

**ON THE ROLE OF TEMPERATURE AND  
PRESSURE IN THE ARTIFICIAL EVOLUTION  
OF ORGANIC MATTER OF THE PULA OIL SHALE  
(HUNGARY)**

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**INTRODUCTION**

The Upper Pannonian oil shale of Pula (Hungary, Transdanubia) provides advantageous material for the experiments investigating the evolution of the sedimentary organic matter since it contains considerable amount of organic matter of algal origin being in the initial stage of evolution.

Factors determining the evolution of organic matter are the environmental conditions being changed during sedimentation and subsidence, the increase of pressure and temperature, as well as the geological time during which the degradation of organic matter proceeds just on the effect of above parameters. Under natural conditions the three influences cannot be separated from each other, moreover other factors (e.g. mineral components, water) should also be taken into account. Only the laboratory experiments make possible to study the independent effects of these parameters. In order to study the possible widest interval of evolution process, kerogen of early evolutionary stage is to be used as raw material.

The physical and chemical analysis of samples of great number taken from different depths of sedimentary basins, as well as the laboratory experiments showed that the process of degradation is determined primarily by the temperature. Temperature plays such an important role that the economically most important stage of kerogen evolution, i.e. the catagenesis can be simulated by means of thermal degradation. This artificially produced process provides possibility to follow the change of kerogen during evolution. The chemical composition of products and of oil formed during the laboratory and natural degradation, slightly differs just because of temperature differences [TISSOT and WELTE, 1978]. Higher temperatures favour the formation of products of smaller C-number. The basis of this simulation is the reaction kinetics of the process. According to most of researchers the transformation of the organic matter is a first-order or at least a pseudo-first-order reaction [DI RICCO, 1956; CANE, 1948, 1976; CONNAN, 1974; WEITKAMP *et al.* 1970; CUMMINS and ROBINSON, 1972; TISSOT and WELTE, 1978].

In accordance to the ARRHENIUS-equation the temperature and the reaction time may mathematically compensate each other. This makes possible to approach certain stages of natural processes by means of model experiments of much shorter time but at somewhat higher temperature.

As it was emphasized by TISSOT and WELTE [1978] and STRAKHOV [1962], temperature is of decisive role in the first stage of evolution of organic matter (called diagenesis after STRAKHOV), but it is only one and not the primary parameter. Having studied the role of pressure in the degradation of kerogen, temperature values were chosen with changing pressures, which fall to the temperature range of experimental

simulation of diagenesis. It seems to be expedient to study the effect of pressure in the stage of diagenesis where temperature plays less important role, since according to the uniform view of researchers pressure plays subordinate role as compared to that of the temperature concerning the whole process. Within the given stage, however, relatively high temperature was chosen in order to observe the changes. At low temperature the preformed hydrocarbon of the sample is released, the gases however, produced at about 150—200°C are undoubtedly the degradation products of kerogen [ABELSON, 1967]. At this temperature the carbon dioxide production exceeds that of the hydrocarbons, at 300°C, however, the hydrocarbon production is considerably accelerated, too.

The limit of experimental simulation of diagenesis and catagenesis, as well as the upper limit of catagenesis were determined by TISSOT and WELTE [1978] at about 350°C and between 470 and 500°C, respectively. The validity of these values were experimentally verified in case of Pula oil shale used as raw material in the measurements to be discussed below [HETÉNYI, 1980].

Taking into account these facts, measurements aiming the investigation of the effect of temperature were carried out between 325 and 500°C at different temperatures, starting somewhat lower temperatures than the lower limit. The effect of pressure was studied at 260°C at overpressure 0, 200, 300, 400 bars. In the case of latter experiments special attention was taken to the gaseous products. In all measurements the unconverted organic matter was characterized and the quantity of bitumen was determined which is usually believed to be an intermediate product produced during the evolution of kerogen [ABELSON, 1967; VITOROVIĆ and JOVANOVIĆ, 1968; CARLSON *et al.*, 1937; CANE, 1951]. The role of degradation time was studied and kinetic calculations were also made.

## EXPERIMENTAL

The air-dried oil shale sample was ground to the grain size of 0.05—0.15 mm, then the bitumen was extracted in Soxhlet extractor in two stages: first by chloroform (Bit-A), then by benzene:acetone:methanol mixture of 70:15:15 ratio (BAM-bitumen). After the extraction kerogen was isolated from the inorganic components by means of physical enrichment, *i.e.* by specific gravity separation.

The thermal degradation was carried out in a furnace provided by programmed heating, in an ignition glass tube, in nitrogen stream. The oil was collected in an air-cooled and adjoining trap cooled with salted ice.

The investigation of the effect of pressure was carried out in a special GEOTERD equipment (*Fig. 1*). During measurements the required pressure was assured by a hydraulic compressor and a suitably processed membrane. The sample was diluted with glass beads in order to eliminate the compaction of the sample caused by the pressure effect.

The most important parts of GEOTERD device are as follows:

- the GEOTERD cell with a hot trap mounted to the output;
- air thermostate with „kaowool” isolation (only indicated on the figure),
- hydraulic compressor (adjoining the pressing rod „15”, not indicated in the figure),
- gas flow meter and the liquid air-cooled cold trap (not indicated in the figure).

Between the conical piston and the pressing rod, between the upper margin of the cell and the top cover an elastic gas-insulating membrane is built in which en-

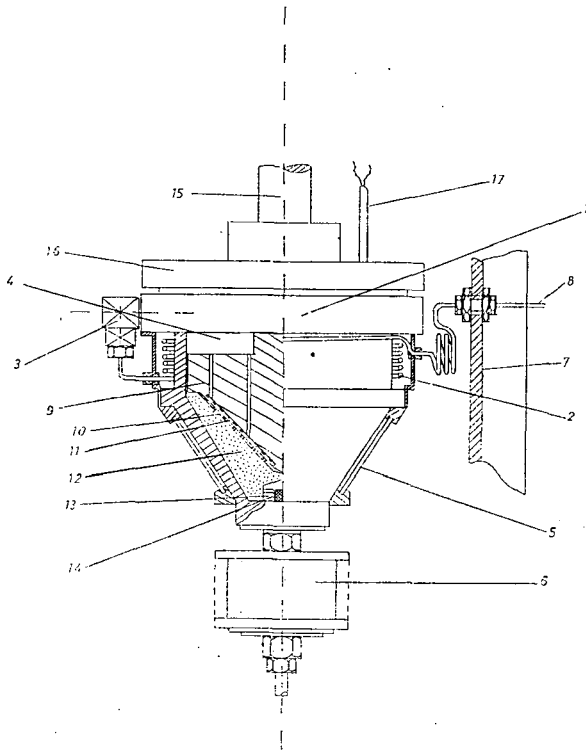


Fig. 1. Sketch of the GEOTERD device

1. Cell of GEOTERD
2. Preheating tube-coil (stainless steel, i.d. 2.2 mm)
3. Gas inlet port
4. Space filled with the eluent gas
5. Cell heating elements
6. Hot trap
7. Steel frame of the device
8. Gas inlet tube
9. Conical pressing pistone
10. Perforated stainless steel cover
11. Stainless steel mesh ( $45 \mu\text{m}$ )
12. Test sample mixed with glass beads
13. Gas outlet port
14. Sintered glass filter
15. Pressing rod
16. Cover flange
17. Pt thermometer

sure the flushing gas to flow only through the bores of the piston. The temperature is controlled by a two-stage electronic thermoregulator operated by a Pt-resistivity thermometer. The high temperature gas when leaving the cell, flows through the labyrinth-like hot-trap then gets the liquid air cooled special cold-trap where the hydrocarbons heavier than methane will be released. The cooled gas flows through

a rotameter which serves to control and state the 7—9 litre/min velocity of the flushing gas.

According to Fig. 1 the device operates as follows: the moisture-free flushing gas is directed first through the adsorber, than through the (8) inlet tube into the (2) tube coil, which is dimensioned that the gas should reach the experimental temperature up to the (3) gas inlet port. The flushing gas gets the (4) gas space, from here it passes the vertical bores of the conical pressing piston, the (11) mesh tissue, the (10) perforated steel cover through the (12) mixture of powdered sample and glass beads, the (13) outlet port and (14) glass filter and finally gets into the hot and cold traps. In the sample the pressure is assured by the hydraulic compressor joining the (15) pressing rod. The heating elements are found at the lower conical part of the cell, their on and off stages are controlled by the electronic thermoregulator according to the sign of the Pt resistivity thermometer.

The bitumen formed during degradation was extracted in solvent mixture in Soxhlet extractor.

The hydrogen and carbon contents were determined by CHN—1 analyser.

The degradation factor denotes the carbon content ( $C_R$ ) of the sample after thermal treatment at 500°C for 30 minutes in inert atmosphere, as compared to the carbon content before thermal treatment (Standard Methods of Laboratory Sampling and Analysis of Coal and Coke D 271—48, in 1952, Book of ASTM Standard, 1952).

The gas chromatographic analyses were made with a Hewlett—Packard 5750 GC equipped with flame ionization detector, electronic integrator and gas feeding apparatus. The column packing: Porapack Q, 100—120 mesh, length: 2 m, diameter 3,2 mm. Temperature: 120—170°C, 8°C/min programmed heating velocity, then at 170°C isothermal conditions. Base gas: helium 30 ml/min, auxiliary gas: helium 20 ml/min. To determine qualitatively and quantitatively the desorbed hydrocarbons external or absolute calibration method was used. Natural gas sample of known composition served as standard.

## RESULTS

### *Characterization of the kerogen*

Kerogen used in the measurements was isolated from the Pliocene (Upper Pannonian) oil shale of Pula (Hungary, Transdanubia). This oil shale was generated as a filling material of a volcanic crater lake, at 10 to 12°C, in semi-haline water. Its biological precursor proved to be the *Botryococcus braunii* KÜTZ alga [JÁMBOR and SOLTI, 1976; NAGY, 1976]. It is rich in organic matter and proves to be a near-surface alginite. According to the palynological investigations carried out on the kerogen, the preservation state of the microscopic plant remnants is excellent. The *Botryococcus* alga predominates, in addition small amount of *fungi* is found. The preservation state of *Botryococcus* coloniae and sporomorphs relates to biologically inactive sedimentation conditions.

The composition of sporomorphs according to the personal communication of M. KEDVES is as follows:

#### *Pteridophyta*

Polypodiaceae 0.8%

some perisporium specimen also occurred supporting the favourable sedimentation conditions.

## *Gymnospermatophyta*

Abietaceae	
Pinus haploxyton type	17.7%
Pinus diploxyton type	18.7%
Tsuga	10.0%
Picea	26.3%
Pseudotsuga-Larix	0.8%
Abies	18.7%
Taxodiaceae-Cupressaceae	1.4%

## *Angiospermatophyta*

### *Dicotyleodonopsida*

Tiliaceae	
Tilia	0.4%
Ulmaceae	0.4%
Betulaceae	
Corylus	2.6%
Fagaceae	
cf. Quercus	0.8%
Juglandaceae	
Carya	1.4%

Only a few sporomorphs relate to shallow bog or bog forest vegetation (Taxodiaceae-Cupressaceae, Polypodiaceae with underwood). *Monocotyledons*, the *Cyperaceae*, *Gramineae*, as well as the dicotyledons of this biotope, e.g. *Nymphaeaceae*, the *Alnus* or *Salix* referring to bog forest, are absent. The proportion of dicotyledons are negligible, in general.

The predominance of pines is conspicuous. Among others, the pollen grains of *Tsuga*, *Picea*, *Pseudotsuga-Larix* and *Abies* relate to mountain forests [KEDVES, 1981, personal communication].

According to the technological tests, the oil shale can be qualified as an oil shale of progressed polymerization and of high kerogen content (according to the ratio of bitumen of the Fisher-distillation to that of the bitumen is greater than 2; [ARATÓ and BELLA 1976]. The organic carbon content of the average sample is 27.4%, Bit-A=3.3%, BAM-bitumen=1.3%.

Based on the behaviour during the gradual  $\text{KMnO}_4$  oxidation the organic matter is an "A<sub>1</sub>-type kerogen" according to the CANE [1976] classification [HETÉNYI and SIROKMÁN, 1978] which probably developed from algal fatty acids.

The H/C atomic ratio (1.76), the degradation factor ( $T_D < 0.10$ ) as well as the results of IR and NMR analyses relate to the fact that the studied kerogen is in rather immature state at the initial stage of evolution and it consists mainly of long-chain paraffin hydrocarbons built up by organic polymers.

### *Thermal degradation of kerogen*

At low temperature (325 and 350°C) medium quantity of gas and water, small quantity (<40 mg/g organic carbon) of oil were formed during 1,5 and 10 hours. The two temperature values fall to the I stage of experimental simulation of kerogen evolution, i.e. to the range of diagenesis, and represent the boundary between dia-

TABLE 1

## Results of thermal degradation of kerogen from Pula

Temperature		Time (hr)	Oil	BAM-bit.	Gas + water	Unconverted matter
(°C)	(K)		(mg/l g organic carbon)			
325	598	1	—	19	—	1329
		5	28	21	86	1288
		10	28	20	114	1267
350	623	1	—	26	—	1270
		5	37	30	177	1180
		10	—	29	—	1111
375	648	1	11	44	174	1197
		5	67	51	246	1063
		10	87	31	367	981
400	673	1	24	64	246	1089
		2	83	86	245	1011
		5	145	63	282	852
450	723	1	251	449	461	264
		2	413	339	522	~150
		5	616	133	522	~150
500	773	1	466	20	716	222
		2	541	29	641	214
		5	688	4	492	224

genesis, and represent the boundary between diagenesis and catagenesis, respectively. Above 350°C the oil formation becomes more intense (Table 1). The amount of oil formed during the 5 hours of thermal treatment suddenly increases as a function of temperature between 375 and 450°C. The increase of temperature of 50°C between 450 and 500°C promotes the oil production only to a restricted extent.

Oil, gas and water are the products of the degradation of organic matter and bitumen of changing quantity can be extracted after experimental evolution in addition to the more coalified kerogen. This bitumen is probably an intermediate product according to the basic scheme of kerogen → bitumen → oil + gas + more coalified organic matter. In case of investigating the oil shale itself the verification is hindered by the fact that in the sample there is also soluble organic matter and in case of the oil shale of Pula its quantity represents high amount, *i.e.* about 4.6%. When degrading the kerogen, however, bitumen may have formed obviously during the thermal treatment of the insoluble organic matter (Table 1).

When comparing thermal treatments of same duration (5 hours), the quantity of the unconverted organic matter decreased up to 400°C. Between 400 and 500°C the degradation proved to be more intense, while between 450 and 500°C equilibrium followed (Fig. 2).

The range of diagenesis is characterized mainly by the diminishing of oxygen-containing groups, thus the H/C atomic ratio expressing the relation of H- and C-content of the organic matter, slightly changed between 325 and 350°C. Above 350°C, in the range of catagenesis the release of hydrocarbons follows consequently the H/C ratio of remaining matter which considerably decreased between 375 and 500°C (Fig. 2). When comparing the results comprehended in Table 2 with the data obtained by TISSOR *et al.* [1974] in the experimental simulation of kerogen of type-II, it was observed that the H/C ratios of the kerogen of type-I degraded by ourselves are somewhat higher at all temperatures, but the difference is not remarkable.

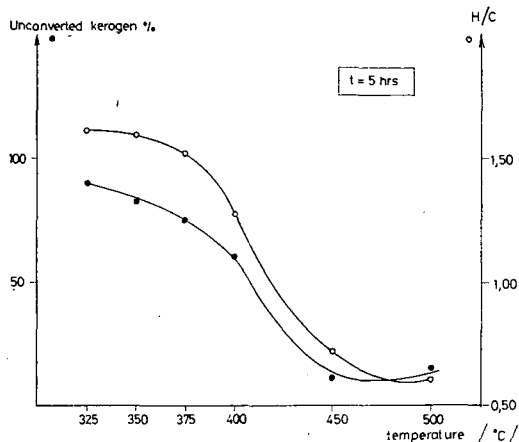


Fig. 2. Changes in the quantity and H/C atomic ratio of unconverted kerogen upon the thermal degradation

E.g. the H/C ratio of the kerogen of type-II is 0.50 and 0.61 at 500°C, at 400°C the difference is greater, *i.e.* 1.07 and 1.27.

The temporal change of the H/C atomic ratio during the experimental degradation indicates that at higher temperature the hydrocarbon production starts only after certain time interval, and this is valid also for the absolute and relative decrease of hydrogen content of remaining organic matter. At 375 and 400°C the H/C ratio scarcely changed after 1 or 2 hours, at higher temperatures not only the measure

Characterization of unconverted kerogen

TABLE 2

Temperature (°C)	Temperature (K)	Time (hr)	Quantity (%)	H/C	T <sub>D</sub>
Unheated kerogen			—	1.76	<0.10
325	598	1	93.4	1.76	
		5	90.5	1.72	
		10	89.0	1.70	
350	623	1	89.2	1.75	
		5	82.9	1.70	
		10	81.6	1.65	
375	648	1	84.1	1.71	0.16
		5	74.7	1.63	0.21
		10	68.9	1.45	0.41
400	673	1	76.5	1.71	0.19
		2	71.0	1.70	0.44
		5	59.8	1.27	0.53
450	723	1	18.5	1.64	0.42
		2	~10.7	1.28	0.70
		5	~10.7	0.73	0.72
500	773	1	15.6	0.67	0.67
		2	15.0	0.64	1.00
		5	15.7	0.61	1.00

but the rate of the change proved to be also greater. At lower temperature, *i.e.* in the temperature range of experimental simulation of diagenesis, the chemical change of the unconverted organic matter proceeded during much longer time but showed the same tendency (Table 2). At 300°C and during 336 hours the H/C atomic ratio is the same as at 375°C during 10 hours, *i.e.* H/C=1.45 [HETÉNYI, 1979].

The change of degradation factor expressing the degree of degradation of organic matter ( $T_D = C_R/C_T$  at 500°C) as a function of degradation time and temperature, is in accordance to the data above and indicates the development of thermal transformation.

TABLE 3  
*Kinetical data on thermal degradation of kerogen from Pula*

Temperature (°C)	Temperature (K)	Time (hr)	$-\log(1-x)$	$r^2$	$-10^3 m$	$k$ (per hr)
325	598	1	0.0246	0.97	0.29	$6.7 \cdot 10^{-3}$
		5	0.0400			
		10	0.0506			
350	623	1	0.0453	0.95	0.57	$1.3 \cdot 10^{-3}$
		5	0.0783			
		10	0.0969			
375	648	1	0.0670	0.99	1.10	$2.5 \cdot 10^{-2}$
		5	0.1203			
		10	0.1669			
400	673	1	0.1118	0.99	1.75	$4.03 \cdot 10^{-3}$
		2	0.1267			
		5	0.1739			
450	723	1	0.3468	0.98	13.7	$3.16 \cdot 10^{-1}$
		2	0.5607			
		5	0.9172			

The thermal degradation of kerogen, the quantity of the products as well as the chemical features of unconverted organic matter depend also on the duration of degradation and in addition to the temperature. The two parameters may compensate each other to a certain extent. From kinetic point of view the process assumed to be a first order one. Data concerning the degradation between 325 and 450°C are shown in Table 3. The quantity of the original material is taken as unit,  $x$  denotes the quantity of gas+water+oil produced during the conversion. In calculations bitumen was regarded as an intermediate product. The degradation time *vs.*  $\log(1-x)$  relation is linear at all temperatures with good approximation (*Fig. 3*), the correlation coefficient ( $r^2$ ) is 0.95—0.99. Knowing the temperature dependence of specific reaction constants ( $k$ ) computed from the slopes of curves, the apparent activation energy can be calculated from the Arrhenius-equation.

Regarding the apparent activation energy, the literature data extend over a rather wide range, *i.e.* from kJ up to 251.0—334.7 kJ. Its value may change between the low energy necessary to the decomposition of the weak, *e.g.* adsorption bonds and the 251.0—334.7 kJ required to the break of C—C bonds. It depends on the applied temperature as well as on the type of kerogen. 41.8—62.8 kJ is the apparent activation energy of the start of oil formation [TISSOT, 1969; CONNAN, 1974]. Concerning the Green River kerogen and its experimental degradation between 150 and 350°C CUMMINS and ROBINSON [1972] calculated 79.5 kJ. In case of the kerogen



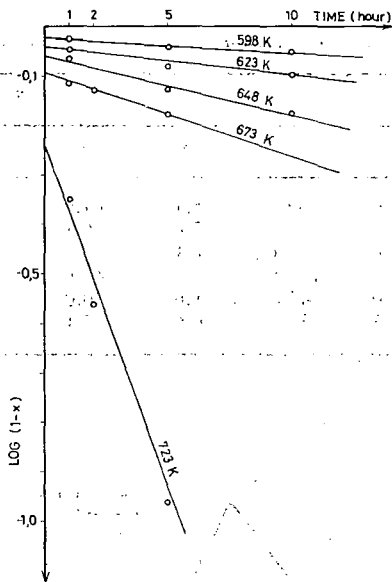


Fig. 3. First-order plot for 598 and 723 K (325°–450°C) data

of type-I according to the VAN KREVELEN diagram, TISSOT and WELTE [1978] found 125.5 and 292.8 kJ for the apparent activation energy, in addition to the 41.8–62.8 kJ mentioned above.

The values calculated for the degradation in wider temperature interval are the average values of the activation energy of different types of processes. Together with the data obtained at 300°C, the measurement results produced  $E=92.0$  kJ average activation energy for the temperature range of from 300 to 450°C. Based on the same data  $E=50.2$  kJ and 146.4 kJ at from 300 to 350 and from 375 to 400°C, respectively. The lower value agrees fairly well with the  $E=41.8$ –62.8 kJ apparent activation energy of TISSOT [1969] and CONNAN [1972] for the start of oil formation. The  $E=146.4$  kJ determined at higher temperature slightly exceeds the value concerning the kerogen type-I (125.5 kJ) and is somewhat lower than the  $E=167.4$  kJ determined by ABELSON [1967] in the course of experimental degradation of Green River oil shale between 185 and 400°C.

#### *Effect of pressure on the kerogen degradation*

When studying the role of pressure in the experimental evolution of diagenesis, the kerogen was degraded at 260°C at overpressure 0, 200, 300 and 400 bars. In this process considerable amount of gas was developed, and its hydrocarbon content was determined by means of gas chromatography ( $C_2$ – $C_6$  hydrocarbons).

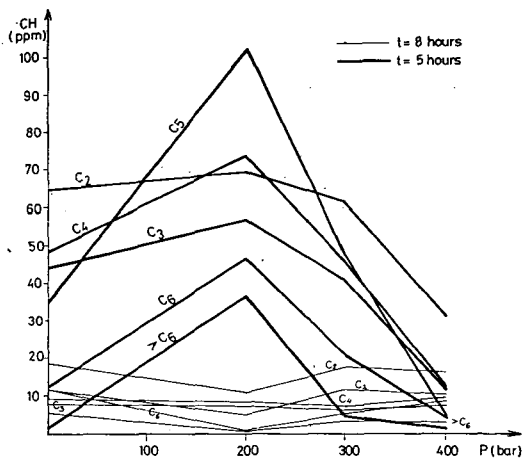
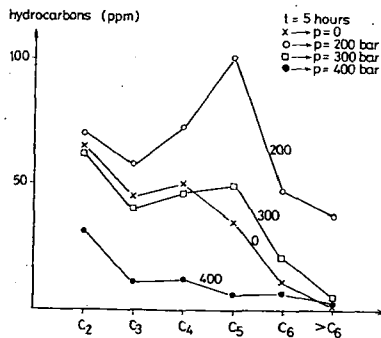
The degradation time of first series was 8 hours, gas sample was taken in the 5th and 8th hours. The  $C_2$ – $C_6$  hydrocarbon quantities produced from 1 g kerogen are shown in Table 4, the change as a function of pressure is seen in Fig. 4.

The hydrocarbon production proved to be more intense during the first five hours than between the 5th and 8th hours. In the first sampling the quantity of the  $C_2$ – $C_6$  hydrocarbons changed according to a maximum curve as a function of pressure. The maximum is more conspicuous in case of higher carbon number, it

TABLE 4

## Hydrocarbons yielded by degradation of kerogen from Pula at 260°C

PRESSURE (bar)	0		200		300		400	
TIME (hr)	5	8	5	8	5	8	5	8
C <sub>2</sub> (ppm)	64.5	12.0	69.5	5.1	61.9	12.5	31.1	10.6
C <sub>3</sub>	44.7	7.8	57.6	7.6	40.1	6.1	11.3	7.4
C <sub>4</sub>	49.4	9.6	73.1	8.1	46.2	7.8	12.2	9.0
C <sub>5</sub>	34.7	18.6	101.4	11.2	48.6	17.9	5.8	16.7
C <sub>6</sub>	12.2	12.0	47.0	1.6	20.6	6.5	7.6	8.0
>C <sub>6</sub>	1.8	6.3	37.5	0.6	5.1	4.0	2.1	4.0

Fig. 4. Changes in the quantity of hydrocarbons (C<sub>2</sub>—C<sub>6</sub>) as a function of the pressureFig. 5. The quantity of hydrocarbons (C<sub>2</sub>—C<sub>6</sub>) yielded by degradation of kerogen at different pressures and T = 260°C

can be hardly observed in the lower carbon number range. The quantity of hydrocarbons produced at 300 and 0 bar proved to be nearly the same (*Fig. 5*), the pressure of 200 bar was especially favourable to the formation of  $C_2$ — $C_6$  hydrocarbons, while their quantity decreased to minimum at high pressure (400 bar).

In the given range, the hydrocarbon content of gas sample taken in the 8th hour proved to be much lower and scarcely changed as a function of pressure. The change is so slight (*Fig. 4*) that the quantity of hydrocarbons is practically independent of the pressure or concerning its tendency is opposite to that of the previous sampling.

Hydrocarbons yielded by degradation of kerogen from Pula  
at  $P=200$  bar  $T=260^\circ C$

TABLE 5

HC (ppm)	$C_2$	$C_3$	$C_4$	$C_5$	$C_6$	$>C_6$
TIME (hr)						
5	66.5	24.7	26.0	8.2	0.5	0
8	34.8	28.1	28.6	31.7	8.5	3.2
11	14.0	11.2	13.4	18.5	12.5	5.5
14	10.3	8.9	9.8	12.1	3.2	0.7
29	126.0	112.3	73.1	32.3	7.9	0.4
37	23.3	21.1	17.0	12.3	29.7	—
53	8.5	7.8	8.2	12.0	8.2	0.9
61	5.2	3.4	3.9	8.9	2.4	0.2
77	16.7	16.1	16.6	23.0	10.6	3.6
85	7.4	10.1	9.8	12.5	5.4	0.5
101	13.6	14.3	14.4	21.8	13.2	4.0
109	2.1	0.8	0.8	4.1	0.8	—
114	16.7	10.5	11.9	18.8	8.9	1.7
122	28.2	31.3	20.6	26.1	14.1	1.4
138	68.1	78.6	66.5	53.8	29.3	5.3
146	77.1	94.6	68.9	34.5	4.0	0.3
162	94.8	127.4	98.7	37.5	1.7	1.9
170	43.5	58.4	50.6	39.7	23.5	3.4
186	26.3	31.9	25.5	24.8	9.1	0.7
193	5.1	6.6	9.7	13.8	7.7	1.1

The difference observed in the quantities of hydrocarbons taken in the 5th and 8th hour rose the question how this value will change as a function of degradation time. At 200 bar producing extreme value in the first series, the kerogen was degraded in the second series at  $260^\circ C$  and during 193 hours. Gas samples were taken 20 times and the quantities of  $C_2$ — $C_6$  hydrocarbons were determined (Table 5; *Fig. 6*). Their quantity and its change as a function of time seems to be independent of the carbon number. It is a low value, in general, in the given time interval with two maxima in the 29th and 162nd hours, in case of  $C_2$ ,  $C_3$  and  $C_4$ . The quantity of  $C_5$  and  $C_6$  is less than that of the lighter hydrocarbons, during the whole process. This difference could be observed also in the tendency of change: the maximum is much lower, the average values proved to be somewhat higher, especially in case of  $C_5$ . In order to control the results, the first phase of the experiment series above was repeated and though some difference could be detected between the two series regarding the absolute value, the tendency was the same and the maximum observed in the 29th hour could be reproduced. Under the given experimental conditions the formation of  $C_2$ ,  $C_3$  and  $C_4$  hydrocarbons is periodical.

The dependence on pressure of the intermediate bitumen was also followed (Table 6, Fig. 7). When comparing the character of the Fig. 7 with the data of the Table it is obvious that the increase of pressure and temperature produced increased bitumen quantity up to a certain value, then the bitumen quantity decreased presumably due to the increased rate of further transformation.

Similarly to these two parameters, the increase of degradation time also affected the change of bitumen quantity. At  $P=300$  bar it proved to be 1.9% after 4 hours degradation, and 2.2% after 8 hours degradation. At  $P=200$  bar the reaction time of 8, 33 and 193 hours produced 2.0, 1.5 and 1% bitumen.

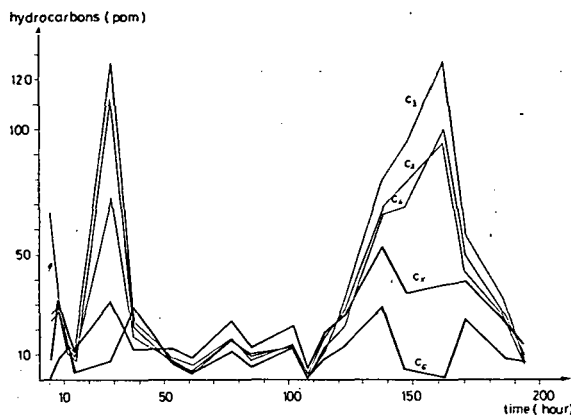


Fig. 6. The quantity of hydrocarbons ( $C_2-C_6$ ) as a function of the time of degradation at  $T=260^\circ\text{C}$  and  $p=200$  bar

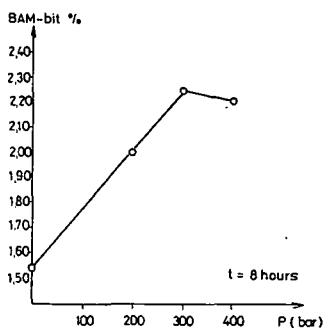


Fig. 7. The quantity of BAM-bitumen extracted from kerogen degraded at  $T=260^\circ\text{C}$  and at different pressures

The value of the  $T_D=C_R/C_T$  expressing the degree of degradation of the unconverted matter relates to the fact that when comparing with the effect of degradation temperature and time, the role of pressure is less significant. The value of this quotient (Table 6) indicates "immature" kerogen even after degradation at 400 bar. The insoluble organic matter seemed to be unchanged even after 33 hours as a

Effect of the change of pressure and degradation period on the soluble and insoluble organic material

Temperature (°C)	Pressure (bar)	Time (hr)	BAM-bit. %	T <sub>D</sub>	H/C
260	0	8	1.5	0.11	1.73
	200	8	2.0	0.13	1.70
	300	8	2.3	0.13	1.68
	400	8	2.2	0.14	1.68
	200	33	1.5	0.14	1.65
	200	193	1.0	0.24	1.54
	300	4	1.9	0.14	1.71

function of degradation time, only the considerable increase of time (193 hours) produced fairly well observable progress in the experimental evolution.

The H/C atomic ratio corresponded to the experimental temperature (260°C), its change as a function pressure can be neglected.

#### SUMMARY

The oil shale of Pula was generated in a special geological environment, in a Pliocene crater lake surrounded by tuff rings. The organic matter, the precursor of which is the *Botryococcus braunii*, accumulated in a biologically less active environment. The kerogen isolated from the oil shale is an immature geopolymer being in the initial stage of evolution, thus it proved to be suitable to the experimental study of effect of evolution parameters.

In the course of transformation of the insoluble organic matter soluble bitumen was formed as an intermediary product. Its quantity first increased, then decreased as a function of increasing temperature and pressure. The effect of pressure is negligible, that of temperature proved to be significant.

The process of degradation started in all cases by fairly well observable gas development. The concentration of C<sub>2</sub>—C<sub>6</sub> hydrocarbons showed periodicity as a function of degradation time, with definite maxima in case of hydrocarbons of C=2—4, and with less variance in case of those of C=5—6. Maxima occurred in the 29th and 162nd hours. The increase of pressure promoted the formation of C<sub>2</sub>—C<sub>6</sub> hydrocarbons in the first phase (P=200 bar), the further increase of pressure resulted in minimum quantity of hydrocarbons.

In the experimental temperature range of diagenesis the shale oil production proved to be small, increased above 350°C and intense increase could be observed between 400 and 450°C. At given temperature the quantity of shale oil increased as a function of increasing degradation time.

The quantity of unconverted kerogen decreased practically linearly as a function of temperature between 325—400 and 400—450°C, during 5 hours degradation time, but the change was steeper in the latter interval. Between 450 and 500°C the progressing oil production with constant unconverted matter is verified by the progress of bitumen transformation. In addition to the temperature defining the process of conversion, the role of degradation time cannot be neglected, and difference could

be observed especially in the temperature dependence of degradation of 1 and 5 hours.

When comparing the qualitative change of the unconverted kerogen in the process of degradation produced by the temperature and pressure, the widely accepted view, *i.e.* pressure plays subordinate role against temperature during the evolution of organic matter, can be fairly well illustrated. The value of the degradation factor, being  $T_D < 0.10$  in the starting material, slightly changed as a function of increasing pressure (between 1 and 400 bar  $T_D = 0.11-0.14$ ), but showed considerable increase as a function of increasing temperature (e.g. at 500°C  $T_D = 0.67$  after degradation of 1 hour).

On the basis of the values of H/C atomic ratio of unconverted kerogen determined in the course of experimental thermal degradation the zones of diagenesis and catagenesis of experimental evolution were simulated between 325 and 500°C during the maximum 10 hours, at higher temperature 5 hours thermal treatment. According to this quotient, the sample degraded at 350°C represents the zone of diagenesis, the sample degraded at 375°C during 10 hours belongs to the zone of catagenesis.

The apparent activation energy of thermal degradation is 50.2 kJ within the temperature range of 300—350°C, and 146.4 kJ between 365 and 450°C.

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