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Investigation of the Effect of Grinding Parameters of Brown Coal on the Yield and Structural Group Composition of Humic Acids

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Abstract

The influence of the dry (in the air, without water) and wet (in water) method of brown coal grinding on the extraction efficiency and structural group composition of the extracted humic acids (HA) was studied. The samples of liquid and powder humic preparations (HP) from brown coal of the Tisulskoye deposit (Kaychakskiy site) were produced. The samples were obtained using the original set-up, which allowed us to achieve the high yield of HA by means of ultrafine grinding of the raw material in the dry form or in the aqueous solution of an alkali. The technical characteristics and regimes of equipment operation are presented. All the samples were characterized by means of technical and elemental analysis, ^{13}C NMR (CPMAS) and FTIR spectroscopy. Granulometric composition and specific surface area of coal samples after dry and wet grinding were determined. It was established that the wet method allows achieving more complete extraction of HA from brown coal due to an increase in the surface area of the contact between coal and the alkali. Both methods of grinding do not have a significant effect on the structural group composition of extracted HA and their biological activity.

Keywords: brown coal, humic acids, humic preparations, crushing, structural parameters

INTRODUCTION

Attention to humic substances (HS) used in a number of branches of industry, in particular in agriculture, as highly efficient plant growth stimulators, has substantially increased during the recent years [1–4].

An increase in demand for HS is accompanied by the search for promising kinds of raw material and modernization of the technological schemes of obtaining them [1]. At the present stage of the scientific and technical progress, the most promising humate-containing raw material is brown coal, which may be used not only as low-grade fuel but also as a source of biologically active substances [5].

The major direction of the further development of technologies for obtaining HS is the achievement of the maximal yield of the target product. The major technological operation aimed at the isolation of HS from caustobioliths is alkaline extraction – the alkaline hydrolysis of the organic mass of coal and the extraction of humic preparations (HP) in the form of water-soluble salts – sodium, potassium, ammonium humates *etc*.

It was established previously [6, 7] that the parameters of alkaline extraction (amount of alkali, temperature and duration of the process) affect the structural group composition of HS: relatively rigid conditions of alkaline extraction (the concentration of the aqueous solution of NaOH 5 %, temperature 98 °C, process duration 5.5 h) have a positive effect on the yield but a negative on the content of aromatic fragments in the extracted HA. The presence of these fragments depicts the degree of aromaticity f_a – a parameter calculated on the basis of the data obtained by means of ^{13}C (CPMAS) NMR spectroscopy. In turn, a decrease of this parameter in HA causes a decrease in their biological activity with respect to plants [8–10]. This dependence may be explained by the fact that parameter f_a shows the content of aromatic fragments in HA molecule, in particular phenol hydroxyl groups that are able to participate in oxidation-reduction processes in a plant cell and to enhance these processes according to the theory proposed by Bach–Paladin–Sent-Dierdi [11].

So, during the development of new technological approaches to the extraction of biologically active HA, aimed at an increase in the yield of the product, it is recommended to control the content of aromatic fragments in HA (f_a parameter) and avoid its decrease during the extraction of humic acids.

It is known that the activity of alkaline extraction changes in phase with the changes of the surface area of the solid raw material [12]. So, it is possible to increase the yield of HA through multistage grinding of brown coal, which helps reaching high fineness. There are two major methods of particle grinding: dry (in air or in an inert gas) and wet (in water or in another liquid) [12, 13].

It is assumed that in the case of fine and superfine grinding of brown coal the yield of HA increases significantly, with the conservation of the high content of aromatic fragments, therefore, with high biological activity with respect to plants [8–10]. The maximal degree of coal grinding may be achieved with the help of wet grinding, which is often more rational than the dry procedure [12, 13]: the process is optimized due to the purification of the surface of milling bodies by the liquid and due to the absence of agglutination and pressing of the particles, minimal heating and dusting of the material under grinding, simplified unloading and transportation along the technological line *etc*. Wet grinding is also distinguished by decreased specific energy consumption (up to 30 % in comparison with dry grinding) and more uniform particle size at the outlet [14].

The goal of the work was to compare the dry and wet methods of coal grinding; to test the original set-up made for the purpose of achieving the maximal yield of HA from brown coal by means of superfine grinding using the dry procedure (to obtain powdered HP) and the wet procedure (to obtain liquid HP); to investigate the obtained large-scale HP samples by means of ^{13}C NMR (CPMAS) and IR Fourier spectroscopy in order to evaluate the effect of coal grinding parameters on the structural and group composition and therefore on the biological activity of HA.

EXPERIMENTAL

To determine the influence of the presence of liquid on the extent of brown coal extraction and the yield of HA, coal grinding was carried out using the dry method (powder HP) and wet method (liquid HP) combined with alkaline extraction. It is assumed that the addition of

TABLE 1

Results of technical and elemental analysis of brown coal samples (BCTS), residual coal and HA, %

Sample	W^a	A^d	V^{daf}	C^{daf}	H^{daf}	$(O + N + S)^{daf}$, found from the difference	$(HA)_t^{daf}$, (HumNa)
BCTS	8.3	10.3	48.3	61.4	5.0	33.5	22.1
HA HumNa BCTS	3.8	1.9	n/d	59.8	3.5	36.7	n/d
C_{res} HumNa BCTS	2.8	16.4	49.5	52.3	4.3	43.5	n/d

Note. W^a is analytical moisture, A^d is ash content per dry sample, V^{daf} is the content of volatile substances, daf is dry ash-free state of the sample, C, H, O, S, N are element contents; $(HA)_t^{daf}$ is the yield of free humic acids (according to GOST 9517-94 [15]); HumNa is sodium humate; HA are humic acids; C_{res} HumNa is residual coal after the extraction of HumNa; n/d means determination was not carried out.

water will affect the degree of coal grinding and the yield of HA, provided that the performance parameters of the equipment remain unchanged.

The characteristics of HP samples obtained from brown coal of the Tisulskoe deposit (Kaychakskiy site) (BCTS) are presented in Table 1. Humic acids isolated from sodium humates (HA HumNa) were obtained for analytical purposes according to the procedure of the determination of the yield of free HA (1 % solution of NaOH, 98 °C, 2 h) [15].

Investigation methods

The high-resolution ^{13}C NMR spectra in the solid state were recorded with the help of a Bruker Avance III 300 WB instrument (Germany) at the frequency of 75 MHz with the sample rotation frequency of 5 kHz using the procedure of cross polarization with magic-angle spinning (CPMAS).

The structural group parameters of HA samples were calculated from the ^{13}C NMR spectra using the formulas reported in [16, 17]:

1) aromaticity degree f_a:
$f_a = C_{Ar-O} + C_{Ar}$;

2) the hydrophilic-hydrophobic parameter $f_{h/h}$:
$f_{h/h} = (C{=}O + COOH + C_{Ar-O} + C_{O-Alk-O} + C_{Alk-O})/(C_{Ar} + C_{Alk})$;

3) aromaticity/aliphaticity $f_{ar/al}$:
$f_{ar/al} = (C_{Ar-O} + C_{Ar})/(C_{O-Alk-O} + C_{Alk-O} + C_{Alk})$

IR spectra were recorded in dry KBr with the help of an Infralyum FT-801 IR Fourier spectrometer (Russia) with the resolution of 4 cm and accumulation of 64 scans within the range 4000–500 cm^{-1}. The ratio KBr/sample = 1 : 200. Spectra were interpreted according to the literature sources [18, 19].

Synthesis procedure

Liquid and powdered HP were manufactured using the equipment of the experimental-industrial stand for the basic technologies of HP at the Institute of Coal Chemistry and Chemical Materials Science of the Federal Research Centre for Coal and Coal Chemistry, SB RAS, according to technological scheme (Fig. 1).

The vertical centrifuge was not used for manufacturing powdered HP.

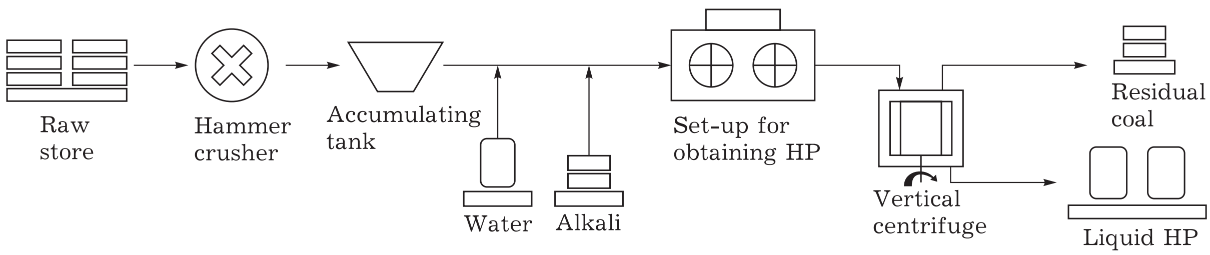
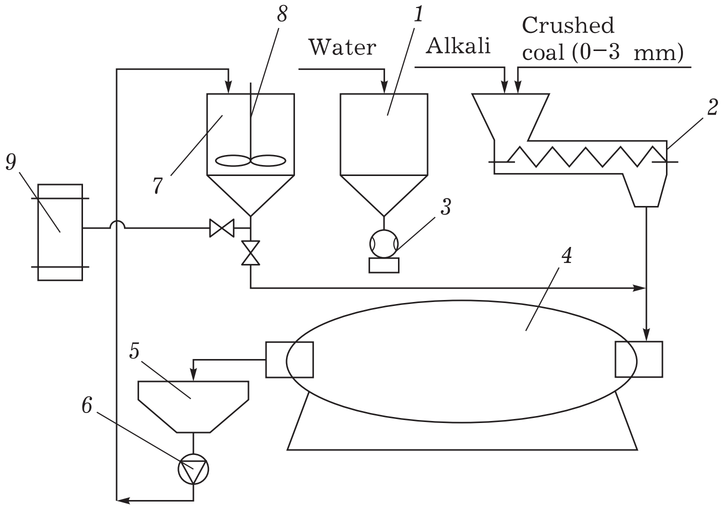


Fig. 1. Technological scheme of obtaining HP.



Specification

1 – tank with water
2 – dosage hopper
3 – liquid flow meter for dosing
4 – ball vibrocentrifugal mill
5 – suspension receiving vessel
6 – gerotor pump
7 – intermediate vessel
8 – blade mixer
9 – tank for final product (suspension)

Fig. 2. Original set-up for obtaining liquid humic biostimulator [20].

TABLE 2

Technical characteristics of the equipment

Parameter	Value
Hammer crusher	
Rotor size, mm:	
diameter	300
length	200
The size of a piece of the loaded material, not more, mm	50
The size of a mesh of the fire-grate, mm	3
Frequency of rotor rotation, r.p.m.	3000
Installed power, kW	4.0
Crushed coal, mm	0–3
Ball vibrocentrifugal mill (JSC Novits) included in the original set-up	
Number of milling cylinders, pc.	2
Number of milling chambers in a cylinder, sp.	2
Diameter/mass of milling bodies, mm/kg:	
The first chamber	15/9.1
The second chamber	10/14.6
The volume of milling chambers in the cylinder, dm^3:	
The first chamber	2.85
The second chamber	7.12
Installed power, W	11

The HP samples were obtained in two stages: preliminary crushing and fine grinding of coal combined with alkaline extraction.

Preliminary crushing. This is a common stage for both the wet and dry methods. It is carried out with a hammer crusher. The data included in the certificate of this equipment, operation mode and requirements to the raw material are presented in Table 2.

Then an original set-up was used to obtain the liquid and powdered HP as shown in Fig. 2. The set-up included a ball vibrocentrifugal mill (JSC Novits, Russia) (see Table 2), supplemented with auxiliary equipment fixed on a special frame. For this structure, the authors have obtained an RF Patent on the utility model “Set-up for obtaining liquid humic biostimulator” [20]. The set-up may be run either in the dry mode (without the addition of water) or in the wet mode (with the addition of water).

Dry grinding. To obtain the dry HP, brown coal was crushed preliminarily with a hammer crusher to particle size not more than 3 mm and loaded into a dosage hopper (*2*) of the original set-up (see Fig. 2) with the addition of NaOH. The ball mill (*4*) and the weighing dosage hopper (*2*) are put into operation, so that the dry mixture is supplied along the flexible pipeline into the loading section of the milling cylinders of the ball mill (*4*). Then fine grinding of coal particles and alkali is carried out with the help of milling bodies, which are metal balls in two milling sections. Grinding is carried out due to the total action of vibroimpact, crushing and comminuting load.The productivity of the mill is directly dependent on the amount of the supplied material and the frequency of cylinder vibrations. At the outlet, powdered HP gets into the receiving tank (*5*), then into the transportation container.

Wet grinding. The operation of the set-up (see Fig. 2) is quite different in the case if liquid HP is to be obtained. A tank for water (*1*) with a dosing device (*3*) is filled with the necessary amount of water. A mixture of brown coal and alkali with particle size not more than 3 mm is loaded into the weighing dosage hopper (*2*). Ball mill (*4*) is switched on. Water is let to pass by gravity along the pipes into the loading section of milling cylinders. Then the weighing dosage hopper (*2*) is put into operation, the dry mixture falling along a flexible pipeline meets with water from dosing device (*3*) and is transferred into the loading section of milling cylinders of the ball mill (*4*). Grinding and mixing of the particles of solid fossil fuel and alkali in the aqueous medium occur in the milling cylinders. As a result, extraction of HS by the water-alkali solution proceeds. The resulting fine suspension passes through the flexible pipeline and enters the suspension-receiving tank (*5*) equipped with a gerotor pump (*6*). Then the suspension is pumped by the gerotor pump (*6*) into an intermediate vessel (*7*) equipped with a mixer (*8*), to prevent sedimentation of the suspension. From the intermediate vessel (*7*), the suspension is let by gravity along the pipeline into the vessels (*9*) for the final product. Then unreacted residual coal is separated from the liquid HP at the vertical centrifuge.

In both cases, grinding of coal particles is combined with leaching, which allows the interaction of the newly formed coal contact surfaces with alkali. This process causes a substantial decrease in the time of HA leaching in comparison with the traditional technology which involves three discrete stages: preliminary crushing, fine grinding, and alkaline extraction of HA from brown coal.

Analysis of biological activity

The liquid HP obtained as described above was tested for the biological activity with respect to the seeds of spring wheat Iren. The biological activity of HP was determined according to the procedure described in [4, 8], relying on the index of phytoactivity (IP) and taking into account the energy seed germination (EG), root length (RL) and seedling height (SH). The index of phytoactivity is a generalizing index and is calculated as a mean of the sum of EG, SH and RL expressed in the fractions of unit:

$$IP = (EG + SH + RL)/(3 \cdot 100)$$

Here EG, SH and RL are average values over three trays (in per cent with respect to the reference).

The seeds were germinated in special germinating trays between the layers of wetted filter paper. The repetition of the experiment was triple, with 50 seeds in each tray for each HA concentration and the same number for the reference. EG, SH and RL were measured at the fifth day. The seeds were germinated at a constant temperature of 20 °C in the dark. Some seeds were treated (once) with the 0.0005, 0.005 and 0.01 % solution of the liquid HP, while some seeds were wetted with distilled water (reference).

The relative error was 3–5 % in all experiments, for the significance level $\alpha = 0.05$.

RESULTS AND DISCUSSION

The formulations and the parameters of equipment operation are presented in Table 3.

The manufactured HP were characterized with the help of technical and elemental analysis (Table 4).

To evaluate the efficiency of BCTS grinding after preliminary crushing with a hammer

TABLE 3

Formulations and the parameters of the original set-up

Characteristics	Dry grinding	Wet grinding
Formulation		
Mass ratio of raw material (coal/alkali/water)	4 : 1 : 0	4 : 1 : 40
Parameters of the original set-up		
Granulometric composition of coal at the input, μm	0–3000	0–3000
The same, at the outlet, μm	0–160	0–50
The degree of coal grinding	107	137
The productivity of the set-up, kg/h:		
with respect to coal	15.0	20.0
with respect to HA (100 %)	2.3	5.5
Number of passes of the raw material through milling chambers	1	1
Frequnecy of milling cylinder vibrations, Hz	7.5	7.5
Additional heat input	Absent	Absent

TABLE 4

Results of technical and elemental analysis of the obtained HP, HA and residual coal (C_{res}), %

Sample	W^a	A^d	C^{daf}	H^{daf}	$(O + N + S)^{daf}$, from difference	$(HA)_t^{daf}$, (HumNa)
Dry grinding						
Dry HP	7.5	32.5	69.3	5.4	25.3	20.4
HA from dry HP	5.2	1.7	64.5	4.0	31.5	н/о
C_{res} of dry HP	9.3	20.8	67.5	5.4	27.1	н/о
Wet grinding						
HA from liquid HP	6.1	1.1	56.1	5.1	38.8	н/о
C_{res} of liquid HP	11.8	27.4	53.7	6.0	40.4	н/о

Note. n/d means that the determination was not carried out..

crusher followed by the dry and wet fine grinding in the original set-up, determination of the particle size in the samples was carried out (Table 5): in BCTS after hammer crusher; dry HP washed with water from alkali and HA (C_{res} of dry HP); residual coal separated from liquid HP with the centrifuge, washed with water from alkali and HA (C_{res} of liquid HP). The sieve analysis was carried out according to GOST [21].

The results of the sieve analysis showed that the content of the 0–50 mm fraction in the wet-ground sample is higher by 16.7 % in comparison with the dry-ground sample (see Table 5), which is the evidence of higher grinding efficiency and the formation of the surfaces for HA leaching.

If we know the granulometric composition (see Table 5) and the true density of brown coal, it is possible to calculate [22] the area of specific surface of coal at each stage of grinding. Coal porosity was not taken into account in the calculations of specific surface. The true density of brown coal was accepted to be 1.25 according

TABLE 5

Fraction content, % of total mass

Sample	Fraction of particles on sieve, μm							Degree of coal grinding
	0–50	50–100	100–160	160–200	200–500	500–1000	1000–3000	
	Hammer crusher							
Crushed coal	**9.4**	**6.1**	**8.0**	**6.0**	**28.7**	**34.7**	**7.2**	10
	Hammer crusher + dry grinding in the original set-up							
C_{res} of dry HP	**75.8**	**11.1**	**10.8**	1.5	0.7	0.03	0.01	107
	Hammer crusher + wet grinding in the original set-up							
C_{res} of liquid HP	**92.5**	2.3	1.3	1.4	0.8	0.4	0.1	137

Note. The content of the main fractions is shown in bold.

TABLE 6

Efficiency of wet and dry grinding

Sample	Specific surface of coal particles, cm^2/g	$(HA)_t^{daf}$, % (per initial coal)
Coal after hammer crusher	328	–
C_{res} of dry HP	1571	18.8
C_{res} of liquid HP	1801	33.7

TABLE 7

Integral intensities of the spectral regions and structural parameters of the samples of coal and humic acids according to the ^{13}C NMR spectra, %

Sample	Chemical shift, ppm							Structural parameters	
	220–187 C=O	187–165 COOH	165–145 C_{ar}–O	145–108 C_{ar}	108–90 $C_{O-alk-O}$	90–48 C_{alk}–O	48–5 C_{alk}	f_a	$f_{a/al}$
	Initial coal								
BCTS	0.4	3.2	7.0	54.9	3.3	10.1	21.1	61.9	1.8
HA from HumNa	1.0	8.2	6.7	51.0	3.4	7.3	22.4	57.8	1.7
C_{res} HumNa	0.7	4.6	5.9	51.7	2.4	11.7	23.0	57.7	1.6
	Hammer crusher + dry grinding in the original set-up								
Dry HP	0.8	6.2	5.9	52.1	3.1	11.9	20.1	58.0	1.7
HA of dry HP	0.9	8.2	6.4	51.7	3.4	6.4	23.0	58.1	1.8
C_{res} of dry HP	1.4	5.0	6.8	52.5	3.8	13.0	17.5	59.3	1.7
	Hammer crusher + wet grinding in the original set-up								
HA of liquid HP	1.1	8.2	6.4	51.9	3.4	6.7	22.1	58.3	1.8
C_{res} of liquid HP	1.9	6.0	8.0	50.6	6.7	14.4	12.5	58.6	1.7

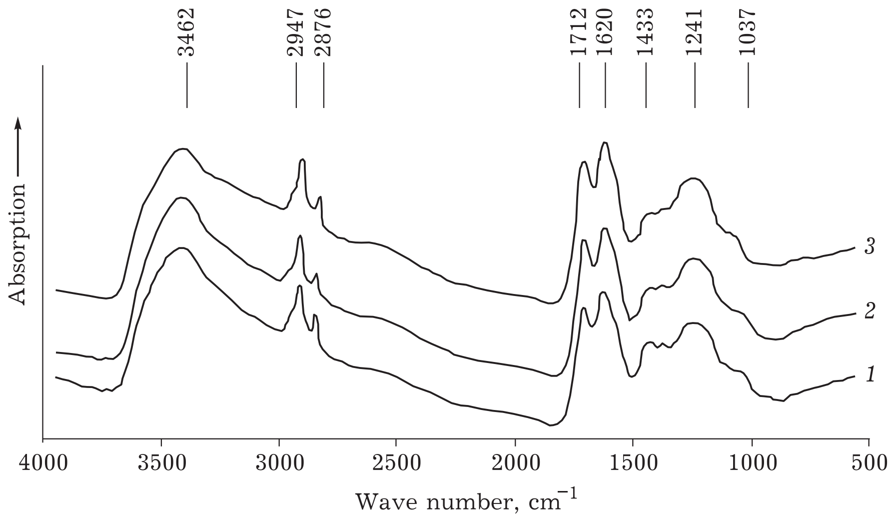


Fig. 3. IR spectra of HA from HumNa of BCTS (*1*), liquid HP (*2*) and powdered HP (*3*).

to the literature sources [23, 24]. It was established that the use of the wet grinding method leads to an increase in the specific surface of coal particles by 14.6 % in comparison with dry grinding (Table 6). Due to this fact, a higher yield of HA from brown coal can be achieved. For the dry method, the yield of HA per initial coal was 18.8 %, while for the wet one it was 33.7 % of daf. It should be stressed that the yield of HA in the case of liquid GP (33.7 %) exceeds the analytical yield according to the procedure described in GOST 9517–94 (22.1 %), by 52.5 %.

As stressed above, the structural group composition is subject to changes during alkaline extraction [6, 7]. To study the effect of coal grinding method on the composition of extracted HA, the HP samples were studied with the help of ^{13}C NMR and IR spectroscopy. The results of ^{13}C NMR spectroscopy showed that the degree of brown coal grinding and the presence of water during the manufacture of HP have only weak effect on the structural group composition of HA (Table 7).

These results were confirmed by the data of IR spectroscopy (Fig. 3). For HA (*1*) obtained from brown coal according to the procedure described in GOST 9517–94 [15], and HA obtained from the liquid (*2*) and powdered (*3*) HP, an intense absorption band at 3462 cm^{-1} is characteristic, which is attributed to the stretching vibrations of OH groups bound through molecular hydrogen bonds. Absorption bands within the ranges of 2947, 2876 and 1433 cm^{-1} are characteristic of HA and mean the presence of CH_3 and CH_2 groups. The presence of carbonyl groups (C=O) was established (1712 cm^{-1}), as well as unsaturated and aromatic C=C bonds (1620 cm^{-1}). The presence of aromatic fragments may also be indicated by the absorption band at 1465 cm^{-1}, but it is often overlapped with the band of bending vibrations of CH_2 group. The absorption band at 1241 cm^{-1} is the evidence of the presence of C–O bond of carboxylic acids, esters, OH bonds in phenols. The band at 1037 cm^{-1} may be the evidence of the presence of mineral components.

So, the method of brown coal grinding has a weak effect on the functional group composition of the extracted HA. The high content of aromatic fragments (f_a = 57.9) in HA from BCTS is the reason of the enhanced phytoactivity (IP) with respect to plants. The treatment of the seeds of Iren wheat with 0.0005, 0.005 and 0.01 % HA solutions within the liquid HP allowed an increase in the parameters of seed germination (EG, RL and SH) up to 19 %. The value of IP for these concentrations of solutions is 1.04, 1.19 and 1.08, respectively.

CONCLUSION

Investigation of the granulometric composition of brown coal showed that the content of the 0–50 mm fraction in the case of wet grinding is higher by 16.7 % in comparison with the dry method, which points to a higher efficiency of grinding and the formation of new surfaces of HA leaching. The operation of the original set-up in the mode of wet grinding causes an increase in the specific surface of coal particles in comparison with dry grinding by 14.6 %, which allows achieving a higher yield of the target product, HA. or the dry method, the yield of HA per initial coal is 18.8 %, while for the wet method it is 33.7 % of daf. The productivity (kg/h) of the original set-up with respect to coal in the mode of wet grinding is higher by 33 %, and with respect to HA by 139 % in comparison with the dry mode. The yield of HA in the case with the liquid GP (33.7 %) exceeds the analytical yield according to the procedure described in GOST 9517–94 (22.1 %) by 52.5 %. The results of ^{13}C NMR and IR spectroscopy showed that both grinding methods do not have a substantial effect the structural group composition of HA, therefore, the high biological activity of humates is conserved. For instance, the degree of aromaticity f_a for HA obtained using the standard method is equal to 57.8, for HA of the liquid and powdered HP it is 58.3 and 58.1, respectively. The high values of this parameter explain increased phytoactivity of liquid HP with respect to wheat seeds (IP = 1.19 for HA concentration 0.005 %).

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