

H. LUIK**THERMAL DESTRUCTION METHODS
FOR CHARACTERIZING KEROGEN****Abstract**

Thermal destruction (fragmentation) in a variety of its methods is the main technique for analytical and geochemical characterization of oil shales. The yield of the fragmentation products as well as their molecular and structural distribution and degree of conversion can be very different. For that reason there arises the inescapable question about the alterations which will occur in the composition of the products when using different thermal destruction methods and just what kind of general strategy should be used for the analytical investigation of sedimentary rocks.

In this article, data for gas extraction and hydrogenation of two shales are provided. These results are from tests with variables optimized in order to achieve maximum yield of liquid product, as compared to results from Fischer Assays. It is shown that 97 % conversion of kukersite kerogen into benzene-soluble liquid product is feasible with CO_2 extraction (this process achieved solid-residue free product and with only 3% by-product gas formation). The Dzham shale (Uzbekistan) does not liquefy as readily, providing a maximum yield of benzene-soluble product of only up to 55% of the feed kerogen. These tests used hydrogen as produced from HCOONa .

Distribution of heteroelements (O, N, S) among destruction products depends on the method of thermal destruction. It was shown to be quantitatively different: as a result of semi-coking, 50 % of kukersite and 69 % of Dzham kerogen heteroelements were transformed into gaseous products, but using gas extraction or hydrogenation under the mild conditions (360 °C, 4-6 hours) to destruct Dzham shale, 86 % of heteroelements remain in the kerogen and they do not combine with the gaseous or liquid products.

Conversion rates for liquefaction of different kerogens can vary, even when they are treated under the same conditions. As a result, non-comparable products are obtained. This precludes a successful categorization of kerogens. Yield of the liquid product with gas extraction is considerably higher than with a semi-coking process. This is caused by retention of intermediate fractions - asphaltenes and highly-polar malthenes in the extract. With further thermal treatment the asphaltenes and highly-polar compounds, which are thermally unstable, form gas and coke. The asphaltene content is highest in the extract and lowest in the semi-coking oil (49 and 3 % for Kukersite and 7 and 0 % for Dzham shale, respectively). A significant observation is that the produced alkenes and homologous series of *n*-alkanes, *n*-alkanones and alkylarenes have characteristics which are different than those in the primary product. As a result of continual formation and accumulation of identical primary and secondary compounds during thermal treatment, similarities in the concentrations of those compounds reflect the degree of destruction of the kerogen and its fragments. But they are not characteristic of the kerogen composition.

Char produced from Dzham kerogen by gas extraction or hydrogenation, unlike semi-coke, is capable of producing liquid product in higher yield. This potential for additional liquid product can be realized under special experimental conditions. Therefore, effective

liquefaction of different kerogens can be accomplished using a multi-stage thermal destruction procedure.

It is shown that numerous essential differences in the composition of the liquid products from gas extraction, hydrogenation and semi-coking are mainly caused by different yields of liquid products. This is based on tests using physico-chemical, chromatographic and infrared spectroscopic methods.

To reflect the original kerogen structure and to understand the changes taking place during destruction, all structural units and fragments of kerogen decomposition should be taken into account. It is shown that the higher the yield of liquid product, and the value of physico-chemical parameters (such as d_{20}^{20} , n_D^{20} , and M), the higher the content of asphaltenes and the concentration of odd carbon-number homologues in the fractions of *n*-alkanes, alkanones and *n*-alkylarenes. The value of the H/C ratio approaches that of the source kerogen. Results of the quantitative interpretation of infrared spectra show that the concentrations of -OH and -C=O functional groups increase in conjunction with $-(CH_2)_n$ - concentrations, as the yield of liquid product increases.

The yield and extent of destruction of liquid product from gas extraction, hydrogenation and pyrolysis is very different and ambiguous. Ideas about structure are achieved when either a single method is used or various methods are applied in parallel.

A stepwise scheme for effective thermal destruction of kerogen is suggested in order to optimize kerogen transformation into the liquid product. Hence, the liquid product contains the identity of the source kerogen within its composition.

The mechanism of kerogen destruction could be controlled by using a multiple-step destruction process on the intermediate compounds.

Various kerogens could be adequately categorized on a common basis: equal (and maximal) yield of liquid product.

Up to now, thermal destruction in its variety of applications, has been most commonly applied method for characterization and geochemical investigation of kerogen - fossilized, insoluble organic matter of caustobioliths. The reason for the success of thermal treatment is that it transforms the kerogen into soluble and volatile products. This occurs to a greater or lesser extent, depending upon the treatment conditions. The less common compounds from dia- and catagenesis of kerogen could be detected and identified using state-of-the-art instruments.

All destruction products must be taken into account in order to adequately reflect the source kerogen and its complicated structure. Initial fragments ruptured from the kerogen have subsequently undergone alterations and have been distorted to varying degrees during thermal destruction. Thus, they do not provide meaningful information. The best thermal destruction methods used for the characterization of kerogen are those which yield to a maximal extent liquid product as the most informative one, and to a minimal extent gaseous and solid products as poorly informative ones. Such high-yield processes include, semi-coking by Fischer Assay, gas extraction in dense vapour media, and hydrogenation for kerogen liquefaction. Advantages and shortcomings of these methods are described by Klesment (1984) [1].

The liquid product of thermal destruction is thus the main bearer of kerogen identity. It is a complex mixture of kerogen-derived fragments and complex chemical compounds which have been formed from these intermediate fragments. The composition of this mixture depends upon the conditions of thermal destruction and the characteristics of the kerogen under study.

The aim of the present work is to compare the liquid products obtained from kerogen by different thermal destruction methods. This will show how each method alone, and methods applied in combination, could reflect the complicated structure of kerogen. This work also shows how the methods could complement each other and what kind of distortions have been transferred into the liquid products.

1. Experimental

Estonian kukersite and Dzham shale (Uzbekistan) kerogens were studied. Their genesis and chemical composition are presented in Table 1. The various thermal destruction methods including treatment conditions are identified in Table 2.

The liquid product analysis was patterned after the well-known analytical technique described by Klesment (1974) [2].

Table 1. Comparative Characterization of Shales Analyzed

Parameter	Kukersite	Dzham shale
Geological period of formation	O ₂	P ₂
Kerogen content, wt. %	35.5	31.0
C _{organic} , wt. %	27.4	18.8
Heteroelements, wt. %	4.3	9.7
H/C in kerogen	1.47	1.60
Mineral matter	carbonaceous	clayey

Table 2. Parameters of Thermal Destruction for Obtaining the Maximal Yield of Liquid Product from Kukersite (numerator) and Dzham Shale (denominator)

Parameter	Gas extraction in CO ₂	Hydrogenation <i>in situ</i> with HCOONa
Autoclave volume, cm ³	20/20	20/20
Temperature, °C	350/360	370/360
Duration, h	4/6	4/4
Autoclave free volume, %	64/45	45/45
Shale/CO ₂ or HCOONa ratio, g/g	1:3/1:2	1:2/1:2

2. Results and Discussion

2.1. Indications of kukersite and Dzham shale kerogen structures based on liquid product yields from liquefaction

Thermal destruction of kerogen yields gaseous and solid by-products in addition to the desired liquid product. The proportions of these products depend on the character of the liquefaction process and the conditions used (see Table 3).

Table 3. The Yield of the Thermal Destruction Products and Composition of Liquid Product (kukersite - numerator, Dzham shale - denominator), %*

Product	Semicoking** in Fischer assay	Hydrogenation <i>in situ</i> with HCOONa	Gas extraction with CO ₂
	1	2	3
Gas	23/32	15/4	3/5
Liquid	61/28	78/55	97/44
Solid residue	16/40	7/40	0/51
Composition of the liquid product:			
Alkanes and alkenes (TLC-1)***	7/5	7/13	7/6
Monocyclic alkylarenes (TLC-2)	4/1	2/2	1/2
Polycyclic (alkyl)arenes (TLC-3)	9/13	4/8	4/8
Alkanones-2 and dialkylalkanones (TLC-4)	15/4	5/11	8/8
High-polar compounds (TLC-5, start line)	23/5	33/17	28/13
Asphaltenes	3/0	27/4	49/7

*Percentage here and later on is given on kerogen basis.

**Dzham shale [3].

***Thin-layer chromatography, the number indicates the sequence of fractions on the plate in descending order.

Up to now, it has been considered that coke and gas formation is unavoidable when applying thermal destruction methods. The presumption was made that all of the numerous thermal methods must be used in order to provide a thorough characterization of the kerogen. Each method defined some aspect of the kerogen structure. For categorization of different types of kerogen on a common basis, similar conditions of liquefaction must be used. The expectation was based on the supposition that coke and gas are not formed from the same fragments of kerogen under different destruction conditions.

However, among the methods of thermal destruction, there is one which brings about an unique distribution of kerogen among the products. This can be seen in Table 3. The CO₂ extraction method leads to the fast, and almost total, conversion of kukersite kerogen into liquid product. This occurs at a temperature close to that of kukersite thermal bituminization.

Thus, another hypothesis could be presented. An adequate characterization of kerogen does not necessarily depend on applying the utmost number of different destruction methods but on the possibility to transform the product fragments, *in corpore*, into liquid product. In this case one will obtain and rally into liquid product compounds associated not indirectly but directly and mutually. To characterize different kerogens from the liquid product composition, as proposed in this work, one must achieve common (maximum) yields of product and not necessarily common fragmentation conditions.

Which one of the presumptions proposed above would be more veracious will be seen below in this paper.

2.2. General characteristics and elemental composition of the liquid product

Liquid products of kerogen thermal destruction are often characterized by several physico-chemical parameters. The basic parameters for liquid products obtained from kukersite were defined. As can be seen in Fig. 1, there clearly exists a proportional dependence between the yield of the liquid product and its density (d_{20}^{20}), refractive index (n_D^{20}) and molecular weight (M): the higher the yields, the higher the values of those parameters. This also means that at higher yields of liquid product, a closer and more adequate relationship with source kerogen could be obtained. The respective heavy products contain more initial fragments of kerogen.

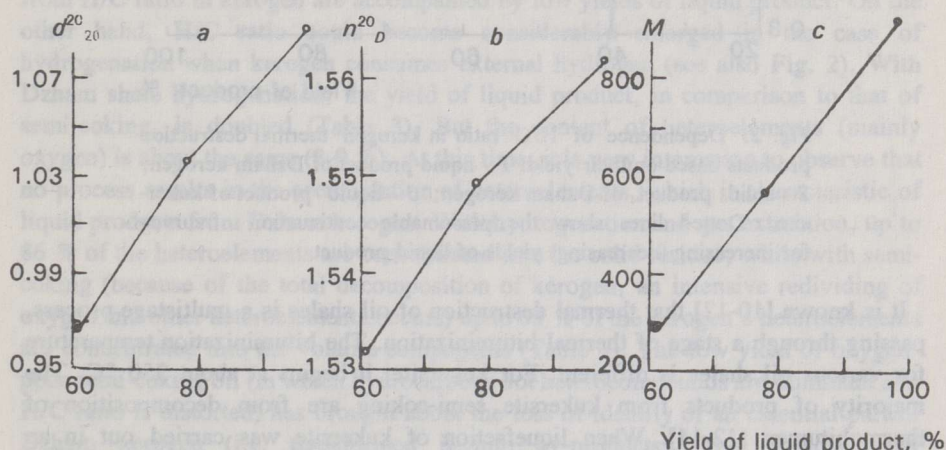


Fig. 1. Dependence of liquid product yield from kukersite thermal destruction as a function of (a) density, (b) refractive index, and (c) molecular weight

It must be mentioned that liquefaction of 90 % or more of the kerogen, even with gas extraction, is a complicated problem and sensitive to applied conditions. Four main factors (temperature, duration, density and origin of solvent) influence the efficiency of gas extraction [4-6]. The first three of the above-mentioned factors are the physical ones and, in case when kerogens are liquefied in closed vessels for obtaining maximum yield of liquid product, are conjuncted with each other [6]. For maximum transformation of kerogen into liquid product with extraction, it must be taken into account and the optimum conditions must be found in order to effectively apply the process.

The conditions established for effective thermal destruction of kukersite are not suitable for other shales. Kerogens rich in heteroelements ($O+N+S = 20-33\%$) are transformed into liquid products - oil, hydrogenisate, extract - to a limited degree

because their heteroelements are only minimally transformed into liquid product. This affects Dzham kerogen (see Table 4) as well as Sysola and Krassava kerogens, per investigations by Urov, et al., Luik and Klesment, and Nappa, et al. [3, 7-9].

Figure 2 shows the dependency of H/C ratio in the liquid product on its yield from Dzham kerogen (curve 1) and kukersite (curve 3). Various thermal destruction methods were used. One can see that the curves vary, depending on the content of heteroelements and H/C ratio in liquid products (see Table 4 and Fig. 2). It could be claimed that information about the kerogen structure, as based on the analysis of liquid products, is not adequate.

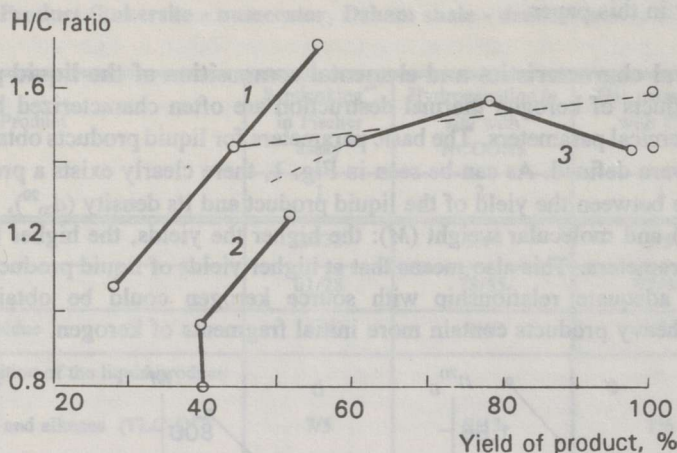


Fig. 2. Dependence of H/C ratio in kerogen thermal destruction products based on their yield: 1 - liquid product of Dzham kerogen; 2 - solid product of Dzham kerogen; 3 - liquid product of kukersite. Dotted lines show the presumable continuation of curves for increasing (decreasing) yields of liquid product

It is known [10-12] that thermal destruction of oil shales is a multistage process, passing through a stage of thermal bituminization. The bituminization temperature for various oil shales is different. For kukersite, it begins at about 350 °C. The majority of products from kukersite semi-coking are from decomposition of thermobitumen [12-14]. When liquefaction of kukersite was carried out in an autoclave at 350-370 °C, then changes in the composition of thermobitumen, if they took place at all, were not caused by temperature but by the residence time factor and the type of extractant which was present. In the case of kukersite, the value of the H/C ratio, for the so-called "primary" and "secondary" products of thermal destruction (thermobitumen and semi-coking oil), is 1.45-1.47. This value is close to that of kerogen (1.45). During semi-coking, elements in the kerogen (H, C, O) are first transferred into the thermobitumen and then channelled disproportionately into its decomposition products - oil, gas and semi-coke. Oil as the product of semi-coking aimed at includes only 40 % of the source kerogen's oxygen. Thus, various liquid forms of kerogen in different yields - bitumens, oils and extracts of specific process origin - having modified elemental proportions and being more or less distorted during destruction stages (see the molecular weight curve in Fig. 1) are not of equal value in reflecting the structure of kerogen. Kerogen-derived thermobitumen, or extract, obtained in 97% yield reflect kerogen structure more adequately than the thermobitumen-derived oil, gas or solid residue could ever do.

Table 4. Content of Heteroelements (O+N+S) in Thermal Destruction^a Products of Kukersite and Dzham Kerogen

Product	Kukersite			Dzham kerogen		
	1	2	3	1	2	3
Gas	50	10	1	69	5	4
Liquid	40	77	99	8	9	10
Solid	10	13	0	23	86	86

^aThe method of destruction find in accordance with the number in Table 3.

In comparison with kukersite, Dzham shale kerogen liquefies very little and the yield of liquid product is considerably less. In Figure 2, one can see that the H/C ratio versus yield of liquid product curve obtained for Dzham kerogen ends at the point (55 %) where the kukersite curve has just begun (60 %). It is logical to suppose that the missing parts of the curves - the end of one and the beginning of the other curve - could be interpolated by dotted lines. That is, major deviations from H/C ratio in kerogen are accompanied by low yields of liquid product. On the other hand, H/C ratio could become considerably enlarged in the case of hydrogenation when kerogen consumes external hydrogen (see also Fig. 2). With Dzham shale hydrogenation, the yield of liquid product, in comparison to that of semi-coking, is doubled (Table 3). But the content of heteroelements (mainly oxygen) is about the same (8-9 %). At this time, it is very interesting to observe that no process results in the accumulation of heteroelements, which is characteristic of liquid products from Dzham kerogen. With hydrogenation and gas extraction, up to 86 % of the heteroelements are concentrated into the solid residue, while with semi-coking (because of the total decomposition of kerogen, an intensive redividing of oxygen and other heteroelements occurs) up to 69 % of the kerogen's heteroelements are concentrated into the volatile components (Table 4). The low yield of oxygen-poor semi-coking oil (in which hydrocarbons not heterocompounds are dominant and H/C ratio is distorted) has brought about the loss of identity of an essential part of Dzham kerogen (i.e. transformed it into by-products). The abundance of heteroelements is a specific feature of Dzham shale and, in dependence on the thermal destruction method used, expressed not in liquid product, but in either the gas or solid residue composition.

2.3. Additional liquid product yield from the solid residue

The solid residue (char) of Dzham kerogen, formed from hydrogenation or gas extraction (unlike the semi-coke) represents incompletely decomposed kerogen. This has maintained its characteristic oxygen-containing structures. It is noticeable (Fig. 2) that H/C ratio in solid residue has a maximum value at the maximum yield of char, 1.25 at 51 %. An H/C ratio of 1.25 surpasses the value for several shales and brown coals (Carpathian menilite, Kenderlyk shale, liptobioliths from Tkibuli and Lipovetsk deposits). Each of these comparative materials yields a considerable amount of liquid product upon thermal destruction, in spite of their low H/C ratio. Applying liquefaction in inert media, these shales yield 9-17 %, and the liptobioliths,

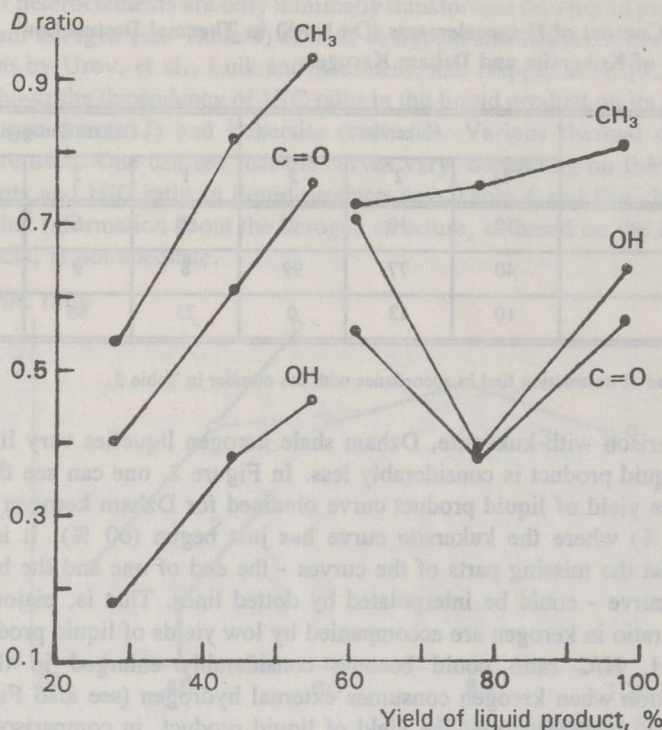


Fig. 3. Dependence of the (1) -CH₃, (2) -C=O, and (3) -OH functional group content as a function of the yield of liquid product of thermal destruction for both Dzham (curves on the left) and kukersite (curves on the right) kerogens, as developed from quantitative infrared spectroscopic analysis

24-34 %. With hydrogenation up to 70 % liquid product yield can be achieved [15]. Comparison of the H/C ratios leads to the conclusion that chars are candidates for yielding an additional amount of solubles upon supplementary thermal treatment. Indeed, our recent results confirm that conclusion [16]. In that regard, in analogous cases to Dzham kerogen investigated in this paper, a stepwise mode of destruction is proposed to liquefy kerogen more completely. This would use both internal and external combination of individual methods of extraction, hydrogenation and semi-coking. The proposed approach would maintain the structure of the source kerogen within the composition of the liquid product. This would avoid transformation into gaseous or solid by-products. With consecutive processing, using various methods of thermal destruction successively, the number of steps (methods) for effective kerogen liquefaction depends on the sequence and kinds of steps used. Instead of a series of different methods, multiple applications of the same method could be put to use as well, e.g. extraction at several temperatures or with different solvents. It is impossible to give an universal recipe for best results, but it should be obvious that the semi-coking step should be left for last. This is the case since semi-coke, unlike char, is not convertible into liquid product.

Kerogens, as well as their fragments of decomposition, have different thermal stability and that is why liquefaction at common conditions never provides equal

yields nor comparable data. As a result of gradual destruction, summarizing the yields of liquid product in the range of 90-97 % would be possible for all kerogen types. At the same time, pathways of destruction would be controlled, avoiding intensive gas and coke formation. This would allow detection of their precursors. In this manner, different kerogens might be investigated on a common basis (equal yields).

2.4. Chemical group composition of the liquid product

Infrared spectroscopy was used to characterize the content of chemical functional groups in liquid products. An attempt was made to identify the source of additional liquid product yield using quantitative interpretation of the infrared spectra [17]. As an example for Dzham kerogen, increasing yield of liquid product and oxygen content had a corresponding marked increase in the content of -OH and OC-groups (Fig. 3 and Table 4). Presumably, during kerogen decomposition, a higher yield of liquid is produced at the cost of phenols, alkanones and other oxygen compounds. This results from the increase in terminal -CH₃ groups. In the case of kukersite, values of *D* (Fig. 3) (which characterize the relationship between carbonyl and carboxyl groups to long-chain alkyl groups) are the same for semi-coking oil and extract. This supports the concept of an equi-proportional formation of those groups during the destruction in inert media. During thermochemical destruction, the chemicals present in the autoclave and the operating conditions, are both important parameters. During mild *in situ* hydrogenation (with HCOONa as the H-donor) the primary carbon skeletons of the compounds are maintained, though the content of functional groups containing oxygen decreases slightly. This is based on an analysis of -CH₃/CH₂, and is contrary to the results with catalytic destructive hydrogenation at high hydrogen pressure.

The group composition of compounds in liquid products is presented in Table 3. We can see that the content of aliphatic hydrocarbons derived from kukersite is 7 %, irrespective of the yield of liquid product and method used. This confirms their formation in an initial stage of the treatment. Otherwise, the numerical value of that constant would be noteworthy provided that the total potential of kukersite would have been expressed. In the case of Dzham kerogen, the concentration of aliphatic hydrocarbons in liquid products from semi-coking or extraction is 5-6 %, while with hydrogenation that number exceeds 13 %. With increasing the yield of liquid product on hydrogenation by 11 % concentration of mono- and polycyclic arenes in it does not alter in comparison with the results obtained on extraction in CO₂. An increase in the share of aliphatic compounds with long straight chains (alkanes and alkanones) is a peculiarity to Dzham kerogen during the final stage of thermal destruction in an hydrogen atmosphere. A common characteristic for both kerogens is that the content of asphaltenes increases with increasing liquid product yield (Table 3). Whereas high yields of liquid product were obtained at low-temperature and prolonged hydrogenation and gas extraction processing, asphaltenes (as well as the other highly polar compounds) decompose upon semi-coking at elevated temperatures yielding various secondary products. Liquid products of semi-coking contain less alkanones but considerably more aromatic hydrocarbons.

In the composition of liquid products of extraction, hydrogenation and semi-coking the specificity of each method rather than the virtual potential of kerogen to produce whatever compounds mentioned above is expressed.

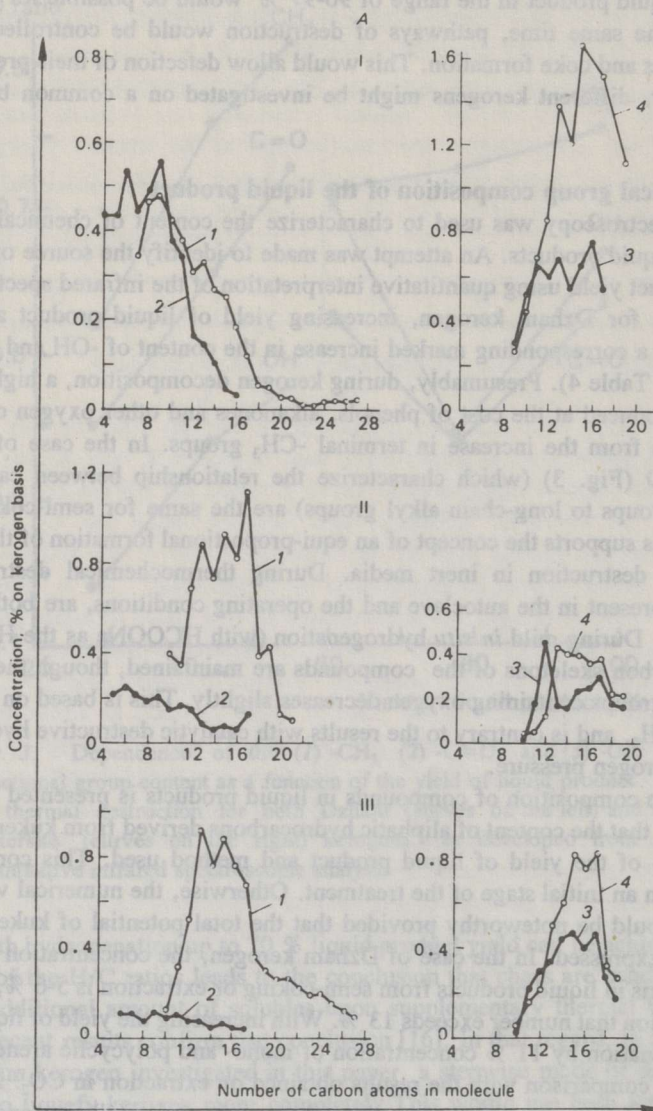


Fig. 4A. Concentration (on a kerogen basis) of (1) *n*-alkanes, (2) alkylarenes, (3) 2-alkanones, and (4) dialkylalkanones (having carbonyl group close to the center of the chain) for: (I) 61 %, (II) 78 %, and (III) 97 % yield of liquid product from kukersite thermal destruction

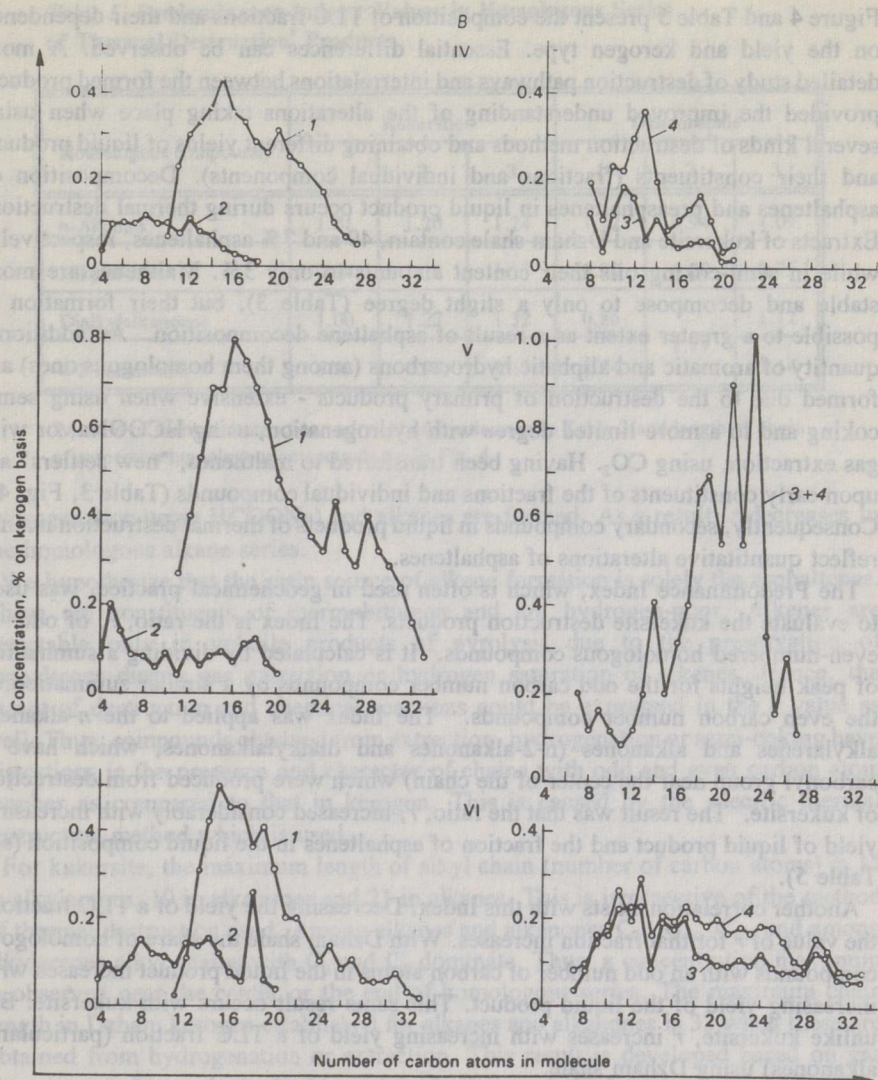


Fig. 4B. Concentration (on a kerogen basis) of (1) *n*-alkanes, (2) alkylarenes, (3) 2-alkanones, and (4) dialkylalkanones (having carbonyl group close to the center of the chain) for: (IV) 28 %, (V) 44 %, and (VI) 55 % yield of liquid product from Dzham kerogen thermal destruction

2.5. Composition of liquid products and the role of asphaltenes and other intermediates on distribution of homologous compounds

Figure 4 and Table 5 present the composition of TLC fractions and their dependence on the yield and kerogen type. Essential differences can be observed. A more detailed study of destruction pathways and interrelations between the formed products provided the improved understanding of the alterations taking place when using several kinds of destruction methods and obtaining different yields of liquid products and their constituents (fractions and individual components). Decomposition of asphaltenes and preasphaltenes in liquid product occurs during thermal destruction. Extracts of kukersite and Dzham shale contain, 49 and 7 % asphaltenes, respectively, while in semi-coking oils their content amounts to only 3 %. Malthenes are more stable and decompose to only a slight degree (Table 3), but their formation is possible to a greater extent as a result of asphaltene decomposition. An additional quantity of aromatic and aliphatic hydrocarbons (among them homologous ones) are formed due to the destruction of primary products - extensive when using semi-coking and to a more limited degree with hydrogenation, using HCOONa , or with gas extraction, using CO_2 . Having been transferred to malthenes, "new settlers" act upon early constituents of the fractions and individual compounds (Table 3, Fig. 4). Consequently, secondary compounds in liquid products of thermal destruction mainly reflect quantitative alterations of asphaltenes.

The Predominance Index, which is often used in geochemical practice, was used to evaluate the kukersite destruction products. The Index is the ratio, r , of odd- to even-numbered homologous compounds. It is calculated by dividing a summation of peak heights for the odd carbon number compounds by a similar summation of the even carbon number compounds. The Index was applied to the n -alkanes, alkylarenes and alkanones (n -2-alkanones and dialkylalkanones, which have a carbonyl group near the center of the chain) which were produced from destruction of kukersite. The result was that the ratio, r , increased considerably with increasing yield of liquid product and the fraction of asphaltenes in the liquid composition (see Table 5).

Another correlation exists with this Index. Decreasing the yield of a TLC fraction, the value of r for that fraction increases. With Dzham shale the share of homologous compounds with an odd number of carbon atoms in the liquid product increases with increasing yield of the liquid product. This same result occurs with kukersite. But unlike kukersite, r increases with increasing yield of a TLC fraction (particularly alkanones) using Dzham shale.

For the homologous series mentioned above, r depends on the extent of kerogen conversion, temperature used and presence of reagents during thermal destruction. Compounds with even number carbon atoms prevail, among homologous aliphatic and aromatic hydrocarbons, when they are formed as a result of the destruction of asphaltenes. Kukersite pyrolysis, including semi-coking, produces abundant n -1-alkenes. This phenomenon is explained by the high temperature of the retorting processes and with the fact that kerogen becomes hydrogen-deficient in the final stage of thermal treatment [19]. Even-numbered carbon atoms prevail in the n -1-alkene homologous series.

During thermal destruction in closed systems, alkenes are saturated with hydrogen either from the kerogen (with extraction in CO_2) or from the hydrogen donor (with

Table 5. Predominance Index r Values in Homologous Series of Thermal Destruction* Products

Homologous compounds	Kukersite			Dzham shale		
	1	2	3	1	2	3
<i>n</i> -Alkanes	1.01	1.20	1.24	1.02	0.94	1.09
Alkylarenes	0.94	1.16	1.17	0.90	1.00	0.75
Dialkylalkanones	1.00	1.27	1.32	0.86	1.17	1.12
<i>n</i> -2-Alkanones	0.93	0.98	1.13	0.74		1.14

*Method of thermal destruction and yield of fraction see in Table 3 and length of chain of respective homologous compounds see in Fig. 4.

hydrogenation using HCOONa) and alkanes are formed. As a result, r decreases in the homologous alkane series.

We hypothesize that the main source of alkene formation is solely the asphaltenes. These are constituents of thermobitumen and are hydrogen-poor. Alkenes are detectable only in volatile products of pyrolysis due to the preservation of asphaltenes during gas extraction or hydrogen saturation of alkenes. Hence, the extent of destruction and chemical reactions could be expressed in the r value as well. Thus, compounds obtained from extraction, hydrogenation or semi-coking have distortions in the presence and character of chains with odd and even carbon atom number as compared to that in kerogen. This is caused by the specific thermal destruction method which is used.

For kukersite, the maximum length of alkyl chain (number of carbon atoms) is 17 in alkylarenes, 19 in alkanones and 21 in alkanes. This is irrespective of the method of thermal destruction used. Among alkanes and alkanones C_{13} , C_{15} , C_{17} , and among alkylarenes alkyl chains with C_6 and C_9 dominate. Thus, a concentration maximum is observed near the center or the end of homologous series. The maximum chain length in Dzham kerogen established for alkanes and alkanones is 33 when these are obtained from hydrogenation or extraction. This result is developed based on gas chromatographic analysis. In this case, side chains of alkylarenes contain 20 carbon atoms. With semi-coking, the following maximum lengths of alkyl chains were determined: 27 C atoms in alkanes, 21 in alkanones and 18 in arenes. Consequently, cracking of long chains into shorter ones during thermal destruction is possible. If this occurs, alterations in r value might be brought about (i.e. hydrocarbon C_{30} is cut up in two C_{15} instead of C_{16} and C_{14}). As seen in Fig. 4, this does not result in a rearrangement of relative maxima and minima, i.e. the reflection of the kerogen structure is not beyond its recognition limits in the products of severe thermal treatment. Klesment, et al., [20-21] have shown that destruction of kukersite-derived heavy oil produced by semi-coking (both its neutral and acid parts) yields similar compounds. These have boiling points up to 300 °C and concentration similarities to the primary oil. The aforementioned facts coincide with the results obtained in the

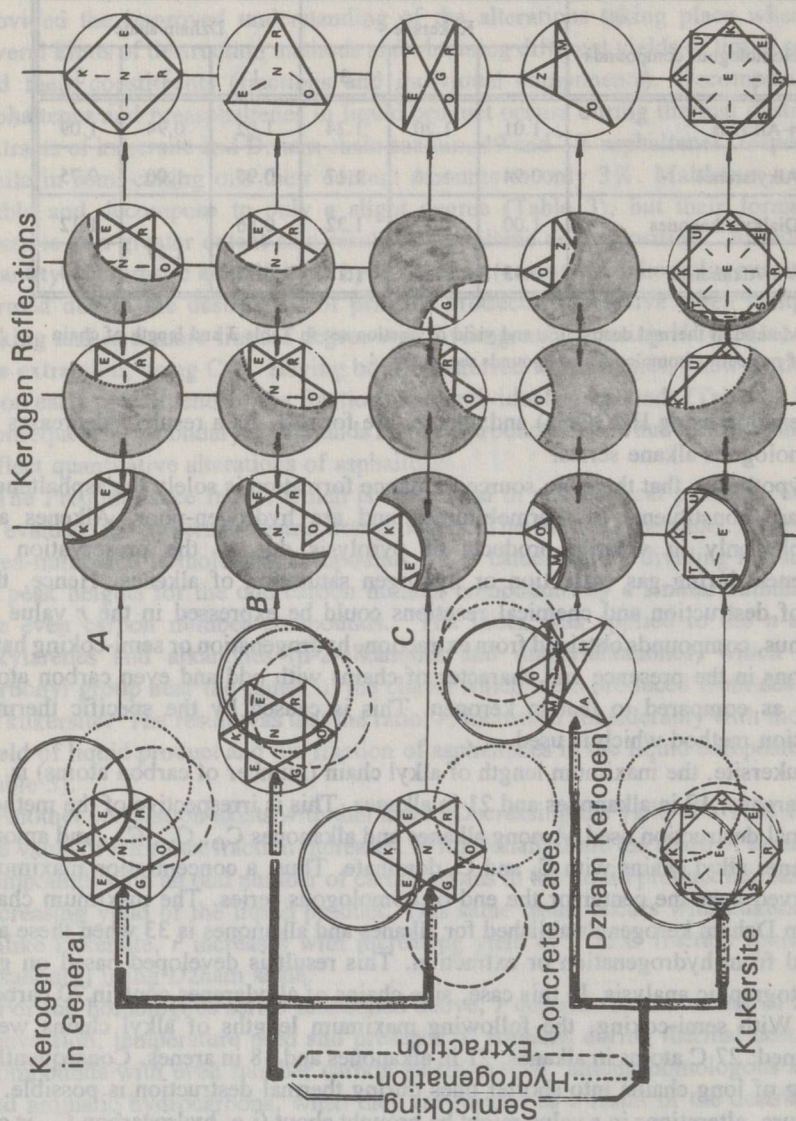


Fig. 5. Possible reflections of kerogen structure using different thermal destruction methods for kerogen study

present work concerning asphaltenes and TLC-5. This might represent the incompletely decomposed kerogen - the intermediates between kerogen and light oil.

Total yield of asphaltenes and TLC-5 during hydrogenation or extraction of Dzham kerogen is quadruple that of the yield with semi-coking (Table 3). Obviously, they decompose, forming gas and semi-coke sooner than the lighter liquid products. The yield of semi-coking oil is moderate. Gas chromatographic studies show that 1.5 to 2 times more extracts and hydrogenisates are obtained than semi-coking oil. In addition, they contain considerably more long-chain compounds in comparison to semi-coking oil. In the latter, it is observed that there is a tendency towards carbon chain lengthening in a compound with a corresponding decrease in its concentration. The concentration of the first members in a homologous series increases due to the cracking reactions. The final products of kerogen thermal destruction - which provide the information source for further geochemical conclusions - include both altered and re-altered products. The type of method used sets its specific stamp upon the extent of alterations.

2.6. Possible kerogen structure using individual liquefaction methods separately or in combination

A summary of obtained results and the author's idea are presented briefly in Fig. 5. When any kerogen is liquefied using a combination of thermal destruction methods, three pathways A, B and C are possible: A - methods applied in combination complement each other, B - methods duplicate or repeat each other, C - methods counteract each other. An erroneous reflection of structure is obtained (note the horizontal lines in Fig. 5) when using a combination of thermal methods in parallel. This develops a kerogen structure which does not mirror the original material. As parts of the kerogen fragments are repeatedly included in, or totally excluded from, the liquid product composition, the recognition of the kerogen under study is indefinite. Likewise, the categorization of different kerogens, though liquefied under common conditions (i.e. at the same parameters for semi-coking, extraction or hydrogenation - per the vertical lines in Fig. 5), is impossible. But categorization of kerogen distortions (oils under different yields) is possible.

During liquefaction of Dzham shale, the thermal destruction methods somewhat duplicate and somewhat complement each other (A and B in combination); the kerogen was described from different aspects, but the real image of its structure was not obtained.

During kukersite extraction, kerogen is totally transformed into liquid product and consequently there is no need for using additional methods. Using the methods of thermal destruction in parallel results in variant B. Also, labile intermediates are maintained in liquid form in the kukersite extraction product. The latter is the source of gas and (semi)coke formation during further thermal treatment. Separation of intermediate fractions, such as asphaltenes and TLC-5, from liquid products, including kukersite extract, is analytically simple. It enables their stepwise destruction, separately from the remaining primary ones, in order to study the mechanism of thermal destruction. If the decrease of the amount of liquid product is caused by gas and coke formation resulting from primary fragments, it raises the question about the adequacy of the proposed kerogen structure.

3. Conclusions

1. The yield and extent of destruction of liquid product during gas extraction, hydrogenation or pyrolysis are very different. This leads to insufficient and ambiguous, rather than close and reproducible, images of kerogen structure. This result is attained when either an individual method is applied or various methods are used in parallel.

Liquefaction of various kerogens under common conditions produces differences between conversion rates. As a result, noncomparable products are obtained. A successful categorization of kerogens is not possible.

2. Yield of the liquid product during gas extraction or hydrogenation is considerably higher than with semi-coking because intermediate fractions (preasphaltenes, asphaltenes, high-polarity malthenes) have maintained their initial composition.

Applying further thermal treatment, only the intermediates are the precursors for formation of gas and coke. Significantly, alkenes and the homologous series of *n*-alkanes, *n*-alkanones and alkylarenes are formed. These do not have characteristics which are similar to those already existing in the primary product. As a result of the continual formation and accumulation of primary and secondary identical compounds during thermal destruction, commonalities in their concentration reflect the degree of destruction of kerogen and its fragments. But they are not characteristic of the kerogen.

3. The stepwise scheme for an effective thermal destruction of kerogen is suggested in order to optimize kerogen transformation into the liquid product, thereby carrying the identity of the kerogen in its composition.

During stepwise destruction of the intermediates, the mechanism of kerogen destruction can be controlled.

Various kerogens can be categorized on a common basis — equal (and maximal) yield of liquid product.

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