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Chemical Transformations of Waxes in the Process of Mechanochemical Treatment of Peat in Aqueous Alkaline Media

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Abstract

Chemical transformations of petroleum extracts of peat wax occurring in the process of mechanochemical treatment (cavitation) of the most typical types of high-moor peat for the territory of Khanty-Mansiysk Autonomous Okrug – Ugra were studied. It was demonstrated that hydrolysis of ester bonds in the composition of wax molecules proceeded in alkaline media resulting from mechanochemical treatment of peat raw materials. Alcohol groups of waxes formed as result of hydrolysis are subjected to oxidation to aldehyde groups followed by condensation. Peat waxes are capable of entering into reactions with ammonia molecules, which is confirmed by elemental analysis results when flowing the processes listed. It was suggested that free-radical states, as well as hydrogen peroxide formed due to mechanochemical treatment of aqueous alkaline media were a source of an oxidizing agent. Additionally, based on elemental analysis data and IR spectra obtained, a hypothesis was put forward of mainly the aldol condensation mechanism for processes initiated by mechanochemical treatment. A preliminary conclusion was made of the fact that only a part of peat waxes participates in the stated processes, which allows using this type of raw materials more rationally, simultaneously obtaining humic acids and bitumenols from it. It was demonstrated that qualitative characteristics of peat wax isolated from oxidative aminolysis products met requirements for technical conditions imposed on raw peat wax.

Key words: peat wax, mechanochemical treatment, cavitation, oxidation, condensation, oxidative ammonolysis

INTRODUCTION

An integrated approach to peat processing suggests the preparation of peat wax as one of the types of production [1]. Traditional raw materials suitable for its preparation is high-moor peat, the ash content of which does not exceed 6 %, and the content of bitumenols is no less than 4 % [2]. A low level of economic efficiency of the production of raw peat wax from this type of raw materials led to its complete replacement by less expensive analogs that are petroleum paraffin [3], therefore, to increase the economic efficiency of processing of peat raw materials currently implemented technologies mainly seek for the integrated approach.

The main slope in the search for economically viable methods of peat processing is currently made in the direction of the preparation of humic fertilizers with higher quality indicators [4, 5]. Thus, the study of the range of issues related to the nature of chemical transformations of bitumenols in the process of aqueous alkaline mechanochemical treatment of peat is of practical and scientific interest. From the practical viewpoint, this sort of studies is most interesting for peat deposits of Khanty-Mansiysk Autonomous Okrug (KhMAO) – Ugra, since about 10 % of the world reserves of peat, the main part of which refers to high-moor and transitional types of peat, is concentrated within its territory [6]. However, valley peat with a high degree of decomposition is used as raw materials for the preparation of humic acids in the frameworks of the existing technologies [1]. Thus, traditional approaches upon processing of peat resources of KhMAO are not applicable. A new technological solution of peat processing considering peculiarity of regional peat resources and based on the integrated approach to raw materials processing is required.

The goal of the present work was a preliminary assessment of an opportunity for uniting extraction preparation of raw peat wax and mechanochemical preparation of humic acids [5] into common technological processes directed at the integrated use of peat raw materials.

The study purpose is the detection of the major regularities of chemical transformations of waxes happening in the process of such influences.

MATERIALS AND METHODS

High-moor oligotrophic peat of the Ob-Irtysh floodplain with a decomposition degree (R) of 20 %, as most common in the territory of KhMAO – Ugra was used as raw materials in the experiment.

The botanical composition and the decomposition degree of peat were determined by the macroscopic method according to GOST 28245–89. The extraction method defined the content of waxes according to Grefe with petroleum ether 40–70. The elemental composition of waxes was studied using EuroVector EA 300 analyzer by burning and subsequent quantitative analysis for the content of carbon, hydrogen, and nitrogen in a sample weight according to the technique [7]. Determining the oxygen mass fraction when studying the elemental composition were performed by the difference.

Infrared spectra were produced using a PerkinElmer Spectrum One FTIR spectrometer taking spectra was carried out in a mixture of potassium bromide with a mass fraction of the sample of 3 %. Alongside with peat, the solid residue (SR) formed resulting from mechanochemical treatment of peat in an aqueous ammonium solution was used as raw materials. To obtain it a sample weight of peat was treated with ammonia with a concentration of 1 mol/L for 10 min in rotor cavitation apparatus designed by A. D. Petrakov [8] with a rotor speed of 3000 min^{-1} followed by separating the mixture by centrifugation. The SR isolated was washed with distilled water until obtaining colourless washings with the neutral reaction of the medium. Afterwards, the SR was dried and brought to the constant mass, and then it was subjected to the same studies similarly to the initial peat.

Determining chemical constants of bitumens (acid number, saponification number, ester number, and iodine value) was carried out by conventional methods [7] and dropping temperature – by State Standard GOST 6793–73.

RESULTS AND DISCUSSION

The isolated yield of wax from the initial peat was (2.57±0.30) %, from the SR – (2.34±0.39) %, and in terms of the initial substance – 1.17 %. One can suggest that alkaline hydrolysis of ester bonds flows intensively in the composition of wax under oxidative ammonolysis conditions. Resulting from this process, over a half of wax contained in the samples under study can participate in the formation of the peripheral part of humic acids formed or be removed with washings, since it

TABLE 1

Elemental composition and atomic ratios of wax

Samples	Content, %				H/C	O/C	N/C
	N	C	H	O			
1	0	77.2±0.9	10.9±1.4	12.6±2.3	0.847	0.058	0.000
2	0.4±0.0	79.0±0.7	12.6±0.1	8.0±0.7	0.957	0.038	0.004

Note. Sample No. 1 is wax isolated from the initial peat; sample No. 2 is wax isolated from hydroxy ammoniated peat.

has surface properties. One may also suggest that some amount of hydrolysis products of peat waxes is susceptible to secondary oxidation processes that also increase their hydrophilicity.

To study the nature of major changes in the chemical structure of peat wax subjected to cavitation elemental analysis of two samples of the substance under study before and after mechanochemical impact was performed (Table 1). According to the data presented in Table 1, mechanochemical treatment of peat contributes to intensive flowing of condensational processes of wax molecules and is accompanied by a decrease in the number of oxygen-containing groups and by the formation of an additional number of carbon-carbon bonds. A decrease in the number of oxygen atoms indicates the prevalence of condensation processes over oxidation processes of wax transformation. An increase in the atomic O/C ratio points out at the participation of oxygen-containing groups in condensation processes.

According to the literature data [9], initiation of a complex process of waxes transformation by the action of free-radical states generated by mechanochemical effects in aqueous alkaline media may be suggested. Since oxygen atoms are active acceptors of free-radical states, one can also assume that the process of their transition from solutions onto wax molecules that contain molecules of alcohols and carboxylic acids.

It is on record that primary monohydric alcohols can oxidize to aldehydes [10]. It is also

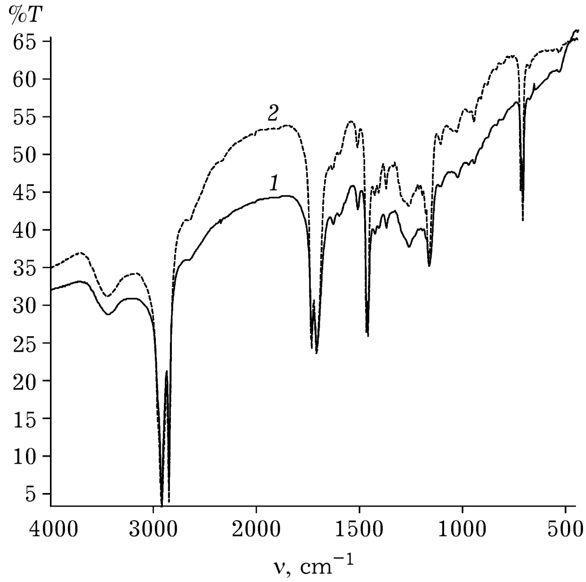

Fig. 1. IR spectra of waxes obtained from the initial (*1*) and hydroxy ammoniated (*2*) peat.

known that aldehydes containing hydrogen atoms at the α-carbon atom are prone to an aldol condensation in aqueous alkaline solutions at a temperature close to room [10]. Thus, the aldol condensation will be the most probable mechanism of condensation transformations of wax peats during mechanochemical treatment.

The formation of organically bound forms of nitrogen should also be noted, characterizing the elemental composition of waxes isolated from hydroxy ammoniated peat. On the assumption of the general perceptions of the chemical composition of wax one can assume

TABLE 2

Characteristic frequencies of IR spectra of peat waxes

Maximum of adsorption bands, cm^{-1}		Assignment of absorption bands
Wax of hydroxy ammonolysis product	Peat wax	
3402	3383	Stretching vibrations of OH groups
2970	2970	Stretching vibrations of C–H methyl
2870	2870	and methylene groups (and (or) aldehydes)
2607	2607	Stretching vibrations of OH groups
1720	1720	Stretching vibrations of carboxyl and carbonyl groups
1462	1462	Deformation vibrations of C–H bonds
1420	1420	Methylene groups bound to carboxyl or carbonyl groups
1266	1266	Stretching vibrations of CO bonds of ethers
1080	1080	Deformation vibrations of CO bonds in secondary alcohols
720	720	Stretching vibrations of C–C bonds

TABLE 3

Properties of waxes isolated from the initial peat and its hydroxy ammonolysis products

Samples	Acid number, mg KOH/g	Saponification number, mg KOH/g	Iodine number I_2/100 g	Dropping point, °C
Initial peat	51	155	18	71
Hydroxy ammonolysis product	54	155	26	77

the interaction of some number of carboxylic groups formed resulting from oxidation with ammonium molecules leading to the formation of imines. Nitrogen fixation through the formation of carbamide groups can also be presumed.

Since unambiguous features of occurring transformations of wax are impossible without the data of the functional composition of oxidative aminolysis products, further studies were related to the study of qualitative changes in the chemical composition of wax based on IR spectroscopy data.

Figure 1 shows IR spectra of the sample under study and initial peat wax. The assignment of the absorption bands in spectra is given in Table 2.

Characterizing the IR spectra obtained the absence of significant difference on the total number of adsorption bands and their mutual location in spectrum should be noted first. With the reservation about the impossibility of the qualitative determination of imine and carbamide groups on the background of organically bound oxygen, it can be argued about the preservation in a constant kind of the qualitative set of other functional groups. The major differences consist in the intensity of adsorption bands in spectra. Thus, an increase in adsorption bands at a wavelength of 720, 1462, 2920 и 2850 cm^{-1} is observed for wax subjected to mechanochemical effects. This points out at an increase in the number of methylene groups in the structure of wax molecules. The formation of an additional number of carbonyl and carboxyl groups happens resulting from mechanochemical treatment, which is especially indicated by a significant increase in adsorption bands at 1720 and 1740 cm^{-1}, respectively. An increase in the intensity of the band at 1080 cm^{-1} points out at the formation of an additional number of hydroxyl groups bound with a secondary carbon atom.

Thus, IR spectroscopy data confirm the assumption made earlier about alkaline hydrolysis accompanied by oxidation of alcohols to aldehydes followed by their aldol condensation.

In accordance with requirements TU 6-15-1228–80 imposed on raw peat wax, it should meet the following indicators: acid number – from 30 to 60 mg KOH/g, saponification number is from 100 to 160 mg KOH/g, the iodine number from 15 to 30 g I_2/100 g, the Ubbelohde dropping point is from 70 to 80 °C. Properties of wax isolated from the product of cavitation of peat meet these requirements (Table 3).

CONCLUSIONS

1. The feasibility of wax isolation from products of oxidative ammonolysis of peat carried out under mechanochemical conditions treatment was demonstrated.
2. It was detected that noticeable amounts of peat waxes were prone to the oxidative and hydrolytic degradation and removed from a solid phase with washings.
3. It was found that the main areas of chemical transformations of waxes during mechanochemical treatment were alkaline hydrolysis and condensation.
4. The suggestion was made about the aldol mechanism of condensational transformations of waxes prone to mechanochemical treatment.

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