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Thermogravimetric analysis of brown coals and also humic acids as well as their extracted bitumens in the Circumpolar Urals

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ABSTRACT

The purpose of this work is to study the thermal stability of humic acids and bitumens extracted from brown coals of the Circumpolar Urals in the Khanty-Mansi Autonomous Okrug-Ugra. Waxes, bitumens and resins were extracted from brown coals with benzene on Soxhlet apparatuses. Extraction of humic acids was carried out by the Instorf method. Thermal analysis of all humic acid samples was performed at Novosibirsk Institute of Organic Chemistry in the Siberian Branch of the Russian Academy of Sciences on a STA 409 PC Luxx synchronous thermal analyser (Netzsch Company) in an inert atmosphere in a platinum crucible. It was found that thermal stability of humic acid macromolecules obtained from brown coals is characterized by typical thermal effects and quantitatively different value of macromolecule destruction within the ranges from 220 to 400 °C and from 400 to 800 °C.

Keywords: Brown coals, Bitumens, Humic Acids, Khanty-Mansi Autonomous Okrug - Yugra, Circumpolar Urals.
Article type: Short Communication.

INTRODUCTION

In the second half of the 20th century on the territory of Berezovsky District of Khanty-Mansi Autonomous Okrug - Ugra, 8 brown coal deposits were identified and explored, three of which are geographically close to the largest settlement in the northwestern part of Berezovsky District, i.e. Saranpaul village: Lyulyinskoe, Tolyinskoe, and Otoryinskoye. The central part of the Otoryinskoye field deposit is located 8 km to the east of the Tolya settlement and 280 km to the north along a straight line from the nearest railway station, Polunochnoye. The distance from the deposit to the city of Ivdel along the winter road is 370 km. The geographic coordinates of the central part of the field deposit are as follows: 63°14' north latitude and 60° 21' east longitude. Otoryinskoye field deposit is located on the eastern wing of the Otorinskaya anticline and is bounded to the west by the axial part of the anticline structure, where it runs along the erosive section of the coal-bearing strata. Realization of local heat and electricity supply when not importing hard coal and fuel oil for local boiler stations is the basic idea laid down in many reporting and design documents of the Khanty-Mansi Autonomous Okrug-Yugra. However, we propose to evaluate the possibility of deep processing of brown coals with obtaining a wide range of end products. Studies are aimed at creating technologies for obtaining new target products of their processing, in particular humic preparations.

Field deposit geology

The coal-bearing rock formation lies on the dislocated Paleozoic rocks represented in the area by diabases, diabase porphyrites with interlayers of clay shales and quartz sandstones, or on the products of their weathering. Some places in the eastern part of the deposit, where the Paleozoic basement is somewhat elevated, the coal sequence is wedged, and the weathering crust is covered with coal-laid argillites. The coal-bearing formations are everywhere

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covered by the aforementioned coal-laid mudstones, as well as by clays along their section. In the western elevated axial part of the anticline, where these sediments are eroded, coal-bearing sediments in places come to the day surface or are covered with Quaternary glacial or interglacial sediments. According to prospecting works (Denisov *et al.* 1986; Denisov *et al.* 1993), the Otoryinskaya rock formation contains eight coal seams. The most mature of these is the "Main Layer". Coal seams deposited below the "Main layer" are, as a rule, poorly sustained along the strike and dip and are distributed in small limited areas (Table 1).

Table 1. Data on the structure and thickness of the coal seams of Otoryinskoye field deposit according to prospecting data.

Rock formation	Layer No. and name	Power counts from and to the average (number of intersections)	Layer structure	Normal distance between layers
1	2	3	4	5
Otoryinskoye	Main "A"	1.8 (I)	Simple	3.0
	Main	1.0-9.7 3,75 (16)	Complex	7.0
	№14	1.1-4.8 2.5 (8)	Simple	8.0

Fig. 1. Geographical location of the Otoryinskoye field deposit.

Ханты-Мансийск	Khanty-Mansiysk
Курган	Kurgan
Магнитогорск	Magnitogorsk
Тюмень	Tyumen
Челябинск	Chelyabinsk
Екатеринбург	Ekaterinburg
Уральский федеральный округ	Ural Federal District
Салехард	Salekhard
Северо-Сосьвинская электростанция	North-Sosva power plant
Оторьинское месторождение бурого угля	Otorinsky brown coal field

RESULTS

The thermal analysis results shown below were performed using modern simultaneous thermal analysis instruments, which provide accurate data with high accuracy and at low sample flow rates (Tikhova 2007) Thermal analysis of all humic acid samples was performed on a STA 409 PC Luxx thermal analyser (Netzsch company) in an inert atmosphere in a platinum crucible at the Novosibirsk Institute of Organic Chemistry in the Siberian Branch of the Russian Academy of Sciences. Similar studies were carried out for humic acids of peats and sapropels (Sartakov 2007; Tikhova & Sartakov 2009; Evgeny *et al.* 2019) The works by V.A. Chernikov and N.V.

Chukhareva deserve special attention in the field of studying the thermal characteristics of humic acids (Chernikov 2001; Chukhareva & 2019) Transformation of high-molecular-weight organic compounds occurs under the influence of regional climatic factors (Vasilevich & Lodygin 2021) The data of obtained thermograms were summarized and presented in Table 2.

Table 2. Results of thermal analysis.

Specimen	**Mass loss (%)**		**Total mass loss (%)**	**Z**	**Maximum temperature of thermal effects in the high-temperature region (°C)**		**Calorific value (J/g)**
	Up to 400	**Higher than 400**			**I**	**II**	
Guimatomelanic acid - 2nd drain	22.37	77.31	99. 68	0.29	435. 4	445.0	25232
Hymatomelanic acid - 1st drain	20.06	79.29	99.35	0.25	445.0	−	24019
Himatomelanic acid - 3rd drain	21. 66	75.13	96. 79	0.29	439.1	454.8	25028
Humic acid - 2nd drain	16. 72	79.95	96. 67	0.21	425.8	432.9	24588
Humic acid - 1st drain	15.85	82. 57	98. 42	0.19	417. 4	426.3	24343
Humic acid - 3rd drain	18.69	76.34	95.03	0.24	431.8	−	24883
Bitumens	26.44	72.81	99.25	0.36	471.3	−	23216
Brown coals	7.15	74. 74	81.89	0.09	328.5	367. 5	22449

Note: Z is the ratio of mass loss in the low-temperature region to mass loss in the high-temperature region.

Preliminarily, the correlation dependence of the index Z in relation to the maximum temperature of thermal effects was built in order to see if there is a relationship between these parameters. Index Z and maximum temperature of thermal effects for brown coal, bitumen, humic acid of 1st drain and hypomelanic acid of 1st drain values were taken for construction of correlation dependence (Table 3). We find the correlation coefficient ($R^2 = 0.9419$) from the graph (Fig. 2). Since the correlation coefficient is positive and tends to 1, we can talk about the dependence of the index Z and the maximum temperature of the thermal effects of the target products.

Table 3. Thermal characteristics of group components of brown coals.

Specimen	**Z**	**T_{max} (°C)**
Brown coals	0.09	367.5
Bitumen	0.36	471.3
Humic acid - 1st drain	0.19	426.3
Hymatomelanic acid - 1st drain	0.25	445

Note: Z is the ratio of mass loss in the low-temperature region to mass loss in the high-temperature region. T is the maximum temperature of the thermal effect.

As shown in Table 4, the highest Z-index value corresponds to the hymatomelanic acid of 2nd and 3rd drains, and the lowest Z-index value corresponds to the humic acid of 1st drain. The smaller the Z-index value, the more thermally stable and more aromatic the preparation. Consequently, of the extracted humic acids, thermally stable is the humic 1st drain acid (Z-index value = 0.19). Notably, the least thermally stable are the hymatomelanic acids of 2nd and 3rd drains (Z-value is 0.29). Noteworthy, the thermal stability of humic acids decreases by the elevation in the number of drains. Humic acid of the 1st, 2nd and 3rd drains exhibited the index values of Z = 0.19, Z = 0.21 and Z = 0.24 respectively. The following is observed in the group of the hymatomelanic acids: The Z-index value for hymatomelanic acid of the 1st drain was 0.25, while those of the 2nd and 3rd were not different (0.29).

Table 4. Thermal characteristics of humic acids.

Specimen	**Z**	**T_{max} (°C)**
Guimatomelanic acid - 2nd drain	0.29	445
Hymatomelanic acid - 1st drain	0.25	445
Himatomelanic acid - 3rd drain	0.29	454.8
Humic acid - 2nd drain	0.21	432.9
Humic acid - 1st drain	0.19	426.3
Humic acid-3rd drain	0.24	431.8

Note: Z is the ratio of mass loss in the low-temperature region to mass loss in the high-temperature region.

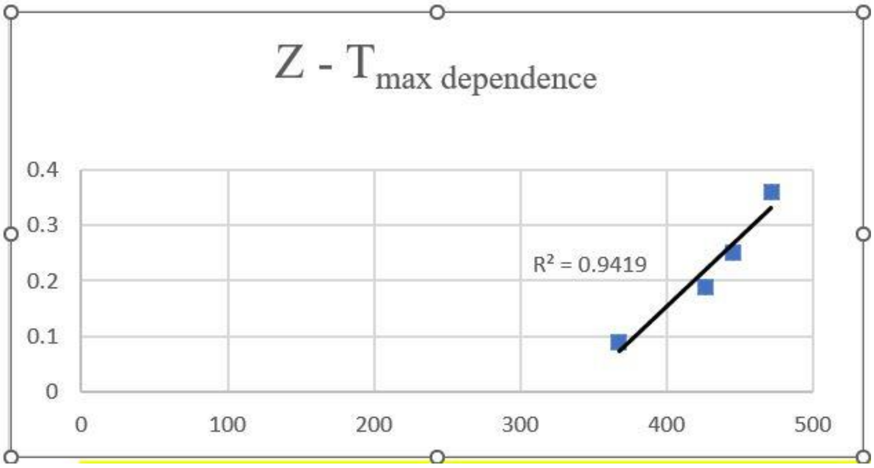

Fig. 2. Correlation relationship between the Z indicator and the maximum temperature of thermal effects of brown coals, bitumen, humic acid 1st drain and hydromelanic acid 1st drain.

The greater the temperature of the thermal effects, the greater the Z-index value, i.e., for the maximum temperature (454.8) it corresponds to the Z-index value (0.29), or for the hymatomelanic acid of the 3rd drain. The correlation coefficient for the Z index dependence on the maximum temperature of the thermal effects for hypatomelanic acids (1-3 drains) and humic acids (1-3 drains) was0.8043 (Fig. 3)

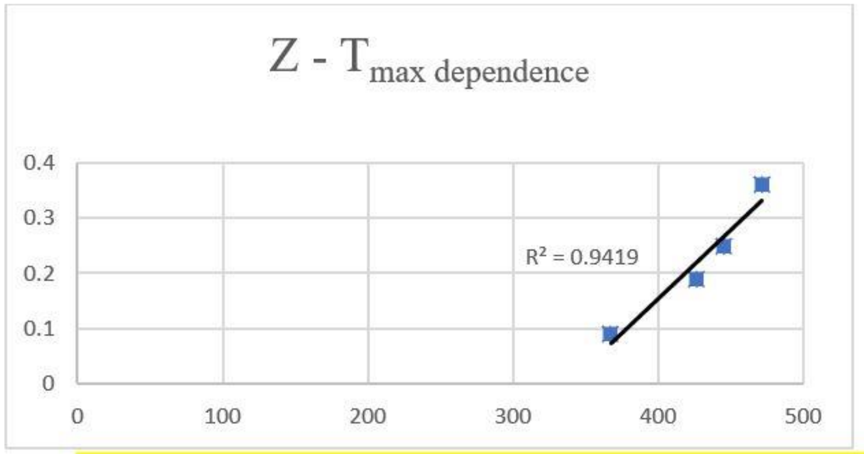

Fig. 3. Correlation dependence for Z index on the maximum temperature of the thermal effects for HMA-1.2.3 drains and HA-1.2.3 drains.

The results of the study on thermal characteristics of brown coals have complemented our earlier research on the elemental composition of brown coals (Gurova *et al.* 2021)

CONCLUSION

The thermal stability of humic acids macromolecules obtained from brown coals is characterized by typical thermal effects and quantitatively different value of macromolecule degradation within the ranges from 220 to 400 °C and from 400 to 800 °C, which confirms the two-member structure of macromolecules. The difference between humic acids is especially pronounced in the differential-scanning curves abstraction. Humic acids are more aromatically arranged in comparison with hymatomelanic acids, which is reflected in their thermal characteristics. The results of the work can be used for large-scale evaluation of raw brown coals and serve as a source of information for humic preparations.

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