

## **SIMULATED MATURATION PROCESS OF THE BITUMENS OF THE PULA OIL SHALE, HUNGARY**

L. PÁPAY

### **ABSTRACT**

Maturation processes were carried out between 200 and 500 °C in the bitumens of the Pula oil shales, the alteration was traced partly by the thermal residue, partly by the IR and C—H analyses of the organic condensate.

It was stated that the relatively high oxygen content of the Bit—A and BAM-bitumen is gradually lost by the release of compounds of different oxygen contents (carboxylic acids, ketons etc.) and by their decomposition, respectively. Above 400 °C no oxygen-bearing compound could be identified in the thermal residue.

In case of both bitumens considerable part of the long paraffin chain and alicyclic skeleton is preserved up to 400 °C. At 450 °C the thermal residue contains very small quantities of paraffinic part in case of Bit—A, at the same temperature more paraffinic compounds survive the thermal effect in case of the BAM-bitumen. At 500 °C the difference between their thermal resistivity is manifested by the coke-like thermal residue of Bit—A and by the product of BAM-bitumen being similar to that of 450 °C.

At lower temperatures the condensates are characterized by large quantities of oxygen-bearing compounds. The amount of these compounds is decreasing as a function of increasing temperature and mainly above 400 °C this value becomes ever lower, but the compounds can be detected even at 500 °C. The quantity of terminal olefines increases parallel with the temperature.

In the course of the simulated maturation processes the changes followed in the bitumen structure of the Pula oil shale show considerable similarities to those described in the thermal investigations of kerogens.

### **INTRODUCTION**

The methods used in the research of insoluble organic matter (kerogen) are applied in the investigations of bitumens, too. So the artificial diagenesis of soluble esters isolated from the chloroform extract of brown coals (BROOKS and SMITH, 1969) as well as the solid phase functional group extraction for bitumens and kerogens (COSTA NETA *et al.*, 1978) were studied.

Due to the high organic matter content, out of the sedimentary rocks the oil especially suitable to yield kerogen concentrate or after extraction to produce greater quantities of bitumen, since a part of them bears bitumen content of percentual order of magnitude (YEN, 1976). Nevertheless, formations with extremely high bitumen content also exist, *e.g.* coorongite. The solubility of coorongite in common organic solvents likewise varies from over 50% when reasonably young to less than 15% for old material (CANE, 1969).

In the Transdanubian Central Mountains (Hungary) in the vicinity of Pula, Upper Pannonian oil shale was found as filling of a basalt crater (JÁMBOR, SOLTI,

\* Department of Mineralogy, Geochemistry and Petrography, Attila József University, H-6701 Szeged, Pf. 651, Hungary

1975). Its biological precursor proved to be the *Botryococcus braunii* KÜTZ. alga (NAGY, 1976).

Since this discovery in 1973, several oil shale beds were found in Hungary (JÁMBOR, 1980), the studies of the oil shale of Pula and of the kerogen isolated from it, however, are most complete (GRASSELLY *et al.*, 1978; HETÉNYI *et al.*, 1977, 1978, 1982; HETÉNYI, 1979, 1980). Since the investigations needed the isolation of kerogen from year to year, the first step of this process being the extraction of the soluble matter of the oil shale, the possibility has been provided to carry out the simulated evolution experiments also with the bitumens. These investigations aimed to determine the thermal features of the bitumens as intermediary products of kerogen decomposition under the conditions when due to the lack of mineral matrix neither their catalytic, nor their retention effects should be taken into account.

## EXPERIMENTAL

The starting material was obtained by long extraction from the Pula oil shale, by chloroform in Soxhlet extractor (Bit-A) and subsequently by the mixture of benzene-acetone-methanol of 70:15:15 ratio (BAM-bitumen).

The thermal treatment was carried in a Heraeus-type furnace in oxygen-free nitrogen flow. Out of the experiments of different durations only the samples are discussed which underwent five hours thermal treatment. Bitumens were put in a boat made from Pyrex glass and this was put in the heating tube consisting of the same material, and the trap at its end collected the condensates, *i.e.* the brownish-black fat-like organic part and water. The organic matter was separated from water in a filler by means of chloroform, the organic solvent was evaporated at 60 °C in a drying chamber.

Analyses were carried out partly on the thermal residue remained in the glass-boat, partly on the organic condensates. These materials were characterized by IR spectra and C—H analyses.

The IR spectra of the original bitumens and thermal residues were recorded by the Specord 75 IR (Carl Zeiss, Jena), in the wavenumber range of 4000 to 400  $\text{cm}^{-1}$  using the KBr disc method, except the thermal residues of Bit-A of 375 and 400 °C, since their spectra could be recorded only by means of film techniques because of the sticky state of the material.

In addition to the qualitative evaluation, by means of the base-line method the extinction ratios of the carbonyl group (1710 and 1720—40  $\text{cm}^{-1}$ ) and of the methylene group (1460  $\text{cm}^{-1}$ ) of the corresponding compounds were calculated. These indices can be fairly well applied to characterize genetically the bitumens (GLEBOVSKAYA, 1971), and in addition to other indices these are used in the studies of hydrocarbon generation (BRUKNER-WEIN and VETŐ, 1981), as well as when qualifying the organic matter of core samples (BRUKNER-WEIN and SZÜCS, 1982).

The hydrogen and carbon contents were determined by CHN—1 analysator. In case of some samples of high carbon content, the determination of carbon was carried out by Carmhograph 8 (Wösthoff) in oxygen flow at 1000 °C.

The nitrogen determination was carried out by the Kjeldahl-method. Measurements were carried out after destruction in concentrated sulfuric acid in form of ammonium ion, using ion-selective electrodes in an equipment of OP—264 type.

## RESULTS

The data of elementary analyses of starting bitumens as well as the extinction ratios of carbonyl and methylene groups of the corresponding compounds measured at the given wavenumber are shown in Table 1, the data concerning the C, H and S contents were published earlier (PÁPAY, 1979).

Based on the IR spectra of the thermal residues of Bit-A (Fig. 1) it can be stated that the long unbranched alkyl-chain (strong aliphatic C—H absorption bands at 2920, 2860 and 1460  $\text{cm}^{-1}$ , moderate absorption at 1370 and 720  $\text{cm}^{-1}$ ) and the cycloparaffin skeleton (965  $\text{cm}^{-1}$ ) are mostly preserved up to 400 °C, the major part of the oxygen-bearing functional groups is broken off, while at higher temperatures being absent.

TABLE I

*The data of elementary analyses and extinction ratios of carbonyl and methylene groups of the corresponding compounds measured at the given wavenumber of starting bitumens*

	C %	H %	N %	S %	O (diff.) %	$\frac{E_{1710}}{E_{1460}}$	$\frac{E_{1720-40}}{E_{1460}}$
Bit-A	72.9	11.8	0.05	0.14	15.09	0.92	0.86
BAM-bitumen	72.6	11.2	0.07	0.17	15.96	1.08	1.02

It is to be noted that when interpreting the band at about 970  $\text{cm}^{-1}$  the other part of the spectrum should also be taken into account, since the bands at 965  $\text{cm}^{-1}$  (DOUGLAS *et al.*, 1970) and at 978  $\text{cm}^{-1}$  (CANE and ALBION, 1973) were interpreted as trans-olefines, the band at 970  $\text{cm}^{-1}$  (GLEBOVSKAYA, 1971) as naphthenic structure. In case of the Pula bitumens the presence of trans-olefines cannot be unambiguously excluded, but the NMR studies of the Pula paraffin oils revealed large amounts of cycloparaffins (PÁPAY, 1982), thus the IR-band of 965  $\text{cm}^{-1}$  is believed to be produced by cycloparaffin skeletons.

At 450 °C the overwhelming majority of the paraffin chains was broken off. At 500 °C the spectrum indicates strongly coaly (coke-like) state. Out of the oxygen-bearing compounds a small quantity of alcohol-type matter is preserved at 200 °C (3450  $\text{cm}^{-1}$ ) while out of the esters representing the major part (1720—40  $\text{cm}^{-1}$ ) the ketons are more resistive to temperature. The thermal effect of 400 °C is endured only by a few keton-types out of the oxygen-bearing compounds, the quantity of esters becomes minimal already after the thermal treatment at 375 °C.

It is characteristic of the thermal residues of BAM-bitumens (Fig. 2) that at 450 °C a part of the unbranched long paraffins and of the alicyclic skeletons is preserved. The functional groups with oxygen content are broken off above 400 °C. The residue obtained at 500 °C is not coke, but similar to the spectrum of Bit-A at 450 °C.

In case of both bitumens (Bit-A and BAM), especially at 375 °C and above, the spectra of the thermal residues show a small band at 1600  $\text{cm}^{-1}$  which is usually attributed to aromatic structures. Though in the course of the former IR and NMR analyses no aromatic structure could be identified in the Bit-A and BAM bitumens, the fact cannot be excluded that small quantity of aromatic compounds occurs in the starting bitumens, since palynological studies revealed pollens of higher plants

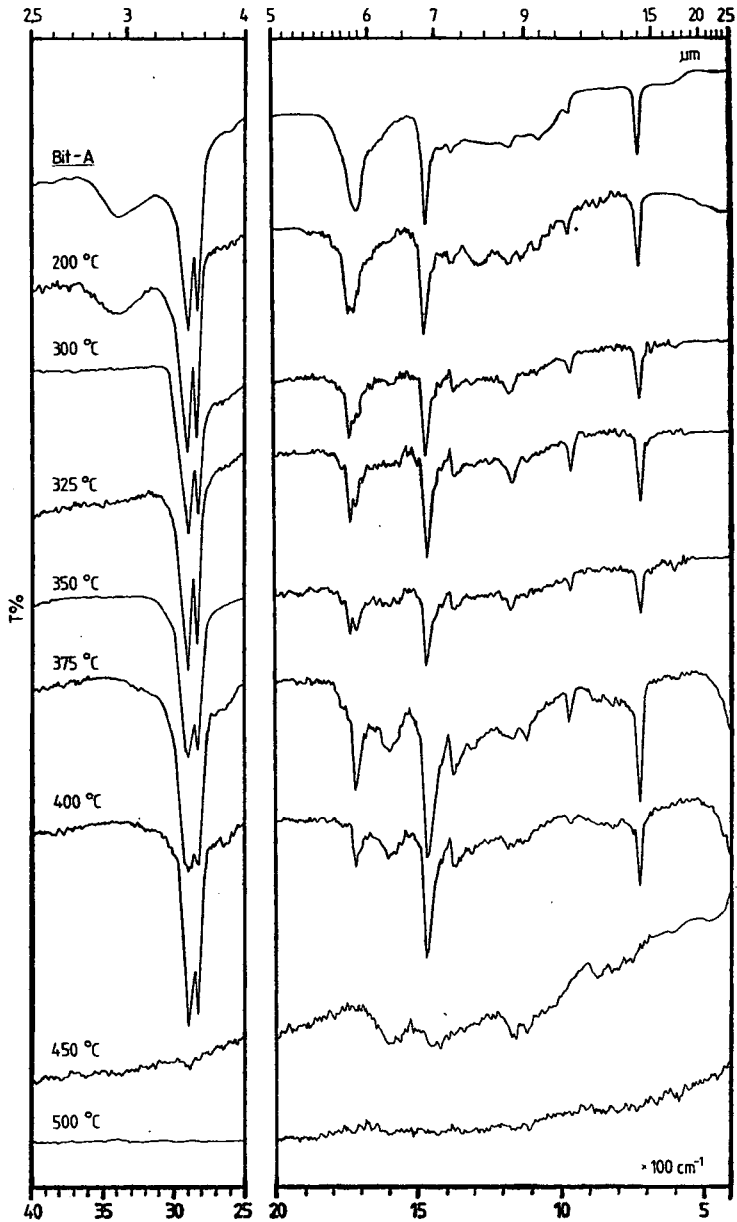


Fig. 1. The IR spectra of starting and thermal residues of Bit-A

(pines and deciduous trees), in addition to the predominance of *Botryococcus braunii* Kütz. algae (NAGY, 1976). It is to be taken into consideration, however, that due to the thermal effect in case of Bit-A a relative concentration increase of a factor of two (375 °C) and of twenty (450 °C), in case of the BAM-bitumen that of ten (450 °C) followed as a result of coalification, as compared to the initial state. More-

over, the spectra of Bit-A were made by film-technique at 375 and 450 °C, thus in case of these records the material quantity is greater than in case of the KBr disc records.

Based on the C—H analyses the maturation (coalification) processes can also be followed (Table 2). In the thermal residues of Bit-A, the thermal treatment at

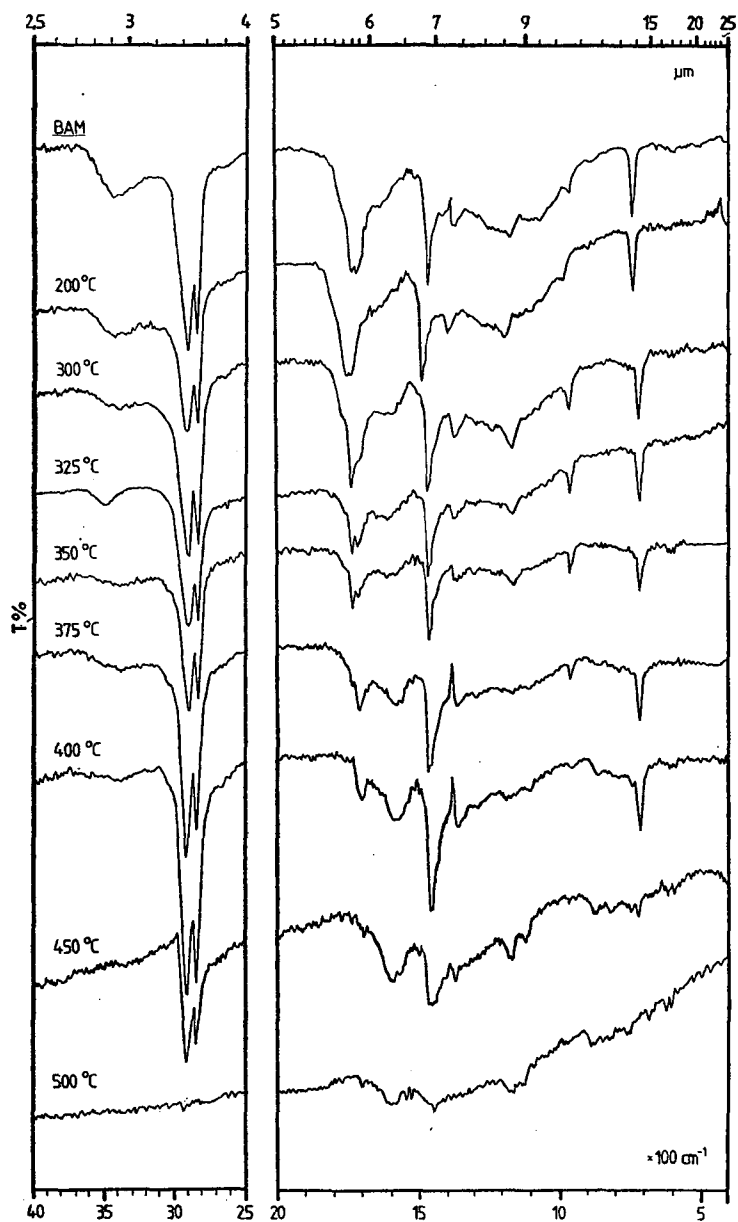


Fig. 2. The IR spectra of starting and thermal residues of BAM-bitumen

TABLE 2

*C—H analyses and variation of the ratio of the extinction coefficients of bitumens after thermal treatment*

Temperature °C	Bit—A				BAM—bitumen			
	C %	H %	$\frac{E_{1710}}{E_{1460}}$	$\frac{E_{1720-40}}{E_{1460}}$	C %	H %	$\frac{E_{1710}}{E_{1460}}$	$\frac{E_{1720-40}}{E_{1460}}$
200	78.2	12.6	0.76	0.76	73.2	12.2	1.09	1.09
300	81.0	13.8	0.52	0.71	80.4	12.8	0.81	1.02
325	81.6	13.9	0.46	0.59	81.4	14.0	0.62	0.71
350	83.4	14.0	0.48	0.50	82.9	14.1	0.55	0.62
375	84.7	13.7	0.46	0.14	85.2	13.2	0.48	0.28
400	86.1	12.9	0.25	0.00	84.9	12.2	0.29	0.00
450	96.0*		0.00	0.00	87.6	10.3	0.00	0.00
500	100.0*		0.00	0.00	91.1*		0.00	0.00

\* The carbon contents were determined by Carmhograph 8 apparatus.

200 °C caused considerable oxygen loss, which continued somewhat moderately up to 350 °C. From 375 °C the records refer to the break off of smaller carbon chains in addition to the process above.

On the contrary, in case of the thermal residues of the BAM-bitumen the thermal treatment of 200 °C did not produce remarkable change in the state of bitumen as compared to the initial one. (At this temperature no condensate could be collected.) Nevertheless, the oxygen loss at 300 °C proved to be considerable, then parallel with increasing temperature this trend is continued somewhat more moderately up to 350 °C. At 375 °C and above the decrease of hydrogen quantity refers to the break off of units for smaller carbon chains. Data obtained at 450 °C support the information indicated by the IR spectra, *i.e.* a part of the paraffinic and alicyclic skeletons survived the thermal effect.

Under increasing thermal conditions the qualitative changes of the thermal residues are fairly well indicated by the extinction ratios of carbonyl and methylene groups of the given compounds measured at given wavenumber. The overall tendency is that the band of 1710  $\text{cm}^{-1}$  decreases to greater extent in case of Bit-A up to 300 °C and in case of BAM-bitumen up to 325 °C, than the band of 1720—40  $\text{cm}^{-1}$ . Up to 375 °C the measure of decrease is reversed, while the intensity of the band of 1710  $\text{cm}^{-1}$  is nearly constant or decreases only to small extent. This fact was concluded from the fact that up to 300 and 325 °C, respectively, mostly carboxylic acids, subordinately esters are released from the bitumens. After the loss of carboxylic acids the decomposition of the esters is accelerated from esters and residues consisting of ketons, up to 375 °C, while the quantity of the keton-type matter remains nearly constant or shows some decrease. Taking into account the C—H data it can be stated that about one-fifth of the original oxygen-bearing compounds of the bitumens are preserved after the thermal treatment at 400 °C.

Based on the IR spectra, the condensate produced by Bit-A at 200 °C consists mainly of the mixture of carboxylic acids, esters and hydrocarbons (*Fig. 3*). Between 300 and 350 °C in the spectra the band of carboxylic acids in dimeric cyclic association (3500—2400  $\text{cm}^{-1}$ ) gradually disappears, the base-line of the fingerprint range is increasing, *i.e.* the quantity of the oxygen-bearing compounds of the condensate is decreasing. At 375 °C and above the long unbranched hydrocarbons and cycloparaffins are predominating, in addition to the small quantities of ketons and ester

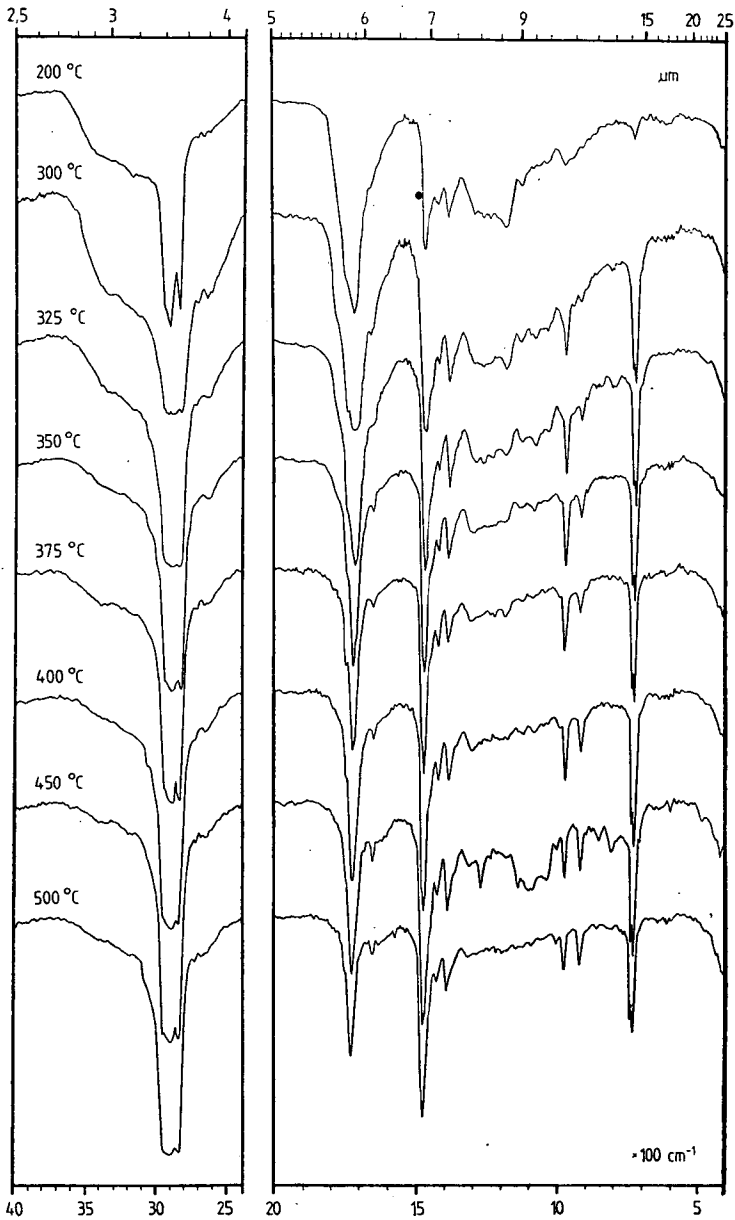


Fig. 3. The IR spectra of the condensate produced by Bit-A at different temperatures

type compounds. In the spectra of the Pula Bit-A condensates the bands characteristic of the aromatic structure are lacking. In all spectra bands referring to isolated double bonds are found, at 200 °C as a shoulder at  $1640\text{ cm}^{-1}$  and as small band at  $910\text{ cm}^{-1}$ , while at 500 °C in form of bands at  $1640$ ,  $990$  and  $910\text{ cm}^{-1}$ . The band pair of  $990\text{--}910\text{ cm}^{-1}$  is characteristic of the matter of  $\text{RHC}=\text{CH}_2$  type.

In the degradation processes related to kerogen the occurrence of terminal vinyl groups is also well-known. This is the result of the homolytic scission of C—C bonds (HENDERSON *et al.*, 1968; BROOKS and SMITH, 1969; DOUGLAS *et al.*, 1970; CONNAN, 1973; ESNAULT, 1973; KIRAN and GILLHAM, 1976; LARTER, 1978; see in: ALLAN *et al.*, 1980), and the lack of these terminal olefins is just surprising. Taking into account the qualitative composition of the Pula bitumens it seems to be very probable that the occurrence of terminal vinyl groups is caused by the degradation of fatty acids and carbonic acid esters, respectively, disregarding the reaction mechanism of degradation (DOUGLAS *et al.*, 1970; JURG and EISMA, 1970; BASET *et al.*, 1980).

The peculiarities determined for the Bit-A condensates are characteristic also of the condensates of BAM-bitumen (*Fig. 4*), only the temperature values are different. At 200 °C no condensate could be collected. Between 300 and 375 °C in the condensates much carboxylic acid and esters are found, in addition to hydrocarbons. Above 400 °C the hydrocarbon character predominates, the quantities of ketons and esters are subordinate. Between 300 and 500 °C the amount of terminal vinyl groups is increasing parallel with the temperature. No aromatic compounds are indicated by the spectra.

The C—H analyses as well as the ratios of carbonyl and methylene groups of the corresponding compounds measured at given wavenumber (Table 3) indicate

C—H analyses and variation of the extinction coefficients of organic condensations generated from bitumens after thermal treatment

TABLE 3

Temperature °C	Bit—A				BAM—bitumen			
	C %	H %	$\frac{E_{1710}}{E_{1460}}$	$\frac{E_{1720-40}}{E_{1460}}$	C %	H %	$\frac{E_{1710}}{E_{1460}}$	$\frac{E_{1720-40}}{E_{1460}}$
200	72.7	11.6	2.80	1.78	—	—	—	—
300	79.6	13.4	1.21	0.98	72.9	11.5	2.93	1.45
325	80.0	14.1	0.90	0.40	76.6	11.4	1.95	0.84
350	79.7	13.8	0.97	0.33	78.6	13.2	1.26	0.76
375	80.9	14.0	0.77	0.27	81.2	13.1	1.01	0.39
400	80.1	13.9	0.66	0.18	79.9	12.8	0.96	0.40
450	80.5	14.0	0.66	0.22	80.1	13.0	0.63	0.21
500	79.8	14.0	0.58	0.18	79.3	12.6	0.48	0.16

that the condensate produced by Bit-A at 200 °C contains considerable amounts of oxygen-bearing compounds. As compared to 200 °C, the oxygen quantity is considerably decreased at 300 °C, then between 325 and 500 °C a decrease of smaller extent can be observed, while the C and H values are constant within the measurement error values. In the condensate of the BAM-bitumen the amount of oxygen-bearing compounds is high at 300, 325 and 350 °C, further it decreases with increasing temperature. Above 375 °C the oxygen loss is of smaller extent than at lower temperatures and the C and H values vary only within narrow extreme limits. In the condensates no aromatic compounds are indicated by the IR spectra, *i.e.* it can be assumed that without catalysis no aromatic compounds are generated from the alkyl and cycloalkyl compounds of bitumens within the temperature range applied.



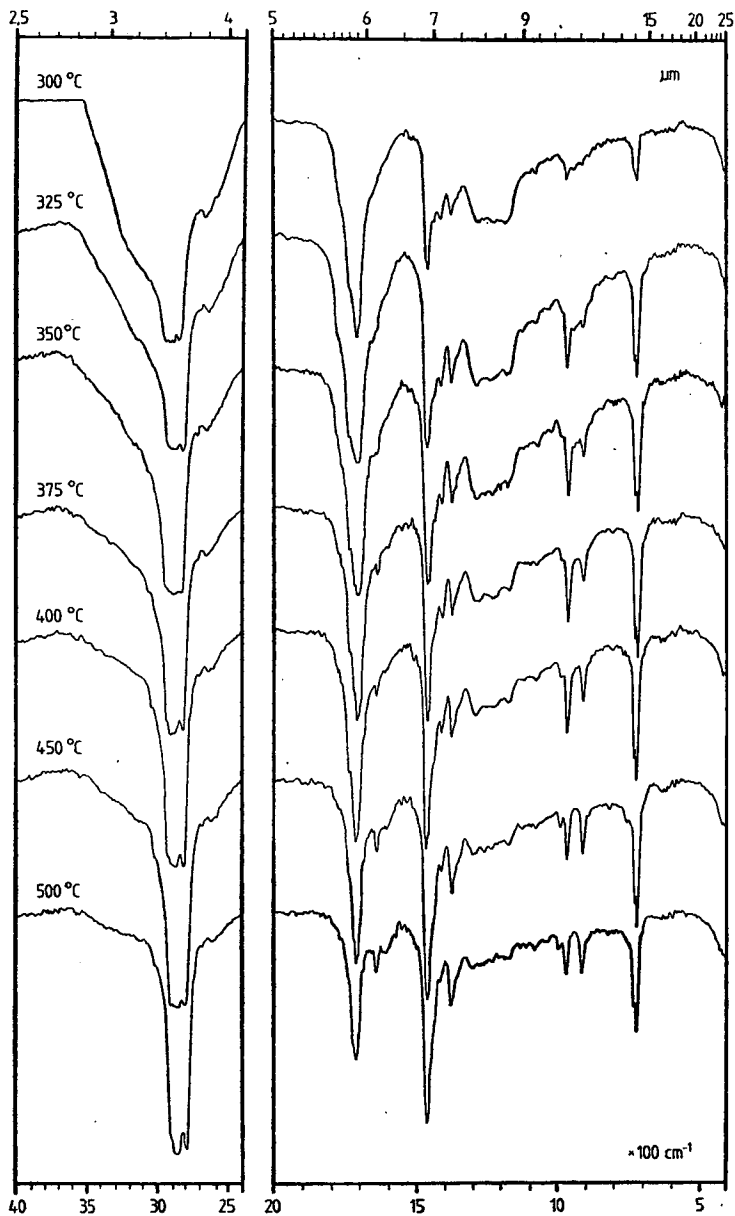


Fig. 4. The IR spectra of the condensate produced by BAM-bitumen at different temperatures

#### SUMMARY

Based on the simulated maturation processes of the Pula bitumens it can be stated that both the Bit-A and the BAM-bitumen loss their relatively high oxygen content only gradually. At lower temperatures the oxygen is released mainly in

form of carboxylic acid, esters and ketons. Above 400 °C all the oxygen-bearing compounds are lacking in the thermal residue. Considerable parts of the long unbranched paraffin chain and of the alicyclic skeleton are preserved up to 400 °C, though when condensates are generated the scission of C—C bonds can also be presumed at 200 °C in case of Bit-A and at 300 °C in case of BAM-bitumen, being indicated by the occurrence of terminal vinyl groups. At 450 °C small amounts of paraffinic parts can be observed in case of Bit-A, while at the same temperature much more paraffins survive the thermal effect. The difference between their thermal resistivity can be observed also at 500 °C, because the thermal residue of Bit-A is strongly coalified (coke-like), the residue of the BAM-bitumen is similar to that of 450 °C.

The condensates produced by bitumens and isolated from water are characterized by remarkable amounts of oxygen-bearing compounds (carboxylic acids and esters). This value decreases with increasing temperature and mainly above 400 °C it comes close to the oil state of paraffin base, though the products generated at 500 °C contain also some oxygen-bearing compounds. The quantity of terminal olefins increases with increasing temperature. No aromatic compounds could be identified in the condensates.

As a function of increasing temperature, the oxygen loss of bitumens, the break off of aliphatic units, the simultaneous increasing coalification of the thermal residue and the trend towards the graphite-state, as well as the occurrence of terminal olefins in the condensates are experimental results showing similarities to the data described from the thermal investigation of kerogens (HARWOOD, 1974; TISSOT *et al.*, 1974; 1978; DURAND and ESPITALIÉ, 1976; ROBIN and ROUXHET, 1978; TISSOT and WELTE, 1978; ALLAN *et al.*, 1980; MONIN *et al.*, 1980; ROUXHET *et al.*, 1980).

Nevertheless, the aromatization in case of bitumens is less unambiguous. In the condensates no aromatic compounds could be determined, in the thermal residues aromatic compounds were indicated by the IR spectra at 375 °C and above. The appearance of these compounds in the spectra, however, is not due to aromatization, but rather to the relative concentration increase of the aromatic compounds of the starting bitumens, generated by the thermal effect.

#### ACKNOWLEDGEMENTS

I am thankful to dr. M. HETÉNYI, for the thermal investigations and to dr. L. KÖRMÖCZI (Department of Botany) for making the nitrogen determination.

#### REFERENCES

- ALLAN, J., M. BJØROY and A. G. DOUGLAS (1980): A geochemical study of the exinite group maceral alginite, selected from three Permo-Carboniferous torbanites. In: *Advances in Organic Geochemistry 1979* (eds. A. G. DOUGLAS and J. R. MAXWELL), Pergamon Press. p. 599—618.
- BASET Z. H., R. J. PANCIROV and T. R. ASHE (1980): Organic compounds in coal: Structure and origins. In: *Advances in Organic Geochemistry 1979* (eds. A. G. DOUGLAS and J. R. MAXWELL), Pergamon Press. p. 619—630.
- BROOKS J. D. and SMITH J. W. (1969): Diagenesis of plant lipids during the formation of coal, oil and gas—II. Coalification and formation of oil and gas in the Gippsland Basin. — *Geochim. Cosmochim. Acta* **33**, p. 1183—1194.
- BRUKNER-WEIN, A. and I. VETŐ (1981): Origin and migration of hydrocarbons in the southeastern Danube-Tisza Interfluvium (in Hungarian with English resume). — *Bull. of the Hungarian Geol. Soc.*, **111**, p. 98—118.

- BRUKNER-WEIN A. and I. SZÜCS (1982): Bitumen contents of the fish-scale clay-marl in the Mecsek mountains, S Hungary (in Hungarian with English resume). — Annual Report of the Hungarian Geological Institute of 1980, p. 487—500.
- CANE, R. F. (1969): Coorongite and the genesis of oil shale. — *Geochim. Cosmochim. Acta* 33, p. 237—265.
- CANE, R. F. ALBION, P. R. (1973): Organic geochemistry of torbanite precursors. — *Geochim. Cosmochim. Acta* 37, p. 1543—1550.
- CONNAN, J. (1973): Diagenese naturelle et diagenese artificielle de la matiere organique a elements vegetaux predominants. In: *Advances in Organic Geochemistry, 1973* (eds. B. TISSOR and F. BIENNER) Editions Technip, Paris. p. 73—96.
- COSTA NETO, C., A. M. P. MACAIRA, R. C. P. PINTO, H. T. NAKAYAMA and J. N. CARDOSO (1980): New analytical approaches to organic geochemistry: solid phase functional group extraction for bitumens and functional group markers for kerogens. In: *Advances in Organic Geochemistry* (eds. A. G. DOUGLAS and J. R. MAXWELL), Pergamon Press. p. 249—263.
- DOUGLAS, A. G., EGLINTON, G. and W. HENDERSON (1970): Thermal alteration of the organic matter in sediments. In: *Advances in Organic Geochemistry, 1966* (eds., G. D. HOBSON and G. C. SPEERS), Pergamon Press. p. 369—388.
- DURAND, B. and ESPITALIÉ, J. (1976): Geochemical studies the organic matter from the Duala Basin (Cameroon)—II. Evaluation of kerogen. — *Geochim. Cosmochim. Acta* 40, p. 801—808.
- ESNAULT, C. (1973): Evolution thermique des acides gras combinées genése des paraffines normales dans las sédiments. Ph. D. Thesis L 'Université de Pau et des Pays de l'Adour.
- GLEBOVSKAYA, E. A. (1971): *Primenenie infrakrasnoy spektrofotometrii v neftyanoy geohimii*. Nedra, Leningrad.
- GRASSELLY, GY., M. BERTALAN and Cs. SAJGÓ (1977): Contributions to the knowledge of the Hungarian oil shale kerogen II. Results of preliminary DTA and IR-investigations on the kerogen of the oil shale occurrence at Pula. — *Acta Miner. Petr.*, XXIII/1, p. 177—196.
- HARWOOD, R. J. (1977): Oil and gas generation by laboratory pyrolysis of kerogen. — *AAPG Bull.*, 61, p. 2082—2102.
- HENDERSON, W., EGLINTON, G., SIMMONDS, C. and LOVELOCK, J. E. (1968): Thermal alteration as a contributory process to the genesis of petroleum. — *Nature*, 219, p. 1012—1016.
- HETÉNYI, M., K. MAITZ and É. TÓTH (1977): Contributions to the knowledge of the Hungarian oil shales kerogen I. Preliminary report on the results of the pyrolysis and selective oxidation. — *Acta Miner. Petr.*, XXIII/1, p. 165—175.
- HETÉNYI, M. and K. SIROKMÁN (1978): Structural information on kerogen from the Hungarian oil shale. — *Acta Miner. Petr.*, XXIII/2, p. 211—222.
- HETÉNYI, M. (1979): Thermal degradation of the oil shale kerogen of Pula (Hungary) at 473 and 573 K. — *Acta Miner. Petr.*, XXIV/1, p. 99—111.
- HETÉNYI, M. (1980): Thermal degradation of the organic matter of oil shale of Pula (Hungary) at 573—773 K. — *Acta Miner. Petr.*, XXIV/2, p. 301—314.
- HETÉNYI, M., J. TÓTH and GY. MILLEY (1982): On the role of temperature and pressure in the artificial evolution of organic matter of the Pula oil shale (Hungary). — *Acta Miner. Petr.*, XXV/2, p. 131—146.
- HOLLY, S. and P. SOHÁR (1975): Absorption spectra in the infrared region. *Akadémiai Kiadó*, Budapest.
- JÁMBOR, Á., G. SOLTÍ (1975): Geological condition of the Upper Pannonian oil shale deposit recovered in the Balaton Highland and Kemeneshát (Transdanubia, Hungary). — *Acta Miner. Petr.*, XXII/1, p. 9—28.
- JÁMBOR, Á. (1980): The results of oil shale exploration in Hungary (1980) (in Hungarian). — *Földt. Kutatás XXIII/4*, p. 5—8.
- JURG, J. W. and E. EISMA (1970): The mechanism of the generation of petroleum hydrocarbons from a fatty acid. In: *Advances in Organic Geochemistry, 1966* (eds. G. D. HOBSON and G. C. SPEERS), Pergamon Press. p. 367—368.
- KIRAN, E. and GILLHAM, J. K. (1976): Pyrolysis-molecular weight chromatography: a new on-line system for analysis of polymers. II. Thermal decomposition of polyolefins: polyethylene, polypropylene, polyisobutylene. *J. appl. polymer Sci.*, 20, p. 2045—2068.
- LARTER, S. R. and DOUGLAS, A. G. (1978): Low molecular weight aromatic hydrocarbons in coal maceral pyrolysates as indicators of diagenesis and organic type. In: *Environmental Biogeochemistry and Geomicrobiology. Vol. 1. The Aauatic Environment* (ed. W. E. KRUMBEIN) p. 373—386. *Ann Arbor, Sci. Pub. Inc.*, Michigan.
- MONIN, J. C., B. DURAND, M. VANDENBROUCKE and A. Y. HUC (1980): Experimental simulation of the natural transformation of kerogen In: *Advances in Organic Geochemistry 1979* (eds. A. G. DOUGLAS and J. R. MAXWELL), Pergamon Press. p. 517—530.

- NAGY, E. (1976): Palynological investigation of Transdanubian oil-shale exploratory boreholes (in Hungarian with English resume). — Annual Report of the Hungarian Geological Institute of 1974, p. 247—262.
- PÁPAY, L. (1979): Several features of the oil shale and oil-shale-kerogen bitumen of Pula (Hungary). — Acta Miner. Petr., XXIV/1, p. 113—124.
- PÁPAY, L. (1982): IR and NMR characterization of oil generated from some Hungarian oil shale at 773 K. — Acta Miner. Petr., XXV/2, p. 147—156.
- ROBIN, P. L., and ROUXHET, P. G. (1978): Characterization of kerogens and study of their evolution by infrared spectroscopy: carbonyl and carboxyl groups. — Geochim. Cosmochim. Acta 42, p. 1341—1349.
- ROUXHET, P. G., P. L. ROBIN and G. NICAISE (1980): Characterization of kerogens and their evolution by infrared spectroscopy. In: Kerogen insoluble organic matter from sedimentary rocks (ed. B. DURAND) Éditions Technip, Paris. p. 163—190.
- TISSOT, B., B. DURAND, J. ESPITALIÉ and A. COMBAZ (1974): Influence of nature and diagenesis of organic matter in formation of petroleum. — AAPG Bull., 58, p. 499—506.
- TISSOT, B., G. DEROO, A. HOOD (1978): Geochemical study of the Uinta Basin: formation of petroleum from the Green River formation. — Geochim. Cosmochim. Acta 42, p. 1469—1485.
- TISSOT, B. P. and D. H. WELTE (1978): From kerogen to petroleum. In: Petroleum formations and occurrence (eds. B. P. TISSOT and D. H. WELTE), Springer-Verlag, p. 148—184.
- YEN, T. F. (1976): Structural aspects of organic components in oil shales. In: Oil shale (eds. T. F. YEN and G. V. CHILINGARIAN), Elsevier Scientific Publishing Company, p. 129—148.

*Manuscript received, July 31, 1984*