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PRODUCTION OF CELLULOSE-CONTAINING INTERMEDIATES FROM THE WOOD OF BROAD-LEAVED AND CONIFEROUS SPECIES USING ITS TREATMENT UNDER THE CONDITIONS OF EXPLOSIVE AUTOHYDROLYSIS

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The influence of the technological parameters of the process of explosive autohydrolysis of the wood of aspen, pine, and spruce on the yield and composition of cellulose-containing intermediates has been studied. It has been established that with a rise in temperature and an increase in the time of explosive autohydrolysis the yield of technical cellulose falls and the content of Kürschner cellulose rises. The optimum parameters have been found for the oxidative destruction of the residual lignin in the cellulose-containing intermediates by hydrogen peroxide in an alkaline medium, which enables their cellulose content to be raised to 95—96%.

It is known that explosive autohydrolysis permits lignocellulosic raw material to be separated into its main components [1, 2]. A detailed analysis of the water-soluble substances and the sold products of autohydrolyzed aspen, pine, and spruce woods [3—6] has shown that the main processes involved are the hydrolytic cleavage of hemicelluloses and the depolymerization of the wood lignin with the formation of low-molecular-mass fragments capable of being removed from the autohydrolyzed material by solutions of alkalis. In view of this, the given method of treating wood biomass may be considered as one of the promising ways of delignification with the production of cellulose-containing intermediates, and then, after certain treatments, of cellulose itself. In the light of the fact that the degree of hydrolytic cleavage of hemicelluloses and of the depolymerization of wood lignin is determined by the parameters of the process of explosive autohydrolysis, it is obvious that after aqueous and alkaline extraction (elimination of water-soluble substances and low-molecular-mass lignin) the autohydrolyzed material will contain various amounts of cellulose with residual lignin and hemicelluloses as impurities.

In the present paper we give the results of a study of the influence of the technological parameters of the process of explosive autohydrolysis of aspen, pine, and spruce woods on the yields of cellulose-containing intermediates and on their component composition and of the possibility of raising the cellulose content after the stage of oxidizing the residual lignin with hydrogen peroxide in an alkaline medium. The amounts of the main components in the initial woods are given in Table 1.

TABLE 1. Chemical Compositions of the Initial Raw Materials, % on the Absolutely Dry Weight of the Wood

Wood	Cellulose	Hemicellulose with uronic acids	Lignin	Extractive substances
Aspen	46.3	24.5	21.8	7.8
Pine	52.2	13.5	26.3	7.6
Spruce	51.0	15.3	27.3	6.4

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TABLE 2. Yields of Technical Cellulose from Autohydrolyzed Aspen, Pine, and Spruce Woods Obtained under the Conditions of Explosive Autohydrolysis at 187—240°C, and Amounts of the Main components* in It

Parameters of the process		Yield of technical cellulose, % on the wood			Amounts of the components in the technical cellulose, %								
					cellulose			lignin			hemicellulose		
T, °C	Time, s	1	2	3	1	2	3	1	2	3	1	2	3
187	180	61.1	83.3	85.6	73.6	54.1	51.6	19.4	30.0	33.6	6.6	15.2	14.7
187	180	61.3	74.6	78.2	74.2	57.7	55.8	18.7	29.6	31.7	6.5	12.4	12.2
187	300	63.0	68.8	70.2	72.1	61.6	61.5	16.6	28.3	28.4	8.8	9.6	9.9
220	60	70.6	74.8	74.3	67.3	57.6	59.5	27.2	37.5	36.8	5.1	4.5	3.4
220	120	71.0	69.1	71.6	65.6	63.5	61.8	31.6	32.0	35.1	2.2	4.2	3.0
220	180	61.7	65.4	68.5	75.2	67.3	64.0	22.3	29.3	33.2	2.1	3.2	2.6
240	60	64.6	68.4	67.5	74.5	69.4	71.9	25.0	30.4	27.9	0	0	0
240	120	57.2	62.1	62.6	84.8	77.5	75.9	14.7	22.2	23.9	0	0	0
240	180	57.2	62.5	62.6	85.1	75.8	78.8	14.4	23.8	21.0	0	0	0

* 1) aspen; 2) pine; 3) spruce.

TABLE 3. Content of Kürschner Cellulose after the Treatment of Technical Cellulose with Hydrogen Peroxide in an Alkaline Medium under Various Conditions

Solution used for treatment	T°, C	Time, min	Content of Kürschner cellulose, %
	Sample 1		
A*	40	60	83.6
A	40	180	84.2
B	60	60	84.6
B	60	180	85.7
B	90	180	85.3
B	90	240	88.0
C	60	60	83.7
C	90	180	84.6
	Sample 2		
A	40	60	86.0
B	40	240	90.3
B	60	60	91.4
B	90	60	90.8
B	90	240	92.4
B	90	180	96.1
C	90	60	90.4
C	90	180	93.6

*A - 1% H_2O_2+1% NaOH; B - 2% H_2O_2+1% NaOH; C - 3% H_2O_2+ 1% NaOH.
Content of Kürschner cellulose in the technical cellulose: sample 1) 74.5%; sample 2) 84.8%.

It can be seen from the results given in Tables 2 and 3 that the yield of technical cellulose from autohydrolyzed aspen,

pine, and spruce woods and the amounts of cellulose, lignin, and hemicelluloses in them are determined by the parameters of explosive autohydrolysis. Here we must mention a general tendency: with a rise in the temperature of the process the yield of technical cellulose falls while the amount of Kürschner cellulose in it rises.

Thus, the yield of technical cellulose from pine wood autohydrolyzed at 187°C was 68.8—83.3% and its content of Kürschner cellulose was 54.1—61.6%. At 220°C, the yield of technical cellulose was 65.4—74.8% and the content of Kürschner cellulose had increased to 57.6—67.3%. And, finally, at 240°C the yield of technical cellulose amounted to 62.5—68.4% and the content of Kürschner cellulose had risen to 69.4—75.8%.

An analogous relationship between the yield of technical cellulose and the amount of Kürschner cellulose in it was observed with an increase in the time of activation of the wood at fixed process temperatures.

The given relationships are fully understandable, since with an rise in the temperature of explosive autohydrolysis and with an increase in the time of activation, the amount of hemicelluloses in the solid residue falls and the proportion of low-molecular-mass lignin removable by alkaline extraction rises. This also leads to a fall in the yield of technical cellulose from the autohydrolyzed wood and to an increase in the amount of Kürschner cellulose with a rise in the temperature of explosive autohydrolysis and with increasing time of treatment.

In the case of autohydrolyzed aspen wood the dependence of the yield of technical cellulose and the amount of Kürschner cellulose in it on the parameters of the process of explosive autohydrolysis have a more complex nature. The yield of technical cellulose from pine wood autohydrolyzed at 187°C amounted to 61.1—63.0% and the Kürschner cellulose content to 72.2—74.2%. With a rise in the temperature of autohydrolysis to 220°C the yield of technical cellulose did not fall but rose, while its content of Kürschner cellulose fell somewhat because of the large amount of residual lignin in aspen wood autohydrolyzed at these temperatures. At 240°C the yield of technical cellulose amounted to 57.2—64.6%, while the amount of Kürschner cellulose in it reached 74.5—85.1%.

Thus, after the elimination of water-soluble substances and low-molecular-mass lignin from autohydrolyzed pine, spruce, and aspen woods it is possible to obtain technical cellulose with a yield of 57—68% that contains up to 75—85% of Kürschner cellulose. Such cellulose intermediates can be used as the starting material for obtaining high-purity cellulose or valuable chemical substances — glucose, levulinic acid etc.

It must also be mentioned that the technical cellulose is characterized by a fairly high content of residual lignin. As can be seen from Tables 2 and 3, its amount was smallest when the wood was treated at 240°C, being 14.4% in the case of aspen wood and 21—23% for pine and spruce woods.

As is known, the quality of the cellulose-containing intermediates used in various branches of industry is determined by the residual lignin content. When the lignin content is zero, the product obtained is pure cellulose.

It is also well know that cellulose-containing intermediates with higher cellulose contents can be obtained by the oxidative destruction of the residual lignin — for example, with hydrogen peroxide in acid and alkaline media [8—10].

In order to obtain information on the efficacy of the oxidative destruction of the residual lignin in technical cellulose, we investigated the component composition of the technical cellulose from aspen wood after its treatment with hydrogen peroxide in an alkaline medium. For the investigation we took technical cellulose obtained under conditions of explosive autohydrolysis at 240°C, since it contained the highest amount of cellulose. The optimum consumption of hydrogen peroxide for the effective oxidative destruction of the residual lignin apparently amounted to 2—3% on the weight of the initial technical cellulose at 60—90°C with a treatment time of 3—4 h (Table 3).

EXPERIMENTAL

As the initial raw material we used aspen, pine and spruce woods in the form of chips with dimensions of 25 × 20 × 4 mm. Explosive autohydrolysis was performed in a batch apparatus with a reactor volume of 0.8 liter, described in detail in [3], in the temperature range of 180—240°C at a pressure of saturated steam of 12—34 atm., with treatment times of 60—180 s. The autohydrolyzed material was expelled from the apparatus into a receiver, collected quantitatively, and subjected to stagewise analysis for its individual components according to generally adopted methods of wood analysis [7]. The autohydrolyzed material obtained was subjected to extraction with hot water to eliminate water-soluble substances and to exhaustive extraction with 0.1 N NaOH at 20°C for the complete elimination of low-molecular-mass lignin. After the aqueous and alkaline extractions, the cellulose-containing material was called "technical" cellulose. The lignin, hemicellulose, and cellulose contents of the technical cellulose were determined as described in a handbook [7].

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