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PRODUCTION OF LEVULINIC ACID FROM WOOD RAW MATERIAL IN THE PRESENCE OF SULFURIC ACID AND ITS SALTS

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The catalytic activities of sulfuric acid and of cobalt(II), iron(III), and aluminum sulfates in the thermal splitting of the cellulose and wood of various species in the presence of superheated steam at 250-350°C under flow conditions and at 150-250°C under autoclave conditions have been studied. The yield of levulinic acid from cellulose reaches 35 wt-% and from wood 16.0-18.0 wt-%.

At the present time, great interest is being aroused by the use of lignocellulosic materials as the initial source for the production of valuable organic substances. One of such products is acetylpropionic, or levulinic, acid, which finds wide use in the cosmetic, food, and medicinal industries [1].

Levulinic acid is one of the end-products of the hydrolytic decomposition of hexose carbohydrates in the presence of catalysts of the acid type under autoclave conditions. It has been proposed to use both strong mineral acids [2] and aqueous solutions of their salts [3] as catalysts. The use of aqueous solutions of salts forming ions of alkali metals and aluminum — the chlorides and sulfates — has increased the yield of levulinic acid to 19% [3].

We have previously [2] discussed the catalytic activity of the strong mineral acids HCl, HBr, and H_2SO_4 in the formation of levulinic acid from aspen wood and cellulose. It was shown that the most active among the catalysts studied is H_2SO_4, which ensures levulinic acid yields of about 16 and 28.8% from the wood and the cellulose, respectively.

In the present work we have compared the catalytic activities of H_2SO_4 and Co, Fe, and Al sulfates in the formation of levulinic acid from cellulose and have investigated the yields of levulinic acid from the woods of birch, aspen, pine, and fir* in the presence of the most active catalyst, H_2SO_4.

The formation of levulinic acid from lignocellulosic material is a complex and multistage process. It is generally accepted that levulinic acid is formed directly from hydroxymethylfurfural [1], which is obtained in the dehydration of glucose — a product of the acid cleavage of the hexosans of the raw material. However, the formation of hydroxymethylfurfural from glucose includes stages of the dehydration of glucose with the splitting out of three molecules of water, while, as is known, the incomplete dehydration of glucose leads to the formation of levoglucosenone [4].

Thus, levoglucosenone and hydroxymethylfurfural may be precursors of the formation of levulinic acid, and, as has been shown in [5], levoglucosenone is actually converted into levulinic acid with a yield of about 80%. The formation of levulinic acid from hexosan-containing raw material takes place at elevated temperatures and pressures. As a rule, when the process is performed without pressure in continuous flow regimes no levulinic acid is formed from wood and only very small amounts from cellulose (Table 1).

The main products of the cleavage of cellulose under continuous-flow conditions are furfural, levoglucosenone, hydroxymethylfurfural, levulinic acid, and a sugar (RV and RVI). The most active of the catalysts studied in this case was $CoSO_4$. The highest yield of all the main liquid products was observed in its presence. The high yield of sugars, levoglucosenone, and hydroxymethylfurfural in thermocatalytic transformations of cellulose under conditions of continuous flow

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*Spruce, according to Table 3 and the experimental part — Translator.

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TABLE 1. Yields of Liquid Products in Thermocatalytic Transformations of Cellulose under Continuous-Flow Conditions, wt.-% on Absolutely Dry-Cellulose

Product	Without catalyst			H_2SO_4			$Fe_2(SO_4)_3$			$CoSO_4$			$Al_2(SO_4)_3$		
	Temperature, °C														
	250	300	350	250	300	350	250	300	350	250	300	350	250	300	350
Isopropanol	–	–	0.1	–	–	0.1	–	0.2	0.1	–	–	0.2	–	0.2	-0.2
Acetone	–	–	0.1	–	–	0.1	–	0.2	0.1	–	–	0.2	–	0.1	0.1
Furfural	1.3	1.5	1.5	3.2	3.0	2.8	5.5	3.4	2.8	5.5	5.2	4.6	3.3	1.8	3.0
Levoglucosenone	0.9	1.3	0.7	1.8	1.1	2.7	6.9	8.4	6.5	6.9	7.7	8.7	3.0	4.5	7.0
Hydroxymethyl-furfural	–	0.9	1.8	0.5	0.6	0.9	1.0	–	–	1.0	1.0	1.6	–	0.3	–
Levulinic acid	–	1.2	0.5	2.3	–	–	1.5	–	–	1.5	1.4	1.3	1.1	0.6	–
RVI	12.0	13.2	–	5.4	4.4	5.6	13.1	10.5	7.2	13.1	15.1	9.6	5.3	6.7	11.2
including RV	–	–	–	3.7	3.8	0.9	13.1	5.5	4.7	13.1	15.1	9.6	5.3	5.0	4.7
Degree of conversion of the cellulose, %	41.3	75.3	69.9	52.7	65.8	66.7	50.4	64.2	68.7	48.2	61.9	70.2	50.7	65.3	65.4

TABLE 2. Yields of Liquid Products in Thermocatalytic Transformations of Cellulose under Autoclave Conditions, wt.-% on Absolutely Dry Cellulose

Product	Without catalyst			H_2SO_4			$Fe_2(SO_4)_3$			$CoSO_4$			$Al_2(SO_4)_3$		
	Temperature, °C														
	150	200	250	150	200	250	150	200	250	150	200	250	150	200	250
Isopropanol	–	2.5	2.1	3.3	0.4	–	0.6	1.6	0.2	–	1.1	0.8	0.8	0.3	0.1
Levoglucosenone	–	0.3	–	–	–	–	–	0.4	–	–	0.2	0.5	–	–	–
Hydroxymethyl-furfural	–	0.3	2.1	–	–	–	–	1.1	–	–	0.3	1.0	–	0.2	–
Levulinic acid	–	–	0.6	–	22.1	25.2	–	1.8	4.7	–	–	–	–	16.6	18.4
RVI	0.6	9.7	–	–	–	–	3.9	10.1	–	0.7	4.3	–	3.8	6.4	–
including RV	0.4	8.7	–	–	–	–	6.0	10.1	–	0.5	4.2	–	3.7	6.4	–
Degree of conversion of the cellulose, %	0.0	14.5	23.8	21.7	62.6	67.3	1.2	26.7	52.9	0.0	11.0	19.3	6.4	58.1	58.6

TABLE 3. Yield of Levulinic Acid from Wood by Thermocatalytic Transformations in the Presence of 5% of H_2SO_4 as Functions of the Temperature and the Solid/Liquid Ratio of the Reaction Mixture, wt.-% on the Absolutely Dry Weight

Temperature, °C	Beech		Aspen		Pine		Spruce	
	liquor ratio	yield	liquor ratio	yield	liquor ratio	yield	liquor ratio	yield
200	1:5	16.3	1:5	15.5	1:5	14.6	1:5	13.2
	1:5	16.5	1:5	15.7	1:5	15.3	1:5	13.4
	1:10	16.2	1:10	15.7	1:10	15.8	1:10	13.4
240	1:5	17.2	1:5	15.6	1:5	15.4	1:5	14.6
	1:5	17.3	1:5	15.8	1:5	15.6	1:5	15.3
	1:10	17.8	1:10	16.0	1:10	16.0	1:10	15.6

TABLE 4. Chemical Composition of the Initial Wood, % of the Initial Weight

Wood	Cellulose	Hemicelluloses and uronic acids	Lignin	Extractive substances
Pine	52.2	13.5	26.3	7.6
Fir	50.3	15.4	27.7	6.8
Aspen	46.3	24.5	21.8	7.8
Beech	48.5	24.0	23.9	2.5

shows that in this case their secondary transformations cannot take place completely because of the removal of the above-mentioned compounds from the reaction zone.

Experiments performed with $CoSO_4$ and $Fe_2(SO_4)_3$ in a continuous-flow regime in the temperature interval of 250-350°C at pressures of from 5 to 20 atm. showed that the maximum yield of levulinic acid amounted to 10 wt.-%.

The same yield of levulinic acid (10-12 wt.-%) can be achieved if the solutions obtained in continuous-flow conditions are heated to 250°C under autoclave conditions. Then the products formed are present in the reaction zone during the whole of the process and the occurrence of secondary reactions involving the successive transformations of levoglucosenone and hydroxymethylfurfural into levulinic acid is possible.

In actual fact, analysis of the products formed in the thermocatalytic transformations of cellulose under autoclave conditions in the presence of the same catalysts has shown that in this case levoglucosenone and hydroxymethylfurfural are formed in only small amounts, and the main product is levulinic acid. Its yield is a maximum on the use of H_2SO_4 and $Al_2(SO_4)_3$ (Table 2).

On the basis of the results obtained, we have made an attempt to optimize the yield of levulinic acid while using sulfuric acid as catalyst. Supplementary investigations showed that the maximum yield of levulinic acid is achieved (in 4 h at 230°C) when 3 wt.-% of H_2SO_4 is added to cellulose (at 230°C for 4 h) and amounts to 35.1% on the weight of absolutely dry cellulose.

Since sulfuric acid is the most active catalyst for the production of levulinic acid, it appeared of interest to determine its yield from the woods of various tree species.

It was established by physicochemical methods of analysis (GLC, ^1H and ^{13}C NMR, and others) that the main liquid products of the thermocatalytic transformations of aspen, pine, fir, and beech woods in the presence of H_2SO_4 were methanol, isopropanol, acetic acid, furfural, levulinic acid, and mono- and oligosugars. We may note that in the products formed no account has been taken of water and uncondensable gases, represented mainly by CO and CO_2.

As can be seen from the facts given, the yield of levulinic acid depends on the temperature of the process and is practically independent of the type of raw material used and on the solid/liquid ratio of the reaction mixture, between 1:5 and 1:10 (Table 3). The maximum yield of levulinic acid from wood amounted to 16.0-18.0 wt.-%.

Thus, as a result of the investigations performed we have found the optimum conditions for performing thermocatalytic transformations of cellulose and the wood of various species in autoclave reactors. The maximum yield of levulinic acid, 35.1 wt.-%, was obtained at a reaction temperature of 230°C with the addition of 3 wt.-% of H_2SO_4. When the wood of various species was used as the raw material, the highest yield of levulinic acid amounted to 16.0-18.0 wt.-% at a process temperature of 240°C with the addition of 5 wt.-% of H_2SO_4 to the initial raw material.

EXPERIMENTAL

As the initial raw material we used aspen, beech, spruce, and pine woods (Table 4) ground to a particle size of 0.5-2.0 mm, and 99.6% pure cellulose from the Krasnoyarsk Pulp and Paper Combine. The raw material was dried at 105°C to constant weight. The investigations were performed both in the absence of catalysts and in the presence of H_2SO_4 and Co(III), Fe(III), and Al sulfates.

Thermocatalytic Transformations of Cellulose under Continuous-Flow Conditions. The dried raw material was impregnated with 3 wt.-%, on the absolutely dry cellulose, of the catalyst calculated as H_2SO_4 or as anhydrous sulfate, the ratio of the weight of raw material to the weight of solution being 1:2.5-3.0. After impregnation the cellulose was dried at 25°C for a day and was charged into a titanium reactor. The process was carried out in the temperature interval of from 250 to 350°C at a rate of feed of steam of 4-5 liters/min. The time of the process was monitored by the GLC of the hydrolysate until the evolution of volatile liquid products ceased, and amounted to 1-2.5 h.

Thermocatalytic Transformations under Autoclave Conditions. Wood and cellulose in 8- to 10-g batches were impregnated with aqueous solutions of catalysts in calculated amounts of 1, 3, and 5%, as anhydrous catalyst, on the absolutely dry weight of the raw material, the ratio of the weight of raw material to the weight of the solution (liquor ratio of the process) being 1:5-1:10. After the addition of the catalyst, the raw material was charged into a 120-cm^3 titanium autoclave which was then placed in a gradientless furnace controlled by a RIF-101 thermoregulator capable of maintaining the given temperature to within 1°C. Catalytic thermolysis was carried out at 150-250°C. The time of the process was 7 h at 150°C, 4 h at 200°C, and 2 h at 250°C.

After the end of the reaction, the contents of the autoclave were worked up by the procedure given in [2].

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