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COMPARATIVE CHARACTERIZATION OF ORGANIC MATTER OF OIL SHALES FROM THE MAIN DEPOSITS IN BULGARIA

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Abstract. *The organic matter of oil shale samples from four major Bulgarian deposits was investigated using thermal and oxidative treatments. Neutral oils from oil shales were obtained by low-temperature pyrolysis. Gas chromatography-mass spectrometry (GC-MS) was used to study the oxidation products and their chemical composition. A stepwise alkaline permanganate degradation of oil shale concentrate at ambient temperature was carried out, affording a high total yield (90 %) of oxidation products and a minimum yield of gas products. Two different types of high molecular substances were detected in oil shales. The results allowed conclusions to be made about the utilization of prospective Bulgarian oil shale deposits as energy sources.*

Keywords*: oil shale pyrolysis, organic matter, extraction, oxidative destruction, alkaline permanganate degradation.*

1. Introduction

In the last decades, scientists worldwide have made efforts to search for alternative energy sources. It has also been aimed to increase the resource base by using potentially energy-rich materials, such as oil shale, biomass, agricultural waste, polymer waste, etc., as well as to develop new effective technologies for the treatment of these materials. The development of methods for utilization of oil shales started in the 18th century, but in the last years greater attention has been paid to oil shale as a prospective material for obtaining liquid fuels and valuable chemical products. Some researchers claim that the world reserves of oil shale may exceed the potential resources of petroleum oil. In comparison with coals, oil shale can produce a high

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yield of liquid products, and its composition is suitable for treatment to produce liquid fuels with appropriate composition, as well as different chemical products and gas mixtures [1–3].

There are over 30 oil shale deposits registered in Bulgaria. According to organic matter content, some of them are prospective for the industry, especially Krassava, Borov dol, Mandra and Pirin.

Possibilities to obtain liquid fuels from Bulgarian oil shales have been extensively investigated since the 1900s. Being mostly paleogenic, Bulgarian oil shales have different geological age [4, 5]. The locations of the main oil shale deposits in Bulgaria are shown in Figure 1.

The present work includes investigations of the most prospective oil shale deposits for obtaining liquid fuels and sources for the chemical industry.

The main characteristics of the investigated oil shale samples are given in Table 1.

The oil shale samples from Krassava, Mandra and Pirin deposits have a higher content of organic matter in comparison with that from Borov dol.

Table 1. Characteristics of Bulgarian oil shales

Parameter\Oil shale	Krassava	Borov dol	Mandra	Pirin
Moisture W^a, %	1.4	3	0.8	2.8
Ash A^d, %	55.9	73.3	58.7	60.9
CO_2, %	15.6	6.8	13.6	4.6
OM, %	28.5	19.9	27.7	34.5
Sulfur total, S_t^d	1.72	2.6	2.6	2.2
S_p^d, %	0.80	1.4	1.8	1.0
V^{daf}, %	81.8	70.57	83.0	72.5
C^{daf}, %	75.8	73.10	77.2	71.1
H^{daf}, %	8.7	8.10	10.4	7.9
N^{daf}, %	1.9	1.72	1.0	2.0
S^{daf}, %	3.2	2.00	2.6	3.0
O^{daf} (diff.)	10.4	15.08	8.8	16.0
H/C	1.38	1.33	1.66	1.35
Q^{daf}, kJ/kg	38247	36193	38456	35948

W^a – moisture
OM – content of organic substances
S_t^d – total content of sulfur
S_p^d – content of pyrite sulfur
a – ash free base
d – dry base
daf – dry ash free base
V^{daf} – weight content of volatile components
Q^{daf} – calorific content

Fig. 1. Map of oil shale deposits in Bulgaria. The samples under investigation were taken from the following deposits: 1 – Krassava; 2 – Borov dol; 3 – Mandra; 4 – Pirin.

2. Methods, results and discussion

2.1. Pyrolysis of oil shale at moderate temperatures

Pyrolysis at moderate temperatures (400–500 °C) is an important thermo-chemical method for investigation of oil shale structure. During pyrolysis the dominant part of organic matter (almost 50%) is converted to an oil product – a precursor for obtaining liquid fuels and other chemical products. Studying the composition of the obtained oil is important for the selection of the methods for oil shale utilization, as well as for the elucidation of the nature and processes of destruction of organic matter. This will help to adjust the process of thermal destruction in order to obtain more liquid products – this method is applied for oil shales from different deposits [6–8]. The pyrolysis at 450 °C is performed in order to convert oil shale organic matter to liquid products. Solid-liquid chromatography on silica gel has been used to study the chemical group composition of oils. Separation of the neutral part of shale oil was performed similarly to the procedure of Sawatsky et al. [9], but at atmospheric pressure and in a glass column filled with Al_2O_3 and silica gel. The scheme of the separation of neutral shale oil is shown in Figure 2.

Gas-liquid chromatography has been applied to determine the individual paraffin substances in the paraffinic-naphthenic fractions. The results presented in Table 2 show that all oils are of dominantly aliphatic character. The aromatic carbon content is lower, and it decreases in the following order: Borov Dol (16.87%), Krassava (12.77%), Mandra (10.16%), and Pirin oil shale (8.74%). The aromatic carbon content of pitch ranges from 18.60% for Pirin oil shale, down to 6.92% for Mandra oil shale.

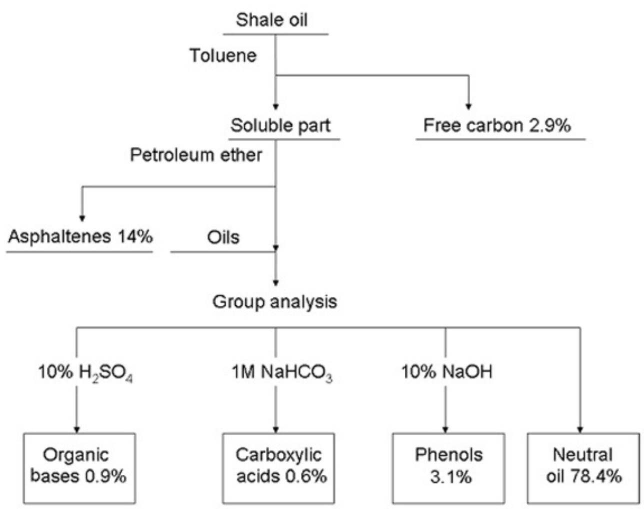

Fig. 2. Scheme of the chemical group analysis of shale oil.

Table 2. Chemical group composition determined by solid-liquid chromatography

Fraction	Oil shale from different deposits, %			
	Krassava	Borov dol	Mandra	Pirin
Paraffinic-naphtenic	79.56	70.31	80.03	70.94
Aromatic	12.77	16.87	10.16	8.74
Pitches	7.23	11.37	6.92	18.60
Losses	0.44	1.45	2.89	1.72

Sixteen different n-paraffins have been indentified in the fractions from oil shales of Mandra, Krassava and Borov dol deposits, and seventeen in oil shale from Pirin deposit (Fig. 2).

The content of straight-chain paraffins determined by gas chromatography-mass sepectrometry (GC-MS), depending on carbon atom number, is shown in Figures 3 and 4.

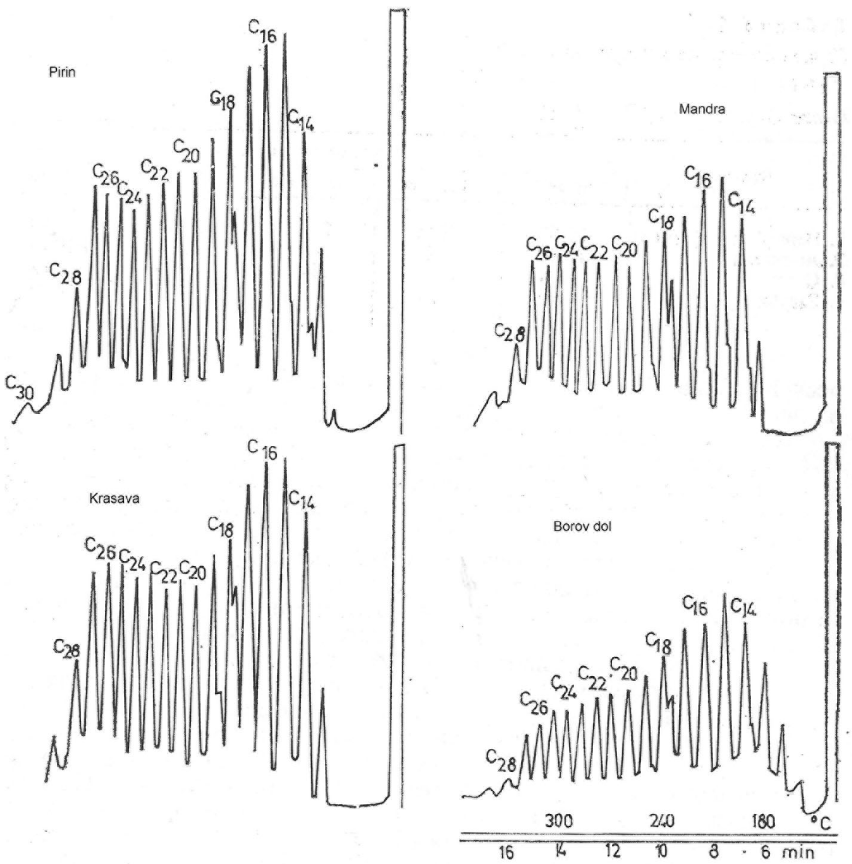

Fig. 3. Chromatograms of paraffinic-naphthenic fractions from oil shales of Pirin, Mandra, Krassava and Borov dol deposits.

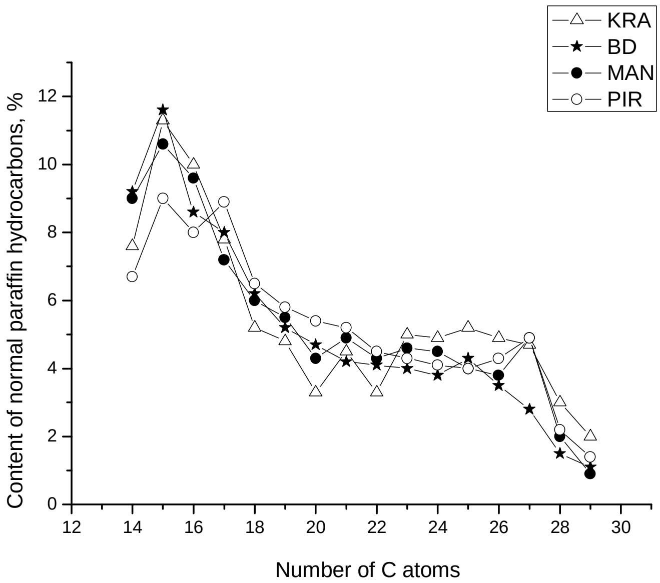

Fig. 4. Dependence of straight-chain paraffins content on carbon atom number (The abbreviations used: KRA – Krassava, BD – Borov dol, MAN – Mandra, PIR – Pirin.)

All the investigated oil samples exhibit a similar distribution of hydrocarbons. The content of pentadecane (C_{15}) is the highest. The decrease of the hydrocarbon content from light hydrocarbons to eicosane is well demonstrated. The content of long-chain hydrocarbons from eicosane (C_{20}) to hexacosane (C_{26}) differs little (Fig. 4).

The performed investigations allow us to draw some conclusions about the composition of organic matter of oil shales. In the first place, it should be noted that the organic matter of the investigated oil shales has a dominantly aliphatic character. The aliphatic structural elements are present mainly in the matrix of oil shales. Aromatic structures are present in considerably lower amounts. It should be mentioned that the aliphatic character of the OM of oil shale from Mandra deposit is more clearly expressed, which determines the higher yield of liquid products from the thermal treatment (almost 65% of organic matter) and the higher yield of the paraffinic-naphthenic fraction of natural oil. The content of pitches (heavy fractions) is the highest in neutral oils obtained from oil shale of Pirin deposit, which is an indication of the presence of a higher amount of aromatic structures and existence of neutral oxygen compounds in this oil shale. This explains the low content of paraffinic-naphthenic hydrocarbons and the comparatively low yield of liquid products. These results show that the organic masses of oil shales of Krassava and Borov dol deposits have a middle position, while the organic mass from oil shale from Krassava deposit is close to that of oil shale from Mandra deposit, and the organic mass from Borov dol oil shale is close to that from Pirin oil shale.

2.2. Oxidative treatment of oil shales

2.2.1. Oxidation in alkaline medium with potassium permanganate

Literature data show that oxidation is the most promising method for investigation of the structure of oil shale organic matter, involving a stepwise oxidative destruction with potassium permanganate in alkaline medium [10–15]. The stepwise destruction at ambient temperature allows performing destruction in mild conditions and obtaining products, which preserve the structural features of the initial organic matter.

The concentrates of Krassava, Mandra, Pirin and Borov dol oil shales were, after demineralization with 10% HCl, subjected to the oxidation procedure till a complete destruction of organic mass. The number of steps of the oxidation procedures performed was different, due to the different stability of organic mass of oil shales: 15 steps for Krassava, 13 steps for Borov dol, 12 steps for Pirin and 16 steps for Mandra oil shale. Demineralization with 10% HCl was carried out before the oxidative treatment of oil shale concentrates, which allowed elimination of carbonates, sulfates, chlorides, etc., and increase of the organic content of the remaining matter. We consider that this approach, demineralization with 10% HCl, did help us in achieving a more complete preservation of the characteristic features of the initial organic matter, in comparison with deep demineralization with hydrofluoric acid. The concentrate after demineralization, around 10 g, was further oxidized and approximately 95% of OM was decomposed. In Table 3 the distribution of carbon in the products after oxidation is given. The low degree of the oxidation of organic matter to CO_2 is due to the mild conditions of the oxidation process. The products of oxidation were analyzed according to the scheme shown in Figure 5.

The ether extracts as well as volatile acids with water vapor (after water vapor distillation) contain low molecular products (LMP). The acetone extracts contain so-called polyfunctional acids (PFA). PFA have a relatively high molecular mass and are considered to be the primary products of oxidation (Fig. 5).

Table 3. Distribution of carbon in the products of oxidation

Oil shale sample	Carbon evolved as CO_2, %	Carbon insoluble in acid solution (PFA), %	Carbon soluble in acid solution, %	C in solid product after extraction, %
Krassava	2.4	70.4	25.1	2.0
Borov dol	1.2	68.1	19.1	2.0
Mandra	1.3	79.7	17.0	2.0
Pirin	1.5	66.2	18.0	2.1

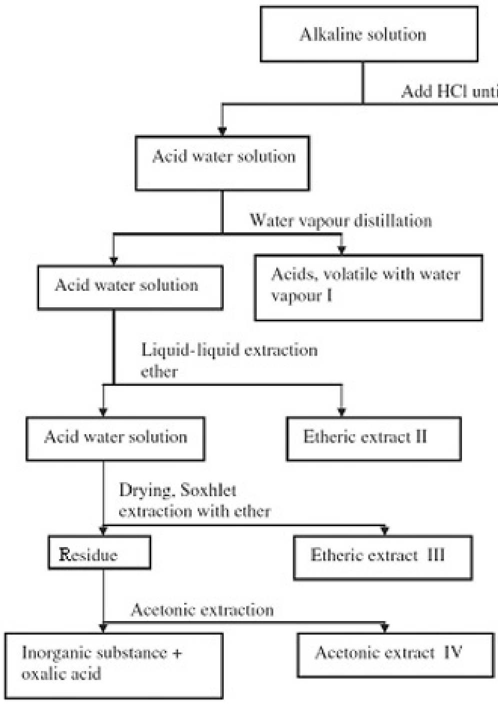

Fig. 5. Scheme of separation of the products after oxidation for each step.

The results show that the main part of organic matter is present in low molecular products (soluble in acid solution) and polyfunctional acids (insoluble in acid solution). In comparison with the oxidation procedure at 65 °C of oil shale from Krassava deposit [15], the oxidation at room temperature gives the possibility to increase the carbon content in PFA, which implies that during this oxidation procedure reactions connected with organic matter destruction via breaking of weaker bonds occur. The results obtained are very important for elucidation of the structure of organic matter of oil shales.

The spectroscopic investigations were performed in order to characterize the products obtained [15, 16]. The IR spectra of extracts II–VI show that the products contain dominantly carbonyl and aliphatic structures. The adsorption band at 1740–1710 cm^{-1} is more intensive in comparison with those for other oil shales. The band at 3400 cm^{-1}, which is characteristic of –OH groups, is present in all spectra. All spectra are characterized by the adsorptive bands at 1465 cm^{-1} and 2940 cm^{-1} that are typical of CH_2 aliphatic and alicyclic structures, respectively, while CH_3 groups are also detected at 1380 cm^{-1} and 2860 cm^{-1} [16, 17].

The bands at 730–720 cm^{-1} are visible in extracts II, V and VI, which is due to the presence of paraffin structures. The band at 970 cm^{-1} appearing in the spectrum is connected with the presence of naphthenic cycles. A weak band at 1700 cm^{-1} due to the presence of aromatic structures is weakly present for Krassava oil shale sample, while in Pirin and Borov dol oil shale samples these structures are present in higher quantities.

The IR spectrum of PFA (extract VI) shows these acids to have a higher content of aliphatic and lower content of aromatic structures compared to PFA (extract IV). The bands at 1465 cm^{-1} and 2880 cm^{-1} are characteristic of aliphatic structures, whereas the bands at 1780 cm^{-1} and 3600–3300 cm^{-1} are due to the presence of carboxylic and associated hydroxyl structures.

The study of the distribution of molecular mass of soluble PFA shows that they contain products with a molecular mass from 200 to 7000 Da. This indicates that the extensive oxidation does not influence the size of individual molecules.

The ^{1}H NMR spectra contain signals for CH_3 and CH_2 groups, connected with an aromatic ring, as well as for phenolic groups related to soluble PFA (extract IV).

The ^{1}H NMR spectra for PFA (extract VI) insoluble in acid solution show the content of aromatic hydrogen to be insignificant (95.5%). The main part of protons is associated with aliphatic groups [17].

The analysis of fractions I, II, III and V by GC-MS gives evidence of the prevailing presence of aliphatic dicarboxylic acids (DCA, 20.1%), and an insignificant content of monocarboxylic (MCA) and benzenecarboxylic (BCA) acids. The amount of oxalic and malonic acids decreases with the prolongation of the oxidation procedure, while the distribution of the other acids is constant in all steps.

The distribution of dicarboxylic, monocarboxylic and benzencarboxylic acids in Bulgarian oil shales is given in Table 4 and for Krassava oil shale shown additionally in Figure 6.

The hydrocarbon chain length of the obtained acids increases with the prolongation of oxidation from the 1st step to the 3rd step as follows: from C_{22} to C_{26} for Krassava oil shale, from C_{20} to C_{29} for Borov dol oil shale, from C_{20} to C_{24} for Pirin oil shale and from C_{23} to C_{31} for Mandra oil shale. MCA are evenly distributed in all oil shales, while their quantity is similarly very low, about 1%. MCA are represented by homologues up to C_{27} for Krassava, up to C_{31} for Borov dol, up to C_{25} for Pirin and up to C_{30} for

Table 4. Distribution of monocarboxylic, dicarboxylic and benzencarboxylic acids in Bulgarian oil shales

Oil shale sample	MCA	DCA	BCA
Krassava	C_2–C_{10}	C_{10}–C_{27}	All homologues
Borov dol	C_2–C_{10}	C_{10}–C_{31}	All homologues
Pirin	C_2–C_{10}	C_{10}–C_{30}	All homologues
Mandra	C_2–C_{10}	C_{10}–C_{28}	All homologues

The abbreviations used: MCA – monocarboxylic acids, DCA – dicarboxylic acids, BCA – benzenedicarboxylic acids.

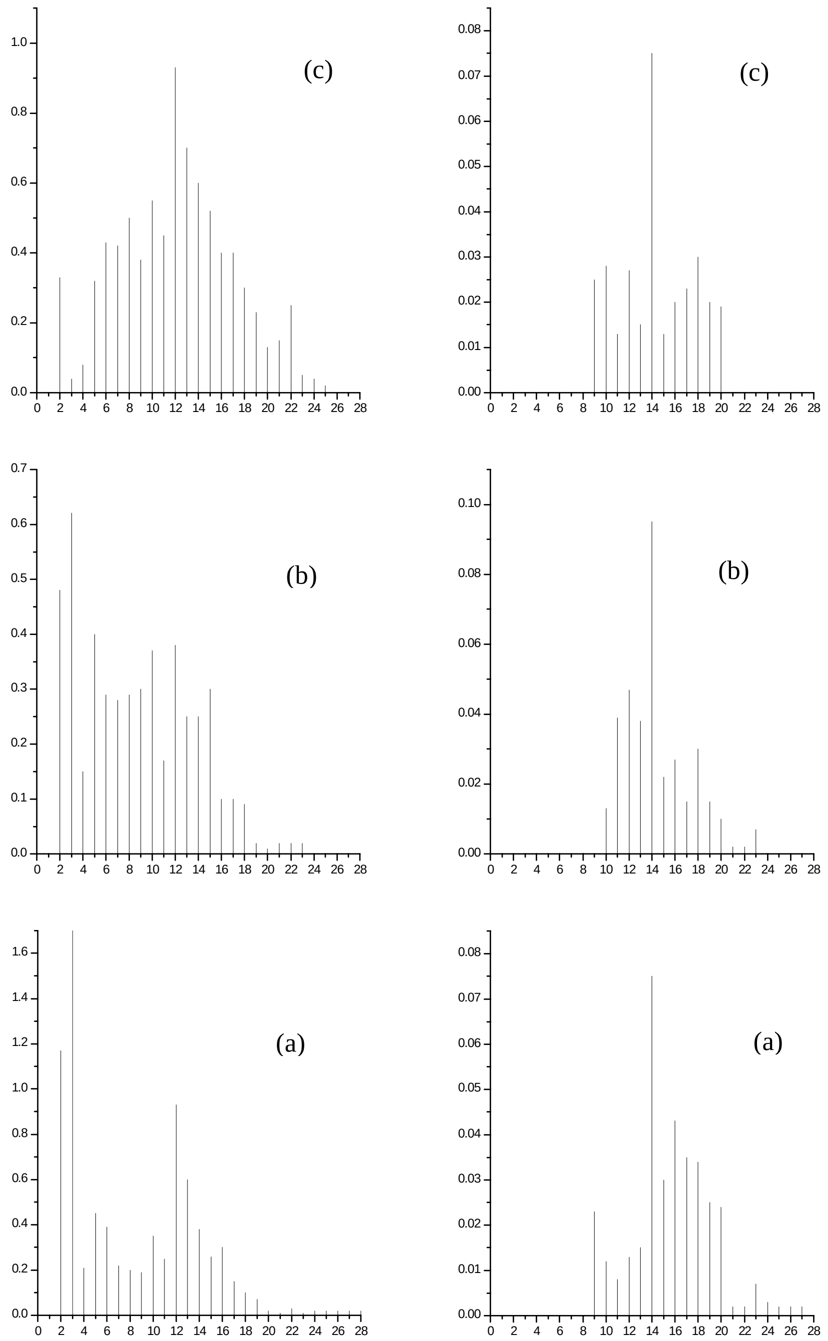

Fig. 6. Distribution of aliphatic carboxylic acids in Krassava oil shale at different stages of oxidation, %: a) MCA, b) DCA, c) BCA. (The abbreviations used: MCA – monocarboxylic acids, DCA – dicarboxylic acids, BCA – benzenedicarboxylic acids.)

Mandra oil shale. The amount of BCA is approximately 1.2% of organic matter in Mandra oil shale, 3% in Krassava, 3.5% in Borov dol and 4 % in Pirin oil shale. All BCA homologues have been indentified in the products of oxidation [18–20].

The proportion of the acids and their composition indicate that the qualitative and quantitative characteristics of the organic matter of Borov dol oil shale are similar to those of Pirin oil shale, both having a relatively high content of aromatic components. At the same time, the amount of aromatic structures in Krassava oil shale is lower than that in Mandra oil shale, but higher than that in Borov dol and Pirin oil shales.

The mild conditions of oxidation and step-wise oxidative destruction of oil shale organic matter macromolecules give us the reason to propose that the oxidation products, PFA and low molecular products, are fragments of the macromolecule. The scheme of the oxidative destruction of oil shale organic matter macromolecules is shown in Figure 7.

The results from the experiments on the destruction of oil shale organic matter with alkaline permanganate demonstrate that the dominant part of OM (40%) is composed of high molecular fragments and contains two types of structures. The structures of the first type are primarily of aliphatic character – they are high molecular structures and are formed in the successive steps of oxidation.

Formed in the first step of oxidation, the structures of the second type contain a considerable amount of phenolic groups and exhibit a well-expressed aromatic character. These specific features are due to the different places the structures occupy in the macromolecule of the organic matter of oil shales. Most probably the fragments with a well-expressed aromatic character occupy chiefly the peripheral part of the macromolecule. Hydrocarbons with straight-chain homologues up to C_{31} are present in almost 20% of OM, which is established by the yield of α,ω-dicarboxylic acids. These hydrocarbons perform connecting and cross-connecting functions. The low content of monocarboxylic acids up to C_{27} is the evidence for the low content of branches in the macromolecule (almost 1%).

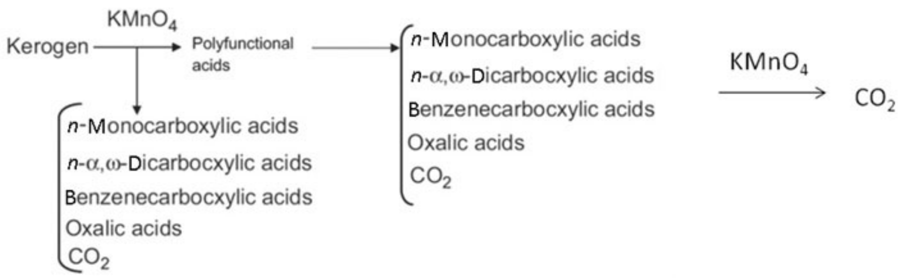

Fig. 7. Scheme of the destruction of oil shale organic matter macromolecules.

3. Conclusions

The investigations performed of the products from pyrolysis and oxidation of the organic matter of oil shales from different deposits in Bulgaria show that they are a complicated mixture of different compounds in which polymethylene chains prevail. This is evidence for the dominantly aliphatic character of the organic matter of investigated oil shales. The aliphatic character of organic matter is very well expressed especially in Mandra oil shale sample, which is distinguished by a high yield of liquid products after pyrolysis, almost 65% of organic matter, whereas aromatic hydrocarbons are obtained in insignificant amounts. The organic matters of Borov dol and Pirin oil shales have a similar composition, they are distinguished by a high content of aromatic components (yield of solid coke is almost 49%), a considerably low yield of paraffinic-naphthenic hydrocarbons (40%) and a high content of phenols.

The investigations carried out allow us to characterize the organic matter of oil shales from the most prospective Bulgarian deposits. Despite the similar chemical composition, the investigated oil shales differ in organic composition, which determines their different properties and reveals possibilities for their utilization.

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