Changes in the Chemical Composition of Wood during Mechanochemical Treatment

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(Received November 29, 2001)

Abstract

Changes in the chemical composition of aspen wood after grinding in the ball, planetary, and vibrational centrifugal mills are estimated from the copper number, contents of water-soluble substances, monosaccharides in water-soluble substances, and the amount of easily hydrolyzed polysaccharides. It is stated that the destruction of polyoses and lignin occurs more intensively during the grinding of wood in the presence of sodium hydroxide.

INTRODUCTION

Chemical processing of the plant raw material, particularly wood, occurs in two stages, as a rule. The first stage is activation, *i. e.* preparation of the raw material to the chemical interaction. The second stage is chemical reaction itself. If the process is carried out in the solid phase, these two stages can be united.

Mechanochemical methods of preliminary treatment involve grinding of the plant raw material in various mills (ball, colloid, or vibrational), disintegrators and crushers, dispersing in rolls, *etc.* [1]. The increase of the available surface of the material under treatment causes substantial increase of its reactivity (by a factor of 10 and more) [1–3].

The use of mechanochemical activation methods leads to the destruction of cell walls hardly changing the chemical composition of wood. However, this process is accompanied by degradation of lignin, cellulose, hemicelluloses [4].

We were the first to use the vibrational centrifugal and other mills, designed and built at the Institute of Solid State Chemistry, SB RAS, for preliminary activation of wood and for direct solid-phase carboxymethylation [5]. An advantage of these mills, unlike those used and described in the literature earlier, is that the products with the desired properties can be obtained within short time intervals (up to half an hour). The investigation of chemical transformations in the wood during the treatment in these mills is of both the scientific and practical interest.

The goal of the present work is the investigation of the changes in the chemical composition of wood after grinding in ball, planetary, and vibrational centrifugal mills, estimated according to the copper number (CN), the content of water-soluble substances (WSS), and monosaccharides within the total WSS content, as well as by the amount of easily hydrolyzed polysaccharides (EHP).

EXPERIMENTAL

Chips of air-dry aspen wood (fraction with particle size not larger than 0.5 mm) was used in the investigation. Grinding was performed in a vibrational centrifugal mill of the VTsM-5 type, ball mill (BM), and planetary mill (PM) manufactured at the Institute of Solid State

Chemistry and Mechanochemistry, SB RAS. For the experiments, the VTsM-5 type mill was adjusted for the periodic operation; the effective volume of the drum was 800 ml; balls 10 mm in diameter with the total mass of 1.1 kg or a steel cylinder 30 mm in diameter with the total mass of 1.1 kg were used as milling bodies at the 40 g efficient load of the material under treatment and the motor shaft rotation frequency of 1500 rpm.

The volume of the ceramic drum of the BM-type ball mill was 1800 ml; steel balls 20 mm in diameter with the total mass of 2.4 kg were used as milling bodies; the total load of the material to be treated was 50 g; rotation frequency was 118 rpm. The planetary mill of the AGO-2 type had a drum of the 30 ml effective volume; the total mass of balls 5 mm in diameter was 75 g; total amount of the material to be treated was 2 g; acceleration was 60 *g*.

In all the mills described above, the material was subjected to mechanical shock-attrition action. The differences in the construction features of mills and the use of milling bodies of different types allowed us to perform experiments applying varied frequencies and intensities of mechanical action.

The determination of the copper number, lignin content according to Komarov, the content of EHP, water-soluble substances and monosaccharides in WSS of the ground wood (the humidity being 6.0 %) was performed using the standard procedures described in [6].

RESULTS AND DISCUSSION

Mechanical shock-attritions actions on the wood material help changing its structure and chemical composition. An increase of the accessibility of the reaction centers of the plant cell components under mechanical treatment occurs due to the rupture of lignocarbohydrate bonds in the wood matrix. This parameter can be characterized by comparing the lignin content (in per cent of the mass of initial wood) extracted by the 90 % aqueous solution of dioxane from the initial and mechanically activated plant materials, which was described by us earlier [7]. The solubility of lignin in the aqueous solution of dioxane after mechanical grinding depends on the type of raw material and changes in the row: spruce < poplar < pine < aspen < reed. It should be noted that the mechanical treatment of this kind allows extracting smaller amount of lignin from wood than other activation methods do. For example, in the case of the treatment of wood with steam explosion, more intensive destruction of the lignocarbohydrate matrix and lignin occurs. Mechanical treatment is preferable for more complete utilization of all the components by chemical modification of plant materials.

TABLE 1

Effect of mechanical treatment on the properties of wood

Mill	Grinding time, min	WSS content, %	Lignin content (determined by Komarov's procedure), %
Ball	315	7.6	20.4
Planetary	2	10.2	13.9
VTsM (balls)	15	23.5	8.6
VTsM (cylinder)	15	9.1	17.2

Note. The lignin content of the initial wood (as determined by Komarov's procedure) is 22.4 %.

Substantial changes in the content of lignin isolated according to Komarov's procedure (acid-insoluble lignin) are observed in the case of wood treatment in the mills used by us (Table 1). Maximal residual lignin content (20.4 %) is present in the sample ground in the ball mill; it is comparable with the acid-insoluble lignin content of the initial sample (22.4 %). The lowest residual amount of lignin (8.6 %) is present in the wood sample ground in VTsM with balls used as the milling bodies. If the cylinder was used in this mill as a milling body, the residual lignin content was about 2 times higher. It is evident that the treatment of wood in VTsM with balls causes more intensive destruction of lignin, accompanied by depolymerization, which results in the increased solubility of its low-molecular fragments in 72 % sulphuric acid.

Maximal content of the substances soluble in water was detected after grinding the wood with balls as milling bodies in VTsM mill.

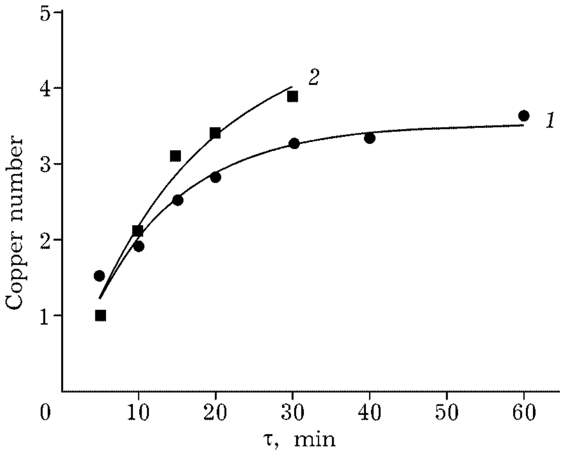

Fig. 1. Changes of copper number for aspen wood (*1*) and for a mixture of aspen wood with NaOH (OH_{wood} : NaOH = 1 : 0.5) (*2*) *vs.* the time of grinding in VTsM (balls).

The destruction of cellulose and hemicelluloses is accompanied by the appearance of an additional amount of carbonyl groups, which is reflected in the copper number [8]. An increase of the copper number is observed for the samples ground both in ShRM for 15 min [7], and in VTsM with balls as MB (Fig. 1).

Copper number of the sample treated in VTsM for 0.5 h is 3.25, which is 4 times more than the CN value for the initial sample. CN of the sample ground for 1 min is 4.5 times more than that of the initial sample. The carbonyl groups of lignin bring a definite contribution into the determined CN; however, their presence in the initial lignin is insignificant; in the air, they will be oxidized into carboxyl groups more rapidly.

The wood samples ground in VTsM for different time intervals were investigated by means of IR spectroscopy. No substantial changed were detected in the spectra of samples. The spectra of the initial samples are identical with those of the ground samples, independently of grinding time. This proves that no new substances different from the monomeric fragments of cellulose (hemicelluloses) are formed during destruction. We only observed the changed in the region of absorption band responsible for the vibrations of OH groups. Thus, the destruction is likely to proceed via the rupture of the glycoside bonds of carbohydrate-type macromolecules.

Aspen wood samples ground in VTsM with balls, either in the presence or in the absence of NaOH, contain water-soluble substances. In the presence of NaOH, the dynamics of the accumulation of WSS is much more intensive (Fig. 2). The highest WSS content is observed when wood is ground in VTsM with balls and in PM (see Table 1). A sharp increase of the solubility points to the fact that the destruction of polysaccharides has proceeded till water-soluble oligomers. The decrease of the content of acid-insoluble lignin in the treated samples in comparison with the initial wood is one more evidence of its substantial destruction.

It was stated in [5] that the mechanical treatment of wood affected the content of lignin and uronic acid in the material under investigation. After mechanical treatment of the spruce wood, 60 % of its lignin passes into solution when treated with a 0.05 M solution; at the same time, the number of methoxy groups changes. Chemical transformations that occur with lignin during vibrational grinding are characterized by the decrease of methoxy group content. For example, it was discovered [10] that with the increase of treatment time from 48 to 200 h, the methoxyl group content changes from 4.34 to 4.01 %, which makes 0.33 %.

By means of GLC, we discovered 1.76 % CH_3OH, calculated for the wood mass, in aqueous extracts from the wood sample ground in VTsM with balls for 1 h. Wood sample ground

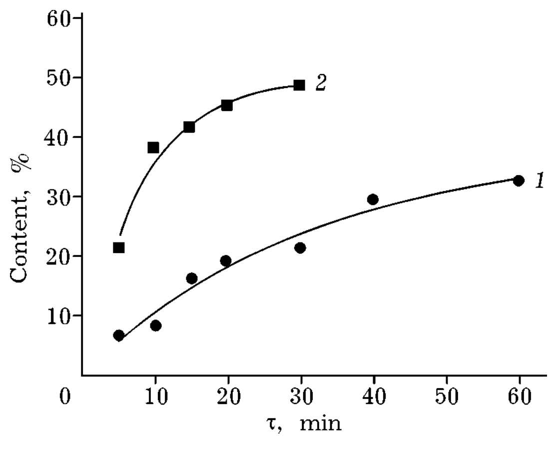

Fig. 2. Changes in the content of water-soluble substances *vs.* the time of grinding in VTsM (balls) for aspen wood (*1*) and a mixture of aspen wood with NaOH (*2*).

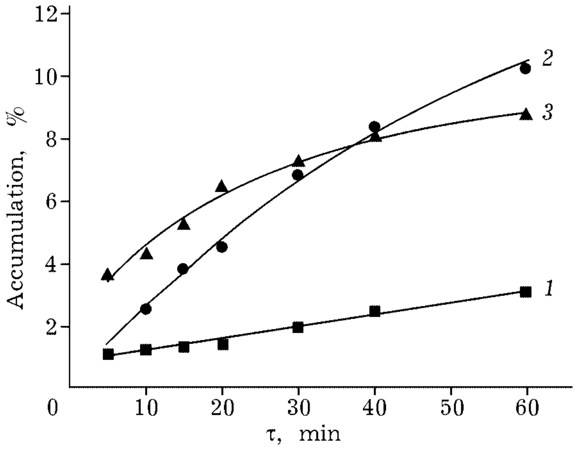

Fig. 3. Accumulation dynamics of monosaccharides present in water-soluble substances of wood after grinding in VTsM: *1* – arabinose, *2* – glucose, *3* – xylose.

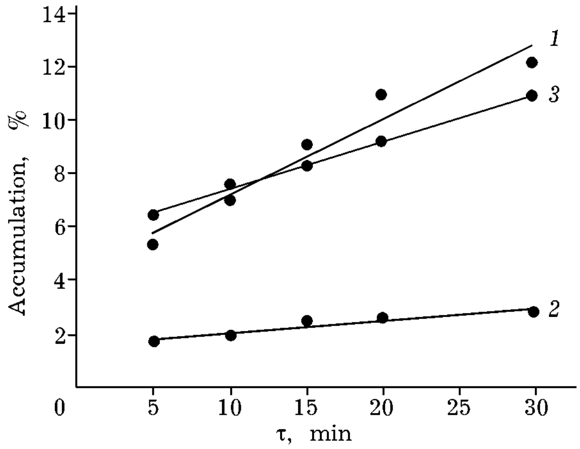

Fig. 4. Accumulation dynamics of monosaccharides present in water-soluble substances of wood after grinding in VTsM in mixture with NaOH: *1* – arabinose, *2* – glucose, *3* – xylose.

for 0.5 h in VTsM with balls in the presence of an alkali contains 1.45 % CH_3OH. The appearance of CH_3OH is likely to be connected with demethoxylation of lignin. It should be noted that in the case under consideration more intensive destruction occurs within very short time, unlike the case described in literature [10]. The reason is that we used the mill of the new type.

More intensive destruction processes accompanied by the formation of WSS occur during the grinding of wood in the presence of NaOH. Water-soluble substances extracted from the ground wood were hydrolyzed. By means of paper chromatography, we quantitatively identified the following monosaccharides in the hydrolyzate solution: glucose, arabinose, xylose (Figs. 3, 4).

The presence of glucose is most likely connected with the destruction of cellulose to oligomers. Hemicelluloses exhibit higher stability during grinding in VTsM both in the presence of alkali or in its absence. Generally speaking, there is some correspondence with the regularities established for the treatment of wood with alkali solutions.

The content of easily hydrolyzed polysaccharides in the initial wood and in the wood ground in VTsM with and without NaOH is shown in Table 2. One can see that it increases with increasing the time of wood treatment in VTsM. An interesting experimental observation is that the increase of treatment time leads to an increase of glucose content of the EHP; glucose is a monomeric fragment of cellulose

TABLE 2

Content of easily soluble polysaccharides after grinding wood with NaOH and without it in VTsM with balls, %

τ, min	Without NaOH			In the presence of NaOH		
	Gl	Ar	Xyl	Gl	Ar	Xyl
0	8.5	5.5	17.5	8.5	5.5	17.5
5	8.8	6.3	17.1	9.8	6.3	17.3
10	16.3	6.3	17.6	13.1	6.7	17.2
15	17.2	6.4	17.5	17.2	6.6	17.3
20	18.5	6.5	17.5	20.6	6.2	17.3
30	20.4	6.5	17.5	21.4	6.8	17.4
40	21.8	6.5	17.6			
60	23.9	6.6	17.6			

Note. Gl is glucose, Ar is arabinose, Xyl is xylose.

macromolecule. The presence of monosaccharides incorporated in hemicelluloses remains practically constant. This is in agreement with the conclusion concerning the relative stabilization of hemicelluloses during alkaline treatment, as well as with the data obtained earlier [11, 12]. The density of the cellulose ground in the laboratory vibrational mill decreases from 1.55 to 1.50 g/cm^3, according to [11]; as reported in [12], it decreases by 12 %. It is also stated in [12] that the ground cellulose consists of two fractions differing in density: easily-hydrolyzed fraction (cellodextrin, mass fraction: 35 %, density: 1.506 g/cm^3), and difficultly hydrolyzed one (65 % mass, density: 1.517 g/cm^3).

CONCLUSIONS

The comparative analysis of the experimental data on chemical transformations of wood after mechanical treatment in the mills of different types shows that the maximal changes within a short time interval occur in the planetary mill while the minimal ones occur in the ball mill. Chemical composition of wood after grinding depends on the type of mill used for treatment. The data obtained in the present study can be used to choose a method of preliminary treatment of wood or directly to conduct the reaction with it in order to obtain products with the required properties. In order to obtain more delignified products, mechanical treatment should be performed in a planetary or vibrational-centrifugal mill using balls as milling bodies. Products with reduced molecular mass can be obtained by treating the wood in the presence of sodium hydroxide because this case involves the most intensive processes of polyose destruction, accompanied by the formation of water-soluble substances.

The use of VTsM for the preliminary treatment of wood allows performing continuous technological processes, thanks to the mill design. Mechanochemical treatment of wood in VTsM involves substantial structural and chemical transformations within a short time interval, in comparison with the grinding of plant polymers in ball mills.

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