CONTRIBUTIONS TO THE KNOWLEDGE OF THE HUNGARIAN OIL SHALE KEROGEN I

PRELIMINARY REPORT ON THE RESULTS OF THE PYROLYSIS AND SELECTIVE OXIDATION

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INTRODUCTION

"As petroleum is a natural resource that is being rapidly consumed, there are widespread efforts to seek possible substitutes for it. The reserves of oil shale stand out as a very important source of substitutes for petroleum" [YEN and CHILINGARIAN, 1976]. Recently, the energy crisis and the increasing oil prices throw gradually light upon the problem, i.e. to find other energy resources. Thus, in addition to the productive oil shale occurrences, the research of smaller occurrences of local importance may arise partly from economic, partly from prospecting points of view. It can be assumed that the results of scientific researches explore new profitable possibilities of application which are recently more or less unknown. The investigations of FOMINA [1968] show this trend, resulting the chemical-industrial and agricultural utilization of oxidation products of the Estonian kukersit kerogen.

GENERAL REMARKS ON THE OCCURRENCE

In Hungary oil shale was found in a Pliocene basin in 1973 by the experts of the Hungarian State Geological Institute [JÁMBOR *et al.* 1975]. The rock filling up the basin is greyish-green, apparently light and of lamellar stratification, it is of characteristic smell and combustible. 10 to 70 per cent of it is of algal origin. Its inorganic components are clay minerals, fine-grained sand deriving from the region of the neighbouring basalts, and limy material. Out of its organic components the *Botryococcus braunii* planktonic alga is predominant, further the pollens of terrestrial plants are frequent [JÁMBOR *et al.* 1975]. According to the detailed investigations of algal and pollen remnants these oil shale strata were formed in the Pliocene, in semi-haline water of 10 to 12° C of a crater lake of appropriate pH, salinity and temperature, and which proved to be suitable to abundant production of protophytes. Since the protophytes in question are highly sensible to the factors mentioned above, their large-scale destruction was probably caused by cold-water inundations and by the change of salinity. On the basis of the calcite/aragonite ratio determined by means of X-ray diffractometer two sedimentation cycles can be distinguished in the basin: the boundary of the cycles is in a depth of 19 to 20 metres, the start of the first cycle is probable in a depth of about 40 metres [MEZŐSI, 1976].

Part of the oil shales and of other sediments, i.e. the bitumen fraction is soluble in the common organic solvents. The other part is insoluble in organic solvents, this is usually called kerogen. The bitumen fraction of oil shales is max. 20 per cent of the total organic matter content, however, its value is less, in general. Consequently, the major part of the organic matter is kerogen, thus if the oil shale is to be

characterized, its kerogen should be studied. Unfortunately, while the bitumen fraction can be easily separated by extraction, the isolation of kerogen is troublesome and hardly can be carried out without the decomposition of the original matter by using chemical methods. This is why efforts are made to characterize the kerogen content of the oil shales, and which do not need the preliminary removal of inorganic components, e.g. measurement of reflectance of vitrinite, determination of reduction capacity of the organic matter by means of selective oxidation, pyrolysis, etc.

The results of the preliminary investigations on the kerogen of the Hungarian oil shale are summarized. These investigations were carried out according to the scheme shown in *Fig. 1*. It is to be noted here, that certain measurements were carried out only in some representative samples. In Table 1 some characteristics of the samples investigated are demonstrated.

The peculiarities of the oil shale kerogen depend on the diagenesis, on the chemical features of the sedimentary environment, on the geological conditions (closed bay, or inland sea, etc.) and on the biological source matter. The data of the elemental analysis are used to characterize these materials (H, C, N, O, S), or as an approach, the hydrogen and carbon content, resp., the H/C atomic ratio is given.
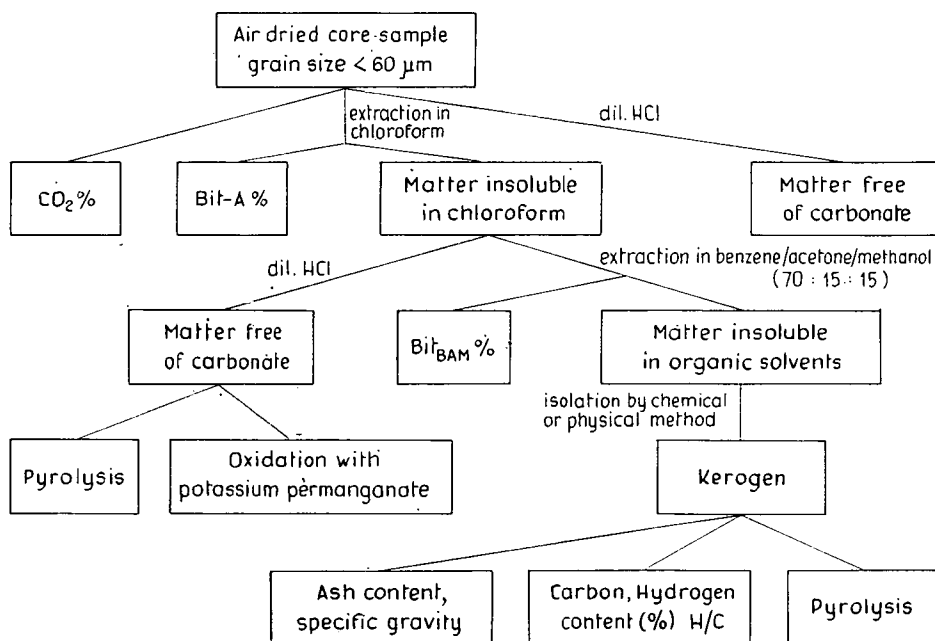

Fig. 1. Investigation scheme of organic matter of the Hungarian oil shale.

Having removed the bitumen fraction from the samples by means of repeated extraction, the kerogen has been isolated. This has been carried out by physical methods in most of the cases: flotation in calcium chloride solution in order to avoid the chemical transformation of the organic matter. The concentrate, however, will contain inorganic matter of small quantity, especially in the samples of low organic carbon content. The samples of C_{org} content less than 10 per cent do not produce kerogen concentrate of required purity, their data are published only

TABLE 1

Carbon dioxide (CO_2), organic carbon content (C_{org}), organic matter soluble in chloroform (Bit—A) and organic matter soluble in organic solvents (Bit_{BAM}) of samples from the borehole Put-7

Sample No	Depth m	CO_2 (%)	C_{org} (%)	Bit—A (%)	Bit_{BAM} (%)
5	4,8— 5,4	18,5	2,27	0,14	0,07
7	6,0— 6,5	17,3	1,69	0,11	0,08
11	8,0— 8,5	11,2	6,88	0,61	0,19
14	9,5—10,0	9,5	11,30	1,40	0,54
18	11,5—12,0	16,1	7,69	0,84	0,55
22	13,4—14,0	18,0	8,94	1,80	0,43
24	14,5—15,0	6,7	32,56	3,61	2,04
26	15,5—16,0	3,7	45,61	5,12	1,73
27	16,0—16,5	4,3	45,68	3,95	2,01
28	16,5—17,0	4,8	28,89	4,98	1,54
32	18,5—19,0	15,5	11,44	1,35	0,79
33	19,0—19,5	21,4	9,89	0,55	0,49
35	20,0—20,5	22,1	11,80	1,15	0,32
38	21,5—22,0	14,7	16,74	3,99	1,18
42	23,5—24,0	17,4	18,64	1,56	0,95
45	25,0—25,5	11,8	30,09	2,99	0,85
49	27,0—27,5	16,1	21,16	4,77	1,49
55	30,0—30,5	22,2	8,74	0,47	0,05
59	32,0—32,5	21,5	10,54	0,67	0,27
62	33,5—34,0	23,7	6,80	0,53	0,38
69	37,0—37,5	24,6	5,00	0,28	0,17
73	39,0—39,3	29,8	6,15	0,43	0,23

for comparison. In the samples No. 14 and 18, the carbon content of which proved to be relatively low, kerogen was isolated by chemical method.

The carbon and hydrogen contents as well as the H/C ratios of the concentrates are shown in Table 2. The average value of the *H/C* ratio is 1.77. It is low in case

TABLE 2

Carbon, hydrogen content, H/C atomic ratio and method of isolation of the kerogens

Sample No	Method of the isolation	C (%)	H (%)	H/C atomic ratio
14	chemical	67,5	9,5	1,6
18	chemical	73,0	8,5	1,4
24	physical	72,9	11,6	1,9
26	physical	69,2	11,2	1,9
27	physical	73,6	11,7	1,9
28	physical	76,7	12,7	2,0
32	physical	72,6	11,7	1,9
33	physical	74,5	11,5	1,8
35	physical	80,5	12,5	1,8
38	physical	72,9	10,0	1,7
42	physical	69,6	10,2	1,8
45	physical	73,5	10,5	1,7
49	physical	65,6	9,8	1,8
55	physical	17,6	2,8	1,9
62	physical	57,3	8,1	1,7
69	physical	12,4	1,8	1,7

of the two chemically isolated samples (1.4–1.6), in case of the other no significant deviation is found.

The *H/C* ratios of the Hungarian oil shale were compared with those of other kerogens, the source matter of which has been also *Botryococcus* alga. In Table 3 the values from the literature as well as that of our samples are shown. The H/C ratio of the Hungarian oil shale agrees with that of the Coorongite of Australia. Coorongite represents a rather early stage in the formation of the algal kerogen, it is the occurrence of *Botryococcus braunii* in form of free colonies. "Coorongite should be considered similarly to the peat state when the algal shales are coalified" — writes CANE [1969].

Age, precursors, carbon, hydrogen content and H/C atomic ratio of some kerogens

Name and location of kerogen	Age	Precusor	C (%)	H (%)	H/C
Torbanite Scotland	Permian	*Pilaminima P. scotica (Botryococcus)*	79,1	9,8	1,49
Marahunite Brazil	Tertiary	*Botryococcus braunii*	58,9	5,5	1,12
Autun Boghead France	Permian	*Pila bibractensis (Botryococcus)*	76,9	10,4	1,62
Alginite Australia	Permian	*Pila reinschia (Botryococcus)*	72,5	9,1	1,28
Coorongite Australia	Recent	*Elasophyton coorongina (Botryococcus)*	76,1	11,2	1,77
Alginite Hungary	Pliocene	*Botryococcus braunii*			1,77

INVESTIGATION OF ORGANIC MATTER BY PYROLYSIS

To study the character, composition and degree of diagenesis of the organic matter, pyrolysis is one of the most wide-spread method. Similarly to other methods, this method is also unable to describe alone the structure and evolution of organic matter of the oil shales but provides satisfactory informations as a first approach.

Pyrolysis is an artificial evolution process, i.e. the evolution taking place in the nature at low temperature, high pressure and during long time can be modelled by pyrolysis carried out at higher temperatures in laboratory conditions. TISSOT et al. [1974] evidenced that the high temperature eliminates the time and pressure factors of evolution. The conditions of heating (vacuum or inert atmosphere, solvent medium, temperature) determine the mechanism of the process, the quality and quantitative distribution of its products. Certain part of the pyrolysis investigations try to explore the structure of kerogen. The different groups and radicles produced by the low temperature pyrolysis are detected by gas chromatographs or mass spectrometers. When applying low temperature (200 to 300° C) the paraffin or aromatic

character of the organic matter can be determined, further data can be obtained concerning the gas and oil potential, and the kinetics of the decomposition process can also be studied [CANE, 1948; DI RICCO and BARRICK, 1956; GIRAUD et al. 1970].

By means of higher temperature pyrolysis (500 to 600° C) the evolution processes can be followed [TISSOT et al., 1974; GIRAUD et al., 1970].

GRANSCH and EISMA [1966] characterized the source and evolution degree of the kerogen by the C_R/C_T quotient were C_R denotes the carbon content after the pyrolysis at 900° C and during 90 minutes and C_T is the total carbon content. GIRAUD et al. [1970] measured the C_R/C_T quotient at 500°C and this was called degradation factor (T_D). These methods are favourable since the preliminary removal of the inorganic compounds can be neglected.

Our investigations were carried out according to GRANSCH and EISMA [1966] with the only modification that pyrolysis was performed not only at 900° C but also at 300, 400, 500 and 600°C. Pyrolysis was carried out in an electric furnace, in a quartz tube. The furnace was heated to the required temperature, then the weighted sample was taken into the furnace where it was pyrolized during 90 minutes in nitrogen atmosphere. Cooling to room temperature was carried out also in nitrogen atmosphere, then the sample was weighted again. The carbon contents obtained before and after pyrolysis at different temperatures, respectively, were determined (signs of the values: C_T, C_{300}, C_{400}, ... C_{900}). The degradation factor (T_D) was computed for all temperatures: $T_{300} = C_{300}/C_T$, etc. (Table 4). According to GRANSCH and EISMA [1966] in case of alginite the value of C_{900}/C_T measured at 900° C is 0.05–0.27, in case of peat, lignite and humic coals 0.60–1.00. In the samples investigated containing alginite the C_{900}/C_T value proved to be 0.09–0.24, in samples

TABLE 4

Degradation factors $\left(T_D = \dfrac{C_R}{C_T} \right)$ measured by pyrolysis at different temperatures

Sample No	T_{300}	T_{400}	T_{500}	T_{600}	T_{900}
5	0,83	0,83	0,77	0,54	0,34
7	0,86	0,86	0,74	0,49	0,42
11	0,96	0,95	0,86	0,32	0,16
14	0,98	0,94	0,81	0,28	0,24
18	0,99	0,94	0,79	0,49	0,35
22	0,92	0,87	0,81	0,40	0,32
24	0,98	0,83	0,71	0,15	0,11
26	0,95	0,95	0,81	0,17	0,12
27	0,96	0,96	0,86	0,13	0,09
28	0,96	0,96	0,96	0,17	0,15
32	0,96	0,91	0,80	0,31	0,10
33	1,00	0,98	0,82	0,51	0,27
35	1,00	0,89	0,84	0,49	0,23
38	0,95	0,91	0,81	0,23	0,14
42	0,97	0,95	0,82	0,33	0,20
45	0,96	0,95	0,87	0,18	0,13
49	0,97	0,98	0,74	0,21	0,16
55	0,92	0,90	0,78	0,53	0,28
59	0,93	0,91	0,75	0,45	0,40
62	0,95	0,90	0,74	0,48	0,29
69	0,99	0,99	0,71	0,48	0,14
73	0,92	0,92	0,85	0,59	0,41

rich in organic matter around 0.10. The T_D values were plotted as a function of temperature and some characteristic curves are seen in *Fig.* 2. It is characteristic of all the samples that the transformation of the organic matter follows mostly between 500 and 600° C but in case of a few samples this section is steeper than in case of others. Further differences are found, *i.e.* in certain samples pyrolysis seems to be completed at 600° C, in others the curve is steep also between 600 and 900° C. To make easier the comparison, the characteristic curves of the samples were described by a figure, thus the rise of the curves between 500 and 600° as well as between 600 and 900° C being apparently characteristic of the samples were also determined
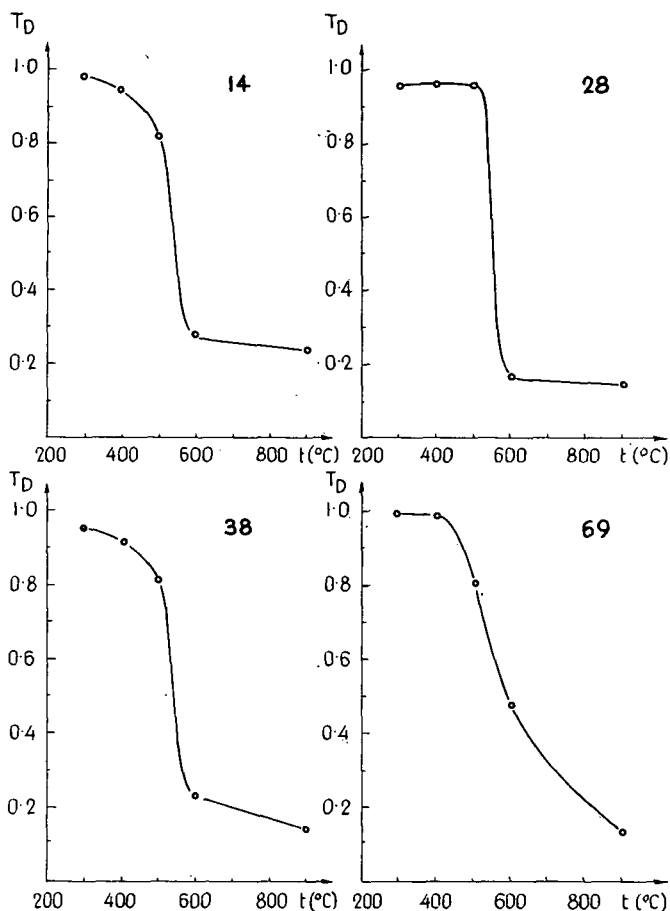

Fig. 2. Pyrolysis curves of some samples of the borehole Put-7. $T_D = C_R/C_T$ degradation factor t (°C) temperature of pyrolysis.

(marked by m_1 and m_2), finally their quotient (m_1/m_2) was formed. On the basis of these values the investigated samples can be assigned to three groups (Table 5). In the first group the value of m_1/m_2 is 2.0 to 7.0; in the second group it is 10.4–19.3 while in the third group it is greater than 33. The distribution of the samples among the three groups seems to be concordant with the geological view developed on the

TABLE 5

Slope of the pyrolysis curves of the samples from boreholes Put-7

	I		II		III
Sample No.	$\dfrac{m_1}{m_2}$	Sample No.	$\dfrac{m_1}{m_2}$	Sample No.	$\dfrac{m_1}{m_2}$
69	2,0	11	10,4	49	33,1
55	3,0	7	10,9	26	40,0
5	3,5	42	12,0	14	40,8
33	3,9	22	15,4	24	43,0
35	4,1	59	18,8	45	43,1
73	4,3	38	19,3	27	56,2
18	6,0			28	>60,0
32	7,0				

basis of the stratigraphic and X-ray diffractometric investigations. As it has been emphasized in the introduction, the Hungarian oil shale was formed in a small bay surrounded by the ring-shaped tuff barriers of a volcanic crater [JÁMBOR *et al.*, 1975]. Smaller cold-water inundations caused periodic temperature and salinity changes in several phases and this had been responsible for the destruction of the *Botryococcus* colonies [MEZŐSI, 1976]. Out of our samples those of No. 24, 26, 27, 28 and 14 derive from the depth corresponding to such inundation periods. This may explain the fact that the sample No. 14 of relatively low carbon content (C=11.3%) and the samples of high carbon content (C=20.45%) form the third group characterized by the highest m_1/m_2 value. Samples being assigned to the first group $(m_1/m_2<7)$ derive from the boundaries of the sedimentation cycles, their organic carbon content is low and is composed more or less of coalified plant remnants.

The transitional samples lying between the two extreme values belong to the second group.

Comparing our measurement results with the data of the literature, e.g. with those of TISSOT *et al.* [1974] it is apparent that according to the authors above significant change follows during pyrolysis between 400 and 500° C while according to our data this occurs only between 500 and 600° C. It was thought that the difference can be attributed to the inorganic components. To prove this assumption the pyrolysis was carried out on some kerogen concentrates by means of the method described above. The specific gravity and ash content characteristic of the purity of the concentrates as well as the degradation factors determined by pyrolysis are shown in Table 6. Since the kerogen investigated was concentrated by means of physical

TABLE 6

Specific gravity, ash content and degradation factors of the kerogens isolated from samples of the borehole Put-7

Sample No.	T_{300}	T_{400}	T_{500}	T_{600}	T_{900}	Specific gravity	Ash content %
26	0,91	0,38	0,07	0,06	0,03	0,89	10,56
28	0,91	0,40	0,05	0,05	0,03	0,99	7,67
38	0,92	0,47	0,05	0,04	<0,03	1,12	9,18
55	0,94	0,55	0,47	0,36	0,09	1,65	64,7
69	0,91	0,78	0,70	0,44	0,24	1,48	71,10

method, in case of the samples No. 55 and 69 of lower organic matter content the concentration is only partial, the specific gravity and ash content are fairly high. In case of these samples the rise of the curves is similar to that of the original matter, the main thermal process takes place also between 500 and 600° C and 600 and 900° C, resp. In case of the samples No. 26, 28 and 38 the concentrate is somewhat purer, and pyrolysis seems to be completed at 500° C and this is in accordance with the data of references. On the basis of this measurement series it is believed that the difference of about 100° C is caused by the inorganic components and this problem will be investigated in detail.

CLASSIFICATION OF THE ORGANIC MATTER BY MEANS OF SELECTIVE OXIDATION METHOD

On the basis of the wide-spread methods applied in carbon chemistry numerous authors studied the effect of different oxidizing media on oil shales, especially that of potassium permanganate. "This research had the very important result that it clearly differentiated oil shale kerogens into two types depending upon whether benzenoid acids were formed or not. Further research has led to the belief that at least two types of kerogen are likely to be present in oil shales: 1. an algal portion which may or may not be oxidation resistant and 2. a quasi-aromatic portion the nature of which is more humic or coaly" [CANE, 1976]. As an improvement of the method and to avoid the further oxidation of the transitional products either special oxidation medium is used, e.g. the acetonic solution of potassium permanganate of STEFANOVIČ and VITOROVIČ [1959] being specific of double bonds, or the oxidation is carried out step by step. To classify the petroleum source rocks and to estimate the oil potential an empirical formula was elaborated by KHALIFEH and LOUIS [1961]; the method is based on the analysis of the non-oxidized residue of the step by step oxidation. Acidic potassium permanganate was used as oxidizing medium, and after oxidation the reduction capacity (PR) and carbon content (C) of the organic matter remained in solid phase were determined. In case of our investigations this latter method has been used. Samples were prepared in the manner shown in *Fig. 1*. Since the matter of about 3 per cent organic carbon content is most favourable for the measurements, the oil shale was "diluted" by kaolinite by five to ten times. (The selective oxidation was carried out, of course, also by kaolinite and while no change in the parameters needed by our measurements could be measured during the process, it proved to be a suitable diluting medium.) The quotient of reduction capacity and organic carbon content ($C_R=PR/C$) was plotted against the organic carbon content. Seven samples were chosen, three from the second sedimentation cycle, the samples No. 24 and 28 being characterized by numerous large-sized *Botryococcus* colonies, and finally the sample No. 32 deriving from the lower boundary of the sedimentation cycle. The carbon content of this latter sample is lower and contains a few coalified plant fragments. In the first sedimentation cycle samples No. 38, 42 and 49 represent the relatively enriched organic matter content, out of the investigated samples that of No. 69 is of lowest carbon content ($C=5\%$).

The C_R-C curves obtained as a result of selective oxidation are of the same rise in the sample No. 24 and 28 out of the seven investigated samples *(Fig. 3a)*, and they are nearly parallel with the abscissa. The curve of the sample No. 38 seems to be divided into two sections, i.e. up to about $C=50\%$ it is parallel with the abscissa, then it turns steeply downward *(Fig. 3b)*. The curves of the samples No. 42 and 49

(Fig. 3c) incline gradually downward but after about C=60% the sudden decrease of the C_R-values follows. The change of the C_R values of the samples No. 32 and 69 is nearly linear as a function of C. The reduction capacity of the samples decreases in the order described above, *i.e.* initially the *Botryococcus braunii* remnants determine the character of the organic matter, and parallel with their gradual decrease the coalified plant remnants become predominant out of the components of the organic matter. Consequently, the rise of the curves will be determined by the maturity of the organic matter and not by the absolute value of the organic carbon content, since regarding *e.g.* the sample No. 32 (C=11.44%) lies closer the sample No. 38 (C=16.74%) than the sample No. 69 (C=5.00%). Nevertheless, the reduction capacity of the samples No. 32 and 69 shows similar features as a function of the carbon content while the sample No. 38 is transitional between the sample No. 24 and 28 rich in organic matter and those of No. 42 and 49.
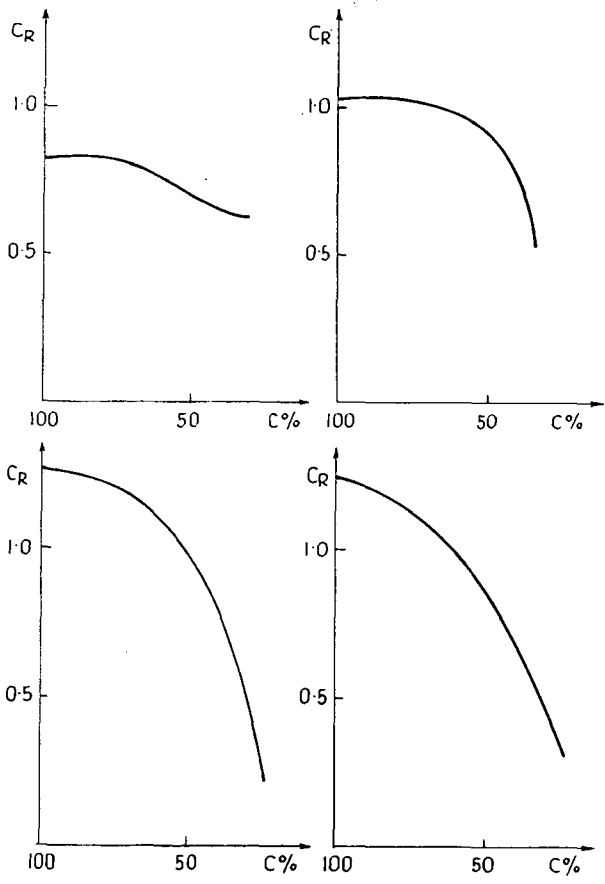

Fig. 3. Change of reduction capacity of the organic matter during selective oxidation in some samples of the borehole Put-7.
a) samples No 24 and 28;
b) sample No 38;
c) samples No 42 and 49;
d) samples No 32 and 69.

SUMMARY

The kerogen of the Hungarian oil shale tried to be characterized by several methods.

Kerogen was isolated, its carbon and hydrogen contents were measured, its H/C ratio was calculated and these were compared with the same data of other oil shales known from literature. The H/C ratio depends on the maturity of the kerogen and on its diagenetic state. The source material as well as the sedimentation conditions and chemical parameters of the environment also affect on this ratio. According to GRANSCH and EISMA [1966] in case of alginites the H/C ratio moves between 1.4 and 1.8. In case of the Hungarian oil shale this ratio proved to be 1.77, in average. Lower values were obtained in case of chemically isolated samples (1.4–1.6) and somewhat higher in case of samples isolated by means of physical methods. When comparing these samples with other alginites the source matter of which was also Botryococcus alga, the obtained average value is close to that of the Australian coorongite.

Further, methods were applied to determine the character of the organic matter which do not need the preliminary separation of the organic matter, but after removing the bitumen fraction and the carbonates, the measurement can be carried out just on the original rock. Though no information was obtained regarding the chemical composition and structure of kerogen by means of these methods, so these provide only preliminary informations, distinction can be made within one borehole in the character of the organic matter (in our case also within 40 metres).

Pyrolysis is such a method which is suitable to describe the source material and degree of evolution of the kerogen. The samples were pyrolised step by step at 300, 400, 500, 600 and 900° C. At 900° C the ratio of the bound carbon content to the total carbon content is 0.05 to 0.27 in case of alginites [GRANSCH and EISMA, 1966]. In the investigated alginite-bearing samples the C_{900}/C_T value proved to be 0.09 to 0.24, in the samples most abundant in organic matter around 0.10. The degradation factors determined at different temperatures were plotted against the temperature and on the basis of the rise of the curves characterized by the slope of each curve, the samples could be divided into three groups. The samples containing only coalified plant remnants and the samples of algal origin and rich in organic matter belong to the two extreme groups. The second groups contains the samples of transitional character. The samples assigned to the first group correspond to the depth intervals determining the start and end of each sedimentation cycle. The samples of the third group derive from a depth where, as a result of the gradual changes of chemical parameters of the crater lake, the Botryococcus colonies were destroyed in large masses.

The character of the organic matter can be described by selective oxidation as a first approach, since the resistance capacity of the organic matter against the oxidizing agents is in relationship with the kerogen structure and source material and the diagenetic process affects them only to a smaller extent [YEN and CHILINGARIAN, 1976]. On the basis of the C_R—C curves the samples containing different kinds of organic matter can be decisively separated and the curves of the samples of the two sedimentation cycles rich in organic matter (samples No. 24, 28, resp. 42, 49) are also different. On the basis of the sedimentological investigations the following difference can be found among the samples mentioned above: in the depth interval of 13 to 19 m (samples No. 24 and 28) the Botryococcus colonies occur in large masses, while the samples No. 42 and 49 are characterized by lamellar formation and only Botryococcus colonies of smaller size can be observed in them. Further

174

investigations extending also over the analyses of the oxidation products will throw light upon the problem that the differences in the features of the samples can be attributed to the smaller differences in the kerogen structure, or this is caused by the "advantage" of the investigation method (which may occur here as a failure) that the inorganic components were not preliminarily separated from the organic matter.

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