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ORGANIC GEOCHEMICAL CHARACTERIZATION OF BROWN COALS BY TERMAL DEGRADATION AND MODIFIED ROCK-EVAL METHOD

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ABSTRACT

The relationships between the organic geochemical features of brown coals and the peculiarities of the formation micro-environment determined on the basis of miscroscopic plant remnants of the samples have been studied.

Samples were brown coals of Eocene age from the Dorog and Tatabánya basins (Hungary, Transdanubia).

The organic matter falls between the types II and III (i.e. between oil prone and gas prone). The more exact position of the samples within the group is determined mainly by the macro-environment (i.e. the locality). Within a given locality some relationships could be observed also among the microenvironmental features.

The hydrocarbon genetic potential of the samples was characterized by experimental thermal degradation and step-by-step Rock-Eval pyrolysis. In case of Rock-Eval pyrolysis the isotherm temperature between the steps was increased by 20 °C. Based on the results it is plausible that the hydrocarbon genetic potential of brown coals and the oil quantity to be obtained by experimental thermal degradation are considerably influenced by the chemical-biological features of the micro-environment. The value of the gas-hydrocarbon genetic potential and its change as a function of temperature are unambiguously determined by the character of the micro-environment.

Keywords: modified Rock-Eval pyrolysis, brown coal, hydrocarbon genetic potential, thermal degradation, plant remnants.

INTRODUCTION

Rock-Eval pyrolysis is a rapid and effective means of characterizing the quality and thermal maturity of kerogens and perspective source rocks. The procedure and apparatus has been developed by ESPITALIÉ *et al.*, (1977). In Rock-Eval pyrolysis pulverized rock samples are progressively heated to 550 °C under an inert atmosphere. The quantity of the hydrocarbons which have been released in this temperature programmed pyrolysis is mentioned as genetic potential (TISSOT and WELTE, 1984), petroleum potential (ESPITALIÉ, 1977) or petroleum generative potential (PETERS, 1986) of the sediments. During the assay, the hydrocarbons already present in the rock in a free or adsorbed state are volatilized at a moderate temperature. This is the first peak of the pyrogram (S1). The second peak of the pyrogram (S2) represents the hydrocarbons generated by the cracking of kerogen. The temperature at which the maximum cracking of the organic matter occurs is called T_{max}. The pyrolysis of the organic matter results in generating oxygen containing volatiles (S3), too. On the basis of S1, S2, S3, T_{max} and the total organic carbon content (TOC), the

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This sample is very rich in sporomorphs, but the number of the species is few. The spores of tropical ferns (Schizaeaceae, Anemia, Cicatricosisporites dorogensis, Plate I—9) are dominant: 44.5%, the quantity of the "tranquillus type" palm pollen grains is nearby the same, 42.4% (Plate I—10, 11). Sporomorphs occurring in a small quantity: Lygodium (3.0%) tropical fern genus (Plate I—7, 8), Cycadopites minor (2.7%), Cycadopites kyushuensis (1.7%), "granulatus type" palm pollen grains (1.4%), (Plate I—12), Fagaceae Cupuliferoipollenites pusillus (1.4%).

This spore-pollen spectrum reflects the "tranquillus type" palm forest, with fern (Anemia-Mohria, Lygodium) undergrowth.

Sample No T—6

The plant tissue remnants (Plate II—3) are degraded, with a high quantity of fungous remnants. Very often the hyphae penetrate the tissue remnants (Plate II—4, 7). The resinous drops are few.

The sample is in general poor in sporomorphs, but the number of the species is relatively high. It is worth of mentioning that there is not a single species with predominant quantity. The important percentage of the palynomorphs is as follows: Monocolpopollenites tranquillus (Palmae) 24%, Fagaceae: Cupuliferoipollenites pusillus (20.0%), C. oviformis (15.5%), Myricaceae (20.0%), the presence of the pollen grains of the form-genus Plicatopollis (Juglandaceae) is also important.

The destroyed organic material blead with fungous hyphae indicates an intense biological activity during the sedimentation process. Before this there was a strong oxidation, as an antecendent of the microbial activity. The spore-pollen spectra suggest in inundated open swamp, the pollen grains fell in the sedimentary basin, from the vegetation zones of the river side.

EXPLANATION OF PLATES

Plate I

1. Degraded plant tissue remnants, fibres or vascular elements. Slide: D—3—1, cross-table number 13.3/111.2.
2. Remnants of vascular tissue. Slide: D—16—3, cross-table number, 19.2/118.3.
3. Degraded parenchyma cells. Slide: D—3—2, cross-table number, 19.7/113.2.
4. Burnt prosenchyma cells. Slide: D—16—2, cross-table number, 15.1/104.6.
5. Stoma bearing epidermis remnant. Slide: D—3—3, cross-table number, 21.8/104.0.
6. Fungous remnant, Pluricellaesporites fsp. Slide: D—3—1, cross-table number, 13.3/108.5.
7. Leiotriletes dorogensis (Kds. 1960) Kds. 1961, Schizaeaceae, cf. Lygodium. Slide: D—3—2' cross-table number, 9.6/103.8.
8. Leiotriletes adriennis (R. Pot. et Gell. 1933) W. Kr. 1959, Schizaeaceae, cf. Lygodium. Slide: D—3—1, cross-table number, 10.7/114.9.
9. Cicatricosisporites dorogensis R. Pot. et Gell. 1933 subfsp. dorogensis, Schizaeaceae, Anemia. Slide: D—3—1, cross-table number, 11.9/105.6.
10. Monocolpopollenites tranquillus (R. Pot. 1931) Th. et Pf. 1953 subfsp. tranquillus, Palmae. Slide: D—3—1, cross-table number 19.5/112.1.
11. Monocolpopollenites tranquillus (R. Pot. 1931) Th. et Pf. 1953 subfsp. tranquillus, Palmae. Slide: D—3—2, cross-table number, 13.6/113.1.
12. Arecipites granulatus (Kds. 1961) L. Rákosi 1973, Palmae, massula of pollen grains. Slide: D—3—2, cross-table number, 10.3/119.9.
13. Cupuliferoidaepollenites liblarensis (Thoms. in Pot., Thoms. and Thierg. 1950) R. Pot. 1960, Fagaceae v. Leguminosae (left), Cupuliferoipollenites pusillus (R. Pot. 1934) R. Pot. 1960, Fagaceae (right). Slide: D—16—1, cross-table number, 22.1/113.6.

Plate I

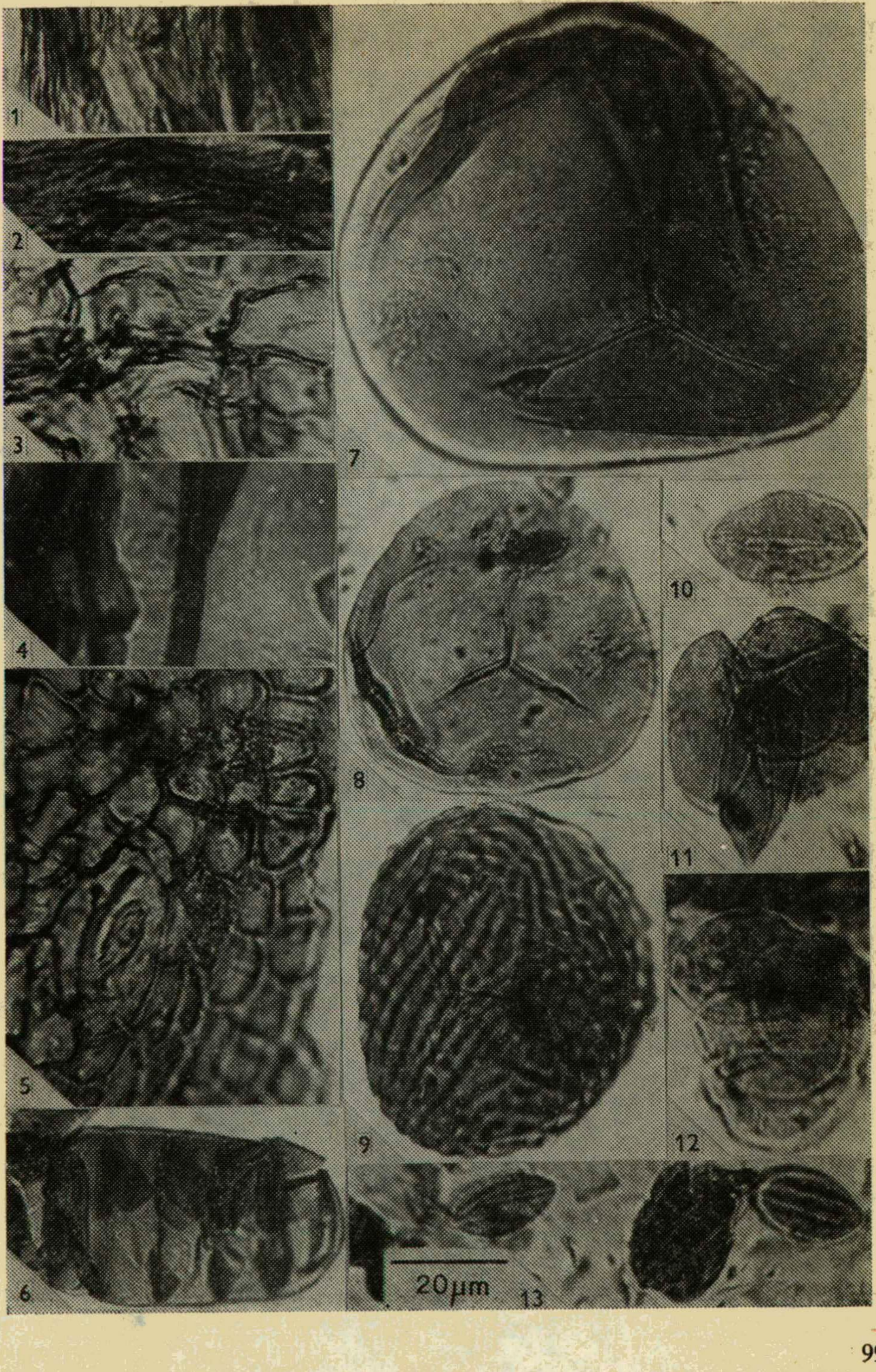
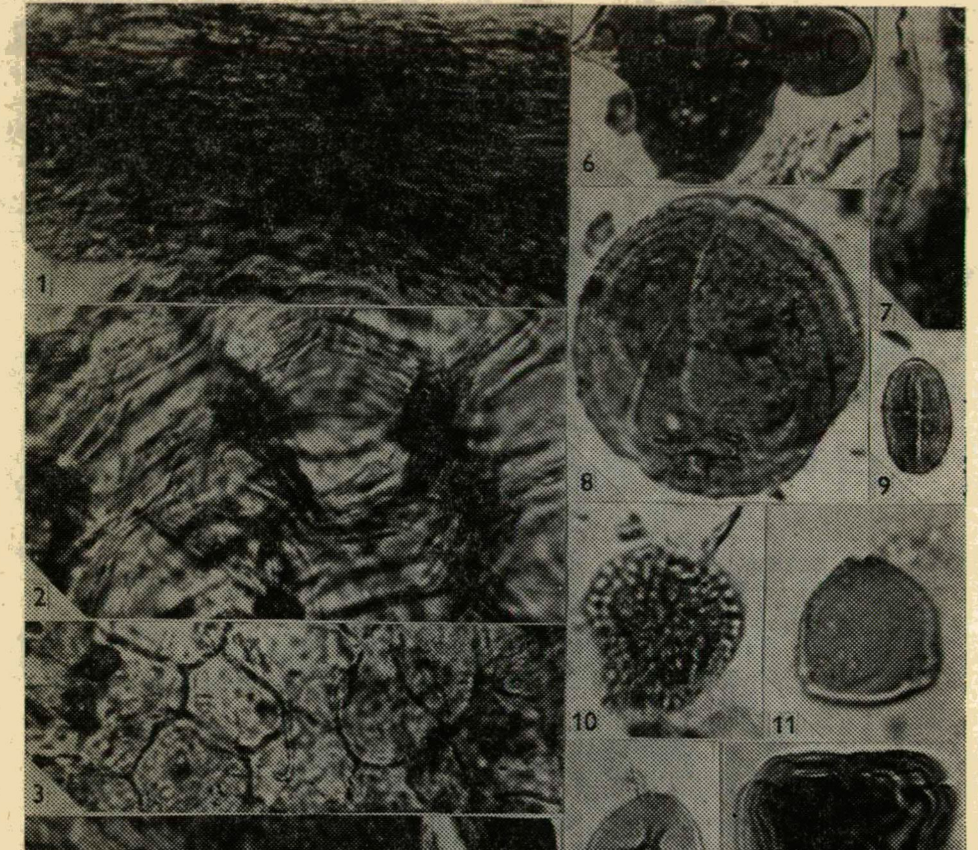


Plate II



Organic geochemical features

To describe the geochemical features of the organic matter brown coals were chosen that display similar organic carbon contents. As it is shown in Table 1: TOC=65—73%, the hydrogen content varies between 5.7 and 6.7%. In favour of exact comparison, the elementary composition is given to moisture and ash-free state. Ash content varies within wide extreme values, i.e. between 6.8 and 28.9%. When comparing the two coal seams the samples from the Dorog basin (marked by D) display higher ash and H-contents than the samples from Tatabánya (marked by T). The ash contents of the latter ones shows only slight changes and their H-contents are nearly the same, i.e. 5.69, 5.84 and 5.89%. Concerning the organic carbon content, the TOC-contents show lowest and highest values in the D-samples and medium values in the T-samples. With respect to the two most significant element, i.e. C and H, the difference can be neglected.

TABLE 1

Moisture- and ash-content of samples, elemental analysis of organic matter (OM)

Sample	Moisture %	Ash %	Elemental analysis of OM C %	H %	N %	S %
D—16	8.66	19.70	73.22	6.39	0.15	4.61
T—1	13.64	7.03	71.05	5.84	0.61	3.03
T—2	14.37	6.77	72.48	5.69	0.93	5.33
D—3	8.94	28.87	65.44	6.74	0.43	7.88
T—6	11.28	13.73	68.84	5.89	2.63	5.73

Plate II

1. Degraded plant tissue remants, probably fibres or tracheids. Slide: T—1—1, cross-table number 18.1/106.7.
2. Thick walled parenchyma tissue remnants. Slide: T—1—1, cross-table number, 16.1/110.4.
3. Thin walled parenchyma cells. Slide: T—6—4, cross-table number, 17.4/109.4.
4. Hyphae penetrated into degraded plant tissue remnants. Slide: T—6—2, cross-table number, 11.4/105.2.
5. Fossilized resinous cell material. Slide: T—1—1, cross-table number, 18.2/103.8.
6. Resinous drop. Slide: T—2—3, cross-table number, 8.7/117.3.
7. Hyphae penetrated into degraded plant tissue remnants. Slide: T—6—2, cross-table number, 12.7/106.2.
8. Granotricolporites semiglobosus (Kds. 1963) Kds. 1974, Sterculiaceae. Slide: T—2—1, cross-table number, 9.3/118.4.
9. Cupuliferoipollenites pusillus (R. Pot. 1934) R. Pot. 1960, Fagaceae. Slide: T—1—3, cross-table number, 4.2/109.2.
10. Ilexpollenites margaritatus (R. Pot. 1931) Thg. 1937 f. medius, Aquifoliaceae, Ilex. Slide: T—2—3, cross-table number, 20.9/117.8.
11. Labraferoidaepollenites pseudogranulatus (Gladkova 1965) n. comb., Myricaceae. Slide: T—2—3, cross-table number, 9.9/115.6.
12. Plicatopollis lunatus Kds. 1974, Juglandaceae. Slide: T—2—3, cross-table number, 17.2/116.2.
13. Ericipites longisulcatus Wodeh. 1933, Ericaceae. Slide: T—1—1, cross-table number 17.2/113.3.
14. Ericipites longisulcatus Wodeh. 1933, Ericaceae. Immature massula of pollen grains. Slide: T—1—2, cross-table number 4.9/117.9.

Nevertheless, the quantitatively similar carbon and hydrogen contents imply remarkable qualitative difference. In harmony with the Rock-Eval records carried out by the usual programme (isothermal temperature = 300 °C) the organic geochemical features of the samples are different. All samples are immature, these did not reach the main CH-generation zone *Fig. 1.* As compared to the evolution path determined for the dispersed organic matter, based on the HI-OI indices all the five samples fall between type II and III *(Fig. 2)*. Nevertheless, the H-index of the D-samples is higher than that of the T-samples, in harmony with the hydrogen content of the samples (Tables 1 and 2). The ability for pyrolysis of the organic matter is similar. The organic carbon content of the D-samples can be pyrolized to 20—22%, that of the T-samples to 13—17%. Within a given locality, e.g. comparing the three T-samples, the PC/TOC value is highest in the sample T—1 deriving from inundated deep swamp ecological conditions, and lowest in the sample T—6 formed in the environment characterized by intense microbial activity.

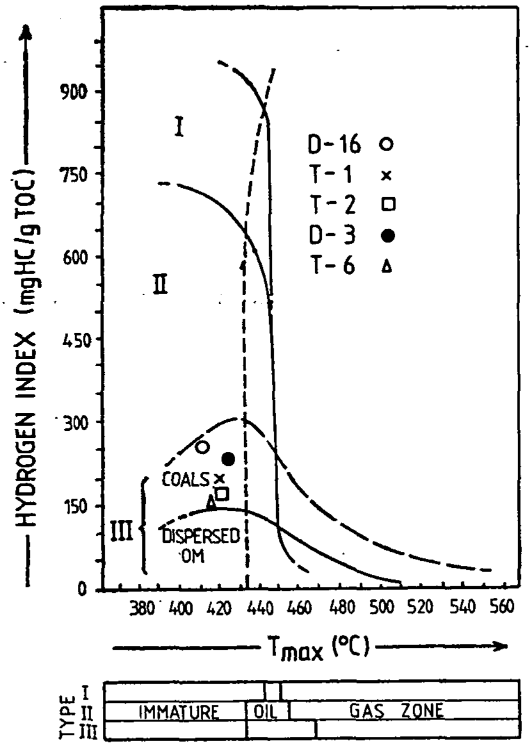


Fig. 1. Diagram of Hydrogen Index versus T_{max} for the brown coals examined

The genetic potential of the samples (Table 2) show definite relationship with the formation micro-environment. Sample D—16 deriving from an inundated deep swamp displays the highest genetic potential: 136 mg HC/g. The second highest value is displayed by the sample T—1 (114 mg HC/g) formed in very humid environment. The samples T—2 deriving from a myricaceous swamp, and D—3 referring

TABLE 2

Rock-Eval pyrolysis results for brown coal samples (isothermal temperature = 300 °C)

Sample	T_{max} °C	S1	S2	Gen. pot.	PI	S2/S3	PC/TOC	HI	OI
D—16	411	4.08	132.36	136.44	0.03	11.95	21.7	252	21
T—1	419	3.86	110.68	114.54	0.03	6.96	16.9	196	28
T—2	418	2.71	95.06	97.77	0.03	7.13	14.2	166	35
D—3	423	3.08	94.56	97.64	0.03	8.75	20.0	232	26
T—6	415	1.61	79.43	81.04	0.02	5.66	13.1	153	27

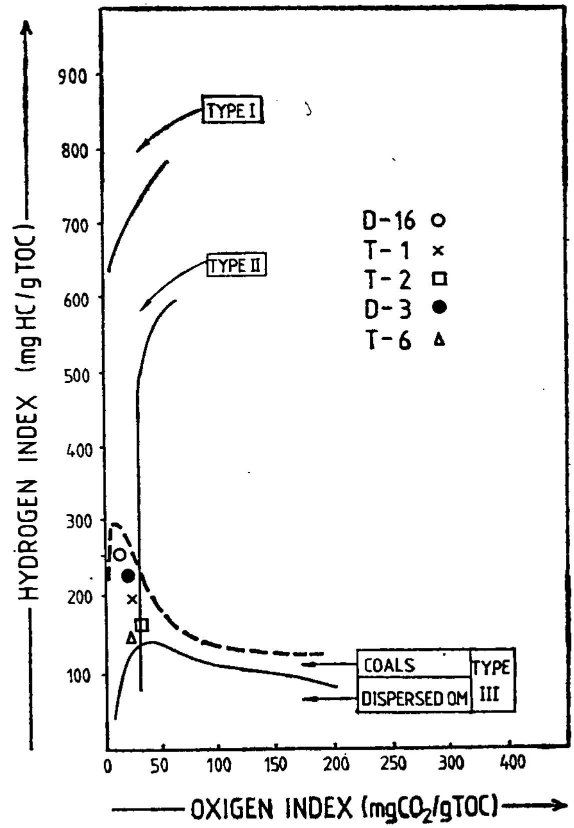


Fig. 2. Diagram of Hydrogen Index versus Oxygen Index for the brown coals examined

to tranquillus type palm forest show the same genetic potential (97.7 mg HC/g). The potential value is lowest in case of the sample T—6 (81 mg HC/g) the features of wich referring to strong oxidation and high frequence biological activity.

Based on the H-index, on the genetic potential and on the PC/TOC ratio all the studied samples are favourable from the hydrocarbon generation point of view. In the HI-OI diagram *(Fig. 2)* these lie between the so-called oil prone and gas prone kerogens. Consequently, in the zone of catagenesis both oil and gas generation can be expected from them. The S2/S3 values that are greater than 5 in all samples (Table 2) indicate also oil prone organic matter. PETERS (1986), however, stated that "the results overestimate the liquid-hydrocarbon-generative potential of these types of coals". Thus, in order to determine the liquid-hydrocarbon-genetic potential of the studied brown coal samples, experimental thermal degradation was carried out. Samples were heated at 500 °C for one hour, in inert gas atmosphere. Results are shown in Table 3. For comparison, the products of a type II, immature dispersed organic matter developed under similar conditions, are also demonstrated. In the course of degradation relatively large amounts of oil were generated from the brown coal samples: 54—160 mg oil/g TOC. The quantity of liquid hydrocarbon generated from the sample D—16 is the same as that generated from the type II OM. Under the same conditions, 500—550 mg oil/g TOC was obtained from the oil shale containing kerogen of type II (HI=440 mg HC/g TOC). About 40 mg oil/g TOC was generated by the lignite, displaying organic geochemical features similar to the kerogens of type III (HETÉNYI, unpublished data).

TABLE 3

Yield of thermal degradation (T=500 °C. period=1 hour)

Sample	Unconverted matter %	Gas+Water %	Oil mg/g	Bitumen TOC
D—16	68	23.5	160	4.8
T—1	62	30.0	122	4.1
T—2	64	31.0	85	3.0
D—3	72	23.5	108	3.2
T—6	65	32.1	54	2.7
OM, type II. (Mecsek Mts)	92	6.8	163	47.0

The oil quantity generated from brown coals is also related to the plant remnants. Greatest amounts of oil were generated by the pyrolysis of samples D—16 and T—1. The oil production of the samples T—2 and D—3 shows medium values and lowest quantity of oil was generated during the thermal degradation of sample T—6 deriving from an environment of high biological activity. On the contrary, the total amounts of gas+water generated during the process did not show relationships to the palynological features. 23.5% gas+water was generated from the D-samples and 30—32% from the T-samples. This value represents the total amounts of water, hydrocarbon and non-hydrocarbon gases.

The S1 value provides information on the hydrocarbon gases, i.e. on the gas-hydrocarbon-genetic potential (measured in the course of Rock-Eval pyrolysis). Similarly to the genetic potential (S1+S2), the S1 value shows relationship with the palynological features of the samples (Table 2). In order to study the change of gas-hydrocarbon quantity as a function of temperature, step-by-step Rock-Eval pyrolysis was carried out having changed the isothermal temperature by 20 °C between 180 and 340 °C.

The difference of data obtained by the lowest (180 °C) and highest (340 °C) isothermal temperature programme is shown in Table 4. Based on the change of the genetic potential, on the Δ(S2/S3), on the Δ(PC/TOC) and on the ΔHI value, the samples can be divided into two groups and the groups correspond to the localities. The measure of change concering the data in relation with the genetic potential is

TABLE 4

Change of the Rock-Eval pyrolysis data between 180 °C and 340 °C isothermal temperature

Sample	Change of data between 180—340 °C							
	S1	S2	Gen. pot.	PI	S2/S3	PC/TOC	HI	OI
D—16	−22.46	49.29	26.83	−0.16	9.25	4.2	94	−10
T—1	−18.03	26.30	8.27	−0.15	4.38	1.3	46	−12
T—2	−12.54	19.06	6.52	−0.13	3.73	1.0	33	−29
D—3	−11.16	21.65	10.46	−0.12	6.02	2.2	53	−17
T—6	− 9.41	16.93	7.52	−0.12	3.44	1.2	33	−14

greater in the D- and smaller in the T-samples. At the same time, the change of the S1: ΔS1 (180°—340 °C) being characteristic rather of the gas-hydrocarbon-genetic potential shows relationship unambiguously with the palynological features of the samples.

The values of the change followed in the 20 °C steps are shown in Table 5. In this respect, the S1 value of the sample T—6 formed in an environment of strong biological activity displays different changes as compared to those of the other samples. In case of the sample in question, the gradual increase of ΔS1 can be observed as a function of the increasing temperature interval. In case of the other samples maxima can be observed between 220 and 240 °C.

TABLE 5

Relative change of S1 between the following steps of modified Rock-Eval pyrolysis. (Difference of S1-values measured at 180° and 340 °C isothermal temperature = 100%

Temperature (°C) \ Sample			−ΔS1 (%)		
	D—16	T—1	T—2	D—3	T—6
180—200	0.9	0.9	0.6	0.1	0.4
200—220	0.4	1.2	0.6	1.1	0.2
220—240	3.3	5.5	4.4	3.4	1.7
240—260	1.4	1.4	0.1	1.0	1.9
260—280	5.5	6.2	3.3	5.1	3.1
280—300	6.5	6.2	12.7	15.2	9.4
300—320	39.3	20.2	23.3	15.9	22.0
320—340	42.7	58.4	55.0	58.2	61.3
180—340	22.46	18.03	12.54	11.16	9.41

The close interrelation between the palynological features and the change of the gas-hydrocarbon-genetic potential of the samples as a function of temperature can be clearly seen in Fig. 3. The S1 value is negligible and falls behind the determination limit between 180 and 200 °C, in case of all samples. The curves of the samples deriving from very humid inundated regions (D—16, T—1) are separated from those of the others. Three curve types can be distinguished after 220 °C: the curves of the mentioned inundated deep swamps, the curve of the fungiferous sample T—6 referring to the region of strong biological activity, and the common curve of samples

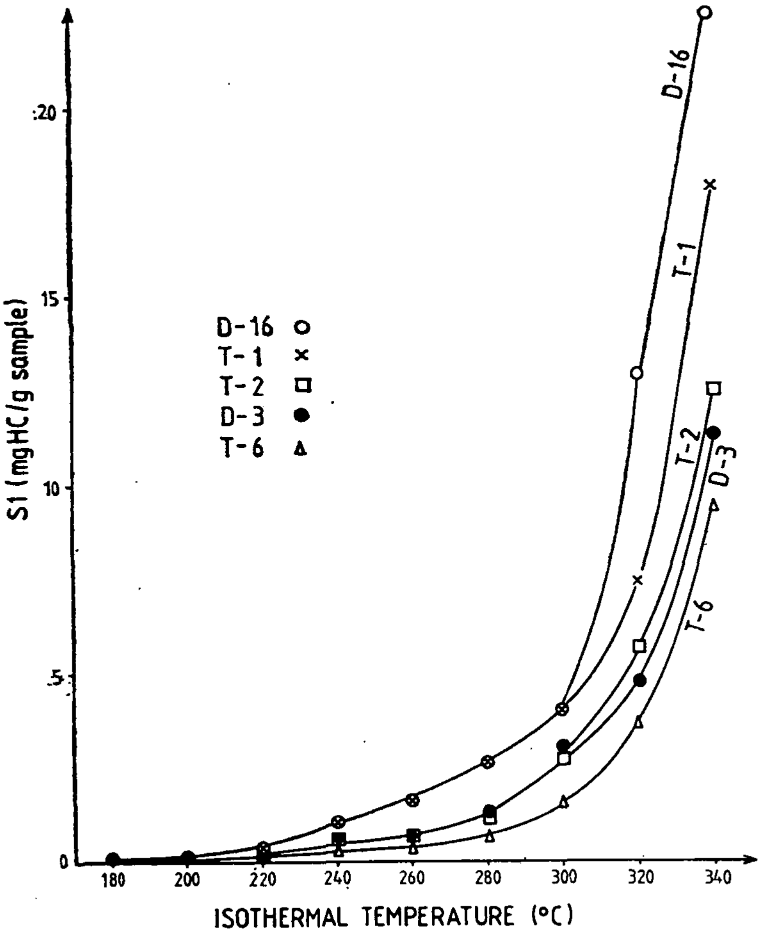


Fig. 3. The change of the gas-hydrocarbon-generative potential of the samples as a function of isothermal temperature

T—2 and D—3 being intermediary between the two preceding curves. Consequently, the hydrocarbon quantity generated between 220 and 300 °C is related first of all to the features of the environment of formation. Above 300 °C all samples display different curves, i.e. the individual features become predominating. At these temperatures (over 300 °C) probably small amounts of liquid hydrocarbon are also generated in addition to the gas-hydrocarbon. The sample sequence corresponds to the sequence obtained according to the S2 quantities (Table 2) by the Rock-Eval basic programme (isothermal temperature = 300 °C).

SUMMARY

The organic geochemical features of several Hungarian brown coals were studied by Rock-Eval pyrolysis and experimental thermal degradation. We tried to find relationships between these features and the microscopic plant remnants of the samples:

Brown coals derive from two different localities: Dorog and Tatabánya. In case of both localities samples were chosen that derive from periodicaly inundated deep swamp ecological conditions (D—16, T—1). One sample from each region formed in shallow moor characterized mostly by tranquillus type palm forest (D—3, T—2). The sample T—6 derives from an environment characterized by intense biological activity during sedimentation. In this sample great amounts of fungous remnants were found.

We tried to characterize the different environmental conditions by samples that display minimum differences with respect to the organic matter quantity. TOC equals 68—72% in the T-, and 65—73% in the D-samples.

As a first approximation, the quality of the organic matter proved to be similar. All samples are immature containing organic matter between type II and type III. Within the group, however, samples being closer either to type II or to type III could be distinguished. The D-samples were closer to type II and the T-samples to type III organic matter. Relationship between the H-index and the features of the microscopic plant remnants could be ovserved only within one locality.

The position of the samples in the evolution paths and the high S2/S3 value indicated organic matter suitable to generate both gas and oil. By means of experimental thermal degradation 54—160 mg oil was generated from 1 g organic carbon. Greatest amounts of oil were generated during the pyrolysis of the samples deriving from swampy inundated region, and lowest amounts were experienced in case of samples deriving from the region of high frequence biological activity, independently of the locality.

The gas-hydrocarbon-genetic potential was studied by step-by-step Rock-Eval pyrolysis. The isothermal temperature was increased by 20 °C between 180 and 340 °C. At the beginning, the S1 value proved to be negligible, between 200 and 300 °C isothermal temperatures it displayed close relationship with the features of the ecological conditions. The S1 isothermal temperature curves of the samples that showed similar microscopic plant remnants coincide *(Fig. 3)*. Above 300 °C isothermal temperature the curves become separated. In this range the increasing sequence of D1 value is the same as that of S2 value and roughly corresponds to the sequence of increasing oil production, as well.

The results of these investigations suggest that the microscopic plant remnants of the samples, i.e. the ecological conditions are related to the hydrocarbongenetic potential of the organic matter. This relationship is characteristic especially in case of gas-hydrocarbon-genetic potential as a function of temperature.

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REFERENCES

Espitalité, J., Madec, M. and Tissot, B. (1977): Source rock characterization method for petroleum exploration. Offshore Technology Conference.

Espitalié, J., Deroo, G. et Marquis, F. (1985): La pyrolyse Rock-Eval et ses applications, I—II. Revue de L'Institut Francais du Pétrole 40, 5, 6 563—579, 755—784.

ESPITALIÉ, J., DEROO, G. et MARQUIS, F. (1986): La pyrolyse Rock-Eval et ses applications, III Revue de L'Institut Francais du Pétrole **41**, 1, 73—79.

FORSBERG, A., and BJORØY, M. (1981): A sedimentological and organic geochemical study of the Botneheia formation, Svalbard, with special emphasis on the effects of weathering on the organic matter in shales. In: Advances in Organic Geochemistry, 1981, ed. by M. BJORØY, 60—68.

FREDERIKSEN, N. O. (1985): Review of Early Tertiary sporomorph paleoecology. — AASP Contribution ser., **15**, 92.

KEDVES, M. (1960): Etudes palynologiques dans le bassin de Dorog — I-. — Pollen et Spores **2/1**, 89—118.

KEDVES, M. (1963): Contribution la flore éocène de la Hongrie sur la base des examens palynologiques des couches houillères du puits III. d'Oroszlány et du puits XV/b de Tatabánya. — Acta Bot. **9/1—2**, 95—130.

KEDVES, M. (1969): Palynological Studies on Hungarian Early Tertiary Deposits. — Akadémiai Kiadó Budapest.

ORR, W. L. (1983): Comments in pyrolytic hydrocarbon yields in source-rock evaluation. In: M. Bjorøy et al, eds., Advances in organic geochemistry, 1981, New York, Wiley, 775—787.

PETERS, K. E. (1986): Guidelines for evaluating petroleum source rock using programmed pyrolysis. AAPG Bulletin **70**, 3, 318—329.

RÁKOSI, L. (1973): Palynologie des formations paléogènes du bassin de Dorog. — Ann. Inst. Geol. Publ. Hung., **55**, 500—575.

SAXBY, J. D., BENNETT, A. J. R., CORCORAN, J. F., LAMBERT, D. E. and RILEY, K. W. (1986): Petroleum generation: Simulation over six years of hydrocarbon formation from torbanite and brown coal in a subsiding basin. Org. Geochem., **9**, 2, 69—81.

SPIRO, B. and AIZENSHTAT, Z. (1981): Natural combustion and pyrolysis of bituminous rocks at the margin of Hatrurium, Israel. In: Advances in Organic Geochemistry, 1981, ed. by M. BJORØY, 799—807.

TEICHMÜLLER, M. and DURAND, B. (1983): Fluorescence microscopical rank studies on liptinites and vitrinites in peat and coals, and comparison with results of the Rock-Eval pyrolysis. Int. J. Coal Geol., **2**, 197—230.

TEICHMÜLLER, M. and R. TEICHMÜLLER (1979): Diagenesis of coal (coalification) In: G. LARSEN and G. V. CHILINGAR: Diagenesis in sediments and sedimentary rocks. Developments in Sedimentology, Elsevier, 1979, 207—218.

VERHEYEN, T. V., JOHNS, R. B. and ESPITALIÉ, J. (1984): An evaluation of Rock-Eval pyrolysis for the study of Australian coals including their kerogen and humic acid fractions. Geochimica et Cosmoshimica Acta **48**, 63—70.

TISSOT, B. P. and WELTE, D. H. (1984): Petroleum formation and occurrence: New York, Spinger-Verlag, 699.

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