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COMPOSITION OF THE WATER-SOLUBLE PRODUCTS FROM THE THERMOCATALYTIC ACTIVATION OF ASPEN WOOD

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The compositions of the water-soluble substances formed on the thermocatalytic activation of aspen wood under the conditions of explosive autohydrolysis at temperatures of 187, 220, and 240°C and, correspondingly, saturated steam pressures of 1.2, 2.4, and 3.4 MPa have been studied. The water-soluble compounds are formed as the result of hydrolysis reactions of the components of the wood catalyzed by organic acids produced in the decomposition of hemicelluloses. It has been established that the main water-soluble compounds are true sugars, low-molecular-mass lignin, acetic acid, furfural, and sugar degradation products. Methanol, isopropanol, propionic acid, and hydroxymethylfurfural are present in minor amounts. Raising the temperature of the autohydrolysis of wood intensifies the degradation of sugars and increases the degree of their depolymerization to form water-soluble low-molecular-mass fragments.

The industrial processes for the chemical treatment of wood do not ensure the waste-free utilization of all the main components of the wood biomass. In view of this, the search for new approaches to the problem of the complex use of wood raw material is an urgent one. Directions of investigations connected with the use of thermocatalytic methods of acting on wood biomass appear extremely promising [1]. Recently, the explosive autohydrolysis of wood, which permits its waste-free processing to give cellulose, active lignin, and fodder additives has been undergoing intensive development [2-5]. The essence of the method consists in the partial hydrolysis of the wood raw material by its brief treatment with superheated steam, followed by a sharp release of pressure. The efficacy of the process depends on two main factors: the hydrolysis of weak bonds in the matrix of the wood biomass, and the mechanical disruption of the solid raw material during the sharp drop in pressure. With a rise in the temperature of the steam activation process a deacetylation of the polysaccharides of the hemicelluloses takes place with the formation of acetic acid. Small amounts of formic acid are also formed, obviously as a result of thermal transformations of sugars. During the steam treatment, the organic acids catalyze the hydrolysis of ester and other weak bonds in the lignocarbohydrate complex of the wood. As a result of this activation it is possible to raise the degree of extraction of the main components of the wood biomass: the hemicellulose is isolated in the form of an aqueous solution of sugars, dilute solutions of alkali extract low-molecular-mass lignin, and, as a solid product, technical cellulose with minor amounts of lignin and hemicelluloses is obtained.

An important criterion of the hydrolytic degradation of the lignocellulose complex of the plant biomass under conditions of explosive autohydrolysis is the nature of the water-soluble substances. Analysis of the literature shows that the composition of the water-soluble substances is largely determined by the conditions of performing the process (temperature and time of treatment, steam pressure) and the nature of the plant biomass [6-9]. The composition of these substances may include mono- and oligosaccharides, water-soluble lignin, acetic acid, methanol, and furfural. However, there is practically no information on the nature of the other organic products formed in autohydrolysis under various conditions of conducting the process.

In the present paper we give the results of a study of the composition and information on the yield of the water-soluble products formed in the thermocatalytic activation of, as an example, aspen wood under conditions of nonisobaric autohydrolysis performed with a variation in the temperature and the pressure.

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TABLE 1. Composition of the Water-Soluble Substances Formed under the Conditions of the Explosive Autohydrolysis of Aspen Wood

Time of treatment, sec	Total amount,* %	Composition of the water-soluble substances †								
		RSF	RS	LML	CH_3OH	i-C_3H_7OH	acetic acid	propionic acid	furfural	HMF	Σ
		Temperature 187°C, steam pressure 1.2 MPa									
120	15.7	10.87	1.77	0.50	0.04	0.01	3.85	0.003	0.033	0.006	15.31
180	13.0	9.93	1.30	1.33	0.03	0.01	1.60	0.003	0.010	0.006	12.92
300	10.0	5.47	1,17	1.61	0.03	0.02	2.54	0.006	0.025	0.014	9.71
		Temperature 220°C, steam pressure 2.4 MPa									
60	15.21	6.89	3.44	0.6	0.08	0.03	5.05	0.004	2.21	0.008	15.33
90	14.34	7.18	3.31	0,84	0.12	0.04	4.78	0.005	1.54	0.010	14.52
120	11.77	4.61	2.94	0.90	0.22	0.07	4.62	0.005	1.64	0.012	12.08
150	15.70	8.87	3.46	1.13	0.26	0.09	4.32	0.007	1.38	0.009	16.07
180	17.44	10.26	7.56	1.53	0.30	0.10	3.63	0.007	2.03	0.018	17.88
		Temperature 240°C, steam pressure 3.4 MPa									
60	16.22	10.08	5.68	5.89	0.09	0.04	0.06	0.005	0.19	0.01	16.4
90	21.39	12.99	7.21	7.88	0.13	0.06	0.11	0.006	0.41	0.02	21.6
120	17.62	9.67	5.39	7.22	0.20	0.07	0.30	0.006	0.43	0.02	17.9
150	15.66	8.07	4.62	6.56	0.24	0.10	0.21	0.008	0.33	0.02	15.5
180	14.79	7.66	5.11	6.34	0.32	0.12	0.13	0.009	0.34	0.03	14.9

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*Here and in Table 2, in percentages of the absolutely dry weight of the autohydrolyzed wood.

†RSI — reducing substances after inversion; RS — reducing substances; LML — low-molecular-mass lignin; HMF — hydroxymethylfurfural; Σ — total amount of the individual compounds.

TABLE 2. Composition of the True Sugars in the Water-Soluble Substances Formed from Aspen Wood under the Conditions of Explosive Autohydrolysis

Temperature,* °C	Time of treatment, sec	RSI content	Composition of the true sugars in the RSI					
			arabinose	xylose	glucose	mannose	galactose	total amount
187	120	10.87	0.40	2.82	3.14	0.87	Abs.	7.23
	180	9.93	0.23	2.66	3.45	0.53	Abs.	6.87
	300	5.47	0.02	1.84	1.65	0.18	Abs.	3.69
	60	6.89	-	2.05	Tr.	-	0.06	2.11
	90	7.18	-	3.22	Tr.	-	0.16	3.38
220	120	4.61	-	2.22	Tr.	-	0.10	2.32
	150	8.87	-	2.67	Tr.	-	0.12	2.79
	180	10.26	-	4.10	Tr.	-	0.31	4.41
	60	10.08	-	3.79	0.12	-	0.24	4.15
	90	12.99	-	3.49	0.14	-	0.22	3.85
240	120	9.67	-	3.07	0.34	-	0.31	3.72
	150	8.07	-	1.52	0.33	-	0.32	2.17
	180	5.11	-	1.46	0.29	-	0.34	2.09

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*Steam pressure 1.2 MPa at 187°C, 2.4 MPa at 220°C, 3.4 MPa at 240°C.

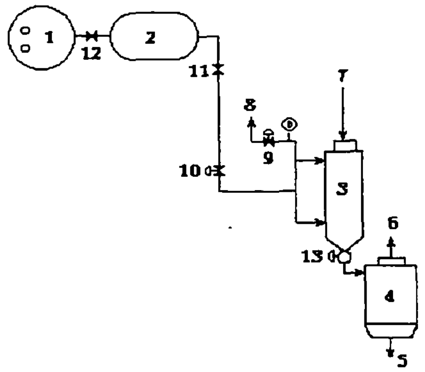

Fig. 1. Basic scheme of the apparatus for the nonisobaric steam cracking of plant biomass: 1) steam generator; 2) steam accumulator; 3) reactor (0.85 liters); 4) cyclone (25 liters); 5) discharge of autohydrolyzed mass; 6) discharge of uncondensed gases; 8) discharge of steam; 9-12) stop-valves; 13) ball valve for the discharge of the product.

Table 1 shows the composition of the water-soluble substances of aspen wood subjected to explosive autohydrolysis at temperatures of 197-240°C and steam pressures of 1.2-3.4 MPa. The autohydrolyzed wood mass had a moisture content of 56-64%, the moisture content of the product rising with an increase in the time of treatment. Conversely, the amount of water-soluble substances fell with an increase in the time of activation of the wood.

As follows from an analysis of the literature [6-9], the water-soluble substances formed under the conditions of the explosive autohydrolysis of wood may include: mono- and oligosaccharides, water-soluble low-molecular-mass lignin, alcohols, acids, furfural and its homologs, levulinic acid, and other compounds. In view of the relatively low temperature of the process, one must expect small amounts of the above-mentioned products formed in the autohydrolysis of wood at 187°C.

In actual fact, according to Table 1, the amount of reducing substances (RS) in the solution was not more than 1.77% of the weight of the initial wood. At the same time, the amount of RS in the water-soluble substances rose substantially after the performance of inversion — i.e., after additional hydrolysis — and reached 5.47-10.87%. The complete hydrolysis of aspen formed: arabinose, 0.47%; xylose, 16.67%; mannose, 1.74%; glucose, 56.31%; and galactose, 1.05%, on the weight of the dry wood. Under the conditions of explosive autohydrolysis, the sugars formed from wood may undergo further transformations. In particular, xylose may be converted into furfural, and glucose into hydroxymethylfurfural and levulinic acid [13]. Resinification and destructive processes are also possible under these conditions.

As has been shown in [4-6], with a rise in the temperature of autohydrolysis the degree of degradation of the lignocellulose complex of wood increases. We obtained a similar result. It was established that at process temperatures of 220°C and above the formation of liquid organic degradation products took place even at a treatment time of 30 sec.

As can be seen from Table 1, the amount of water-soluble substances in the products obtained at 220°C was 17.44%.

The main components of the water-soluble substances of aspen wood after autohydrolysis under these conditions were RS, low-molecular-mass lignin, acetic acid, and furfural. The yield of all the organic products in these experiments was considerably higher than at 187°C. This difference was shown particularly clearly for the cases of RS, acetic acid, furfural, and methanol.

After the autohydrolysis of aspen wood at 240°C and a steam pressure of 3.4 MPa, the amount of water-soluble substances determined from the loss in weight of the autohydrolyzed wood after extraction with water was 21.39%. This figure agrees satisfactorily with the sum of the independently determined individual substances and is appreciably higher than that found at lower process temperatures.

The water-soluble substances from wood autohydrolyzed at 240°C contained a higher amount of RS and of low-molecular-mass lignin. The amount of the latter was 6-8% of the weight of the initial wood. At the same time, the yield of acetic acid and furfural under these conditions was considerably lower than after the treatment of the wood at 220°C. This fact

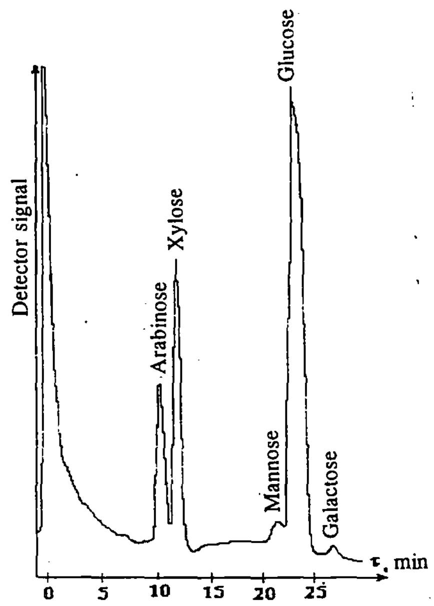

Fig. 2

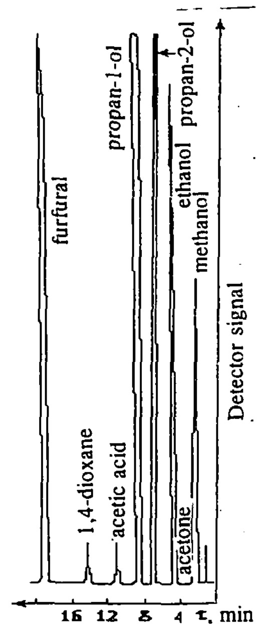

Fig. 3

Fig. 2. Chromatogram of the individual sugars after the complete hydrolysis of the initial aspen wood and their conversion into acetoaldononitriles. Conditions of analysis: column 2 m long; sorbent Chromaton N-AW-HMDS, 0.20-0.25 mm fraction, with the liquid phase 5% XE-60, $T_{evap} = T_{det} = T_{col} = 220°C$.

Fig. 3. Chromatogram of an artificial mixture of the main volatile organic products obtained under the conditions of nonisobaric steam cracking of aspen wood (internal standards ethanol and 1,4-dioxane). Conditions of analysis: glass column 1 m long; sorbent Separon-BD, 0.125-0.200 mm fraction, $T_{evap} = 210°C$, $T_{det} = 230°C$, column temperature 100°C with a programmed rise of 6°C per minute.

may witness a participation of the acetic acid in polysaccharide hydrolysis reactions [1, 4-6], while the furfural suffers degradation [2-5] or condenses with lignin fragments, thereby increasing the amount of low-molecular-mass lignin. The amount of methanol, isopropanol, propionic acid and hydroxymethylfurfural increased with a rise in the temperature of wood autohydrolysis from 220 to 240°C.

Table 2 gives information on the composition of the true sugars in the water-soluble substances of autohydrolyzed aspen wood, obtained by the GLC method. It was found that the true sugars included arabinose, xylose, glucose, and mannose. Consequently, even at 187°C the pentosans underwent hydrolysis, with the formation of arabinose and xylose, and so did part of the hexosans, with the formation of glucose and mannose.

It must be mentioned that with an increase in the time of autohydrolysis a tendency was observed to a fall in the yield of sugars. This fact may show their further transformations with the formation of furfural, hydroxymethylfurfural, and other products. The condensation of sugars with lignin to form so-called "pseudolignin," as has been reported, for example, by Brownell and Sadler [13], is also possible. A study of the individual composition of the true sugars in the water-soluble substances before inversion showed that the amount of RS agreed well with the total of the individual sugars: on treatment for 2 min the RS amounted to 1.77% and the total sugars to 1.63%; after 3 min, RS 1.30% and total sugars 1.63%; after 5 min RS 1.17%, total sugars 1.02%.

In view of the fact that the total amount of true sugars in the water-soluble substances after inversion was not more than 67-69% of the reducing substances after inversion (RSI), it may be assumed that part (31-33%) of the oligosaccharides underwent degradation under the conditions of autohydrolysis with the formation of carbohydrates capable of titrating as sugars but not being true sugars. In other words, part of the reducing substances formed at an activation temperature of 187°C did not consist of true sugars. Thus, the water-soluble substances from aspen wood autohydrolyzed at 187°C were made up of true sugars (about 7.23%), oligosugars (about 3.64%), low-molecular-mass lignins (about 1.61%), and acetic acid (about 3.85%). Present in minor amounts were methanol (0.03-0.04%), isopropanol (0.01-0.02%), propionic acid (0.002-0.007%), furfural (0.01-0.03%), and hydroxymethylfurfural (0.006-0.03%).

The amount of true sugars formed in the autohydrolysis of wood at 220°C was substantially smaller than the amount of RSI. The true sugars made up only 31-50% of the RSI. This indicates that with a rise in the temperature of the process the proportion of sugars undergoing degradation increases. Thus, a rise in the temperature of autohydrolysis from 187 to 220°C did not only increase the degree of degradation of the initial lignocarbohydrate complex of the wood but also led to the degradation of the resulting sugars with the formation of fragments of the RS.

A rise in the temperature of treating the wood to 240°C led to an increase in the degree of degradation of the true sugars, and their proportion in the RS determined fell. The proportion of true sugars in the water-soluble substances of wood autohydrolyzed at 240°C amounted to 27-41% of the total amount of RSI.

It follows from Table 1 that the amount of water-soluble low-molecular-mass lignin formed in autohydrolysis at 187°C was likewise small and rose with an increase in the time treatment of the wood from 0.5% at 2 min to 1.6% at 5 min. The increase in the level of lignin substances may take place either through an increase in the degree of degradation of the lignocarbohydrate complex of the wood or as the result of condensation of the sugars formed with low-molecular-mass lignin.

It was established by GLC that the water-soluble substances from autohydrolyzed wood contained not only sugars and low-molecular-mass lignin but also volatile products. In an investigation of the volatile components of the water-soluble organic substances by GLC using various columns, the following were identified: methanol, isopropanol, acetic acid, propionic acid, furfural, and hydroxymethylfurfural (see Table 1). Under the given conditions of explosive autohydrolysis the bulk of the volatile water-soluble substances consisted of acetic acid (about 3.85%), and the amounts of the other organic substances were only hundredths and thousandths of a percentage part.

EXPERIMENTAL

The initial raw material used was aspen wood with the following composition (%) on the weight of the absolutely dry wood: cellulose, 46.3; lignin, 21.8; hemicelluloses, 25.5. It also contained 7.8% of extractive substances, of which 5.8% was extracted by water, and 2.0% by diethyl ether. A sketch of the apparatus for activating wood by nonisobaric autohydrolysis is shown in Fig. 1. Reactor 3 with a volume of 0.85 liters, previously heated to the given temperature was charged with wood chips (dimensions not greater than 25 × 20 × 4 mm, dried to the air-dry state at 105°C). The reactor was tightly closed and superheated steam from steam accumulator 2 was fed in through valves 10 and 11. The required pressure of saturated steam was maintained for a predetermined time (from 0.5 to 5 min). Then the pressure was rapidly released through steam valve 13. This led to the "explosive discharge" of the autohydrolyzed material into the receiver 4. The autohydrolyzed material was collected quantitatively and subjected to stepwise analysis for individual substances according to generally adopted [10], and our own, methods.

The amount of water-soluble substances was determined by extracting the autohydrolyzed wood by boiling 10-20 g of material with 100 ml of distilled water in a flask with a reflux condenser for 30 min. The cooled solid residue was filtered off, washed with water, and dried to constant weight at 105°C, and the amount of water-soluble substances was calculated from the loss in weight with allowance for the moisture content of the initial sample. Mean values were determined from three parallel experiments (agreement 1-2%). The volume of the aqueous extract obtained was measured, and the composition of its organic components was determined.

The amounts of RS and RSI were determined by an ebulliostatic method [10] and were calculated in relation to the concentration of glucose. In the measurement of the RSI, 40 ml of aqueous extract was heated in the boiling water bath with the addition of 1.25 ml of 72% H_2SO_4.

The amounts of the individual true sugars were determined in the form of acetoaldononitriles by GLC as in [11]. The analysis was performed on a Chrom-5 chromatograph using a flame-ionization detector and a glass column (4 mm × 2.0 m) filled with Chromaton 4N-AW-HMDS (0.20-0.25 mm fraction) with the liquid phase XE-60, 5 wt.% (Fig. 2).

The volatile organic compounds in the water-soluble substances were determined by GLC, with the injection of 1-10 μl of the basic working solution into the evaporator of the chromatograph. Analysis was carried out both on the column with

5% XE-60 and with the use of a glass column (4 mm × 2.0 m) containing the phase Separon-BD, 0.125-0.200 mm fraction, at 100-200°C with a programmed rise in temperature (6°C per minute). Helium was used as the carrier gas (Fig. 3).

In the aqueous extracts we also determined low-molecular-mass lignin (degradation products of native lignin having an aromatic nature) using UV spectroscopy. To determine the extinction coefficients of the water-soluble low-molecular-mass lignins, we isolated native lignins using the procedure of [12] and established that the concentration of low-molecular-mass lignin in the solution is determined by the expression:

$$C_{(\mathrm{g/liter})}=0.0515 \bullet D,$$

where D is the optical density of the lignin solution at 280 nm in a cell 10.0 mm thick.

For the quantitative determination of low-molecular-mass lignin, solutions were evaporated to dryness in a rotary evaporator at 60-70°C with the aim of the complete elimination of furfural and its homologs, which distill with steam well. The completeness of their elimination was monitored by GLC. The dry residue was dissolved in a definite volume of distilled water, and the amount of low-molecular-mass lignin was determined by UV spectroscopy on a Shimadzu instrument in cells 10.0 mm thick.

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