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Thermolysis Dynamics of Bituminous Sandstone from the Bayan-Erkhet Deposit (Mongolia)

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Abstract

The dynamics of thermolysis was studied for the bituminous sandstone taken from the Bayan-Erkhet deposit (Mongolia). It has been demonstrated that the thermolysis procedure could be used for the isolation of bituminous component from these raw materials to obtain valuable intermediates for coal chemistry and motor fuels.

Key words: bituminous sandstone, thermal analysis, thermolysis, low-melting fraction, sublimates, cinder

INTRODUCTION

Under the conditions of the intensive exploitation of the world reserves of hydrocarbon fuel-and-energy resources, the depletion thereof becomes more and more obvious every year. In this situation, of especial urgency is to search for alternative sources of energy as an additional resource with respect to available energy raw. These sources could be presented by rich bituminous sandstone.

According, for example, to data from [1], the world's reserves of oil shale and bituminous sandstone are estimated ranging within 700–800 billion tons, which is 7–8 times greater than all the world's oil reserves surveyed by now. Russia is among the countries those possess large-scale reserves of such natural resources.

In the territory of Mongolia there are also reserves of bituminous sandstone [2], among those there are bituminous sandstone deposits at Bayan-Erkhet most well-studied from the geological standpoint.

According to the current classification, the bituminous sandstone species of the Bayan-Erkhet deposit can be attributed to the epigenetic type of tabular oil sandstone species [3, 4]. The binding part of the sandstone deposits (bitumen) belongs to the asphalts [5]. The authors of [6] demonstrated that such sandstone could be used as a component of hot dense asphalt-concrete for different road climatic zones with not additional introduction of petroleum bitumen therein. However, under appropriate conditions, bituminous sandstone species could be an alternative source of hydrocarbon feedstock [1, 5].

The aim of this work consisted in studying the thermal decomposition of bituminous sandstone taken from the Bayan-Erkhet deposit.

EXPERIMENTAL

A sample of sandstone represented a fatty to the touch, solid, tightly compressed viscous

black matter that can be subjected to deformation and cutting with a spatula and other auxiliary tools. Studying the dynamics of the thermolysis was carried out using a Paulik–Paulik–Erdey MOM-1000 derivatograph (Hungary). A weighed sample portion with the mass up to 1.0 g was placed into a special quartz crucible to heat to a temperature of 950–1000 °C at a heating rate of about 10 and 5 °C/min.

The determination of the aggregate state of the thermolysis products was carried out *via* stepwise heating a weighed sample portion with the mass of 40–60 g in an evacuated quartz tube-ampoule with the system for suction and trapping the fusible fractions of the material and sublimation products. The ampoule with the sample placed therein in a quartz boat was heated using a muffle furnace. In order to separate the fusible components of the material, the ampoule in the furnace was mounted in a horizontal position with an inclination towards the cold end thereof protruding from the furnace.

The experiments were repeated several times in order to obtain relatively reliable and reproducible results.

RESULTS AND DISCUSSION

Differential thermal and gravimetric analysis

The preliminary thermal analysis demonstrated that at a heating rate of about 10 °C in the sample within the temperature range 400–480 °C (see Fig. 1, *a*, DTA curve) there occurs a transformation with heat absorption of at a

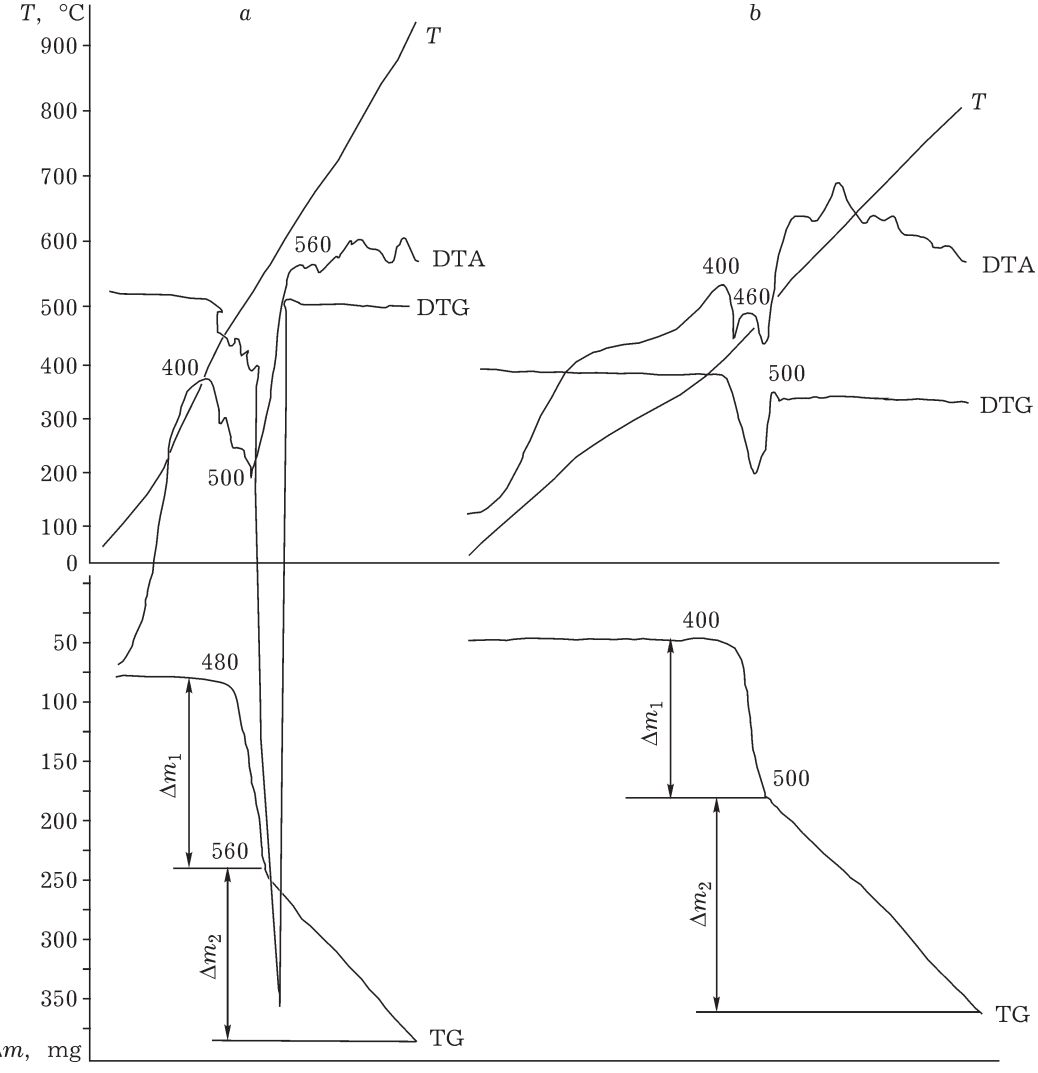

Fig. 1. DTGA of bituminous sandstone in the experiments at a heating rate equal to 10 (*a*) and 5 °C/min (*b*).

constant mass. Further, the mass change curve (TG) as well as differential mass change (DTG) and differential temperature (DTA) curves exhibit initially smooth, then turning to the explosion-like endothermic process of changing the state of the sample material with an abrupt diminution of the mass, which culminates within the temperature range of 560 °C. Then, the TG curve exhibit monotonic mass loss upon heating the sample, whereas the DTA curve demonstrate some minor endoeffects, those, to all appearance, correspond to the phase transition and the decomposition of the mineral components of the sample. The mass loss within the temperature range of 560 °C was equal to 8 mass %, whereas the total mass loss upon heating the sample up to 950 °C reached 14.6 %.

In the course of performing the experiments with a heating rate of 5 °C/min (see Fig. 1, *b*), the processes of melting and sublimation take place in a quiet mode, with no explosive effect. The formation of the liquid phase, *i. e.* melting the bituminous component, to all appearance, occurs in a mode of gradual softening the bulk with the transition to the liquid state. The DTA curve confirms this by the presence of saddle endothermic deflection within the temperature range of 200–400 °C and by the absence of any thermal effects on the TG and DTG curves obtained. The endothermic effect within the temperature range of 400–435 °C, to all appearance, relates to the decomposition reaction of the resulting liquid phase, whereas the endothermic effect at 470–500 °C concerns a final process of the sublimation of a low-boiling product formed. As one could see from the course of the DTA curve, the two processes occur almost simultaneously: with beginning the decomposition process, simultaneously there is boiling the product formed observed, whose distillation is completed at 470–500 °C. The subsequent rising the temperature of the material the residual coal component is monotonously removed, which is exhibited on the TG curve within the temperature range 500–800 °C.

Determining the aggregate state of the thermolysis products

According to the results of DTGA we performed a stepwise heating of the material up to the temperature values of 360 and 490 °C in an alundum crucible (with a lid made of foamed corundum to provide free diffusion of gaseous thermolysis products and to provide limit an access from the ambient air to the sample). As the result of heating up to 360–370 °C and a subsequent cooling, the sample material being tightly sintered due to melting and subsequent solidification of a low-melting component of the bituminous sandstone. After heating up to 500 °C and subsequent cooling the sample material represents a sand bulk (especially in the upper part thereof) that can be relatively easily removed from the crucible before until complete cleaning the crucible walls. At that, he lower part of the sample has black anthracite colour, whereas the top part has the colour of light-brown sand (see Fig. 2).

Further, the sample of the original material in a quartz boat was placed into a quartz ampoule in order to obtain the products of thermolysis: a mineral component, as well as fusible and sublimating bitumen fractions. In the course of heating the ampoule, there was a permanent suction of formed sublimates carried out through a system of trapping bottles with the help of a water-jet pump.

Initially, the experiments were carried out as it follows: heating to a temperature of 550 °C for 1 h with further holding at this temperature for 4 h with cooling after that down to a room temperature (sample PB-3).

As the result, we obtained the cinder of anthracite colour, effortlessly malaxed to give a loose bul as well as distilled oily viscous liquid similar to waste engine oil. The latter included the sublimate condensate from the absorbency bottles and a more viscous fluid that flowed into a cold end of the ampoule, protruding out of the furnace. The solid mass loss was equal to approximately 15 %. It should be noted that on the wall of the quartz tubular ampoule, in the hot zone there formed a black thin layer, *i. e.* carbon “mirror” that exhibits a complete burnout upon heating in air up to 800–850 °C. Furthermore, under heating a sample swells, whereas the molten fraction flows down along the inclination of the boat, so a part of the material appears outside the boat. This, to all appearance, one could consider an explanation of appearing the liquid fraction in the cold zone of the ampoule (see Fig. 3).

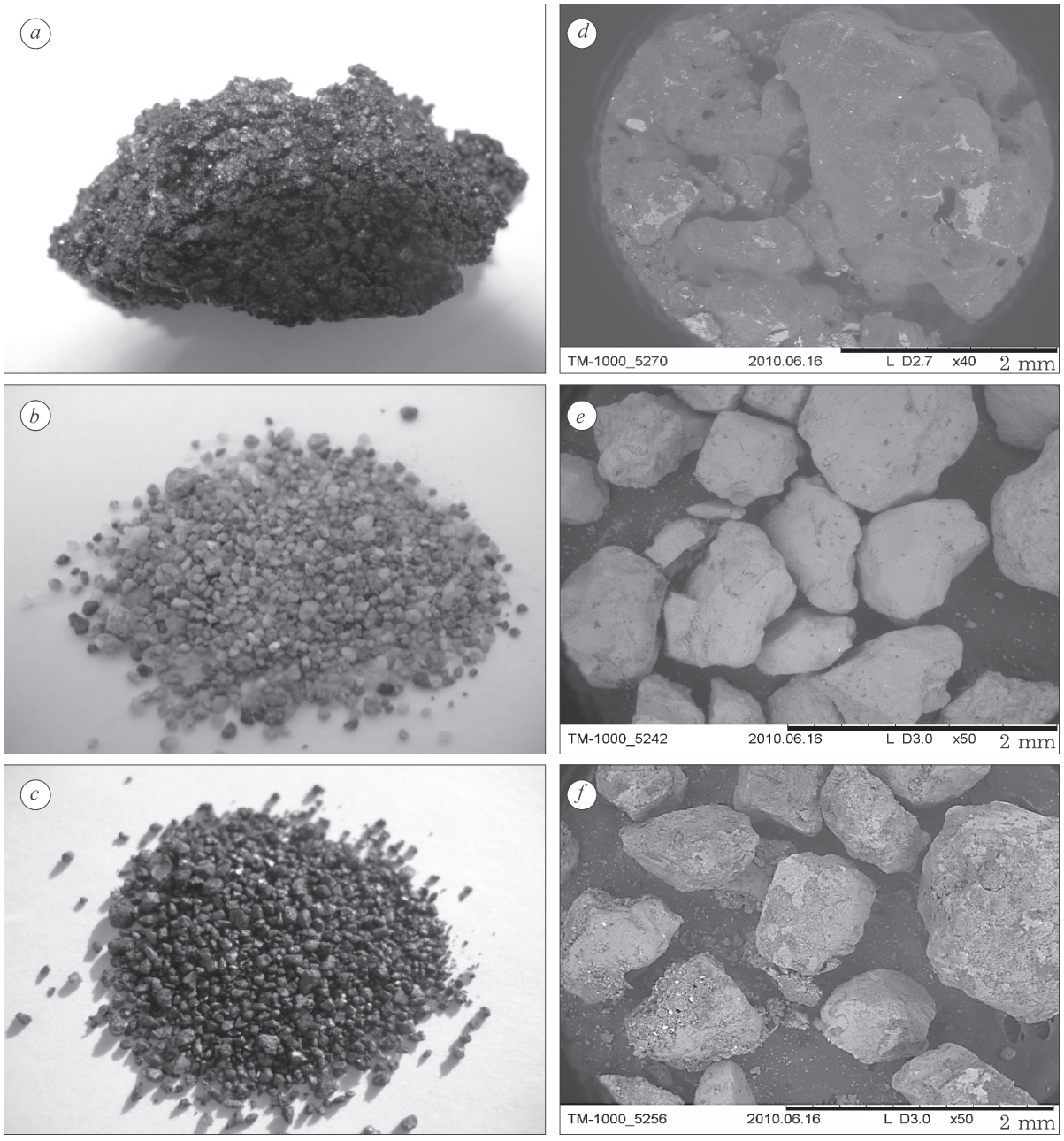

Fig. 2. Products of sandstone heat treatment at 500 °C: *a*, *d* – original sandstone (general view and binocular shot image at a 40-fold magnification, respectively); *b* – general view of the top of the cinder; *d* – binocular shot image at 50-fold magnification; *c*, *e* – the same for the bottom of the cinder.

From the series of experiments with gradual heating the material and registering the liquid fraction formed, the condensate of sublimates and the change in the mass of remaining solid material we have found that holding the material within the temperature range up to 400 °C (sample PB-4) results in melting the fusible bituminous component of the original material to occur. The fraction obtained in the experiments represents a low-viscosity, oily liquid at the temperature values of 350–200 °C, whereas on the verge of solidifying at the temperature close to a room temperature it is a viscous, thick black bulk. Sublimates formed under boiling within the temperature range of 420–600 °C represent light yellow liquids at a room temperature (sample PB-6).

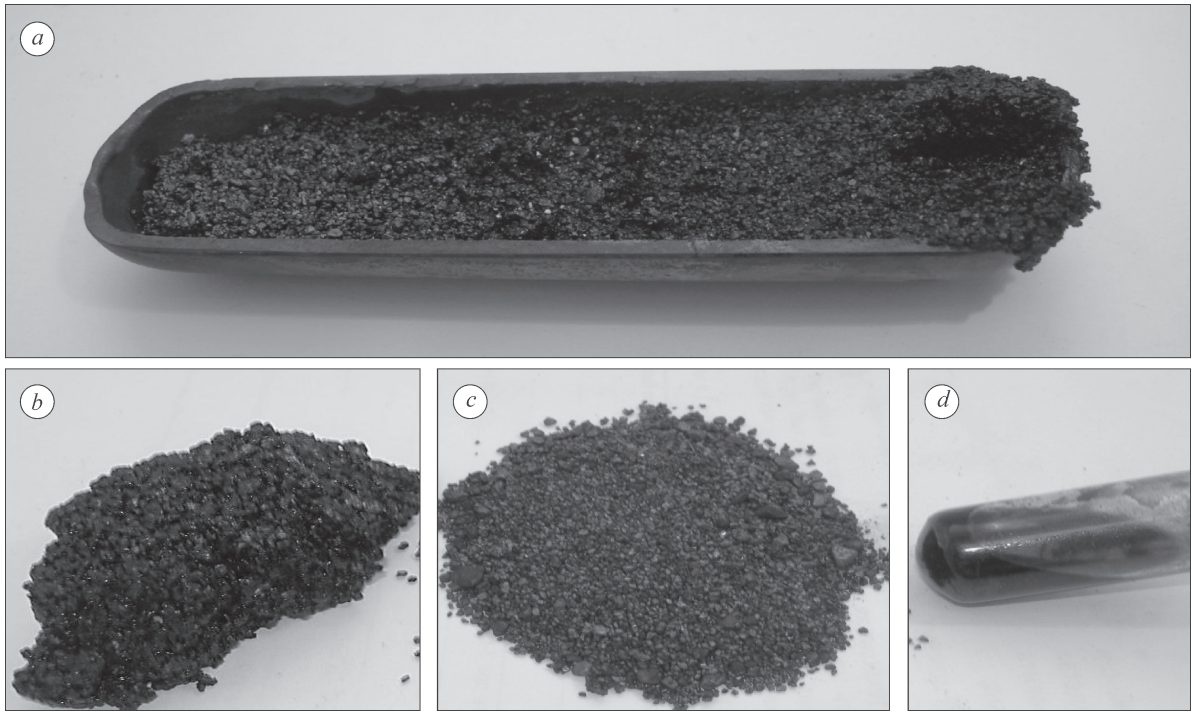

Fig. 3. Thermolysis products: *a* – boat with a cinder; *b* – the cake of cinder with the remnants of the bituminous component, appeared out of the boat when the liquid substance runoff towards the cold part of the ampoule; *c* – friable cinder from the boat; *d* – the condensate of sublimates.

The experiments, wherein the liquid component was removed from the test sample at the melting temperature of the bituminous material did not resulted in obtaining sublimates upon further heating the sample to the temperature up to 660 °C. Therefore, the sublimation occurs with the phase that, when exposed to a lower exhibits melting to begin to boil and to sublimate at the temperature above 400 °C and begins to boil sublimes. To all appearance, the composition thereof differs from that of fused phase, since this phase has different colour and different fluidity (solidification temperature). Maybe, at the sublimation temperature the liquid decomposes to give a subliming liquid and a solid component that is deposited onto a solid mineral part of the original material (cinder) and onto the walls of the ampoule (in this case – in the form of carbon "mirror").

It should be noted that the temperature values of the observed thermolysis processes inherent in the bituminous sandstone obtained by DTGA and in the experiments with suction, are slightly different, because DTGA provides more difficult conditions for the diffusion process of sublimation comparing to the experiments with the suction of sublimates. This is just that that determines the somewhat higher temperature data in DTGA.

The bituminous part isolated from sandstone (amounting to 15–16 % of the total composition) is characterized by the following features [7]: the average molecular mass – 578 amu, substantial composition (mass %): oil species 36.76, resins 56.30, asphaltenes 5.94, paraffin waxes 1.15; elemental composition (mass %): C 85.26, H 13.26, S 0.45, N 0.98, O 0.23; H/C ratio = 1.83, the proton deficiency $Z = 2C–H = 6.84$.

The IR spectral analysis of the liquid products of thermolysis demonstrated that in the IR spectra exhibit the absorption bands of alkanes, cycloalkanes and aromatic structures. A low intensity of the absorption bands inherent in the functional groups of hetero compounds in the vibrational spectra of oil species could be, to all appearance, caused by a minor concentration of nitrogen-, sulphur- and oxygen-containing components therein.

The substantial composition of sandstone thermolysis products and their behaviour in the

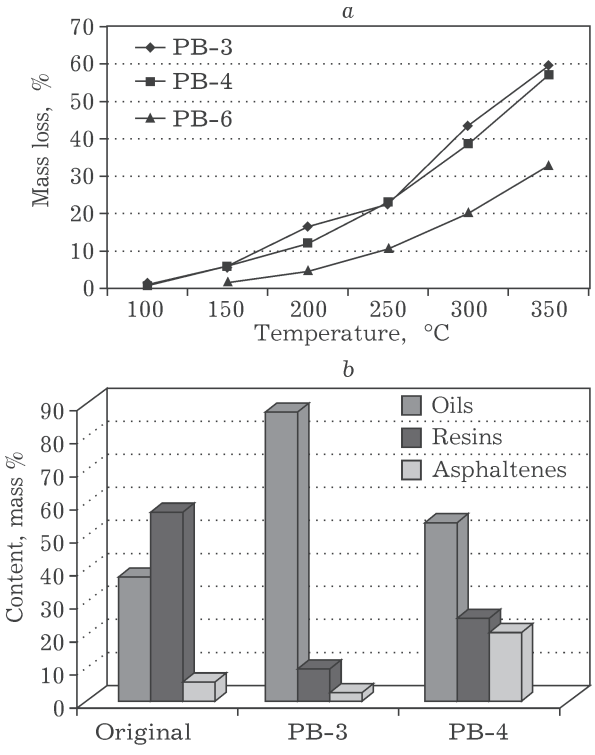

Fig. 4. Properties (*a*) and composition (*b*) of sandstone thermolysis products. Process temperature, °C: 550 (PB-3), 350–400 (PB-4), 600 (PB-6).

course of heating significantly differ from the composition and behaviour of the original bituminous component of sandstone (Fig. 4).

Thus, the original bituminous component exhibit the mass change to begin under heating to the temperature higher than 450–480 °C, whereas the thermolysis products (see Fig. 4, *a*) begin to lose the mass even at the temperature values of 100 °C or higher, with the mass loss reaching 60 % at 350 °C (for sandstone thermolysis temperature equal to 400–550 °C) or at 150 °C or higher, reaching the mass loss of about 30 % at 350 °C (for sandstone thermolysis temperature equal to 600 °C and higher).

The substantial composition of sandstone thermolysis products also differ from the composition a binder sample isolated from sandstone (see Fig. 4, *c*) being determined by the thermolysis temperature. So, at the temperature values lower than 400 °C (sample PB-4) we observed approximately twice decreasing the resin content, decreases to 1.4-fold increasing the oil content and an almost five-fold increase in the content of asphaltenes. At higher thermolysis temperature values, (550 °C and above, sample PB-3) the oil concentration in the product of thermolysis increases up to ~85 % (2.3-fold increase), while dramatically reducing the content of resins and asphaltenes (down to several percent).

This could indicate that the thermolysis of sandstone, alongside with the distillation of the components of the bituminous fraction, exhibits chemical reaction with the oil-based formation of a new homogeneous phase to occur in the sandstone material.

CONCLUSION

Studying the thermolysis of bituminous sandstone from the Bayan-Erkhet deposit (Mongolia) demonstrated that heating within the temperature range 200–400 °C causes initially a gradual softening, with further fluidizing the bituminous component of the material. At the temperature values equal to 400 °C and above, the bituminous melt begins decomposing to form a low-boiling phase. In this case, finely divided solid carbon is formed, to deposit onto the hot surface of the working quartz ampoule and onto mineral sandstone cinder as a thin layer. The resulting low-boiling phase is subjected to sublimation within the temperature range of 460–500 °C to be condensed in a trap in the form of an oily yellowish liquid. Subsequent heating causes the residual bituminous component to remove from the material with obtaining a graphite-coloured particulate cinder.

According to the data of the investigation, the content of the bituminous component for this raw material amounts to about 15 %. The composition thereof changes significantly in the course of the thermolysis. With increasing the thermolysis temperature, the liquid products exhibit a 1.4–2.3-fold increase in the content of oily species with decreasing and reducing the content of resins comparing to the initial composition of the bitumen. Increasing the thermolysis temperature up to 400 °C also results in an increase in the concentration of the asphaltenes in the melt. However, on further heating (up to 550–600 °C) the content of asphaltenes, just like the content of resins decreases abruptly with an abrupt increase in the concentration of oils. To all appearance, in this case, under the influence of heat

input there takes place a chemical decomposition of the components of the liquid to form new reaction products, which is in a good agreement with the data of the thermal analysis.

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