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THERMOCATALYTIC TRANSFORMATIONS OF WOOD AND CELLULOSE IN THE PRESENCE OF HCl, HBr, AND H_2SO_4

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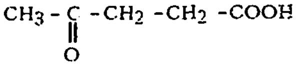
The compositions of the liquid organic products formed from aspen wood and cellulose at 150, 200, and 250°C in the presence of 1, 3, and 5% of HCl, HBr, and H_2SO_4 have been studied. The yield of levulinic acid from wood reached 13.0-15.5%, and from cellulose 28.8%.

The complex utilization of wood and its wastes presupposeses increases both in the variety of valuable chemical substances obtained from it and in the yields of known organic compounds, with a fall in the total cost of their production and a decrease in the amount of ecologically harmful wastes. One of the products the output of which can be organized from wood wastes is acetylpropionic (γ-ketovaleric) or levulinic acid



$$CH_3-\underset{\underset{O}{\|}}{C}-CH_2-CH_2-COOH$$

It is one of the final products of the hydrolytic decomposition of hexose carbohydrates (glucose, fructose, sucrose, cellulose, and other polymeric materials) in the presence of strong mineral acids [1]. Thus, it is reported in patents [2, 3] that the yield of levulinic acid from plant material processing-wastes (maize cobs, oat or rice husks, wood cellulose) in the temperature interval of 150-200°C in the presence of sulfuric acid reaches 10-20% of the weight of the dry material.

When lignocellulose material (wood, straw, bagasse, etc.) is to be used, it is proposed to perform the process in the presence of sulfuric acid in the temperature interval of 160-210°C with the production of furfural and levulinic acid in yields of 8-10% and 12-17%, respectively [4]. A method has been proposed for obtaining levulinic acid from cellulose previously dissolved in the cold in concentrated hydrochloric acid, with a yield of 68% of theoretical [5].

It must be mentioned that in the publications mentioned above only the yield of levulinic acid is given and the composition of the other organic products formed in the process is not reported; furthermore, there are no comparative characteristics on the yields of levulinic acid when other mineral acids are used.

In [6] the composition of the organic products formed from aspen wood under autoclave conditions at 150, 200, and 250°C in the presence of 3% by weight of H_2SO_4 and of Fe, Co, and Al sulfates is given: the liquid products included methanol, isopropanol, furfural, acetic and levulinic acids, and mono- and oligosugars. The yield of levulinic acid was not more than 4.3% in the presence of salts, and 5.6% in the presence of sulfuric acid.

We have studied the compositions and yields of the liquid products of the thermocatalytic transformations of wood and cellulose in the temperature interval of 150-250°C, with variations in the catalyst used (HCl, HBr, and H_2SO_4), in the time of the process, and in the amount of catalyst added to the raw material.

Table 1 gives figures for the conversion of wood and cellulose in the presence of HCl, HBr, and H_2SO_4 at temperatures of 150, 200, and 250°C under autoclave conditions. It can be seen that at 150°C the conversion of wood considerably exceeded the corresponding figure for cellulose. This is understandable in view of the fact that, together with the partial hydrolysis of hexosans of the wood, there is also intensive hydrolysis of its pentosans. Actually, analysis of the solid residues of wood treated under the given conditions at 150°C in the presence of HCl, HBr, and H_2SO_4 showed that the pentosans of the wood had undergone complete conversion into gaseous and liquid products. Intensive decomposition of the hexosans of wood and cellulose

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TABLE 1. Degrees of Conversion of Wood and Cellulose in Thermocatalytic Transformations under Autoclave Condition in the Presence of HCl, HBr, and H_2SO_4 at Temperatures of 150-250°C (in % on the absolutely dry weight of raw material)

Raw material and catalyst	Conversion		
	150°C	200°C	250°C
Wood+1% HCl	37.5	56.3	57.4
Wood+3% HCl	40.3	55.3	57.8
Wood+5% HCl	43.3	56.8	58.2
Wood+1% HBr	37.0	40.1	54.2
Wood+3% HBr	37.8	56.7	58.7
Wood+5% HBr	37.7	55.9	58.0
Wood+1% H_2SO_4	36.4	40.8	55.2
Wood+3% H_2SO_4	36.4	42.9	56.6
Wood+5% H_2SO_4	35.9	57.4	58.0
Cellulose+1% HCl	20.0	68.2	68.4
Cellulose+3% HCl	26.0	70.4	79.2
Cellulose+5% HCl	29.1	79.2	79.6
Cellulose+1% HBr	19.6	58.6	79.6
Cellulose+3% HBr	25.6	77.2	79.4
Cellulose+5% HBr	27.4	78.8	79.8
Cellulose+1% H_2SO_4	16.2	61.2	68.4
Cellulose+3% H_2SO_4	21.7	62.6	67.3
Cellulose+5% H_2SO_4	21.8	69.1	70.2

was observed at 200°C, the hexosans being converted under these conditions into liquid, gaseous, and solid thermolysis products.

It is interesting to note that the conversion of wood at 250°C was practically independent of the nature of the acid used and amounted to 54-58%, while in the case of cellulose its conversion reached 70.2% for H_2SO_4 and 79.8% for HCl and HBr.

It was found by gas-liquid chromatography and ebulliostatic titration that the main liquid products of the thermocatalytic transformations of wood in the presence of the given catalysts under autoclave conditions were methanol, isopropanol, acetic acid, furfural, levulinic acid, and mono- (RV) and oligosugars (RVI). In addition, when water and uncondensable gases were ignored, the products formed consisted mainly of CO and CO_2.

In the case of the thermocatalytic transformations of cellulose, the liquid products were represented by furfural, levulinic acid, and oligosaccharides (Tables 2 and 3).

Analysis of the results obtained shows that the formation of levulinic acid at 150°C from wood in the presence of HBr and H_2SO_4 took place only when 5% of catalyst was added to it, while in the presence of HCl levulinic acid was formed on the addition of 1 and 3%, as well as 5%. Nevertheless, the yield of levulinic acid at 150°C was low, amounting to not more than 3.4% in the presence of 5% of HCl. At the same time, at 150°C the formation of a considerable amount of mono- and oligosaccharides was observed. For example, in the presence of 1 and 3% of HBr the products contained 23.5-26.9% of sugars. This may be evidence in favor of the hypothesis that the main process in the thermocatalytic transformations of wood at 150°C in the presence of HCl, HBr, and H_2SO_4 is the hydrolysis of the wood carbohydrates with the formation of sugars, while the rate of formation of levulinic acid from the sugars is low.

In the case of cellulose, the yield of levulinic acid at 150°C was also low, amounting to 7.1% in the presence of 5% of HCl; however, there were practically no sugars in the products. With a rise in the temperature of the process to 200°C the yield of levulinic acid from the wood rose considerably, with a simultaneous fall in the yield of sugars, the greatest yield of the acid being observed in the presence of 5% of HBr and 5% of H_2SO_4, then amounting to 13.0 and 15.5%, respectively.

The yield of levulinic acid from cellulose also rose appreciably at 200°C and reached a maximum (26.8%) on the addition of 5% of HBr.

A further rise in the temperature of the process increased the yield of levulinic acid when 1 and 3% of catalyst was added to the wood and cellulose but hardly did so on the addition of 5% of catalyst.

When larger amounts of HBr and H_2SO_4 (up to the same molar ratios of raw material to catalyst) were added, the yield of levulinic acid did not increase at low temperatures and decreased at high temperatures. It was established that in the case of H_2SO_4 the yield of levulinic acid falls because of the oxidation of the initial raw material by the acid. This was shown experimentally by the presence of hydrogen sulfide among the reaction products.

It is most likely that when 5% of a mineral acid is added to cellulose, as well as the formation of levulinic acid more far-reaching transformations both of the hexosans of the raw material and, possibly, of the levulinic acid formed take place.

TABLE 2. Yields of Liquid Products of the Thermocatalytic Transformations of Aspen Wood in the Presence of HCl, HBr, and H_2SO_4 under Autoclave Conditions (in % on the initial weight)

Products	1% HBr			3% HBr			5% HBr		
	150°C	200°C	250°C	150°C	200°C	250°C	150°C	200°C	250°C
Methanol	0.2	0.4	0.6	0.3	0.5	0.5	0.3	0.5	0.7
Isopropanol	-	0.4	0.2	-	0.5	0.3	-	0.4	0.3
Furfural	1.6	2.7	0.9	3.3	0.8	0.8	2.0	0.4	0.3
Acetic acid	3.2	3.8	3.7	3.3	4.0	3.7	3.5	4.6	3.3
Mono- and	13.6	14.5	2.8	12.3	7.5	-	11.1	-	-
oligosugars	26.9	20.9	2.9	23.5	9.4	-	11.9	-	-
Levulinic acid	-	1.0	4.8	-	8.6	8.7	0.4	13.0	8.1
	1% HCl			3% HCl			5% HCl		
	150°C	200°C	250°C	150°C	200°C	250°C	150°C	200°C	250°C
Methanol	0.2	0.3	0.4	0.2	0.4	0.5	0.3	0.4	0.6
Isopropanol	-	0.3	0.3	-	0.4	0.3	-	0.5	0.4
Furfural	2.3	2.3	1.0	1.5	0.5	1.1	1.0	0.5	0.4
Acetic acid	3.8	3.7	3.5	3.1	3.7	3.4	3.9	3.6	3.8
Mono- and	0.7	4.5	-	6.7	-	-	9.8	-	-
oligosugars	16.0	10.2	-	7.5	-	-	15.7	-	-
Levulinic acid	0.7	4.5	7.4	0.5	9.7	9.7	3.4	11.3	12.4
	1% H_2SO_4			3% H_2SO_4			5% H_2SO_4		
	150°C	200°C	250°C	150°C	200°C	250°C	150°C	200°C	250°C
Methanol	0.4	0.5	0.5	0.5	0.5	0.6	0.5	0.6	0.7
Isopropanol	-	0.4	0.4	0.3	0.4	0.4	0.4	0.4	0.4
Furfural	0.4	3.4	0.5	0.6	2.8	0.3	2.3	2.2	2.8
Acetic acid	1.7	2.3	2.7	2.2	2.9	3.0	3.9	3.8	3.9
Mono- and	8.6	3.0	-	16.0	5.2	-	12.7	-	-
oligosugars	12.6	6.3	-	16.0	10.2	-	17.3	-	-
Levulinic acid	-	1.1	8.6	-	7.2	9.4	0.8	15.5	13.9

TABLE 3. Yields of Liquid Products of the Thermocatalytic Transformations of Cellulose in the Presence of HCl, HBr, and H_2SO_4 under Autoclave Conditions (in % on the initial weight)

Products	1% HBr			3% HBr			5% HBr		
	150°C	200°C	250°C	150°C	200°C	250°C	150°C	200°C	250°C
Furfural	1.3	1.8	1.3	0.8	0.7	0.6	0.7	0.8	0.8
Mono- and	5.0	41.8	11.8	-	-	-	-	-	-
oligosugars	5.2	11.8	13.5	-	-	-	-	-	-
Levulinic acid	1.0	6.0	11.5	1.8	24.9	26.9	2.6	26.8	22.0
	1% HCl			3% HCl			5% HCl		
	150°C	200°C	250°C	150°C	200°C	250°C	150°C	200°C	250°C
Furfural	0.3	0.3	-	-	0.7	-	-	0.8	0.6
Mono- and	-	-	-	-	-	-	-	-	-
oligosugars	-	-	-	-	-	-	-	-	-
Levulinic acid	-	12.2	12.5	-	18.9	28.8	7.1	21.5	21.9
	1% H_2SO_4			3% H_2SO_4			5% H_2SO_4		
	150°C	200°C	250°C	150°C	200°C	250°C	150°C	200°C	250°C
Furfural	2.2	2.4	0.8	3.3	0.4	-	2.3	2.6	0.5
Mono- and oligosugars	0.8	6.8	-	0.6	9.7	-	1.2	9.2	-
Levulinic acid	-	18.2	23.2	-	22.1	25.2	3.6	23.6	24.8

In the light of this, it may be concluded that the maximum yield of levulinic acid from wood and cellulose must be expected in the temperature interval of 200-250°C by varying the amount of mineral acid used from 3 to 5% and also by changing the time of the process and the liquor ratio of the reaction mixture.

EXPERIMENTAL

We used aspen wood ground to dimensions of 0.5-2.0 mm and pure cellulose from the Krasnoyarsk Pulp and Paper Combine containing 99.6% of the main substance. According to chemical analysis performed in accordance with [7], the wood contained (%): cellulose, 45.7; pentosans, 24.5; lignin, 21.8; uronic acids, 6.3; and water-soluble substances 1.4. As catalysts for the process we used the mineral acids HCl, HBr, and H_2SO_4 of kh.ch. [chemically pure] grade.

Amounts of 8-10 g of wood and cellulose dried at 105°C were impregnated with an aqueous solution of catalyst in proportions of 1, 3, and 5% of anhydrous catalyst on the weight of the raw material, the ratio of the weight of raw material to the weight of the solution being 1:10.

After the addition of the catalyst, the raw material, in a titanium autoclave with a volume of 120 cm^3, was placed in a gradientless furnace controlled by a RIF-101 thermoregulator with an error of maintaining a given temperature of 1°C. Catalytic thermolysis was carried out in the temperature interval of 150-250°C, the time of the process being 7 h at 150°C, 4 h at 200°C, and 2 h at 250°C. After the end of the reaction, the autoclave was cooled to 20°C, and the solid residue was filtered off and washed with distilled water. The conversion of the initial raw material was determined from the loss in weight of the original sample, and the liquid phase obtained was analyzed for its content of organic products by gas-liquid chromatography, as in [8, 9]. The amount of mono- and oligosugars in the aqueous phase was determined by Felling's method of ebulliostatic titration [7] and were calculated as glucose.

REFERENCES

1. B. M. Levitin, Levulinic Acid, its Properties, Production, and Use [in Russian], ONTiTÉI Mikrobioprom, Moscow, Ser. 3 (1976).
2. A. P. Dunlap and P. A. Wells, US Patent No. 2813900 (1957).
3. R. H. Leonard, US Patent No. 2840605 (1958).
4. E. Ramos-Rodrigues, US Patent No. 3701789 (1970).
5. A. V. Fomichev, S. Ya. Livshits, R. G. Kasimov, V. I. Chirtsov, N. N. Vdovenko, A. M. Mezheritskii, and S. M. Yudin, USSR Inventors' Certificate 249364 (1969); Byull. Izobret., No. 25 (1969).
6. A. A. Efremov, G. A. Slashchinin, E. D. Korniets, and B. N. Kuznetsov, Khim. Drev., No. 5, 57 (1990).
7. A. V. Obolenskaya, V. P. Shchegolev, G. L. Akim, É. L. Akim, N. P. Kossovich, and I. Z. Emel'yanova, Practical Work in the Chemistry of Wood and Cellulose [in Russian], Moscow (1965).
8. A. A. Efremov, B. N. Kuznetsov, S. A. Kuznetsova, I. V. Krotova, and V. A. Vink, Khim. Prir. Soedin., 20 (1995).
9. A. A. Efremov, A. P. Konstantinov, and B. N. Kuznetsov, Zh. Anal. Khim., **49**, No. 8, 822 (1994).