Environmentally Friendly Catalytic Production of Cellulose by Abies Wood Delignification in "Acetic Acid – Hydrogen Peroxide – Water" Media

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Abstract

The paper concerns the environmentally benign method of catalytic cellulose production by wood delignification over various catalysts using sulfur-free reagents – acetic acid and hydrogen peroxide. The optimum operation conditions (temperature and time of the process, H_2O_2/CH_3COOH and liquor/wood ratios) of abies wood delignification using sulfuric acid as reagent and TiO_2 as catalyst which allow reaching the acceptable yields of cellulosic product with high content of cellulose were selected.

INTRODUCTION

The industrial processes of cellulose production have a negative influence on an environment since they use the sulfur-containing reagents for removing lignin from a wood biomass. A variety of catalysts and catalytic additives for wood delignification process are known [1–3], but only a few of them have found at present the industrial application [4, 5].

Organosolvent wood delignification (for example using acetic acid) is considered as a promising direction in the ecologically safe cellulose production [6, 7]. In comparison with traditional sulfate and sulphite pulping technologies organosolvent wood delignification allows to utilize by-products from hemicelluloses and from lignin into valuable chemicals, to reduce energy consumption for solvent regeneration and to move away from the use of sulfur-containing reagents.

The oxidative wood delignification with acetic acid and hydrogen peroxide is of apparent interest, since under these conditions the intensive oxidation of lignin units is observed [8–11]. The goal of the ongoing research is to optimize the process of abies wood delignification with acetic acid and hydrogen peroxide in the presence of various catalysts.

EXPERIMENTAL

Abies wood was used as a raw material. The content of main chemical components in abies wood, % mass: cellulose – 50.3, lignin – 27.7, hemicelluloses – 15.4, extractives – 6.8.

Wood sawdust with particle sizes $2 < d < 5$ mm were used in pulping experiments with H_2O_2/CH_3COOH mixture. The delignification process was carried out in a static reactor made from titanium having a volume of 200 cm^3 within the temperature range 120–150 °C and liquid to solid ratio 5 : 1 – 20 : 1 during 1–5 h. The ratio H_2O_2/CH_3COOH varied in the range 0.1–0.9. Acid type and oxide catalysts were used for wood delignification process. The characteristic of used reagents: acetic acid, CH_3COOH, 99.8 % mass; hydrogen peroxide, H_2O_2, 35–40 % mass solution in water; sulfuric acid, H_2SO_4, 93.6–95.6 % mass; titanum (IV) oxide, TiO_2, 99.9 %.

The main components of cellulosic material obtained were analyzed using chemical methods [12]. FTIR spectroscopy and γ-ray diffraction technique were used for microcrystalline cellulose characterization.

IR spectra were recorded on spectrometer Vector 22 (Bruker) with scans number 150 and with resolution 4 cm^{-1}. Program Opus/IR, version 2.2 was used for spectroscopic data processing.

γ-Ray diffraction spectra were recorded on DRON-3 diffractometer (CuK_α radiation).

RESULTS AND DISCUSSION

Wood represents a mixture of natural polymers – cellulose, lignin and hemicelluloses – in the approximate ratio 50 : 25 : 25, depending on genetic differences within tree species and growing conditions. Cellulose and hemicelluloses are polymers of carbohydrate nature built up from molecules of simple sugar, and lignin is a polymer consisting of phenylpropane units [13]. Lignin structure also varies between hardwoods and softwoods. The phenyl groups in hardwood lignins are substituted with methoxyl groups to a greater extent than in softwood lignins. The consequence of this difference is that hardwood lignins are less cross-linked and they can be more easily depolymerized by delignification agents.

The target transformations in the processes of cellulose production from wood are connected with depolymerization of lignin macromolecules with the formation of low-molecular weight fragments.

Acid catalysts can promote the destruction of alkyl-aryl ether bonds in wood lignin [14]. Oxidative degradation of lignin proceeds through radical-type transformations with a participation of such highly reactive radicals as hydroxy radical $OH^{\cdot}$ and oxygen radicals [15]. In this case the oxide catalysts can promote the lignin depolymerization reactions.

It is reasonable to expect that the combination of acid catalysts and oxidative reagents will increase the intensity of lignin destruction process owing to a combination of heterolytic and homolytic type reactions of lignin depolymerization. The catalytic properties of different catalysts were compared in the process of abies wood delignification with hydrogen peroxide/acetic acid mixtures.

The operating parameters of the catalytic process of abies wood delignification by acetic acid/hydrogen peroxide mixtures were optimised in order to obtain the acceptable yield of cellulosic product with high cellulose content.

The data illustrating an effect of (different catalysts) reaction time and temperature on the pulp yield and on the composition of cellulosic product obtained from abies wood are given in Table 1.

Sulfuric acid (2 % to mass of absolutely dry wood (a. d. w.)) and TiO_2 (0.5 % to mass of a. d. w.) catalysts were selected for detail investigation since they provide high degree of wood delignification.

The optimum parameters of abies wood delignification process (pulping temperature and time, liquor composition, H_2SO_4 and TiO_2 concentration, pulping liquor/wood ratio), corresponding to the acceptable yields of cellulosic product with high content of cellulose have been determined.

The increase of temperature from 120 up to 150 °C decreases the yield of cellulosic material from 55.2 to 36.8 %. The observed decrease of cellulosic product yield at 140–150 °C is associated with the intensive oxidation of lignin, hemicelluloses and amorphous cellulose to soluble low-molecular mass compounds. The highest cellulose content (71.9 %) in the cellulosic product was observed at 130 °C, it decreased to 63 % at 150 °C. At the same time, a little increase of lignin content was observed. The content of hemicelluloses in the cellulosic product was as low as 3.9 % at 120 °C and even less (2.7 %) at 150 °C. This observation corresponds to the known fact that pentoses are less stable then hexoses at the acetic acid pulping [16].

Data presented in Fig. 1 show that the optimum temperature of delignification process is 130 °C which corresponds to high cellulosic product yield (55.2 %) and cellulose content in this product (71.9 % mass).

Figure 2 demonstrates the effect of pulping liquor composition on the yield of cellulosic

TABLE 1

The influence of temperature and process time of abies wood delignification on cellulosic product yield and composition. H_2O_2/CH_3COOH mole ratio 0.5, catalyst TiO_2 0.5 % on a. d. w., liquor/wood ratio 15 : 1

Temperature of pulping, °C	Process time, h	Yield of cellulosic product, %*	Content of cellulose, %**	Content of lignin, %**	Delignification degree, %
90	2	92.6	45.9	26.7	12.9
	3	91.6	49.1	26.8	13.6
100	2	88.7	45.4	25.7	19.7
	3	81.9	48.6	19.9	42.6
110	2	71.8	57.7	22.4	43.4
	3	60.0	68.8	15.7	66.8
120	2	40.5	87.6	2.7	96.1
	3	38.6	89.4	0.8	98.9
130	2	36.5	84.6	5.3	93.7
	3	34.0	87.9	4.8	94.1
140	2	36.2	80.8	6.7	91.2
	3	32.5	82.7	4.4	94.8

*To the mass of a. d. w.
**To the mass a. d. cellulosic product.

product and on the content of cellulose and lignin in this product.

The increase of oxygen peroxide concentration increases the wood delignification degree but at the same time reduces the cellulosic product yield. At high H_2O_2/CH_3COOH mole ratios the formation of peracetic acids is possible which is known as a good delignification agent [17]. This results in the intensive oxidative destruction of lignin, especially under conditions of acid catalysis. Thus, at the high H_2O_2/CH_3COOH mole ratio, the decreased yield of pulp and lignin content in cellulosic product were observed. For example, pulp yield and lignin content were 64.5 and 31.1 %, respectively, at H_2O_2/CH_3COOH mole ratio 0.1, and 31.7 and 3.3 %, respectively, at H_2O_2/CH_3COOH mole ratio 0.7. Upon the increasing of H_2O_2 concentration the oxidation of wood carbohydrates occurs along with the oxidation of wood lignin. Pentosanes content also reduces with the increase of H_2O_2/CH_3COOH mole ratio. For example, pentosanes content was 2.8 % at H_2O_2/CH_3COOH mole ratio 0.1 and only 0.2 % at mole ratio 0.7. According to the data obtained the optimal H_2O_2/CH_3COOH mole ratio

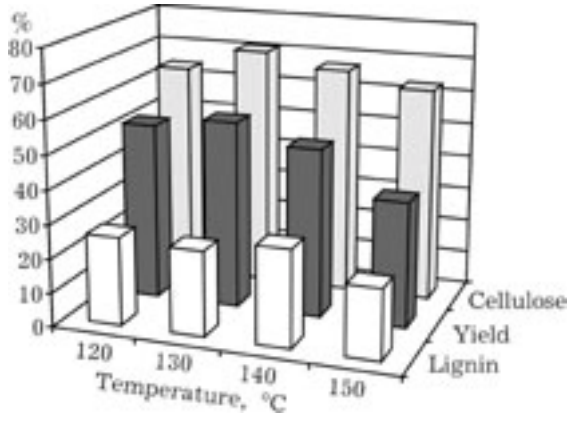

Fig. 1. Influence of the temperature of abies wood delignification on the yield and composition of cellulosic product. H_2O_2/CH_3COOH mole ratio 0.3, catalyst H_2SO_4 2 % on a. d. w., liquor/wood ratio 10 : 1, process time 3 h.

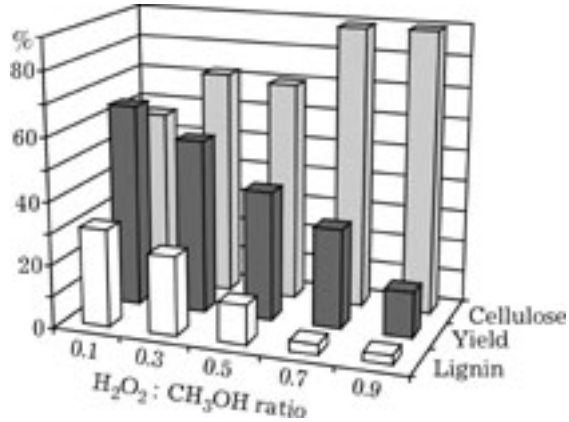

Fig. 2. Influence of H_2O_2/CH_3COOH mole ratio in pulping liquor on the yield and composition of cellulosic product from abies wood. Catalyst H_2SO_4 2 % on a. d. w., liquor/wood ratio 10 : 1, process time 3 h, temperature 130 °C.

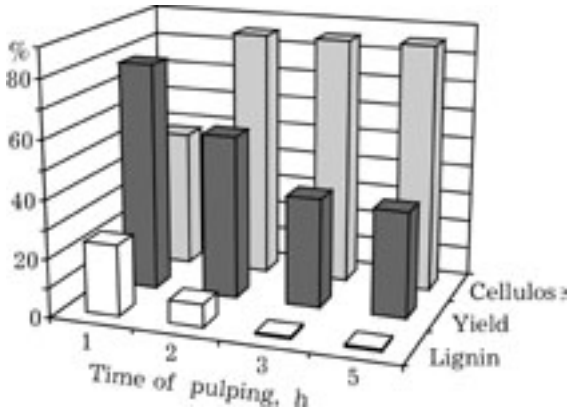

Fig. 3. Influence of the process time on the pulp yield from abies wood and on composition of cellulosic product. H_2O_2/CH_3COOH mole ratio 0.3, catalyst H_2SO_4 2 % on a. d. w., liquor/wood ratio 20 : 1, temperature 130 °C.

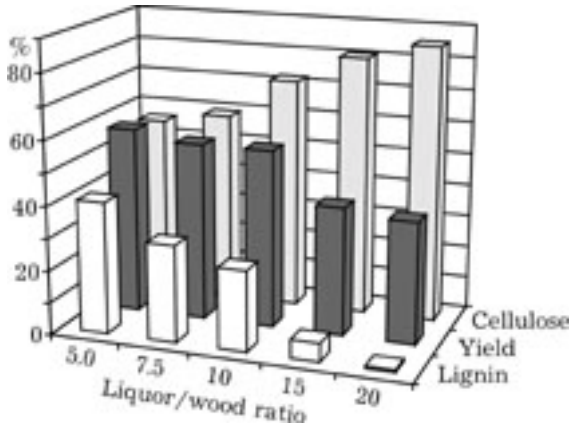

Fig. 4. Influence of liquor/wood ratio on the pulp yield from abies wood and on composition of cellulosic product. H_2O_2/CH_3COOH mole ratio 0.3, catalyst H_2SO_4 2 % on a. d. w., process time 3 h, temperature 130 °C.

is 0.3. This ratio corresponds to rather high yield of pulp (55 % mass) and increased cellulose content (72 % mass) in cellulosic product.

The yield of cellulosic product and its composition varies with the process time (Fig. 3). Increasing of the reaction time from 1 to 5 h increases the degree of wood delignification but decreases the yield of cellulosic product.

It is known [6] that the rate of organosolvent pulping of wood at liquor/wood ratio 5 : 1 can be limited by diffusion of lignin destruction products from wood matrix into pulping liquor. But at higher liquor/wood ratios the diffusion processes are accelerated. Therefore the most pronounced catalytic effects should be expected upon wood delignification at high liquor/wood ratios.

According to data presented in Fig. 4 the increase of liquor/wood ratio from 5 to 20 increases significantly the degree of wood delignification but also reduces the yield of cellulosic product. At high liquor/wood ratios (20 : 1 or 15 : 1) the time of delignification may be decreased up to 2 h. Under these conditions the yield of cellulosic product was near 56 % and content of cellulose and lignin in solid product – 85.6 and 7.9 % mass, respectively.

The data obtained show that the most appropriate concentration of H_2SO_4 catalyst in pulping liquor is near 2 % mass to a. d. w. The increase of the catalyst concentration up to 3.5 % reduces the cellulosic product yield to 48.4–52.9 % mass to a. d. w. as a result of cellulose degradation. Cellulosic product obtained at lower catalyst concentration (1.5 %) contains higher amount of lignin (17.2–17.8 % mass).

The cellulosic products containing 85.2–86.4 % of cellulose were obtained with the yields up to 72 % at optimum conditions of abies wood delignification (H_2O_2/CH_3COOH mole ratio 0.3, H_2SO_4 2 % on a. d. w., liquor/wood ratios 10–20, temperature 130 °C, pulping time 2–3 h).

The application of heterogeneous catalyst instead of soluble sulfuric acid gives some advantages connected with the decrease of a corrosion activity of pulping liquor and with catalyst reuse.

The detail study was accomplished to optimize the operating parameters of abies wood delignification by acetic acid/hydrogen peroxide mixture in the presence of titanium dioxide catalyst.

Data presented in Table 1 show that the products with high content of cellulose are obtained at 120–130 °C and process time 2–3 h.

Table 2 illustrates the influence of TiO_2 catalyst concentration, temperature and process time on the pulp yield and on the composition of cellulosic product obtained from abies wood.

The optimum concentration of TiO_2 is 0.5 % and optimum time of pulping is 3 h. Under these conditions the cellulosic products with yield 52.3 % and delignification degree 96.2 % are produced.

TABLE 2

The influence of TiO_2 concentration, and time of abies wood pulping at 120 and 130 °C on the yield and composition of cellulosic product. H_2O_2/CH_3COOH mole ratio 0.5, liquor/wood ratio 15 : 1.

Parameter	Temperature, °C											
	120						130					
Concentration of TiO_2 catalyst, % mass*	0.5	0.5	1.0	1.0	2.0	2.0	0.5	0.5	1.0	1.0	2.0	2.0
Process time, h	2	3	2	3	2	3	2	3	2	3	2	3
Cellulosic product yield, % mass*	65.7	52.3	8.7	49.0	40.5	38.6	53.6	48.4	42.6	39.8	36.5	34.0
Cellulosic product composition, % mass**:												
Cellulose	70.3	81.7	76.5	86.1	87.6	89.4	83.5	89.5	84.7	83.9	84.6	87.9
Lignin	11.4	2.1	6.4	1.4	2.7	0.8	4.4	0.8	4.5	1.8	5.3	4.8
Hemicelluloses	73.7	96.2	86.9	97.5	96.1	98.9	91.8	98.7	93.7	97.3	93.7	94.1

*To the mass of a. d. w.
**To the mass of a. d. cellulosic product.

Fig. 5. The influence of H_2O_2 /CH_3COOH mole ratio on the cellulose product yield (*1*), cellulose and lignin content (*2*, *3*) in solid product in the process of abies wood delignification. Catalyst TiO_2 0.5 % on a. d. w., liquor/wood ratio 15 : 1, process time 3 h, temperature 130 °C.

Figure 5 demonstrates the influence of H_2O_2/CH_3COOH mole ratio on the abies wood delignification process.

The yield of cellulosic product decreases with the increase of H_2O_2/CH_3COOH mole ratio from 0.1 to 0.7 owing to the increase of concentration of hydroperoxide anions HOO^- promoting the intensive destruction of lignin and amorphous part of cellulose. The optimum H_2O_2/CH_3COOH mole ratio providing high delignification degree (91.8–98.7 %) and the acceptable yield of cellulosic product (53.6–48.4 %) is nearly 0.5.

As in the case of sulfuric acid catalyst cellulosic product yield and composition change upon the variation of liquor/wood ratio (Table 3).

In the result of the accomplished study the optimum parameters of abies wood delignification, corresponding to the highest content of cellulose in the solid product (88.4–89.5 % mass to dry wood) were selected: temperature 130 °C, H_2O_2/CH_3COOH mole ratio 0.3, liquor/wood ratio 15 : 1. The highest cellulose content in cellulosic product was observed for TiO_2 catalyst at concentration 0.5 % mass and pulping time 2 h. In the case of H_2SO_4 catalyst its optimum concentration was 2.0 % mass and pulping time 3 h.

The developed methods of catalytic organosolvent delignification were adapted to production of microcrystalline cellulose (MCC) which is widely used in medicine, pharmaceu-

TABLE 3

The influence of liquor/wood ratio and time of delignification on the yield and composition of cellulosic product obtained from abies wood. H_2O_2/CH_3COOH mole ratio 0.5, catalyst TiO_2 0.5 % on a. d. w., temperature 130 °C

Parameter	Liquor/wood ratio					
	7.5 : 1		10 : 1		15 : 1	
Process time, h	2	3	2	3	2	3
Yield of cellulosic product, % mass*	53.6	55.6	56.6	54.3	53.6	48.4
Composition of cellulosic product, % mass**:						
Cellulose	58.3	59.6	66.1	69.4	83.5	89.5
Lignin	34.4	429.8	25.9	22.0	4.4	0.8
Delignification degree, %	35.1	41.7	48.4	57.9	91.8	98.7

*To the mass of a. d. w.
**To the mass of a. d. cellulosic product.

tical and food industries and in the preparation of sorbents, emulsions, dyes, polymeric covering *etc.* (Fig. 6).

The novel method of MCC production combines the stages of wood catalytic delignification by H_2O_2/CH_3COOH mixture and following solvolysis of obtained cellulosic product. The solvolysis is used for removing of amorphous cellulose from cellulosic product.

MCC with polymerization degree near 240 can be obtained from abies wood sawdust with a rather high yields, depending on the parameters of delignification and solvolysis processes. The highest yield of MCC (35.4 % on dry wood was obtained at the following delignification parameters: T = 130 °C, H_2O_2/CH_3COOH mole ratio 0.3, catalyst concentration 2 % for H_2SO_4 or 0.5 % for TiO_2, liquor/wood ratio 15: 1, 2 h and solvolysis parameters: T = 120 °C, H_2O_2/CH_3COOH mole ratio 0.3, liquor/wood ratio 15 : 1, 1 h.

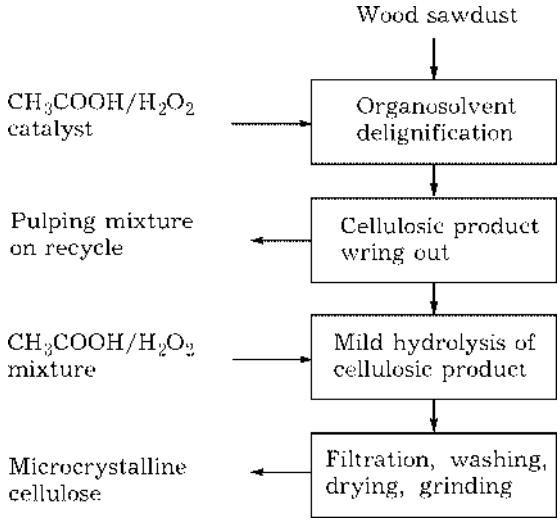

Fig. 6. Scheme of MCC producing from wood sawdust.

The structural characteristics of obtained MCC were studied using γ-ray diffraction and FTIR techniques. It was shown that their spectra are similar to spectra of the standard samples of MCC.

CONCLUSION

The process of abies wood delignification with acetic acid/hydrogen peroxide mixtures is sensitive to such parameters, as temperature, time of pulping, H_2O_2/CH_3COOH mole ratio, liquor/wood ratio, catalyst nature and concentration. In order to obtain cellulosic product of high quality with the acceptable yield the following parameters of wood delignification process should be used: mole ratio H_2O_2/CH_3COOH 0.3, temperature 120–130 °C, pulping time 2–3 h, catalyst concentration 2 % for H_2SO_4 or 0.5 % for TiO_2, liquor/wood ratio from 10 : 1 to 20 : 1.

The use of catalyst at high liquor /wood ratio makes it possible both to reduce the pulping process time and to increase the degree of wood delignification.

The novel ecologically safe method of microcrystalline cellulose production from wood waste material – sawdust was suggested and optimized. It combines the processes of wood catalytic delignification by acetic acid/hydro-

gen peroxide mixture at 130 °C and mild solvolysis of obtained cellulosic product with H_2O_2/CH_3COOH mixture at 120 °C.

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REFERENCES

1 I. A. Weinstok, R. H. Atalla, R. S. Reiner *et al.*, *J. Mol. Catal. A*, 116 (1997) 59.
2 D. V. Evtugin, N. C. Pascoal, *Holzforschung*, 51 (1997) 338.
3 R. R. Hames, B. Kurek, B. Pollet *et al.*, *J. Agric. Food Chem.*, 46 (1998) 5362.
4 J. M. MacLeod, *J. Pulp. Pap. Sci.*, 13 (1987) 44.
5 T. Vourinen, *J. Wood Chem. Technol.*, 13 (1993) 97.
6 G. B. Timirmane, L. T. Purina, M. Ya. Ioelovich, A. P. Treimanis, *Khimiya drevesiny*, 4–5 (1992) 46.
7 J. C. Parajo, J. L. Alonso, V. Santos, *Ind. Eng. Chem. Res.*, 34 (12) (1995) 4333.
8 S. A. Kuznetsova, V. G. Danilov, B. N. Kuznetsov, Book of Proceedings of the Sixth European Workshop on Lignocellulosics and Pulp, Bordeaux, France, 2000, p. 421.
9 H. J. Mielisch, O. Kordsacchia, R. Patt, *Paper*, 50 (10A) (1996) 16.
10 R. Z. Pen, V. R. Pen, M. O. Leonova *et al.*, *Russ. J. Appl. Chem. Eng. Tr.*, 72(9) (1999) 1629.
11 B. N. Kuznetsov, A. A. Efremov, S. A. Kuznetsova *et al.*, *Khimiya rastitel'nogo syr'ya*, 2 (1999) 85.
12 A. V. Obolenskaya, Z. P. El'nitskaya, A. A. Leonovich, Laboratory Work on Chemistry of Wood and Cellulose, Ecology, Moscow, 1991 (in Russian).
13 D. Fengel, G. Wegener, Wood (Chemistry, Ultrastructure, Reactions), Walter de Gruyter, Berlin, New York, 1984.
14 S. K. Bose, R. C. J. Francis, *Pulp. Pap. Sci.*, 25 (12) (1999) 425.
15 Y. H. Ni, A. R. P. VanHeiningen, G. J. Kang *et al.*, *TAPPI J.*, 81(10) (1998) 165.
16 M. A. Zilbergleit, T. V. Korneichik, V. M. Reznikov, *Khimiya drevesiny*, 6 (1988) 44.
17 V. A. Demin, V. V. Shereshovez, Yu. B. Monakov, *Uspekhi khimii*, 68 (11) (1999) 1029.