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Petroleum Hydrocarbons

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The review considers the present state of research on petroleum hydrocarbons and presents the results of studies on the individual hydrocarbons in various fractions of petroleum as well as individual types of petroleum hydrocarbons; in some cases, the possible pathways to the formation of the hydrocarbons are considered. The general characteristics of the distribution of hydrocarbons in petroleum are discussed and certain features of further research on petroleum hydrocarbons are outlined.
The bibliography includes 85 references.

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I. INTRODUCTION

The studies on petroleum hydrocarbons (and other components) are of exceptionally great theoretical importance, since they extend our knowledge concerning the nature and origin of one of the commonest mineral fuels. At the same time the results of such research have been assuming increasing practical importance.

The main raw material for the petroleum processing and petrochemical industries consists of hydrocarbons isolated from petroleum distillates, liquid and gaseous hydrocarbons formed in different thermal and catalytic types of petroleum processing, as well as the hydrocarbons in natural gases. The study of the chemical composition of petroleum—the determination of the nature and structure of hydrocarbons and other petroleum components, the study of the products of the processing of petroleum, the study of natural gases, and the development of new methods for the separation and investigation of complex mixtures of hydrocarbons—is one of the most important fields in petrochemical research. The investigation of the hydrocarbon composition of petroleum is of primary importance also for the development of new methods whereby one can obtain the principal products of the petroleum industry—fuels and lubricating oils, the properties of which are determined in the first place by their chemical composition.

The study of petroleum hydrocarbons has a relatively long history and in our country has always been considered as one of the most interesting fields of chemical science both as regards theory and practice. It is sufficient to point out that research on petroleum hydrocarbons is associated with the names of F.F.Bel'shtein, A.A.Kurbatov, D.I.Mendeleev, A.A.Markovnikov, V.Ogloblin, M.I.Konovalov, N.D.Zelinskii, S.S.Nametkin, B.A.Kazanskii, and others.

Research by foreign scientists has made a significant contribution to our knowledge of petroleum hydrocarbons. Here mention should be made of the systematic investigation of the composition of petroleum based on the programme of the American Petroleum Institute Project 6, carried out from 1928 under Washburn's supervision, from 1935 under Rossini's supervision, and at the present time under Mair's supervision, as well as the research of Waterman, Vlugter, and coworkers (1928–1940), van Nes and van Westen (1950–1959), etc.

The modern period (from 1960) of research on petroleum hydrocarbons is characterised by the application of various physicochemical methods. Techniques for the isolation and separation of hydrocarbons have been improved: different versions of adsorption chromatography, the thermal diffusion method of separation, and methods based on the formation of clathrate compounds—the clathrate method (the use of urea and thiourea), etc. Gas–liquid chromatography, spectroscopic methods, including infrared and ultraviolet absorption spectroscopy, mass-spectrometry, and nuclear magnetic resonance have found very extensive applications in the characterisation and identification of hydrocarbons.

One should note here that progress in the study of petroleum hydrocarbons is to a large extent determined by the development and application of new research techniques. The use of a new, effective method usually leads to a deepening of our knowledge of petroleum hydrocarbons. A striking example is the application of chromatographic methods to the investigation of such hydrocarbons.

Since the present issue of the journal is devoted to the hundredth anniversary of the birthday of the outstanding scientist Sergei Semenovich Nametkin, a separate section of the review describes the fundamental results of the research by Nametkin together with his pupils and coworkers in the field of petroleum hydrocarbons.

Nametkin's Contribution to Research on Petroleum Hydrocarbons

At the beginning of his scientific career, while still a student at Moscow University, Sergei Semenovich Nametkin already wrote his Diploma Thesis "Hydrocarbons in the Caucasus Petroleum, Their Properties and Chemical Reactions" (1902)†. Before entering his chosen

† Nametkin's work quoted in this section has been published in special collections [1].

field of study, the young scientist surveyed in this report the results of previous investigations of the hydrocarbons in Caucasus petroleum.

The first studies on the Caucasus petroleum, carried out at the time when petroleum processing consisted merely in the preparation of lighting kerosene and fuel mazut, already yielded general ideas about the chemical nature of petroleum. It was established that petroleum includes hydrocarbons of three different series: aromatic hydrocarbons, hydrocarbons of the methane series or paraffins, and other saturated hydrocarbons, which Markovnikov called naphthenes. Nametkin, who already showed his characteristic thoroughness and objectivity in the solution of scientific problems, summarised the results of research on petroleum hydrocarbons, and outlined the problems which required further development. The classical studies by the first investigators of Caucasus petroleum had a strong and fruitful influence on his future career.

In 1907, Nametkin began his research, related to Konovalov's familiar studies, on the interaction of dilute nitric acid with hydrocarbons. These experiments, which were initially undertaken to investigate the hydrocarbons in the Caucasus petroleum, led him to new views on the mechanism of the nitration reaction. The mechanism of the nitrating and oxidising action of nitric acid on saturated hydrocarbons, which Nametkin proposed and justified experimentally, is undoubtedly one of the greatest generalisations in organic chemistry. Nametkin described the fundamental results of this research in his Master's Dissertation (1911). He subsequently used the nitration reaction to investigate petroleum hydrocarbons—paraffin and ceresin.

The range of Nametkin's interest in the field of petroleum chemistry was extremely wide, and in the second half of his career embraced the most important types of research on petroleum chemistry, among which studies on the chemical composition of petroleum occupied an exceptional place. These studies may be conventionally combined in the following groups: methodological problems; investigation of petroleum, petroleum fractions, and natural gases; investigation of certain types of hydrocarbons; the synthesis and study of model petroleum hydrocarbons.

Natural gases from a number of deposits in different regions (Baku, Daghestan, Groznyi, Melitopol, Taman', and Chusov), were investigated for the first time in the Soviet Union on a wide scale under Nametkin's supervision (1931–1933) (together with Zabrodina, Karkanas, Kursanov, Sokolov, and Uspenskii). This systematic research was of interest as regards its methodological aspects and at the same time yielded valuable information about the composition of natural gases, which was also of practical importance. Apart from the main component of the gas (methane), ethane, propane, butane, higher hydrocarbons, and carbon dioxide were determined.

The series of Nametkin's studies was devoted to the investigation of petroleum from new and relatively little investigated deposits in the Soviet Union (1928–1930), Sakhalin petroleums (from the Okha, Nutovo, Katangli, Ekhabi, Chakry, and Lyangri deposits) (together with Putsillo, Shakhnazarova, Abakumovskaya, and Nifontova), Kamchatka petroleum {the Bogachev [tentative transcription] deposit}, and the Urals (Perm) petroleum {the Chusovsko [tentative transcription] settlements}. It is noteworthy that the study of the petroleum from the Chusovsko settlements constituted the first research on petroleums from Second Baku. The petroleum investigated had a high content of sulphur compounds (which reached approximately 5.5%) and in this respect differed sharply from the familiar Caucasus petroleums.

An exceptional growth of production of petroleum from the deposits of Second Baku faced investigators with a new problem—the utilisation of the most effective methods for the processing of sulphur-containing petroleums. Nametkin frequently pointed out that this important problem can be solved only on the basis of a comprehensive study of the chemical composition of sulphur-containing petroleums and their sulphur compounds. The nature of the sulphur compounds in the petroleums from Second Baku was almost unknown.

Nametkin and his coworkers obtained the general characteristics of the first petroleum from Second Baku. Subsequently research was undertaken on the sulphur compounds contained in distillates from certain sulphur-containing petroleums. In the first study, on the kerosene distillate from the Urals petroleum (the Chusovsko settlement deposit), it was already shown that thiophans constitute a considerable proportion of the sulphur compounds of petroleum. This conclusion was reached indirectly, on the basis of the results of the oxidation of sulphur compounds by nitric acid. Subsequent investigations confirmed this conclusion. Thus, hexyl-, heptyl-, and octyl-thiophans were isolated from the light distillates of Ishimbai petroleum (via the corresponding mercury complexes). In addition an aliphatic sulphide (dipropyl sulphide) and mercaptans (butane-2-thiol and pentane-1-thiol) were isolated (together with Sosnina; 1948). Together with Putsillo, Nametkin undertook a systematic study of the proposed methods for the group analysis of sulphur compounds (1943). Tests of the methods, using a wide assortment of synthetic materials comprising individual sulphur compounds, made it possible to establish the limits of the applicability of the individual methods and to outline ways whereby an improved analytical technique for complex mixtures of sulphur compounds could be developed.

Further investigation of the nature of sulphur compounds in petroleum, the development of methods for their isolation from petroleum, and methods for their analysis, which were all problems featuring in Nametkin's research, constitute at the present time one of the most urgent problems in the chemistry of petroleum.

The general research on petroleum convinced Nametkin of the necessity for a more detailed investigation of the chemical composition of the petrol, kerosene, and oil distillates from petroleum. Even an approximate knowledge of the chemical composition of the higher distillates of petroleum is of great significance for the solution of many important theoretical and practical problems. At the same time, investigators in this field encountered the greatest methodological difficulties due to the extreme complexity of the objects of study. On the other hand, it was necessary to refine the existing methods for the determination of the group composition of petroleum distillates, and in many cases to develop new methods. Nametkin's methodological research is in fact associated with this period.

Together with Abakumovskaya (1926–1929), he proposed a new method for the determination of unsaturated compounds in petroleum products—the method of oxygen numbers based on the Prilezhaev reaction (the interaction of benzoyl hydroperoxide and unsaturated hydrocarbons with formation of epoxyalkanes). Together with Robinzon (1928–1938), a method was also developed for the quantitative determination of unsaturated and aromatic hydrocarbons in petrols, which was widely used at the time.

Apart from research on petroleum and the group chemical composition of various petroleum distillates, two other types of research feature in Nametkin's work. The first concerns the isolation of hydrocarbons from petroleum fractions and their identification and the second the synthesis and investigation of the properties of "model" hydrocarbons corresponding to petroleum hydrocarbons as regards their structure and molecular weight. Both these types of research have greatly developed in recent years and are of fundamental importance in the study of the structure of petroleum hydrocarbons.

As an example of the first type of research, one may quote Nametkin's investigations (together with Pokrovskaya and Stepantseva; 1949–1950) on hydrocarbons belonging to the naphthalene series. The picrate method was used; the corresponding petroleum fractions were treated with a solution of picric acid and the resulting alkylnaphthyl picrates were isolated in a pure form after recrystallisation and identified; in some cases, the picrates were decomposed (by steam distillation) and the alkylnaphthalenes isolated were also identified. It was possible to establish in this way the presence of naphthalene, β-methylnaphthalene, and 1,6-dimethylnaphthalene in the middle fractions of the light oil from Surakhany petroleum (the 190–252°C distillate) and of naphthalene, monomethylnaphthalenes, 1,6- and 1,7-dimethylnaphthalenes, trimethylnaphthalenes, and other higher naphthalene homologues in Maikop petroleum (185–265°C and 105–135°C distillates at 2 mmHg). Alkylnaphthalenes constitute 15–20% of all the aromatic hydrocarbons in the middle fractions of the above petroleums. At the same time it was shown that the middle fractions of Emba petroleums (the Dossor and Makat deposits) contain virtually no naphthalene or its homologues. These differences in the content of naphthalene homologues are apparently consistent with the general chemical compositions of the petroleums and are possibly due to their age—the Maikop petroleum deposit belongs to the Tertiary Period and that of Emba petroleums belongs to the Jurassic Period.

Studies on the high-molecular-weight hydrocarbons comprising paraffin and ceresin (together with Nifontova; 1936) should be included in the same group of Nametkin's investigations. They constitute an excellent application of the nitration of saturated hydrocarbons with dilute nitric acid, which had been comprehensively studied by Nametkin in his previous work. It was postulated that it is possible to approach in this way a solution to the problem of the structure of the paraffin and ceresin hydrocarbons, which are difficult to investigate chemically. Nitration under appropriate conditions might lead to the formation of secondary and tertiary nitro-compounds and hence to an experimental solution of the problem of whether or not these hydrocarbons contain tertiary carbon atoms.

It was established that, following the nitration of the hydrocarbons of petroleum paraffin, tertiary nitro-compounds as well as secondary nitro-compounds are formed; the hydrocarbons of petroleum ceresin give rise almost exclusively to tertiary nitro-compounds under the same nitration conditions. Thus it was shown that petroleum paraffins and ceresins contain hydrocarbons with a tertiary carbon atom or, in other words, branched hydrocarbons.

These results constituted a new stage in the understanding of the chemical structure of the hydrocarbons in paraffins and ceresins and stimulated chemists to undertake further research on these complex natural petroleum products. It has now been established that paraffins and ceresins contain, apart from saturated hydrocarbons with normal and branched structures, also high-molecular-weight cyclic hydrocarbons (with long paraffinic chains), this is fully consistent with Nametkin's research—cyclic hydrocarbons in paraffins and ceresin also contain a tertiary carbon atom.

Nametkin's study (together with Pokrovskaya; 1937 to 1938) on the synthesis and properties of hydrocarbons in cyclohexylbenzene and cyclopentylbenzene series as well as other polycyclic hydrocarbons constitutes one of the most important stages in the synthesis of model petroleum hydrocarbons. In terms of their molecular weight, these hydrocarbons serve as models of lubricating oils. The hydrocarbons of the cyclohexylbenzene series were obtained by the condensation of benzene with cyclohexene in the presence of aluminium chloride (the Friedel–Crafts reaction). Cyclohexylbenzene ($C_{12}H_{16}$), 1,4-dicyclohexylbenzene ($C_{18}H_{26}$), 1,3,5-tricyclohexylbenzene ($C_{24}H_{36}$), and, tentatively, 1,2,4,5-tetracyclohexylbenzene ($C_{30}H_{46}$) were obtained in this way. The structures of the hydrocarbons were confirmed by analysis and by the catalytic dehydrogenation of their cyclohexane rings; subsequent hydrogenation led to the reformation of the initial hydrocarbons. The study of the hydrocarbons (their viscosities, solubilities, etc.) led to conclusions about their properties as models of lubricating oils. The hydrocarbons of the cyclopentylbenzene series were investigated and described in the same way: cyclopentylbenzene, two dicyclopentylbenzene isomers, and two tricyclopentylbenzene and tetracyclopentylbenzene isomers.

It is seen from the brief review of his studies on petroleum hydrocarbons that Nametkin developed various branches of this important field in petroleum chemistry. His broad view of the problem and the depth of his research enabled him to obtain results, which in many instances still remain important. On the other hand, the fundamental types of research on petroleum hydrocarbons begun, or suggested, by Nametkin have now been developed by his students and later investigators. In this we see the main importance of Nametkin's work, which constitutes a remarkable stage in the general understanding of petroleum.

A brief outline of the present state of research on petroleum hydrocarbons is given below. The first studies on each type of petroleum usually begin with its general characteristics which are of practical importance. More detailed investigations of petroleum hydrocarbons carried out in different laboratories are in most instances devoted to the solution of individual aspects of the given problem and systematic studies are unfortunately undertaken extremely rarely. Nevertheless, all the more detailed investigations of petroleum can be conventionally divided into three groups: studies on the individual compositions of petroleums and petroleum fractions; studies on specific types of hydrocarbons; determination of the general structures of individual types of hydrocarbons (the modern version of structural-group analysis). Certain general features of the hydrocarbon composition of petroleum have also been outlined as a result of this research.

II. PETROLEUMS FROM NEW DEPOSITS

In the general research on different types of petroleum, investigation of petroleums from newly discovered deposits occupied a significant place. The main aim of the initial

study of each petroleum is to obtain its general characteristics, to determine the position of the petroleum in the existing classification of different types, and to establish possible procedures for its processing. In order to characterise the petroleum, one employs established methods and procedures, which in some measure determine the extent to which the petroleum is investigated. At the same time, such characteristics of the petroleum must be consistent with the present development of the petroleum processing and petrochemical industry and must therefore be continuously improved.

There exists at the present time an extended programme of research on petroleums from new deposits. There are also shorter programmes of research on such petroleums. Apart from the usual physicochemical characteristics of petroleum and its fractions, whereby their potential content of commercial products (petrols—aviation and automobile fuels, reactive fuel, kerosene, diesel fuel, raw material for catalytic reforming and catalytic cracking, oil fractions, and bitumen) can be found, provision is made in the extended programme for the determination of the group composition of the fractions, for the determination of straight-chain paraffins in certain fractions by the urea method for the elimination of paraffins (for example the paraffins of the 240–350°C fraction used for the microbiological synthesis of protein), the determination of straight-chain paraffins with the aid of molecular sieves (the fraction boiling up to 200°C), and the determination of the structural-group composition of certain oil fractions.

The results of research on petroleums in the individual Republics and Regions of the Soviet Union are reviewed in monographs and handbooks (see, for example, Refs. 2 to 12).

III. INDIVIDUAL PETROLEUM HYDROCARBONS

Quite naturally, complete determination of individual hydrocarbons can be considered only in relation to light petroleum fractions (petrols). On passing to higher-boiling fractions, the number of possible isomers of individual classes of hydrocarbons becomes so great that the determination of the composition in terms of individual compounds is no longer possible.

Systematic studies over a period of many years on the composition of straight-run petrols in terms of individual compounds were undertaken in 1959 under the supervision of Kazanskii and Landsberg [13]. The combined research technique involved accurate fractionisation, the isolation of aromatic hydrocarbons by adsorption chromatography on silica gel, catalytic dehydrogenation of six-membered naphthenes, and analysis of fractions by Raman spectroscopy. In the course of the investigation, approximately 160 individual hydrocarbons were synthesised and the wavenumbers and the line intensities in the spectra of a large number of individual hydrocarbons were obtained. The combined method made it possible to determine hydrocarbons with boiling points up to 125°C and to find qualitatively, and to some extent quantitatively, the contents of a number of hydrocarbons with boiling points between 125° and 150°C.

It was shown with the aid of the combined method, that the composition of straight-run petrols in terms of individual compounds can be elucidated to the extent of 80 to 90%.[14] In the study of a series of petrols from different types of petroleum, up to 90% of the hydrocarbons was determined—alkanes, cyclopentane and cyclohexane hydrocarbons, and aromatic hydrocarbons. Certain characteristics of the distribution of hydrocarbons in petrol as a function of the type of petroleum were established. Of particular interest is the conclusion that, although petrols derived from different types of petroleum contain approximately the same set of hydrocarbons, their quantitative proportions are extremely different, 10 hydrocarbons present in petrol in greatest amounts constituting about 50% of the petrol from each type of petroleum (Table 1).

One should also note a study [15] of the composition of petrols from Nebit-Dag and Romashkino petroleums in terms of the individual hydrocarbons.

Table 1. Hydrocarbons present in greatest amounts in petrols derived from different types of petroleum.

Surakhany (selected)		Tuimazinsk*		Koschagyl	
hydrocarbon	%	hydrocarbon	%	hydrocarbon	%
Methylcyclohexane	20.05	n-Heptane	9.74	Methylcyclohexane	13.06
Cyclohexane	7.37	n-Hexane	8.43	1,3-Dimethylcyclohexane	6.19
1,3-Dimethylcyclohexane	5.68	n-Octane	7.12	Cyclohexane	4.64
1,2-Dimethylcyclopentane	5.49	n-Pentane	6.32	1,2,4-Trimethylcyclopentane	4.10
Methylcyclopentane	4.59	n-Butane	4.69	2-Methylbutane	3.55
1,2,4-Trimethylcyclopentane	3.45	2-Methylheptane	4.69	Methylcyclopentane	3.51
2-Methylhexane	3.16	Methylcyclo-	3.74	1,1,3-Trimethylcyclopentane	3.39
1,1-Dimethylcyclohexane	2.99	hexane		1,2,3-Trimethylcyclopentane	2.52
Ethylcyclohexane	2.23	2-Methylbutane	3.57	1,2-Dimethylcyclopentane	2.39
1,2,3-Trimethylcyclopentane	2.05	3-Methylhexane	3.43	1,2-Dimethylcyclohexane	2.27
		2-Methylpentane	3.06		
Total	57.06		54.79		45.62

*Tentative transcription (Ed. of Translation).

In the determination of the composition of the light fractions of petroleum in terms of individual compounds, aromatic hydrocarbons are nowadays first separated from alkanes and cyclanes by adsorption chromatography, accurate fractionation, and spectroscopic methods. The advances in the development of chromatographic methods have greatly extended the scope of research and at the same time greatly reduced the time required for the determination of the composition of light petroleum fractions in terms of their individual compounds.

Here one should note the investigation of hydrocarbons in the petrol fractions in the "reference" Ponca (Oklahoma) petroleum carried out in accordance with the programme of the American Petroleum Institute Project 6. This programme led to the determination of the first characteristics of the composition of petrol fractions boiling in the range 40–180°C from seven types of petroleum (Rossini et al.[16], p. 345; Rossini and Mair [17]). The composition of the hydrocarbon fractions was characterised in terms of the individual hydrocarbons of five classes: straight-chain paraffins, branched paraffins, alkylcyclopentanes, alkylcyclohexanes, and alkylbenzenes; bicycloparaffins and cycloheptanes were present in extremely low amounts and could be neglected. It was already noted at the time that the petrol fractions from different types of petroleum consist of the same hydrocarbons, differing only in the relative contents of the above five classes; on the other hand, within the limits of each class, the relative amounts of the individual hydrocarbons remain approximately constant and vary within the same limits.

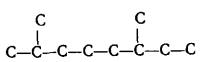
Next a study was made of the 140–180°C distillate from the Ponca petroleum in terms of the individual hydrocarbons, namely branched paraffins and cycloparaffins [18].

The hydrocarbons were isolated by fractionating the distillate (45 litres) on a high-efficiency column using also preparative gas–liquid chromatography; the hydrocarbons were identified by analytical gas–liquid chromatography and by determining the physical as well as spectroscopic characteristics of the hydrocarbons isolated (infrared spectroscopy, NMR, and mass-spectrometry); model hydrocarbons were widely used for identification. 160 fractions, distilling in the range 0.2–0.3°C, were used for the analytical chromatography, which served also for the determination of the quantiative contents of the hydrocarbons. The stationary chromatographic phases were diethylene glycol succinate, silicone nitrile, and *m*-bis-[*m*-(*m*-phenoxyphenoxy)phenoxy]benzene.

As an example of the identification, one may quote 2,4-dimethyloctane[18]. This hydrocarbon was isolated from the fraction boiling at about 156°C and had the refractive index $n_D^{25} = 1.4077$, which is close to the literature value. The mass-spectrometric determination showed that it is a C_{10} paraffin whose molecule contains four methyl groups according to NMR measurements. The results could refer to three hydrocarbons: 2,4-dimethyloctane (b.p. 155.9°C, $n_D^{25} = 1.4069$), 2,2-dimethyloctane (156.9°C and 1.4060), or 1,4-dimethyloctane (157.5°C and 1.4122). The infrared spectrum showed that the hydrocarbon does not contain a tertiary butyl group; the absence of three equivalent methyl groups was likewise confirmed by NMR; thus 2,2-dimethyloctane was excluded. The 4,4-dimethyloctane structure was eliminated by the same type of analysis. At the same time the infrared spectrum showed that the hydrocarbons contain a terminal isopropyl group as well as a butyl group; the structure of the hydrocarbon, corresponding to 2,4-dimethyloctane, was additionally confirmed by the mass spectrum (on the basis of the fragment ions).

Forty-nine paraffins and cycloparaffins, constituting 84% of all possible hydrocarbons in the distillate or 10% in relation to petroleum, were isolated (and identified) from the 140–180°C petroleum distillate, which might contain C_9 and C_{10} hydrocarbons. Six dimethyloctanes of the twelve possible isomers were isolated and identified, namely 2,4-, 2,5-, 2,6-, 3,4-, 4,4-, and 4,5-dimethyloctanes. The remaining six dimethyloctanes, the 2,2-, 2,3-, 2,7-, 3,3-, 3,5-, and 3,6-isomers, are probably present in the petroleum in insignificant amounts only.

It is noteworthy that two paraffins, 2,6-dimethyloctane and 2-methyl-3-propylhexane, were present in petroleum in unusually large amounts (0.55 and 0.64%); the content of each of the other hydrocarbons did not exceed a few hundredths per cent. The first hydrocarbon



can be assigned to isoprenanes—the hydrogenated analogues of acyclic isoprenoids; it was suggested that the second hydrocarbon might have originated from a monocyclic terpene—sylvestrene.

Among the cyclopentanes, 1-methyl-*trans*-2-n-propylcyclopentane, 1-methyl-3-n-propylcyclopentane, and n-butylcyclopentane were identified. Ten of the possible eighteen C_{10} alkylcyclohexanes were also identified. The structural and geometrical isomers of ethylmethylcyclohexane and methylpropylcyclohexane were mainly isolated from C_9 and C_{10} alkylcyclohexanes and identified; also identified were 1-*trans*-2-*cis*-3-trimethyl-, 1-*cis*-2-*trans*-3-trimethyl-, 1,1,2-trimethyl-, and 1,1,3-*cis*-5-tetramethyl-cyclohexanes as well as n-propyl-, isopropyl-, and n-butyl-cyclohexanes.

It is interesting to note that, although the 140–180°C distillate might have contained theoretically a large number of different bicycloparaffins, only nine hydrocarbons belonging to the bicyclo[3,3,0]octane, bicyclo[4,3,0]nonane, bicyclo[3,2,1]octane, and bicyclo[3,3,1]nonane series were isolated and identified:



Judging from the literature data, the hydrocarbon composition of the petrol fractions of petroleum can be found also on the basis of a simplified technique involving only the application of capillary chromatography, the hydrocarbons being identified solely in terms of their retention times without their isolation and characterisation. The saturated hydrocarbons (alkanes and cyclanes) of the 125° to 150°C fraction of the Groznyi petroleum (the Ozek-Suat deposit) were determined in this way[19]. The analysis was carried out using a capillary column equivalent to 60 000 theoretical plates with squalane as the stationary phase. The identification was based on the elution sequence of the hydrocarbons under the chromatographic conditions at 80° and 106°C. The chromatograms of the 125–150°C fraction were interpreted with the aid of a calibration mixture consisting of the products of the isomerisation of n-nonane in the presence of aluminium bromide, which contained a mixture of nonane isomers as well as C_4–C_{10} alkanes (as a result of destructive alkylation). The relative retention times (elution sequence) of the hydrocarbons in the calibration mixture were determined with the aid of model hydrocarbons. After the addition of model hydrocarbons (cyclanes) to the test fraction and the calibration mixture, the cyclanes were identified from the chromatograms. The presence of 61 hydrocarbons (out of the 130 possible compounds), mainly C_9 hydrocarbons, was established in the 125–150°C fraction of the Groznyi petroleum; among the cyclanes, the methyl and ethyl derivatives of cyclopentane and cyclohexane were widely represented.

It is noteworthy that the chromatographic method for the determination of hydrocarbons described above is relatively rapid and is widely used; however, apart from the fact that one cannot characterise hydrocarbons by this procedure (they are not isolated), there are limitations associated with the poor chromatographic separation of certain types of hydrocarbons. Thus the chromatographic peaks of monosubstituted nonane isomers overlap the peaks of cyclopentane hydrocarbons. The six geometrical isomers of 1,2,3,4-tetramethylcyclopentane are also not separated by the chromatographic method.

The research on the hydrocarbons in the petrol fractions of petroleum is related to the research on the hydrocarbons from the gas-condensate deposits. Here mention should be made primarily of extensive systematic investigations of the gas condensates from Central Asian deposits—in Turkmenistan and Uzbekistan[20–23]. A large proportion of the gas deposits which have been prospected and brought into production in recent years are known to be of the gas-condensate type; the gases from these deposits contain 2–5% and more of liquid hydrocarbons. In view of the enormous production of natural gas, amounting to hundreds of thousand millions of cubic metres, liquid hydrocarbons (condensates) are a valuable and readily available raw material for chemical processing. In the study quoted above[19], it was shown that the hydrocarbon composition of the 125–150°C fraction of the condensate from the Shur-Tepe deposit (Turkmenistan) is close to that

of the similar fraction of the Groznyi petroleum (the Ozek-Suat deposit).

The bulk of the condensates from all the gas-condensate deposits in Central Asia investigated (50 different condensates have been studied) consist of ligroin fractions (100–200°C) or C_7–C_{13} hydrocarbons; the content of the lightest fraction in the condensate (boiling up to 100°C) rarely exceeds 10%. Certain condensates are distinguished by a high content of benzene homologues (20–30% and more) and cyclohexane homologues (up to 20–25%); on the other hand, another group of condensates have a low content of these hydrocarbons and a high content of cyclopentane homologues.

Certain general characteristics of the hydrocarbon composition of the condensates may be noted. Among branched paraffins, the monomethyl derivatives predominate, namely 2-, 3-, and 4-methyl-alkanes, the substances present in largest amounts being 2-methylalkanes, namely 2-methylpentane, 2-methylhexane, and 2-methylheptane. The dimethylalkanes contain mainly 2,3- and 2,4-dimethylalkanes. Apart from cyclopentane itself, the cyclopentane hydrocarbons consist mainly of methyl- and ethyl-cyclopentanes as well as 1,2- and 1,3-dimethylcyclopentanes. The condensates usually contain all three dimethylcyclohexane isomers (1,2- 1,3-, and 1,4-), the proportion of 1,3-dimethylcyclohexane ranging from 50 to 70% of the total content of all three isomers. It is of interest that the same proportions have been observed for dimethylbenzenes, the 1,3-isomer (*m*-xylene) predominating. One may also note that toluene and 1,2,4-trimethylbenzene predominates in the condensate.

One can now assume that the determination of the composition of the light petroleum fractions (boiling up to about 150°C) in terms of the individual hydrocarbons presents no difficulties. The study of such composition of the middle petroleum distillates has naturally been carried out on a smaller scale. As an example, one may quote the results of the investigations of the Romashkino[24] and Arlansk[25] petroleums. Both types of petroleum have a high content of sulphur compounds (containing 1.8 and 2.84% of sulphur) and tars (9.9 and 20.3%); they can be classified as paraffinic petroleums (their paraffin contents are 4.9 and 4.7%). The petroleums were investigated on the basis of a single programme. Their general characteristics and information about their composition in terms of individual hydrocarbons were obtained. After deasphalting at a low temperature, the petroleum was distilled with isolation of the 180–350°C fraction (the kerosine–gas oil distillate), which was then investigated further. The distillate contained about 19% of straight-chain paraffins and 20% of aromatic hydrocarbons. Various methods for the separation and identification of the hydrocarbons were used in the course of the investigation: clear-cut fractionation, complex formation with urea, adsorption chromatography, gas–liquid chromatography, spectroscopic methods, and catalytic dehydrogenation.

The 180–200°C, 200–300°C, and 300–350°C fractions of the distillate were separated into two components by adsorption chromatography on silica gel: a mixture of paraffins and cycloparaffins and a mixture of aromatic hydrocarbons and sulphur compounds. The straight-chain paraffins were isolated from the mixture of paraffins and cycloparaffins by complex formation with urea and then identified in the usual way by gas–liquid chromatography. It is noteworthy that the hydrocarbons isolated with urea contained, apart from straight-chain paraffins, a certain amount of branched paraffins and cycloparaffins. For example, it has been established that the hydrocarbons crystallising from the 300–350°C fraction of the Romashkino petroleum and forming a complex with thiourea contained 60% of straight-chain paraffins and approximately 40% of branched paraffins and alkylcycloparaffins. Another method for the isolation of straight-chain paraffins from the mixture of saturated hydrocarbons by adsorption chromatography on activated charcoal was developed in the course of the investigation. Subsequently this method was improved and used to separate naphthenes and branched paraffins—the mixture of petroleum hydrocarbons which is most difficult to separate[26].

The list of straight-chain paraffins contained in the 180–350°C distillate is given below. The boiling points of the hydrocarbons, based on the literature data, make it possible to infer the range corresponding to their ebullition.

Straight-chain paraffins

		B.p., °C
$C_{11}H_{24}$	undecane	195.8
$C_{12}H_{26}$	dodecane	216.3
$C_{13}H_{28}$	tridecane	235.5
$C_{14}H_{30}$	tetradecane	253.6
$C_{15}H_{32}$	pentadecane	270.6
$C_{16}H_{34}$	hexadecane	287.1
$C_{17}H_{36}$	heptadecane	302.7
$C_{18}H_{38}$	octadecane	317.5
$C_{19}H_{40}$	nonadecane	331.7
$C_{20}H_{42}$	eicosane	345.3

Thus the distillate contains all ten possible straight-chain paraffins; the content of each hydrocarbon is about 0.4–0.5% in both Romashkino and Arlansk petroleums.

As mentioned above[24,25], the aromatic hydrocarbons isolated by adsorption chromatography contain an appreciable amount of organosulphur compounds; these were oxidised by hydrogen peroxide in glacial acetic acid to sulphoxides, and the latter were separated from aromatic hydrocarbons by adsorption chromatography on silica gel. The purified aromatic hydrocarbons were separated by adsorption chromatography on alumina gel into aromatic hydrocarbons containing one and two benzene rings. The content of aromatic hydrocarbons in the initial distillate was approximately 20% and most of them (80–90%) consisted of alkylbenzenes. The hydrocarbons were distilled with isolation of narrow fractions (2° and 5°C fractions). They were identified by gas–liquid chromatography and infrared and ultraviolet spectroscopy. Model hydrocarbons were used for comparison.

Twenty benzene homologues, mainly with the composition $C_{10}H_{14}$ and $C_{11}H_{16}$, were determined on the basis of the boiling points of the corresponding 170–215°C fractions:

Benzene homologues in petroleum (b.p.170–215°C)

		B.p., °C
C_9H_{12}	1,2,4-trimethylbenzene	169.35
$C_{10}H_{14}$	s-butylbenzene	173.30
$C_{10}H_{14}$	4-isopropyl-1-methylbenzene	177.25
$C_{10}H_{14}$	1-methyl-3-n-propylbenzene	181.75
$C_{10}H_{14}$	n-butylbenzene	183.85
$C_{10}H_{14}$	1-methyl-2-n-propylbenzene	184.75
$C_{10}H_{14}$	2-ethyl-1,4-dimethylbenzene	186.45
$C_{10}H_{14}$	4-ethyl-1,3-dimethylbenzene	188.45
$C_{10}H_{14}$	2-ethyl-1,3-dimethylbenzene	189.95
$C_{10}H_{14}$	3-ethyl-1,2-dimethylbenzene	193.80
$C_{10}H_{14}$	1,2,4,5-tetramethylbenzene	196.85
$C_{10}H_{14}$	1,2,3,5-tetramethylbenzene	198.15
$C_{10}H_{14}$	1,2,3,4-tetramethylbenzene	205.10
$C_{11}H_{16}$	3-phenylpentane	191.0
$C_{11}H_{16}$	4-s-butyl-1-methylbenzene	192.8
$C_{11}H_{16}$	2-phenylpentane	193.0
$C_{11}H_{16}$	3-n-butyl-1-methylbenzene	205.0
$C_{11}H_{16}$	n-pentylbenzene	205.3
$C_{12}H_{18}$	1,4-di-isopropylbenzene	210.4
$C_{12}H_{18}$	4-s-butyl-1,2-dimethylbenzene	215.1

It is seen from the above list that only a small proportion of the hydrocarbons which may be present in the distillate were determined. This is because the difficulty

of identifying the hydrocarbons increases with increase of their molecular weights and boiling points. It is also well known that the determination of hydrocarbons in petroleum depends directly on the availability of model hydrocarbons, the synthesis of which also becomes more complicated with increase of the molecular weight of the hydrocarbon.

The high content of tetramethylbenzene isomers in petroleum is striking. Whereas the content of each hydrocarbon [of each of the other hydrocarbons?] does not exceed 0.02–0.04%, the contents of 1,2,4,5-, 1,2,3,5-, and 1,2,3,4-tetramethylbenzenes were found to be 0.064, 0.13, and 0.22%. It is interesting to note that high contents of tetramethylbenzenes for the same proportions of the isomers were found by American investigators in the petroleum from the Ponca deposit [17].

As will be shown below, aromatic hydrocarbons with methyl groups in general predominate among the aromatic hydrocarbons in petroleum. Twenty hydrocarbons boiling in the range 215–300°C have been determined in the fractions containing hydrocarbons with two benzene rings. They consist mainly of naphthalene homologues:

Hydrocarbons with two benzene rings (b.p. 215–300°C)

		B.p., °C
$C_{10}H_8$	naphthalene	217.96
$C_{11}H_{10}$	2-methylnaphthalene	241.05
$C_{11}H_{10}$	1-methylnaphthalene	244.64
$C_{12}H_{10}$	biphenyl	254.9
$C_{12}H_{12}$	2-ethylnaphthalene	257.9
$C_{12}H_{12}$	1-ethylnaphthalene	258.7
$C_{12}H_{12}$	2,6-dimethylnaphthalene	262.0
$C_{12}H_{12}$	2,7-dimethylnaphthalene	262.3
$C_{12}H_{12}$	1,7-dimethylnaphthalene	263.0
$C_{12}H_{12}$	1,6-dimethylnaphthalene	264.0
$C_{12}H_{12}$	1,3-dimethylnaphthalene	265.0
$C_{12}H_{12}$	1,5-dimethylnaphthalene	265.0
$C_{12}H_{12}$	1,2-dimethylnaphthalene	266.0
$C_{12}H_{12}$	2,3-dimethylnaphthalene	268.0
$C_{12}H_{12}$	1,4-dimethylnaphthalene	130 (12 mmHg) . *cm.*)
$C_{12}H_{12}$	1,2-dimethylnaphthalene	268.5
$C_{12}H_{12}$	1,5-dimethylnaphthalene	269.1
$C_{13}H_{14}$	1-propylnaphthalene	272.0
$C_{13}H_{14}$	2-propylnaphthalene	273.5
$C_{14}H_{16}$	2-*s*-butylnaphthalene	274—276
$C_{12}H_{10}$	acenaphthene	277.3
$C_{14}H_{14}$	1,2-diphenylethane	284.7
$C_{13}H_{14}$	2,3,6-trimethylnaphthalene	286.0
$C_{13}H_{10}$	fluorene	297.2

Each hydrocarbon of this series was present in the petroleum in an amount corresponding to several thousandths per cent. There were high contents of naphthalene (0.014%), 1-methyl- and 2-methyl-naphthalenes (0.023 and 0.029%) and certain dimethylnaphthalenes.

Of the ten possible dimethylnaphthalene isomers, nine were found in the petroleum, the missing isomer being 1,8-dimethylnaphthalene. The bulk of the dimethylnaphthalenes (70–80% of the total naphthalenes) consisted of four isomers: 1,6-, 2,6-, 2,7-, and 1,7-dimethylnaphthalenes. It is remarkable that the quantitative proportions of the isomers are very similar in a wide variety of petroleums.

Table 2 presents as an example data for two types of petroleum.

It is interesting that the quantitative proportions of the dimethyldecalins found in the petroleums are close to the proportions obtained after prolonged disproportionation of dimethyldecalin isomers on an aluminosilicate catalyst at 450°C. [27] The similarity of the compositions of the dimethylnaphthalenes from different types of petroleum demonstrate yet again the common features in the composition of petroleum hydrocarbons in general.

Apart from naphthalene homologues, biphenyl, 1,2-diphenylethane, acenaphthene, and fluorene were detected in the petroleum. A number of decalin homologues were also determined. For this purpose, the fractions of naphthenoparaffinic hydrocarbons were dehydrogenated in the liquid phase in the presence of an iron-platinum catalyst after the elimination of straight-chain paraffins [28]. The resulting naphthalene homologues were isolated and identified as described above. Many decalin homologues were determined by this indirect procedure in the 200° to 300°C distillate; their structures corresponded to those of the naphthalene homologues determined previously in the petroleum: 2-methyl- and 1-methyl-decalins, 2-ethyldecalin, and all the isomeric dimethyldecalins except 1,8-dimethyldecalin. Using the dehydrogenation reaction, hydrocarbons with mixed structures were also found in the petroleum: cyclohexylbenzene and 1-cyclohexyl-2-phenylethane.

Table 2. The comparative contents of dimethylnaphthalene isomers in different types of petroleum.

Hydrocarbon	Contents of dimethylnaphthalene isomers, wt.% (relative to total content of dimethylnaphthalenes	
	Arlansk petroleum	American petroleum (Ponca)
2,6-Dimethylnaphthalene	17.2	19.4
2,7-Dimethylnaphthalene	13.4	14.4
1,7-Dimethylnaphthalene	14.6	21.2
1,6-Dimethylnaphthalene	27.2	28.2
1,3-Dimethylnaphthalene	7.2	0.2
2,3-Dimethylnaphthalene	5.9	7.2
1,4-Dimethylnaphthalene	4.6	2.8
1,5-Dimethylnaphthalene	2.9	3.7
1,2-Dimethylnaphthalene	7.0	2.4
1,8-Dimethylnaphthalene	nil	nil

Summarising the results of studies on the composition of petroleum hydrocarbons in terms of individual compounds, we see that more than 600 hydrocarbons have now been isolated from petroleum or determined in petroleum. Different classes of hydrocarbons have been investigated to different extents. Paraffinic hydrocarbons with straight-chain structures have been studied most thoroughly. This is understandable, since straight-chain paraffins do not have isomers. Their isolation from petroleum fractions (adsorption chromatography, the formation of a complex with urea, isolation with the aid of zeolites–molecular sieves) and identification (gas–liquid chromatography) do not present difficulties at present, as already mentioned above. Preliminary detailed investigations of the physicochemical properties of straight-chain paraffins, particularly their tendency to form solid solutions, have proved of much assistance in their identification [29].

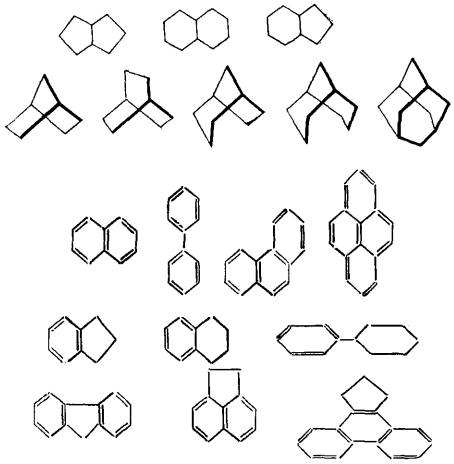
The presence of all straight-chain paraffins from n-butane (b.p. −0.5°C) to n-tritriacontane $C_{33}H_{68}$ (b.p. 475°C) in petroleum has been demonstrated; some of the straight-chain paraffins have been isolated in a pure form with a purity exceeding 99 mole %. The content of straight-chain paraffins in petroleum decreases with increase of their molecular weight; that of the highest straight-chain paraffins is 0.1% or less [30].

It is of interest that, in the solution of the problem of the microbiological synthesis of protein from the paraffinic hydrocarbon of petroleum, the past studies on hydrocarbons of this series made it possible to solve over a short period methodological problems associated with the determination of the paraffins (and to some extent aromatic

hydrocarbons) in the initial fractions used for the synthesis and in the biological products obtained.

The list of the hydrocarbons detected in petroleum shows how limited is our knowledge of the hydrocarbons in the middle fractions of petroleum, particularly of branched paraffins and cyclanes as well as hydrocarbons with mixed structures containing benzene and cycloparaffin rings. Only a few of the hydrocarbons detected in petroleum boil above 200°C.

The structural formulae of the principal types of cyclanes and aromatic hydrocarbons containing two and more rings, which have been detected in the middle fractions of petroleum, are listed below:



Certain homologues of these hydrocarbons and their isomers have been found.

It is of interest to compare the results of the study of the hydrocarbon composition of petroleum obtained in the reserach laboratories of the Soviet Union and abroad, in the first place those of the American Petroleum Institute Project 6.[16,18,30-34] The total numbers of hydrocarbons determined are approximately the same, but the alkyl derivatives of cyclopentane and bicyclanes have been studied more fully in the Soviet Union. Foreign investigators have paid more attention in recent years to the isolation and determination of aromatic petroleum hydrocarbons. It is noteworthy that nowadays investigators endeavour in most cases to determine the hydrocarbon chromatographically without isolating it from petroleum. Because of this, the properties of certain hydrocarbons detected in petroleum have sometimes not been investigated.

The enormous number of structural and geometrical isomers in the middle fractions of petroleum limits the possibility of their determination. Other research techniques described below are of considerable importance in this field.

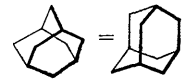
IV. INDIVIDUAL TYPES OF HYDROCARBONS

We may note one group of hydrocarbons in the middle fractions of petroleum, namely methylnaphthalenes, the composition of which in terms of individual compounds was investigated within certain limits as early as the 1950s. Naphthalene homologues form crystalline picrates (molecular compounds) by reaction with picric acid and for this reason they were isolated from petroleum fractions relatively long ago. The modern methods for their identification were described above.

Four types of hydrocarbons, namely alkyl derivatives of adamantane and hydrocarbons which are the hydrogenated analogues of terpenes (isoprenanes, steranes, and triterpanes), have been actively investigated recently.

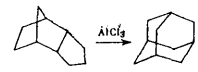
(a) Adamantane and Its Homologues

Adamantane or tricyclo[3,3,1,$1^{3,7}$]decane, which has a very unusual polyhedral structure, has been isolated from Godonin petroleum (Czechoslovakia) and has been investigated by Landa and Machacek[35] in 1933. It is a crystalline substance with a melting point of 269°C (the highest among the known hydrocarbons). The adamantane molecule consists of three condensed cyclohexane rings in the chair form; the steric dispositions of the carbon atoms in the adamantane molecule forming, as it were, a cage closed on all sides, is the same as in the crystal structure of diamond—hence its name:



Mention should be made of yet another factor—the discovery in petroleum of this hydrocarbon with its remarkable structure and properties initiated the development of an extremely important field in modern organic chemistry—the chemistry of adamantane. Adamantane derivatives have now found a wide variety of applications (as medicinal substances, polymers, etc.).

Adamantane is usually obtained by the isomerisation of the fully hydrogenated cyclopentadiene dimer (*endo*-trimethylenenorbornane) in the presence of aluminium chloride[36]:



The isomerisation takes place also over the aluminosilicate catalyst[37]. We are unable to consider here the reaction mechanism, which is discussed by Schleyer and Donaldson[38].

The adamantane content in the middle fractions of Soviet petroleums has been determined by the method of Landa and Hala[39]. The entire distillate which may contain adamantane is obtained from petroleum by steam distillation; adamantane is concentrated by repeated complex formation with thiourea and is isolated by preparative gas–liquid chromatography. The adamantane contents in various Soviet petroleums, even those with a high content of cyclanes such as the petroleums from the Balakhansk [tentative transcription] and Surakhany deposits, are small and usually amount to 0.004–0.01%.[39] Petroleum from the Ponca deposit (USA) was found to contain 0.004% of adamantane[40]. The content of adamantane is somewhat higher in the petroleum from the Godonin deposit, where it was first discovered[41].

The presence of a number of alkyladamantanes in petroleum has now been established. They can be isolated and identified as follows. The petroleum fraction consisting of branched paraffins and cyclanes is separated by thermal diffusion, which yields a concentrate of tricyclic hydrocarbons containing alkyladamantanes. The efficiency of the thermal diffusion method in this case has been confirmed with the aid of artificial mixtures of synthetic hydrocarbons. The concentrate, containing a considerable amount of "non-adamantane" structures in addition to the alkyladamantanes, is subjected to catalytic cracking

and dehydrogenation under pulsed conditions over a platinum catalyst (0.5%) on alumina at 420°C and the resulting unsaturated and aromatic hydrocarbons (formed by the dehydrogenation of the cyclanes containing the cyclohexane ring) are removed by adsorption chromatography on activated silica gel. Under the conditions described, alkyladamantanes, which are very stable, are hardly altered. Only partial epimerisation is observed, for example, there is partial conversion of *cis*-1,4-dimethyladamantane into *trans*-1,4-dimethyladamantane[43]. The alkyladamantanes in the concentrate are then identified by capillary gas–liquid chromatography (with squalene as the stationary phase)[42,43].

The 200–250°C fraction of heavy Balakhansk petroleum (Baku), which might have contained methyl- and ethyladamantanes, was investigated in this way. The yield of the 200–225°C fraction was 2.8% and its content of the mixture of branched paraffins and cyclanes was 85%. A concentrate of tricyclanes was isolated from the mixture and a concentrate of alkyladamantanes was obtained.

Twenty-four C_{11}–C_{14} alkyladamantanes with methyl and ethyl substituents were identified. The total content of alkyladamantanes was 0.02%, which is ten times more than the content of adamantane itself in this petroleum (0.001%).

The presence of mono-, di-, tri-, and tetra-substituted alkyladamantanes, containing methyl and ethyl substituents in various positions in the adamantane ring, has now been established in different types of petroleum[42–46].

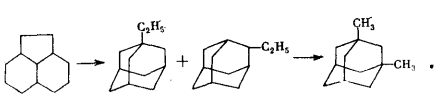
Petroleum alkyladamantanes
(The alkyl groups and their positions in the adamantane nucleus are indicated)

C_{11}	C_{13}	C_{14}
1-methyl-	1,3,5-trimethyl-	1,3,5,7-tetramethyl-
2-methyl-	1,3,6-trimethyl-	1,3,5,6-tetramethyl-
	1,3,4-trimethyl	1-ethyl-2,5-dimethyl-
	1-ethyl-3-methyl-	1,2,3,5-tetramethyl-
C_{12}	4-ethyl-1-methyl-	
	1,2,6-trimethyl-	
1,3-dimethyl-	1,2,4-trimethyl-	
1,4-dimethyl-		
1,2-dimethyl-		
1-ethyl-		
2-ethyl-		
2,2-dimethyl-		
2,4-dimethyl-		

It is remarkable that, together with the most stable alkyladamantanes having substituents at the tertiary bridgehead carbon atoms in the adamantane nucleus (in the 1-, 3-, 5-, and 7-positions), alkyladamantanes with substituents at secondary carbon atoms (in the 2-, 4-, and 6-positions) have been detected in petroleum in considerable amounts. Consequently, the proportions of the alkyladamantane isomers in different types of petroleum do not correspond to equilibrium.

Compounds containing the adamantane nucleus have not been detected among substances of plant and animal origin. One must therefore suppose that the hydrocarbons of the adamantane series have been formed as a result of secondary processes—for example as a result of the isomerisation of other tricyclic hydrocarbons present in petroleum.

Tricyclic (perhydroaromatic) hydrocarbons, namely perhydroacenaphthene (C_{12}), perhydrofluorene (C_{13}), and perhydroanthracene (C_{14}), are known to isomerise to alkyladamantanes in the presence of $AlBr_3$.[47] The mechanism of the process involving perhydroacenaphthene is as follows:



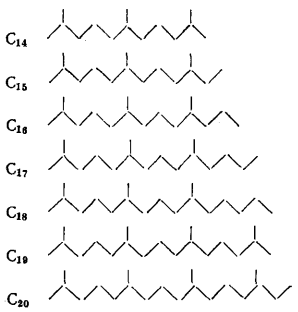
The isomerisation takes place also under the influence of other metal halides[44] and the corresponding bicyclic hydrocarbons are likewise capable of isomerising adamantanes[48].

Tricyclic hydrocarbons undergo an analogous transformation also under the conditions of heterogeneous catalysis over an aluminosilicate catalyst or alumina at moderate (between approximately 180 and 250°C) and higher temperatures[48–51]. The alkyladamantanes formed in the reaction then undergo further isomerisation, there is an increase in the total number of substituents, a decrease in the length of the substituents, and preferential formation of the most stable alkyladamantanes containing methyl or other groups only at the bridgehead positions of the adamantane nucleus.

As already mentioned above, in the series of alkyladamantane isomers with the same molecular weight the proportions of petroleum adamantanes are far from the equilibrium values. Thus the contents of 1,3,5-, 1,3,6-, and 1,3,4-trimethyladamantanes in petroleum were (relative to the sum of C_{13} alkyladamantanes) 21.5, 14, and 28.5%, while the contents in the equilibrium mixture (obtained by isomerisation over alumina) were 92.5, 3, and 3% respectively. At the same time, there is a fairly satisfactory correspondence between the relative contents of petroleum alkyladamantanes and their contents in the non-equilibrium mixtures obtained in the catalytic isomerisation of tricyclanes. Thus, even if alkyladamantanes were formed from tricyclanes, this must have occurred under conditions preventing the completion of the isomerisation reaction with formation of stable isomers alone; kinetic factors may have played a significant role in this process.

(b) Petroleum Isoprenanes

Alkanes with the isoprenoid structure were discovered in petroleum in the 1960s. Aliphatic polyperterpenes, having a polyisoprene skeleton with a characteristic alternation of methyl chain substituents at intervals corresponding to three methylene groups, which may be regarded as isoprene polymerisation products, are classified as aliphatic isoprenoids in organic chemistry. The term "isoprenoid petroleum hydrocarbons" has been very arbitrarily attributed to saturated branched alkanes, which are hydrogenated analogues of isoprenoids. The present author believes that the above hydrocarbons should be called isoprenanes, by analogy with terpanes (hydrogenated analogues of terpenes) and steranes (hydrogenated analogues of steroids). The structures of C_{14}–C_{20} isoprenanes can be represented as follows:

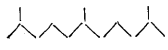


Mainly 2,6-dimethylalkanes, 2,6,10-trimethylalkanes, and 2,6,10,14-tetramethylalkanes are assigned to hydrocarbons of this type.

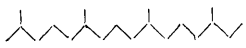
The syntheses of the majority of isoprenane hydrocarbons as models of petroleum hydrocarbons have now been described[52,53]. Thus 2,6-dimethylalkanes (C_{10}–C_{13}) can be obtained from acyclic terpenoids–citronellol, citral, pseudoionone; 2,6,10-trimethylalkanes (C_{14}–C_{18}) can also be obtained from pseudoionone. In a general form, the synthesis of alkanes of this type can be carried out via the following scheme:

corresponding ketone → alcohol → unsaturated hydrocarbon → alkane.

For example the alcohol 2,6,10-trimethylundeca-2,6-diene-10-ol has been obtained by the Grignard reaction from geranylacetone, synthesised by the condensation of linalool and ethyl acetoacetate; the alcohol was then dehydrated to the corresponding triene and the hydrogenation of the latter yielded 2,6,10-trimethylundecene:



Phytane (2,6,10,14-tetramethylhexadecane) can be obtained by the dehydration of isophytol (2,6,10,14-tetramethylhexadec-15-en-14-ol) and subsequent reduction of the resulting tetramethylhexadiene to tetramethylhexadecane:

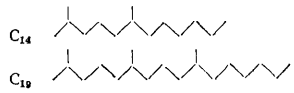


The physicochemical characteristics of the isoprenanes synthesised are listed in Table 3.

Table 3. Physicochemical characteristics of isoprenanes.

Hydrocarbon	B.p., °C (mmHg)	B.p., °C (at 760 mmHg; recalc.)	Solidification temp., °C	n_D^{20}	ρ_4^{20}
2,6,10-Trimethylundecane	103.2–103.8 (11)	236.2–237.5	<–100	1.4270	0.7593
2,6,10-Trimethyldodecane (farmesane)	118.0 (10)	253	<–90	1.4335	0.7714
2,6,10-Trimethyltridecane	123.5 (9)	272	<–90	1.4349	0.7773
2,6,10-Trimethyltetradecane	127.5 (7)	285	<–80	1.4361	0.7806
2,6,10-Trimethylpentadecane	140.3 (8)	300	<–70	1.4400	0.7845
2,6,10,14-Tetramethylpentadecane (pristane)	146–147 (4)	331.2–332.5	<–70	1.4390	0.7845
2,6,10,14-Tetramethylhexadecane (phytane)	139.7–140.2 (3)	352.5–353.0	–70	1.4420	0.7935

Branched alkanes, whose molecules contain only fragments of the isoprenane (polyisoprene) structure have also been synthesised, for example, 2,6-dimethyldodecane, 2,6,10-trimethylhexadecane, etc.[54]:



The isoprenanes pristane and phytane were first detected in Iranian[55] and Western Texas[56,57] petroleums. It has now been established that all petroleums contain some isoprenanes; they have also been detected in shale, bituminous coal, and various bituminous sedimentary rocks[58,59]; their formation is apparently associated with a plant substance (phytol), which has a definite bearing on the problem of the origin of petroleum and caustobioliths in general. The wide occurrence of these unusual hydrocarbons and their biogenic origin ("biological labels") has attracted the attention of investigators.

Various methods, particularly capillary gas chromatography and mass spectrometry, are used to determine isoprenanes. Two approaches to the identification of isoprenanes in petroleum have been devised; the first provides for a preliminary preparation in one way or another of isoprenane concentrates from fairly narrow fractions and their subsequent analysis and the second involves direct determination of isoprenanes in broad fractions with the aid of analytical gas chromatography.

A scheme has been described for the investigation of hydrocarbons of the type of isoprenanes in 180–350°C petroleum fractions, which involves the elimination of aromatic hydrocarbons (adsorption on silica gel) and straight-chain alkanes (complex formation with urea) from the fraction, separation of branched alkanes and cyclanes by adsorption chromatography on activated charcoal, and their vacuum distillation[60]. The development of a method for the separation of branched alkanes and cyclanes presented the greatest difficulties—separation of this kind is still an urgent problem and in this connection we may mention, together with the use of activated charcoal as an adsorbent, the work by American investigators in which Sephadex has been used as the adsorbent[61]. Branched alkane fractions, in which isoprenanes were determined by capillary chromatography and mass-spectrometry, were thus obtained. A mass-spectrometric method has been developed for the quantitative determination of isoprenanes in petroleum[62]. The entire study has been carried out using model hydrocarbons.

Isoprenanes can be determined also by methodologically simpler methods. The 150–350°C broad petroleum fraction, containing the main bulk of petroleum isoprenanes (with the C_{11}–C_{20} composition), was directly analysed for isoprenanes by capillary gas chromatography (with Apiezon L as the stationary phase) after preliminary elimination of aromatic hydrocarbons by adsorption on silica gel[53]. The contents of isoprenanes in various types of petroleum[57,60] are listed in Table 4.

Table 4. The contents of isoprenanes in different types of petroleum (wt.%).

Hydrocarbon	Composition	B.p., °C	Petroleum		
			Romashkino	Irkutsk	Western Texas
2,6,10-Trimethylundecane	C_{14}	236.2–237.5	0.2	0.20	0.10
2,6,10-Trimethyldodecane (farmesane)	C_{15}	253	0.2	0.20	0.20
2,6,10-Trimethyltridecane	C_{16}	272	0.2	0.15	0.20
2,6,10-Trimethyltetradecane	C_{17}	285	0.1	0.10	not found
2,6,10-Trimethylpentadecane	C_{18}	300	0.2	0.30	0.06
2,6,10,14-Tetramethylpentadecane (pristane)	C_{19}	331.2–332.5	0.2	0.30	0.50
2,6,10,14-Tetramethylhexadecane (phytane)	C_{20}	352.5–353	0.4	0.50	0.20

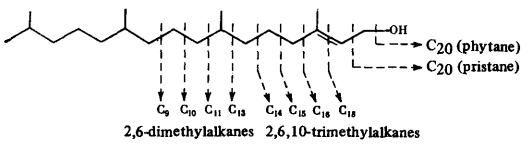
The Table shows that petroleums contain all seven C_{14}–C_{20} isoprenanes (2,6,10-trimethyl- and 2,6,10,14-tetramethyl-alkanes). Their overall content in petroleum is approximately 1.5–2.0% and the amount of each hydrocarbon is approximately 0.2–0.3%. Certain types of petroleum have enhanced contents of pristane (C_{19}) and phytane (C_{20}).

The contents of isoprenane hydrocarbons in four Soviet paraffinic petroleums {Ronashkino, Groznyi, Surgut

(Western Siberia), and Usinsk [tentative transcription] (Ukhta)} have been determined[53], and, apart from the $C_{14}-C_{20}$ hydrocarbons mentioned above, $C_{11}-C_{13}$ dimethylalkanes were found, namely 2,6-dimethylnonane, 2,6-dimethyldecane, and 2,6-dimethylundecane. The overall content of ten $C_{11}-C_{20}$ isoprenane hydrocarbons (2,6-dimethyl-, 2,6,10-trimethyl-, and 2,6,10,14-tetramethylalkanes) was 2–3%.

Thus the petroleums are distinguished by a high content of isoprenanes, the main bulk of which (30–40%) consists of pristane and phytane. The isoprenane contents in petroleum may vary as a function of the overall composition of the petroleum; the largest amounts of isoprenanes are present in paraffinic petroleums. In comparing quantitative contents of isoprenanes in different types of petroleum, account must also be taken of the deviations associated with the characteristics of the methods used to identify the hydrocarbons.

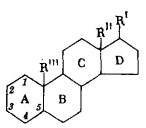
The majority of investigators assume, quite correctly, that the main source of isoprenanes is phytol, an unsaturated aliphatic alcohol, which can be isolated from plant chlorophyll by hydrolysis. Phytane (C_{20}) might have been formed from phytol under appropriate conditions by its dehydration and subsequent hydrogenation of the resulting unsaturated hydrocarbon. The thermocatalytic degradation of phytol itself or phytane (also with subsequent hydrogenation) might have led to the formation of hydrocarbons of this type[57,63,64]. This can be clearly illustrated by the following diagram[64]:



The experimental data for the thermocatalytic degradation of phytol and the composition of the petroleum isoprenanes confirm the validity of the above scheme. However, we may note that some of the isoprenanes might have been formed from the corresponding acids—fornesanoic, phytanic, etc., which have been detected in certain paraffinic types of petroleum.

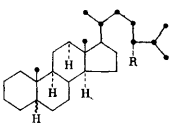
(c) Steranes and Triterpanes

Steranes are saturated tetracyclic hydrocarbons based, like steroids, on the carbon skeleton of cyclopentanoperhydrophenanthrene:



The origin of the steranes detected in petroleum and other caustobioliths is naturally associated with steroids. Steroids are substances of plant and animal origin, which differ in the nature of their substituents (they can contain hydroxy-, keto-, and other groups), the nature of the alkyl groups, and the degree of unsaturation of the tetracyclic nucleus. Thus steranes might have been formed from steroids as a result of a number of chemical transformations, among which reduction (under natural conditions, apparently associated with the disproportionation of hydrogen) should have played a significant role. The biological origin of steranes in fact made it possible to regard them, like isoprenanes, as biological "labels" and to relate the results of the study of petroleum steranes to the general problems of the origin of petroleum.

Steranes have been found in bituminous sedimentary rocks, in oil-bearing shales, in brown coal, and in petroleum. Here special attention must be made of the study of Nigerian petroleum and the oil-bearing shale from the Green River deposit (Colorado), the results of which have been described in reviews[65,66]. Cholestane, ergostane, and stigmastane have been detected in the 458–526°C fraction of Nigerian petroleum:

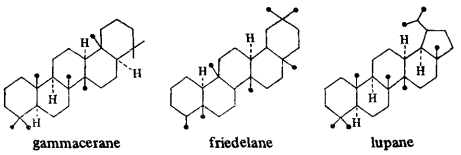


cholestane ($C_{27}H_{48}$), R = H;
ergostane ($C_{28}H_{50}$), R = CH_3;
stigmastane ($C_{29}H_{50}$), R = CH_2CH_3;

The same steranes, as well as lanostane, have been detected in the 450–500°C fractions of the Soviet petroleums from the Gyurgyansk [tentative transcription] and Anastasievsko-Troitsk [tentative transcription] deposits[67].

The hydrocarbon cholestane is an analogue of the steroid cholesterol {$C_{27}H_{46}O$, m.p. 149°C, $[\alpha]_D = -39°$}, which is one of the zoosterols, ergostane is an analogue of ergosterol {$C_{28}H_{50}$, m.p. 165°C, $[\alpha]_D = -130°$}, which is one of the microsterols, and stigmastane is an analogue of stigmasterol {$C_{29}H_{52}$, m.p. 170°C, $[\alpha]_D = -40°$}, which is a well known phytosterol.

A number of analogues of cyclic polyterpenes, namely diterpanes (C_{20}) and triterpanes (C_{30}) have also been detected in petroleum (and other caustobioliths). The pentacyclic triterpanes detected included gammacerane, friedelane, and lupane:



gammacerane friedelane lupane

The presence in petroleum of hydrocarbons with the oleanane (a triterpane) structure has also been established.

Several triterpanes, which are solids melting at relatively high temperatures, have been isolated from Nigerian petroleum[68–70]. The triterpane gammacerane has been isolated from petroleum (and from the bitumen of the Green River shale) and has been thoroughly investigated by mass-spectrometry; it has a melting point of 290°C and $[\alpha]^{21}_{546} = +31.9 \pm 0.4°$.[69] Friedelane has been detected in the petroleums from the Gyurgyansk and Anastasievsko-Troitsk deposits[67]; the triterpanes lupane and moretane have been found in the Baku petroleum from the Surakhany deposit[71]. Furthermore, one should note that an unusual pentacyclic terpane, containing two rings with a spiro-junction, has also been found in Nigerian petroleum[70].

Since steroids and triterpanes consist of condensed alicyclic rings, there is a possibility of their stereoisomerism depending on the *cis*- and *trans*-disposition of the rings relative to one another, similar to the stereoisomerism of perhydrophenanthrene. In natural steroids, ring C occupies the *trans*-position relative to rings B and D, while ring A can have both *cis*- and the *trans*-configuration in relation to ring B. Indeed, it is proved possible to isolate from the Green River shale bitumen two isomers of

cholestane, ergostane, and stigmastane in each case, namely the 5α- and 5β-isomers, depending on the position of the hydrogen atom at the fifth carbon atom. The 5β-isomer (*trans*-junction of rings A and B) usually predominates.

Like steroids, steranes are optically active, since the carbon atoms at the junctions between the rings are arranged asymmetrically. The latter should have led to a large number of stereoisomers. For example, pregnane (a C_{21} sterane) might have 128 isomers due to stereoisomerism alone, and, when two additional asymmetric centres are present (after the introduction of substituents into the ring), the number of possible isomers reaches 512. In reality, steroids are synthesised in nature with considerable selectivity and among the enormous number of steroids only four steric forms of the skeleton, corresponding to the energetically most favourable configuration, have been found. This naturally applies also to steranes.

The optical activity of steranes is of special interest. It has been noted for a long time that petroleums exhibit optical activity, which has served as a basis for the claim that petroleum contains components related to natural organic compounds with asymmetric molecules. The optical activity of petroleum is probably largely caused by the presence in the latter of sterane and triterpane hydrocarbons. More complete data on the optically active substances in petroleum can be found in Louis's paper [72].

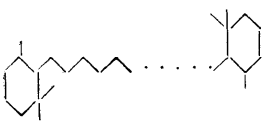
Different methods have been used to isolate and identify steranes and triterpanes. The concentrate of tetracyclic and pentacyclic hydrocarbons is isolated from the corresponding fraction containing branched paraffins and cycloparaffins using separation by thermal diffusion, adsorption chromatography on activated charcoal, gel-penetration chromatography on dextran, etc. Sterane (C_{27}, C_{28}, and C_{29}) and triterpane (C_{30}) concentrates are in their turn isolated from the resulting concentrate by preparative gas–liquid chromatography. Sterane concentrates are sometimes treated with thiourea in order to separate α(*trans*)- and β(*cis*)-steranes [73]. Steranes and triterpanes are identified by analytical gas–liquid chromatography, mass-spectrometry, and chromato-mass-spectrometry. The application of chromato-mass-spectrometry proved to be extremely effective, since the nature of the fragmentation of model steranes and triterpanes under the influence of electron impact had been thoroughly investigated beforehand [66].

It is noteworthy that the preparation of individual steranes and triterpanes, which are absolutely essential model hydrocarbons for their determination in petroleum, involves certain difficulties. The steranes described above (cholestane, ergostane, and stigmastane) are usually obtained from the corresponding sterols, containing double bonds and a hydroxy-group. Sterols are reduced under pressure in an atmosphere of hydrogen in the presence of catalysts or dehydration and hydrogenation are carried out in succession. It is then necessary to maintain reaction conditions such that the resulting saturated hydrocarbon (sterane) has a structure corresponding to that of the initial compound; in other words, one must make sure that there are no rearrangements and especially no rupture of the cyclopentane ring.

As already mentioned, steranes and terpanes have been found in various caustobioliths belonging to different, sometimes extremely ancient geological ages. The bituminous Green River shale, the steranes and triterpanes of which have been most thoroughly investigated, belongs to the Eocene Era in terms of its age (about 52×10^6 years). Steranes and terpanes have been detected in the organic material of more ancient sedimentary rocks in Precambrian deposits (more than 10^9 years old).

It is at present difficult to estimate quantitatively the content of steranes and terpanes in petroleum, since the majority of determinations have been qualitative. One can only note that the extract from the Green River bitumen, consisting of branched paraffins and cycloparaffins (average molecular weight 226–558) consisted to the extent of 10% of hydrocarbons of biological origin, among which there was 10% of isoprenanes, 20% of terpanes, and 20% of steranes. Steranes and triterpanes are probably also present in relatively large amounts in petroleum, at any rate in amounts comparable to that of isoprenanes.

Apart from isoprenanes, steranes, and triterpanes, other biogenic hydrocarbons have been detected in petroleum and other caustobioliths. These include, for example, perhydro-β-carotene [63,66]:



Perhydro-β-carotene ($C_{40}H_{56}$) is a hydrogenated analogue of β-carotene—a plant pigment.

In conclusion of this Section, one must note that further research on biogenic hydrocarbons from different types of petroleum will be useful not only for the extension of our knowledge of the chemical composition of petroleums, but also for the solution of geochemical problems of the origin of petroleum.

V. DETERMINATION OF THE OVERALL STRUCTURE OF INDIVIDUAL GROUPS OF HYDROCARBONS

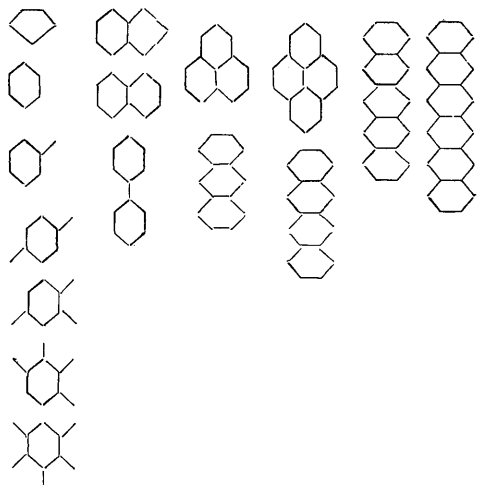
The application of structural-group methods to the analysis of higher fractions of petroleum containing hydrocarbons with relatively high molecular weights was already noted above. These include, for example, the $n-d-M$ method of van Nes and van Westen for the analysis of oil fractions of petroleum [74]. As a result of the extensive application of various methods for the separation of hydrocarbons and the use of spectroscopic research techniques, general and far-reaching characteristics of the structure of different groups of hydrocarbons can now be formulated over a wide range of boiling points.

Paraffinic hydrocarbons and naphthenes can be characterised, cyclopentane and cyclohexane rings can be determined, and the number of rings in the molecule, the number of substituents, and their size can be found from the mass and infrared spectra of the fractions isolated by the appropriate procedure. Mass-spectrometric, ultraviolet spectroscopic, and NMR methods are used to investigate aromatic hydrocarbons. It is then possible to establish the type of aromatic nucleus of the molecule (benzene, naphthalene, phenanthrene, etc.) [75]. The number of rings in polycyclic hydrocarbons and, in only a few instances, their positions have been determined by molecular spectroscopy.

A series of petroleums from different deposits, including fractions boiling at high temperatures (up to 470°C), have been investigated. The structural formulae (fragments) of the hydrocarbons which may be determined by

modern methods are listed below. Polycycloparaffins and mixed hydrocarbons containing cyclohexane benzene rings are shown here by convention in the form of condensed systems.

Cyclanes



Aliphatic chains

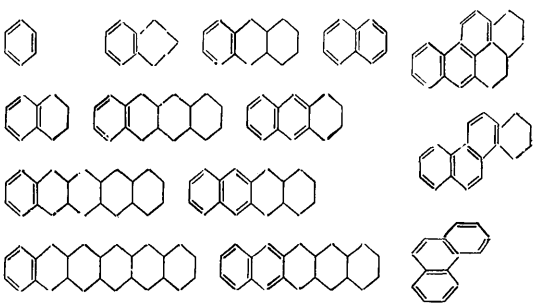
$-CH_2-$

$-CH_2-CH_2-$

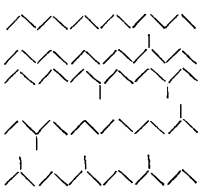
$-CH_2(CH_2)_nCH_2-$

$-CH_3$

Aromatic hydrocarbons



Alkanes



The general characteristics of petroleum hydrocarbons determined by the most modern research techniques are of considerable practical importance apart from their theoretical significance, since the results obtained can be used to assess the fractions processed into fuels and lubricating oils. At the same time, the general characteristics of the petroleum constitute a basis for subsequent more far-reaching research on specific types of hydrocarbons.

VI. CERTAIN REGULARITIES IN THE HYDROCARBON COMPOSITION OF PETROLEUM

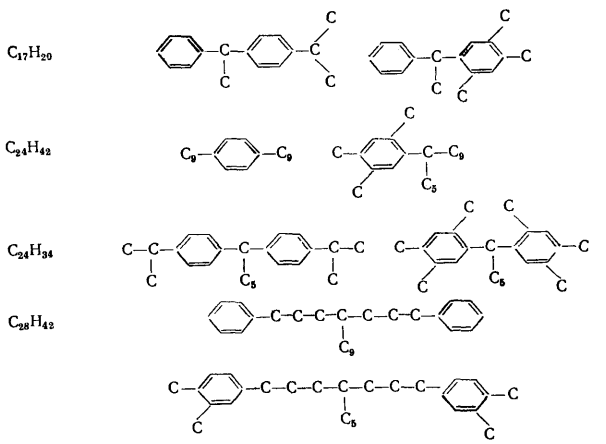
The study of hydrocarbons from the middle and higher fractions of petroleum is extremely difficult owing to the presence in the latter of a large number of isomers. For this reason, chemists have endeavoured for a relatively long time to find regularities in the contents and distribution of various types of petroleum hydrocarbons; such regularities should be observed if the composition of petroleum is determined by certain general conditions governing its genesis from more or less similar organic material. The regularities would naturally facilitate also the investigation of the chemical composition of petroleum.

For example, one can reach an extremely important general conclusion about the composition of aromatic hydrocarbons in petroleum fractions. The studies by the American Petroleum Institute showed at one time that the hydrogenation of synthetic polycyclic hydrocarbons consisting of condensed benzene rings leads to the formation of cyclanes with a reduced viscosity and an enhanced viscosity index, while hydrogenation of aromatic hydrocarbons containing isolated benzene rings actually leads to an increase of viscosity and a decrease of the viscosity index[16,74,76]. It was established at the same time that the hydrogenation of narrow oil fractions leads to an appreciable reduction of their viscosity, which is greater the larger the number of benzene rings in the hydrocarbons. On this basis, it was concluded that polycyclic aromatic hydrocarbons in the oil fractions of petroleum virtually all belong to different kinds of condensed systems (see Rossini et al.[16], p. 327). For example, alkylated derivatives of anthracene, phenanthrene, and naphthacene are such "exceptional" types of polycyclic hydrocarbons, the hydrogenation of which results in a decrease of viscosity. However, it is known that naphthalene homologues containing long alkyl groups ($C_{18}-C_{26}$) behave on hydrogenation like the majority of aromatic hydrocarbons—their viscosity increases. Thus not all aromatic hydrocarbons with condensed benzene rings exhibit a decrease of viscosity on hydrogenation.

The study of the physicochemical properties of about fifty hydrocarbons, namely cyclohexane and benzene homologues, polycyclic (mainly bicyclic) C_{24} and C_{28} hydrocarbons (corresponding to the oil fractions of petroleum) provided grounds for a new interpretation of the structure of aromatic hydrocarbons in higher petroleum fractions[77,78]. It has been established that aromatic hydrocarbons containing methyl groups in the ring are in general anomalously viscous compared with other alkyl-substituted aromatic hydrocarbons having the same molecular weight. Aromatic hydrocarbons containing methyl groups have higher viscosities and refractive indices, smaller molecular volumes, and higher heats of evaporation. Table 5 lists the physicochemical characteristics of certain alkylbenzenes.

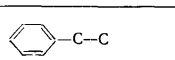
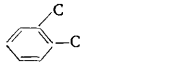
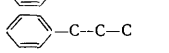
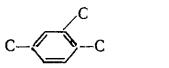
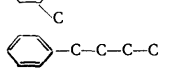
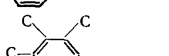
Similar relations have been obtained also for hydrocarbons with a different structure, differing in the number

of methyl groups in the molecule; some of these are indicated below:



The increased viscosity of aromatic hydrocarbons with methyl groups in the benzene rings is due to increased intermolecular interaction (a relatively smaller molecular volume and a higher heat of evaporation). On hydrogenation, such hydrocarbons give rise to cyclanes, the viscosity of which is lower rather than higher than that of the initial aromatic hydrocarbons.

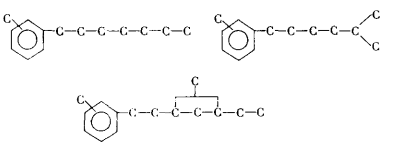
Table 5. Physicochemical characteristics of aromatic hydrocarbons.

Formula	Structure	ρ_4^{20}	n_D^{20}	Molecular volume, ml	Heat of evaporation, kcal mole^{-1}		Viscosity, cP	
					50° C	0° C	50° C	0° C
C_8H_{10}		0.8670	1.4959	122.5	9.70	10.35	0.48	0.87
C_8H_{10}		0.8802	1.5055	120.6	10.05	10.63	0.56	1.06
C_9H_{12}		0.8620	1.4920	139.5	10.65	11.18	0.58	1.18
C_9H_{12}		0.8758	1.5048	137.2	11.06	11.64	0.72	1.32
C_9H_{12}		0.8944	1.5139	134.6	11.31	11.86	0.82	1.82
$C_{10}H_{14}$		0.8601	1.4898	155.9	11.67	12.29	0.68	—
$C_{10}H_{14}$		0.8904	1.5130	150.7	12.77	13.35	0.82	1.86

Thus the decrease of viscosity on hydrogenation of petroleum fractions indicates primarily the presence in these fractions of considerable amounts of methyl-substituted aromatic hydrocarbons (including polycyclic condensed aromatic hydrocarbons). The cause of this characteristic of methyl-substituted aromatic hydrocarbons is unknown and requires separate examination. Here one can only note that the phenomenon of hyperconjugation has been observed for molecules containing methyl groups linked to the benzene ring, which may be reflected also in certain features of their physicochemical properties.

The conclusion reached concerning the structure of aromatic hydrocarbons in petroleum has been confirmed also by certain data obtained in direct studies on petroleum hydrocarbons. For example, C_{10} benzene homologues with methyl groups predominate among the aromatic hydrocarbons of Romashkino petroleum. On passing to higher petroleum fractions, the benzene homologues may contain also higher alkyl groups. According to non-Soviet investigators, hydrocarbons containing methyl groups and one larger alkyl group, do indeed predominate in the alkylbenzenes in petroleum [33].

Thus aromatic hydrocarbons, the alkylbenzenes in the light gas oil from American petroleum boiling in the range 230–305°C (from the Ponca deposit), have been investigated [33]. The light gas oil constituted 70% of the petroleum and the aromatic hydrocarbons isolated constituted 19.6% of the light gas oil. Adsorption chromatography on silica gel, adsorption on molecular sieves, and gas–liquid chromatography were used to isolate and separate the hydrocarbons; low-voltage mass-spectrometry and NMR were employed to determine the structure of the "average" molecule. It was established that the C_{13}–C_{15} alkylbenzenes in the light gas oil consist mainly of di- and trisubstituted derivatives. The disubstituted alkylbenzenes usually contain one methyl group and one long C_7 or C_8 alkyl group in the 1,3- and 1,2-positions. The typical dialkylbenzenes can be represented as follows:



Two possible locations of the methyl group in the alkyl chain are indicated in the last formula.

A similar study of aromatic hydrocarbons containing a single benzene ring, isolated from the heavy gas oil and the light oil distillate (305–405°C) of the same petroleum, showed that these distillates contain approximately 75% of C_{24}–C_{26} alkylbenzene with a single long alkyl group and several, sometimes three or four, methyl groups; some of these alkylbenzenes can also contain ethyl groups [34]. It is interesting to note that optically active C_{25}–C_{26} hydrocarbons of the type of tetra- or penta-cyclanobenzenes with $[\alpha]_D^{25} = 6$ were detected in the same distillates.

Systematic research on petroleum hydrocarbons carried out in accordance with the programme of the American Petroleum Institute Project 6 permitted a number of conclusions concerning the hydrocarbon composition of different types of petroleum. Particular mention should be made of the conclusion that the relative quantitative contents of hydrocarbons within the limits of each type of hydrocarbons (straight-chain paraffins, branched paraffins, alkylcyclopentanes, alkylcyclohexanes, and alkylbenzenes) are approximately the same in different types of petroleum. Certain specific instances of this general conclusion have already been noted.

We shall now consider the possible cause of the above similarity of the compositions of different types of petroleum, namely whether this generalisation is applicable only to petrol fractions, whether it can be extended also to hydrocarbons with higher molecular weights, and whether it is valid for petroleums of sharply different ages.

It was noted a comparatively long time ago that petroleum consists of an equilibrium mixture of hydrocarbons formed as a result of various catalytic reactions occurring, for example, under the influence of aluminosilicates

(natural clays) at certain temperatures near 150–250°C. Thus Frost [79] and Obryadchikov [80] established for the first time that the contents of cyclohexane and methylcyclopentane in a wide variety of petroleums corresponded to their equilibrium concentrations at temperatures in the range ~150° to 300°C.

The relative equilibrium concentrations of cyclohexane and methylcyclopentane (the K_e values) at different temperatures between 150° and 300°C are as follows:

T, °C	K_e
150	1.38
200	0.89
250	0.63
300	0.48

Approximately the same relations are observed also for the contents of both hydrocarbons in different types of petroleum. The knowledge of the temperatures in the formation of petroleum with allowance for the possible transformations of hydrocarbons (or the initial compounds) under the influence of natural catalysts of the aluminosilicate type seemingly might have accounted for the differences between the chemical compositions of different types of petroleum and might have led to the discovery of new possibilities for the investigation of the chemical composition of petroleum itself. Having established the equilibrium proportions of the hydrocarbons within the limits of the particular group at a given temperature, for example at 200°C, and having determined the thermodynamically most stable structures of the hydrocarbons, it might be possible to predict beforehand their contents and proportions in petroleum; this would be particularly useful in the determination of the contents in petroleum of the structural and steric isomers of different types of hydrocarbons.

There are a number of publications on the stereochemistry and relative stabilities of hydrocarbons [46,64,81,82]. The stereochemistry and equilibrium proportions (relative stabilities) of a series of C_7–C_9 alkylcyclopentanes, C_8–C_{12} alkylcyclohexanes, various C_8–C_{10} bicyclanes, C_{11}–C_{12} alkyldecalins, and C_{11}–C_{13} alkyladamantanes have now been investigated. The conformational characteristics of alkanes and cyclanes are being widely studied.

The results obtained are undoubtedly valuable for the characterisation of certain types of hydrocarbons and for their determination in petroleum. For example, in many instances it has indeed been found that the thermodynamically most stable bicyclanes predominate in petroleum.

The study of the relative stabilities of the isomeric forms of methylbicyclo[3,2,1]octanes and methylbicyclo-[2,2,1]octanes in synthetic model hydrocarbons [83] permitted the subsequent identification of nine methylbicyclo[3,2,1]-octanes and methylbicyclo[2,2,2]octanes in Soviet petroleums of different origins. It was established that, among identified hydrocarbons of the 125–150°C fraction of the Gryazevaya Sopka petroleum [84] and the 70–180°C fraction of Balakhansk petroleum [85], the most stable 1-methylbicyclo[3,2,1]octane is present in the largest amount, while the contents in the petroleums of the relatively less stable 2,3- and 6-substituted methylbicyclo[3,2,1]octanes are smaller. There are other examples of this kind.

Thus the above type of research on hydrocarbons, based on the determination of the equilibrium proportions of hydrocarbons and their relative thermodynamic stabilities at specific temperatures, yields valuable evidence for subsequent direct studies on petroleum hydrocarbons.

At the same time one must note that the limits of the applicability of this approach to the investigation of petroleum hydrocarbons are still not clear. It is not known which types of hydrocarbons are present in petroleum in equilibrium proportions corresponding to a specific temperature. Nor can the temperature limits corresponding to the formation of petroleum hydrocarbons be regarded as rigorously established. The thermodynamic stability of hydrocarbons depends to a large extent on temperature.

Presumably petroleum contains three groups of hydrocarbons. The first includes biogenic hydrocarbons which retain the structure of the initial natural products, for example, isoprenanes, steranes, triterpanes, and other still unknown hydrocarbons, the proportions of which may not, of course, correspond to equilibrium. They are determined by the contents of the natural products in the initial material from which petroleum originated. The hydrocarbons whose proportions correspond to equilibrium (at a specific temperature) may be included in the second group; the third group consists of hydrocarbons formed as a result of a number of transformations which do not retain the initial structure and whose composition does not correspond to equilibrium for one reason or another, which has not as yet been elucidated. One must bear in mind that the proportions of hydrocarbons might have altered also as a result of secondary processes (adsorption on rocks, particularly during the migration of petroleum, etc.).

Further research on biogenic petroleum hydrocarbons and the determination of the types of hydrocarbons whose proportions may correspond to equilibrium is necessary; this requires in its turn further far-reaching investigation of the hydrocarbon composition of petroleum as a whole. Such research will make it possible also to obtain more refined data on one of the most important problems in the geochemistry of petroleum—the problem of the temperatures at which petroleum was formed.

The discussion of these aspects of the hydrocarbon composition of petroleum frequently involved certain problems which have some bearing on the origin of petroleum. It is becoming increasingly necessary that investigators concerned with the study of the chemical composition of petroleum should examine new data on its composition from the standpoint of general modern ideas about its origin. The most important generalisations will probably be made on these lines.

The present review has dealt only with certain problems associated with the investigation of petroleum hydrocarbons and petroleum fractions. The extremely important questions in the field of petroleum chemistry, such as the investigation of the chemical composition of the oil fractions and lubricating oils, the study of high-molecular-weight compounds (including hydrocarbons) in petroleum, and others require separate consideration.

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