Thermal analysis of mechanochemically activated humic acids of brown coal

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Abstract. Humic acids of brown coal before and after mechanochemical treatment under various conditions were studied by TG and DSC (carried out both in air and in an inert atmosphere, with the temperature range of 300–800 K), and gel permeation chromatography. The obtained data were used to calculate the values of the energy of activation and the thermal effects for each stage of thermal decomposition. Influence of mechanochemical treatment upon humic acids thermolysis stages was shown. Hypothesis of thermal stages chemical interpretation was proposed. The staged decomposition of humic acids includes the stages of decarboxylation of acid groups of various types. A change in the staging of decomposition is observed upon mechanochemical introduction of alkali into humic acids, associated with the conversion of acid groups to the salt form.

1. Introduction
Brown coal is a widely used fuel both in Russia and abroad. In recent years, brown coal is increasingly subjected to preliminary mechanical and mechanochemical activation to improve thermal properties, such as temperature of ignition, yield of volatiles, etc. [1]. During mechanochemical activation of brown coal, humic acids, which are an irregular polyphenolic polymer with a wide range of oxygen-containing groups, undergo the greatest changes [2]. Transformations in an oxidizing environment determines the behavior of HA during coal combustion. Thermal decomposition in a neutral environment simulates the presence of HA during storage without air. In works devoted to the thermal decomposition of HAs from peat and coals of various origin [3, 4], it is indicated that decomposition passes through a number of stages, ranges of decomposition temperatures at various stages are given, some decomposition products and mass loss rates at various temperatures are determined under these conditions. The determination of kinetic parameters at the selected stages is not carried out usually.

The objective of this study was to investigate the thermal decomposition of humic acids (HA) at the level of isolation of individual stages and determination of the thermochemical parameters, and to study the effect of mechanochemical activation on these stages.

2. Experimental
Brown coal humic acids were subjected to mechanical activation in the presence of air without any additions (sample marked as "MA") and with 5% of NaOH (MA-alk) in the laboratory mechanochemical mill-activator of the planetary type AGO-2. The acceleration of grinding bodies in the case of MA
sample was of 20g. The acceleration of grinding bodies in the case of MA-alk was 20 and 40 g (MA-alk-20g and MA-alk-40g). The ratio of the mass of the sample and grinding media was 1: 150. Steel grinding bodies and drums were used.

The last index in the description of the samples shows the gas atmosphere of thermolysis: oxidizing (oxi) or neutral (He). Thermal analysis of humic acids was carried out on a STA 409 PC Luxx thermal analyzer (Netzsch) in synchronous mode, which allows simultaneous recording of mass loss, determination of characteristic temperatures and thermal effects. Decomposition was carried out both in air and in an inert atmosphere, in a platinum crucible; the heating rate was 10 K min⁻¹, temperature range was 300–800 K; sample of the test substance was ~ 2 mg; sensitivity of scales was 0.002 mg.

The methodology for calculation of thermal analysis results was as follows. Data from the TG-DSC instrument was obtained in text format. The number and approximate position of the peaks (maxima of the decomposition rates) were determined from the graphs “DTG-temperature” and “DSC-temperature”. An approximation curve was plotted for the found number of peaks. Further data calculation included varying the parameters of the position and shape of the curves of each peak until the maximum of the $R^2$-compliance criterion was reached. After that, for thermogravimetric results and the weight loss curves for each stage were synthesized. For each of the stages, at the site of the maximum reaction rate, the activation energy was calculated according to the Erofeev – Kolmogorov equation [5]. The number and position of peaks were also determined for DSC curves, the general curve was presented as the sum of the individual curves, at the final stage, the area under each curve was calculated. The criterion for evaluating the suitability of the model was the $R^2$ criterion and the achievement of equality of the sum of the peak areas and the area of the total curve. The normalizing mechanism was the result of determining the total thermal effect in the temperature range of 463 – 803 K, presented by the DSC analysis instrument software.

The molecular mass distribution of humic acids samples were determined by gel chromatography using an Agilent 1200 chromatograph (USA) equipped with an isocratic pump and a refractometric detector. The samples were prepared by dissolving a 2 g portion of humic acids in 1 L of borate buffer solution with pH 9.18 and removing the undissolved fraction by decantation. All the subsequent experiments were performed with the dissolved fraction. Samples were introduced manually. Borate buffer solution (pH 9.18) was used as eluent. The sample volume was 20 μL. Analysis was performed with a PL-aquagel OH-30 chromatographic column of 300 × 7.5 mm [6].

3. Results and discussion

The TG and DSC thermolysis curves of the samples in an oxidizing and neutral atmosphere are shown in figures 1a and 1b, respectively.

It can be noted that up to about 800 K in the oxidizing atmosphere, four exopics are noticeable, while in a neutral medium this number decreases to 2. In turn, thermal decomposition in an oxidizing atmosphere allows us to divide the samples into two groups. In the first group (the initial, Ini-oxi and mechanically activated without alkali, MA-oxi samples) four stages with thermal effects are noticeable (table 1). The second group is represented by samples mechanically activated with the addition of alkali; for this group three stages of thermolysis are characteristic.

The determined values of the activation energy for thermal decomposition are given in table 1 (the average error is less than 2%, the error in determining the peak temperature is about 3 K), the thermal effects of various stages are also presented there. The selected temperature range (up to approximately 800 K) in an oxidizing atmosphere is characterized by the release of water and carbon oxides during the thermal decomposition of HA. It is believed that the side structural elements are degraded and the core condensation increases. Upon transition to a neutral atmosphere of thermolysis, the values of thermal effects are leveled to insignificant values. Possible reactions of side chain degradation are decarboxylation of carboxylic acids. The decarboxylation temperature range lies in a very wide range of 320–700 K. The decarboxylation process itself depends on many factors and is facilitated by flowing in an oxidizing atmosphere, with the introduction of alkalis and catalysts (carbonates, for example).
Figure 1. TG and DSC thermolysis curves of samples of humic acids: a – oxidizing atmosphere, b – neutral atmosphere (exo direction – up).

The decarboxylation temperature of aromatic carboxylic acids depends on the particular position of the other substituents in the arene ring and decreases when the hydroxyl groups are in the ortho and para positions. The thermal decomposition of the carboxyl group at the benzene core with the formation of carbon dioxide occurs at a temperature of 450–710 K, while the decomposition of benzenepolycarboxylic acids of HA with carboxyl groups in the ortho position is observed at 370–550 K and proceeds through the formation of pyrogenetic water [7].

Table 1. Activation energies and thermal effects of thermal decomposition of HA samples.

| Sample          | $E_a$, kJ·mol$^{-1}$ | $T_{max}^a$, K | $Q$, kJ·g$^{-1}$ | $T_{max}^b$, K |
|-----------------|----------------------|----------------|------------------|----------------|
| Ini-oxi         | 61.7                 | 579            | 7.84             | 578            |
|                 | 153.3                | 674            | 5.80             | 674            |
|                 | 362.7                | 709            | 2.26             | 709            |
|                 | 441.6                | 759            | 1.85             | 757            |
| MA-oxi          | 59.2                 | 573            | 8.67             | 586            |
|                 | 231.2                | 643            | 5.78             | 643            |
|                 | 497.0                | 664            | 1.67             | 663            |
|                 | 386.9                | 753            | 2.35             | 747            |
| MA-alk-20g-oxi  | 71.7                 | 561            | 7.80             | 573            |
|                 | 303.0                | 712            | 0.10             | 628            |
|                 | 207.9                | 739            | 9.64             | 733            |
| MA-alk-40g-oxi  | 63.2                 | 564            | 8.49             | 578            |
|                 | 234.7                | 709            | 0.21             | 634            |
|                 | 212.7                | 728            | 8.77             | 718            |
| Ini-He          | 102.3                | 533            | 0.16             | 640            |
|                 | 96.1                 | 601            | 0.09             | 707            |
| MA-He           | 53.3                 | 558            | 0.46             | 611            |
|                 | 71.4                 | 708            | 0.37             | 693            |
| MA-alk-20g-He   | 69.3                 | 527            | 1.03             | 609            |
|                 | 86.1                 | 577            | 0.33             | 687            |
|                 | 65.6                 | 712            |                  |                |
| MA-alk-40g-He   | 66.2                 | 566            | 0.67             | 630            |
|                 | 85.6                 | 680            | 0.14             | 711            |

*a The temperature value was determined using the TG curve.

*b The temperature value was determined using the DSC curve.

The mechanical activation of HA in the presence of alkali leads to the conversion of acid residues of arene acids to the salt form, the process of decarboxylation of the actual acids becomes less noticeable as compared to the decarboxylation of salts, which is recorded in our case as a change in the shape of
the TG-DSC curves (the combination of peaks with a decrease in activation energy and growth thermal effects).

Figure 2 demonstrates that molecular mass distribution of humic acids does not change in the result of mechanical and mechanochemical treatment under investigated conditions. All the studied samples are characterized by a large set of molecular masses, merging into one wide peak with an average value of 49.5 kg/mol. This is consistent with the fact that the effects of mechanochemical activation affecting thermal decomposition are also related to the decomposition of the structure of humic acids, but rather are explained by the oxidation of groups at the periphery of the molecules and the conversion of acids to salt forms, which is also not associated with significant changes in molecular weights.

Thus, it can be concluded that the staged decomposition of humic acids includes the stages of decarboxylation of acid groups of various types. A change in the staging of decomposition is observed upon mechanochemical introduction of alkali into humic acids, associated with the conversion of acid groups to the salt form. The values of activation energy for thermal decomposition are determined and the thermal effects of individual stages of decomposition of HA are presented.

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References
[1] Burdukov A P, Butakov E B, Kuznetsov A V and Chernetskiy M Y 2018 Combust., Explos. Shock Waves 54 20
[2] Skripkina T S, Bychkov A L, Tikhova V D and Lomovsky O I 2018 Solid Fuel Chem. 52 356
[3] Francioso O, Ciavatta C, Montecchio D, Tugnoli V, Sanchez-Cortes, S and Gessa C 2003 Bioresour. Technol. 88 189
[4] El Ouaqoudi F Z, El Fels L, Winterton P, Lemée L, Amblès A and Hafidi M 2014 Compost Sci. Util. 22 188
[5] Gorbachev V M 1978 J. thermal anal. 13 509
[6] Urazova T S, Bychkov A L and Lomovskii O I 2014 Russ. J. Appl. Chem. 87 651
[7] Chukhareva N, Sartakov M, Korotchenko T 2016 MATEC Web of Conferences 85 01004