

## **THERMAL DEGRADATION OF THE ORGANIC MATTER OF OIL SHALE OF PULA (HUNGARY) AT 573—773 K**

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### **INTRODUCTION**

The thermal degradation of oil shales is worthy of mention partly from the point of view of their industrial utilization, partly as the most important parameter of the evolution of the organic matter.

Shale oil and gas can be produced from the oil shale with best efficiency at the temperatures between 743 and 823 K. Thus the thermal treatment has been studied so far in this temperature range and the investigations aimed first of all the increase of the quantity of products *i. e.* of the shale oil and gas. In spite of the efficiency of the conversion of organic matter the considerable amount of mineral components highly lowers the efficiency of the process. It seemed to be obvious to eliminate the mining, transport and storing of these components. Consequently especially in case of large scale fields the *in situ* production is favoured both by researchers and by economic experts. In addition to numerous technological researches the processing *in situ* requires the investigation of the degradation process at lower temperatures, as well. Studies dealing with the thermal degradation of the Green River kercgen between 423 and 623 K were published by CUMMINS and ROBINSON [1972] CUMMINS, DOOLITTLE and ROBINSON [1974].

At the same time, the evolution of the organic matter and the formation of petroleum and natural gas have been one of the fundamental problems of organic geochemistry. The kercgen of strongly polycondensated structure being formed at low temperature and pressure under surficial conditions is in metastable state. The temperature and pressure increase produced by deposition and subsidence breaks the equilibrium between the kercgen and its environment. The progression of the evolution of kercgen is manifested by the effort to re-establish the equilibrium between the kercgen and its continuously changing environment. Most of the authors believe the temperature to be the most important factor among the environmental parameters. In first approximation the laboratory simulation of the thermal degradation seems to be improbable just because of the incommensurability of the geological and human ages. Nevertheless, numerous experiments and reaction kinetic calculations prove that by increasing the temperature the reaction rate can be increased to such an extent that the degradation process can be simulated even under laboratory conditions, as well. Observations concerning the possibility of time-temperature replacement are only qualitative, the numeric relationships are not cleared yet (TISSOT and WELTE, 1978).

According to the observations concerning the mechanism of decomposition, bitumen soluble in organic solvents develops from kercgen, together with CO<sub>2</sub>,

H<sub>2</sub>S, H<sub>2</sub>O and occasionally with hydrocarbons of shorter chains; then the bitumen is degraded to oil the phenomenon being accompanied by gas formation, and a more coalified organic matter remains [CANE, 1951; ABELSON 1967; VITOROVIĆ and JOVANOVIĆ, 1968].

Having compared the experiences of laboratory simulation of the kerogen evolution with the maturity of the organic matter of sediments TISSOT and WELTE [1978] found that when treating the kerogen of type II at normal pressure and in neutral gas atmosphere, the temperature ranges of the phases of evolution can be determined even in laboratory. By means of degradation below 623 K the diagenesis, between 623 and 773 K the catagenesis and above 773 K the metagenesis can be simulated.

This paper gives a summary of the observations concerning the thermal degradation of the oil shale of Pula (Hungary) with special regard to the distribution of products of temperature, as well as to the change of character of the non-converted organic matter during the artificial genesis. Since the oil shale of Pula is a near-surface alginite rich in organic matter, it may be suitable for these experiments. The sample deriving from small depth (0—45 m) did not endure considerable changes of temperature and pressure, thus it contains organic matter of immature state being at the beginning of its genesis, as it has been proved by the preliminary investigations [HETÉNYI and SIROKMÁN, 1978]. The kerogen isolated from the oil shale has been degraded already at 473 and 573 K [HETÉNYI, 1979]. In the experiments in question the oil shale was degraded at different temperatures between 573 and 773 K and at different durations. We aimed the laboratory simulation of the process of catagenesis and to determine the transition between the dia- and catagenesis in case of the studied organic matter, of course under laboratory conditions. Further, at several characteristic temperatures based on the experiences of the measurements above the kerogen isolated from the oil shale was also degraded in order to determine the coal rank and H/C atomic ratio of the non-converted organic matter.

## EXPERIMENTAL

The sample in question is a Pliocene (Upper Pannonian) oil shale of Pula (Hungary) which was formed in a miohaline crater lake of 283—285 K, and the precursor of which is the *Botryococcus braunii* KÜTZ. [JÁMBOR and SOLTÍ, 1976]. During the measurements air-dried sample of 0.05—0.15 mm diameter was used, its ash content is 49.9%, C<sub>inorg</sub> = 2.6%, C<sub>org</sub> = 27.4%. Before isolating the kerogen the bitumen was extracted in Soxhlet extractor by means of chloroform (Bit-A = 3.3%). Based on the differences in specific gravity, the kerogen was enriched physically. Parameters of the kerogen are: ash content = 9.0%, C<sub>inorg</sub> = 0.6%, C<sub>org</sub> = 70.2%.

Thermal degradation was carried out in a glass-made heating tube and the samples were measured in boats made from the same glass. The heating tube was surrounded by a programmed furnace. Heating and cooling to room temperature were carried out in continuous nitrogen flow. The products were collected in two traps. The first was air-cooled in which the oil was practically precipitated. The second collector was cooled by salted ice where first of all the water and a small quantity of oil precipitated. Gases were not measured. The oil shale and the kerogen were extracted in the mixture of benzene:acetone:methanol of 75:15:15 ratio after degradation.

The determination of hydrogen and carbon contents was carried out by means of CHN-1 analyser.

The degree of degradation was determined according to the ASTM-standard [CUMMINS *et al.*, 1974]; taking the carbon content (C<sub>R</sub>) of the sample after heating

at 773 K in inert atmosphere during 30 minutes and referring this value to the carbon content ( $C_T$ ) before the thermal treatment.

The products of thermal degradation of the oil shale, i. e. the quantities of gas + water, oil, bitumen, non-converted matter and the quantity of the non-converted organic carbon are summarized in Table 1.

TABLE 1

*Different matters originated from oil shale by thermal degradation*

Heating		Gas + water (%)	Shale oil (%)	Bitumen (%)	Unconverted	
temperature (K)	period (h)				oil shale (%)	$C_{org}$ (%)
573	48	8,1	0,9	1,4	89,6	21,9
	96	11,2	0,9	0,5	87,4	17,6
	336	12,8	1,2	0,5	85,5	16,6
598	5	7,9	1,1	2,9	88,1	18,7
	10	7,9	1,1	2,4	88,6	17,0
	24	8,3	1,7	2,4	87,5	15,7
	48	10,3	2,7	2,4	84,6	13,1
623	1	8,1	0,9	3,6	87,4	14,4
	5	9,6	1,4	3,0	86,0	13,2
	10	13,3	2,7	2,8	83,2	13,6
	24	12,0	4,0	3,4	82,6	—
648	1	8,1	1,9	3,3	86,7	16,6
	5	9,9	5,1	5,3	79,7	12,4
	10	11,3	6,7	4,3	77,7	10,6
673	1	12,1	5,9	7,4	74,6	8,3
	5	14,8	10,2	6,4	68,6	8,0
	10	13,6	11,4	2,0	73,0	9,6
723	1	19,4	4,6	1,9	74,1	8,2
	2	22,1	5,9	0,9	71,1	5,8
	5	16,8	12,2	0,7	70,3	5,1
773	1	16,9	12,1	1,6	69,4	4,8
	2	18,2	14,8	0,4	66,6	3,0
	5	19,0	14,0	0,3	66,7	2,8

The formation of the most important product of the process, i. e. of the shale oil could be observed already at the applied lowermost temperature (573 K) and during a relatively short time. During 48 hours 0.9% shale oil was formed. When having increased the duration of thermal treatment, the production has hardly changed, it reached only 1.2% even during 336 hours.

Parallel with the increasing temperature the quantity of the shale oil is rapidly increasing. In Fig. 1 the increase of the quantity of shale oil can be seen as a function of the degradation temperature during thermal treatment of 5 hours. From the temperature of 623 K the production steeply increases, while between 673 and 773 K it is also intense but less rapid than before. Consequently, it seems so that the main oil producing phase of the studied Hungarian oil shale of type I falls between 623 and 773 K under laboratory conditions, i. e. this temperature interval is suitable to the laboratory simulation of the catagenesis.

As it is well-known, the quantity of the oil is increased both by the increase of temperature and of duration of degradation: the change is exponential in the former and linear in the latter case. Under the applied experimental conditions certain overlaps could be observed between each temperature-time pairs. Nearly the same quantity

of oil was formed at 673 K during 10 hours, at 723 K during 2 hours and 773 K during one hour (Table 1). These results refer also to the fact that the results of degradation carried out under laboratory conditions at higher temperatures and shorter duration are commensurable at least concerning the quantitative relations with the evolution under natural conditions at lower temperatures but longer durations.

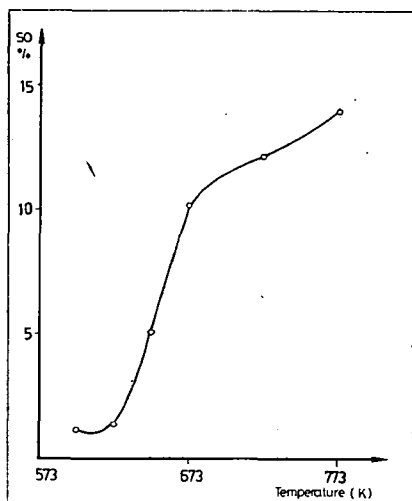


Fig. 1. Yield of the shale oil as a function of temperature of degradation.

In addition to the shale oil being the most important from the industrial point of view, gas and water as well as bitumen were formed at all the studied temperatures and during each degradation time. The temporal change of these products, as well as of the non-converted organic matter, and of the organic carbon content of the latter can be seen in Figs 2—5.

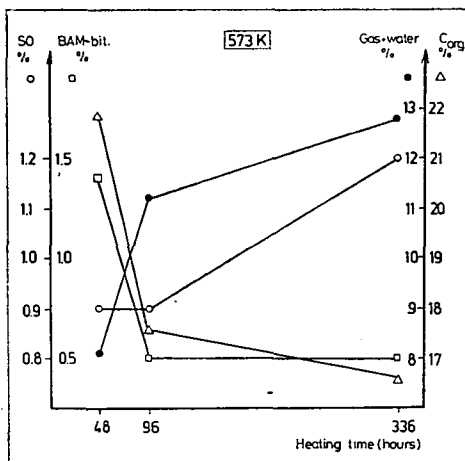


Fig. 2. Materials degraded from oil shale and organic carbon content of the unconverted oil shale in function of the heating period at 573 K.

At 573 K and during 48 hours the bitumen content of 4.6% of the original sample decreased to 1.4%, simultaneously the gas and water release was started and 0.9% shale oil formed. The organic carbon content decreased from 30.0% to 21.9%. When having increased the duration of degradation, between 48 and 96 hours the subsequent bitumen decrease was not accompanied by the increase of the quantity of shale oil, but the quantities of the released gas and water were considerably increased. Between 96 and 336 hours the quantity of bitumen seemed to remain unchanged, but at the same time the oil predominated out of the reaction products, the joint quantity of gas and water was increased only to smaller extent. When characterizing the whole of the conversion by the change of the  $C_{org}$  content the reaction is more intense at the beginning, then the efficiency of transformation seems to decrease. Presumably, the degradation of the bitumen being present in the original sample and of relatively large amount, has started already in the first minutes of thermal treatment, the release of gases could be observed by sense, as well. The transformation of kerogen has presumably also started, but this needs much more time than the decomposition of the bitumen, thus equilibrium between the formation and transformation of bitumen followed only between 96 and 338 hours.

When increasing the temperature the rate of reaction is increased and the oil production becomes more intense. At 598 K (Fig. 3) the character of the process

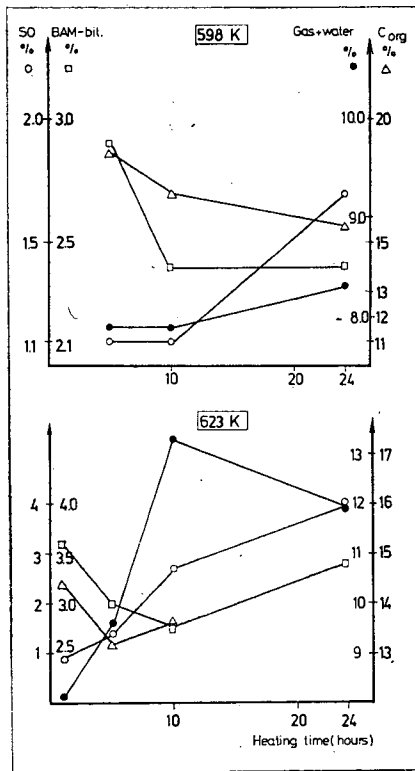


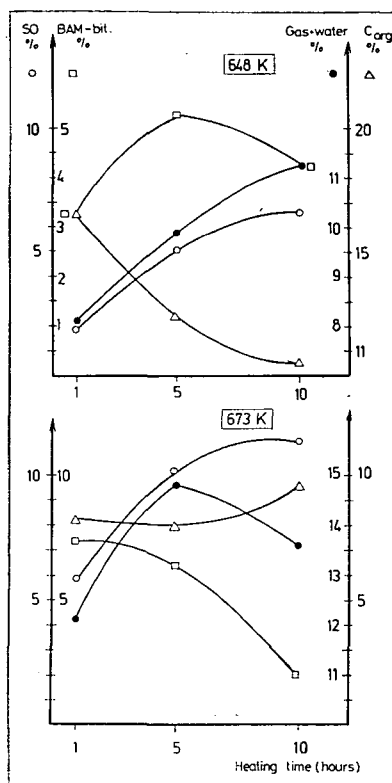
Fig. 3. Materials degraded from oil shale and organic carbon content of the unconverted oil shale in function of the heating period at 598 K and 623 K.

is similar to that observed at 573 K but all changes take place within a much shorter duration. The increase of oil production becomes stronger and the formation of water and gas is less significant.

At higher temperature already from 623 K (*Fig. 3*) the equilibrium followed previously in the formation and decomposition of bitumen seems to be disturbed. After the initial decrease (between 1 and 10 hours) the bitumen content increases again between 10 and 24 hours. The quantity of shale oil increases as a function of time already from the start of the reaction as against the constant value observed at 96 and 10 hours, respectively. The gas and water content increases first as a function of time, then shows a decreasing tendency. This is valid not only at 623 K but also at higher temperatures, i. e. at 673 and 723 K.

At 648 K (*Fig. 4*) the bitumen content shows a relatively high value during the whole process of degradation. It decreases down to 3.3% at the end of the first hour while in the 5th hour it exceeds the 4.6% of the original sample, but between 5 and 10 hours it is slightly decreasing again. Simultaneously, the quantities of oil, gas + water increase continuously, presumably due to the more intense degradation of bitumen between 5 and 10 hours.

At 673 K (*Fig. 4*) considerable quantities of bitumen and oil developed during 1 and 5 hours. Between 5 and 10 hours the transformation of bitumen into oil is



*Fig. 4.* Materials degraded from oil shale and organic carbon content of the unconverted oil shale in function of the heating period at 648 K and 673 K.

stronger, the bitumen content considerably decreased. Under the studied experimental conditions, at this temperature considerably greater quantity of bitumen could be extracted as compared with the results of other degradation processes carried out at other temperatures but during the same duration.

At 723 and 773 K (Fig. 5) the character of the changes is nearly the same. The tendency seems to predominate that some equilibrium should develop in the quantitative ratios of all products studied. Of course, at higher temperature this may follow during shorter durations.

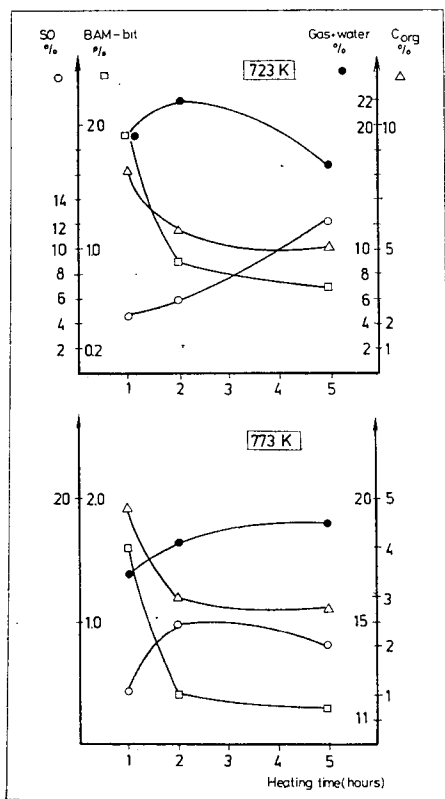
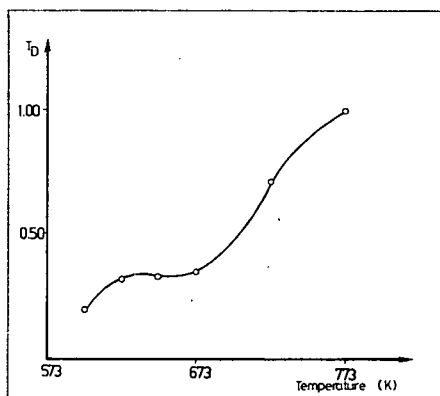


Fig. 5. Materials degraded from oil shale and organic carbon content of the unconverted oil shale in function of the heating period at 723 K and 773 K.

As it has been demonstrated above, during the natural and artificial degradation gas, water and oil develop depending on the conditions of the process (e. g. temperature, time). Their ratio is not constant. In the meantime, by means of gradual elimination of the smaller, shorter carbon-chain units the organic matter is also transformed and a more condensed and more complex matrix remains. Since at the beginning of the process the units more abundant in hydrogen are released, the unconverted kerogen becomes ever more coalified. To characterize the unconverted organic matter the degree of degradation ( $T_D = C_R/C_T$ ) is given. In Table 2 the quotients are listed which derive from the samples of 5 hours thermal treatment and extracted in BAM,

Degradation coefficient ( $T_D$ ) of unconverted oil shale

Heating period (h)	Heating temperature (K)	Degradation coefficient $T_D = C_R/C_T$
5	598	0,20
5	623	0,32
5	648	0,33
5	673	0,35
5	723	0,71
5	773	1,00

Fig. 6. Degradation coefficient ( $T_D$ ) as a function of temperature.

further these are shown as a function of temperature in Fig. 6. The determination  $T_D$  was carried out according to the ASTM-standard at 773 K. Though the type and measure of diagenesis of the organic matter of sediments were characterized by the  $C_R/C_T$  ratio at 1172 K by GRANSCH and EISMA [1966], the temperature value of 773 K proved to be more favourable both numerically and in the subsequent investigations in case of oil shales [GIRAUD, 1970; CUMMINS *et al.*, 1974]. According to the authors above the  $C_R/C_T = 0.09-0.27$  is characteristic of alginites, the values of 0.60-1.00 of humic coals, peat and lignite. Further, in case of  $C_R/C_T > 0.6$ , the organic matter is so highly coalified that it becomes unable to oil production. When making the determination of  $T_D$  at lower temperature the limits above will be probably displaced to higher values. The organic matter of the Hungarian oil shale is alginitic. Knowing its feature conclusions can be drawn from the  $T_D$  value to its degree of diagenesis. The  $T_D \approx 0.10$  value of the original sample is increased during 5 hours only up to 0.25 at 598 K and up to 0.35 at 623, 648 and 673 K. The value given for the alginites hardly exceeds the limit value already in the range of catagenesis. Consequently, the samples degraded for such short durations show only slight transformation already at relatively high temperatures. Above 673 K the conversion considerably increased and at 723 K the sample is hardly able to further oil generation, i. e.  $T_D$  is around the limit value. In case of thermal treatment at 773 K, because the determination of  $T_D$  is carried out at this temperature the  $T_D = 1$  could be expected in all cases. After 5 hours treatment this value was obtained. The  $C_R/C_T$  ratio of the



unconverted oil shale degraded at 773 K during 1 and 2 hours was also determined and this proved to be 0.64 and 1.00. These results, i. e. the quantitative relations of the value reflecting the character of the remaining matter and of the products (see the data of Table 1 and Fig. 5) show that at 773 K practically equilibrium follows after 2 hours. The duration of 2 hours is sufficient to reach the most favourable conversion and when increasing the duration the transformation of the organic matter is not continued at this temperature.

In Fig. 6 showing the change of the unconverted organic matter as a function of the temperature, a break can be seen at 763 K in addition to the approximate temperature of 623 K assumed to be the boundary between the dia- and catagenesis. Similar relationship can be observed also in Fig. 1 showing the relationship between the shale oil quantity and temperature. As to our opinion some change follows in the reaction mechanism at this temperature. The quantity of the extractable bitumen is greatest also at this temperature. Since the evaluation of bitumen quantity is complicated by the fact that not only the bitumen formed during the laboratory degradation but also the bitumen developed during the natural evolution are present in the sample, it proved to be expedient to degrade thermally the kerogen itself also at several characteristic temperatures. For this very reason, the kerogen concentrate was heat-treated at 598, 673 and 773 K during 5 hours. The temperature of 598 K falls to the range of diagenesis as proved by the experiments carried out previously with the oil shale while the values of 673 and 773 K represented the stage of catagenesis. The quantitative distribution of the products are involve in Table 3.

*Different matters originated from kerogen by thermal degradation*

TABLE 3

Heating temperature (K)	period (h)	Gas + water (%)	Shale oil (%)	Bitumen (%)	Unconverted kerogen (%)
598	5	11,1	0,9	1,5	86,5
673	5	39,8	13,2	17,6	29,4
773	5	41,9	38,1	0,3	19,7

In the range of diagenesis (598 K) only a relatively small portion of kerogen, i. e. about 13% was converted. Major part of the products is gas and water, small quantity of shale oil was formed and 1.5% bitumen was extracted. Since the starting matter did not contain bitumen, the total quantity was formed from kerogen as a result of thermal treatment under laboratory conditions. The shale oil of 0.9% is also the product of the artificial evolution of kerogen. It could be assumed that during the degradation of oil shale the subsequent degradation of the original bitumen produced an oil formation. The low temperature degradation of the bitumen-free kerogen, however, proved that the laboratory temperature of diagenesis provided also sufficient energy to start the bitumen and oil formation. According to the experiences of the preliminary measurements bitumen can be observed also at lower temperatures, i. e. at 473 and 573 K, and the generation of oil at 573 K, respectively. These results of the artificial evolution as well as the fact that the studied oil shale being in the initial stage of diagenesis contains large quantities of original bitumen refer to the start of evolution of the organic matter in the stage of diagenesis, and to the start of oil generation at the end of this stage. From the economic point of view this oil quantity is negligible, the phenomenon, however, throws light upon the fact that

though the main phase of oil generation is assigned to the catagenesis, the generation itself cannot be bound only to this stage.

Catagenesis was simulated at 673 and 773 K by means of thermal degradation, with the same durations. The efficiency of conversion has considerably increased, about 70% of the kerogen concentrate was converted at 673 K and about 80% at 773 K. The quantity of the products, first of all that of the shale oil, was multiplied. When comparing the quantities of the products at 673 and 773 K the gas+water quantities are nearly the same, that of the shale oil continuously increases. The quantity of the extracted bitumen, however, changes inversely as a function of temperatures: at 673 K 17.6%, at 773 K very small quantity of bitumen (0.3%) was obtained.

The question is arisen whether only the quantity or probably the quality of bitumen change at 673 K. The bitumen formed during the thermal degradation of kerogen was characterized by its hydrogen and carbon content as well as by its H/C atomic ratio (Table 4). As a comparison: the H/C ratio of the bitumen extracted from the original oil shale is 1.76. The H/C ratio of the BAM-bitumen formed from the kerogen concentrate at 473 K during one day is 1.75. For the bitumens obtained after degradation of seven days the H/C values are as follows: at 573 K 1.69 and at 573 K 1.67. The same, i. e. 1.67 value was obtained for the BAM-bitumen degraded at 598 K during 5 hours. At 673 K the H/C atomic ratio considerably decreases (1.50) while at 772 K the value is some higher again (1.60). Consequently, in case of degradation at 673 K not only more bitumen was formed but its quality also differed from the average. Parallel with increasing temperature presumably ever greater structural units are cut off from the kerogen and become the constituents of the bitumen fraction. At the beginning of the process, at low temperature only the H<sub>2</sub>O, H<sub>2</sub>S, CO<sub>2</sub>, i. e. the most instable groups are eliminated, this is followed by the release of the hydrocarbons of shorter chains. Parallel with increasing temperature the release of ever greater units becomes possible and the character of bitumen follows this change; its H/C atomic ratio is slightly decreased. At 773 K the rate of reaction of bitumen → oil has so considerably increased that the intermediary product can hardly be isolated. The bitumen of very small quantity was more degraded than that of 673 K and its H/C atomic ratio is higher, as well.

TABLE 4

*Hydrogen and carbon content of the bitumen extracted from degraded kerogen*

Heating temperature (K)	Carbon content (%)	Hydrogen content (%)	H/C atomic ratio
598	75,3	10,5	1,67
673	75,1	9,4	1,50
773	67,7	9,0	1,60

In the quality of the unconverted organic matter this type of change could not be observed. The hydrogen and carbon contents as well as the H/C atomic ratios of the unconverted kerogen are shown in Table 5, and a supplement is given consisting of the same parameters of the kerogen concentrate and of the kerogen treated at 473 and 573 K. In the latter cases the duration of thermal treatment was 24 hours [HETÉNYI, 1979]. As it can be seen in Fig. 7 the H/C atomic ratio is nearly constant in the T ≈ 598 K temperature range representing the stage of diagenesis, small decrease with the increasing temperature can be observed. The sudden change observed in the

stage of catagenesis relates to the rapid conversion, "coalification" of the organic matter.

The qualification of the organic matter of sediments is impossible only on the basis of the H/C ratio. On the basis of this series of experiments the conclusion should be drawn that the value of this quotient depends not only on the character of the

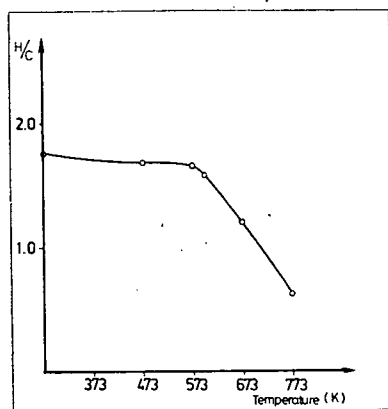


Fig. 7. H/C atomic ratio of the unconverted kerogen as a function of temperature of degradation.

Hydrogen and carbon content of the raw and degraded kerogens

TABLE 5

temperature (K)	Heating		Carbon content (%)	Hydrogen content (%)	H/C atomic ratio
	period (h)				
raw kerogen	—		70,2	10,3	1,76
473	24		71,3	10,0	1,68
573	24		70,7	9,7	1,65
598	5		70,4	9,3	1,58
673	5		59,2	5,9	1,20
773	5		39,7	2,1	0,62

starting organic matter (terrestrial or marine origin, algal or humic constituents, etc.) but also on its evolution. According to the traditional classification the original kerogen and the kerogen treated at  $T \leq 598$  K are "alginite", since their H/C ratios fall between 1.4 and 1.8 [GRANSCH and EISMA, 1966]. On the basis of only this quotient the samples degraded at higher temperatures should be assigned to the group of humic coals, peat and lignite, the H/C atomic ratio of which varies between 1.4 and 0.4. In this case the alginite has considerably transformed during the artificial treatment, so that during the gradual coalification it reached the "peat"-state.

### CONCLUSIONS

The thermal degradation of the organic matter of the oil shale of Pula (Hungary) was simulated under laboratory conditions in the temperature range of 573 to 773 K in neutral gas atmosphere.

The raw material is a Pliocene (Upper Pannonian) near-surface oil shale containing organic matter in the first stage of its evolution. Its H/C atomic ratio is 1.76, the degree of degradation is 0.07. The precursor is the alga *Botryococcus braunii*. As it was proved by the preliminary investigations it is a kerogen formed from strongly polymerized algal fatty acids which is of type I according to the classification of VAN KREVELĚN.

On the basis of the laboratory experiments it can be stated that during the laboratory evolution of the oil shale both the quantity and some qualitative characteristics of the products, and the features of the unconverted organic matter refer to the end of the first phase of genesis to be at 623 K. This temperature may correspond to the simulated boundary between dia- and catagenesis.

With increasing temperature first the smaller peripheral units are cut off from the kerogen during the diagenesis: CO<sub>2</sub>, H<sub>2</sub>O, H<sub>2</sub>S and hydrocarbons of shorter chains are released in form of gas. The temperature of 473 K provides sufficient energy to the degradation of greater units which can be extracted by means of organic solvents and which are the constituents of the so-called bitumen fraction. When increasing the reaction time gas and water are formed again during the subsequent degradation of these units and the bitumen content slightly decreases. Under such conditions remarkable oil generation was observed first at 573 K. The quantity of oil is at 573 K 1% on the average which hardly changes as a function of the degradation time: between 24 and 336 hours it increases from 0.9 to 1.2%. At 598 K this quantity amounts to 1.1 to 2.7% during 5 to 48 hours.

The formation of shale oil is produced by the kerogen of the oil shale and it is the intermediary product of the kerogen oil transformation. In the raw oil shale relatively large quantity of original bitumen is found the transformation of which into oil should have been also taken into account. Presumably, the subsequent transformation of this oil being of much simpler structure and consisting of shorter chains than the kerogen, takes place much more rapidly even at such low temperature than the oil generation from the gel-network (kerogen) of complicated three-dimensional structure. As a function of time an equilibrium follows in the bitumen quantity and both temperatures (573 and 598 K). As it has been proved by the increase of the oil quantity, this equilibrium is dynamic, i. e. the bitumen is continuously formed and transformed.

The H/C atomic ratio of the BAM-bitumen formed in the stage of diagenesis is somewhat lower than that of the original bitumen and when increasing the simulation temperature or the duration, the value of this ratio slightly decreases. This decrease relates to the fact that parallel with both the increasing temperature and duration the bitumen which can be isolated as an intermediary product becomes somewhat more degraded already in this range.

The increase of coalification of the unconverted organic matter is more expressed though as compared to the change in the stage of catagenesis, this can be neglected. The degree of degradation is a low value ( $T_D=0.20$ ) also after 5 hours degradation at 598 K. Taking into account that the degradation degree of the raw material is 0.07, it is fairly demonstrated that the artificial evolution proceeds relatively intensely also during short time.

Based on the H/C atomic ratio and on the  $T_D$  quotient the organic matter of the sample treated thermally at 598 K can be qualified as an "alginitic" sample of diagenetic stage. Taking into consideration the change of products of degradation as well as of the "coalification" of kerogen as a function of temperature (Figs 1—6)

it can be stated that the temperature of 623 K or the higher temperatures show the degradation under catagenic conditions. The transition between the two stages is unbroken and cannot be bound to one temperature value. Under the experimental conditions applied the temperature around 623 K seems to be the probable boundary. This observation is in harmony with the boundary value determined by TISSOT and WELTE [1978] for the kerogen of type II. The authors above studied the degradation during continuously temperature increase. In the experiments discussed above the raw sample was heated to the required temperature only during several minutes and the samples were kept at the temperature in question for different durations. It is remarkable that the two series of experiments differing not only in the raw material but also in their conditions, provided the same results.

Catagenesis was simulated by degradation carried out in the temperature range  $623 \leq T \leq 673$  K. As it is well-known, catagenesis is the main phase of oil generation, accordingly at the temperature  $T > 623$  K sudden increase could be observed in the oil generation. Nevertheless, when investigating the dependence on the temperature the samples treated during the same time (i. e. 5 hours) were compared with each other, while at the given temperature values degradations of three different durations were investigated. Oil generation is increased by the increase of both the temperature and duration, the former showing more rapid, the latter less intense change. At 773 K and after degradation of 2 hours the quantity of shale oil does not increase anymore. At this temperature practically the equilibrium follows concerning all the products and the whole conversion.

The quantity of the bitumen, i. e. of the intermediary product is more varied in this stage than in the stage of diagenesis. The quantity will be nearly constant at the extreme temperature values of catagenesis when increasing the duration. At 773 and 723 K 1% bitumen can be extracted after 2 hours. At the beginning of this stage (623 K) the value varies between 3.0 and 3.5%, i. e. the quantity of bitumen is practically independent of the time. The temperature of 673 K seems to be favourable from the point of view of bitumen formation: during 5 hours 17.6% bitumen was formed from the kerogen concentrate. Presumably, at this temperature and during this duration the further fractionation of bitumen takes place only to relatively small extent. The change of only one experimental parameter, i. e. the increase of duration, however, also promotes the transformation of the intermediary product as it has been proved by the experiments when the oil shale was degraded (Table 1).

In this stage of genesis the conversion of kerogen shows rapid increase. 70—80% of the kerogen concentrate was converted at 673 and 773 K, respectively. The remaining organic matter is more "coalified", its H/C atomic ratios are 1.20 and 0.62, i. e. reaches the characteristic values of the humic coals, peat and lignite.

When having simulated the thermal degradation of kerogen under laboratory conditions we tried to compensate the considerable decrease of duration by applying much higher temperatures. It seems so that the laboratory boundary between the dia- and catagenesis is at around 623 K independently of the duration of degradation and of other experimental conditions (e. g. gradual or sudden increase of temperature) and of the type of the starting material. The quantity of the produced oil increases parallel both with the temperature and with the duration. The experimental parameters affect first of all the formation and further fractionation of the intermediary product, i. e. of the bitumen, as well as the quality of the bitumen extractable in each phase. Except the H/C atomic ratio the qualitative characteristics have been neglected here.

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