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Figure 1

Figure 1: Figure 1

Abstract

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KINETICS OF THERMAL DECOMPOSITION AND STRUCTURAL TRANSFORMATIONS OF FOSSIL COALS

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The process of thermal decomposition of fossil coals is characterized by a number of distinctive features that may be attributed to the peculiarities of the chemical structure of the organic matter of coal. Coal substance, represented by us as aromatic carbon networks spatially connected with one another by side radicals ([1]), combines in its structure a relatively inert, core part (carbon networks) and a reactive, peripheral part (side radicals) ([2]). This feature of the structure can explain the two commonly observed stages of primary and secondary decomposition, which differ sharply in their character. In the stage of primary decomposition, which proceeds rapidly at a relatively low temperature, the main mass of volatiles is liberated, chiefly as a result of destruction reactions of the side radicals. Chemical changes in the core part of the structure are observed at the later stage of secondary decomposition. At the same time, a process of intensive growth of the carbon networks takes place, which is well illustrated by the X-ray method (see Fig. 2). According to the described picture of decomposition, the carbon networks of the original coal substance remain in the solid product

Fig. 1. Kinetic decomposition curves. Left-hand part—yield of volatiles: *a*—shale, —Boghead, —brown coal, —long-flame coal, —gas coal, —coking coal. Right-hand part—rates of volatile evolution: *a*—500°, coking coal; —450°, long-flame coal; —500°, long-flame coal.

(coke), being centers of two-dimensional crystallization of carbon in the process of carbonization of the organic matter of coal.

Fig. 2. Ia and Ib —ordering curves (a —500°, b —425°); II —growth of carbon networks, 500°

In the present study, a comparative investigation was carried out of the kinetics of thermal decomposition of the vitrinitized substance of Donets coals of a metamorphic series, the structure of which is characterized by the presence of atomic carbon networks, and of the organic matter of combustible shales (Estonian) and boghead coal (Olenek), which do not contain carbon networks (^{3}). Structural transformations of coal matter were also studied by X-ray diffraction and infrared spectroscopy.

Measurements of the kinetics of thermal decomposition were made by the method of mass loss in a nitrogen stream at constant temperature, with small samples. To introduce a correction for nonisothermality in the initial moments of decomposition, the temperature course of heating was measured in special experiments by means of a thermocouple immersed in the sample.

Table 1

Sample	300-350° α	300-350° E, cal/mol	350-400° α	350-400° E, cal/mol
Boghead	0.05	14679.2	0.20	28276.8
Boghead	0.10	14352.8	0.30	37170.4
Boghead	0.15	23488.4	0.40	41002.4
Shale	0.05	16962.4	0.15	13795.2
Shale	0.10	21855.4	0.20	14561.6
Shale	0.15	31967.6	0.30	22225.6
Shale	0.20	39470.2	0.40	33338.4
Shale			0.50	39469.6
Brown coal	0.10	5300.0*	0.30	6897.6
Brown coal	0.30	20224.4	0.40	9346.4
Brown coal	0.40	32620.0	0.50	13038.8
Long-flame coal	0.15	7176.4	0.20	7664.0
Long-flame coal	0.20	18267.2	0.30	8813.6
Long-flame coal	0.30	37513.0	0.40	9963.2
Long-flame coal			0.50	18776.8
Gas coal	0.15	3914.4	0.20	3832.0
Gas coal	0.20	15331.4	0.30	14944.8
Gas coal			0.35	29889.6

* According to the data of E. A. Shapatina, V. V. Kalyuzhny, and Z. F. Chukhanov (^{4}).

In Fig. 1 are shown the curves of the yield of volatiles v/v_0 and the rates

Figure 3

Figure 2: Figure 3

of release of volatiles $\frac{1}{v_0}\frac{\Delta v}{\Delta t}$ as a function of the holding time in the furnace (where v_0 is the limiting yield of volatiles, determined by the standard method). Coals of a metamorphic series, in the process of primary decomposition, arrange themselves in a regular sequence depending on v_0, which reflec-

reflects changes in the chemical nature of the side radicals in the structure of the coal substance during metamorphism (Fig. 1). Brown coals fall into this sequence. The exceptions are shales and boghead, which is connected with qualitative differences in the chemical structure of their organic matter from that of coal. During prolonged holding in the furnace, maxima of the rate of evolution of volatiles are observed on the kinetic curves, corresponding to the process of secondary decomposition (Fig. 1). The position of the maxima in time depends on the stage of coal metamorphism and on the temperature. At relatively low decomposition temperatures (300-350°), the monomolecular specific rates of evolution of volatiles, calculated with allowance for the endothermicity at the beginning of decomposition, for fossil coals, in contrast to shales and boghead, have high values and decrease sharply with increasing degree of decomposition $\alpha = v/v_0$. The values of the apparent activation energy (Table 1) for fossil coals have very low values, 4000-7000 cal/mol, at low degrees of decomposition, which indicates the catalytic nature of the process. The observed rapid increase in activation energy as a function of α for low decomposition temperatures of coals, as should be supposed, is associated with the selectivity of the process of primary destruction of the coal substance, in which different atomic groupings are successively split off in order of increasing thermal stability. With an increase in the decomposition temperature, a smoother course of the increase in activation energy as a function of α is observed, which may be attributed to the lower selectivity of the processes of primary destruction, in accordance with the idea of the inclusion of parallel reactions with higher activation energy ([5]).

Fig. 3. Infrared absorption spectra of the solid decomposition products of long-flame coal: a—initial coal; b—$\alpha = 0.024$; v—$\alpha = 0.13$; g—$\alpha = 0.29$; d—$\alpha = 0.79$; e—$\alpha = 0.97$.

An X-ray study of the structural transformations of the coal substance during thermal decomposition was carried out on a series of solid residues from the decomposition of coking coal, obtained after different holding times in the furnace under the conditions described above. X-ray powder patterns were obtained with filtered iron radiation in a cylindrical camera of ordinary radius. Figure 2 shows the dependence of the angular half-width of the 002 interference band (curves Ia and Ib) on the degree of decomposition of coking coal at constant temperature, expressing the change in interlayer ordering ([1]). The observed changes in ordering are associated with the processes of primary destruction of the side radicals and the release of structural units, which are individual carbon networks with side radicals and which, having acquired mobility, during the transition

in the liquid-flowing state tend to arrange themselves parallel to one another under the influence of the molecular force field. Curve *II* depicts the course of change in the linear dimensions of the carbon networks, calculated from the half-width of the second interference band with indices 100. The observed sharp increase in the dimensions of the networks at high degrees of decomposition corresponds to the process of secondary decomposition and serves as a kinetic characteristic of the structural transformations of the nuclear part in the solid residue of decomposition. The X-ray curves of ordering and network growth illustrate the differentiation in time of the processes of destruction and cross-linking in the peripheral part of the structure of the coal substance, as well as the processes of chemical change in the nuclear part of the structure.

Infrared absorption spectra of the solid decomposition residues at different degrees of decomposition under isothermal conditions, obtained by us for the region from 5.7 to 10 μ on an IKS-11 infrared spectrograph with an NaCl prism, characterize substantial changes in the atomic groupings of the coal substance. The samples for spectral investigation were prepared in the form of a paste in paraffin oil. In Fig. 3 the spectral transmittance curves of the solid decomposition residues of long-flame coal are presented. Regular changes in the position and intensity of the absorption bands as a function of the degree of decomposition indicate the relatively lower thermal stability of aromatic simple ethers (band at 9.7 μ) in comparison with aliphatic (8.5 μ) and cyclic (9.2 μ) simple ethers. Oxygen directly bound to the carbon network in the form of phenoxy groups is removed only during secondary decomposition, with which the disappearance of the band at 6.2 μ is associated. The appearance of a band at 6.4 μ at relatively small degrees of decomposition is apparently a consequence of the destruction of radicals that form bonds between carbon networks in the coal substance.

The appearance of the band at 6.0 μ indicates the accumulation of unsaturated C=C bonds in the solid residues. It is possible that the accumulation of unsaturated bonds at high degrees of decomposition is connected with processes that ensure the subsequent intensive growth of carbon networks by their coalescence.

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Note: Figure translations are in progress. See original paper for figures.