

## THE INFLUENCE OF A LIPTOBIOLITH'S MINERAL MATTER ON ITS SEMICOKING PRODUCTS YIELD AND COMPOSITION

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**Abstract.** Upon semicoking a series of model mixtures of the organic and mineral matter concentrates of a Russian Far-Eastern liptobiolith, we have demonstrated that the sorptive mechanism of oil shales mineral matter influence on the thermolysis of their organic portion proposed earlier is also valid in the case of the liptobiolith investigated. Data on the chemical composition of the tars obtained indicate that a considerable part of the caustobiolith originates from aqueous autotrophic organisms and bacterial bioproduction which disagrees with current conceptions.

**Key words:** liptobiolith, origin, thermal decomposition, semicoking, mineral matter.

### INTRODUCTION

For some time already, we have been studying the influence of oil shales mineral components on the distribution of their organic matter between thermal decomposition products, as well as on the chemical composition of the latter; a mechanism of the processes involved has also been proposed [1, 2]. The present work is intended to verify whether the regularities observed while processing oil shales also hold in the case of caustobioliths of other genetic types and, specifically, liptobioliths.

Liptobioliths (sometimes called resinous coals) are a comparatively rare kind of fossil fuels that are supposed to originate mainly from the most stable constituent parts of higher plants such as resins, corky tissue, spores, cuticles, etc. [3]. Though classified as humolites, liptobioliths at the same time resemble oil shales in respect of the high hydrogen content in their organic matter (up to 10%) and, hence, a high yield of tar on semicoking.

As far as we know, the influence of liptobioliths mineral matter on their thermal decomposition processes has not been studied previously. However, their effect cannot be ignored since the mineral compounds content of these coals is often 50% or higher.

## EXPERIMENTAL

A liptobiolith sample from the Lipovetsk (Suifun) deposit, mine No. 4 in the Vladivostok region of the Russian Far-East was studied. Its characteristics are as follows (wt.-%): analytical moisture  $W^a$  1.4, ash  $A^d$  39.9, organic matter (by difference  $100 - A^d$ ) 60.1, mineral carbon dioxide is nearly absent, the ultimate composition of the organic part being the following (wt.-%): C 82.2, H 7.2, N 0.7, S 0.3, O (by difference) 9.6. According to X-ray diffraction analysis, the mineral matter crystalline part (65.8% of the total mineral material) contains (wt.-%): quartz 68.5, kaolinite 20.6, hydromicas 9.7, rutile 1.2, pyrite and anatase in traces.

The rock sample was pulverized in a ball mill to the grain size of 0.1 mm and centrifuged using 8–10% suspensions in aqueous calcium chloride and zinc chloride solutions to obtain concentrates of the liptobiolith organic and mineral parts. The organic rich fraction ( $A^d = 11.7\%$ ; from  $\text{CaCl}_2 \cdot \text{aq}$ ,  $1.25 \text{ g/cm}^3$ ) and the mineral matter concentrate ( $A^d = 76.7\%$ ; from  $\text{ZnCl}_2 \cdot \text{aq}$ ,  $1.70 \text{ g/cm}^3$ ) were combined into a series of model mixtures for thermal treatment.

The thermal decomposition of the mixtures prepared was performed in a Fischer retort according to the standard procedure. The tars obtained were dephenolized using a 10% aqueous sodium hydroxide solution and then separated into the chemical group compounds concentrates by thin layer chromatography on silica gel with *n*-hexane as an eluent. The tar fractions as well as gaseous products were analyzed by gas chromatography in columns of different polarity.

## RESULTS AND DISCUSSION

It follows from the data on the semicoking products yield (Table 1, Fig. 1) that, indeed, the mineral components of the liptobiolith considerably influence the distribution of its organic matter between the decomposition products: with increasing mineral content of the initial mixture for semicoking the tar yield, organic matter basis, decreases, but that of solid residue increases. This agrees with the previously suggested sorptive mechanism [1, 2] of the mineral material effect on the thermolysis of kerogens; the sorption activity coefficient [2] of the liptobiolith's mineral matter is about 0.7. The same applies to the yield, organic matter basis, of different chemical group compounds of tars: the higher the mineral content of the model mixture for semicoking, the higher the yield of non-aromatic hydrocarbons and the lower that of more polar aromatic hydrocarbons and, especially, heteroatomic compounds (Table 2, Fig. 2). For example, the yield of neutral heteroatomic compounds nearly redoubles (from 11.1 to 21.3%, organic matter basis) if the content of the latter in the raw material increases from 23 to 88%. This has been interpreted in terms of a more extensive secondary degradation of relatively polar, as compared with hydrocarbons, heteroatomic compounds of tars, preferentially retained on the solid residue surface. As might be expected, the phenomenon is more pronounced in the case of mineral-rich materials. It is also characteristic of the mineral compounds sorptive effect that with increasing mineral content of the rock to be processed the yield of carbon dioxide and, to a lesser degree, carbon monoxide, organic matter basis, increases (Table 3, Fig. 3), these compounds being typical degradation products of oxygen-containing organic substances.



The composition of model mixtures for semicoking and the thermolysis products yield, wt.-%

Indices	Sample number						
	1	2	3	4	5	6	7
Initial mixture:							
Analytical moisture $W^a$	1.0	0.9	0.9	1.4	1.0	0.9	0.9
Ash $A^d$	11.7	20.7	31.5	38.1	50.5	59.6	76.7
Organic matter, dry material basis (100 — $A^d$ )*	88.3	79.3	68.5	61.9	49.5	40.4	23.3
Yield of semicoking products, dry mixture basis:							
Tar	35.7	30.8	26.3	20.9	17.3	13.3	5.6
Pyrogenetic water	4.4	4.1	3.5	2.7	2.7	1.9	1.4
Solid residue (semicoke)	51.0	55.4	62.1	70.2	74.2	80.5	90.3
Gas and losses (by difference)	8.9	9.7	8.1	6.2	5.8	4.3	2.7

\* Only traces of mineral carbon dioxide are present.

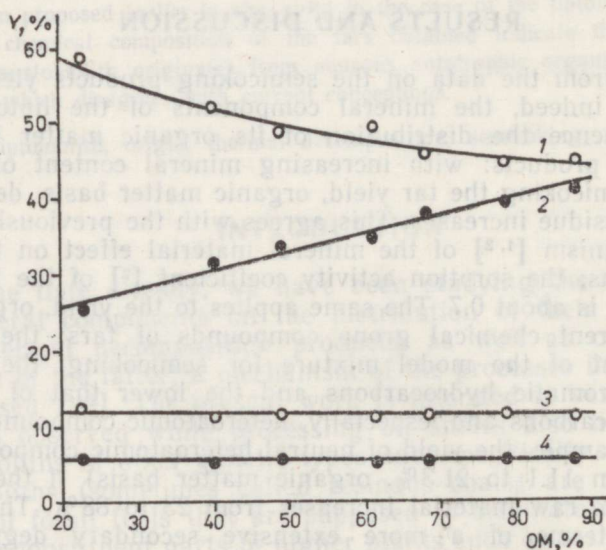


Fig. 1. Dependence of the semicoking products yield, organic matter basis (Y), on its content in the starting mixture (OM): 1 — solid residue (semicoke), 2 — tar, 3 — gaseous products, 4 — pyrogenetic water.

Table 2

The chemical group composition of semicoking tars, wt.-%

Group of compounds	Sample number according to Table 1						
	1	2	3	4	5	6	7
<b>Hydrocarbons:</b>							
Aliphatic and naphthenic	9.0	10.5	8.6	10.8	11.6	12.4	17.7
Monocyclic aromatic	13.3	10.8	6.4	11.7	12.0	13.4	17.4
Bi- and polycyclic aromatic	9.4	10.7	17.5	9.2	9.7	12.2	8.5
<b>Heteroatomic compounds:</b>							
Neutral and basic	52.6	56.9	56.7	57.6	58.3	50.4	46.3
Acidic	15.7	11.1	10.8	10.7	8.4	11.6	10.1

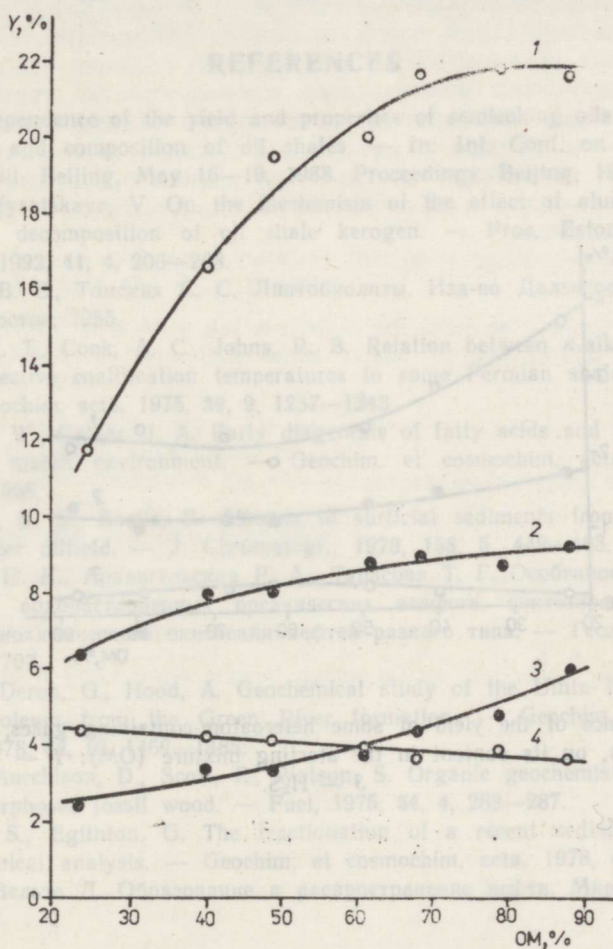


Fig. 2. Influence of the organic matter content (OM) in the initial mixture for semicoking on the yield of the tar chemical group compounds, organic matter basis (Y): 1 — neutral heteroatomic compounds, 2 — aromatic hydrocarbons, 3 — acidic compounds, 4 — aliphatic and naphthenic hydrocarbons.



The composition of semicoking gases (air-free gas basis), vol.-%

Compound	Sample number according to Table 1						
	1	2	3	4	5	6	7
CO <sub>2</sub>	11.3	13.3	11.9	9.6	10.9	16.6	18.1
CO	14.5	7.9	9.9	10.9	10.4	13.8	12.8
H <sub>2</sub> S	1.8	1.8	1.3	2.8	1.8	0.7	0.2
H <sub>2</sub>	4.4	4.9	5.6	4.3	6.7	4.0	5.1
CH <sub>4</sub>	50.5	44.0	48.2	43.6	50.2	42.3	40.8
C <sub>2</sub> H <sub>6</sub>	9.7	12.3	10.6	12.9	10.4	9.7	10.7
C <sub>3</sub> H <sub>8</sub>	2.3	6.2	4.9	6.5	2.7	4.5	3.5
C <sub>4</sub> H <sub>10</sub>	0.9	1.1	0.9	0.9	0.8	0.9	0.7
C <sub>2</sub> H <sub>4</sub>	2.1	2.2	2.3	3.0	2.6	2.5	2.9
C <sub>3</sub> H <sub>6</sub>	1.6	4.1	3.3	4.2	2.7	3.8	3.4
C <sub>4</sub> H <sub>8</sub>	0.9	2.2	1.1	1.3	0.8	1.2	1.8

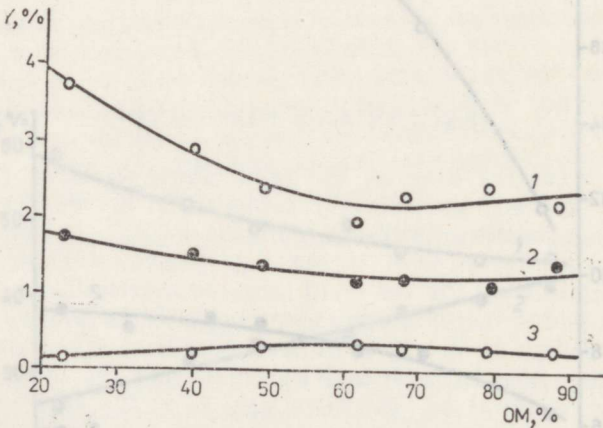


Fig. 3. Dependence of the yield of some heteroatom-containing gases, wt.-% organic matter basis (Y), on its content in the starting mixture (OM): 1 — CO<sub>2</sub>, 2 — CO, 3 — H<sub>2</sub>S.

We can infer from the above experimental data that the effect of mineral material on the thermolysis of the liptobiolith investigated is principally the same as in the case of oil shales. It seems that the mechanism proposed is applicable to a wider scope of fossil fuels than oil shales.

As to the composition of aliphatic hydrocarbons contained in the tars obtained by semicoking the Vladivostok liptobiolith, providing pyrolysis is regarded as an analytical method, it seems that the view on liptobioliths as originating mainly from higher plants should be taken with certain reservations. By and large, the aliphatic chains up to  $C_{17}$  (and the corresponding *n*-alkanes present in mild thermolysis tars) are supposed to originate from the autotrophic marine bioproduction [4], the  $C_{18}$ — $C_{25}$  chains mostly from bacterial production [5-8] and longer chains from higher plants [9-11], the latter being of terrestrial origin. As the concentration ratio of *n*-alkanes of the three aforementioned types is roughly 0.4:0.4:0.2 in the case of the semicoking tars obtained from this liptobiolith, one cannot ignore the primary aquagenous bioproduction and that of microorganisms as a source material for the liptobiolith organic matter.

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## LIPTOBIOLIIDI MINERAALAINETE MÕJU UTTEPRODUKTIDE SAAGISELE JA KOOSTISELE

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Kaug-Ida liptobioliidi orgaanilise ja mineraalne kontsentratsioonidest koostatud mudelsegude utmiskatsetega näidati, et varem tuvastatud sea-duspärasused, mis iseloomustavad mineraalainete mõju põlevkivide ter-molüüsile, kehtivad ka uuritud liptobioliidi termilisel lagunemisel. Lipto-bioliidi uttetõrvade keemiline koostis viitab sellele, et erinevalt levinud seisukohtadest on primaarsel akvageensel ja bakteriaalsel bioprodukt-sioonil liptobioliidi lähteainena oluline osa.

## ВЛИЯНИЕ МИНЕРАЛЬНОЙ ЧАСТИ ЛИПТОБИОЛИТА НА ВЫХОД И СОСТАВ ПРОДУКТОВ ЕГО ПОЛУКОКСОВАНИЯ

Ада СУМБЕРГ, Каарли УРОВ

Полукоксованием модельных смесей из концентратов органического вещества и минеральной части дальневосточного липтобиолита пока-зано, что ранее установленные для горючих сланцев основные законо-мерности воздействия минеральных компонентов на термическое раз-ложение керогена соблюдаются и в случае исследованного липто-биолита. Однако данные о химическом составе полученных дегтей не подтверждают распространенную точку зрения о несущественной роли первичной аквагенной и бактериальной биопродукции в формировании этого липтобиолита.