EXPERIMENTAL EVOLUTION OF OIL SHALES AND KEROGENS ISOLATED FROM THEM

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INTRODUCTION

Nowadays it is generally accepted that petroleum is a product of the evolution of kerogen finely dispersed in sedimentary rocks. The quality of the products depends first of all on the type and chemical composition of kerogen. The most important quantitative feature, i. e. the genetic potential of the evolution process is also determined by the type of kerogen. To answer the question that up to the given date how the genetic potential has been realized, the indices of evolution level of the organic matter are suitable. The evolution level of the organic matter is influenced first of all by the thermal history of sediments including the kerogen, by the geological time as well as by the temperature and pressure. It is of high probability that in addition to the factors listed above the mineral matrix affects both the quantity of the degradation products and their quality. This effect should be taken into account already because of the significance of the inorganic/organic matter ratio, since in all sediments containing organic matter and even in the oil shales being of extreme composition from this point of view, the quantity of the mineral components is several times higher than that of the organic matter. This mineral phase may be of rather varied composition, further even in case of one mineral both the catalytic and retention effects can be presumed, as well. As it was stated by MONIN *et al.,* [1980]: "simulation of maturation by pyrolysis of organic matter in its mineral matrix can, some cases (low carbon content, active mineral matrices), lead to results which are more dificult to interpret."

The effect of mineral components is reflected also by the composition of the so-called lipid fractions extractable from sedimentary rocks, which may be very different depending on the relations of the fraction in question to the type of minerals. As to the investigations of SPIRO [1980] the fractions associated with clays are more aromatic and/or polar than those associated with carbonate minerals. Polar and aromatic compounds are preferentially adsorbed on clay and carbonate minerals. The aliphatic compounds are concentrated in the unadsorbed and therefore more labile fraction. As the lipid adsorption on mineral grains got a saturation level, no compositional discrimination takes place.

To elucidate the role of different mineral components in the oil and gas generation numerous laboratory experiments were carried out. A group of these experiments studied simple chemical compounds (e. g. fatty acids) in presence of clay minerals and carbonates [JURG and EISMA, 1964; SHIMOYAMA and JOHNS, 1972; ALMON and JOHNS, 1977]. In other pyrolysis experiments the kerogen was mixed with different matter: with industrial catalysts [URAND-SOURON *et al.,* 1982], with natural minerals [CONNAN, 1974; HORSFIELD and DOUGLAS, 1980; ERDMAN, 1981], further the prod-

ucts of the organic matter containing rocks and the products of artificial evolution of the kerogen isolated from these rocks, were compared [SPIRO, 1979; ESPITALIÉ *et al.,* 1980; HORSFIELD and DOUGLAS, 1980]. Most of the authors emphasized the catalytic effect of minerals, first of all of clay minerals in the oil generation. Nevertheless, this effect can be observed only at the suitable temperature. As to the results of the pyrolysis experiments of GIRAUD [1970] carried out at 280 °C, the catalytic effect of clay minerals is minimal, the composition of minerals associated with kerogen has no appreciable influence on the pyrolysis products. E. g. as to the statement of SPIRO [1979] the connection between kaolinite and organic matter can be realized in sedimentary rocks only after heating, i. e. due to the partial loss of the adsorbed water.

The catalytic effect of mineral components can be manifested in different manner. As a result of industrial catalysts admixed to kerogen the temperature of hydrocarbon generation was lowered by about 50 °C [DOURAND-SOURON, 1982]. The apparent activation energy values being low as compared to the literature data and to those calculated by CONNAN [1974] to the pyrolysis of the organic matter was attributed also to the catalytic effect of clay minerals. The catalytic effect of mineral components is reflected most obviously by the composition of the generated products. Usually, in the pyrolysate formed from pyrolized organic matter in presence of a mineral matrix the proportion of the compounds of lower molecular weight is less than in the pyrolysis products of the isolated kerogen. HORSFIELD and DOUGLAS [1980] believed that this is due to condensation and gasification of higher molecular weight constituents in the primary pyrolysate.

When comparing the pyrolyses of organic matter in its mineral matrix and of the kerogen isolated from the rock the retention effect of the mineral matrix can also be observed, and when mixing the kerogen with different minerals this effect can be verified by model experiments, as well [ESPITALIÉ *et al.,* 1980]. Due to the retention effect of the inorganic constituents less hydrocarbon can be produced from the rock sample than under the same conditions from the isolated kerogen.

Authors mentioned above called also the attention to the fact that the effect of the mineral matrix exerted on the oil generation depends on the type and quantity of the organic matter, in addition to the mineral composition. As to the observation of CONNAN [1974], in the main zone of oil generation the hydrocarbon generation is catalyzed also by the organic matter itself.

This paper aims to compare the evolution features of the high-grade oil shale and of the kerogen isolated from it, to analyze the possible reasons of differences by means of model experiments, and to throw light upon the relationships between the type of kerogen and the differences experienced during the thermal degradation in laboratory conditions of the oil shale and the isolated kerogen, respectively.

<div align="center">EXPERIMENTAL</div>

Analytical methods

Experimental evolution was carried out between 300 and 500 °C under continuous N_2 flow. Products were collected on a trap cooled by air and by saline ice. The contents of the two traps were unified, the oil was separated from the water and the oil quantity was measured. The remained solid matter was extracted in Soxhlet extractor by benzene: acetone: methanole of 70:15:15 ratio. In this manner the bitumen fraction and the unconverted organic matter were separated.

The starting matter as well as the degradation products were characterized by the elementary composition. Rock-Eval pyrolysis, the CR/CT ratio, the C_{org} content and by the step-by-step oxidation by $KMnO_4$.

The measurement of H- and C-contents was carried out in the CHN—1 analysator.

The C_{org} content was determined at 1000 °C in oxygen flow by means of an instrument of Carmhograph—8 type.

The CR/CT ratio was measured after the ASTM-standard [CUMMINS et al., 1972].

To characterize the type of organic matter and its evolution level the Rock-Eval pyrolysis was carried out [ESPITALIÉ et al., 1977].

The determination of the chemical precursors of kerogen was carried out by step-by-step potassium permanganate oxidation [HETÉNYI et al., 1978].

Description of the samples

The evolution experiments were carried out on maar-type Hungarian oil shales. The maar-type oil shales accumulated in a special environment, in the lake water developed in craters of basalt eruptions [JÁMBOR and SOLTI, 1975; BENCZE et al., 1979]. These are Upper Pannonian formations of 3.05 to 5.34 ± 0.93 my [JÁMBOR et al., 1982]. The C_{org} content of the sample chosen from the maar-type oil shale of high-grade of Pula (Transdanubia, Hungary), amounts to 27.3% (sample is marked *A*). The kerogen isolated from it belongs to type I, its H/C atomic ratio is 1.7, the CR/CT ratio is less than 0.1. The organic matter consists mostly of alginite, the sample contains great amounts of remnants of the *Botryococcus braunii* alga. According to the pollen analyses the alga is well-preserved [HETÉNYI et al., 1982]. The results of experimental evolution of the sample *A* and kerogen *A* were compared with the data of evolution of an other sample and kerogen (sample *B* and kerogen *B*) accumulated under similar geological conditions (Upper Pannonian, maar-type, locality: Várkeszö (Transdanubia, Hungary). In case of the second sample the experimental conditions were the same. Dissimilarly to the sample *A* the sample *B* accumulated under conditions of higher biological activity. The algal remnants are more desctructed and besides them considerable amount of coalified plant remnants can be determined. The organic matter is heterogeneous, it is the mixture of kerogens of type I and II, and based on the results of all of the experiments, it is transitional between the two extreme character and seems to be of type II.

Both samples (*A* and *B*) contain immature organic matter referring to the zone of diagenesis. This is proved in both cases by the high H/C atomic ratios and by the low CR/CT ratios, as well as by the $S_2/S_3 > 5$ measured by Rock-Eval pyrolysis and by the T_{max} values (442 °C for sample *A* and 425 °C for sample *B*). The initial evolution level of the starting matter is indicated by the fact that by means of laboratory evolution nearly the complete evolution path can be construced.

The results of step-by-step oxidation of kerogens by basic potassium permanganate indicate that the organic matter was produced mostly from algal fatty acids [HETÉNYI et al., 1979]. In sample *B* considerable amounts of humin matter was also admixed.

Results of experimental evolution

The products of experimental degradation of the kerogens of two different types (bitumen, oil and gas+water) are shown in Tables 1 and 2. As it is seen in *Fig. 1* the product distribution tendency plotted against the degradation temperature shows close correlation with the kerogen type. Much more oil and bitumen were

formed from the *A*-kerogen of type than from the *B*-kerogen of type II. Nevertheless, the remarkable hydrocarbon generation starts at $T \gtreqqless 375\,°C$ in case of organic matter of type I, while at $T \lesseqgtr 350\,°C$ in case of the other. Based on the experimental evolu-
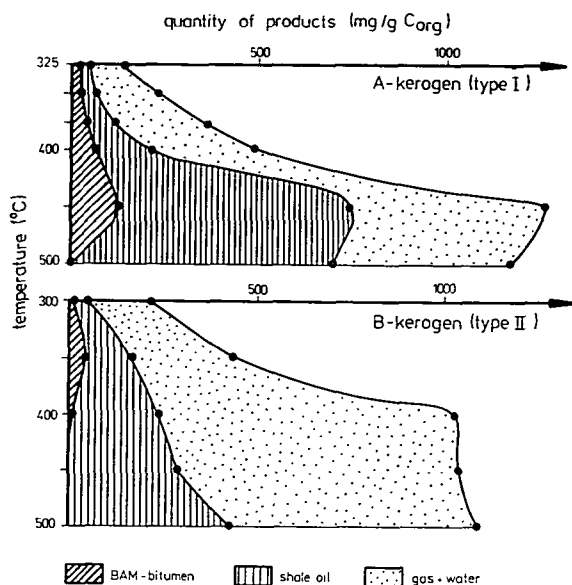

Fig. 1. Yields of pyrolysis of kerogens isolated from maar-type Hungarian oil shales
A-kerogen = a kerogen type I
B-kerogen = a kerogen type II

tion results of the studied kerogens the apparent activation energies calculated for the phase of catagenesis show considerable difference: 146 kJ/mol^{-1} and 75 kJ/mol^{-1} concerning the samples *A* and *B*, respectively. The difference of evolution features of the two kerogens is also demonstrated by the H/C atomic ratio of the unconverted kerogen, by the diagenesis coefficient as well as by the maturity values determined by Rock-Eval pyrolysis as a function of temperature (Tables 3 and 4). As it can be seen in *Fig. 2* the evolution paths obtained by the experimental evolution of the two kerogens also differ from each other. The differences in the evolution paths, in the distribution of products, in the features of the unconverted kerogen as well as in the apparent activation energies calculated for the catagenesis can be attributed to the differences between the types of the two organic matter.

When comparing the products of experimental evolution of the oil shales and of the kerogens isolated from them (Tables 1 and 5, 2 and 6) some difference can be observed between the sedimentary rock and the corresponding organic matter.

To study this problem in detail the sample *A* was chosen as a model. When comparing the tendencies of changes *(Fig. 3)* and emphasizing the shale oil as most important product from the economic point of view *(Fig. 4)* the following main differences can be observed:

— Regarding either the whole of the process, or taking the usual temperature of industrial conversion (450—500 °C) more oil is generated from kerogen than from the oil shale. (Data refer in all cases to 1 g organic carbon.)

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TABLE 1

Pyrolysis of "A-kerogen" (type I) isolated from oil shale

Temperature (°C)	Period (hours)	Gas + water	Oil	Bitumen
			(mg/g organic carbon)	
325	1	75	< 10	19
	5	86	28	21
	10	114	28	20
350	1	114	14	26
	5	177	37	30
	10	228	43	29
375	1	174	11	44
	5	246	67	51
	10	329	87	31
400	1	246	24	64
	2	245	83	86
	5	282	145	63
450	1	461	251	449
	2	522	413	339
	5	522	616	133
500	1	716	466	20
	2	641	541	29
	5	492	688	< 5

TABLE 2

Pyrolysis of "B-kerogen" (type II) isolated from oil shale

Temperature (°C)	Period (hours)	Gas + water	Oil	Bitumen
			(mg/g organic carbon)	
200	5	76	—	56
300	5	269	35	14
350	5	264	131	38
400	5	793	226	12
450	5	745	289	< 5
500	5	669	426	< 5

— On the contrary, at lower temperatures more oil seems to be generated from the oil shale than from the kerogen.

— The maximum of the relationship between the quantities of degredation products and the degradation temperature occurs at lower temperature (400 °C) in case of the oil shale than in case of the kerogen isolated from it (450 °C).

The more intense oil production at lower temperature in presence of the mineral matrix can be explained on the one hand by the probable catalytic effect of the mineral matter, and by the degradation intermediary product, i. e. bitumen being present in the sediment and formed under natural conditions, on the other. The question may arise that the second phase of experimental evolution of the soluble organic matter, i. e. the bitumen to oil transformation would be able to modify the picture developed
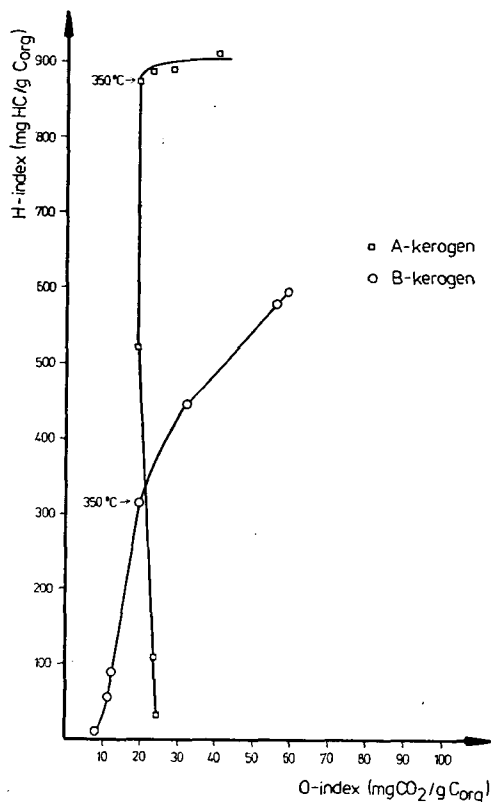
Fig. 7. Artificial evolution path of the kerogens (type I and II) isolated from maar-type Hungarian oil shales

TABLE 3

Characteristics of evolution level of unconverted "A-kerogen" at different temperature of laboratory pyrolysis

Temperature (°C)	Period (hours)	H/C atomic ratio	CR/CT	$\dfrac{PC}{TOC}$ (%)	T_{max} (°C)
Kerogen	—	1.70	< 0.10	77	444
200	5	1.70	0.12	74	443
300	5	1.70	0.13	74	445
325	5	1.70	0.13	74	447
350	5	1.70	0.23	73	447
375	5	1.63	0.41	72	451
400	5	1.27	0.53	44	447
450	5	0.73	0.72	10	454
500	5	0.61	1.00	4	454

on the whole of evolution of the organic matter. In order to analyze the effect to be expected during pyrolysis, the soluble organic matter extracted in two phases from the oil shale *A* (chloroform extracted: Bit-A than solvent-mixture extracted: BAM-

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TABLE 4

Characteristics of evolution level of unconverted "B-kerogen" at different temperature of laboratory pyrolysis

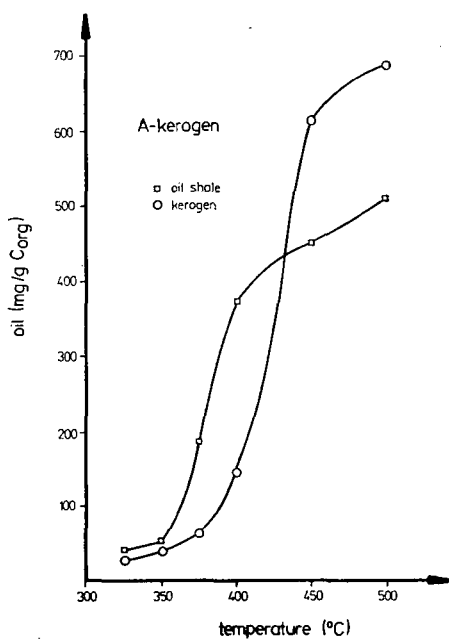| Temperature (°C)	Period (hours)	H/C atomic ratio	CR/CT	$\dfrac{PC}{TOC}$ (%)	T_{max} (°C)
Kerogen	—	1.33	0.43	56	426
200	5	1.30	0.43	54	430
300	5	1.30	0.55	38	428
350	5	1.30	0.65	27	429
400	5	1.30	0.83	9	449
450	5	1.00	0.90	8	535
500	5	0.42	0.95	3	543

Fig. 3. Yields of pyrolysis of oil shale and kerogen isolated from the oil shale

bit.) was degraded under the same conditions as in case of degradation of the sediment and of the kerogen. The quantities of the generated oil and of the unconverted matter are shown in Table 7. Together with the corresponding data of the kerogen and oil shale the increase of oil production as a result of temperature increase of 25—50 °C are shown in *Fig. 5*. It is obvious from the figure that the measure of transformation of kerogen and of the bitumens differ from each other only at lower temperatures, later the conversion is nearly the same. The maximum can be observed in all cases at 450 °C where the bitumen conversion is nearly complete, the quantity of the unconverted matter is low. The reason of the different conversion of bitumen
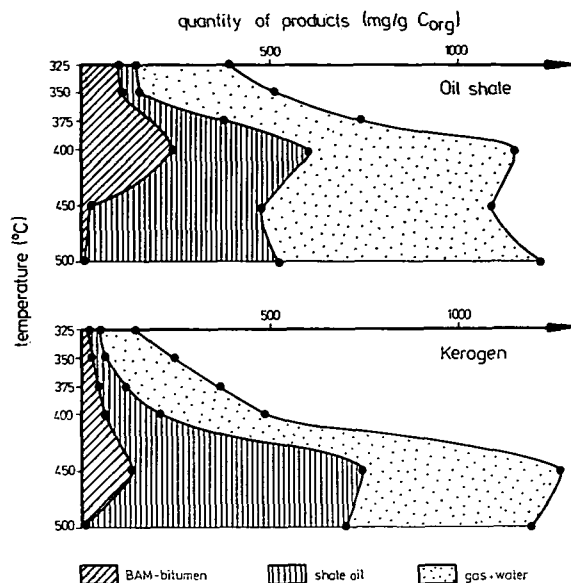
Fig. 4. Oil yielded by the artificial evolution of the Hungarian oil shale and kerogen (type I) isolated from the oil shale

TABLE 5

Pyrolysis of "A-oil shale" (Hungary, Pula)

Temperature (°C)	Period (hours)	Gas + water	Oil (mg/g organic carbon)	Bitumen
300	48	297	33	51
	96	410	33	18
	336	469	44	18
325	5	289	40	106
	10	289	40	88
	24	304	62	88
350	1	297	33	132
	5	352	51	110
	10	487	99	103
375	1	297	70	121
	5	363	187	194
	10	414	245	158
400	1	443	216	271
	5	542	374	234
	10	498	418	73
450	1	711	168	70
	2	810	216	33
	5	615	447	26
500	1	619	443	59
	2	667	542	15
	5	696	513	11

and kerogen at lower temperatures is probably the fact that in spite of all the structural similarity, the bitumen is of much simpler structure.

Thus, the activation energy needed to the subsequent transformation of bitumen is much lower, consequently, a part of the bitumen is able to transform into oil at relatively low temperature. At the same time, the conversion of the complex polymer, i. e. of the kerogen needs higher energy, especially in case of the strongly polymerized kerogen of type I. Probably, on that account a greater quantity of shale oil is generated from the oil shale at $T \leqq 400\,°C$ than from the kerogen isolated from it. This presumption seems to be verified by the fact that in the same temperature range nearly the same quantities of oil were generated from the kerogen B of type II and from the oil shale B (Tables 2 and 6). In the main zone of oil generation the apparent activation energy of kerogen B is 75 kJmol^{-1}, which is about the half of that of the kerogen A (146 kJmol^{-1}). Consequently, in case of kerogen B the lower temperature provides the suitable activation energy to the oil generation from kerogen by thermal degradation.

The catalytic effect of the mineral matrix is probably the other reason of the difference between the oil generations of the oil shale and kerogen A at $T \leqq 400\,°C$.

TABLE 6

Pyrolysis of "B oil shale" (Hungary, Várkesző)

Temperature (°C)	Period (hours)	Gas + water	Oil (mg/g organic carbon)	Bitumen
350	1	791	67	60
	5	776	119	276
	10	791	127	216
400	1	955	201	246
	5	1067	201	149
	10	978	224	97
500	1	1261	231	15
	2	1313	254	< 5
	5	1299	269	< 5

TABLE 7

Oil and unconverted matter (M) yielded by pyrolysis of bitumens extracted from "A oil shale" (Hungary, Pula)
(Degradation period = 5 hours)

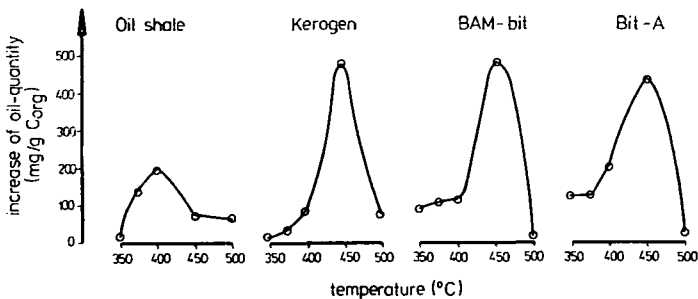| Temperature (°C)	Degradation of Bit − A		Degradation of BAM − bit.	
	oil (mg/g C_{org})	M (%)	oil (mg/g C_{org})	M (%)
200	5.0	96	< 5.0	94
300	53.5	87	39.9	87
325	122.1	81	81.5	80
350	246.9	75	188.8	73
375	370.4	55	287.9	55
400	507.5	37	399.4	45
450	932,8	4	881.5	12
500	960.2	4	852.9	6

Fig. 5. Change in the oil quantity resulting by the rise of the temperature in the course of the artificial evolution

As a result of the catalytic effect too, the degradation proceeds at somewhat lower temperature in presence of the mineral matrix. This latter phenomenon can be observed in case of sample *A* containing of kerogen of type I of higher activation energy *(Fig. 3)*.

Nevertheless, in addition to the catalytic effect of the mineral components, their retention effect should also be taken into account due to the well-known high ad-

TABLE 8

Pyrolysis of mixture of "A-kerogen" and montmorillonite

Temperature (°C)	Period (hours)	Montmorillonite (%)	Bitumen	Oil
			(mg/g organic carbon)	
375	1	0	44	11
		10	44	24
		50	55	17
		90	84	< 5
	2	0	44	63
		10	42	61
		50	60	50
		90	94	26
	5	0	51	61
		10	51	67
		50	63	57
		90	98	28
500	1	0	20	466
		10	21	624
		50	33	463
		90	47	446
	2	0	29	541
		10	29	667
		50	30	533
		90	47	497
	5	0	< 5	688
		10	< 5	751
		50	< 5	660
		90	13	627

sorption capacity of some minerals (e. g. clay minerals). The fact that what of the two opposite effects can be observed, depends on numerous conditions. The quality of the mineral component, the type of the organic matter, the ratio of the inorganic and organic phases as well as the degradation conditions (e. g. degradation temperature, time etc.) may control this dependence. The retention effect can be observed e. g. in the whole temperature range in case of sample B. In case of the sample A, however, the retention can be demonstrated only at higher remperatures where the rate of transformation of the organic matter is high enough.

In order to study the effect of the mineral components in detail, model experiments were carried out. The kerogen A and its mixture with montmorillonite of 9:1, 1:1, 1:9 ratio were degraded. The quantities of the generated bitumen and oil referring to unit organic carbon are shown in Table 8. It is obvious from the data that parallel with increasing montmorillonite quantity, the quantity of extractable bitumen gradually increased at both temperatures. Simultaneously, the decrease of oil quantity can also be observed indicating the fact that the retention effect of montmorillonite retards the transformation of the heavier components by retaining the bitumen, thus decreasing the quantity of the generating oil, as well. The mineral phase of low concentration as compared to that of the organic matter seems to promote the oil generation. In presence of montmorillonite of 10% usually more oil is generated from the unit organic carbon than from the pure kerogen, though the bitumen quantity remains constant.

SUMMARY

To compare the evolution features of the sedimentary rock of organic matter content and of the kerogen isolated from it experimental pyrolysis was carried out.

Samples used in the experiments are Hungarian so-called maar-type oil shales containing immature kerogen. The immaturity of the organic matter provided the possibility to construct the complete evolution paths on the basis of the results of thermal degradation.

To study the catalytic effect presumed for the mineral matrix kerogen of type I was chosen as raw material of the experiments which can be less activated than the kerogens of type II and III. Thus, the activation energy needed for the main hydrocarbon generation can be assured at higher temperature. Due to the catalytic effect of the mineral matrix greater difference can be expected at lower temperatures between the oil generation of the oil shale and the kerogen isolated from it. The apparent activation energy of the kerogen A calculated after the degradation experiments is 146 kJmol^{-1} in the zone of catagenesis.

The results obtained for the experimental evolution of kerogen A and of oil shale A were compared with those obtained from the kerogen of type II of the maar-type oil shale B. The apparent activation energy of kerogen B is 75 kJmol^{-1}, i. e. about the half of the value calculated for kerogen A.

When comparing the oil quantities obtained by the experimental degradation of oil shales and kerogens isolated from them, two temperature ranges can be distinguished: lower and higher temperatures than 400 °C.

At lower temperature ($T \leqq 400$ °C) where only insignificant quantities of oil were generated from the kerogen A, considerable oil generation could be observed when pyrolizing this kerogen in its mineral matrix. This difference can be attributed partly to the catalytic effect of the mineral matrix, partly to the bitumen existing in the rock.

To analyze the catalytic effect of the mineral matrix model experiments were carried out. Kerogen was mixed with montmorillonite in different proportions. The montmorillonite of low concentration as compared to the organic matter seemed to catalyze the oil generation.

To get acquainted with the evolution features of the bitumen which can be regarded as intermediary product of degradation, experimental evolution was carried out on the bitumen extracted from the oil shale A. Considerable difference could be detected between the evolution features of kerogen and of the bitumen just in the afore-mentioned temperature range of $T \leqq 400\,°C$. The conversion rate of bitumen representing the smaller structural units of kerogen proved to be remarkable also at lower temperature.

The two factors, i. e. the catalytic effect of the mineral matrix and the considerable conversion of bitumen into oil at lower temperature, may be responsible for the act that the degradation processes followed at about $50\,°C$ lower in case of the oil shale A than in case of the kerogen isolated from it.

According to the results of the experimental evolution of the kerogen B of type II and oil shale B which can be more easily activated in themselves, the difference mentioned above could not be observed.

In the main zone of hydrocarbon generation greater quantity of oil could be produced from kerogen than from the corresponding oil shale in the course of evolution experiments. In the degradation experiments carried out with the mixture of kerogen and montmorillonite the retention effect of montmorillonite could be detected. Parallel with increasing proportion of montmorillonite the quantity of the products in form of oil decreased. Simultaneously, the quantity of the degradation intermediary product which can be isolated in form of bitumen, gradually increased.

REFERENCES

BENCZE, G., JÁMBOR, Á., PARTÉNYI, Z. [1979]: A Várkeszö és Malomsok környéki alginit- (olajpala) és bentonitkutatások eredményei. A Magyar Állami Földtani Intézet Évi Jelentése az 1977. évröl. Müszaki Könyvkiadó, Budapest, 257—268.

CONNAN, J. [1974]: Time-temperature relation in oil genesis. Am. Assoc. Petr. Geol. Bull., **58**, 2516—2521.

CUMMINS, J. J. and ROBINSON, W. E. [1972]: Thermal degradation of Green River kerogen at 150° to 350 °C. U. S. Bur. Mines. Rep. Invest. 7620, 15.

DURAND-SOURON, C., BOULET, R. and DURAND, B. [1982]: Formation of methane and hydrocarbons by pyrolysis of immature kerogens. Geochim. et Cosmochim. Acta, 46/7, 1193—1202.

ERDMAN, J. G. [1981]: Petroleum exploration, present and future. In: Origin and chemistry of petroleum, ed. by G. ATKINSON and J. J. ZUCKERMAN, Pergamon Press, 89—111.

ESPITALIÉ, J., MADEC, M. and TISSOT, B. [1977]: Source rock characterization method for petroleum exploration. Offshore Technology Conference.

ESPITALIÉ, J., MADEC, M. and TISSOT, B. [1980]: Role of mineral matrix in kerogen pyrolysis: influence on petroleum generation and migration. Am. Assoc. Petr. Geol. Bull., **64**, 59—66.

GIRAUD, A. [1970]: Application of pyrolysis and gas chromatography to geochemical characterization of kerogen in sedimentary rock. Am. Assoc. Petr. Geol. Bull., **54**, 439—455.

HETÉNYI, M. and SIROKMÁN, K. [1978]: Structural information on kerogen from the Hungarian oil shale. Acta Miner. Petr., Szeged XXII/2. 211—222.

HETÉNYI, M. [1979]: Thermal degradation of the oil shale kerogen of Pula (Hungary) at 473 at 573 K. Acta Miner. Petr., Szeged XXIV/1, 99—111.

HETÉNYI, M. [1980]: Thermal degradation of the organic matter of oil shale of Pula (Hungary) at 573—773 K. Acta Miner. Petr., Szeged XXIV/2, 301—314.

HETÉNYI, M., TÓTH, J. and MILLEY, Gy. [1982]: On the role of temperature and pressure in the artificial evolution of organic matter of the Pula oil shale (Hungary). Acta Miner. Petr. Szeged XXV/2, 131—146.

HORSFIELD, B. and DOUGLAS, A. G. [1980]: The influence of minerals on the pyrolysis of kerogens. Geochim. et Cosmochim. Acta 44, 1119—1131.

JÁMBOR, Á., SOLTI, G. [1975]: Geological conditions of the Upper Pannonian oil-shale deposit recovered in the Balaton Highland and at Kemeneshát. Acta Miner. Petr. Szeged XXII, 9 —28.
JÁMBOR, Á., RAVASZ, Cs. and SOLTI, G. [1982]: Geological and lithological characteristics of oil shale deposits in Hungary. 3rd All. Union Meeting on the Geochemistry of Oil Shales, Tallinn.
SPIRO, B. [1979]: Thermal effects in "oil shales" — naturally occurring kaolinite and metakaolinite organic associations. Chemical Geology 25, 67—78.
SPIRO, B. [1980]: Preferential lipid-mineral associations in some "oil shales". Chemical Geology 31/1—2, 27—35.

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