ISSN 0023-1584, Kinetics and Catalysis, 2008, Vol. 49, No. 4, pp. 517–526. © MAIK “Nauka/Interperiodica” (Russia), 2008.
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III INTERNATIONAL CONFERENCE
“CATALYSIS: FUNDAMENTALS AND APPLICATIONS”

New Catalytic Methods for Obtaining Cellulose and Other Chemical Products from Vegetable Biomass

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Received October 12, 2007

Abstract—Experimental data concerning the effects of catalysts are discussed for the oxidative destruction of wood lignin in the acetic acid–hydrogen peroxide–water medium, for lignin oxidation with oxygen into aromatic aldehydes in aqueous alkali, for the acid-catalyzed conversion of carbohydrates into esters of levulinic acid and 5-hydroxymethylfurfural in the two-phase system butanol–water, and for α-angelicalactone polymerization into biodegradable polymers.

DOI: 10.1134/S0023158408040101

Vegetable biomass is a continuously renewable source of organics. The most abundant vegetable polymers are polysaccharides and lignin [1, 2]. In particular, wood contains up to 50% cellulose (hereafter, all concentrations are expressed in weight percent), which is a linear polysaccharide built from $C_6H_{10}O_5$ units. Some kinds of wood contain increased amounts of hemicelluloses, which are branched polysaccharides consisting largely of C_5 units linked into chains shorter than the cellulose chains. The vegetable biomass component next in significance to cellulose is lignin, whose amount in wood can be as large as 30%. Lignin is an irregular, essentially aromatic polymer consisting of phenylpropane fragments.

The present-day wood processing industry consists mainly of pulp-and-paper, hydrolysis, and wood chemical plants.

Wood is delignified to produce cellulose, which is then converted into its derivatives, artificial fibers, and paper [3]. Hydrolysis processes yield cellulose and xylose, which are further processed into ethanol, xylitol, furfural, its derivatives, and organic acids [4, 5]. Extraction technologies are used to obtain tanning agents, essential oils, and biologically active compounds [6].

The conventional commercial technologies used in the deep processing of wood suffer from low capacity, are oriented towards a limited range of products, and are environmentally hazardous.

Promising approaches to the problem of improving the production of cellulose and other chemical products from vegetable biomass are to develop high-performance catalysts and to employ environmentally friendly reagents (oxygen and hydrogen peroxide) and organic and aqueous–organic media [7, 8].

Below, we will consider some advances in the catalytic conversion of vegetable carbohydrates and lignin, illustrating them by recent studies performed at the Institute of Chemistry and Chemical Technology, Siberian Branch, Russian Academy of Sciences.

CATALYTIC DESTRUCTION OF LIGNIN

The main avenue of the chemical processing of wood is cellulose production. The conventional technologies of the pulp-and-paper industry consume high-quality wood and cause damage to the environment by producing sulfur- and chlorine-containing delignifier waste.

Commercial-grade celluloses are usually obtained by the sulfate [9] and sulfite [10] methods and by their modifications [1].

The radically new, environmentally friendly cellulose technologies being developed are based on organic solvent (solvolysis) delignification [11] and on the oxidative delignification of wood with oxygen in a sodium hydroxide or carbonate medium (oxygen–alkali and oxygen–soda delignification) [12]. The advantages of wood delignification with environmentally friendly chemicals, such as dioxygen and hydrogen peroxide, are the absence of smelly sulfur-containing waste gases, the low toxicity of wastewater, and the comparatively whiteness of the resulting cellulose. The last advantage obviates the need for cellulose bleaching with harmful chlorine-containing substances.

The literature contains information concerning the catalytic delignification of wood in a CH_3COOH–H_2O_2 medium at high acetic acid and hydrogen peroxide concentrations [13]. This study was aimed at finding process conditions for efficient lignin destruction

Table 1. Percentages of the main components in the wood species examined

Wood species	Composition, % (of the ADW* weight)			
	cellulose	lignin	hemicelluloses and uronic acids	extractable substances
Common aspen (*Populus tremula* L.)	46.3	21.8	24.5	7.8
Silver birch (*Betula pendula* Roth.)	41.3	19.9	30.3	8.4
Siberian fir (*Abies sibirica* Ledeb.)	50.3	27.7	15.4	6.8
Siberian larch (*Larix sibirica* Ledeb.)	34.5	26.1	27.2	13.0

* ADW, absolutely dry wood.

Table 2. Effects of the fir sawdust delignification temperature and duration on the yield and composition of the fibrous product

Temperature, °C	Process duration, h	Yield of the fibrous product, %*	Cellulose content of the product, %**	Lignin content of the product, %**
120	2	53.6	68.6	8.7
	3	46.2	72.2	4.9
130	2	46.1	77.3	4.7
	3	40.9	82.9	2.5
140	2	36.4	82.7	3.4
	3	32.8	80.0	2.9

Note: Processing conditions: initial concentrations of C_{CH_3COOH} = 23.6%, $C_{H_2O_2}$ = 6.4%, and $C_{H_2SO_4}$ = 2%; WWR = 15.

* Percent of the ADW weight.

** Percent of the absolutely dry fibrous product weight.

with dilute solutions of these delignifying agents (the CH_3COOH and H_2O_2 concentrations were 23.6–25.8 and 4.2–6.4%, respectively).

In order to accelerate wood delignification in this medium, we used the solid catalyst TiO_2 along with the dissolved acid (H_2SO_4) and redox (H_2MoO_4, $Fe_2(MoO_4)_3$) catalysts.

The raw materials were typical Siberian wood species, namely, aspen, birch, fir, and larch. Table 1 lists the percentages of the main components in these wood species.

The chemical composition and the structure of the fibrous products of oxidative delignification were studied by elemental and chemical analyses, x-ray diffraction, and FTIR.

In order to reduce the diffusion limitations, the effects of catalysts on delignification were studied at large water/wood ratios (WWR = 10–15) using wood sawdust (5 × 2 × 0.5 mm fraction). The composition and yield of fibrous products were controlled by varying the catalyst, its concentration, the wood species, and delignification conditions (temperature, reaction medium composition, water duty, and process duration). The studies have demonstrated that, for all of the wood species, the concentration of the sulfuric acid catalyst in the delignifying solution should be at least 1.5–2% of the absolutely dry wood (ADW) weight in order to obtain high-quality cellulose with a low residual lignin content in high yield.

It was found that, as the temperature is raised, the cellulose content of the fibrous content increases and the residual lignin content decreases (Table 2). At the same time, the yield of the fibrous product decreases because the oxidative destruction of lignin, hemicelluloses, and the amorphous part of cellulose are accelerated with an increasing temperature. Similar regularities are observed when the initial hydrogen peroxide concentration in the delignifying solution is increased from 2.0 to 10.2%. The residual lignin content of the fibrous product decreases as the acetic acid concentration in the delignifying solution is increased.

Replacing the sulfuric acid catalysts with soluble redox catalysts (H_2MoO_4 or $Fe_2(MoO_4)_3$) in wood delignification allows the catalyst concentration to be reduced to 0.5% (Table 3).

The effect of the H_2MoO_4 catalyst concentration on the yield and composition of the fibrous product of larch wood delignification is illustrated by the data presented in Table 4. The best quality cellulose (with a lignin content of about 0.5%) is obtained at a catalyst concentration of 0.5–0.7% of the ADW weight. The cellulose yield at this catalyst concentration is rather high (41.5–44.0% of the ADW weight).

It was demonstrated for the first time that high-quality cellulose can be obtained from wood in one step in an acetic acid–hydrogen peroxide medium in the presence of the solid catalyst TiO_2 [14, 15]. An advantage of the TiO_2 catalyst over H_2SO_4 is its higher delignifying activity, which allows its concentration in the reaction mixture to be reduced. Furthermore, TiO_2 is noncorrosive and environmentally nonhazardous.

As follows from our data, the catalysts TiO_2 (0.5%) and H_2SO_4 (2%) show comparable delignifying activities. Delignification at 120°C for 3 h in the presence of TiO_2 affords lignin-free cellulose in 50.5% yield.

The basic regularities of wood delignification in the presence of the TiO_2 catalyst are fairly similar to those observed for the sulfuric acid and molybdenum soluble catalysts. The delignifying activity of the redox catalysts (H_2MoO_4 and TiO_2) is higher than the activity of the dissolved acid catalyst H_2SO_4.

We have optimized the hardwood and softwood delignification conditions for obtaining low-lignin cellulose in an acceptable yield of 44–48%.

Cellulose containing <1% residual lignin can be obtained in 47–50% yield from aspen and birch wood in the presence of 2.0% H_2SO_4 [16, 17].

In order to obtain high-quality cellulose from fir or larch wood, which is richer in lignin than aspen or birch wood, it is necessary to use more active catalysts, such as TiO_2 and H_2MoO_4, and an initial hydrogen peroxide concentration of at least 6.4% (Table 5).

The spent liquor contains various compounds resulting from the oxidative destruction of lignin and polysaccharides [18]. The variation of the chemical composition of the spent liquor is due to the presence of considerable amounts of pentoses and arabinogalactan in birch and larch wood, respectively, and the domination of syringyl and guaiacyl fragments in birch and larch lignin, respectively. The regenerated liquor can be reused in delignification. There are prospects for chemical processing of low-molecular-weight lignin isolated from the liquor and for its use in phenol formaldehyde resin production.

When discussing possible routes of catalytic wood delignification in the acetic acid–hydrogen peroxide–water medium, it is necessary to take into account that different homolytic and heterolytic reactions involved in the oxidative destruction of lignin can take place simultaneously [19, 20].

Table 3. Effects of the nature of the catalyst on the yield and composition of the fibrous product of larch wood delignification

Catalyst	Yield of the fibrous product, %*	Composition of the product, %**	
		cellulose	lignin
H_2SO_4 (2.0%)	38.6	80.3	3.8
H_2MoO_4 (0.5%)	40.0	83.4	absent
$Fe_2(MoO_4)_3$ (0.5%)	39.2	76.4	2.0

Note: Processing conditions: T = 130°C, WWR = 15, τ = 2 h, $C_{H_2O_2}$ = 6.4%, C_{CH_3COOH} = 23.6%.

* Percent of the ADW weight.

** Percent of the absolutely dry product weight.

Table 4. Effects of the H_2MoO_4 catalyst concentration on the yield and composition of the fibrous product of larch wood delignification

H_2MoO_4 concentration in the solution, %*	Yield of the fibrous product, %*	Cellulose content of the product, %**	Lignin content of the product, %**
0.3	45.2	78.2	7.3
0.5	44.0	80.9	0.6
0.7	41.5	81.6	0.4
1.0	41.6	82.4	1.6

Note: Processing conditions: T = 130°C, $C_{H_2O_2}$ = 6.4%, C_{CH_3COOH} = 23.6%, WWR = 10, τ = 2 h.

* Percent of the ADW weight.

** Percent of the absolutely dry fibrous product weight.

The totality of our data and the data known from the literature suggest that the oxidative destruction of lignin in the acetic acid–hydrogen peroxide–water medium in the presence of the above catalysts is dominated by the homolytic route. These catalysts initiate hydrogen peroxide decomposition yielding hydroxyl and peroxyl radicals. These radicals are known to be effective oxidative destructors of lignin via the homolytic mechanism. It is likely that dissolved H_2SO_4 and H_2MoO_4 execute their catalytic action through adsorption on functional groups of lignin. Characterization of metal complexes with model lignin compounds demonstrated that catalytically active metal ions bind to lignin through its hydroxyl and methoxyl groups [21, 22].

In the case of the solid catalyst TiO_2, an indirect catalytic route is possible. The key feature of this mechanism is that the hydroxyl and peroxyl radicals resulting from H_2O_2 decomposition on the TiO_2 surface diffuse into the liquid reaction medium and then to the wood particle surface to execute the oxidative destruction of lignin according to the scheme presented in Fig. 1.

Table 5. Processing conditions for obtaining low-lignin cellulose from various wood species

Wood species	Optimum delignification conditions	Yield of the fibrous product, %*	Cellulose content of the product, %**	Lignin content of the product, %**
Aspen	$C_{H_2SO_4} = 2\%$, $C_{H_2O_2} = 4.2\%$, $C_{CH_3COOH} = 25.8\%$, $T = 130°C$, WWR = 10, $\tau = 3$ h	48.8	79.3	0.8
Birch	$C_{H_2SO_4} = 2\%$, $C_{H_2O_2} = 4.2\%$, $C_{CH_3COOH} = 25.8\%$, $T = 130°C$, WWR = 10, $\tau = 3$ h	47.3	80.9	0.9
Fir	$C_{TiO_2} = 0.5\%$, $C_{H_2O_2} = 6.4\%$, $C_{CH_3COOH} = 23.6\%$, $T = 130°C$, WWR = 15, $\tau = 3$ h	48.4	89.5	0.8
Larch	$C_{H_2MoO_4} = 0.5\%$, $C_{H_2O_2} = 6.4\%$, $C_{CH_3COOH} = 23.6\%$, $T = 130°C$, WWR = 10, $\tau = 2$ h	44.0	80.9	0.6

* Percent of the ADW weight.
** Percent of the absolutely dry fibrous product weight.

The dependence of the quality of the fibrous product on the kind of the initial wood under fixed delignification conditions is due to wood species differing in lignin content. In order to obtain a low-lignin fibrous product from lignin-rich wood (fir or larch), it is necessary to use a more active catalyst and a higher hydrogen peroxide concentration. The effect of the wood density on the quality of the fibrous product, which is clearly observed for large wood chips (20 × 11 × 0.5 mm), is less pronounced for smaller chips (5 × 2 × 0.5 mm) at large WWR values in the delignification process.

The low-lignin fibrous products obtained by the catalytic delignification of wood under the conditions examined can be converted into microcrystalline cellulose (MCC) and thermoreversible gels.

Microcrystalline cellulose is prepared by modifying natural cellulose by means of hydrolytic destruction. It is widely used in medicine; the pharmaceutical, food, chemical, cosmetic, and fragrance industries; thin-layer chromatography; sorbent production; and other applications [23, 24].

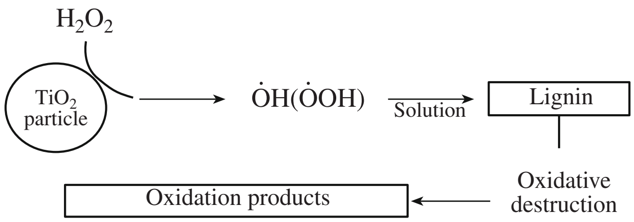

Fig. 1. Oxidative destruction of lignin in the presence of the solid catalyst TiO_2.

Natural cellulose consists largely of defective crystals linked by amorphous interlayers. After the amorphous part of cellulose is removed by hydrolysis, the remaining crystalline part is disintegrated by mechanical and ultrasonic treatments in a hydroxyl-containing medium into particles retaining the initial degree of crystallinity and narrow size distribution. The degree of crystallinity of MCC resulting from hydrolysis is below 100% and is 80% for cotton MCC and 65–70% for wood MCC [24].

The manufacture of MCC from wood cellulose is a multistep and resource-intensive process. Furthermore, it is environmentally hazardous because it employs hazardous chemicals at the cellulose production, bleaching, and acid treatment stages.

The MCC production technology developed at the Institute of Chemistry and Chemical Technology (Siberian Branch, Russian Academy of Sciences, Krasnoyarsk) includes obtaining a fibrous product by the catalytic delignification of wood sawdust in an acetic acid (23.6–25.8%)–hydrogen peroxide (4.2–6.4%) medium, which is followed by finishing delignification in an acetic acid–hydrogen peroxide medium in the absence of a catalyst [25, 26].

The dependence of the MCC yield and degree of polymerization on the MCC preparation conditions for different kinds of wood sawdust is illustrated by the data listed in Table 6. The unit cell of the MCC crystals obtained from birch, aspen, larch, and fir sawdust is identical to the monoclinic unit cell of cellulose I (Fig. 2). The crystallinity indices derived from X-ray diffraction data for birch, aspen, fir, and larch MCC

Table 6. Effects of processing condition on the yield and degree of polymerization of MCC produced from wood sawdust

Wood (catalyst)	Delignification stage						MCC yield, %*	DP** of MCC
	catalytic			finishing				
	T, °C	WWR	τ, h	T, °C	WWR	τ, h		
Aspen (H_2SO_4, 2.0%)	120	12	2.0	120	15	2.0	30.5	127
	130	15	2.0	100	15	1.0	31.7	218
Birch (H_2SO_4, 2.0%)	120	15	2.5	120	10	2.0	31.6	94
	120	15	3.0	120	10	1.5	22.4	146
Fir (TiO_2, 0.5%)	130	15	2.0	120	15	1.0	35.4	246
	130	15	2.0	120	15	2.0	31.0	140
Larch (H_2MoO_4, 0.5%)	120	15	3.0	130	15	2.0	31.2	152

* Percent of the ADW weight.
** DP = degree of polymerization.

samples (0.65–0.74) are similar to the crystallinity index of commercial MCC (0.64–0.80).

Thus, the catalytic organosolvent delignification of wood affords cellulose with a very low residual lignin content. It is, therefore, possible to replace the comparatively expensive cellulosic and cotton materials with cheap wood sawdust in MCC production.

The advantage of MCC production from wood sawdust over the conventional technologies are the low cost of the sawdust; the smaller number of processing steps; the higher purity of the product; and the nonuse of environmentally hazardous chemicals, such as sulfur and chlorine compounds and mineral acids.

The oil recovery of wells is commonly enhanced by using thermoreversible gels. These gels are mostly based on methylcellulose, which is produced from chemically pure cellulose. The comparatively high cost and the limited output of the latter pose the challenging problem of developing new methods for obtaining gelating agents with the desired combination of properties from more widely available and cheaper materials, such as lignocellulose waste.

The method that we developed for obtaining thermoreversible gels from aspen sawdust includes catalytic delignification with an acetic acid–hydrogen peroxide–water mixture in the presence of 2.0% H_2SO_4 as the catalyst, the alkaline processing (mercerization) of the fibrous product using a NaOH solution, and the methylation of the mercerized product with liquid methyl chloride [27]. We studied the chemical reactions that take place in these processing steps and found the processing conditions ensuring the highest yield of the methylated products soluble in cold water. The cold water–soluble methylated products obtained from aspen, whose yield was up to 98% of the ADW weight, undergo gelation upon heating. The properties of the resulting gels are similar to the properties of the commercial low-viscosity methylcellulose MTs-8.

CATALYTIC OXIDATION OF LIGNIN WITH OXYGEN IN AN ALKALINE MEDIUM

Owing to the aromatic nature of vegetable lignin, its oxidative and reductive destruction yields a variety of aromatic and phenolic compounds [2]. The most valuable lignin destruction products are presented in Fig. 3.

Vanillin forms from softwood lignin, while the oxidation of hardwood lignin yields a mixture of syringaldehyde and a minor amount of vanillin.

Aromatic aldehydes are valuable starting chemicals for the pharmaceutical, food, and fragrance industries [28, 29]. For example, vanillin is used in the manufacturing of Papaverine, Ftivazide, and L-DOPA [30]. The presence of reactive functional groups in vanillin allows it to be converted into biologically active derivatives possessing antiseptic, bactericide, and antioxidant properties [31, 32]. Syringaldehyde can be used in the manufacturing of Trimethoprim, Bactrim, Biseptol, and other drugs [33].

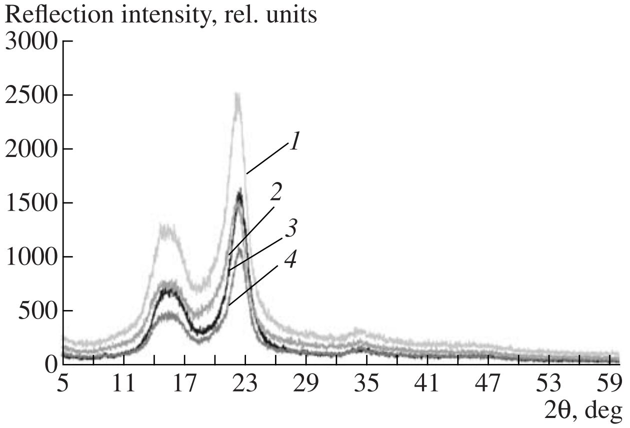

Fig. 2. X-ray diffraction patterns from MCC obtained from (*1*) birch, (*2*) larch, (*3*) aspen, and (*4*) fir wood.

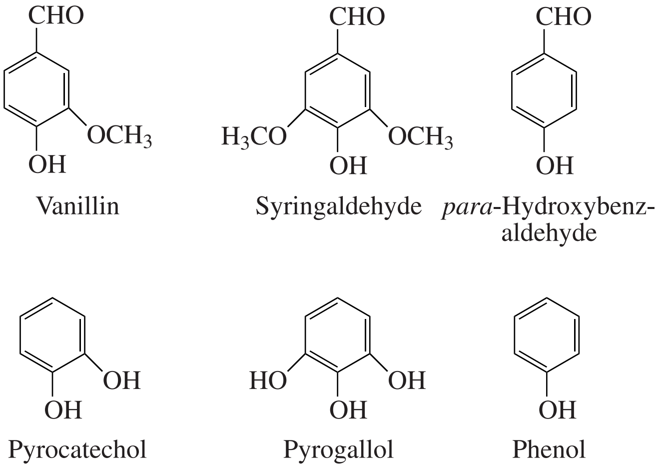

Fig. 3. Some low-molecular-weight compounds obtained by wood lignin destruction.

The nitrobenzene process affords a high aromatic aldehyde yield very similar to the theoretically possible yield for the lignin structure. This process can be used as a reference to evaluate the selectivity of any lignin oxidation process yielding aromatic aldehydes.

The oxidation of lignosulfonates with nitrobenzene into vanillin was carried out as early as the 1930s. However, the high toxicity of nitrobenzene and its reduction products prompts researchers to look for other efficient oxidation systems for obtaining aromatic aldehydes.

Oxidation with dioxygen, though less selective than the nitrobenzene process, is technologically more attractive. Its lower selectivity is primarily due to the considerable contribution from side reactions of free-radical chain oxidation [34, 35].

The aldehyde yield in lignin oxidation with dioxygen can be increased by using some catalysts. Earlier, we attempted the synthesis of syringaldehyde and vanillin by the catalytic oxidation of wood with dioxygen in a flow reactor [36]. A comparison between the total aldehyde yields in this process (35% of the lignin weight) and in the nitrobenzene process (43% of the lignin weight) indicates that the selectivity of the catalytic oxidation of wood lignin with dioxygen in a flow reactor in the presence of a copper catalyst can be as high as 80% of the selectivity of the nitrobenzene process.

Still higher aldehyde yields were achieved by the catalytic oxidation of birch wood with dioxygen in a tilting batch reactor (13% vanillin and 30% syringaldehyde of the lignin yield) [37]. These yields are nearly equal to the yields achieved in the nitrobenzene process (47% aldehydes of the lignin weight).

Thus, under the optimum conditions, the selectivity of the catalytic oxidation of small-leaved wood (birch and aspen) with dioxygen is 80–90% of the selectivity of the conventional nitrobenzene process.

The most efficient catalysts of lignin oxidation are those based on Cu(II). We have recently demonstrated the catalytic activity of copper phenanthroline complexes (0.6 g/l) in the oxidation of pine wood with oxygen at 170°C [38]. With these catalysts, the vanillin yield is 14% of the lignin weight, which is 1.6 times higher than the vanillin yield in the noncatalytic process.

The effect of a catalyst on the oxidation of a lignin-containing material is determined to a considerable extent by the process conditions [39–41]. The reaction temperature, the oxygen pressure, and the alkalinity of the medium are the most significant factors in the oxidation of lignin-containing substrates into aromatic aldehydes (Table 7).

From the nonchain free-radical mechanism of the formation of aromatic aldehydes in lignin oxidation [42], it can be deduced that, in order to raise the aromatic aldehyde selectivity of lignin oxidation with oxygen, it is necessary to increase the oxidation rate by conducting the process under more severe conditions. Elevating the reaction temperature to 160–200°C (at a hydroxide ion concentration of 2 mol/l) dramatically raises the total yield of vanillin and syringaldehyde. The optimum oxidation temperature is between 180 and 200°C.

Until the 1970s, vanillin manufacturing was dominated by lignosulfonate processing. Using this technology, North American companies were producing 2500 t of vanillin per year out of the world vanillin output of 3500 t per year.

In Russia, a pilot plant producing vanillin from lignosulfonates worked at the Syas'skii pulp-and-paper mill until 1994. However, this technology suffered from a number of serious drawbacks [30], namely, a low lignosulfonate oxidation rate (the reactor operation cycle is longer than 1 day) and low selectivity (the vanillin yield is about 3% with respect to the lignosulfonates).

Our studies enabled us to carry out the catalytic oxidation of lignosulfonates with oxygen in a flow apparatus [36, 43–45]. This process is much more efficient than the process used at the Syas'skii pulp-and-paper mill [45, 46]. The highest vanillin concentration attainable in the flow apparatus under the optimum conditions is 12 g/l, which is nearly two times higher than the same parameter of the process used at the Syas'skii pulp-and-paper mill. The production capacity of the flow apparatus is more than one order of magnitude higher than that of the Syas'skii pilot plant.

ACID-CATALYZED REACTIONS OF CARBOHYDRATES

The conventional processes of the hydrolysis industry derive only a limited range of products (glucose, xylose, and furfural) from wood [4]. The wood hydrolysis process is catalytic in nature. Depending on the

Table 7. Lignin oxidation selectivity as a function of the processing conditions

Substrate, catalyst	Temperature, °C	Oxygen pressure, MPa	Maximum selectivity time, min	Aldehyde yield, %*	Reference
Lignosulfonates, no catalyst	160	0.05	180	4.0	[30]
	185	1.1–1.2	70	7.4	[39]
Pine wood, copper oxide	160	0.3	15–20	23.0	[40]
Pine wood, copper phenanthrolinate	170	–	180	14.0	[38]
Pine wood, no catalyst	160	0.3	15–20	12.8	[40]
	170	–	180	9.5	[38]
Birch wood, copper oxide	160	0.3	25	23.4	[37]
	170	0.3	20	43.2	[37]
	180	0.3	15	25.5	[37]
Birch wood, no catalyst	180	0.3	15	11.1	[37]
	190	0.3	10	10.9	[37]
Birch inner bark (bast), copper oxide	160	0.3	40	4.6	[41]
	170	0.3	25	10.0	[41]

* Percent of the lignin weight.

rate of acid hydrolysis, the wood polysaccharides are classified into readily and difficultly hydrolyzable. The readily hydrolyzable polysaccharides are polysaccharides that can be hydrolyzed by dilute mineral acids, namely, hemicelluloses and amorphous cellulose. The difficultly hydrolyzable polysaccharides, namely, crystalline cellulose and cellulosans (hemicelluloses cocrystallized with cellulose) can be hydrolyzed at room temperature only by concentrated mineral acids. The hydrolysis of the difficultly hydrolyzable polysaccharides with dilute mineral acids can be carried out only at elevated temperatures (160–190°C).

It is important to widen the range of chemical products derivable from vegetable carbohydrates. One of these products is levulinic acid (LA), which forms from vegetable hexosans according to the following scheme [8]:

$$\text{hexosans} \longrightarrow \text{levoglucosenone}$$
$$\longrightarrow \text{5-hydroxymethylfurfural} \longrightarrow \text{levulinic acid.}$$

Levulinic acid and its derivatives are used in the food, pharmaceutical, and cosmetic industries and can be used in the synthesis of herbicides, pesticides, plant growth stimulators, antioxidants, and epoxy resins [47].

The maximum yield of LA from wood (~24%) was achieved in the presence of H_2SO_4 (5%) at 220°C and a processing time of about 2 h. The LA yield depends only slightly on the kind of wood (aspen, pine, fir, and birch) and is significantly higher when cellulose is used as the starting material. It was established by investigating LA synthesis from cellulose that the LA yield is determined by the processing temperature and time and by the nature of the catalyst [48–50]. In the presence of sulfuric acid, the highest yield of LA from cellulose is 35–40% at 240°C (Fig. 4).

The low-temperature hydrolysis of carbohydrates (fructose, glucose, and sucrose), cellulose, and fir and aspen wood was also studied [51]. It was found that monosaccharides and disaccharides react at a sufficiently high rate and afford fairly high LA yields. The activity of inorganic acids as catalysts of the conversion of the carbohydrates into LA decreases in the order $HCl > H_2SO_4 > H_3PO_4$ (Fig. 5).

The efficiency of the acid-catalyzed conversion of the hexose carbohydrates into LA in aqueous media is limited by the low selectivity of the process at high sub-

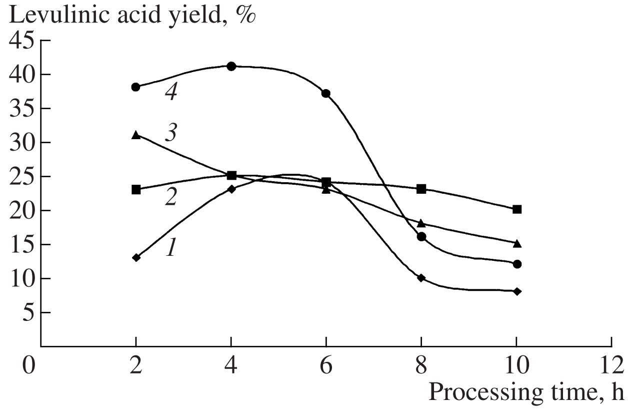

Fig. 4. Yield of levulinic acid forming from cellulose in the presence of 5.0% H_2SO_4 as a function of the processing time at T = (*1*) 210, (*2*) 220, (*3*) 230, and (*4*) 240°C.

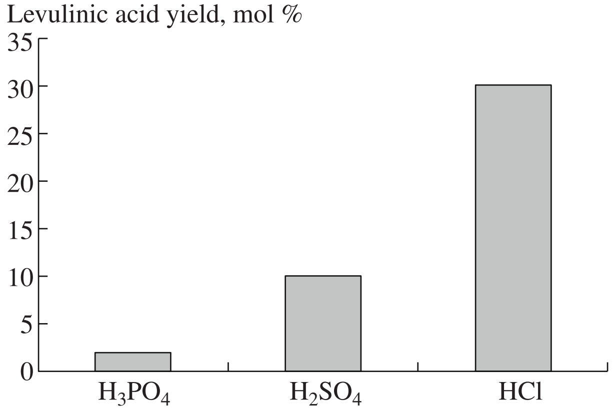

Fig. 5. Effect of the nature of the catalyst on the yield of levulinic acid from glucose at 98°C and a Hammett acidity function of $H^\circ = -2.6$.

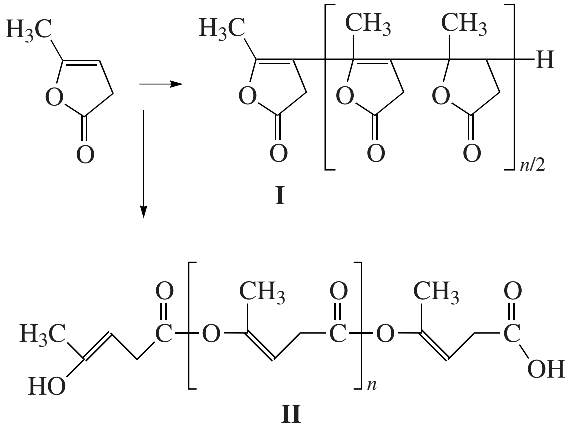

Fig. 6. Possible α-angelicalactone polymerization routes.

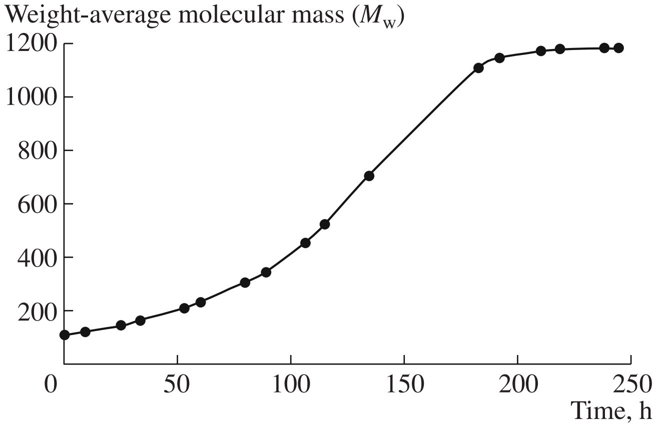

Fig. 7. Weight-average molecular mass of the α-angelicalactone polymerization product as a function of the processing time (T = 18°C, 3 mol % sodium butoxide; M_w is estimated viscometrically).

strate concentrations. High LA and 5-hydroxymethyfurfural (HMF) yields (~90% with respect to the carbohydrate) were reported in the literature, but only for substrate concentrations of 0.1–0.2 mol/l [51, 52]. Raising the carbohydrate concentration to 1 mol/l reduces the LA yield by a factor of 1.5–2 [51, 53]. The catalytic system sodium bisulfate–sulfuric acid in the two-phase medium butanol–water was suggested for enhancing the selectivity of acid-catalyzed carbohydrate conversion. In this medium, high yields of LA butyl esters and HMF (up to 90 mol %) were obtained at a substrate concentration of 1 mol/l [54]. For the constituent homogeneous media—butanol and water—the product yield decreases by a factor of 4 and 6, respectively, as the carbohydrate concentration is raised. Thus, the use of butanol, which serves both as the extractant and as the alkylating agent in the two-phase system, allows the high selectivity of carbohydrate conversion to be maintained at high substrate concentrations.

In order to understand why the selectivity of acid-catalyzed carbohydrate conversion in water decreases with an increasing substrate concentration, we studied the effects of levulinic acid and glucose admixtures on the conversion of fructose.

We found that the main causes of the lower selectivity of the acid-catalyzed conversion of carbohydrates in water are LA condensation and the interaction between LA and the carbohydrate. In order to retard the former process, it is necessary to remove LA from the catalytically active medium; to retard the latter, it is necessary to separate the product from the substrate during the reaction. This is possible with the two-phase system butanol–water.

The lactone of LA, called α-angelicalactone (5-methyl-2(3H)-furanone), has two functional groups capable of participating in polymerization reactions. Accordingly, there are two polymerization routes for this compound, namely, the opening of the double bond with the formation of polyfuranone (**I**) and the opening of the lactone ring with the formation of a polyester (**II**) (Fig. 6).

In the presence of sodium butoxide, a reddish yellow viscous liquid forms, which then turns into a light yellow resin. This resin is soluble in polar solvents and insoluble in water and swells in hydrocarbons.

Figure 7 plots the dependence of the weight-average molecular mass of the α-angelicalactone polymerization product obtained in the presence of 2 mol % sodium butoxide at 18°C.

The ^1H NMR spectrum of the α-angelicalactone polymerization product indicates the presence of olefinic protons, which suggest the presence of polyester units.

Thus, α-angelicalactone homopolymers were synthesized for the first time by opening the lactone ring and the double bond. The proportion of polyester bonds in the resulting polymers exceeds 60%. The polymers are almost completely biodegradable by the yeast *Candida parapsilosis* within 3–20 days.

REFERENCES

1. Fengel, D. and Wegener, G., *Wood: Chemistry, Ultrastructure, Reactions*, Berlin: Walter de Gruyter, 1984.
2. Azarov, V.I., Burov, A.V., and Obolenskaya, A.V., *Khimiya drevesiny i sinteticheskikh polimerov* (Chemistry of Wood and Synthetic Polymers), St. Petersburg: LTA, 1999.
3. Lengyel, P. and Morwai, S., *Chemie and Technologie der Zellstuffherstellung*, Budapest: Akadémiai Kiadó, 1973.
4. Khol'kin, Yu.I., *Tekhnologiya gidroliznykh proizvodstv* (Hydrolysis Technology), Moscow: Lesnaya Promyshlennost', 1989.
5. Morozov, E.F., *Proizvodstvo furfurola: voprosy kataliza i novye vidy katalizatorov* (Furfural Production: Catalysis and New Catalysts), Moscow: Lesnaya Promyshlennost', 1988.
6. Chudinov, S.V., Trofimov, A.N., Uzlov, G.A., et al., *Spravochnik lesokhimika* (Wood Chemist's Handbook), Moscow: Lesnaya Promyshlennost', 1987.
7. Kuznetsov, B.N., *Khim. Interes. Ust. Razv.*, 1998, vol. 6, p. 383.
8. Kuznetsov, B.N., Kuznetsova, S.A., and Taraban'ko, V.E., *Ross. Khim. Zh.*, 2004, vol. 48, no. 3, p. 4.
9. Nepenin, Yu.N., *Tekhnologiya tsellyulozy* (Cellulose Technology), vol. 2: *Proizvodstvo sul'fatnoi tsellyulozy* (Sulfate Pulp Production), Moscow: Lesnaya Promyshlennost', 1990.
10. Nepenin, Yu.N., *Tekhnologiya tsellyulozy* (Cellulose Technology), vol. 1: *Proizvodstvo sul'fitnoi tsellyulozy* (Sulfite Pulp Production), Moscow: Lesnaya Promyshlennost', 1976.
11. Bogolitsyn, K.G., *Ross. Khim. Zh.*, 2004, vol. 48, no. 6, p. 105.
12. Deineko, I.P., Nikol'skii, S.N., Slonim, V.Z., and Zarubin, M.Ya., *Khim. Drev.*, 1984, no. 1, p. 39.
13. Karetnikova, N.V., Pen, R.Z., and Pen, V.R., *Khim. Rastit. Syr'ya*, 1999, no. 2, p. 49.
14. Kuznetsova, S.A., Danilov, V.G., Kuznetsov, B.N., Alexandrova, N.B., Yatsenkova, O.V., and Fat'yanova, Yu.A., *"Towards Molecular-Level Understanding of Wood, Pulp and Paper," 7th Eur. Workshop on Lignocellulosics and Pulp*, Turku, Finland, 2002, p. 281.
15. Kuznetsova, S.A., Danilov, V.G., Alexandrova, N.B., Yatsenkova, O.V., Ivanchenko, N.M., and Kuznetsov, B.N., *Proc. 12th Int. Symp. on Wood and Pulping Chemistry*, Madison, Wis., 2003, p. 135.
16. Danilov, V.G., Kuznetsova, S.A., Kudryashov, A.V., Yatsenkova, O.V., and Nikitina, T.G., *Proc. of the Fourth Int. Symp. on Catalytic and Thermochemical Conversions of Natural Organic Polymers*, Krasnoyarsk, Russia, 2000, p. 185.
17. Kuznetsov, B.N., Kuznetsova, S.A., and Danilov, V.G., in *Green Chemistry in Russia*, Lunin, V., Tundo, P., and Lokteva, E., Eds., Green Chemistry Series, no. 12, Venice: Poligrafica Venezia, 2005.
18. Kuznetsova, S.A., Yatsenkova, O.V., Danilov, V.G., Kalacheva, G.S., Skvortsova, G.P., and Kuznetsov, B.N., *Khim. Rastit. Syr'ya*, 2006, no. 2, p. 19.
19. Reznikov, V.M., *Khim. Drev.*, 1991, no. 2, p. 3.
20. Demin, V.A., *Usp. Khim.*, 1999, vol. 68, p. 1029.
21. Bushkova, E.S., Yusian, T.A., Dorokhova, N.I., Zaletov, V.G., Kuznetsova, S.A., Kuznetsov, B.N., and Garnovskii, A.D., *Koord. Khim.*, 1994, vol. 20, nos. 8–9, p. 630.
22. Kuznetsova, S.A., Bicherov, A.V., Dorokhova, N.I., Kuznetsova, L.I., Amarskii, E.G., Kuznetsov, B.N., Burlov, A.S., and Garnovskii, A.D., *Koord. Khim.*, 1998, vol. 24, no. 1, p. 48 [*Russ. J. Coord. Chem.* (Engl. Transl), vol. 24, no. 1, p. 43].
23. Petropavlovskii, G.A. and Kotel'nikova, N.E., *Khim. Drev.*, 1979, no. 6, p. 3.
24. Ardizzone, S., Dioguardi, F., Mussini, T., Massini, P., Rondinini, S., Vercelli, B., and Vertova, A., *Cellulose*, 1999, no. 6, p. 57.
25. Kuznetsova, S.A., Danilov, V.G., and Yatsenkova, O.V., *Trudy Tret'ei Vserossiiskoi konferentsii "Khimiya i tekhnologiya rastitel'nykh veshchestv"* (Proc. of the Third All-Russia Conf. on Vegetable Compound Chemistry and Technology), Saratov, 2004, pp. 279.
26. Kusnetsova, S.A., Danilov, V.G., Yatsenkova, O.V., Alexandrova, N.B., and Kuznetsov, B.N., *Proc. 8th Eur. Workshop on Lignocellulosics and Pulp*, Riga, Latvia, 2004, p. 177.
27. Kuznetsova, S.A., Vasil'eva, N.Yu., Danilov, V.G., Baryshnikov, S.V., Beregovtsova, N.G., and Sharypov, V.I., *Khim. Rastit. Syr'ya*, 2005, no. 1, p. 71.
28. Erofeev, Yu.V., Afanas'eva, V.L., and Glushkov, R.G., *Khim.-Farm. Zh.*, 1990, no. 7, p. 50.
29. Gogotov, A.F., *Khim. Interes. Ust. Razv.*, 1994, vol. 2, nos. 2–3, p. 597.
30. Chudakov, M.I., *Promyshlennoe ispol'zovanie lignina* (Commercial Use of Lignin), Moscow: Lesnaya Promyshlennost', 1983.
31. Adler, E., *Wood Sci. Technol.*, 1977, vol. 11, no. 1, p. 169.
32. MacRae, W.D., *Phytochemistry*, 1984, vol. 23, p. 1207.
33. Erofeev, Yu.V., *Khim.-Farm. Zh.*, 1990, no. 7, p. 50.
34. Taraban'ko, V.E., Hendogina, Yu.V., Petuhov, D.V., and Pervishina, E.P., *React. Kinet. Catal. Lett.*, 2000, vol. 69, no. 2, p. 361.
35. Khudyakov, I.V., *Kinet. Katal.*, 1987, vol. 17, p. 116.
36. Taraban'ko, V.E., Ivanchenko, N.M., Koropachinskaya, N.V., and Kuznetsov, B.N., *Khim. Interes. Ust. Razv.*, 1996, vol. 4, nos. 4–5, p. 405.
37. Taraban'ko, V.E., Koropachinskaya, N.V., and Chernyak, M.Yu., *Khim. Rastit. Syr'ya*, 2003, no. 2, p. 9.
38. Gogotov, A.F., Rybal'chenko, N.A., and Babkin, V.A., *Khim. Rastit. Syr'ya*, 2001, no. 4, p. 39.
39. Bjorsvik, H.-R. and Minisci, F., *Fine Org. Process Res. Dev.*, 1999, no. 3, p. 330.
40. Taraban'ko, V.E., Koropachinskaya, N.V., Kudryashev, A.V., and Kuznetsov, B.N., *Izv. Akad. Nauk, Ser. Khim.*, 1995, no. 2, p. 375.
41. Koropachinskaya, N.V., Taraban'ko, V.E., and Levdanskii, V.A., *Khim. Rastit. Syr'ya*, 2004, no. 1, p. 27.

42. Taraban'ko, V.E. and Petukhov, D.V., *Khim. Interes. Ust. Razv.*, 2003, no. 11, p. 645.
43. Taraban`ko, V.E., Fomova, N.A., Kuznetsov, B.N., Kudryashev, A.V., and Ivanchenko, N.M., *React. Kinet. Catal. Lett.*, 1995, vol. 55, no. 1, p. 161.
44. Taraban'ko, V.E., Ivanchenko, N.M., Selyutin, G.E., Bezrukova, N.P., Pervyshina, E.P., Kuznetsov, B.N., and Il'ina, I.I., *Khim. Rastit. Syr'ya*, 1997, no. 2, p. 4.
45. Taraban'ko, V.E., Kudryashev, A.V., Kuznetsov, B.N., Gul'bis, G.R., Koropachinskaya, N.V., and Ivanchenko, N.M., *Zh. Prikl. Khim.*, 1996, vol. 69, no. 4, p. 620.
46. Kuznetsov, B.N., Kuznetsova, S.A., Danilov, V.G., Kozlov, I.A., Taraban'ko, V.E., Ivanchenko, N.M., and Alexandrova, N.B., *Catal. Today*, 2002, vol. 7, p. 211.
47. Levitin, B.M., *Levulinovaya kislota. Svoistva, poluchenie i primenenie* (Levulinic Acid: Properties, Synthesis, and Use), Moscow: Mikrobioprom, 1978.
48. Efremov, A.A., Pervyshina, G.G., and Kuznetsov, B.N., *Khim. Prir. Soedin.*, 1997, no. 1, p. 107.
49. Pervyshina, G.G., Efremov, A.A., and Kuznetsov, B.N., *Khim. Rastit. Syr'ya*, 1998, no. 1, p. 9.
50. Efremov, A.A., Pervyshina, G.G., and Kuznetsov, B.N., *Khim. Prir. Soedin.*, 1998, no. 2, p. 226.
51. Taraban'ko, V.E., Chernyak, M.Yu., Aralova, S.V., and Kuznetsov, B.N., *React. Kinet. Catal. Lett.*, 2002, vol. 75, no. 1, p. 117.
52. Kei-ichi, S., Yoshihisa, I., and Hitoshi, I., *Chem. Lett.*, 2000, vol. 73, p. 22.
53. Kuster, B.F.M. and Hessel, S.B., *Carbohydr. Res.*, 1977, vol. 54, no. 2, p. 165.
54. Taraban'ko, V.E., Smirnova, M.A., and Chernyak, M.Yu., *Khim. Interes. Ust. Razv.*, 2005, vol. 3, no. 4, p. 551.