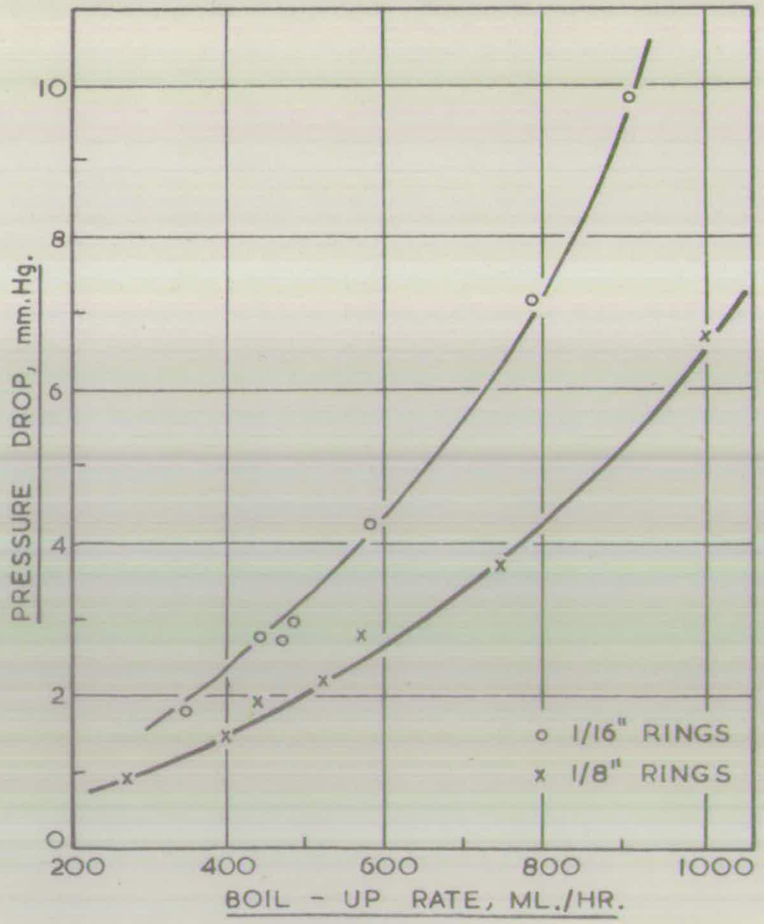


FIGURE 26. PRESSURE DROP IN COLUMN.



sisted of 1/16" Dixon rings, already described on p. 88.

The test mixture charged to the still contained 7.87 mol % n-heptane in methylcyclohexane. The column was flooded, drained and allowed 30 hours to reach equilibrium. The results obtained are given in Table 14, while the variation in the number of plates with boil-up rate is shown in fig. 25.

TABLE 14.

Boil-up rate, ml./hr.	No. of plates	H.E.T.P., cms.	Pressure drop, mm. Hg.
475 ± 5	116	1.46	3.0
480 ±10	116	1.46	3.0
440 ± 5	128	1.33	2.8
340 ± 5	141	1.21	1.9
475 ± 5	116	1.46	3.0
580 ±10	97	1.75	4.3
750 ±10	82	2.08	6.0
910 ±10	71	2.40	9.0

The above results indicate clearly the effect of the smaller diameter packing and of the increased column and packing diameters' ratio on column efficiency. Though flooding was only achieved by allowing the column to prime at a high boil-up rate and without special flooding valves, this procedure was quite satisfactory and yielded a favourably large number of theoretical plates. Boil-up rates above 1000 ml./hr. were difficult to maintain as the column flooded uncontrollably

FIGURE 27. No. OF PLATES vs. RECIPROCAL BOIL-UP RATE.

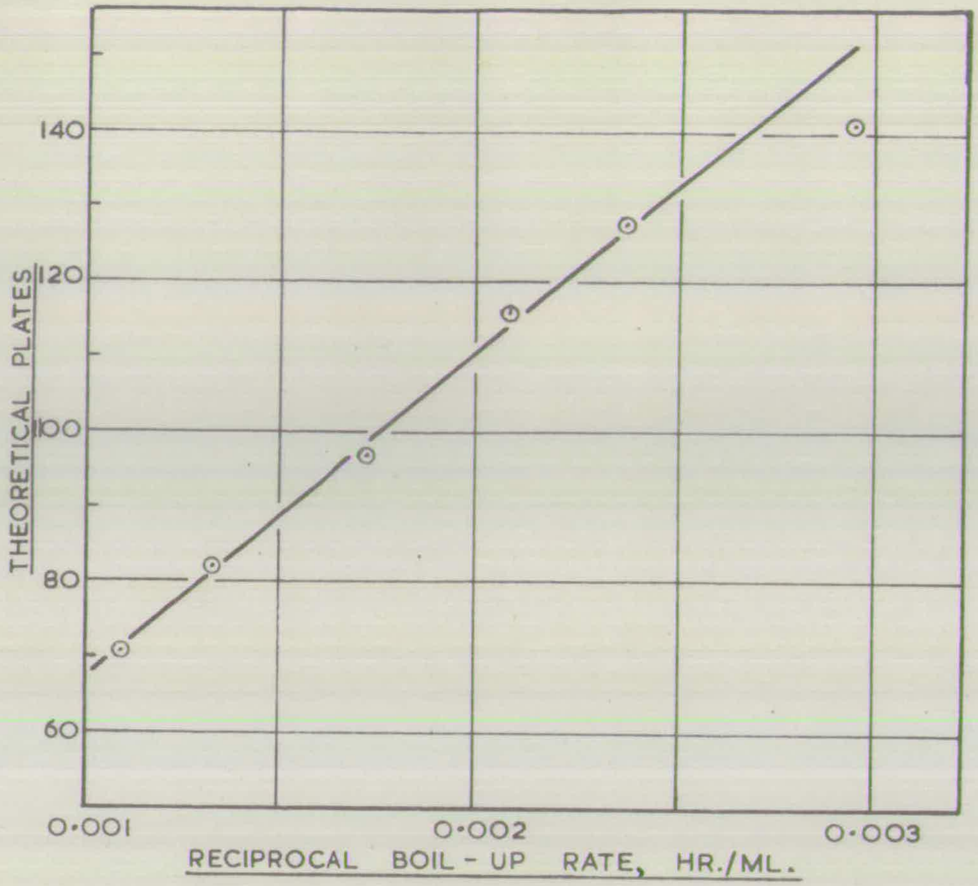


FIGURE 28. EFFECT OF FLOODING ON COLUMN EFFICIENCY.

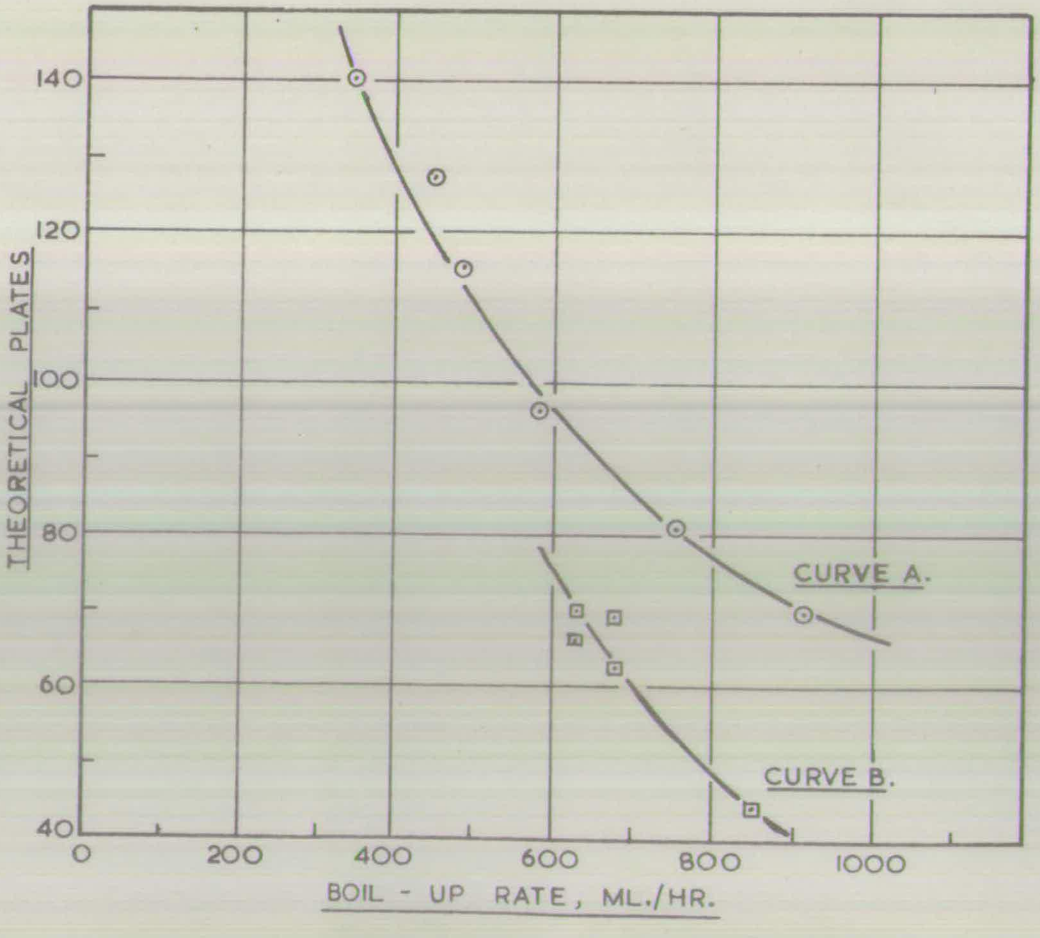


FIGURE 29. EFFECT OF COLUMN JACKETS' TEMPERATURE.

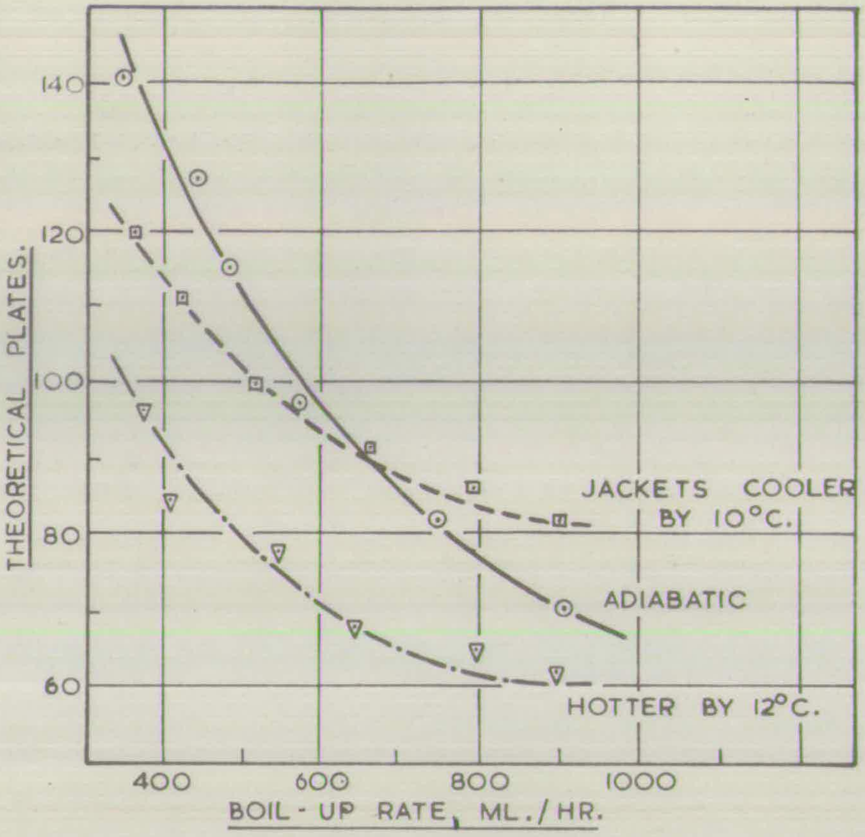
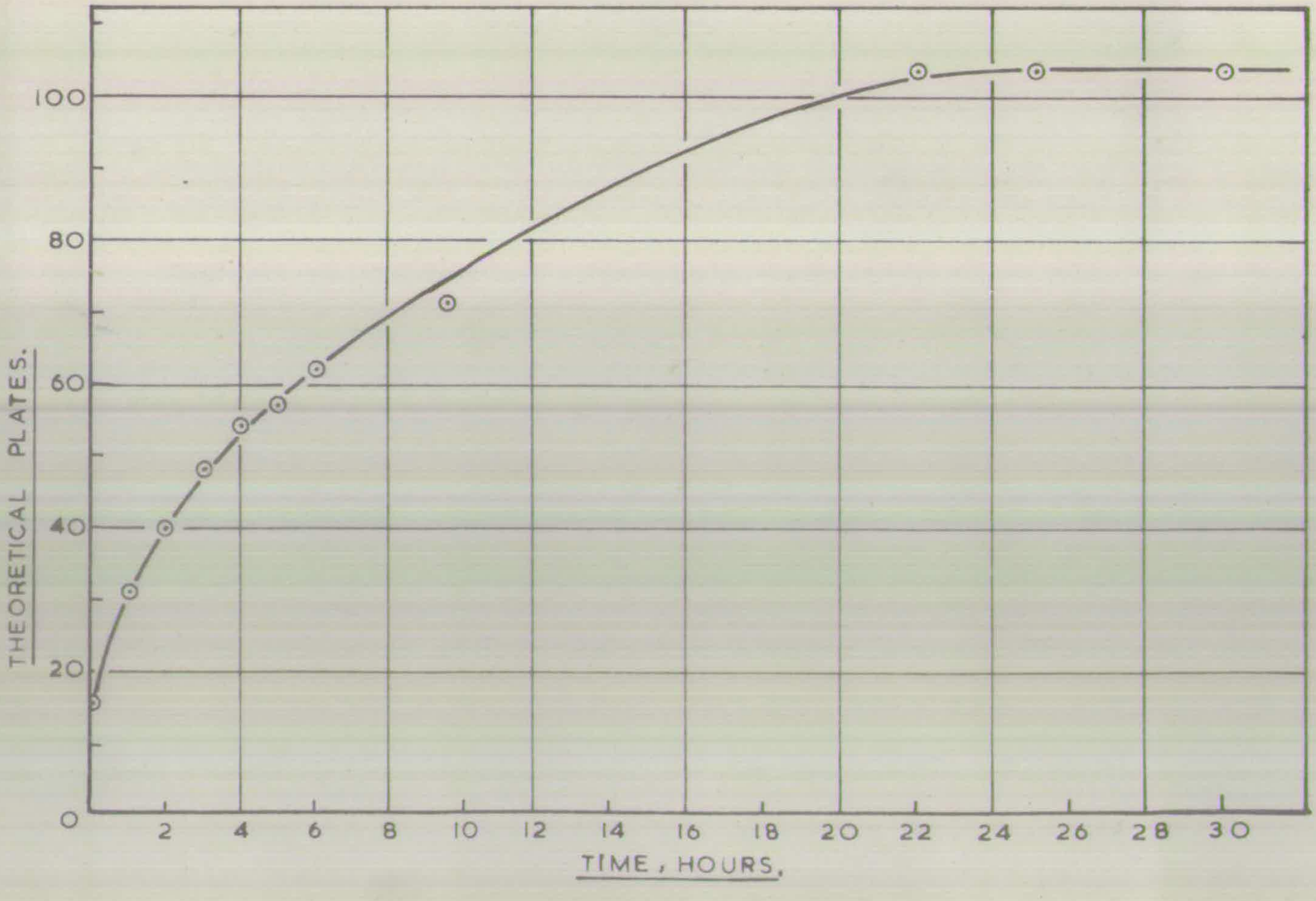


FIGURE 30. ESTABLISHMENT OF EQUILIBRIUM CONDITIONS.



and conditions within the column varied considerably. The low number of theoretical plates at boil-ups of that order was most likely due to the destruction of the liquid film originally imparted on the packing during flooding.

The variation in pressure drop across the column with boil-up rate is shown in fig. 26 (facing p. 108). Fig. 27 shows the linear relationship between the number of theoretical plates and the reciprocal boil-up rate.

Effect of pre-flooding.

The effect of pre-flooding on the efficiency of the column is illustrated in fig. 28, where curve A represents the efficiency in terms of theoretical plates when the column has been flooded in the manner described, while curve B is for a dry column, maintained at a given boil-up rate with the jackets made adiabatic and equilibrium conditions being established before sampling. The efficiency of the column is considerably lower in this case and the values for the number of plates were frequently found to be irreproducible.

Effect of jackets' temperatures on column efficiency.

The effect of column jackets' temperatures on the efficiency of the column was again investigated by operating the column at a given boil-up rate and determining its efficiency when the jackets were adiabatic and when too much and too little heat was being supplied to the jacket heaters. The results are shown in fig. 29. As was expected, the efficiency of the column at total reflux was little altered when the jackets' temperature was of the order of $5^{\circ} - 10^{\circ}$C. below that of the column itself. When operating at finite reflux ratios, however, this may lead to some fluctuations and give erroneous figures for the boil-up rate and hence reflux ratio. Overheating of the jackets, on the other hand, had a more marked effect on column efficiency.

Establishment of equilibrium conditions.

The time necessary for the establishment of equilibrium conditions within the column was determined by operating the column in the usual manner, under adiabatic conditions and a constant boil-up rate. As soon as the column reached operating conditions (i.e. after flooding) the overheads and bottoms were sampled at regular intervals of time until the number of theoretical plates reached a constant value. The results are shown in fig. 30 (facing p. 109), where the number of theoretical plates is plotted against time after operating conditions have been reached. The error involved in these determinations was much larger than in previous cases, since the column was operated at a reflux ratio of approx. 2000:1 instead of infinity.

Hold-up.

No determinations of hold-up, either static or dynamic, were made, and where necessary values quoted by Dixon (26) were used.

Choice of operating conditions.

The choice of most favourable operating conditions was naturally based on the results mentioned above and the properties of material to be distilled.

As the column was made automatic, a fixed rate of take-off of 4 - 5 ml./hr. was most convenient, as it would permit distillations of 1 litre fractions to be completed in 200-250 hrs. Boil-up rates of the order of 500 ml./hr. were considered most suitable, since under these conditions, the column, of efficiency equivalent to about 110 theoretical plates, could be operated at reflux ratios above 100:1.

Adiabatic operation was desirable, though very slight heat losses from the column would not affect the fractionating efficiency to any appreciable extent. A period of 30 hours was to be allowed for establishment of equilibrium conditions.

FRACTIONATION OF CANNEL NAPHTHA DISTILLATES.

The fractionation of cannel naphtha distillates as obtained from batch distillation (B-fractions) and their separation into a number of close-cut fractions were carried out by means of high-efficiency distillation at atmospheric pressure. The apparatus available for this purpose, described in the preceding section, was operated throughout the whole series of distillations (D-distillations) under conditions giving a column efficiency equivalent to at least 100 theoretical plates, at reflux ratios of over 100 to 1.

The object of the distillations was to yield a large number of fractions (D-fractions) consisting of individual hydrocarbons or simple mixtures, which could then be examined with respect to their constituents by adsorption on silica gel and other methods.

(Prefix C- is purposely omitted from the nomenclature of distillations and fractions to avoid confusion with C for carbon).

Distillation procedure.

The general procedure adopted during all distillations was essentially the same and consisted of the following operations. The charge to be distilled was dried over $CaCl_2$, filtered and weighed into the 2 litre still, 20-25 gm. of sample being kept for reference purposes and tests. The still and thermomantle were placed in position under the column. All ground glass joints and taps on the still and the column-head were re-greased and new neoprene gaskets inserted in all flanged joints, the joints made up and tightened. The exposed parts of the still, column and still-head were insulated with asbestos wool or rope and compressed glass wool lagging. The condenser water was turned on and the no-water cut-out device set in position. The push-button control was pressed and the power supply to the heaters and thermomantle turned on to an extent depending on the expected boiling range of the charge. Heating of the charge was adjusted to give a steady rise in temperature of about 40°C. per hour, while the heat input to the jackets was set to give 20° - 25°C. rise per hour. Between two and three hours were required to bring the charge to boiling point and the rate of heating was maintained constant until the vapours entered the still-head. During the latter period (30-45 mins.) the column jacket heaters were set to produce a maximum temperature of about 10°C. below the initial boiling point of the charge. As soon as the charge was at boiling point, the Kent recorder was started.

After the vapours had entered the still-head, the rate of heating of charge was considerably increased so as to force the liquid to the top of the column and flood the packing. The column was flooded for about 15 mins., after which the heat input to the thermomantle was reduced to a value giving approximately the required boil-up rate, as measured by the reflux meter and pressure drop across the column, and the column allowed to drain slowly. After drainage, power supply to all heaters was adjusted to give the necessary conditions and the column was operated at total reflux for a period of at least 30 hours, to permit attainment of equilibrium conditions in the rectifying section. During that period all joints were frequently inspected for leaks and the necessary adjustments made. The boil-up rate was measured at regular intervals by the reflux meter on the still and by noting the pressure drop, and was maintained constant to ± 10 ml./hr. of the required value.

The adiabaticity of the column was also checked frequently by means of the Wheatstone network, and the column was allowed to operate at a maximum deviation of -5°C. from adiabatic; any larger deviation being at once corrected.

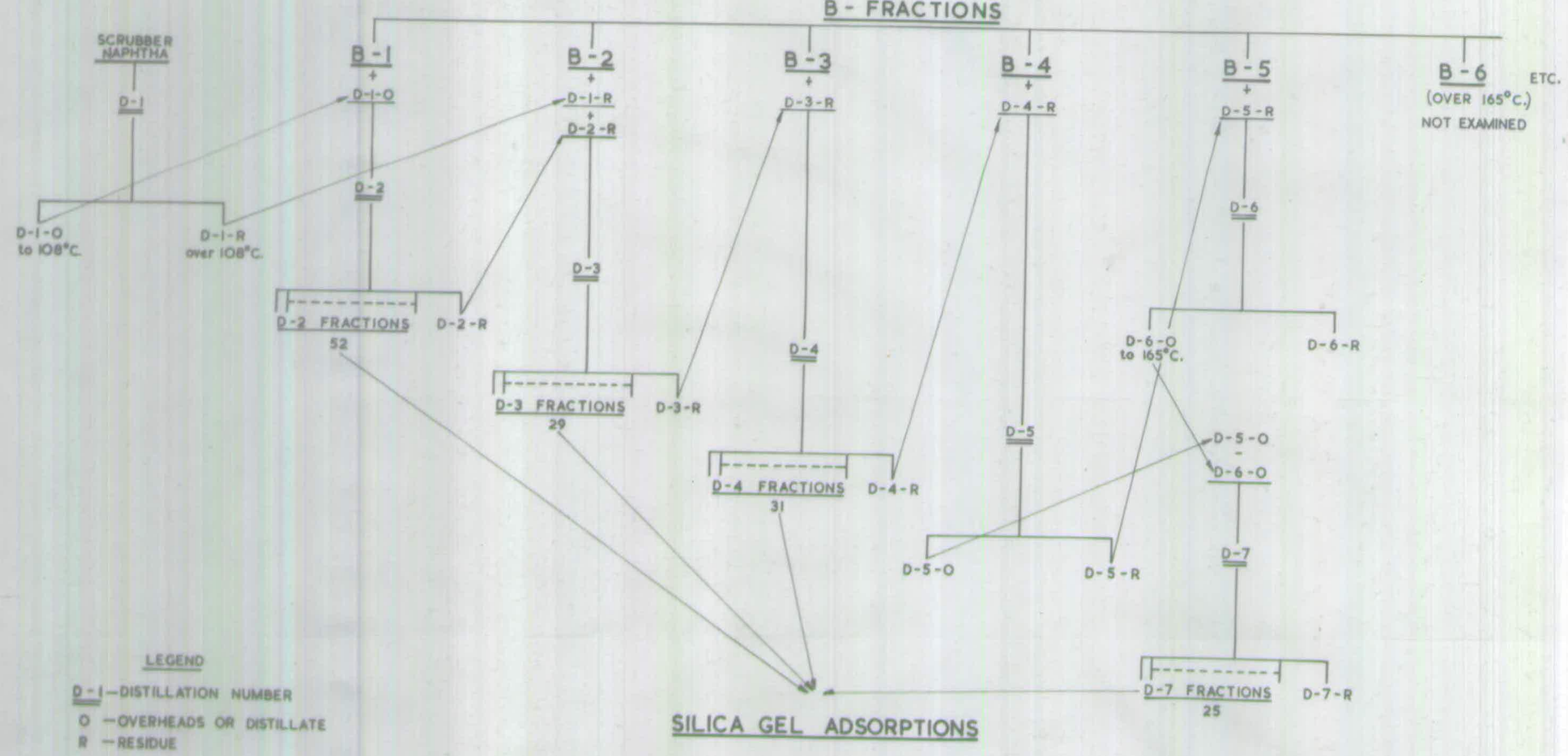
The distillation proper was started after the period at total reflux, by switching on the D.C. supply to the take-off and receiver-changer mechanisms, after previous adjustments to both impulse motors' discs to give the pre-determined take-off rate and distillate fraction volume. Throughout the distillation, readings of boil-up rate, still temperatures, still and barometric pressures etc. were taken and thermal conditions within the column checked. The temperature of the vapours was read-off the recorder chart and converted to degrees C. Owing to small variations in the A. C. frequency the chart had to be adjusted occasionally to read the correct time. All changes in distillation conditions and times when distillate fractions were changed were noted on the chart. Crushed ice for the thermocouple cold junction was changed every 24 hours.

The column was operated continuously day and night until the required quantity of distillate had been collected. The distillate fractions were collected in tared test-tubes suspended from the turntable of the receiver-changer. The weight and volume of each fraction was noted and the fraction transferred to separate test-tubes, while the tared receivers were cleaned, dried and replaced in position.

At the conclusion of a run, the power to all heaters was turned off, the take-off and receiver-changer mechanisms and the D.C. supply switched off, and the column allowed to drain and cool overnight. The Kent recorder was usually stopped when the still-head reached room temperature. The residue remaining in the still was weighed and stored. After every second distillation, the column was cleaned by refluxing acetone for 2-3 hours and dried by compressed air.

The boiling point curve for the distillation was worked out from the recorder chart, corrected to 760 mm. Hg pressure and plotted against % wt.

FIGURE 31.


B - FRACTIONS
SCRUBBER NAPHTHA
D-1
D-1-O to 108°C.
D-1-R over 108°C.
B-1
+
D-1-O
D-2
D-2 FRACTIONS
52
D-2-R
B-2
+
D-1-R
+
D-2-R
D-3
D-3 FRACTIONS
29
D-3-R
B-3
+
D-3-R
D-4
D-4 FRACTIONS
31
D-4-R
B-4
+
D-4-R
D-5
D-5-O
D-5-R
B-5
+
D-5-R
D-6
D-6-O to 165°C.
D-6-R
D-5-O
-
D-6-O
D-7
D-7 FRACTIONS
25
D-7-R
B-6 ETC.
(OVER 165°C.)
NOT EXAMINED
SILICA GEL ADSORPTIONS
LEGEND
D-1 —DISTILLATION NUMBER
O —OVERHEADS OR DISTILLATE
R —RESIDUE

distillate. Knowing the weight and hence, the percentage on charge of each fraction, the boiling ranges of individual fractions were read-off the chart; the range of every fifth fraction being verified by distillation in a 10 ml. flask equipped with a 4" x ½" Vigreux column. Density, refractive index and bromine number of all fractions were measured.

During distillations of the lower-boiling material an activated charcoal scrubber was attached to the top of the main still-head condenser so as to remove all the uncondensed material, such as very low-boiling hydrocarbons and dissolved gases.

D-distillations.

Since it was intended to analyze all low-boiling material derived from the crude cannel oil, the scrubber naphtha collected during carbonizations was included in the range of fractions distilled.

In all, seven major distillations were carried out, by means of which all material boiling to 158.5°C. was distilled and separated into a large number of fractions. The scheme of distillations, shown in the condensed flow diagram (fig. 31) was as follows:-

D-1. Distillation of scrubber naphtha and separation into distillate to 108°C., i.e. corresponding in boiling range to fraction B-1, and residue.

D-2. Distillation of fraction B-1 plus scrubber naphtha distillate ex D-1. Separation of charge into 52 fractions and residue.

D-3. Distillation of fraction B-2 plus residues ex D-1 and D-2. Separation of charge into 29 fractions and residue.

D-4. Distillation of fraction B-3 plus residue ex D-3. Separation of charge into 31 fractions and residue.

D-5. Distillation of fraction B-4 plus residue ex D-4. Separation of charge into distillate to 148°C. and residue.

D-6. Distillation of fraction B-5 plus residue ex D-5. Separation of charge into distillate to 165°C. and residue.

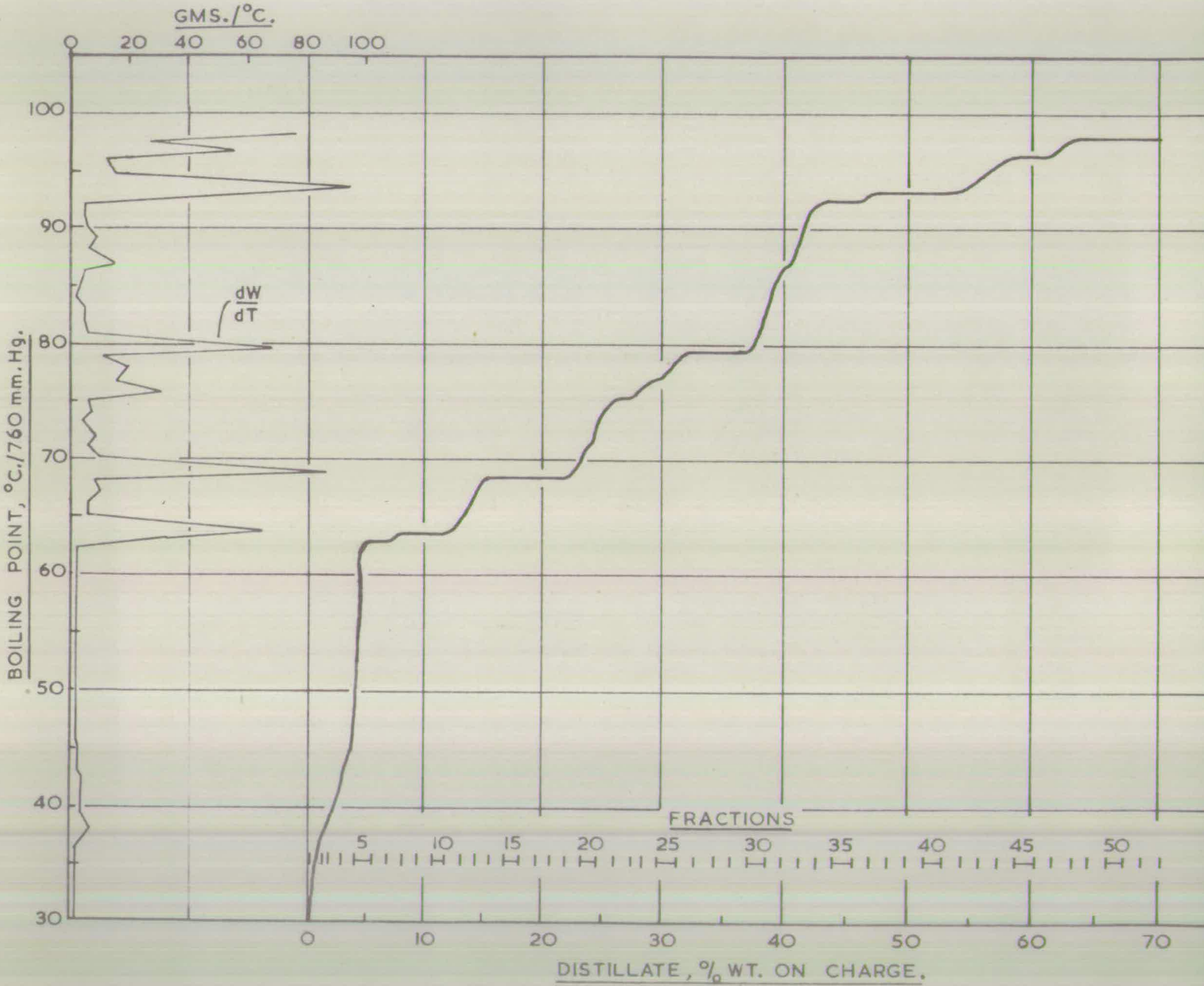
D-7. Distillation of distillates ex D-5 and D-6. Separation of charge into 25 fractions, to 158.5°C., and residue.

Fractions B-6 to B-10 were not distilled. Distillation D-1 was carried out in the column packed with 1/8" Dixon rings, while the remainder of the distillations were performed in the column packed with 1/16" rings.

Of the seven distillations, four (viz. D-2, -3, -4 and D-7) yielded distillate fractions which were subsequently subjected to further separations and analyses with respect to their major hydrocarbon constituents. A more detailed description of the distillations is given below, showing the origin, quantities and boiling ranges of charges and overheads, and conditions under which the distillations were carried out.

FIGURE 32.

RESULTS OF DISTILLATION D-2.



Distillation D-1.

Charge:- 786 gm. of scrubber naphtha. Overall boiling range 36°-131°C.

Distillate:- 590 gm. (75.1% wt. on charge). Boiling range 28.4°-108.2°C.

Residue:- 162 gm. (20.6% on charge).

Loss:- 34 gm. (4.3%)

Conditions:-		
	Duration	135 hours.
	Av-ge rate of boil-up	700±20 ml./hr.
	Av-ge rate of take-off	8.42 ml./hr.
	Reflux ratio	83:1.

Distillation D-2.

Charge:- 1159 gm. combined fraction B-1 plus distillate (to 108°C.) from scrubber naphtha distillation (D-1). Overall boiling range 28°-108°C.

Distillate:- 52 fractions, total weight 809 gm. (69.8% wt. on charge). Total volume 1130 ml. Av-ge volume of fractions 21.8 ml. Overall boiling range 26.9°-98.4°C.

Residue:- 320 gm. (27.6% on charge).

Loss:- 30 gm. (2.6%).

Conditions:-		
	Duration	312 hrs.
	Av-ge rate of boil-up	545 ± 10 ml./hr.
	Av-ge rate of take-off	4.20 ml./hr.
	Reflux ratio	130:1.

The results of the distillation are shown in fig. 32, where the weight percent of total charge and the quantity of material distilling per degree C. $\left[\frac{dw}{dt}\right]$ are plotted against boiling point at 760 mm. Hg.

During the early stages of the distillation a certain amount of gas evolution took place, most of which was adsorbed by the charcoal scrubbers. An interesting feature of this was the appearance, during the first fifteen hours of take-off, of a fine white crystalline solid at the mouth of the spiral distillate cooler. Attempts to examine the solid were unsuccessful as it tended to melt at room temperature and rapidly decompose, giving rise to an oily, water-insoluble liquid. This compound, similar in appearance to the characteristic hydrate "snow", was assumed to be, in fact, a hydrate of one of the butanes. A certain amount of distillate evaporation was taking place at the mouth of the cooler resulting in decrease in temperature and, hence, formation of a fine water mist on the surface of the spout, thus enabling the formation of a hydrate. A literature study on the subject revealed that this was quite likely and could only be due to the presence of butanes in the distillate, since liquid hydrocarbons do not form hydrates, while gaseous hydrocarbons of less than four carbon atoms form hydrates only at low temperatures and relatively high pressures.

Distillation D-3.

Charge:- 1019 gm. combined fraction B-2 plus residues from distillation D-1 (over 108°C.) and D-2. Overall boiling range 98°-131°C.

Distillate:- 29 fractions, total weight 534 gm. (52.4% wt. on charge). Total volume 672 ml. Av-ge volume of fractions 23.2 ml. Overall boiling range 89.3°-117.3°C.

Residue:- 446 gm. (43.8% on charge).

Loss:- 39 gm. (3.8%)

FIGURE 33.

RESULTS OF DISTILLATION D - 3.

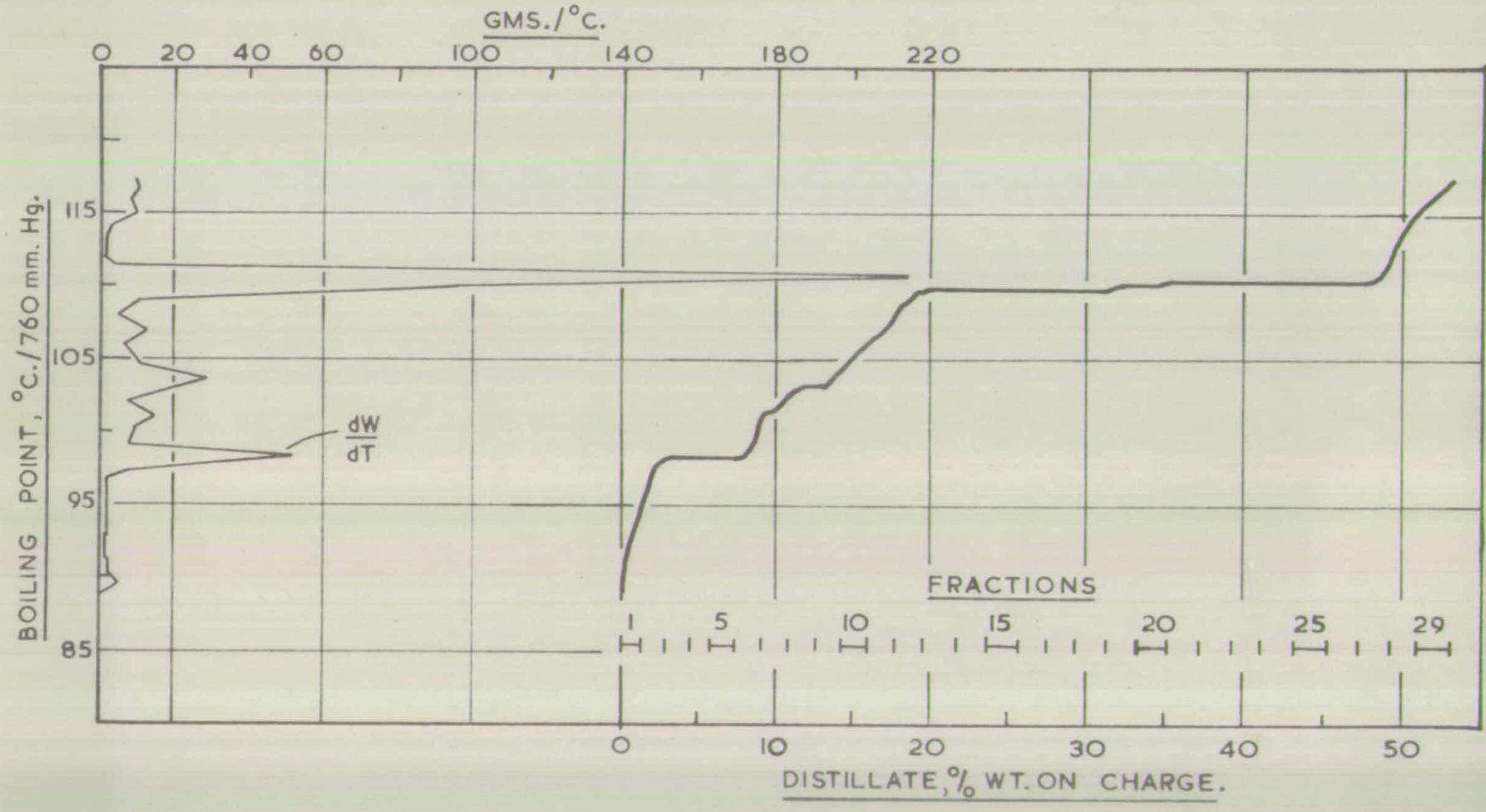
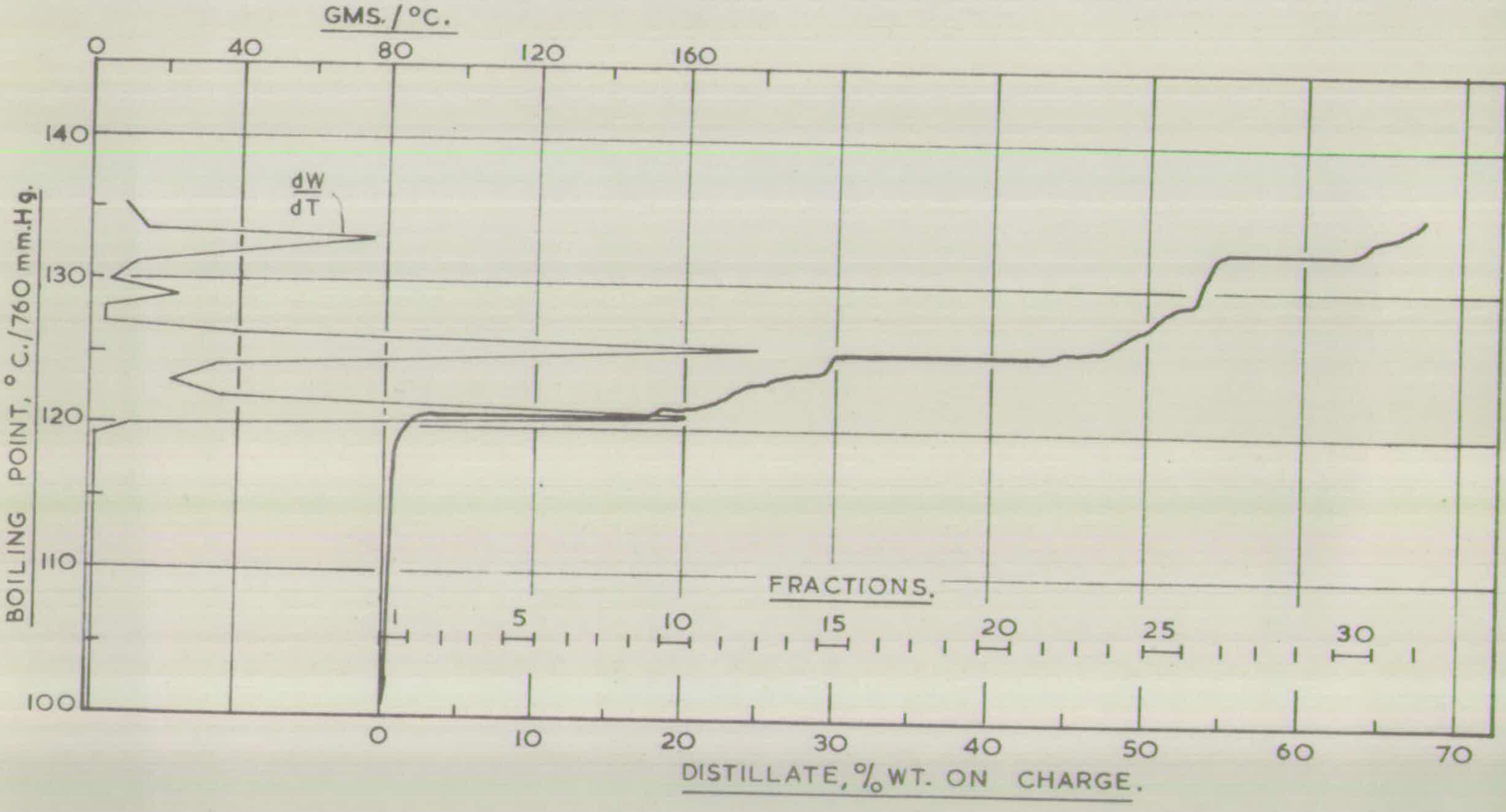


FIGURE 34.

RESULTS OF DISTILLATION D - 4.



Conditions:- Duration 196 hrs.
Av-ge rate of boil-up 580 ± 10 ml./hr.
Av-ge rate of take-off 4.51 ml./hr.
Reflux ratio 128:1.

The results of the distillation are shown in fig. 33.

Distillation D-4.

Charge:- 925 gm. combined fraction B-3 plus residue from distillation D-3. Overall boiling range 117°-145°C.

Distillate:- 31 fractions, total weight 621 gm. (67.2% wt. on charge). Total volume 842 ml. Av-ge volume of fractions 27.2 ml. Overall boiling range 100.9°-134.9°C.

Residue:- 287 gm. (31.0% on charge).

Loss:- 17 gm. (1.8%)

Conditions:- Duration 209 hours.
Av-ge rate of boil-up 600 ± 10 ml./hr.
Av-ge rate of take-off 5.37 ml./hr.
Reflux ratio 112:1.

The results of the distillation are shown in fig. 34.

Distillation D-5.

Charge:- 807 gm. combined fraction B-4 plus residue from distillation D-4. Overall boiling range 135°-157°C.

Distillate:- 623 gm. (77.2% wt. on charge). Boiling range 130.3°-148.2°C.

Residue:- 174 gm. (21.6% on charge).

Loss:- 10 gm. (1.2%).

Conditions:- Duration 190 hrs.
Av-ge rate of boil-up 610 ± 10 ml./hr.
Av-ge rate of take-off 5.41 ml./hr.
Reflux ratio 113:1

Distillation D-6.

Charge:- 824 gm. combined fraction B-5 plus residue from distillation D-5. Overall boiling range 148°-173°C.

Distillate:- 300 gm. (36.4% wt. on charge). Boiling range 144.6°-165.0°C.

FIGURE 35a.

RESULTS OF DISTILLATION D-7.

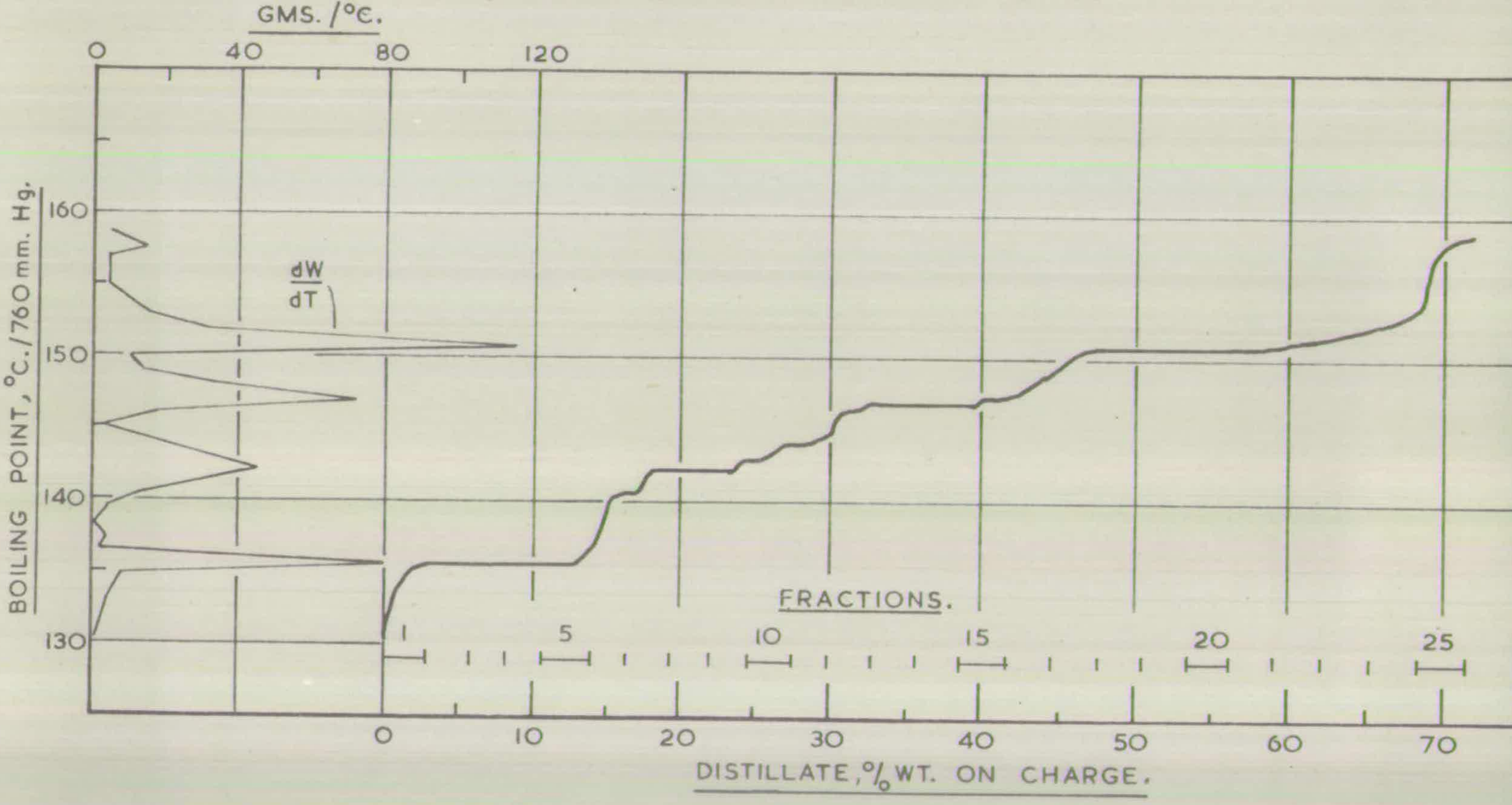


TABLE 15.

No.	Weight of charge, gm.	B.pt. range of charge, °C./760 mm.	B.pt. range of distillate, °C./760 mm.	Weight recovered, gm.		Loss, gm.
				Distillate	Residue.	
D-1	786	36-131	28.4-108.2	590	162	34
D-2	1159	28-108	26.9- 98.4	809	320	30
D-3	1019	98-131	89.3-117.3	534	446	39
D-4	925	117-145	100.9-134.9	621	287	17
D-5	807	135-157	130.3-148.2	623	174	10
D-6	824	148-173	144.6-165.0	300	509	15
D-7	870	130-165	130.1-158.5	548	305	17

Residue:- 509 gm. (61.8% on charge).

Loss:- 15 gm. (1.8%).

Conditions:-	Duration	108 hrs.
	Av-ge rate of boil-up	710 ± 15 ml./hr.
	Av-ge rate of take-off	5.63 ml./hr.
	Reflux ratio	126:1.

Distillation D-7.

Charge:- 870 gm. combined distillates from distillations D-5 and D-6. Overall boiling range 130°-165°C.

Distillate:- 25 fractions, total weight 548 gm. (63.0% wt. on charge). Total volume 715 ml. Av-ge volume of fractions 28.6 ml. Overall boiling range 130.1°-158.5°C.

Residue:- 305 gm. (35.1% on charge).

Loss:- 17 gm. (1.9%).

Conditions:-	Duration	173 hrs.
	Av-ge rate of boil-up	600 ± 10 ml./hr.
	Av-ge rate of take-off	5.73 ml./hr.
	Reflux ratio	105:1

The results of the distillation are shown in fig. 35a.

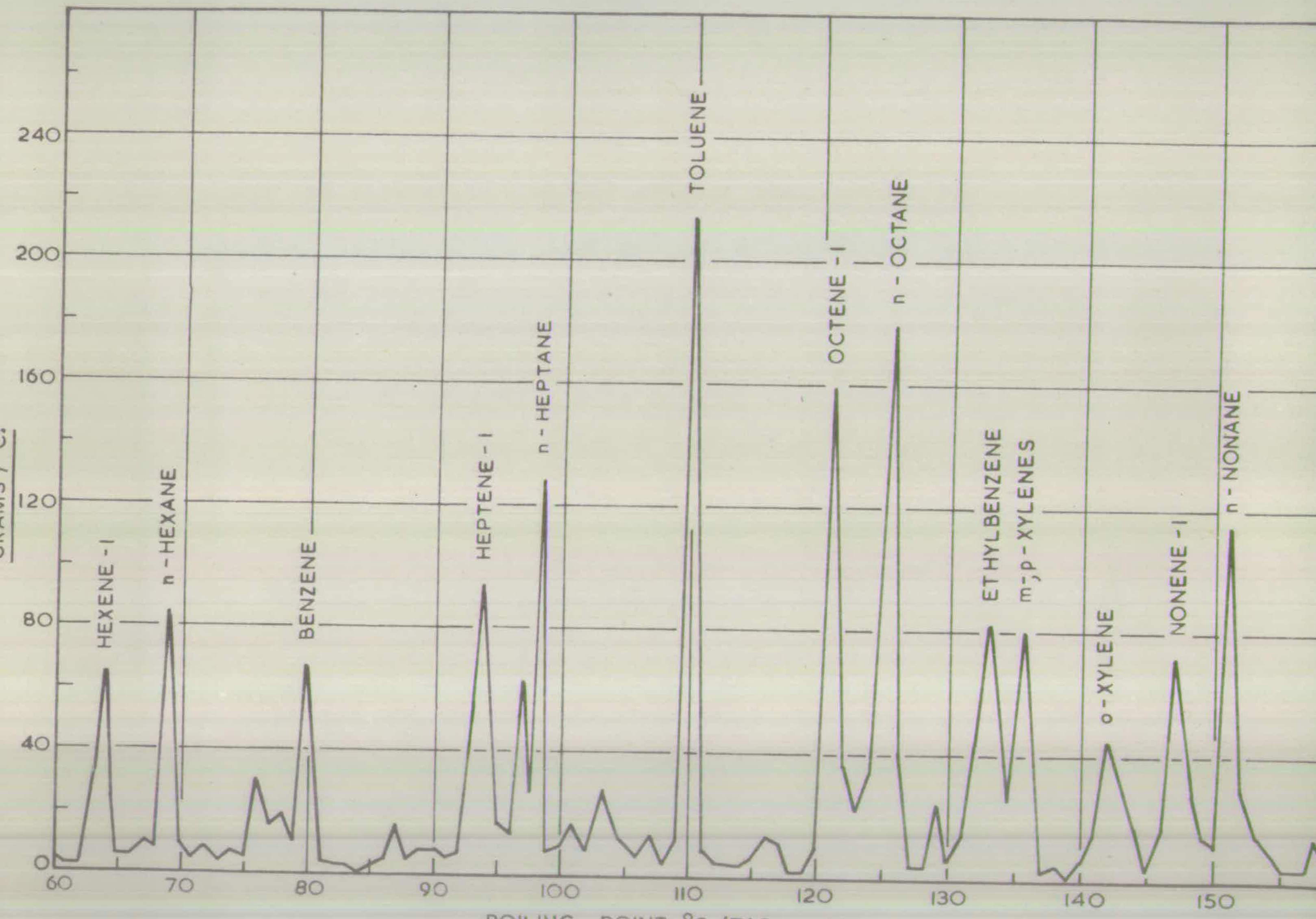
Summary.

The overall weight balances and boiling ranges of charges and overheads for the seven distillations are summarized in Table 15.

Although the overall boiling ranges of distillates from D-2, -3, -4 and D-7 showed a considerable temperature overlap (up to about 17°C.), the material causing the overlaps seldom exceeded 2% of the original charge, and the main body of each distillation curve showed a satisfactory continuation of the preceding curve. The presence in B-fractions of light ends giving rise to these

FIGURE 35 b.

OVERALL YIELDS OF D-DISTILLATIONS.



overlaps was primarily due to inefficient fractioation in the 5 gall. batch still.

The four main distillations yielded as overheads 137 close-cut fractions (totalling 2512 gm. or 3359 ml.); the overall boiling range of the distillate being 26.9°-158.5°C. The overall yields of the distillations are shown in fig. 35b., where the compounds giving rise to the major peaks have also been given (their identification being discussed in the subsequent section).

Material lost during the whole series of distillations amounted to 162 gm. The losses were considered to be due partly to leaks through joints and static hold-up of column, while the fact that losses were heaviest during distillations of low-boiling material indicated that evaporation of distillate was the principal cause of loss.

The weights and volumes of all fractions collected are listed along with the properties of D-fractions in Appendix I. It will be noticed that alternate fractions show similarity in volume; this being due to unequal positioning of pins on disc B (operating the receiver-changer) so that one fraction consisted of 50 while the other consisted of 54 bucket tips. The gradual increase in volume of fractions was assumed to be due to an increase in surface tension of the liquid distilled, resulting in larger quantities being delivered by the bucket. This assumption was confirmed by the fact that during distillation of material of constant boiling point, and hence relatively constant composition, the volume of fractions taken-off showed little variation.

The decrease in operating reflux ratio during a distillation, caused by the increase in fraction volume, was calculated to be about ± 5% of the average value, and was not considered to have a serious effect on the fractionating efficiency of the column.

The determination of properties and composition of fractions from distillations D-2, -3, -4 and D-7, and the examination of their hydrocarbon constituents are dealt with in the following section.

EXAMINATION OF CONSTITUENTS OF D-FRACTIONS AND EVALUATION OF COMPOSITION OF CANNEL NAPHTHA.

The examination of the cannel naphtha distillate (D-fractions) with respect to its composition was principally based on the following operations:-

a. Physical constants of all D-fractions were determined.

b. Selected D-fractions were analyzed by silica gel adsorptions. This comprised:-

   (i) separation of fractions into individual hydrocarbons or hydrocarbon-types,

   (ii) determination of properties of separated hydrocarbons,

   (iii) evaluation of composition of fractions analyzed on SiO_2, and hence calculation of relative amounts of components in each fraction,

   (iv) preliminary identification, on basis of determined properties, of separated components of fractions.

c. The results of adsorption analyses were graphed and the composition of non-analyzed fractions estimated by interpolation.

d. The calculated amounts of hydrocarbons present were summed and hydrocarbon-type composition of total material distilled evaluated, results being expressed in percent by weight and volume on total distillate and original dry crude oil.

e. Major constituents of D-fractions were identified by measurement of physical constants and by ultra-violet spectra.

f. The chemical composition of the cannel naphtha was evaluated.

Determination of physical properties.

The properties of D-fractions and all other material were determined throughout the course of the present work by the following standard methods:-

boiling point - read-off the Kent recorder chart, converted to temperature at 760 mm. Hg and/or determined by distillation in a 10 ml. flask equipped with a 4" x ½" Vigreux column,

density - measured at 20°C. (water thermostat) by means of Perkin's pycnometers of 1 or 2 ml. capacity (restandardized before each set of determinations),

refractive index - measured for the sodium D-line at 20°C. by means of an Abbe refractometer,

bromine number - determined by the McIlhiney method (I.P. - 9/42),

specific dispersion - measured by Grosse and Wackher's methods (43) and calculated from charts supplied by

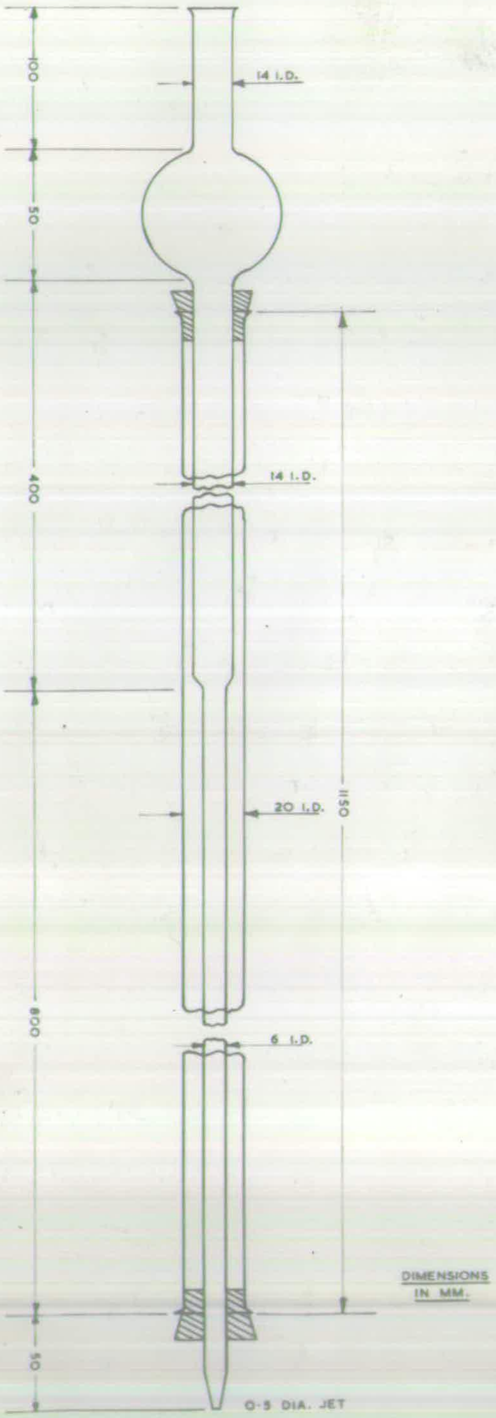


FIGURE 36.

APPARATUS USED FOR

SILICA GEL ADSORPTIONS.

makers of refractometer. Correction for olefins was made as proposed by Groennings (42).

The properties of D-fractions are listed in Appendix I.

Adsorption analyses.

The analyses of D-fractions were performed by means of selective adsorptions on silica gel, using the experimental procedure as proposed by Mair (68) and Dinneen et al. (25), with such modifications as to permit analyses of 5 ml. samples.

General procedure and testing of method.

The apparatus used in all experiments is shown in fig. 36. All tests and analyses were carried out in exactly the same manner, the procedure being as follows:- a few grains of coarse silica gel (ca. 0.5 mm.) were introduced into the tip of a dry column to act as support for the packing and prevent clogging of finer gel in the capillary. Approximately 50 gm. of fine silica gel were poured into the column and the column packed by tapping gently throughout its length with a rubber-covered glass rod until the level of the gel showed no further downward movement. The column was then clamped to a framework and water circulated through the outer jacket for 5-10 mins. before the introduction of sample. The sample to be analyzed was introduced by means of a pipette and nitrogen pressure of 2 p.s.i. applied until the sample had fully entered the gel. 5 - 7 gm. of fresh gel were then added, followed by 50 ml. of ethanol (commercial grade), and nitrogen pressure of 9-10 p.s.i. applied and maintained throughout the duration of analysis. The liquid issuing from the tip of the column was collected in fractions of 4 - 8 drops each (sub-fractions) depending on the volume of the original sample. Between 45 and 55 sub-fractions were taken and their refractive indices at 20°C. determined.

On completion of an analysis the silica gel was washed out from the column by a fine jet of water, the empty column being washed with water and acetone and dried. In the majority of analyses the gel was not recovered. If, however, it was to be re-used, the gel was thoroughly washed with acetone and ethanol, dried and reactivated by heating for 8 - 12 hrs. at 200°C. in a gas-heated oven. Similarly, fresh gel of the required particle size was heated at 200°C. for 12-15 hrs. and stored, ready for use, in a vacuum desiccator.

Assuming the drop size of liquid issuing from the column to remain constant, the volume of each sub-fraction was calculated and the volume sum of the sub-fractions plotted against their refractive indices. The volume and hence, volume percent of the separated hydrocarbons (viz. paraffins and naphthenes, olefins, and aromatics) were then determined from the adsorptogram by assuming a 100% recovery of the sample taken for analysis, and measuring the amount of material on each n_D plateau. The transition between the three groups of hydrocarbons separated was considered to take place between fractions showing the greatest difference in refractive indices.

Prior to application to the examination of cannel naphtha distillates, the method was tested with known hydrocarbon mixtures with a view to determining the efficiency of separation and investigating the conditions under which most satisfactory separations may be accomplished.

As already pointed out, no separation takes place between paraffins and naphthenes, while separations between saturated, unsaturated and aromatic hydrocarbons are usually quantitative, irrespective of the relative proportions of the hydrocarbons present in the sample, provided the silica gel is of the requisite size. It was found that gel of the following particle size:- 100% passing 100 mesh B.S.S., 30% passing 200 mesh, (lot no. 1) greatly retarded an analysis (up to 6 hrs.) and did not improve separations, while gel containing material of which 90% passed 80 mesh, 50% 100 mesh and 1% 200 mesh (lot no. 2) gave very poor and irreproducible analyses. After several tests, it was found that gel of the following particle size distribution produced quantitative separations and at the same time allowed analyses to be completed within 1-2 hrs., depending on size of sample.

Silica gel (lot no. 3 and 4) particle size distribution:-

through 100 mesh B.S.S.		100%
120	"	50 - 60%
150	"	20 - 30%
200	"	13 - 16%

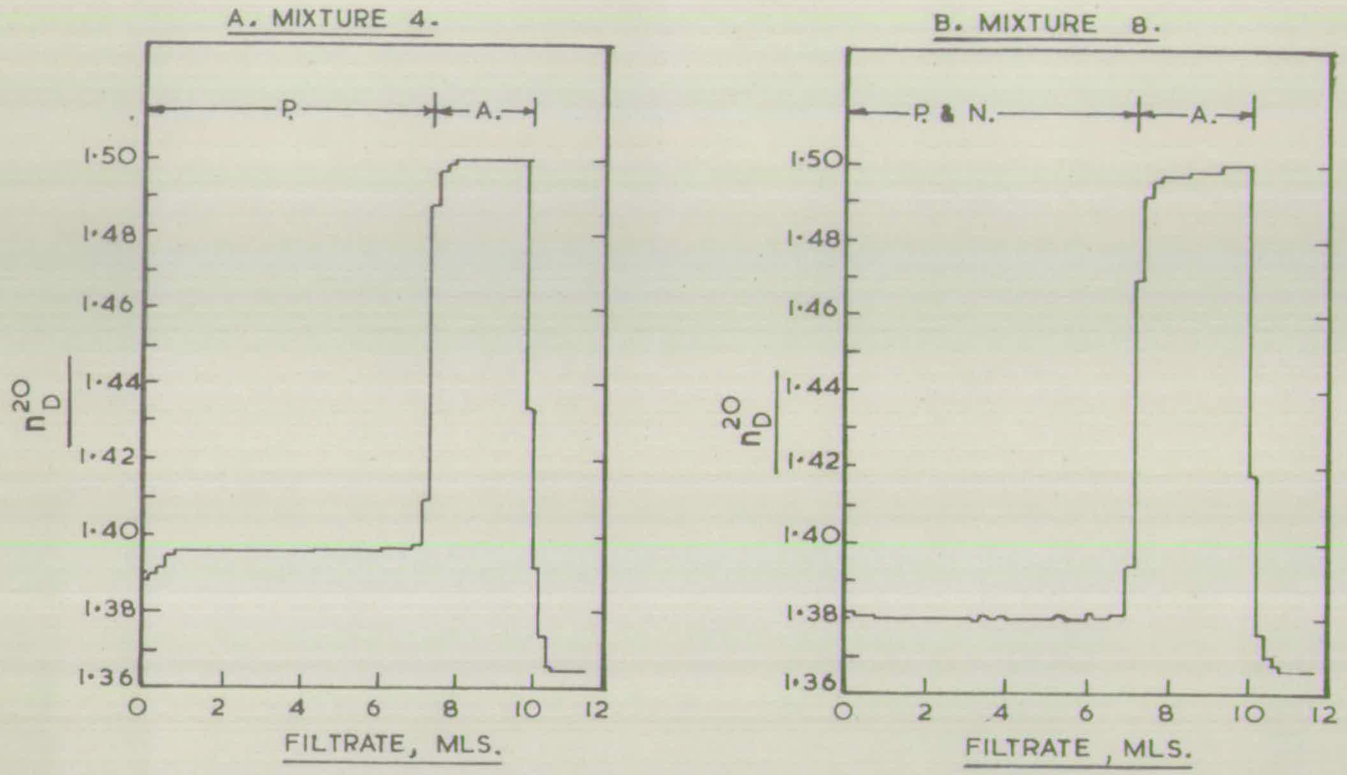
(Initially "Silica gel for chromatographic adsorption" supplied by The British Drug Houses Ltd. was used (lot no. 3). The gel as received required further size reduction, followed by sieving to give the necessary particle size distribution. More recently, however, a finer and higher grade of gel was obtained from Messrs. Silica Gel Ltd. (100-200 mesh grade). This gel (lot no. 4) contained only a small proportion of coarse material, otherwise the particle size being as required.)

In the early experiments, 10 ml. samples of hydrocarbons were analyzed on 50 gm. of gel and it was found that, while satisfactory separations of relatively simple mixtures of hydrocarbons were obtained under these conditions, separations of more complex mixtures could be considerably improved by either increasing the amount of gel used (to 70-80 gm.) or decreasing the sample volume. The latter was preferred, as the duration of an analysis was thus decreased and material requirements, both of gel and sample, were smaller.

External cooling of the gel was necessary to dissipate the heat of adsorption and experiments were carried out in which the effect of cooling

FIGURE 37.

RESULTS OF SiO_2 ADSORPTIONS OF KNOWN MIXTURES.



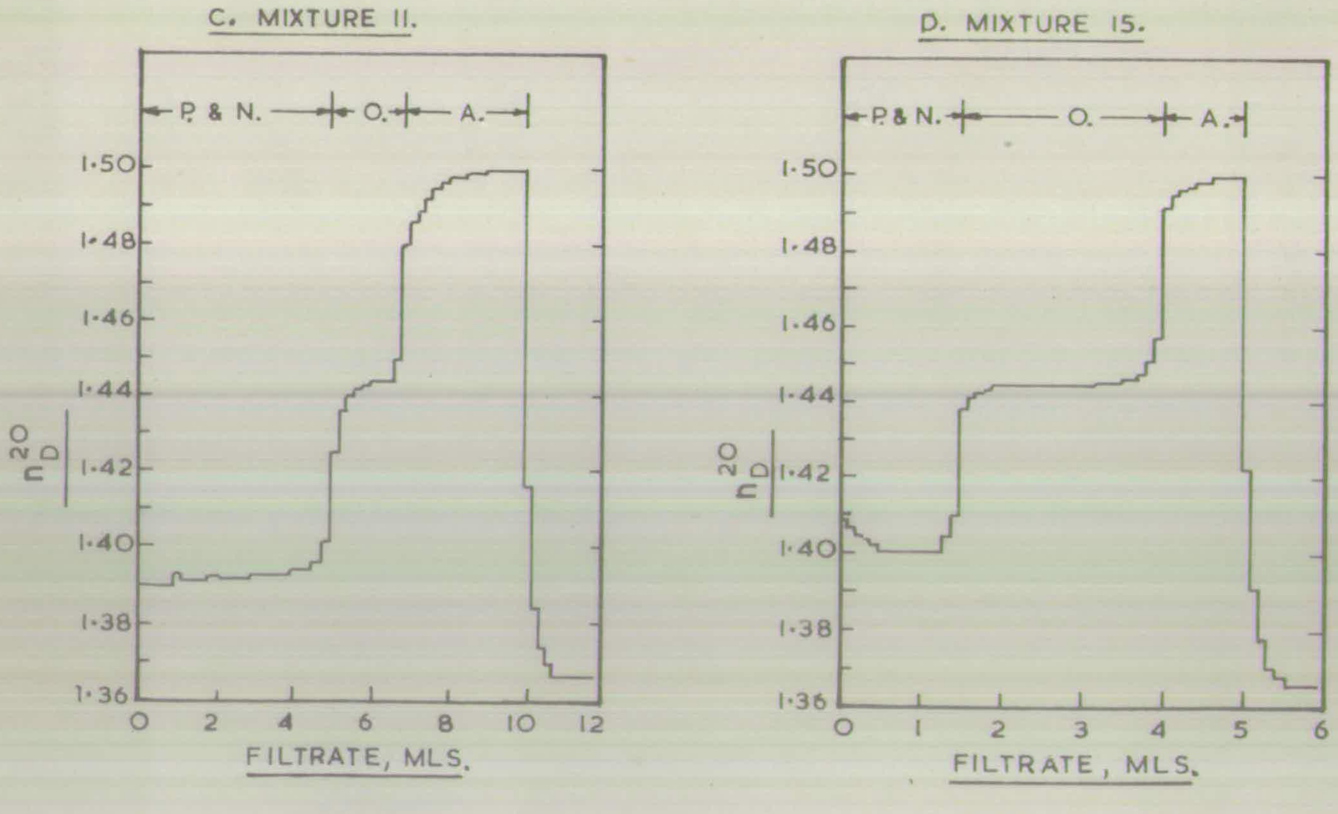


TABLE 16.

Results of Silica gel adsorption tests.

No.	Mixture analyzed	Composition, %			Recovery, %			Silica gel lot no.	Jacket water temp., °C.	Sample vol., ml.
		P.& N.	O.	A.	P.& N.	O.	A.			
1	Paraffin-aromatic	75	-	25	66	-	34	1	14	10
2	Paraffin-aromatic	75	-	25	78	-	22	2	15	10
3	Paraffin-olefin-aromatic	40	30	30	32	36	32	2	7	10
4*	Paraffin-aromatic	75	-	25	75	-	25	3	15	10
5	Paraffin-aromatic	25	-	75	24	-	76	3	10	10
6	Paraffin-naphthene	50:50	-	-	100	-	-	3	15	10
7	Paraffin-olefin	50	50	-	50	50	-	3	16	10
8*	Paraffin-naphthene-aromatic	72	-	28	71	-	29	3	6	10
9	Paraffin-naphthene-aromatic	77	-	23	76	-	24	3	14	10
10	Paraffin-naphthene-olefin-aromatic	25	50	25	24	51	25	3	15	10
11*	Paraffin-naphthene-olefin-aromatic	46	19	35	45	17	38	3	16	10
12	Paraffin-naphthene-olefin-aromatic	50	25	25	51	24	25	3	16	5
13	Paraffin-naphthene-olefin-aromatic	62	17	21	61	18	21	3	17	5
14	Paraffin-naphthene-olefin-aromatic	50	25	25	51	25	24	4	15	5
15*	Paraffin-naphthene-olefin-aromatic	30	50	20	29	50	21	4	15	5

water temperature on efficiency of separation was studied. The results obtained indicated that separations were not improved by circulating water of temperature below 10°C., unless the material analyzed boiled below 60°C., while increase in temperature beyond 20°C. or complete lack of cooling tended to give poor separations. Consequently, in all analyses, the gel was cooled by water at 12°-16°C.

The results of some of the tests are summarized in Table 16, of which tests no. 4, 8, 11 and 15 (marked thus *) are shown graphically in fig. 37.

The results of these tests indicate that satisfactory separations between saturated, unsaturated and aromatic hydrocarbons may be obtained, provided the adsorbent is of the right particle size, is tightly packed in the column, and cooled during percolation.

The maximum error involved in the analyses was considered not to exceed ± 3%. Results given in Table 16 show that the error was actually smaller when the method was applied to synthetic mixtures, but would probably increase to the above value in analyses of more complex mixtures, a fact which has been frequently pointed out by previous workers.

Analysis of D-fractions.

The initial selection of D-fractions for analysis on silica gel was based on the extent of variation in properties of adjacent fractions. Thus, fractions showing a marked difference in properties, and consequently in composition, as compared with their immediate neighbours, were selected for analysis, whereas only every second fraction was analyzed from those series of fractions which showed distinctive similarity in properties and distilled at a constant temperature.

The separation of selected fractions into their individual components or hydrocarbon-types was performed by silica gel adsorptions of 5 ml. samples, using the procedure and under conditions already discussed. Between 44 and 56 sub-fractions of 4-5 drops of filtrate each were collected in an analysis and their refractive indices determined and plotted against volume sum of the sub-fractions. The composition of the analyzed fraction was then determined from the adsorptogram by making the assumptions mentioned, and expressed in percent by volume. The result of the analysis was confirmed by bulking all sub-fractions showing least difference in refractive indices, to give E-fractions, and determining their refractive indices, bromine numbers, and densities if sufficient material was available. This may be illustrated as follows:-

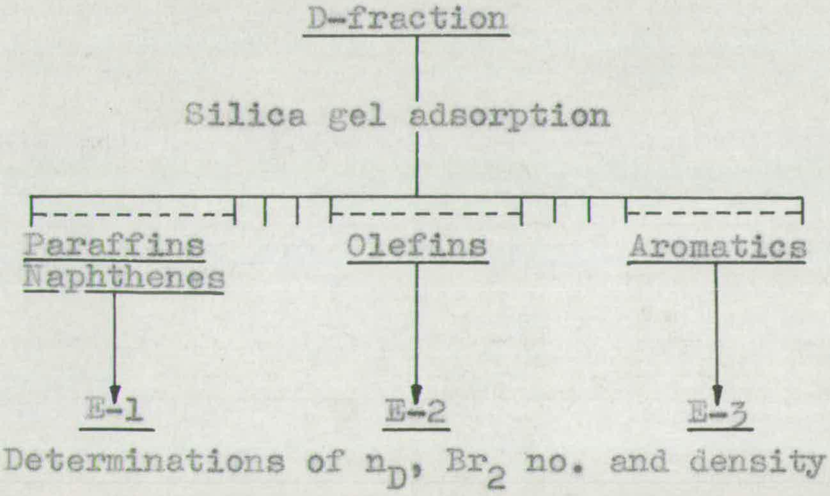


FIGURE 38. ANALYSIS OF FRACTION D-3/11.

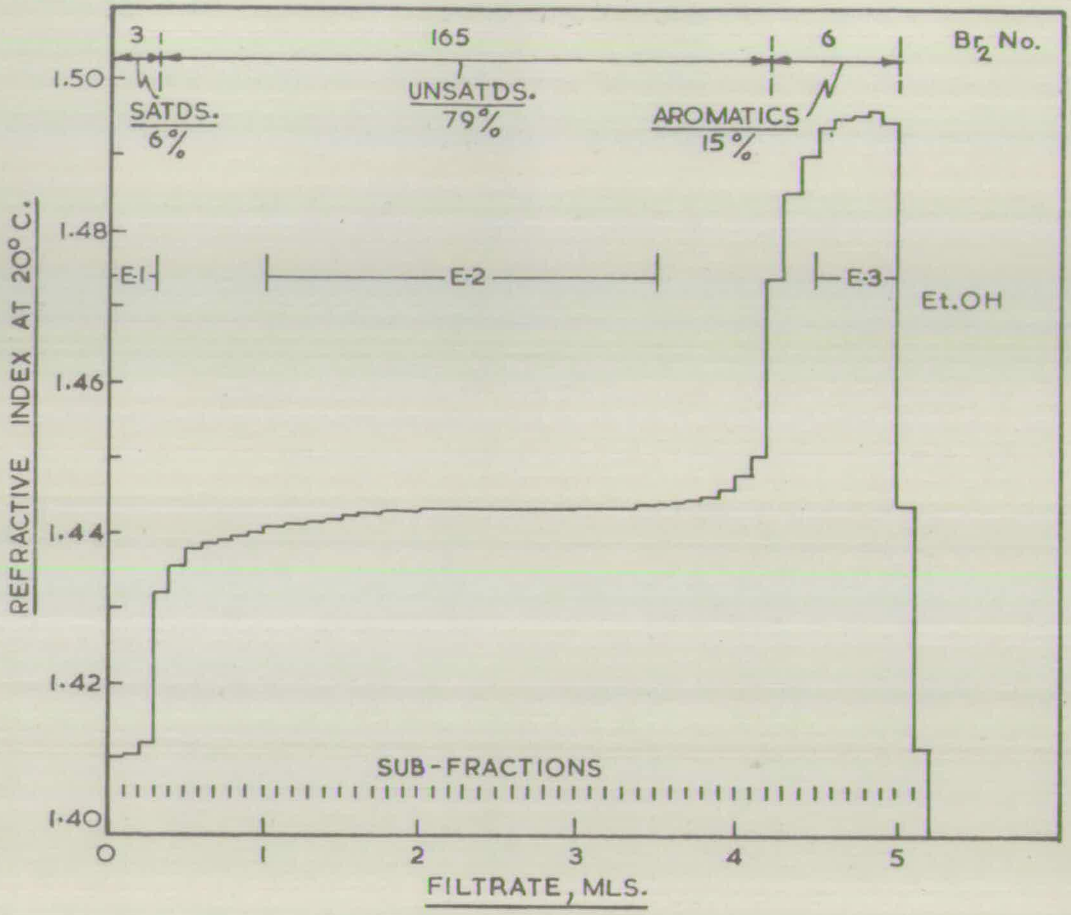
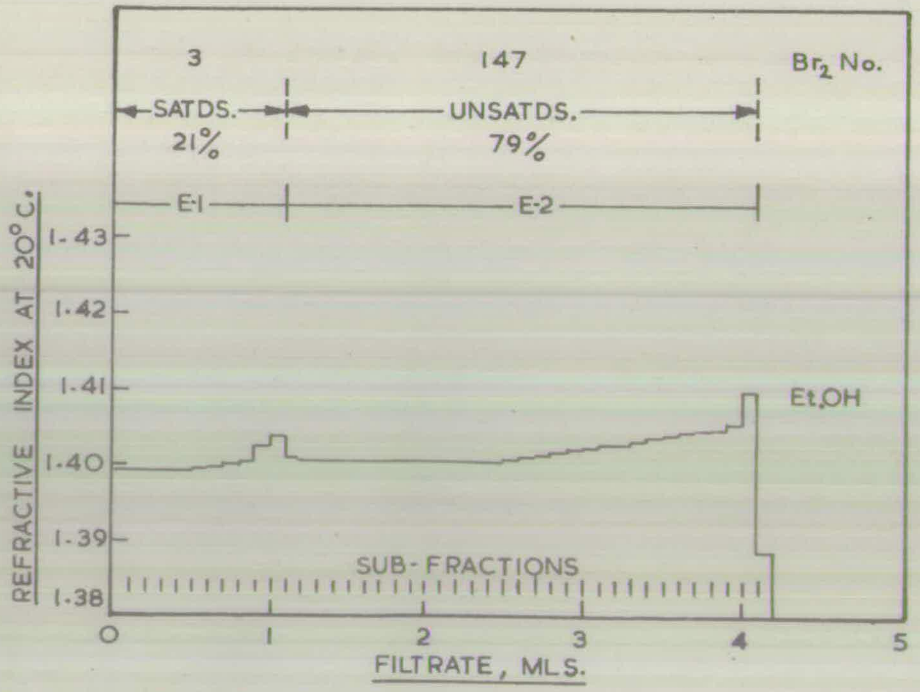


FIGURE 39. ANALYSIS OF FRACTION D-2/33.



For instance, analysis of fraction D-3/11 gave the adsorptogram shown in fig. 38 from which it was assumed that sub-fractions 1 to 3, 4 to 42 and 43 to 50 consisted of saturated, unsaturated and aromatic hydrocarbons, respectively. Sub-fractions 1 to 3, 10 to 35 and 45 to 50 were bulked to give E-1, E-2 and E-3, which were further examined, giving:-

	n_D^{20}	Br_2 No.	d_4^{20}
E-1	1.4114	3	-
E-2	1.4428	165	0.799
E-3	1.4943	6	-

These results indicate that the initial assumption regarding the composition of the fraction was correct, and the composition was calculated to be:-

Saturateds	6% vol.
Unsaturateds	79%
Aromatics	15%

In the above example, the nature of the three classes of hydrocarbons present enabled a very distinct break to be produced between them, with the result that the composition of the fraction could be estimated without the knowledge of the properties of E-fractions. Occasionally, however, the similarity of refractive indices of two hydrocarbon classes necessitated the examination of E-fractions before the composition could be estimated with any degree of certainty. For example, in the case of fraction D-2/33 (fig. 39), the transition between saturated and unsaturated hydrocarbons was suspected to take place after sub-fraction 11. Therefore, sub-fractions 1 to 11 and 12 to 41 were bulked to give E-1 and E-2, respectively, the bromine numbers of which were found to be 3 for E-1 and 147 for E-2, the composition of the fraction being therefore:-

Saturateds	21% vol.
Unsaturateds	79%

The knowledge of the composition, volume and weight of the selected D-fractions permitted the evaluation of the actual volumes and, if density of E-fractions was known, of the weight of constituents of each fraction. In cases where a D-fraction was found to contain two constituents, the density and, hence, weight of one of which was known, the weight of the other constituent was obtained by difference. In all other cases the densities of the constituents were estimated on consideration of the properties and suspected nature of the particular constituents, as discussed below.

The determination of bromine numbers, refractive indices and densities of E-fractions not only served to establish finally the composition of a given fraction, but also afforded a very valuable clue as to the identity of the hydrocarbons present in a D-fraction. Thus, the properties of E-fractions from D-3/11 (p.132) together with the knowledge of the general properties of the D-fraction, and its boiling point in particular, indicated the presence of ethylcyclopentenes in the unsaturated and toluene in the aromatic portions of the fraction; the latter distilling over as an azeotrope. The boiling range of the D-3/11 and the low refractive index of its saturated constituents (ca. 1.411) pointed to the presence of C_8 paraffins, but owing to their low concentration, no further conclusions regarding their nature could be drawn. Occasionally, it was possible, however, to obtain more conclusive evidence of the nature of such components by consideration of general properties and results of adsorption analyses of adjacent fractions.

The nature of the separated constituents of all analyzed D-fractions was estimated in a similar manner. The properties of D-fractions and their boiling characteristics, together with information obtained from adsorption analyses and examination of E-fractions, provided sufficient data to enable a preliminary identification of the major constituents to be made, and, at the same time, to give an indication of the nature of the minor constituents. An additional clue to the composition of a fraction was provided from the actual shape of adsorptograms. It was found that a near-perfect plateau was, without exception, indicative of one compound only, while small variations in refractive index were usually due to two or more hydrocarbons of the same class; this being particularly so in the case of olefins. In such instances, the n_D range plus any other determined properties were considered and compared with published data and with series of charts and tables listing the various properties against boiling point, molecular configuration etc. For example, fraction D-7/7 consisted of 40% unsaturateds and 60% o-xylene. The properties of the former, viz. bromine number of 124, n_D range 1.4208-1.4252 and boiling point of 141°-142°C. pointed to a mixture of branched nonenes, distilling as an azeotrope with o-xylene, an approximate density of 0.74 being assumed for the former. A calculation based on the weights and volumes of the fraction and its aromatic component gave a value for density as 0.743, which agreed well with the assumed value and indicated the correctness of the assumption regarding the nature of the hydrocarbons.

In all cases, where the evidence obtained was not sufficiently conclusive to identify constituent hydrocarbons, the differentiation between various classes of compounds and the estimation of their nature were based on the characteristic ranges of variation of properties of a particular class of hydrocarbons with boiling point and their molecular or skeletal structure (as referred to on p. 42 et seq.). The knowledge of specific dispersion, refractivity intercept and specific refraction frequently facilitated such estimations, especially when separations were poor owing to large numbers of compounds present and wide boiling ranges of D-fractions.

The examinations of saturated and aromatic

FIGURE 40. COMPOSITION OF D-2 FRACTIONS.

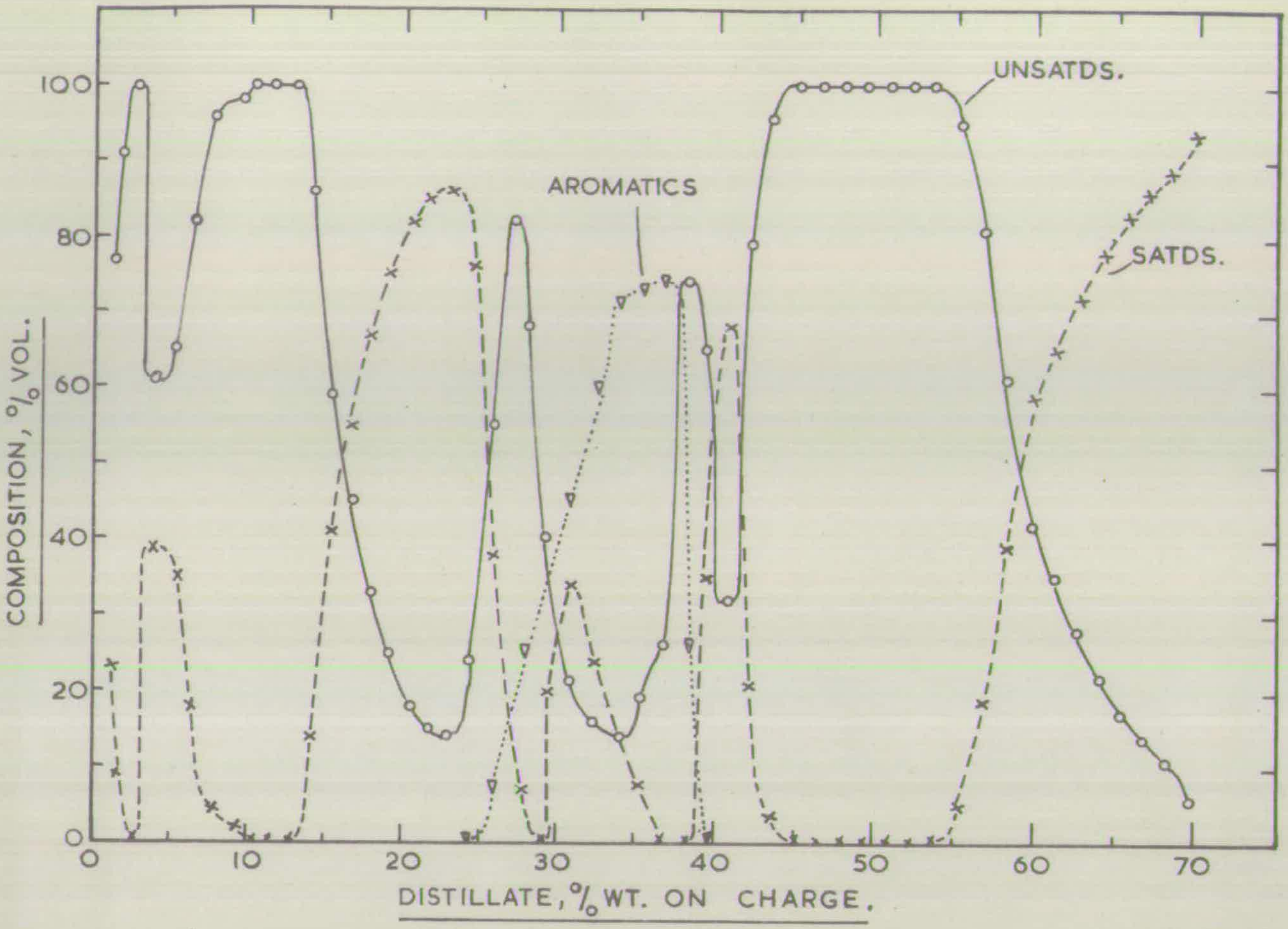


FIGURE 41. COMPOSITION OF D-3 FRACTIONS.

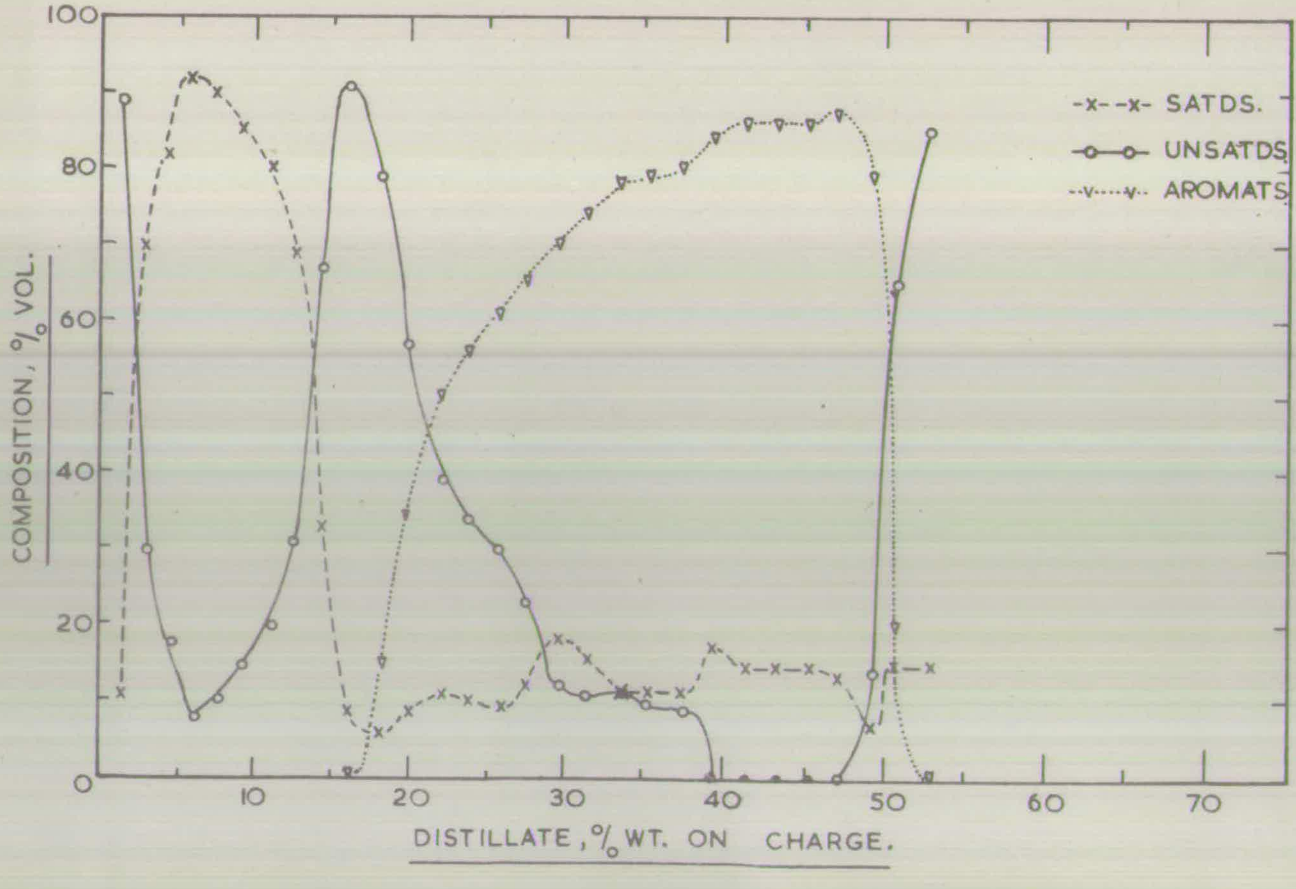


FIGURE 42. COMPOSITION OF D-4 FRACTIONS.

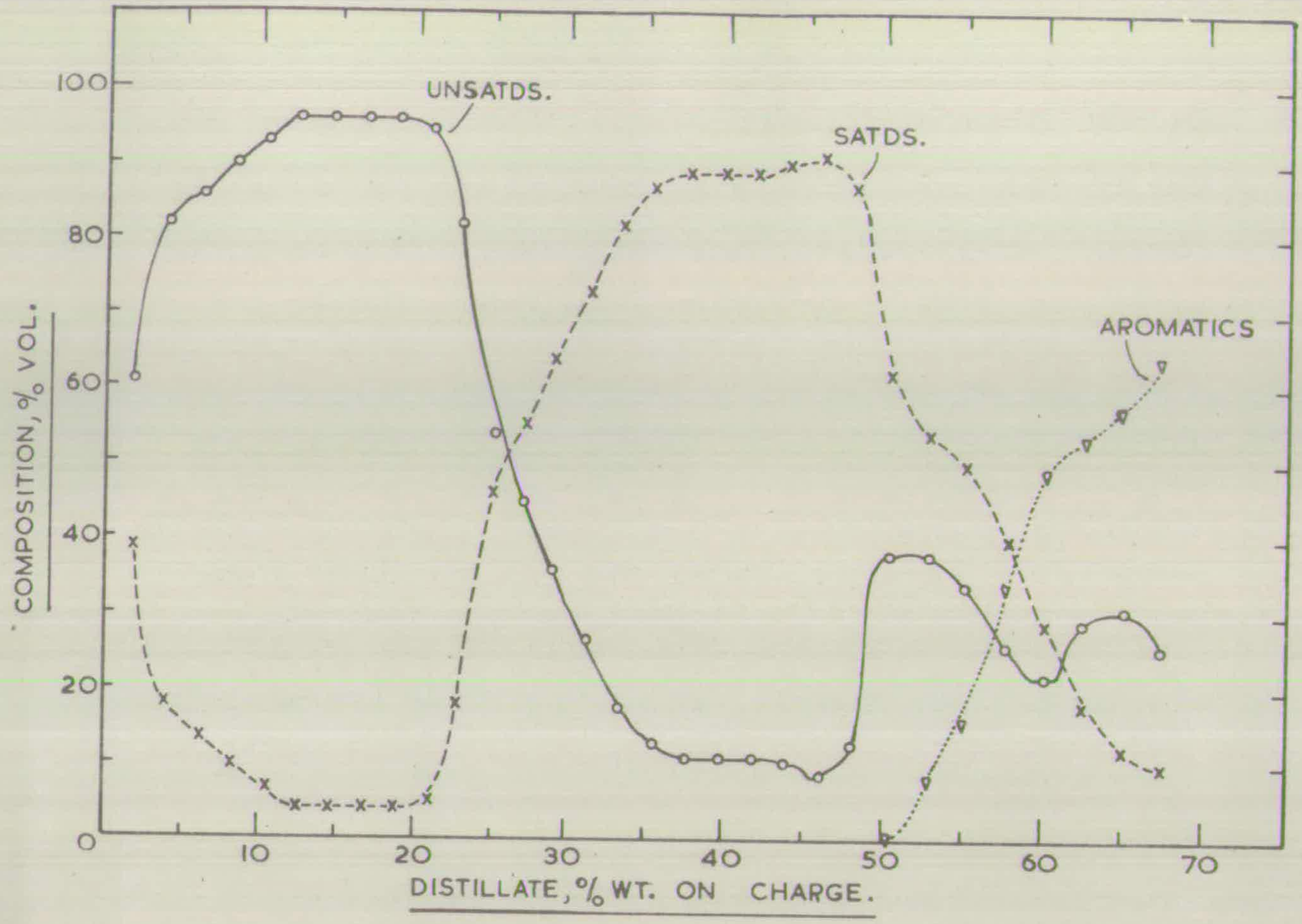
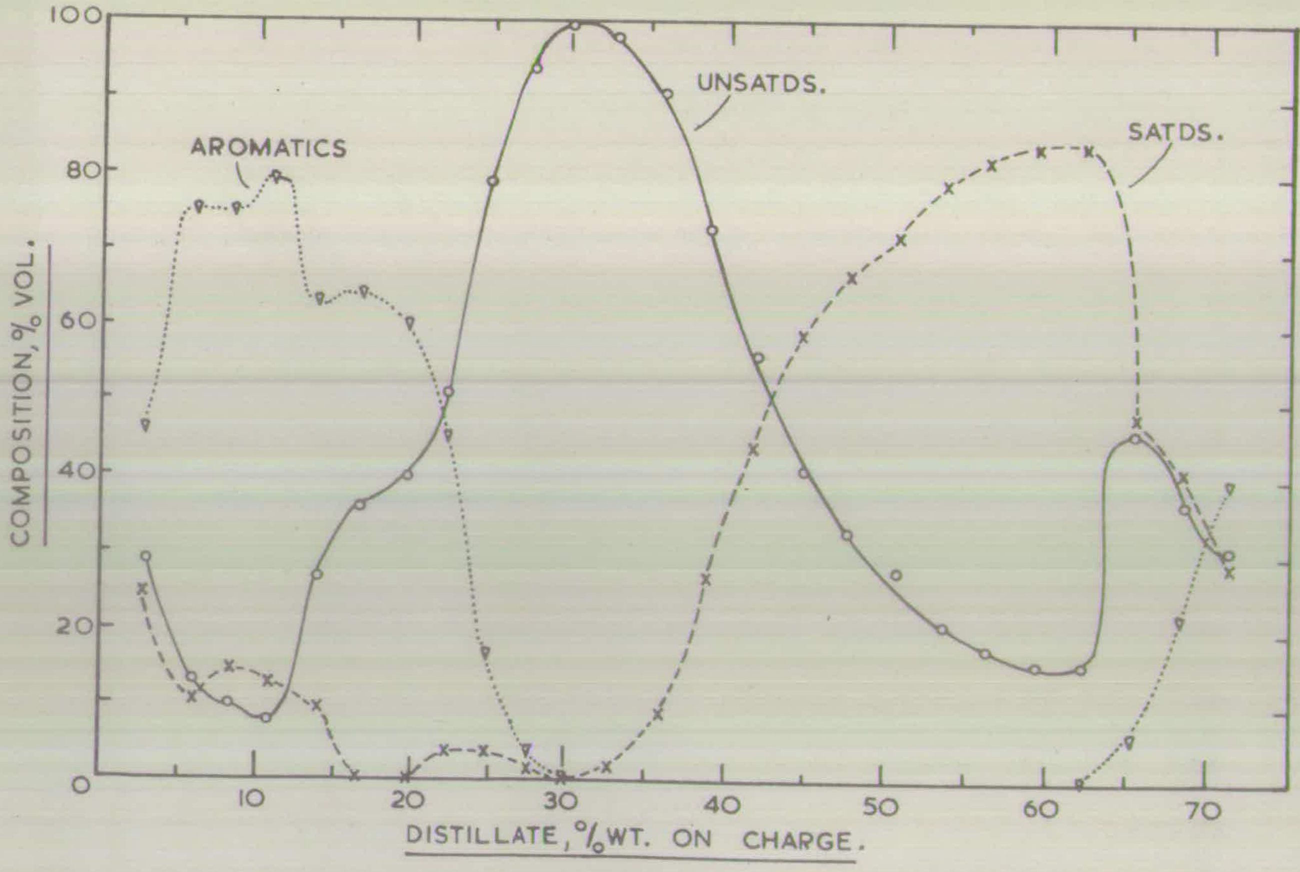


FIGURE 43. COMPOSITION OF D-7 FRACTIONS.



hydrocarbons were relatively straight-forward since physical properties of these compounds, boiling within the range examined, have all been determined and the numbers of possible isomers are not excessively large. The problem, however, became very complex in the case of unsaturated hydrocarbons boiling above 120°C. because of the rapidly increasing number of possible isomers and the almost complete lack of physical data on these compounds, with the result that bromine number and boiling range were, in some instances, the only clues leading to the nature of the compound, which, in these circumstances, could only be expressed in terms of the number of carbon atoms in the molecule.

(The physical and other properties of hydrocarbons were taken from the following sources:- A.P.I. Tables (2), Eaton (27), Forziati and Rossini (33), Huntress (48), Kurtz and Ward (56), Timmermans (93) and Beilstein's "Handbuch").

The results of all adsorption analyses of D-fractions, together with the determined properties of E-fractions, on consideration of which estimates regarding the nature and quantities of constituent hydrocarbons were made, are listed in Table 17 (pp. 137-146). The composition, in percent by volume, of fractions from each of the four D-distillations was plotted against percent by weight of distillate and the resulting graphs for fractions D-2, -3, -4 and D-7 are shown in figs. 40, 41, 42 and 43, respectively.

TABLE 17.

Results of silica gel analyses of D-fractions.

No.	E-No.	B.pt., °C. at 760mm.	n_D range of E-cut	Br_2 No.	d_4^{20}	Compositn., % vol.			Suspected hydrocarbon
						P+N	O.	A.	
D-2									
1.	1	26.9-	1.3578	1	0.626	23	-	-	n-pentane
	2	-36.6	1.3690-1.3748	225	-	-	77	-	pentene-1
2.	1	-37.2	1.3577	2	.628	9	-	-	n-pentane
3.	1	-43.2	1.4150-1.4183	229	-	-	42	-	Mix. of cyclopentene
	2		1.4254-1.4452	204	-	-	58	-	and pentenes-2 ?
4.	1	-58.1	1.4030	3	-	39	-	-	cyclopentane
	2		1.4100-1.4248	210	-	-	61	-	cyclopentene
5.	1	-62.9	1.3734	2	-	35	-	-	C_6 paraffin
	2		1.3877-1.3915	173	.675	-	65	-	hexene-1
7.	1	63.2- -63.8	1.3878	193	.674	-	96	-	hexene-1
9.	1	63.8- -63.8	1.3879	194	.676	-	100	-	hexene-1
11.	1	63.8-	1.3880-1.3898	196	.677	-	39	-	hexene-1
	2	-64.9	1.3904-1.3970	189	-	-	61	-	branched C_6 olefins
12.	1	-67.1	1.3746	3	-	14	-	-	n-hexane
	2		1.3920-1.3988	178	.676	-	86	-	hexenes-2, -3
13.	1	-68.4	1.3750	1	.659	41	-	-	n-hexane
	2		1.3907-1.3994	179	.680	-	59	-	hexenes-2, ?
15.	1	68.7-	1.3750	0	.659	67	-	-	n-hexane
	2	-68.7	1.3930-1.3983	183	-	-	33	-	hexene-2
17.	1	68.7-	1.3750	1	.660	82	-	-	n-hexane
	2	-68.7	1.3928-1.3978	181	-	-	18	-	hexene-2

Table 17.(contd.)

No.	E. No.	B.pt., °C. at 760mm.	n_D range of E-cut	Br_2 No.	d_4^{20}	Compositn., % vol.,			Suspected hydrocarbon
						P+N.	O.	A.	
D-2									
18.	1	68.7-	1.3748	2	0.660	85	-	-	n-hexane
	2	-68.7	1.3930-1.4020	178	-	-	15	-	hexene-2
19.	1	-70.4	1.3760-1.3788	1	.666	86	-	-	n-hexane + ?
	2		1.3910-1.4068	159	-	-	14	-	me.pentenes
20.	1	-72.2	1.3670-1.3906	2	.682	76	-	-	n-hexane + ?
	2		1.4008-1.4162	181	-	-	24	-	C_6 olefins
21.	1	-75.7	1.4090	2	.745	38	-	-	me.cyclopentane
	2		1.4278-1.4422	190	-	-	55	-	1-me.cyclopentene
	3		1.4785-1.4825	-	-	-	-	7	benzene
22.	1	-75.7	1.4308-1.4408	192	.783	-	82	-	1-me.cyclopentene
	2		1.4824-1.4898	-	-	-	-	18	benzene
23.	1	-76.4	1.4193-1.4240	-	-	7	-	-	C_6 naphthene ?
	2		1.4310-1.4365	187	.785	-	68	-	1-me.cyclopentene
	3		1.4824-1.4928	-	-	-	-	25	benzene
25.	1	77.1-	1.4260-1.4251	4	.777	34	-	-	cyclohexane
	2	-78.6	1.4308-1.4402	192	-	-	21	-	C_6 cyclic olefin ?
	3		1.4996-1.5003	6	-	-	-	45	benzene
27.	1	79.6-	1.3950-1.3990	-	-	14	-	-	C_7 paraffins
	2	-79.6	1.4160-1.4430	115	-	-	14	-	C_6 cyclic olefin ?
	3		1.4980-1.4999	-	.878	-	-	72	benzene
29.	1	79.6-	1.4260-1.4486	177	-	-	26	-	C_6 cyclic olefin ?
	2	-79.6	1.4920-1.5004	-	-	-	-	74	benzene
30.	1	-83.1	1.4407-1.4494	179	.810	-	74	-	cyclohexene
	2		1.4932-1.4996	-	-	-	-	26	benzene
31.	1	-86.6	1.3907-1.3950	5	-	35	-	-	C_7 paraffins
	2		1.3995-1.4030	131	-	-	20	-	C_7 olefins
	3		1.4426-1.4472	190	-	-	45	-	cyclohexene

Table 17.(contd.)

No.	E.-No.	B.pt., °C. at 760mm.	n_D range of E-cut	Br_2 No.	d_4^{20}	Compositn, % vol.			Suspected hydrocarbon
						P+N	O.	A.	
D-2									
32.	1	86.6-	1.3907-1.3928	2	0.696	68	-	-	2:3-dime.pentane
	2	-89.4	1.4010-1.4048	148	-	-	32	-	C_7 olefins
33.	1	-92.2	1.3990-1.4007	3	-	21	-	-	C_7 paraffin
	2		1.4000-1.4076	147	-	-	79	-	C_7 olefins
35.	1	92.8- -92.8	1.4000-1.4020	155	.700	-	100	-	heptene-1
37.	1	93.6- -93.6	1.4000-1.4009	161	.698	-	100	-	heptene-1
38.	1	-93.6	1.3998-1.4006	163	.697	-	100	-	heptene-1
39.	1	-93.6	1.3998-1.4009	164	.698	-	100	-	heptene-1
41.	1	93.6- -93.9	1.3999-1.4016	166	.698	-	100	-	heptene-1
43.	1	95.0-	1.3878	3	-	19	-	-	n-heptane ?
	2	-95.9	1.4000-1.4190	156	-	-	81	-	C_7 olefins
45.	1	96.9-	1.3878	2	.684	58	-	-	n-heptane
	2	-96.9	1.4022-1.4180	158	-	-	42	-	C_7 olefins
47.	1	97.5-	1.3877-1.3879	0	.684	72	-	-	n-heptane
	2	-97.8	1.4050-1.4171	156	-	-	28	-	C_7 olefins
49.	1	98.4-	1.3876-1.3880	0	.683	83	-	-	n-heptane
	2	-98.4	1.4020-1.4171	191	-	-	17	-	C_7 olefins
51.	1	98.4-	1.3878	1	.684	89	-	-	n-heptane
	2	-98.4	1.4030-1.4167	148	-	-	11	-	C_7 olefins
52.	1	-98.4	1.3877	2	.683	94	-	-	n-heptane
	2		1.4068-1.4103	97	-	-	6	-	C_7 olefins

Table 17.(contd.)

No.	E. No.	B.pt., °C. at 760mm.	n_D range of E-cut	Br_2 No.	d_4^{20}	Compositn., % vol.			Suspected hydrocarbons
						P+N.	O.	A.	
<u>D-3</u>									
1.	1	89.3-	1.3887-1.3904	1	-	11	-	-	n-heptane ?
	2	-96.4	1.3980-1.4063	153	0.698	-	89	-	C_7 olefins
2.	1	-98.4	1.3877-1.3879	3	.684	70	-	-	n-heptane
	2		1.3980-1.4180	154	-	-	30	-	C_7 olefins
3.	1	-98.4	1.3875-1.3881	3	.684	82	-	-	n-heptane
	2		1.3997-1.4193	162	-	-	18	-	C_7 olefins
4.	1	-98.4	1.3877-1.3880	2	.684	92	-	-	n-heptane
	2		1.3962-1.4162	161	-	-	8	-	C_7 olefins
5.	1	98.4-	1.3877-1.3968	2	.691	90	-	-	n-heptane + ?
	2	-98.4	1.4046-1.4200	137	-	-	10	-	C_7 olefins
7.	1	101.1-	1.4203-1.4211	2	.764	80	-	-	me.cyclohexane + ?
	2	-102.3	1.4368-1.4471	168	-	-	20	-	et.cyclopentene ?
8.	1	102.3- -103.3	1.4230-1.4241	2	.769	69	-	-	me.cyclohexane
9.	1	-104.8	1.4196-1.4200	6	.764	33	-	-	me.cyclohexane + ?
	2		1.4337-1.4448	167	.794	-	67	-	et.cyclopentene
10.	1	-106.8	1.4161-1.4205	-	-	9	-	-	C_8 paraffins ?
	2		1.4418-1.4462	161	.796	-	91	-	et.cyclopentene
11.	1	-108.6	1.4096-1.4144	3	-	6	-	-	C_8 paraffins ?
	2		1.4408-1.4443	165	.799	-	79	-	et.cyclopentene
	3		1.4878-1.4946	6	-	-	-	15	toluene
13.	1	109.8-	1.4128-1.4232	-	-	11	-	-	C_8 paraffins ?
	2	-109.8	1.4410-1.4516	156	-	-	39	-	et.cyclopentene
	3		1.4881-1.4958	-	-	-	-	50	toluene
15.	1	109.8-	1.4037-1.4084	-	-	9	-	-	C_8 paraffins
	2	-109.8	1.4400-1.4523	158	-	-	30	-	et.cyclopentene
	3		1.4906-1.4960	5	-	-	-	61	toluene

Table 17.(contd.)

No.	E. No.	B.pt., °C. at 760mm.	n_D range of E-cut	Br_2 No.	d_4^{20}	Compositn., % vol.			Suspected hydrocarbon
						P.+N.	O.	A.	
D-3									
17.	1	109.8-	1.3970-1.4012	3	-	18	-	-	dime.hexanes
	2	-109.8	1.4418-1.4530	148	-	-	12	-	et.cyclopentene ?
	3		1.4870-1.4963	16	0.866	-	-	70	toluene
19.	1	110.1-	1.3959-1.3978	11	.704	11	-	-	dime.hexanes
	2	-110.1	1.4148-1.4370	-	-	-	11	-	C_8 olefins
	3		1.4910-1.4968	-	-	-	-	78	toluene
21.	1	110.1-	1.3959-1.3966	8	-	11	-	-	dime.hexanes
	2	-110.4	1.4070-1.4298	-	-	-	9	-	C_8 olefins
	3		1.4916-1.4965	-	.866	-	-	80	toluene
22.	1	-110.4	1.3950-1.3977	5	-	17	-	-	dime.hexanes
	2		1.4913-1.4960	7	.866	-	-	83	toluene
23.	1	-110.4	1.3978-1.3993	4	-	14	-	-	dime.hexanes
	2		1.4906-1.4986	9	-	-	-	86	toluene
25.	1	110.4-	1.3987-1.4030	5	-	14	-	-	dime.hexanes
	2	-110.4	1.4912-1.4970	10	-	-	-	86	toluene
26.	1	-110.4	1.3982-1.4020	6	-	13	-	-	dime.hexanes ?
	2		1.4908-1.4980	12	.867	-	-	87	toluene
27.	1	-110.9	1.4038-1.4087	5	-	7	-	-	trime.pentanes ?
	2		1.4172-1.4296	131	-	-	14	-	C_8 olefins
	3		1.4920-1.4978	6	-	-	-	79	toluene
28.	1	-114.9	1.4165-1.4208	11	-	15	-	-	trime.pentanes
	2		1.4250-1.4370	138	.720	-	65	-	C_8 olefins
	3		1.4824-1.4925	-	-	-	-	20	toluene
29.	1	-117.3	1.4176-1.4204	6	-	15	-	-	trime.pentanes ?
	2		1.4170-1.4341	136	-	-	85	-	C_8 olefins

Table 17.(contd.)

No.	E. No.	B.pt., °C. at 760mm.	n_D range of E-cut	Br_2 No.	d_4^{20}	Compositn., % vol.			Suspected hydrocarbon
						P.+N.	O.	A.	
D-4									
1.	1	100.9-	1.4048-1.4098	4	-	39	-	-	C_8 paraffins
	2	-120.4	1.4113-1.4365	132	0.726	-	61	-	C_8 olefins
2.	1	-120.7	1.4205-1.4140	4	-	18	-	-	C_8 naphthenes ?
	2		1.4110-1.4126	134	.725	-	52	-	octene-1 ?
	3		1.4130-1.4183	147	-	-	30	-	C_8 olefins
4.	1	120.9-	1.4177-1.4100	-	-	10	-	-	C_8 paraffins
	2	-120.9	1.4093-1.4098	141	.719	-	90	-	octene-1
6.	1	120.9-	1.4161-1.4115	-	-	4	-	-	C_8 paraffins
	2	-120.9	1.4091-1.4098	142	.718	-	96	-	octene-1
8.	1	120.9-	1.4150-1.4100	-	-	4	-	-	C_8 paraffins
	2	-120.9	1.4091-1.4099	143	.716	-	96	-	octene-1
10.	1	120.9-	1.4035-1.4084	-	-	5	-	-	C_8 paraffins
	2	-121.6	1.4093-1.4144	135	.721	-	95	-	octene-1 + ?
11.	1	-122.5	1.3990-1.4020	5	-	18	-	-	C_8 paraffins
	2		1.4080-1.4180	131	-	-	82	-	octene-1 + ?
12.	1	-123.1	1.3979-1.4000	3	-	46	-	-	n-octane + ?
	2		1.4090-1.4213	131	-	-	54	-	C_8 olefins ?
14.	1	123.7-	1.3979-1.3998	3	.706	64	-	-	n-octane
	2	-124.0	1.4123-1.4230	130	-	-	36	-	octene-2 ?
16.	1	125.4	1.3978-1.3980	5	.704	82	-	-	n-octane
	2	-125.4	1.4120-1.4208	126	.724	-	18	-	octene-2 ?
18.	1	125.4-	1.3977-1.3981	5	.703	89	-	-	n-octane
	2	-125.4	1.4152-1.4223	130	-	-	11	-	octene-2 ?
20.	1	125.4-	1.3975-1.3980	4	.703	89	-	-	n-octane
	2	-125.4	1.4168-1.4267	129	-	-	11	-	C_8 olefins

Table 17.(contd.)

No.	E. No.	B.pt., °C. at 760mm.	n_D range of E-cut	Br_2 No.	d_4^{20}	Compositn., % vol.			Suspected hydrocarbon
						P.+N.	O.	A.	
D-4									
21.	1	125.4-	1.3974-1.3979	4	0.703	90	-	-	n-octane
	2	-125.4	1.4161-1.4270	126	-	-	10	-	C_8 olefins
22.	1	-125.6	1.3976-1.3980	5	.703	91	-	-	n-octane
	2		1.4151-1.4310	130	-	-	9	-	C_8 olefins
23.	1	-125.9	1.3978-1.3986	6	.704	87	-	-	n-octane
	2		1.4265-1.4425	142	-	-	13	-	C_8 cyclic olefins?
24.	1	-127.4	1.4000-1.4076	6	-	62	-	-	branched nonanes
	2		1.4343-1.4502	127	-	-	38	-	C_8 cyclic olefins
25.	1	-129.2	1.4257-1.4276	6	.774	54	-	-	n-propylcyclopentane?
	2		1.4400-1.4480	120	-	-	38	-	C_8 cyclic olefins
	3		1.4758-1.4877	-	-	-	-	8	ethylbenzene
26.	1	-131.2	1.4239-1.4280	7	.776	50	-	-	n-propylcyclopentane
	2		1.4415-1.4507	119	-	-	34	-	C_8 cyclic olefins
	3		1.4900-1.4960	-	-	-	-	16	ethylbenzene
27.	1	-132.6	1.4180-1.4238	8	-	40	-	-	C_9 paraffins + naphthenes
	2		1.4407-1.4468	115	-	-	26	-	C_8 cyclic olefins
	3		1.4913-1.4972	-	.865	-	-	34	ethylbenzene
28.	1	-132.6	1.4280-1.4268	2	-	29	-	-	C_9 paraffins + naphthenes
	2		1.4316-1.4430	84	-	-	22	-	C_8 cyclic olefins ?
	3		1.4912-1.4968	-	-	-	-	49	ethylbenzene
29.	1	-132.6	1.4306-1.4308	7	-	18	-	-	C_9 naphthenes
	2		1.4283-1.4380	93	-	-	29	-	branched nonenes
	3		1.4911-1.4966	12	.866	-	-	53	ethylbenzene
30.	1	-133.2	1.4232-1.4270	9	-	12	-	-	C_9 paraffins + naphthenes
	2		1.4320-1.4442	99	-	-	31	-	branched nonenes
	3		1.4910-1.4962	-	-	-	-	57	ethylbenzene

Table 17.(contd.)

No.	E. No.	B.pt., °C. at 760mm.	n_D range of E-cut	Br_2 No.	d_4^{20}	Compositn., % vol.			Suspected hydrocarbon
						P+N.	O.	A.	
D-4									
31.	1	133.2-	1.4120-1.4187	13	-	10	-	-	branched nonanes
	2	-134.9	1.4226-1.4410	104	-	-	26	-	branched nonenes
	3		1.4918-1.4960	-	0.866	-	-	64	ethylbenzene
D-7									
1.	1	130.1-	1.4203-1.4282	10	-	25	-	-	branched nonanes
	2	-135.2	1.4322-1.4450	97	-	-	29	-	C_8 cyclic olefins
	3		1.4917-1.4966	-	-	-	-	46	ethylbenzene
2.	1	-135.5	1.4082-1.4102	0	-	12	-	-	branched nonanes
	2		1.4147-1.4282	120	-	-	13	-	branched nonenes
	3		1.4922-1.4963	-	.863	-	-	75	m-,p-xylenes
3.	1	-135.5	1.4066-1.4100	3	-	15	-	-	dime.heptanes
	2		1.4220-1.4332	-	-	-	10	-	branched nonenes
	3		1.4928-1.4968	-	.863	-	-	75	m-,p-xylenes
4.	1	-135.5	1.4080-1.4102	3	-	13	-	-	dime.heptanes
	2		1.4241-1.4302	-	-	-	8	-	branched nonenes
	3		1.4929-1.4983	-	.864	-	-	79	m-xylene ?
5.	1	-139.3	1.4135-1.4192	-	-	10	-	-	branched nonanes
	2		1.4252-1.4363	113	-	-	27	-	branched nonenes
	3		1.5003-1.5058	10	.879	-	-	63	o-xylene
6.	1	-141.1	1.4170-1.4290	119	-	-	36	-	branched nonenes
	2		1.5022-1.5062	14	.880	-	-	64	o-xylene
7.	1	-142.0	1.4208-1.4252	124	-	-	40	-	branched nonenes
	2		1.5022-1.5058	-	.880	-	-	60	o-xylene
8.	1	-142.0	1.4223-1.4227	4	-	4	-	-	branched nonanes
	2		1.4180-1.4200	124	.734	-	51	-	nonene-1 + ?
	3		1.5024-1.5065	-	.880	-	-	45	o-xylene

Table 17.(contd.)

No.	E-No.	B.pt., °C. at 760mm.	n_D range of E-cut	Br_2 No.	d_4^{20}	Compositn., % vol.			Suspected hydrocarbon
						P+N	O.	A.	
D-7									
9.	1	142.0-	1.4230-1.4217	4	-	4	-	-	branched nonanes
	2	-142.6	1.4170-1.4187	120	0.731	-	79	-	nonene-1
	3		1.5021-1.5047	-	-	-	-	17	o-xylene
10.	1	-143.7	1.4212-1.4198	-	-	2	-	-	branched nonanes
	2		1.4170-1.4180	122	.730	-	94	-	nonene-1
	3		1.4710-1.4932	-	-	-	-	4	o-xylene
11.	1	-146.0	1.4163-1.4170	122	.729	-	100	-	nonene-1
12.	1	-146.5	1.4120-1.4144	-	-	2	-	-	branched nonanes
	2		1.4162-1.4172	121	.729	-	98	-	nonene-1
13.	1	-146.8	1.4080-1.4127	3	-	9	-	-	branched nonanes
	2		1.4156-1.4177	126	.729	-	91	-	nonene-1
14.	1	-146.8	1.4063-1.4097	1	-	27	-	-	branched nonanes
	2		1.4052-1.4088	127	.729	-	73	-	nonene-1
15.	1	-147.1	1.4058-1.4066	2	.719	44	-	-	n-nonane + ?
	2		1.4122-1.4280	96	.739	-	56	-	nonene-1 + ?
16.	1	-149.3	1.4056-1.4060	2	.719	59	-	-	n-nonane
	2		1.4128-1.4290	115	-	-	41	-	nonene-1 + ?
17.	1	-150.6	1.4055-1.4060	2	.718	67	-	-	n-nonane
	2		1.4160-1.4342	120	-	-	33	-	branched nonenes
18.	1	-150.6	1.4052-1.4060	2	.718	72	-	-	n-nonane
	2		1.4204-1.4420	119	-	-	28	-	branched nonenes
19.	1	-150.6	1.4054-1.4058	2	.718	79	-	-	n-nonane
	2		1.4208-1.4357	122	-	-	21	-	branched nonenes
20.	1	-150.8	1.4058-1.4060	2	.718	82	-	-	n-nonane
	2		1.4217-1.4320	-	-	-	18	-	branched nonenes

Table 17.(contd.)

No.	E-No.	B.pt., °C. at 760mm.	n_D range of E-cut	Br_2 No.	d_4^{20}	Compositn., % vol. P+N	O.	A.	Suspected hydrocarbon
D-7									
21.	1	150.8-	1.4058-1.4064	2	0.718	84	-	-	n-nonane
	2	-151.1	1.4232-1.4325	121	-	-	16	-	branched nonenes
22.	1	-151.4	1.4058-1.4090	2	.724	84	-	-	n-nonane + ?
	2		1.4258-1.4428	-	-	-	16	-	branched nonenes
23.	1	-152.4	1.4145-1.4262	4	-	48	-	-	C_{10} paraffins ?
	2		1.4340-1.4486	88	-	-	46	-	C_9 cyclic olefins
	3		1.4730-1.4906	-	-	-	-	6	C_9 aromatics
24.	1	-154.5	1.4290-1.4350	3	.794	41	-	-	C_{10} paraffins ?
	2		1.4422-1.4580	95	-	-	37	-	C_9 cyclic olefins
	3		1.4940-1.5002	15	-	-	-	22	C_9 aromatics
25.	1	-158.5	1.4203-1.4298	4	-	29	-	-	C_{10} paraffins ?
	2		1.4459-1.4552	88	-	-	31	-	C_9 cyclic olefins
	3		1.4940-1.4997	12	.862	-	-	40	C_9 aromatics

The composition of fractions which were not analyzed on silica gel was determined by interpolation from the composition -% distillate graphs, while the hydrocarbons present in these fractions were assumed to be identical with those in the two adjacent (analyzed) fractions. The initial selection of fractions to be analyzed on silica gel enabled such determinations of the composition of the non-analyzed fractions to be made, as it was found in several instances, that on a boiling point and properties flat, the composition of fractions either remained fairly constant or varied linearly with the quantity distilled. The possibility of a fraction, belonging to a series of fractions of closely resembling properties, having a totally different composition from its two immediate neighbours was considered unlikely, as any such change would be indicated by a marked difference in one or more of its properties. Eventual analyses of fractions which were not selected originally showed, without exception, that the assumptions regarding the composition of these fractions, as well as the nature of their constituents, were fully justified, and the error involved in such determinations was of the same magnitude as that of the adsorption analysis itself. The composition of all D-fractions has been included in the properties tables in Appendix I, the composition of fractions marked thus * having been determined by interpolation.

On the basis of the results quoted in Table 17 (pp. 137-146) and the assumptions made with regard to non-analyzed fractions, the composition of cannel naphtha boiling up to 158.5°C. was calculated in percent by weight and volume on the total material distilled and on the original water-free crude cannel oil. As pointed out already, the volume of a constituent hydrocarbon of a D-fraction was first calculated from the knowledge of composition and volume of the fraction and converted, on consideration of determined or assumed value for density, into grams. If the same hydrocarbon was present in a number of fractions, as was frequently the case, its quantities in each fraction were summed and calculated back as the percentage on total distillate. The hydrocarbon-type composition of the naphtha investigated was, consequently, found to be as given in Table 18.

TABLE 18.

Hydrocarbon-type composition of cannel naphtha.

H'carbon type	Wt. % on distillate	Vol. % on distillate	Wt.% on crude oil	Vol. % on crude oil
Paraffins	28.6	30.7	2.27	2.91
Naphthenes	4.5	4.5	0.35	0.42
Alkane olefins	35.7	37.0	2.82	3.51
Cyclic olefins	10.2	9.8	0.80	0.93
Aromatics	20.9	18.0	1.65	1.71
Total	99.9	100.0	7.89	9.48

(The values quoted for all percentages on crude oil have been obtained from calculations of total material boiling to 158.5°C. (3631 gm. or 4856 ml.) and not the quantity actually distilled (2512 gm. or 3359 ml.). The former figure was obtained by taking material balances on all D-distillations and scaling up proportionately the quantities involved, so as to arrive at true figures for the total naphtha boiling in the range examined. Percentages by volume as well as by weight have been calculated in order to simplify comparisons with values quoted in literature, where compositions are expressed on either of the two bases.)

Identification of hydrocarbons.

The possibility of identifying the majority of hydrocarbons present in the cannel naphtha was extremely remote on account of the following:-

a. small quantities of available material,
b. high complexity of certain fractions,
c. lack of methods and equipment capable of performing separations on very small scales or providing information on the nature of hydrocarbons (e.g. infra-red or mass spectroscopy,) and
d. lack of reliable physical data on some hydrocarbons, particularly olefins.

In view of these considerations, it was decided to attempt an identification of only these hydrocarbons which were present in relatively high concentrations and which could be obtained in a pure state by the application of adsorption methods. The selection of such hydrocarbons was, therefore, based on results obtained from adsorption analyses of D-fractions, together with information derived from boiling point curves and dw/dt vs. b.pt. plots. An examination of these graphs indicated that peaks on the composition - % distillate plots (figs. 40, 41, 42 and 43, facing p. 136) corresponded, in the majority of cases, to a plateau on the boiling point curve and, hence, to a peak on the dw/dt graph (as shown in fig. 35b., facing p. 122), and also, fractions distilling at that temperature showed small differences in properties. For example, fractions D-4/16 to 21, representing 33 to 44 % wt. on D-4 charge, contained a high percentage (ca. 90%) of saturated hydrocarbons, distilled at a constant temperature of 125.4°C. and showed the following range of variation in properties:-

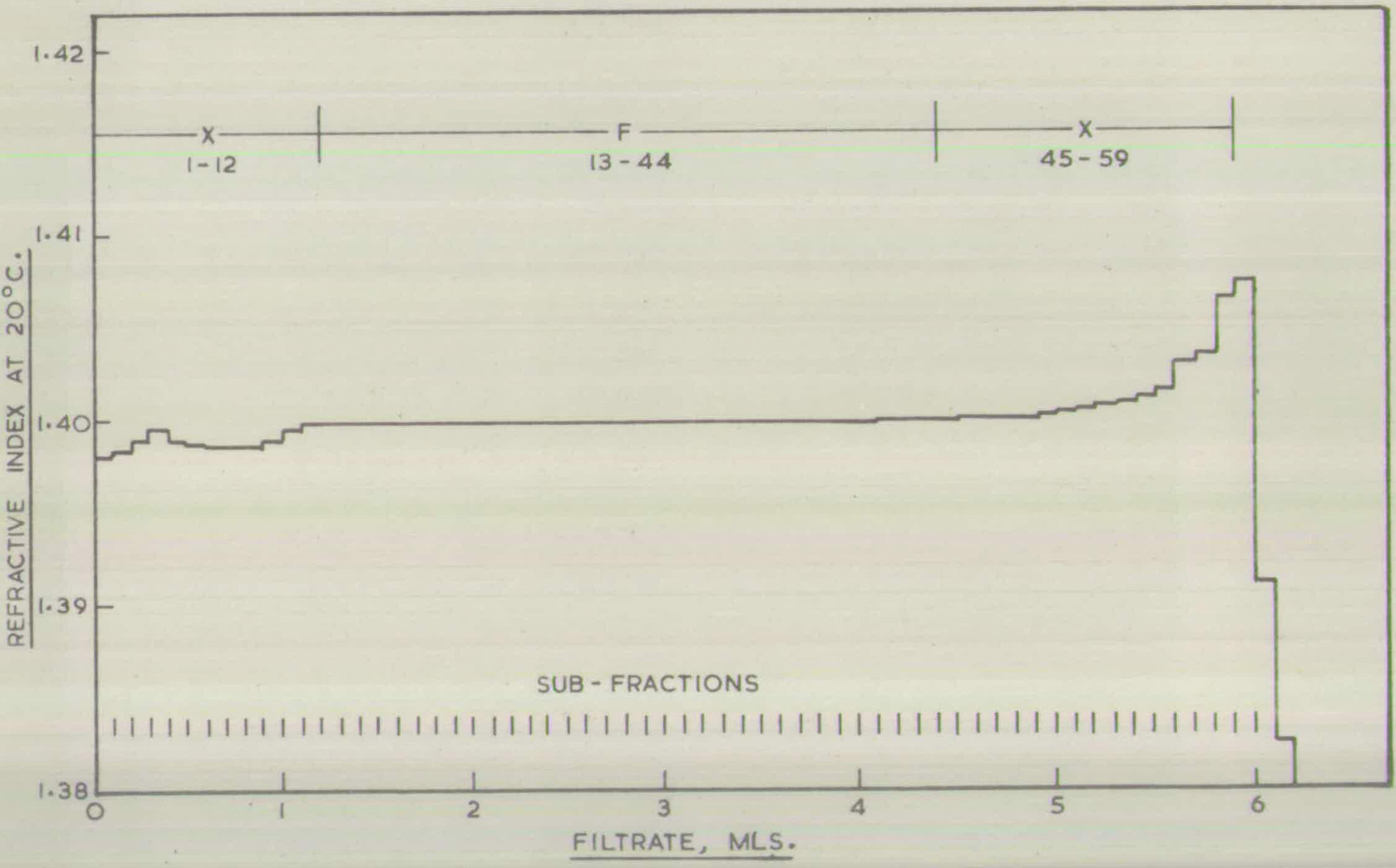
n_D^{20}	1.4033-1.4017
d_4^{20}	0.7139-0.7108
Br_2 No.	33 - 21

Adsorptograms obtained for these fractions consisted of almost perfect flats at 1.3975 to 1.3980, in the saturated portion, while examination of E-fractions pointed to the presence of n-octane.

Similarly, all D-fractions, or series of fractions, containing relatively high concentrations

FIGURE 44.

SEPARATION OF HEPTENE-1.
(FRACTION D-2/39.)

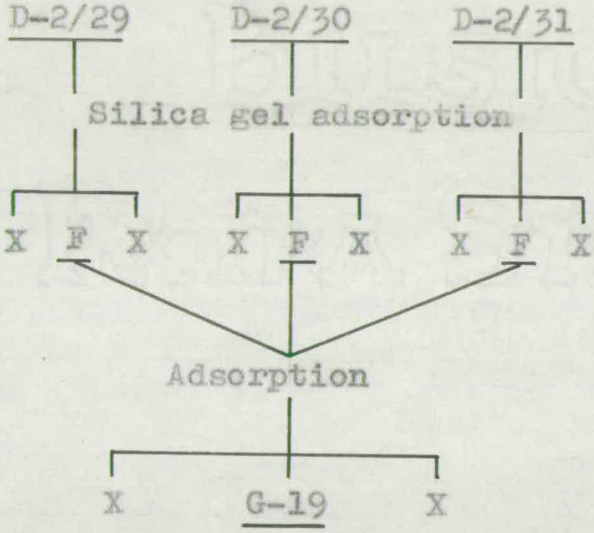


of a suspected hydrocarbon were investigated in this fashion, and, on the basis of the information thus provided, fractions were selected for identification purposes as listed in Table 19.

TABLE 19.

Hydrocarbon	Present in fractions
n-Hexane	D-2/12 - 18
n-Heptane	D-2/45 - 52; D-3/2 - 4
n-Octane	D-4/14 - 23
n-Nonane	D-7/16 - 21
2:3-Dimethylpentane	D-2/31 - 33
Hexene-1	D-2/5 - 11
Heptene-1	D-2/35 - 41
Octene-1	D-4/4 - 10
Nonene-1	D-7/8 - 14
1-Methylcyclopentene	D-2/21 - 23
Cyclohexene	D-2/29 - 31
Ethylcyclopentene-1	D-3/9 - 15
Benzene	D-2/23 - 30
Toluene	D-3/13 - 27
Ethylbenzene	D-4/27 - 31
m-, p-Xylenes	D-7/2 - 4
o-Xylene	D-7/6 - 9

The separation and purification of hydrocarbons present in these fractions was carried out by the following procedure:- a 5 to 10 ml. sample of each selected fraction was percolated through silica gel in the usual manner, followed by determination of refractive indices of all collected sub-fractions, yielding adsorptograms of the type shown in fig. 44. Material marked X, i.e. of varying n_D, was discarded, while material marked F (sub-fractions 13-44), of virtually constant n_D, was bulked to form F-fractions. All F-fractions from one series of selected D-fractions, i.e. consisting of one hydrocarbon, were in turn combined and subjected to a final adsorption, intended as a purification of the hydrocarbon present therein. Material representing not more than the central 60% of a constant n_D plateau was collected and labelled G-fraction, on which all subsequent determinations of properties, leading to identification, were carried out. The following scheme illustrates the procedure in the case of separation and purification of cyclohexene.



(Material marked X was discarded).

The following properties of G-fractions were determined:- boiling point, density, refractive index, bromine number, specific dispersion and refractivity intercept, and the values obtained, along with published data referring to a suspected hydrocarbon, are given in Table 20 (pp.153-154).

The identification of hydrocarbons was, therefore, based on the data presented in the table

TABLE 20.

Identification of hydrocarbons.

G-No.	Hydrocarbon		B.pt., °C/ 760 mm.	d_4^{20}	n_D^{20}	Br_2 No.	δ	R.I.
1		found	68.6	0.6588	1.3750	0	98	1.0456
	n-Hexane	lit.	68.74	0.6594	1.3749	0	99	1.0452
20		found	89.5	0.6962	1.3921	0	99	1.0440
	2:3-Dimethylpentane	lit.	89.78	0.6951	1.3920	0	100	1.0444
6		found	98.4	0.6837	1.3876	0	98	1.0457
	n-Heptane	lit.	98.43	0.6837	1.3876	0	99	1.0457
10		found	125.6	0.7030	1.3976	0	99	1.0461
	n-Octane	lit.	125.67	0.7025	1.3974	0	98	1.0461
12		found	150.5	0.7180	1.4056	2	100	1.0466
	n-Nonane	lit.	150.80	0.7177	1.4055	0	98	1.0466
1		found	63.4	0.6740	1.3883	187	126	1.0511
	Hexene-1	lit.	63.35	0.6736	1.3881	190	128	1.0513
5		found	93.6	0.6971	1.4002	161	124	1.0516
	Heptene-1	lit.	93.64	0.6972	1.3999	163	123	1.0513
9		found	121.1	0.7156	1.4090	141	118	1.0512
	Octene-1	lit.	121.27	0.7152	1.4086	143	119	1.0510
11		found	146.6	0.7300	1.4160	126	115	1.0510
	Nonene-1	lit.	146.87	0.7296	1.4156	127	118	1.0508
18		found	75.6	0.7828	1.4341	194	121	1.0427
	1-Methylcyclohexene	lit.	75.9	0.783	1.434	195	122	1.042
19		found	83.1	0.8100	1.4460	195	119	1.0410
	Cyclohexene	lit.	83.6	0.8088	1.4464	195	117	1.0420
7		found	108.6	0.7977	1.4428	165	120	1.0439
	Ethylcyclopentene-1	lit.	108.9	0.7974	1.4426	166	118	1.0439

Table 20 (contd.)

G-No.	Hydrocarbon		B.pt., °C./ 760 mm.	d_4^{20}	n_D^{20}	Br_2 No.	δ	R.I.
13		found	80.0	0.8785	1.5008	4	189.5	1.0637
	Benzene	lit.	80.10	0.8790	1.5011	0	190.2	1.0634
14		found	110.4	0.8666	1.4970	4	183.5	1.0637
	Toluene	lit.	110.62	0.8668	1.4968	0	184.9	1.0634
15		found	136.1	0.8676	1.4958	5	178.2	1.0620
	Ethylbenzene	lit.	136.19	0.8670	1.4958	0	179.2	1.0623
16		found	138.8	0.8624	1.4965	3	179.5	1.0648
	m-Xylene	lit.	139.10	0.8641	1.4972	0	179.2	1.0651
	p-Xylene	lit.	138.35	0.8610	1.4958	0	179.2	1.0653
17		found	144.2	0.8790	1.5050	3	179.7	1.0655
	o-Xylene	lit.	144.41	0.8801	1.5052	0	179.2	1.0651

and, with the exception of aromatic hydrocarbons, no further confirmation of identity was undertaken. The nature of aromatic hydrocarbons was established by absorption spectra in the ultra-violet, the experimental procedure and results being discussed in Appendix III.

Evaluation of composition.

On the basis of results and information obtained from adsorption analyses and the examination of G-fractions, the chemical composition of cannel naphtha boiling in the range 26.9° - 158.5°C. was found to be as given in Table 21, in which results are classified under hydrocarbon types.

TABLE 21.

Hydrocarbon-type composition.

H'carbon type	Wt. % on distillate	Vol. % on distillate	Wt.% on crude oil	Vol. % on crude oil
n-Paraffins	21.99	23.80	1.74	2.26
Branched-chain paraffins	6.61	6.89	0.53	0.65
Naphthenes	4.54	4.46	0.35	0.42
n-Olefins-1	22.85	23.83	1.81	2.27
Branched-chain olefins	12.87	13.17	1.01	1.24
Cyclic olefins	10.22	9.84	0.80	0.93
Aromatics	20.92	18.01	1.65	1.71
Total	100.00	100.00	7.89	9.48

Table 22 (pp.157-158) indicates the different types of hydrocarbons identified or suspected with the approximate amounts of each, expressed in percent by weight and by volume on total material boiling-up to 158.5°C., and on water-free, crude cannel oil.

TABLE 22.

Composition of Cannel Naphtha boiling up to 158.5°C.

Hydrocarbon	% wt. on distillate	% vol. on distillate	% wt. on crude oil	%vol.on crude oil
Paraffins.	28.60	30.69	2.27	2.91
n-Pentane	0.12	0.15	0.01	0.01
n-Hexane	3.28	3.75	0.26	0.36
C_6 branched paraffins	0.34	0.38	0.03	0.04
n-Heptane	6.60	7.22	0.52	0.68
2:3-Dimethylpentane	0.72	0.77	0.06	0.07
C_7 branched paraffins	0.28	0.32	0.02	0.03
n-Octane	7.33	7.84	0.58	0.75
Dimethylhexanes	1.18	1.28	0.09	0.12
C_8 branched paraffins	1.09	1.09	0.09	0.10
n-Nonane	4.66	4.84	0.37	0.46
C_9 branched paraffins	1.94	2.02	0.16	0.19
C_{10}branched paraffins	1.06	1.03	0.08	0.10
Naphthenes.	4.54	4.46	0.35	0.42
C_5 naphthenes	0.23	0.23	0.02	0.02
C_6 naphthenes	0.64	0.62	0.05	0.06
C_7 naphthenes	1.82	1.78	0.14	0.17
C_8-C_9 naphthenes	1.85	1.83	0.14	0.17
Alkane Olefins.	35.72	37.00	2.82	3.51
Pentene-1	0.57	0.62	0.05	0.06
Hexene-1	3.76	4.11	0.30	0.39
Hexene-2	0.85	0.83	0.07	0.08
C_6 branched olefins	1.12	1.20	0.09	0.11
Heptene-1	5.94	6.29	0.47	0.60
C_7 branched olefins	4.00	4.12	0.31	0.39
Octene-1	7.15	7.34	0.56	0.70
Octene-2	0.72	0.74	0.06	0.07

Table 22.(contd.)

Hydrocarbon	% wt. on distillate	% vol. on distillate	% wt. on crude oil	%vol.on crude oil
Alkane Olefins (contd.)				
C_8 branched olefins	3.09	3.06	0.24	0.29
Nonene-1	5.43	5.47	0.43	0.52
C_9 branched olefins	3.09	3.22	0.24	0.30
<u>Cyclic Olefins</u>.	10.22	9.84	0.80	0.93
Cyclopentene	0.85	0.90	0.07	0.09
1-Methylcyclopentene	1.38	1.39	0.11	0.13
Cyclohexene	1.11	1.08	0.09	0.10
C_6 cyclic olefins	0.33	0.33	0.02	0.03
Ethylcyclopentenes	2.91	2.77	0.23	0.26
C_7 cyclic olefins	0.62	0.58	0.05	0.05
C_8 cyclic olefins	1.76	1.65	0.13	0.16
C_9 cyclic olefins	1.26	1.14	0.10	0.11
<u>Aromatics</u>.	20.92	18.01	1.65	1.71
Benzene	3.12	2.65	0.25	0.25
Toluene	9.74	8.42	0.77	0.80
Ethylbenzene	3.11	2.68	0.24	0.26
m-,p-Xylenes	1.92	1.67	0.15	0.16
o-Xylene	2.38	2.02	0.19	0.19
C_9 aromatics	0.65	0.57	0.05	0.05

PART III.

DISCUSSION OF RESULTS.

General considerations.

As already mentioned in the preceding pages, the evaluation of composition of the cannel naphtha was based on the results of adsorption analyses and was supplemented by identification of a number of hydrocarbons occurring in substantial quantities. These hydrocarbons, separated from the distillate as G-fractions, were examined with respect to their properties and were subsequently identified by comparison of the determined properties with data given in literature, as shown in Table 20 (pp. 153-154). The identity of the aromatic constituents of the naphtha was confirmed by absorption spectra in the ultra-violet.

Agreement between the experimentally determined properties of G-fractions and published data is, in the majority of cases, sufficiently close to justify the establishment of identity of hydrocarbons contained therein, particularly in the case of the major constituents such as n-paraffins or olefins-1. It will be observed, however, that small discrepancies exist between the two sets of values, and these were considered to be due partly to experimental error and partly to the presence of small quantities of impurities, especially as regards constituents present in comparatively low concentrations, such as the three cyclic olefins.

Unfortunately, the quantities of material available made purification by means other than adsorption (e.g. azeotropic distillation) impracticable, while lack of suitable equipment prevented the determination of purity (by freezing points and/or cryoscopic constants) and final identification of the aliphatic members (by infra-red spectroscopy). Consequently, the purity of the hydrocarbons separated as G-fractions could not be established experimentally and it was considered, following a study of the properties of compounds boiling within the range examined, that any impurities, such as close-boiling isomers, present in concentrations exceeding 3-4% would markedly affect one or more of the properties measured, resulting in considerably larger deviations from published values than those given in Table 20 (pp. 153-154). It may be concluded, therefore, that the G-fractions are composed of individual hydrocarbons of a purity not less than 96% mole.

The hydrocarbons, the identity and approximate concentration of which have been established with reasonable certainty (G-fractions) constitute about 70% wt. of the total cannel naphtha distillate to 158.5°C.; the remaining 30% being composed of a large variety of branched-chain and isomeric compounds, present in inadequate concentrations to permit separation and detailed examination. Information with regard to the character and concentration of the latter has been supplied from silica gel adsorptions and examinations of the separated hydrocarbon types. Data thus obtained, together with the knowledge of the properties of D-fractions, were insufficient, in the majority of cases, to permit the assignment of one particular structure to a separated hydrocarbon or a mixture thereof. It was possible, nevertheless, on the basis of the information at hand, to express their nature in terms of carbon atoms in the molecule and hydrocarbon class. In some instances, as for example in the case of dimethylhexanes (present in fractions D-3/17-26) sufficient evidence was available to suggest the presence of one or a series of hydrocarbons, though it was impossible to separate these compounds and establish their identity with any degree of certainty.

Conclusions.

On the basis of the results and considerations given above, the following conclusions may be drawn with regard to the chemical composition of the cannel naphtha examined during the course of this research:-

Overall composition.

The total material boiling in the range 26.9°-158.5°C., and representing 7.89 percent by wt. or 9.48 percent by vol. of the original dry crude cannel oil, consists of mono-olefins, paraffins, aromatics and naphthenes in the ratio of approximately 10:6:4:1. The fractional distribution of the three main classes of hydrocarbons is as shown in Table 23, where the composition is expressed as wt. percentages on each fraction.

TABLE 23.

Fraction, °C.	Composition, % wt.		
	P.& N.	O.	A.
27 - 75	36	64	-
75 - 100	34	53	13
100 - 125	19	47	34
125 - 158.5	43	35	22
Total fraction	33	46	21

From the standpoint of hydrocarbon-type composition, cannel naphtha resembles closely shale oil distillates and cracked petroleum stocks of similar boiling range, inasmuch as all these products contain high percentages of unsaturated hydrocarbons and relatively low concentrations of aromatics. This similarity may be best illustrated by the following table.

TABLE 24.

Material	End pt., °C.	Composition, % wt.				Ref.
		P.	N.	O.	A.	
Cannel naphtha	158.5	28	5	46	21	-
Shale oils.						
Scottish Shale oil	175	37	9	43	11	45
Green River (U.S.) shale oil	200	33		48	19	92
Petroleum.						
Av-ge composition of cracked gasolines:-						
Mixed-phase cracked	200	46	16	32	6	83
Vapour-phase cracked	200	17	20	45	18	83
Catalitically cracked	200	44	20	18	18	83
Thermally reformed	200	40	15	35	10	83

The remarkable similarity between cannel and shale oil distillates is not surprising when the origin, petrology and constitution of both minerals are taken into consideration.

The comparison between cannel and cracked petroleum distillates is much more difficult to draw, since not only does the composition of the charging stocks (e.g. gas or fuel oils) vary considerably with the origin of the crude, but also the conditions under which cracking takes place have a pronounced effect on the resulting material.

Predominance of straight-chain hydrocarbons.

Straight-chain paraffins and olefins-1, containing from five to nine carbon atoms in the molecule, predominate in cannel naphtha to the extent of approximately 45% wt. on total distillate.

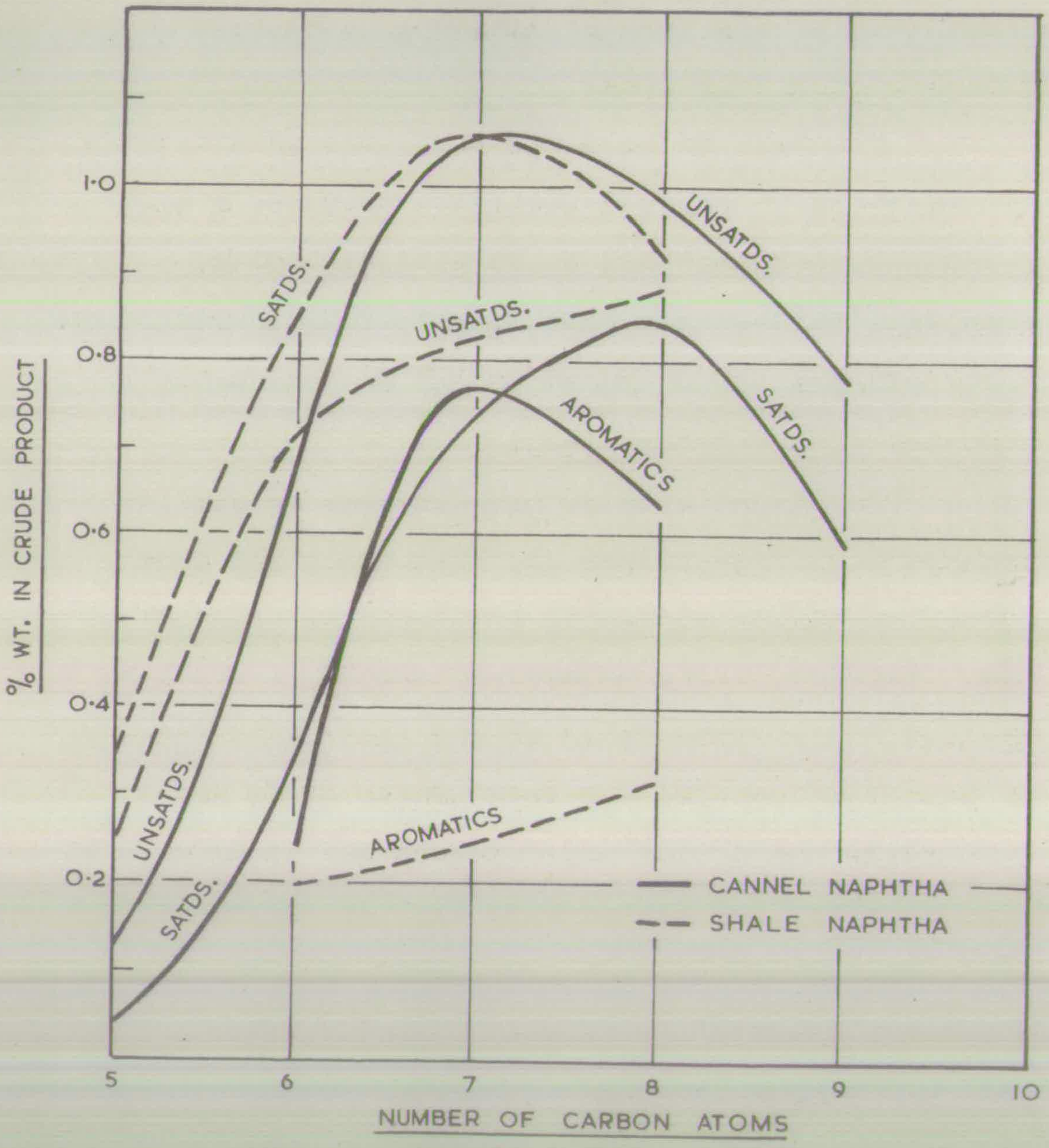
TABLE 25.

Normal constituents of light distillates.

Material	End pt., °C.	Composition, % wt.				
		C_5	C_6	C_7	C_8	C_9
n-Paraffins.						
Cannel naphtha	159	0.12	3.28	6.60	7.33	4.66
Scottish shale oil	150	2.25	5.32	6.37	5.89	-
Green River shale oil (app.)	200	-	0.1	0.2	1.5	3.1
Straight-run petroleum gasolines:-						
(a) Paraffinic -						
Ponca City	180	-	6	7	7	-
Michigan	180	-	12	14	-	-
Bradford	180	-	6	8	4	-
Grozny (U.S.S.R.)	150	6	8	10	9	6
Maikop (U.S.S.R.)	150	5	9	11	8	4
Bucsañi (Rumania)	150	-	5	8	8	6
(b) Naphthenic -						
Midway	180	-	2	1	-	-
Baku (U.S.S.R.)	150	2	3	3	6	3
Merisor (Rumania)	150	-	5	5	3	1
Olefins-1.						
Cannel naphtha	159	0.57	3.76	5.94	7.15	5.43
Scottish Shale oil	150	0.87	3.48	2.91	2.51	-
Green River shale oil (app.)	200	-	-	0.6	2.3	3.8

FIGURE 45.

HYDROCARBONS IN CANNEL AND SHALE NAPHTHAS.



Shale oil and cracked petroleum distillates exhibit very similar properties with respect to both hydrocarbon classes, while straight-run gasolines contain relatively high percentages of straight-chain paraffins only. For the sake of comparison, Table 25 lists the percentages by weight on total distillate of the straight-chain constituents of a number of distillates.

The lack of detailed knowledge of individual hydrocarbons in cracked gasolines prevents a comparison of compositions to be made, although, according to Sachanen (83), straight-chain paraffins and olefins-1 preponderate in all cracked material.

Distribution of hydrocarbons.

The quantities of hydrocarbons of similar chemical characteristics, and containing the same number of carbon atoms, do not increase proportionally with increasing molecular weight, as would be expected on consideration of the increasing numbers of possible isomers, but show maxima at C_8 for saturateds and C_7 for unsaturateds and aromatics. This distribution is shown in fig. 45, where, for comparison purposes, the composition of Scottish shale oil distillates is also included.

Paraffinic hydrocarbons.

The total paraffins present in the cannel naphtha represent 2.27% wt. on crude oil or 28.60% wt. on the total distillate, and are composed to the extent of 77% of normal paraffins, having from five to nine carbon atoms. Branched-chain paraffins are present in comparatively small quantities (ca. 23% of total paraffins).

The normal members of the series, with the exception of n-pentane, were separated by distillation from the naphtha as constant-boiling concentrates, and were further purified by adsorption and subsequently identified.

Of the branched-chain paraffins, 2:3-dimethylpentane was the only compound identified.

Naphthenic hydrocarbons.

Cyclic paraffins or naphthenes represent a very small fraction of the material investigated (4.54% wt. on distillate or 0.35% wt. on crude), and consist of a complex mixture of members containing non-condensed cyclopentane and cyclohexane rings with or without short (up to C_3) paraffinic side-chains.

Strong evidence for the presence of cyclopentane, cyclohexane and methylcyclohexane was obtained in several fractions containing fairly high concentrations of these hydrocarbons, which, however, it was impossible to isolate in sufficiently pure form to permit identification.

Open-chain olefinic hydrocarbons.

Alkane mono-olefins constitute the largest single group of hydrocarbons present in the naphtha (35.72% on distillate or 2.82% on crude). Similarly to paraffins, normal olefins, and in particular olefins-1. having from five to nine carbon atoms in the molecule, predominate to the extent of 68% of the total olefins. Four of the hydrocarbons, viz. hexene-1, heptene-1, octene-1 and nonene-1 were identified following separation (by distillation), as close-or constant-boiling concentrates, and purification (by adsorption).

Straight-chain members containing the double bond in positions other than 1 were indicated in several instances, especially hexene-2 and octene-2, but attempts at separation and purification were unsuccessful.

The remainder of the olefins (approx. 32%) is composed of a large variety of branched-chain compounds, the identity of which, in terms other than the number of carbon atoms in molecule, it was impossible to establish.

Conjugated and non-conjugated di-olefins, such as penta and hexadienes, were not found in the material examined. The presence of dienes was initially suspected in the very low-boiling material (27°-50°C.), which was thoroughly examined and found to contain C_5 olefins only. Similarly, acetylenes were not found in the naphtha.

Closed-chain olefinic hydrocarbons.

As compared with naphthenes, cyclic mono-olefins are present in the naphtha in considerably larger quantities (10.22% wt. on naphtha, or 0.80% wt. on crude). Three of the hydrocarbons, viz. 1-methylcyclopentene, cyclohexene and ethylcyclopentene-1 present in relatively high concentrations, were isolated from the naphtha and their identification attempted. The main difficulty associated with the identification of these hydrocarbons was the inability to obtain high-purity samples and the lack of reliable and accurate physical data on these compounds. Consequently, the position of the double bond in methyl and ethylcyclopentenes is rather doubtful.

Cyclic conjugated dienes were not detected in the naphtha.

Aromatic hydrocarbons.

Aromatic hydrocarbons constitute approximately one-fifth of the total distillate (20.92% wt. on distillate or 1.65% on crude). Toluene, the largest single component of the naphtha, represents about 50% of the aromatics (0.77% wt. on crude); the remainder being composed of benzene and simple benzene derivatives, such as ethylbenzene, the three xylenes and C_9 aromatics, all of which, except the latter, were identified by ultra-violet absorption spectra.

It will be observed that m- and p-xylenes were not separated and their relative concentrations could not be determined by the usual procedure. Attempts to carry out such determinations by spectroscopic means were also unsuccessful.

Owing to the strong azeotrope-forming tendency, all of the aromatic hydrocarbons distilled over rather wide boiling ranges, this effect being particularly pronounced in the C_8 members.

The percentage of total aromatics in the cannel naphtha is rather high as compared with shale naphthas and most straight-run and cracked gasolines, though it does not bear comparison with light oils from high- or low-temperature bituminous coal tars, where the aromatics average up to 90%.

It is interesting to note, however, that while benzene is the major constituent of coal tar distillates (32), toluene is the predominant aromatic constituent of cannel as well as shale oil and straight-run and cracked petroleum distillates.

Comparison of cannel and shale naphthas.

Several comparisons have been drawn on the foregoing pages between cannel naphtha and similar products derived from petroleum or shale oil, with the object of indicating the similarities, as regards overall compositions and certain individual constituents, existing between the various hydrocarbon mixtures. While cannel naphtha resembles straight-run or cracked gasolines in one respect or another, it shows greatest resemblance to shale naphtha, not only in overall composition, but also in the relative quantities of the various constituent hydrocarbons and hydrocarbon classes. In Table 26 (pp. 169-170) are given the compositions, in % by wt. on total crude product, of cannel naphtha as determined during this work, and of a typical Scottish shale naphtha, as reported by Haresnape and Lowry (45).

TABLE 26.

Composition of cannel and shale naphthas.

Hydrocarbon	wt. % on total crude oil	
	Cannel naphtha	Shale naphtha
Paraffins.	2.27	2.80
n-Pentane	0.01	0.27
Iso-pentanes	-	0.03
n-Hexane	0.26	0.64
Iso-hexanes	0.03	0.09
n-Heptane	0.52	0.76
Iso-heptanes	0.08	0.11
n-Octane	0.58	0.71
Iso-octanes	0.18	0.14
n-Nonane	0.37	-
Iso-nonanes	0.16	0.05
Iso-decanes	0.08	-
Naphthenes.	0.35	0.56
C_5 naphthenes	0.02	0.04
C_6 naphthenes	0.05	0.12
C_7 naphthenes	0.14	0.18
C_8-C_9 naphthenes	0.14	0.22
Alkane olefins.	2.82	2.32
Pentene-1	0.06	0.10
Other pentenes	-	0.12
Hexene-1	0.39	0.42
Hexenes-2 and -3	0.08	0.27
Iso-hexenes	0.11	-
Heptene-1	0.60	0.35
Heptenes-2 and -3	-	0.30
Iso-heptenes	0.39	0.03
Octene-1	0.70	0.30
Octene-2	0.07	0.13
Octenes-3 and -4	-	0.07
Iso-octenes	0.27	0.23
Nonene-1	0.52	-
Other nonenes	0.30	-

Table 26 (contd.)

Hydrocarbon	wt. % on total crude oil	
	Cannel naphtha	Shale naphtha
Cyclic olefins.	0.80	0.36
Cyclopentene	0.07	0.03
1-Methylcyclopentene	0.11	-
Cyclohexene	0.09	0.03
C_6 cyclic olefins	0.02	-
Ethylcyclopentenes	0.23	-
C_7 cyclic olefins	0.05	0.15
C_8 cyclic olefins	0.13	0.15
C_9 cyclic olefins	0.10	-
Aromatics.	1.65	0.79
Benzene	0.25	0.20
Toluene	0.77	0.27
Ethylbenzene	0.24	0.16
o-Xylene	0.19	0.05
m-Xylene	0.15	0.08
p-Xylene		0.03
C_9 aromatics	0.05	-
Total	7.89	6.83

It will be observed from the above table, that the nature and relative quantities of constituent hydrocarbons of cannel and shale naphthas show a marked similarity, and that both materials contain predominating amounts of straight-chain paraffins and olefins. The only instances where the two naphthas vary are in the quantities of aromatic constituents, and in the fact that certain low-boiling fractions of shale naphtha contain small quantities of conjugated di-olefins (45); these compounds having been shown to be absent in cannel naphtha.

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APPENDIX I.

Properties and composition of D-fractions.

No.	B.pt., °C. at 760mm.	d_4^{20}	n_D^{20}	Br_2No.	Wt., gm.	Vol., ml.	Compositn., % vol.		
							P.& N.	O.	A.
D-2									
1.	26.9-36.6	0.6546	1.3700	151	12.76	19.0	23	77	-
2.	-37.2	.6491	1.3749	142	4.75	7.0	9	91	-
3.	-43.2	.7013	1.4120	209	12.90	18.4	-	100	-
4.	-58.1	.7411	1.4070	116	14.30	19.6	39	61	-
5.	-62.9	.6898	1.3828	104	14.86	21.6	35	65	-
6.*	-63.2	.6926	1.3860	147	15.26	22.2	18	82	-
7.	-63.8	.6778	1.3880	170	15.30	22.2	4	96	-
8.*	-63.8	.6726	1.3888	177	14.48	21.3	2	98	-
9.	-63.8	.6756	1.3890	187	15.34	22.4	-	100	-
10.*	-63.8	.6790	1.3900	189	13.29	19.8	-	100	-
11.	-64.9	.6861	1.3925	192	14.64	21.3	-	100	-
12.	-67.1	.6920	1.3948	162	14.42	20.8	14	86	-
13.	-68.4	.6811	1.3880	114	14.89	21.8	41	59	-
14.*	-68.7	.6761	1.3850	84	14.51	21.6	55	45	-
15.	-68.7	.6747	1.3838	64	14.77	22.0	67	33	-
16.*	-68.7	.6716	1.3823	50	14.29	21.3	75	25	-
17.	-68.7	.6716	1.3817	40	15.06	22.4	82	18	-
18.	-68.7	.6716	1.3810	33	14.24	21.3	85	15	-
19.	-70.4	.6781	1.3843	35	14.86	22.0	86	14	-
20.	-72.2	.7319	1.4089	45	15.38	21.2	76	24	-
21.	-75.7	.7679	1.4288	111	17.23	22.6	38	55	7
22.	-75.7	.7879	1.4398	138	16.61	21.3	-	82	18
23.	-76.4	.7934	1.4432	134	9.86	12.6	7	68	25
24.*	-77.1	.8058	1.4501	93	16.42	20.6	20	40	40
25.	-78.6	.8166	1.4572	40	17.34	21.4	34	21	45
26.*	-79.6	.8281	1.4692	46	17.40	21.2	24	16	60
27.	-79.6	.8360	1.4747	47	17.77	21.4	14	14	72
28.*	-79.6	.8392	1.4777	54	16.55	19.6	8	19	73

No.	B.pt., °C. at 760mm.	d_4^{20}	n_D^{20}	Br_2No.	Wt., gm.	Vol., ml.	Compositn.,% vol.		
							P.& N.	O.	A.
D-2									
29.	79.6-79.6	.8433	1.4787	67	17.13	20.4	-	26	74
30.	-83.1	.8196	1.4579	135	16.17	20.0	-	74	26
31.	-86.6	.7471	1.4153	121	14.42	19.6	35	65	-
32.	-89.4	.7336	1.3990	60	15.35	21.0	68	32	-
33.	-92.2	.7233	1.4060	130	16.28	22.4	21	79	-
34.*	-92.8	.7114	1.4048	154	16.48	23.2	4	96	-
35.	-92.8	.7094	1.4036	160	17.55	24.6	-	100	-
36.*	-93.6	.7049	1.4028	164	16.98	24.0	-	100	-
37.	-93.6	.7026	1.4021	168	17.15	24.3	-	100	-
38.	-93.6	.7013	1.4020	167	16.18	23.0	-	100	-
39.	-93.6	.7013	1.4011	167	17.10	24.4	-	100	-
40.*	-93.6	.7017	1.4012	171	16.64	23.8	-	100	-
41.	-93.9	.7028	1.4020	169	17.51	25.0	-	100	-
42.*	-95.0	.7117	1.4057	162	16.79	23.8	5	95	-
43.	-95.9	.7181	1.4076	126	17.40	24.4	19	81	-
44.*	-96.9	.7134	1.4030	92	17.02	23.8	39	61	-
45.	-96.9	.7039	1.3989	74	17.45	24.8	58	42	-
46.**	-97.5	.6995	1.3963	62	16.31	23.3	65	35	-
47.	-97.8	.6947	1.3948	52	17.24	24.8	72	28	-
48.*	-98.4	.6966	1.3955	56	15.80	22.6	78	22	-
49.	-98.4	.6921	1.3924	38	16.58	24.0	83	17	-
50.*	-98.4	.6916	1.3913	31	16.28	23.6	86	14	-
51.	-98.4	.6907	1.3909	25	16.87	24.5	89	11	-
52.	-98.4	.6902	1.3903	23	17.16	24.9	94	6	-
D-3									
1.	89.3-96.4	0.7136	1.4045	137	13.62	19.0	11	89	-
2.	-98.4	.7049	1.3973	62	15.43	22.0	70	30	-
3.	-98.4	.6985	1.3943	38	15.99	23.1	82	18	-
4.	-98.4	.6965	1.3935	32	15.26	22.2	92	8	-
5.	-98.4	.7030	1.3961	28	16.05	23.1	90	10	-
6.*	-101.1	.7440	1.4138	31	16.10	22.0	85	15	-
7.	-102.3	.7736	1.4277	52	17.28	22.4	80	20	-

No.	B.pt.,°C. at 760mm.	d_4^{20}	n_D^{20}	Br_2No.	Wt., gm.	Vol., ml.	Compositn.,% vol.		
							P.& N.	O.	A.
D-3									
8.	102.3-103.3	0.7816	1.4312	72	17.30	22.2	69	31	-
9.	-104.8	.7884	1.4363	95	18.38	23.4	33	67	-
10.	-106.8	.7986	1.4430	124	17.82	22.4	9	91	-
11.	-108.6	.7991	1.4476	124	18.92	23.6	6	79	15
12*	-109.8	.8128	1.4580	97	18.77	23.0	9	57	34
13.	-109.8	.8215	1.4653	84	19.91	24.3	11	39	50
14*	-109.8	.8250	1.4680	74	19.62	23.6	10	34	56
15.	-109.8	.8258	1.4697	61	19.98	24.4	9	30	61
16*	-109.8	.8285	1.4716	48	19.19	23.2	12	23	65
17.	-109.8	.8296	1.4728	42	19.72	24.0	18	12	70
18*	-110.1	.8314	1.4739	35	19.21	23.2	15	11	74
19.	-110.1	.8324	1.4747	28	19.98	24.2	11	11	78
20*	-110.1	.8351	1.4754	25	19.40.	23.2	11	10	79
21.	-110.4	.8360	1.4766	22	20.41	24.6	11	9	80
22.	-110.4	.8439	1.4780	19	19.74	23.6	17	-	83
23.	-110.4	.8422	1.4793	18	20.36	24.4	14	-	86
24*	-110.4	.8459	1.4810	18	19.29	23.0	14	-	86
25.	-110.4	.8504	1.4828	18	20.38	24.2	14	-	86
26.	-110.4	.8547	1.4836	24	19.47	23.0	13	-	87
27.	-110.9	.8610	1.4805	52	20.51	24.0	7	14	79
28.	-114.9	.8026	1.4392	91	18.22	23.0	15	65	20
29.	-117.3	.7683	1.4227	114	17.80	24.0	15	85	-
D-4									
1.	100.9-120.4	0.7591	1.4189	100	17.00	21.2	39	61	-
2.	-120.7	.7518	1.4180	117	20.15	27.4	18	82	-
3*	-120.9	.7367	1.4147	126	19.29	26.5	14	86	-
4.	-120.9	.7330	1.4139	133	19.77	27.6	10	90	-
5*	-120.9	.7324	1.4135	132	19.00	26.2	7	93	-
6.	-120.9	.7298	1.4132	135	19.40	27.2	4	96	-
7*	-120.9	.7288	1.4130	135	19.04	26.7	4	96	-
8.	-120.9	.7297	1.4130	134	19.85	28.0	4	96	-
9*	-120.9	.7297	1.4133	132	19.06	26.5	4	96	-
10.	-121.6	.7319	1.4140	129	19.98	27.8	5	95	-

No.	B.pt., °C. at 760mm.	d_4^{20}	n_D^{20}	Br$_2$No.	Wt., gm.	Vol., ml.	Compositn.,% vol.		
							P.& N.	O.	A.
D-4									
11.	121.6-122.5	0.7330	1.4134	103	19.31	27.0	18	82	-
12.	-123.1	.7288	1.4109	73	19.94	27.9	46	54	-
13:	-123.7	.7236	1.4078	59	18.90	26.7	55	45	-
14.	-124.0	.7207	1.4071	55	17.73	24.7	64	36	-
15:	-125.4	.7188	1.4058	43	19.37	27.5	73	27	-
16.	-125.4	.7139	1.4033	33	19.95	28.5	82	18	-
17:	-125.4	.7119	1.4027	29	19.26	27.3	87	13	-
18.	-125.4	.7109	1.4020	27	19.87	28.2	89	11	-
19:	-125.4	.7108	1.4018	24	19.22	27.2	89	11	-
20.	-125.4	.7109	1.4014	21	19.97	28.4	89	11	-
21.	-125.4	.7108	1.4017	21	18.90	27.0	90	10	-
22.	-125.6	.7112	1.4021	21	19.91	28.2	91	9	-
23.	-125.9	.7191	1.4052	31	19.15	27.1	87	13	-
24.	-127.4	.7603	1.4231	60	21.26	28.5	62	38	-
25.	-129.2	.8015	1.4404	57	21.52	27.4	54	38	8
26.	-131.2	.8106	1.4452	52	22.30	28.3	50	34	16
27.	-132.6	.8194	1.4540	43	22.13	27.3	40	26	34
28.	-132.6	.8294	1.4613	34	23.25	28.5	29	22	49
29.	-132.6	.8347	1.4653	35	22.20	27.2	18	29	53
30.	-133.2	.8310	1.4660	49	22.88	28.1	12	31	57
31.	-134.9	.8247	1.4660	44	21.11	26.3	10	26	64
D-7									
1.	130.1-135.2	0.8224	1.4620	38	22.32	27.5	25	29	46
2.	-135.5	.8271	1.4706	22	23.04	28.1	12	13	75
3.	-135.5	.8341	1.4742	15	17.92	22.0	15	10	75
4.	-135.5	.8397	1.4740	23	19.05	23.4	13	8	79
5.	-139.3	.8341	1.4708	45	23.90	29.0	10	27	63
6.	-141.1	.8314	1.4728	46	20.00	24.3	-	36	64
7.	-142.0	.8258	1.4718	48	23.74	28.8	-	40	60
8.	-142.0	.8114	1.4607	65	19.09	24.8	4	51	45
9.	-142.6	.7736	1.4376	98	20.12	26.4	4	79	17
10.	-143.7	.7544	1.4273	110	22.30	29.8	2	94	4

No.	B.pt., °C. at 760mm.	d_4^{20}	n_D^{20}	Br_2No.	Wt., gm.	Vol., ml.	Compositn.,% vol.		
							P.& N.	O.	A.
D-7									
11.	143.7-146.0	0.7492	1.4253	110	17.74	25.0	-	100	-
12.	-146.5	.7471	1.4252	108	22.12	29.8	2	98	-
13.	-146.8	.7499	1.4259	98	23.25	31.3	9	91	-
14.	-146.8	.7509	1.4256	78	22.52	30.3	27	73	-
15.	-147.1	.7519	1.4250	59	23.52	31.2	44	56	-
16.	-149.3	.7539	1.4253	48	22.60	30.1	59	41	-
17.	-150.6	.7396	1.4174	40	23.00	31.5	67	33	-
18.	-150.6	.7345	1.4145	34	21.99	30.3	72	28	-
19.	-150.6	.7324	1.4130	27	22.89	31.6	79	21	-
20.	-150.8	.7324	1.4122	22	22.09	30.4	82	18	-
21.	-151.1	.7316	1.4122	20	22.89	31.7	84	16	-
22.	-151.4	.7308	1.4157	25	22.03	30.4	84	16	-
23.	-152.4	.7925	1.4395	57	24.14	30.8	48	46	6
24.	-154.5	.8194	1.4533	52	23.92	29.5	41	37	22
25.	-158.5	.8196	1.4580	44	21.73	26.8	29	31	40

APPENDIX II.

Examination of alkali- and acid-soluble materials.

Tar acids.

The acidic material present in the overheads from continuous distillation of crude cannel oil (A-fraction) was extracted with 20% sodium hydroxide and recovered from the separated liquor by means of 30% hydrochloric acid. The tar acids thus obtained totalled 1.25 kg. or 2.72% wt. on total crude oil, of which 1.07 kg. were subjected to an examination with respect to their approximate composition.

A preliminary removal of water and pitch was accomplished by simple distillation during which two cuts were taken:-

a. up to 175°C.
b. 175° to 305°C.

Distillation beyond 305°C. resulted in considerable decomposition of the residue as indicated by a copious evolution of light-brown fumes. Phenols present in cut a. were extracted and combined with cut b. which constituted the main bulk of tar acids, boiling up to 305°C.

The working up of the crude acids was carried out by a preliminary distillation, followed

FIGURE 1. FIRST FRACTIONATION OF TAR ACIDS.

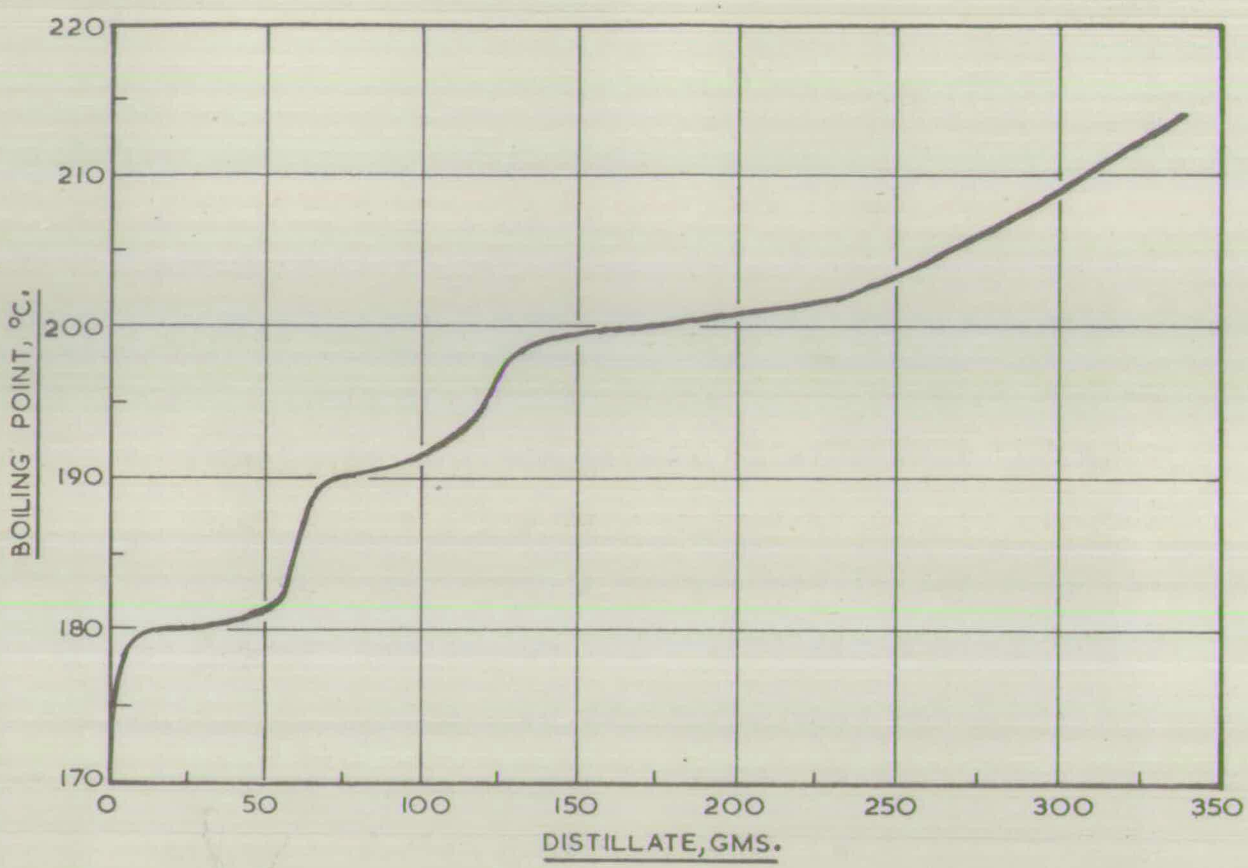
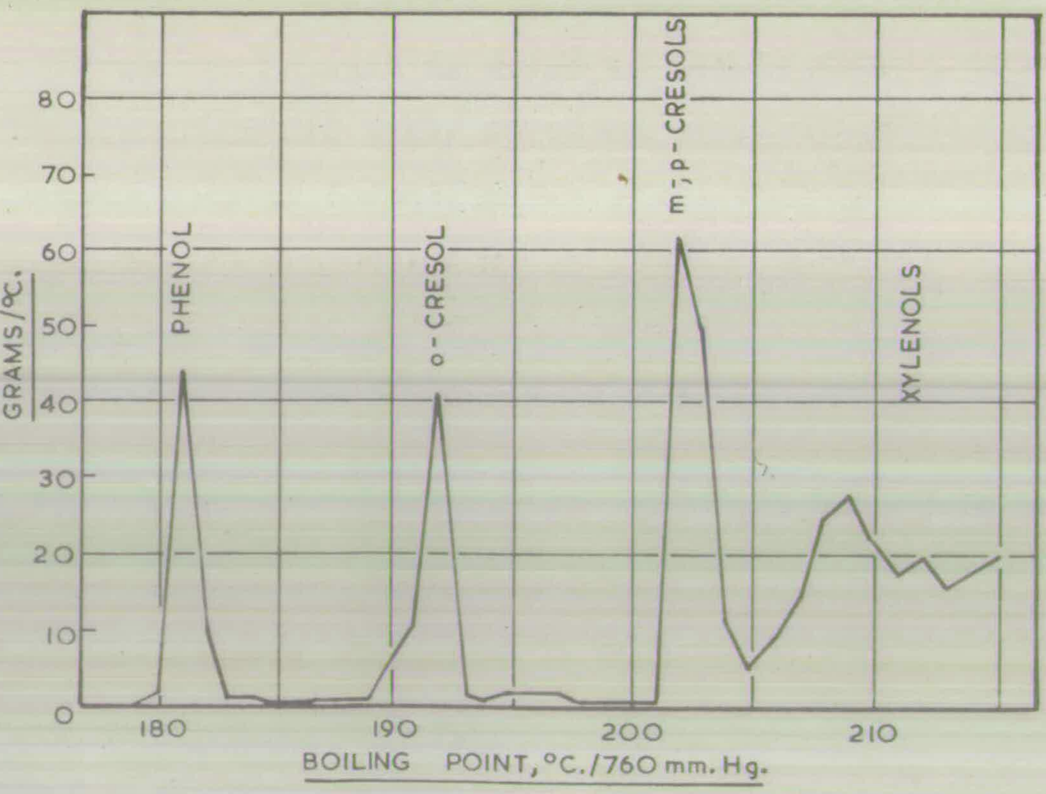


FIGURE 2. OVERALL YIELDS OF TAR ACIDS' FRACTIONATIONS.



by bulking of fractions of similar boiling range and re-distillation of the concentrates to yield readily identifiable material.

First fractionation.

The total quantity of the tar acids, as contained in cut b., was distilled at atmospheric pressure in 300 gm. batches in a 30" x 1" column, packed with ⅛" Dixon gauze rings, carrying a 500 ml. capacity electrically heated still of the Anglo-Iranian Oil Co.'s design (35) and a column head of the parallel condensing surface type, developed by Berg and Smith (7). The column was flooded in the usual manner and brought to equilibrium, after which take-off was started and continued at a rate of 30-35 gm./hr. The operating reflux ratio was approximately 15:1.

A certain amount of separation of the lower members took place, as shown in fig. 1, but no separation could be achieved above 198°C.

The distillate was collected in 1°C. cuts and these were bulked, on consideration of boiling range, to form the charges for the second distillations and separations of the lower-boiling constituents.

Second fractionation.

The final fractionation of the bulked 1°C. cuts and the separation of the lower phenols was accomplished by distillation in a 18" x ⅜" column, packed with 1/16" gauze rings and provided with a total condensate, variable take-off still-head of the type developed by Dixon (26). The column, still-head and condenser were sealed together to form a single unit; the column being surrounded by an electrically heated jacket of standard design. 50 or 100 ml. gas-heated stills were used, depending on quantities of material distilled.

The column was flooded, run to equilibrium and operated at a reflux ratio of approximately 30:1 and at a rate of take-off of 10-15 ml./hr. The bulked 1°C. cuts from the preliminary distillations were charged to the still and distilled until approximately 80% of the charge were taken-off. The next higher-boiling fraction was then charged on top of the residue and the material distilled. This procedure was carried on until all the tar acids were fractionated, leaving a final residue of about 2% of the total material. The overall boiling point curve for the low-boiling material is given in fig. 2 (facing p. 7) and is shown as a plot of gm./°C. (dw/dt) against boiling point. The final fractions containing the separated tar acids were redistilled, and only the heart of each fraction, amounting to about 60% of the charge, was collected.

In this way, phenol, o-cresol and a mixture of m- and p-cresols were separated from the tar acids and subsequently identified by the determination of physical and chemical propertis; the results being given below . No separation of xylenols could be accomplished.

Phenol.

B.pt.	181°C.
M.pt.	41°C.
Mixed m.pt.	41°C.

Derivatives:-	m.pt.
Benzoyl	68°C.
2:4:6-Tribromophenol	118°C.
Aryloxyacetic acid	98°C.

o-Cresol.

B.pt.	192°C.
M.pt.	31°C.
Mixed m.pt.	31°C.

Derivative:-	m.pt.
Aryloxyacetic acid	151°C.

m-, p-Cresols.

B.pt.	202°- 203°C.
d_4^{20}	1.034
n_D^{20}	1.5396

Unfortunately, owing to lack of time, no separation and final identification of the m-, p-cresol mixture could be undertaken, nor was it possible to investigate the nature of the higher-boiling materials, and the xylenols in particular.

Conclusion.

A preliminary investigation of the tar acids, separated from a light oil fraction of crude cannel oil, resulted in the separation of the four lowest-boiling compounds, representing approximately 20% of the total material, while the properties of the remaining material suggest the presence of a complex mixture of xylenols and higher-boiling phenolic compounds.

On the basis of the results obtained, the composition of the total acidic material is as follows:-

Total crude tar acids 1250 gm. ≡ 2.72% wt. on crude cannel oil.

	gm.	% wt. on tar acids	% wt. on crude oil
Phenol	70	5.6	0.15
o-Cresol	73	5.8	0.16
m-, p-Cresol	146	11.7	0.32
Higher-boiling tar acids	656	52.5	1.42
Pitch	125	10.0	0.27
Water	150	12.0	0.33
Losses	30	2.4	0.07

It is interesting to note that by far the greatest part of the tar acids is composed of high-boiling phenols, while the more common compounds total less than a quarter of the material. This is in agreement with the fact that low-temperature carbonization (below 550°C.) does not lead to high percentages of the lower members, since thermal conditions are too mild to effect a decomposition of the highly substituted phenols. (The rate of increase of decomposition reaches a high figure only at temperatures above 500°C. and is at maximum at 750°C.)

Tar bases.

The recovery of tar bases extracted from the cannel distillate by 20% sulphuric acid was accomplished by neutralizing the acidic solution with dilute sodium hydroxide and gaseous ammonia, followed by steam distillation of the resulting alkaline liquor. The basic material was thus regenerated and was separated from the distillate by decantation, yielding a total of 126 gm. of tar bases containing 12.2% vol. of water (Dean and Stark). The bases were dried over calcium chloride and examined with respect to their general characteristics; these being given below.

Density at 20°C.	1.006
Refractive index, n_D^{20}	1.5147
Distillation:-	
I.B.P., °C.	112
5% vol. distilled at °C.	128
10% "	139
20% "	158
30% "	166
40% "	175
50% "	187
60% "	196
70% "	208
80% "	219
90% "	236
F.B.P., °C.	262
Total distillate, %	93
Residue, %	6
Loss, %	1

The freshly distilled bases were of pale yellow colour, slowly darkening to light-brown on standing and possessed the characteristic "sooty" or pyridine odour. Owing to the very small quantities obtained no further examination of the bases was undertaken and it is impossible to give, at this stage, any indications as to their composition, though the properties of the material suggest a complex mixture of heterocyclic bases of the pyridine and, probably, quinoline types.

Materials balance.

Total material removed on acid and alkali washing of cannel distillate to 262°C. (A-fraction)	= 2100 gm.	≡ 4.6% wt. on crude oil
Dry tar acids recovered	1070 gm.	2.33%
Dry tar bases recovered	111 gm.	0.24%
Total water in acids and bases	165 gm.	0.36%
Losses	754 gm.	1.66%

It is reasonable to assume that the nature and distribution of basic material in crude cannel oils is similar to that of crude shale oils, in which the basic tar amounts to approximately 1.5% by volume. It has been shown by Nisbet et al. (73) that volatile bases derived from this material and boiling below 260°C. amounted only to about 12% of the basic tar, or 0.18% of the total crude oil.

In view of these considerations, the low quantity of volatile bases recovered from the cannel distillate boiling to 262 C. is not surprising, and is considerably larger than the figure quoted for shale oil.

The considerable quantity of material lost during the washing process (754 gm.) was assumed to consist of water, drying losses and, probably, small amounts of acid- and alkali-soluble compounds other than tar bases and acids. It must be remembered that the figure of 2.1 kg., quoted for the material removed on washing, represents the difference between unwashed and washed, dry distillate, and is, therefore, bound to include water and material lost during drying.

APPENDIX III.

Ultra-violet absorption spectra of aromatic hydrocarbons.

The final establishment of identity of aromatic hydrocarbons, separated from the cannel distillate, was accomplished by the measurement of their ultra-violet absorption spectra, the following hydrocarbons being examined:-

benzene
toluene
ethylbenzene
o-xylene
m-xylene
p-xylene

The spectroscopic analysis was performed on samples of G-fractions, the separation and purification of which have already been described (p. 149 et seq.).

The apparatus used in this investigation was a standard ultra-violet Hilger quartz spectrograph and Spekker photometer, supplied with tungsten steel electrodes producing a line spectrum. The usual experimental procedure associated with this type of equipment was followed. A series of photographs of twin spectra in close juxtaposition of pure solvent and solvent + hydrocarbon were taken on a single plate with the variable aperture set to different densities, ranging from 0.1 to 1.5. The exposure times were correspondingly varied with density, from 1 to 31.5 secs. The cells containing the liquids under examination were of 1.00 cm. length. The solvent used was n-hexane, specially purified for spectroscopic analysis and supplied by The British Drug Houses Ltd. Two or three series of spectra were taken of solutions of varying concentrations of hydrocarbons. The absorption characteristics in the range 2300 to 2800 A° were then determined visually from the photographic plates and molecular extinction coefficients calculated by the relation

$$\epsilon = \frac{d}{c.l}$$

where ϵ = molecular extinction coefficient,

d = density = $\log \frac{I_o}{I}$ = photometer drum reading,

c = hydrocarbon concentration in gm.moles/l.,

l = cell length in cm. = 1.00 cm.

The results of the spectroscopic measurements are given in Table 1 (p. 16), where are listed the values of wavelengths for the characteristic absorption bands and the corresponding maximum molecular extinction coefficients of the absorption peaks. For comparison purposes, published values of λ and ϵ are also given, these having been taken from data reported by Henri (46), Tunnicliff et al. (94), Vaughn and Stearn (98) and from various references quoted by Jones (51).

TABLE 1.

Hydrocarbon	Found		Literature	
	λ, A°.	ε	λ, A°.	ε
Benzene	2485	170	2485	175
	2543	235	2545	230
	2607	192	2605	180
Toluene	2621	217	2620	210
	2687	217	2685	210
Ethylbenzene	2623	183	2620	185
	2681	163	2680	160
o-Xylene	2630	220	2630	220
	2708	180	2710	180
m-Xylene	2649	245	2650	240
	2722	223	2725	230
p-Xylene	2687	900	2685	900
	2743	700	2745	700

It will be observed that although no separation of m- and p-xylenes could be achieved, the presence of the two hydrocarbons was satisfactorily confirmed from their absorption spectra.