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New catalytic processes for a sustainable chemistry of cellulose production from wood biomass

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Abstract

The present paper describes the results of studies directed to novel catalytic processes design for the environmentally friendly production of cellulose. The new delignification catalyst which is produced by chemical interaction of elemental sulfur with hydrazine in superbase medium was used for the improvement of efficiency and ecological purity of the conventional pulping process. This catalyst reduces the concentration of polysulfides in pulping liquor and the yield of side sulfur-containing compounds (by 1.5 times). The processes of wood delignification with sulfur-free reagents based on catalytic pulping with acetic acid and hydrogen peroxide and on the delignification of steam-activated wood with NaOH or Na_2CO_3 solutions have prospects for the environmentally benign production of cellulose. The new catalytic process of vanillin production by oxidation of lignosulfonates with molecular oxygen was described. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Catalytic delignification; Oxidation; Wood; Cellulose; Lignosulfonates; Environmentally benign processes

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1. Introduction

At present the cellulose production is the most developed industry of wood biomass chemical processing [1]. The conventional sulfate and sulfite pulping processes make negative influence on an environment since they use the sulfur-containing reagents for removing lignin from a wood biomass. The various approaches are elaborated at present in order to prevent the ecological damage of pulp and paper industry.

The use of catalysts makes it possible to increase the efficiency of wood delignification processes. Two catalysts: anthraquinone and 1,4-dihydro-9,10-dihydroxyanthracene disodium salt are used for the cellulose production in industry [2–4]. But the many other different catalysts were successfully tested on a laboratory scale at the conditions of alkaline pulping [5] and oxidative delignification in the presence of metal salts [6], polyoxometalates [7–9], manganese complexes [10,11], etc.

This paper describes the new environmentally benign methods of cellulose production based on:

- application of new catalyst decreasing the yield of sulfur-containing side-products in the conventional alkaline pulping processes;
- use of catalysts and sulfur-free reagents—acetic acid and hydrogen peroxide for wood delignification;
- use of wood pre-treatment by steam for promoting a delignification process;
- utilization of the lignin-origin side-products by the catalytic oxidation process.

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2. Experimental

2.1. Delignification with new sulfur-based catalyst

Isothermal pulping of deresinated wood chips with sizes 2–4 mm was carried out in 20 ml autoclave specially designed for kinetic studies [14]. Pine-wood with composition: cellulose 52.8 wt.%, hemicellulose 16.3 wt.%, lignin 26.6 wt.% and extractives 4.3 wt.% were used as starting raw material. Alkali amount per one cooking experiment was 20% Na_2O. Catalyst concentration was 0.6–1.0 wt.% on absolutely dry wood (ADW).

Pulping temperature was varied between 150 and 180 °C, pressure 0.9–1.2 MPa and time of pulping from 5 min to 20 h. The used liquor:wood ratio was 5. The samples of cellulosic product were selected every 5 min for the analysis of residual lignin content. Rate constants and activation energies of a wood delignification process were calculated from curves describing the variation of residual lignin with pulping time.

The ^{1}H and ^{13}C NMR spectra of lignin samples were obtained on Varian VXR-500S spectrometer at resonance frequency 500 MHz (^{1}H) and 125.5 MHz (^{13}C). The ^{13}C NMR spectra of lignin specimens were recorded with proton decoupling according to IGD method. Subspectra of the primary, secondary, tertiary and quaternary carbon atoms obtained by method of spin echo with multiplet de-phasing (CSE and GASPE) were recorded at 5000 accumulations (relaxation delay 2.5 s, 90° pulse). DMSO-d_6 was used as a solvent.

2.2. Delignification with acetic acid and hydrogen peroxide

Aspen wood and silver-fir wood were used as initial raw materials. Aspen wood chemical composition: cellulose 46.3%, lignin 21.8%, hemicellulose 24.5% and extractives 7.8% on mass of ADW. Silver-fir wood chemical composition: cellulose 50.3%, lignin 27.7%, hemicellulose 15.4% and extractives 6.8% on mass of ADW.

Wood chips with sizes $20 \times 11 \times 0.5$ mm were used in pulping experiments. The pulping liquor composition: 30% acetic acid + 35% hydrogen peroxide (H_2O_2/CH_3COOH molar ratio was varied in the range 0.1–0.9). Sulfuric acid with concentration 1–2.5 wt.% on ADW and TiO_2, Na_2MoO_4 with concentration 2 wt.% on ADW were used as delignification catalysts (DCs).

The pulping process was carried out in a static reactor with volume 200 cm^3 at the temperatures 120–150 °C and liquor ratios 5:1–20:1 during 1–5 h as described in [12]. The main components of cellulosic material obtained were analyzed using chemical methods according to [13].

2.3. Delignification of steam-activated wood

The procedure of wood activation by steam at the conditions of “explosive autohydrolysis” was described in [15]. Air dry sawdust (350 g) was loaded into the metallic reactor with volume 0.8. The overheated steam was injected into the sealed reactor from a steam collector. The duration of treatment was varied between 30 and 300 s and then a pressure of the steam was dropped by spherical stopcock. This resulted in a fast transfer of activated wood material into the blow tank. The following parameters of steam activation were used: temperature 187–240 °C, pressure 1.2–3.4 MPa and time of treatment 30–300 s. The solutions of 0.1 N NaOH or 0.5 N Na_2CO_3 were used for the activated wood delignification.

2.4. Lignosulfonates oxidation to vanillin

Sodium-base spent sulfite liquors (SSLs) produced from softwood at Syas’ Pulp and Paper Plant (PPP, Leningrad region, Russia) and from the mixture of hardwood and softwood at Krasnoyarsk PPP were used as starting raw materials. The content of dry residue in SSL from Syas’ plant was 52 wt.% and from Krasnoyarsk plant 54 wt.%. Mass fraction of lignosulfonates in dry residue was 65% for SSL from Syas’ plant and 49% from Krasnoyarsk plant. The flow system with two tubular vertical reactors of 1.0 and 0.25 l was applied for catalytic oxidation of lignosulfonates at 170 °C, 1 MPa and flow rate 1.8 l/h. The reactors were filled by the copper catalyst particles. The products of lignosulfonates oxidation were analyzed by GLC. The procedure of catalytic measurements was described in [16].

3. Results and discussion

3.1. Catalytic delignification of wood in alkaline medium

The novel DC which is produced by the chemical interaction of elemental sulfur with hydrazine in the superbase medium was used for the improvement of efficiency and ecological purity of wood delignification in an alkaline medium [14,20].

Two clearly displayed kinetic areas corresponding to the fast and slow rates of delignification process were found (Fig. 1). Both of them are described by the equations of the first order reaction. The existence of two kinetic areas can serve as an indication of chemical heterogeneity of wood lignin.

Kinetic parameters of pine-wood delignification and polysaccharides dissolvation in the presence of DC catalysts are presented in Table 1. They were compared with kinetic parameters of the conventional polysulfide and alkaline pulping processes. Obtained data show that the rate constants of catalytic delignification (both at fast and slow kinetic areas) are higher than those of conventional polysulfide and alkaline pulping.

The decrease of reaction activation energy from 145 to 97 kJ/mol in the first kinetic area and from 196 to 158 kJ/mol in the second one was observed in the presence DC catalyst in comparison with non-catalytic alkaline pulping. The DC does not promote the process of polysaccharides destruction. According to Table 1 data the rate constants and the activation energies of polysaccharides dissolvation are similar for catalytic and non-catalytic processes.

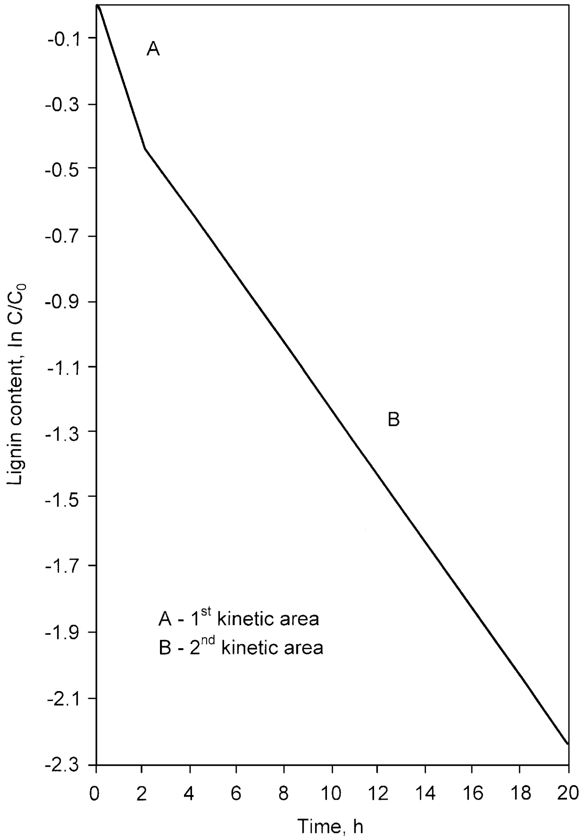

Fig. 1. Typical kinetic curve of pine-wood alkaline delignification with DC catalyst concentration 0.6 wt.% at 150 °C.

But DC catalyst increases the degree of pine-wood delignification to 20–30 Kappa units at 170 °C and pulping time 150–180 min. Optimum concentration of DC catalyst have to be defined around 0.6–1.0 wt.%.

Table 1
Kinetic parameters of pine-wood pulping in the presence of novel DC

	Polysulfide pulping			Alkaline pulping		
	150 °C	170 °C	180 °C	150 °C	170 °C	180 °C
Rate constant[a] of delignification ($\mathrm{min}^{-1} \times 10^2$)	$\frac{0.54}{0.09}$	$\frac{2.2}{0.6}$	$\frac{3.4}{1.0}$	$\frac{0.26}{0.05}$	$\frac{1.2}{0.3}$	$\frac{3.1}{0.9}$
Rate constant of polysaccharides dissolvation ($\mathrm{min}^{-1} \times 10^2$)	$\frac{0.8}{0.02}$	$\frac{3.9}{0.12}$	$\frac{7.9}{0.21}$	$\frac{0.9}{0.02}$	$\frac{3.4}{0.1}$	$\frac{6.8}{0.21}$
Activation energy of delignification (kJ/mol)	$\frac{125}{186}$			$\frac{145}{196}$		
Activation energy of polysaccharides dissolvation (kJ/mol)	$\frac{89}{188}$			$\frac{91}{187}$		

[a] Numerator: the first kinetic area, denominator: the second kinetic area.

Table 2
Relative number of bonds breaking down in lignin on the main stage of pine-wood delignification (wt.% relative to native sample)

Type of bond	Method of delignification		
	Soda	Kraft	Soda + catalyst (DC)
α,β-O-4	60	73	83
4-O-5	77	6	19
$-C_\alpha-C_\beta$, $C_\beta-C_\gamma-$	43	12	70

The cellulose yields are comparable for catalytic and non-catalytic delignification processes and they were varied mainly between 43 and 46 wt.% on ADW at temperature 170 °C and pulping time 150–180 min.

Some data about mechanism of DC catalyst action were obtained from of ^1H and ^{13}C NMR spectra of lignins isolated from pine-wood by different delignification methods. Analysis of NMR data (Table 2) makes it possible to draw the conclusion that the wood lignin depolymerization in the presence of DC catalyst goes mainly via the rupture of alkyl–aryl ether bonds and $-C_\alpha-C_\beta$ bonds in the side chain of lignin macromolecule. At the same time the reactions of aromatic ring demethoxylation and oxidation at C_α, C_β positions of aliphatic chain take place. These reactions were not detected in the conventional pulping processes.

DC catalyst reduces by 15% the concentration of polysulfides in pulping liquor and it reduces also by 1.5 times the yield of side sulfur-containing products. Obtained cellulose has the same characteristics as cellulose produced by conventional sulfate pulping.

3.2. *Wood delignification with acetic acid and hydrogen peroxide*

Organosolvent pulping is considered as an environmentally friendly way of cellulose production [17,18]. Methods of wood organosolvent delignification allow to utilize side-products from hemicellulose and lignin into valuable chemicals, to decrease the energy expenses for solvent regeneration and to avoid the sulfur-containing reagents as compared to conventional sulfate and sulfite pulping technologies. The oxidative delignification of wood with peracetic acid, which can be formed in situ in the pulping liquor at proper molar ratio of acetic acid and hydrogen peroxide, is of apparent interest, since under these conditions the intensive oxidation of lignin units was observed [12,18].

This part of the work was started in order to optimize the process of aspen and silver-fir wood delignification with acetic acid and hydrogen peroxide mixtures in the presence of different catalysts.

The process of wood delignification was optimized on the pulping liquor composition (H_2O_2/CH_3COOH ratio), sulfuric acid catalyst concentration, temperature and the process time. The rise of delignification temperature from 120 to 150 °C decreases the pulp yield and the cellulose concentration in obtained product. The following parameters of aspen wood pulping, which correspond to the highest yield of cellulose (86.6 wt.%) were selected: temperature 130 °C, process time 3 h, H_2SO_4 concentration 2 wt.% and H_2O_2/CH_3COOH molar ratio 0.3. The highest cellulose content (70 wt.%) in cellulosic product from silver-fir wood was observed at 130 °C.

It is known [19] that the rate of organosolvent pulping of birch wood at liquor ratio 5:1 can be limited by diffusion of lignin destruction products from wood matrix into pulping liquor. But at the higher liquor ratios the diffusion processes are accelerated. Therefore the most pronounced catalytic effects should be expected at the conditions of wood delignification at the high liquor ratios. The positive effect of catalytic additives (H_2SO_4, TiO_2, Na_2MoO_4) on silver-fir wood delignification process was observed at liquor ratio (20:1) (Table 3). The use of these catalysts makes it possible both to cut down the pulping process time and to increase the degree of wood delignification.

3.3. *Delignification of steam-activated wood*

The activation of wood by "explosive autohydrolysis" process was intensively studied in order to elaborate an environmentally friendly way of cellulose production. This method includes a short time treatment of wood chips by steam at elevated temperature and pressure, followed by a fast decompression.

The efficiency of this activation process is determined by two main factors [21,22]:

- organic acids produced during a steam treatment of wood act as the hydrolysis reaction catalysts;

Table 3
Influence of catalysts and process time on the pulp yield and on the composition of cellulosic product from silver-fir wood (130 °C, H_2O_2/CH_3COOH mole ratio 0.3, liquor ratio 20:1, catalyst 2 wt.% on ADW)

Parameters	Catalyst							
	Blank		H_2SO_4		TiO_2		Na_2MoO_4	
	1 h	2 h	1 h	2 h	1 h	2 h	1 h	2 h
Cellulosic product yield (% on ADW)	86.3	65.3	78.7	56.4	88.4	58.8	56.7	45.4
Cellulose content (%)[a]	47.3	60.3	47.6	85.5	49.5	71.1	71.4	84.6
Lignin content (%)[a]	25.9	20.3	24.4	7.9	27.6	15.7	9.0	7.6

[a] Relative to cellulosic product mass.

- a mechanical loosening of wood material is accomplished during a fast pressure drop.

As a result of this treatment, the main wood components: cellulose, solubilized sugars and low molecular mass lignin are easily isolated from activated wood with sulfur-free reagents.

The composition of water-soluble compounds isolated from steam-activated wood with yields from 5.3 to 18.8 wt.% depending on the temperature of treatment (187–240 °C) was studied by chemical and chromatographic methods [23].

This part of a paper describes some features of cellulose isolation from steam-activated wood of Siberian origin (pine, fir and aspen).

The cellulose content in wood was not significantly changed after pine, fir and aspen wood treatment by water-steam at 187–240 °C. But hemicelluloses are very sensitive to the activation procedure. About 50% of the native hemicelluloses content was depolymerized at a relatively low temperature (187 °C) and short duration of activation process. The hemicelluloses were hydrolyzed completely by wood treatment with steam at 240 °C.

The important effect of wood treatment by steam is connected with the formation of low molecular mass lignin, which is isolated easily from activated wood with solutions of 0.1 N NaOH or 0.5 N Na_2CO_3. The amount of low molecular mass lignin is increased with the growth of temperature of wood steam treatment.

After the extraction of steam-activated wood with 0.1 N solution of NaOH the solid product was obtained with the yield from 60 to 85 wt.% and with the cellulose content up to 85 wt.% (Table 4).

Table 4
The influence of steam treatment on the yield of lignocellulosic product from wood and on the cellulose content in obtained product

Parameters of steam treatment		Solid product yield (wt.% ADW)[a]			Cellulose content in solid product (wt.%)		
Temperature (°C)	Time (min)	Pine	Fir	Aspen	Pine	Fir	Aspen
187	2.0	83.3	85.6	61.1	54.1	51.6	73.6
	3.0	74.6	78.2	61.3	57.7	55.8	74.2
	5.0	68.8	70 2	63.0	61.6	61.5	72.1
220	1.0	74.8	74.3	70.6	57.6	59.5	67.3
	1.5	72.2	72.2	68.6	61.5	62.4	69.5
	2.0	69.1	71.6	71.0	63.5	61.8	65.6
	2.5	67.6	70.2	65.5	65.4	63.0	75.3
	3.0	65.4	68.5	61.7	67.3	64.0	75.2
240	1.0	68.4	67.5	64.6	69.4	71.9	74.5
	1.5	60.0	63.6	56.1	79.7	75.4	82.4
	2.0	62.1	62.6	57.2	77.5	75.9	84.8
	2.5	62.6	62.9	58.9	77.5	76.8	83.7
	3.0	62.5	62.6	57.2	75.8	78.8	85.1

[a] After steam-treated wood extraction with 0.1 N solution of NaOH.

Table 5
Vanillin and syringaldehyde production from lignosulfonates (SSL) in the flow unit at 170 °C

SSL origin	Catalyst applied[a]	Working pressure (MPa)	Oxygen rate (l/h)	Product concentration (g/l)		Total yield of aldehydes (wt.%)
				Vanillin	Syringaldehyde	
Krasnoyarsk	3	1.10	38	1.70	0.24	1.36
	3	1.20	38	2.20	0.30	1.75
	3	1.34	38	1.53	0.16	1.18
	1	1.10	38	1.75	0.35	1.47
	1	1.20	38	3.82	0.41	2.96
	1	1.35	38	2.35	0.35	1.89
Syas	1	0.9	30	3.7	0.3	2.8
	1	0.9	35	6.2	0.6	4.8
	1	0.9	38	9.8	1.0	7.7
	2	1.1	38	5.6	0.7	4.5
	2	1.1	55	12.4	1.1	9.6
	2	1.1	59	11.9	1.0	9.3
	2	1.1	128	7.5	0.7	5.8

[a] 1: the first reactor of 1.0 l volume was filled with pieces of copper wire 10 × 5 × 1 mm (3.7 kg); 2: the first reactor was filled with pieces of copper wire (14.1 kg) and the second with cupric oxide wire 10 × 5 × 1 mm (0.6 kg); 3: blank experiments with cuts of stainless steel.

3.4. *The utilization of side lignin-origin products by catalytic oxidation*

The influence of process parameters on the efficiency of lignosulfonates oxidation into vanillin in a static swinging reactor was studied earlier [24]. Maximum vanillin yield obtained by catalytic oxidation of SSLs from PPP was 13.1% on lignin mass.

This part of the work describes the process of lignosulfonates oxidation with molecular oxygen in a continuous flow catalytic reactor.

According to the data presented in Table 5 the non-catalytic oxidation of Krasnoyarsk' SSL provides relatively small yields of vanillin and syringaldehyde. The copper catalyst increases the aldehydes yield by 1.5 times. The oxidation of SSL from Syas' PPP gives higher vanillin concentrations under similar conditions. Vanillin yield was optimized by the selection of proper operating parameters for oxidation process. The maximum vanillin yield was obtained at oxygen pressure 1.2 MPa and flow rate 38 l/h. The increase of catalyst charge from 3.7 to 4.7 kg results in the growth of vanillin yield.

The attained productivity of a flow reactor exceeds by 20 times the productivity of the static stirred reactor at the Syas' PPP. This advantage was achieved at the comparable level of alkali consumption due to the increased oxygen pressure and to the higher selectivity of catalytic process.

4. Conclusion

Since a big variety of catalysts and catalytic additives promoting the delignification process are known only few of them have found at present the industrial application. The wide use of catalysts in pulping industry is restricted by different reasons: their high cost, low efficiency, some difficulties with catalyst regeneration, the necessity to change the conventional cycle of pulping reagent regeneration, etc.

But the catalytic processes described in this paper have prospects in industrial production of cellulose from wood by environmentally friendly way. The new DC, suggested by authors increases the efficiency of pulping process in an alkaline medium and reduces significantly the yield of sulfur-based side-products. Some other advantages of DC catalyst are connected with the use of non-expensive and accessible reagents for its preparation. Besides, this catalyst does not make any problems with the reagent regeneration in industrial pulping processes.

Fundamental decision of ecological problem connected with the emission of dangerous sulfur-containing side-products is based on the application of sulfur-free delignification reagents. Such methods as organosolvent pulping, oxidative delignification, "explosive autohydrolysis " can serve in principle, as the alternatives to conventional pulping processes taking into account the absence of sulfur-containing reagents and the possibility of complete utilization of lignin-based products.

According to the data, described at present paper the efficiency of wood delignification with acetic acid was increased in the presence of oxidative and catalytic additives. But the novel processes of organosolvent delignification differ significantly from traditional pulping processes; therefore they could not be applied without the change of technological equipment used at present in pulping industry.

The sulfur-free process including the stage of wood short-treatment by steam with following delignification of activated wood by alkaline solutions can be more easy adopted to the conventional industrial technology. But this process demands the development of new type of equipment for the stage of wood activation at the conditions of "explosive autohydrolysis". Besides, the cellulosic products obtained by methods of "explosive autohydrolysis" and organosolvent delignification can have the other characteristics than those produced by conventional pulping. Therefore the additional efforts are needed for the adoption of these novel processes to the demands of pulping industry.

Developed by authors the process of catalytic oxidation of SSLs to vanillin with molecular oxygen makes a valuable contribution to the utilization of SSLs in pulping industry. The advantages of developed process in comparison with industrial Russian process of lignosulfonates oxidation are the higher productivity and selectivity for vanillin, lower yield of side-products and the absence of dangerous reagents (for example, benzol).

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