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Modification of Peat Humic Acids.

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ABSTRACT

The solution of a number of the tasks directed on optimization of processes of complex processing of peat for needs of industries and agricultural production includes technologies of regulation of an exit of valuable group components one of which are peat humic acids (HA). The analysis of the methods directed on increase in extent of extraction of humic acids presented in article showed the most optimum way of temperature impact on a feed stock as a result of which there is a change of structure and properties of the modified HA. By a complex of physical and chemical methods it is established that the preliminary thermolysis of peat is method of modification of structure of HA leading to removal of unstable side structural fragments in a macromolecule and to increase in a share of nuclear part.

Keywords: peat, heat treatment, humic acids, element and functional structure, thermolysis, thermal stability, decomposition gases, structure.

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INTRODUCTION

The thermal instability of peat is its reference property. Under the influence of temperature light-end, fluid and solid products of a thermolysis are formed. More than half a century back, scientists begin actively research processes of thermal decomposition. Summarizing scientific works on this subject, it should be noted that a number of transformations of mother substance of peat is resulted by transformation of its separate components. The structure and properties of a fixed residue change. But data are ambiguous as proceeding from objectives, conditions of heat treatment of peat can be various. In the real work as a primal problem gain in yield from peat of humic acids (HA) which as testify [1-5], is possible at heat treatment of peat up to the temperatures of 250-280 °C in various environments is: to the CO₂ environment or in the environment of characteristic gases of decomposition. As showed researches [6], application of other environments of heat treatment (N₂ or steam), and also use of isothermal endurance when heating peat, cannot lead to a positive take at the solution of an objective.

Besides, for a choice of conditions of heating of peat for gain in yield of humic acids, for the purpose of experiment optimization, it is necessary to carry out heat treatment on different processing equipment.

Research objectives

Justification of a choice of optimum conditions of heat treatment of peat for the purpose of gain in yield of humic acids; studying influence of preliminary heating of peat on their structure and property.

OBJECTS AND RESEARCH TECHNIQUES

As positively the humic acids influencing gain in yield from peat, heat treatment conditions in the environment of characteristic gases of decomposition were chosen. For the solution of an objective on optimization of a way of heating, authors used four installations of a thermolysis. As the studied objects used chosen samples to depth of 0,5 meters from peat fields of Western Siberia upper peat of extent of decomposition of 25% (the code of H-25) and low-lying sedge peat of extent of decomposition of 35% (the code of L-35).

The characteristic of objects of research was carried out by a technique [7] and the content of humic acids on the dry deashed substance (% for daf) is defined. Results are presented in table 1.

Table 1: The characteristic of peat for receiving humic acids

Code of an exemplar	Commercial analysis, %			GR assay, % for daf
	humidity	ash content	exit of the volatile	
H-25	8,2	1,9	73,5	25,0
L-35	7,6	6,1	70,4	38,3

Air-dried peat crushed 0,25 mm to fraction and heated with a step in 50⁰C to temperatures of 100 ... 400 °C in the following conditions: 1) in the rotating drum in the environment of characteristic gases of decomposition (on the installation developed in Tomsk polytechnical university [6, 8]) without pressure surplus where excess light-end products of a destruction were removed through an opening in a drum with a diameter of 2 mm; 2) on installation of a thermolysis in a retort without hashing with catching of steam-gaseous mix; 3) in the autoclave in the conditions of the continuous hashing and an overpressure in 1 atmosphere; 4) on installation of high-speed heating with branch of excess volatile products of a destruction.

Heat treatment of peat in a drum. The drum with a torus shot to 50 g was placed in the electric furnace. Proceeding from the maximal generation rate of gases of decomposition [8], heat rate was chosen 5 degrees a minute. This moment is very important because the uniform course of thermochemical reactions promotes receiving the homogeneous exemplar. Speed of the rotation of the drum having internal ribbings was chosen 90 revolutions per minute. After heating to the given temperature, the drum was cooled with water to ambient temperature within 20 minutes, then disconnected and took a ready exemplar of peat.

Heat treatment of peat in the autoclave differed from heat treatment in a drum in that peat is located in the autoclave, its heating happened to the same speed, as well as in a drum, but without partial venting of decomposition with an overpressure in 1 atmosphere.

Heat treatment of peat in a retort. Statement series of experiments were made on the installation described in work [8]. A shot no more than 5 g heated peat, and follow-up made catching of pitch by means of the wadded filter and catching of H₂O by means of anhydron. It allowed to determine the volume of the allocated gas without water of decomposition by a difference between the mass of an initial shot, fixed residue, pitch and H₂O.

Heat treatment of peat on the installation of high-speed heating (HSH). In a receiving bin filled up to 50 g of peat. Installation was blown beforehand helium (an expense of 200 ml/min.) for a deaerating from a heat treatment zone by means of a vacuum pump. The electric furnace was heated to the necessary temperature controlled by the thermocouple. Included a mixer. The mixed peat particles, with an expense of 1,5-2 g/min., came to the reactor 2 m high, with a diameter of 20 mm where heated up in an incident layer. The exemplar accumulated in the bunker which is warmed up to 150 °C. After the end of experiment the bunker was cooled to ambient temperature by about 1,5 h, unloaded an exemplar.

The ultimate analysis of humic acids on carbon content, Hydrogenium, nitrogen and the cooperative content of oxygen and sulfur was carried out on the automatic EURO EA3000 analyzer by a technique by [9] method of combustion of an exemplar in an oxidizing tube reactor of vertical type at a temperature of 1050 °C in the inert atmosphere of helium with an additive of oxygen and a full oxidation of pyrolyzed species oxide-coated and catalytic composition; their further passing through the reduction zone (the copper restored beforehand in Hydrogenium current at 500 °C) for transformation of nitrogen oxides and sulfur into N₂ and SO₂. The formed N₂, CO₂, H₂O, SO₂ were divided on a column with Porapak Q and determined by means of the detector by heat conductivity (katharometer).

The functional analysis was carried out according to a technique [7], the thermal complex analysis was carried out on the combined derivatografic installation allowing to record change of an exit of gases of decomposition (CO, H₂, CH₄) in the conditions of thermal decomposition in the environment of nitrogen at heat rate of 5 deg/min.

RESULTS AND DISCUSSION

In table 2 data on an exit of products of heat treatment of peat are provided in small shots. Proceeding from a percentage ratio between the received termination products of thermal decomposition of riding and low-lying peat, follows that the larger exit of gases of decomposition and pyrogenous water and a smaller exit of a fixed residue is characteristic for peat of riding type. It specifies smaller thermal stability (higher degree of a destruction) of this exemplar in comparison with low-lying peat at its heating in the environment of characteristic gases of decomposition up to the temperature of 400 °C.

Table 2: Exit of products of thermal degradation of peat

Code of peat	Heating temperature, °C	Products of thermal decomposition, % for daf			
		pitch	H ₂ O	fixed residue	gas
H-25/ L-35	100	-/-	0,7/0,5	99,0/99,3	0,3/0,2
	150	1,9/0,8	2,9/2,5	93,7/96,0	1,5/0,7
	200	3,0/2,6	3,9/3,4	88,7/91,0	4,4/3,0
	250	6,9/5,7	4,4/4,0	75,2/80,0	13,5/10,3
	300	12,5/11,0	5,9/5,1	66,5/72,0	15,1/11,9
	350	19,9/19,2	5,9/5,2	56,3/60,4	17,9/15,2
	400	23,3/22,2	5,8/5,0	52,0/56,6	18,9/16,2

Results of research of the content of humic acids in peat, after its heat treatment in the reel, the autoclave, a retort and UVN which testify are presented in table 3 that the received regularities of change of an exit of the NA humic acids from temperature of heat treatment of peat at various ways of heating, have identical character.

The experimental data testify that the maintenance of HA in heated exemplars by means of a drum and a retort is more, than when heating peat in the conditions of overpressure in the autoclave. For the specified three ways of heat treatment (except conditions of high-speed heating) the maximal exits of humic acids are received at a temperature of 250 °C. It is 26,4 ... 31,0% for daf (for a H-25₂₅₀ peat exemplar) and 41,4 ... 43,4% for daf (for an exemplar of L-35₂₅₀ peat).

Table 3: Influence of a way and temperature of heat treatment of peat in the environment of characteristic gases of decomposition on the content of humic acids

Code of peat	Heating temperature, °C	Way of heating	Exit of humic acids, % for daf
upper cotton-grass acid peat			
H-25	-	-	25,0
H-25 ₁₀₀	100	drum/autoclave/retort/UVN	25,2/25,0/25,3/24,5
H-25 ₁₅₀	150	drum/autoclave/retort/UVN	27,0/25,8/26,6/24,1
H-25 ₂₀₀	200	drum/autoclave/retort/UVN	28,7/26,2/28,9/23,7
H-25 ₂₅₀	250	drum/autoclave/retort/UVN	31,0/26,4/30,9/22,5
H-25 ₃₀₀	300	drum/autoclave/retort/UVN	29,4/22,4/29,0/16,7
H-25 ₃₅₀	350	drum/autoclave/retort/UVN	21,9/17,5/22,2/12,5
H-25 ₄₀₀	400	drum/autoclave/retort/UVN	16,7/14,5/17,0/8,2
low-lying sedge peat			
L-35	-	-	38,3
L-35 ₁₀₀	100	drum/autoclave/retort/UVN	38,9/38,3/38,9/38,0
L-35 ₁₅₀	150	drum/autoclave/retort/UVN	41,0/39,0/41,3/37,3
L-35 ₂₀₀	200	drum/autoclave/retort/UVN	42,7/40,7/42,2/36,5
L-35 ₂₅₀	250	drum/autoclave/retort/UVN	43,2/41,4/43,4/35,0
L-35 ₃₀₀	300	drum/autoclave/retort/UVN	29,6/25,1/30,0/22,2
L-35 ₃₅₀	350	drum/autoclave/retort/UVN	18,6/15,5/17,0/15,4
L-35 ₄₀₀	400	drum/autoclave/retort/UVN	9,0/7,4/8,9/10,0

It is possible to explain received by the following: 1) during the using of a retort and small shot of peat, heat treatment was exposed thin, quickly and evenly warmed up layer; 2) heating in the rotating drum allowed to be, taking into account low heat conductivity of peat, to its particles in process of heat treatment in the "waterfall" mode and to receive the uniform and fast warming up; 3) in the conditions of heat treatment in the autoclave, unlike other ways of heating, there is a fiber hashing of an exemplar that, apparently, not fully provides uniform of a temperature profile, and leads to receiving mix of the nonuniform structure; 4) the selfcontained zone heating of peat in the autoclave with an overpressure $P = 1 \text{ atm.}$, influences the speed of course of reactions of thermochemical transformations (a decomposition reaction of group components of peat and reaction of formation of new humic acids from products of a destruction [4-7, 10-14]) and therefore the under content of humic acids at the specified way of heating, can be caused by more high speed of reactions of their decomposition unlike reactions of the second group.

The experimental data according to the maintenance of HA in peat after its high-speed heating, differ from other ways of heat treatment. At temperature influence to 250 °C HA exit slightly decreases (for an exemplar of upper cotton-grass acid peat with 25,0 to 22,5% for daf and for an exemplar of sedge low-lying peat with 38,3 to 35,0% for daf, table 3), at further temperature increase – decreases more than twice (to 8,2 and 10,0% for daf). The tendency similar for heat treatment of peat in the environment of nitrogen established in works [2, 14] is observed. Received it is possible to explain with low bond energy of the majority of the functional groups of HA, and, as a result, their thermal instability. In other words, eliminating of side oxygen-containing functional groups of side chains of a macromolecule of HA under the influence of temperature, leads to formation of light-end products, mostly, of pyrogenous water and carbon dioxide. High speed of heating of particles of peat at their small time spent in a heat treatment zone, positively influences the speed of reactions of a destruction. Fusion reactions of new HA under existing conditions – are improbable.

Thus, optimum conditions of heat treatment of peat for the purpose of gain in yield of humic acids can be considered heat treatment in the rotating drum and heat treatment in a retort. But taking into account the larger volume of the received exemplar ON in one shot heating of peat – heat treatment in a drum.

Studying of structure and properties of humic acids HA H-25, HA H-25₂₅₀, HA L-35, HA L-35₂₅₀ by means of technical, element, functional, thermal analyses was the following investigation phase.

The ultimate analysis (table 4) showed that carbon content, Hydrogenium and oxygen lies in limits, the reference for peat humic acids and makes from 59,98 to 63,59% for daf (C), from 4,70 to 5,23% for daf (N) and from 27,99 to 32,16% for daf (O+S).

Table 4: Influence of heat treatment of peat on composition of humic acids

Code of humic acids	Commercial analysis, %		Element structure, % for daf				The functional structure, mol/g	
	ashes	moisture	C	H	N	O+S*	COOH	OH _{fen.}
HA H-25	0,83	5,66	59,98	5,23	2,64	32,16	3,2	3,1
HA H-25 ₂₅₀	0,21	3,07	60,70	4,94	2,65	31,71	3,5	3,0
HA L-35	0,38	9,42	61,23	4,70	3,20	30,87	3,1	3,4
HA L-35 ₂₅₀	0,02	5,12	63,59	5,00	3,42	27,99	3,3	3,3

* the content of sulfur in exemplars did not exceed 0,8% for daf (on the dry and deashed weight)

Comparison of element structure for exemplars of HA and HA₂₅₀, allowed to note increase in carbon content, decrease in the content of Hydrogenium and oxygen. Thus, the calculated nuclear ratio of N / With made 1,04 for HA N-25; 0,97 for HA H-25₂₅₀; 0,91 for HA L-35; 0,86 for HA L-35₂₅₀. The received results can be a consequence of increase in cyclic components in structure of HA H-25₂₅₀ and HA L-35₂₅₀. Change of element structure of exemplars under the influence of preliminary heating of peat in the environment of characteristic gases of decomposition can be "as a first approximation" a basis for problem solving of mathematical model operation of processes of the natural humification which is followed by changes of mother organic matter of peat and its group components. It is known that HA peat of higher degree are characterized by large volume of nuclear part in comparison with the volume of peripheral fragments in a macromolecule HA.

By results of the functional structure (table 4) it is shown that in exemplars of HA H-25₂₅₀ and HA L-35₂₅₀ humic acids the maintenance of phenolic hydroxyl groups decreases and the maintenance of SOON-groups increases. On the one hand, it can be a consequence of interaction of products of thermal decomposition HA (esters, aldehydes, ketones) with water with formation of new carboxyl groups. With another – in their education the hydrolyzed ester groups existing between other components of peat can make the contribution.

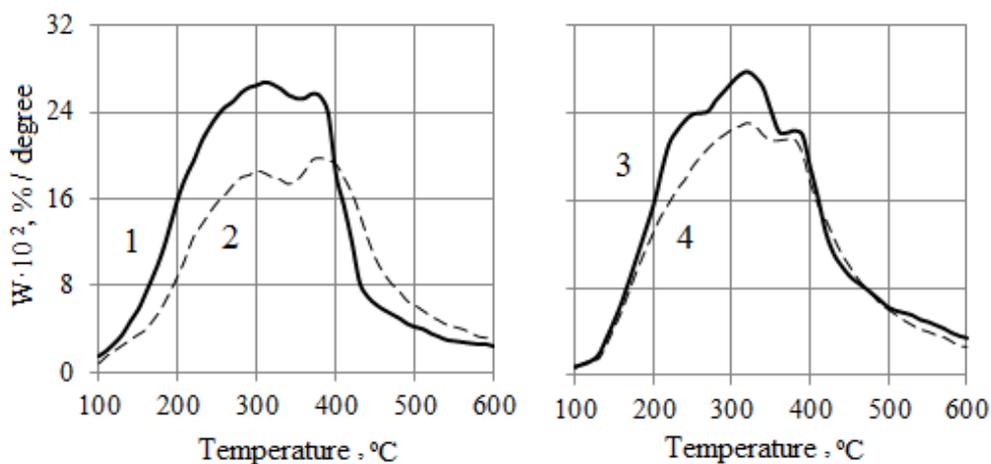
The increase in the contents as a part of humic acids of the functional sour SOON-groups can increase their reactivity.

Besides, the obtained data as it is stated above, also allow to assume possibility of model operation of processes of natural humification by means of simulated heating of peat in the above-stated conditions. These assumptions are based on earlier conducted author's researches [15] which indicate decrease of phenolic hydroxyls and increase in carboxyl sour groups in structure HA upon transition from peat of small extent of decomposition (R = 5-10%) with HA peat of higher R = 30-50%.

Studying of influence of heat treatment of peat on properties of humic acids by a thermal method of the analysis (table 5, figure 1) showed: 1) kinetic curve speeds of loss of weight for NA N-25 and NA N-25₂₅₀ are same and are characterized by existence of two maxima located in temperature areas 300-310 °C and 370-380 °C; 2) the differences between exemplars of HA L-35 and L-35₂₅₀ Group expressed in lack of a maximum at 240 °C for humic acids of wrought peat of low-lying type that is a consequence of removal of less heat-resistant structural fragments (side base units) as a result of preliminary heat treatment of peat are received; 3) temperature areas of two other maxima on curves of speeds of loss of mass of HA L-35 and HA L-35₂₅₀ are close to exemplars of NA N-25 and NA N-25₂₅₀ that testifies to similarity of a structure of more heat-resistant nuclear part of their macromolecule; 4) for exemplars of HA L-35₂₅₀, NA N-25₂₅₀ decrease of speed of decomposition and smaller loss of weight in comparison with exemplars of HA L-35, NA N-25 is received.

Table 5: Thermal analysis of humic acids

Code of humic acids	Loss of weight at 600 °C, % for daf	Change of loss of weight, % .	Temperature of the maximal speed of loss of weight, °C			Maximal speed $W \cdot 10^2$, %		
			1max	2max	3max	1max	2max	3max
HA H-25	59,9	-15,2	-	310	370	-	26,8	25,7
HA H-25 ₂₅₀	50,8		-	300	380	-	18,6	19,8
HA L-35	57,9	-11,2	240	320	380	21,2	27,8	22,4
HA L-35 ₂₅₀	51,4		-	310	380	-	23,1	21,6


 Fig.(1) – Change of speed of loss of mass of exemplars of humic acids:
 HA H-25 (1), HA H-25₂₅₀ (2), HA L-35 (3), HA L-35₂₅₀ (4)

Filing of gases of decomposition of humic acids (CO, H₂, CH₄) on complex derivatographic installation allowed to establish the most expressed changes for process of formation of carbon dioxide (table 6, figure 2).

Table 6: Kinetic parameters of a generation rate of white damp, Hydrogenium, methane at thermal degradation of humic acids

Code of humic acids	Temperature of the maximal generation rate of gases of decomposition, °C				Maximal speed $W \cdot 10^2$, %				
	CO		H ₂	CH ₄	CO		H ₂	CH ₄	
	1max	2max	1max	1max	1max	2max	1max	1max	
HA H-25	370	510	640	450	13,5	11,8	27,0		10,6
HA H-25 ₂₅₀	415	525	680	480	18,2	16,6	26,3		10,4
HA L-35	380	520	640	460	11,7	15,6	30,0		9,8
HA L-35 ₂₅₀	390	530	650	480	14,2	16,6	30,5		10,4

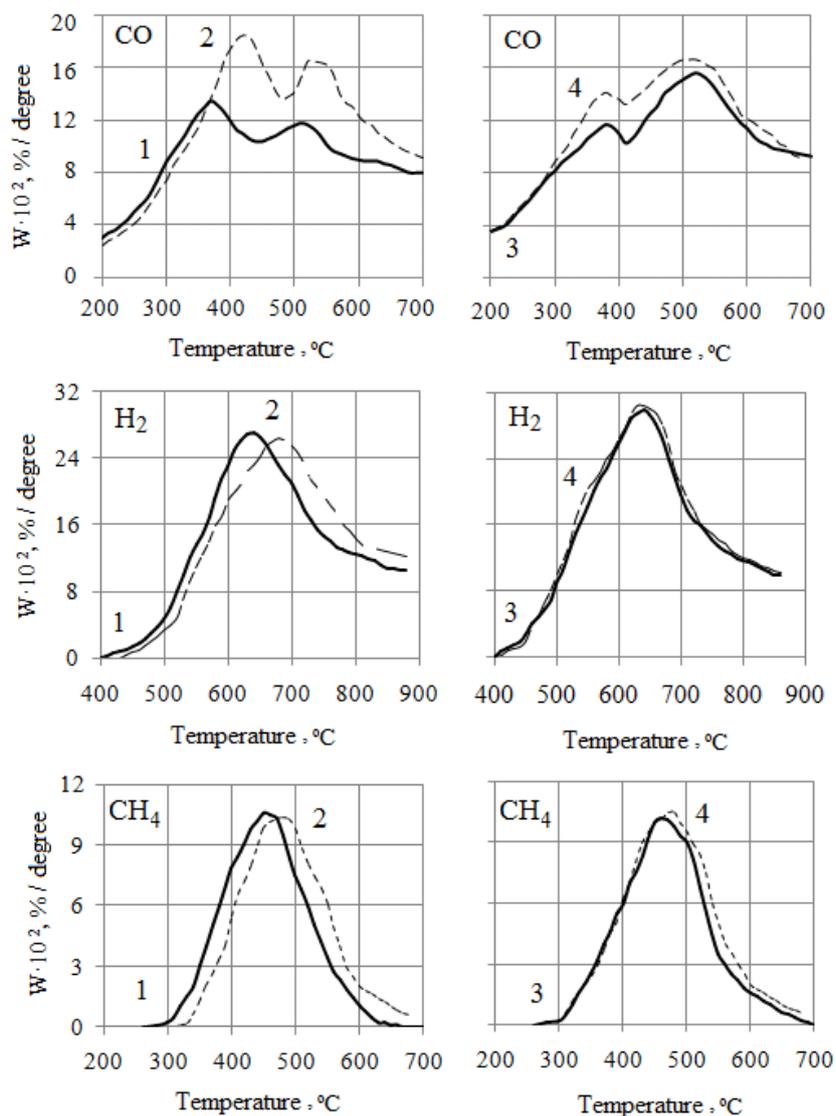


Fig.(2) – Kinetic curve formations of gases of decomposition at thermal degradation of humic acids:
 HA H-25 (1), HA H-25₂₅₀ (2), HA L-35 (3), HA L-35₂₅₀ (4)

As a result of comparison of kinetic curves 1, 2, 3, 4 (figure 2, table 6) it is received: 1) as a result of preliminary heat treatment of peat for objects of HA H-25250 and HA L-35250 the increase in a generation rate is registered CO; 2) kinetic curve formations of CO, H₂, CH₄ for objects of HA H-25250 and HA L-35250 have the maxima displaced in area of more high temperatures in comparison with exemplars of NA N-35, HA L-35; 3) more expressed shift of maxima is characteristic for humic acids of upper peat as a result of its heat treatment; 4) forms of curve generation rates of CO, H₂, CH₄ for all objects of research are identical (for CO existence of two well expressed maxima in temperature areas of 370-420 °C and 510-560 °C is characteristic; for H₂ and CH₄ existence of one maximum in temperature areas of 640-680 °C and 450-480 °C, respectively is characteristic).

If to accept that Hydrogenium source in gas of decomposition of humic acids are fusion reactions and condensations of aromatic compounds, (for example $R-CH=CH-R_{HA} \rightarrow R-Ar-R_{HA} + 3H_2$), that it follows from this that in humic acids of the HA H-25₂₅₀ wrought riding peat the larger maintenance of heat-resistant aromatic fragments in comparison with other exemplars (temperature of the maximal speed of H₂ = 680 °C, table 6, figure 2).

The received results indicate various thermal stability of the reactionary centers CO, H₂ and CH₄ in a macromolecule of humic acids also confirm change in different degree of their quantity as a result of preliminary heat treatment of peat.

SUMMARY

- It is shown that optimum conditions of heat treatment of peat for the purpose of gain in yield of humic acids and receiving a larger shot of an exemplar in one shot of heating, is its heating to 250 °C in the environment of characteristic gases of decomposition at a speed about 5 °C in the rotating drum with partial branch of products of a destruction for decrease in influence of an overpressure.
- It is established that preliminary heat treatment of peat in a macromolecule of humic acids is resulted by change of a share of peripheral base units and nuclear part, towards increase in the last.
- For exemplars of humic acids of heated peat the larger maintenance of the fissile sour SOON-groups in their functional structure is received.
- Decrease of speed of decomposition of humic acids of wrought peat indicates increase of their thermal stability.
- Humic acids heated peat are more enriched with the oxygen-containing structures capable during thermal decomposition to eliminate CO.
- Influence of heat treatment of peat on a generation rate CO, H₂, CH₄ it is more expressed for humic acids of riding peat.

CONCLUSION

Thus, gain in yield of humic acids of methods of preliminary heating of peat in the environment of characteristic gases of decomposition, allows to change structure and the chemical nature of the received objects. On the basis of the above it is possible to draw a conclusion on prospects of use of this method for the purpose of studying of specifics of macromolecules of humic acids and receiving on their basis of preparations with new properties.

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