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Influence of UV pretreatment on the abies wood catalytic delignification in the medium "acetic acid–hydrogen peroxide–TiO_2"

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Abstract Some regularities of abies-wood oxidative delignification by acetic acid–hydrogen peroxide mixture under the action of suspended TiO_2 catalyst and UV pretreatment of wood pulp were studied. The combined action of TiO_2 catalyst and of UV-pretreatment of abies-wood allow to produce at optimal conditions of the delignification process the chemically pure cellulose containing no residual lignin. The major characteristics of cellulose product obtained from abies-wood correspond to the characteristics of microcrystalline cellulose.

Keywords Abies-wood oxidative delignification · UV pretreatment · TiO_2 catalyst

Introduction

New ecology friendly methods of wood delignification use sulfur-free reagents: molecular oxygen, hydrogen peroxide, ozone [1, 2]. The delignification activity of these "green reagents" is increased in the presence of different catalysts [3–5]. In our previous study [6], the intensive delignification of abies-wood was found when the wood sawdust was treated in the acetic acid–hydrogen peroxide solution with powdery TiO_2 catalyst. The optimal conditions were elucidated for the abies-wood delignification with TiO_2 catalyst resulting in a reasonable yield of the cellulosic product with a low content of residual lignin.

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It is well established that TiO_2 is the mostly used photocatalyst [7]. When TiO_2 is irradiated with wavelength lower than 390 nm, electron–hole pairs are generated. They promote the formation of active radical species in the presence of water molecules. Besides, UV irradiation intensifies the destruction of wood lignin [8]. Therefore, the application of photochemical treatment has prospects in wood pulping and bleaching.

This paper describes some regularities of abies-wood delignification by acetic acid–hydrogen peroxide mixture under the action of TiO_2 catalyst and UV pretreatment of the wood pulp.

Experimental

Air-dried abies-wood (*Abies sibirica* Ledeb.) harvested in a suburb of Krasnoyarsk city was used as the initial raw material. The chemical composition of abies-wood (wt%): 50.3 cellulose, 27.7 lignin, 15.4 hemicelluloses, 6.8 extractive substances. Abies-wood sawdust with the average particle size 2–5 mm was used in delignification experiments.

The delignification medium was composed of acetic acid of "chemically pure" grade (GOST 61-75), hydrogen peroxide of medical grade (GOST 177-88) and distilled water (GOST 6709-72).

Industrially produced TiO_2 powder (GOST 9808-84) with an average particle size of about 10 μm, phase composition: rutile 92%, anatase 8% and with the BET surface 3 m^2/g was applied as a catalyst.

Before the delignification process, the reaction medium containing wood sawdust and TiO_2 catalyst was pretreated by UV-irradiation in a quartz reactor with the use of ultraviolet lamp power 850 W.

Delignification of the pretreated reaction medium containing wood sawdust and TiO_2 catalyst was carried out in a metal shaking reactor of 200 cm^3 volume at temperatures 110–140 °C process time 2–3 h, liquid/wood ratios 7.5–20, concentrations of CH_3COOH 21.8–28.5 wt%, H_2O_2 1.5–8.2 wt% and TiO_2 0.5 wt%. Such parameter as a residual lignin content in cellulosic product of wood delignification was used to evaluate the delignification activity of TiO_2 catalyst.

The yield of cellulosic product was estimated by weight method. The contents of cellulose and lignin in this product were determined by standard chemical analysis. The structural characteristics of cellulosic products were studied by FTIR (Vector-22, Bruker) and γ-ray (Dron-4) methods.

Results and discussion

The combined action of TiO_2 catalyst and photochemical pretreatment of reaction mixture was investigated. It was found that the UV-activation of wood promotes the delignification process (Table 1).

The comparison of the efficiency of different methods of wood delignification (Table 1) shows that the combined action of UV irradiation and TiO_2 catalyst allow

Table 1 Comparison of different methods of abies wood delignification in acetic acid–hydrogen peroxide mixture (130 °C, 2 h, CH_3COOH 23.6 wt%, H_2O_2 6.4 wt%, liquid/wood ratio 15)

Parameters	Without catalyst	UV irradiation (10 min) without catalyst	TiO_2 catalyst (0.5 wt%)	UV irradiation, TiO_2 catalyst (0.5 wt%)
Cellulosic product yield (wt%)[a]	51.5	38.2	53.6	35.7
Cellulosic product composition (wt%)[b]				
Cellulose	64.6	81.0	83.5	82.9
Lignin	27.4	6.6	4.4	0

[a] Relative to a.d. wood

[b] Relative to a.d. product

to produce the chemically pure cellulose containing no residual lignin. But the UV pretreatment reduces the yield of cellulosic product down to 35.7 wt% with the liquid/wood ratio of 15 (Table 1).

Kinetic curves of the lignin isolation from UV-irradiated abies-wood look like curves for non-treated abies-wood pulp [6]. The shape of these curves indicates the heterogeneous composition and non-uniform accessibility of wood lignin.

Figure 1 demonstrates the effects of pulping temperature of on the residual lignin content and cellulosic product yield from UV-activated abies wood.

According to the results obtained, the optimal delignification temperature is 120–130 °C and the pulping time is 2–3 h. At these conditions, the cellulosic products with low content of residual lignin (2.7–0.8%) were obtained.

The residual lignin content in cellulosic products was increased at the further growth of the delignification temperature. This can be interpreted by the intensification of condensation reactions among the degraded lignin fragments in the pulping liquor with formation of condensed lignin moieties (so-called "pseudo-lignin") at the pulping temperature higher than 120 °C [9].

The increase of H_2O_2 concentration in the initial reaction medium from 1.5% to 8.2% promotes the delignification process (Fig. 2). Residual lignin is practically

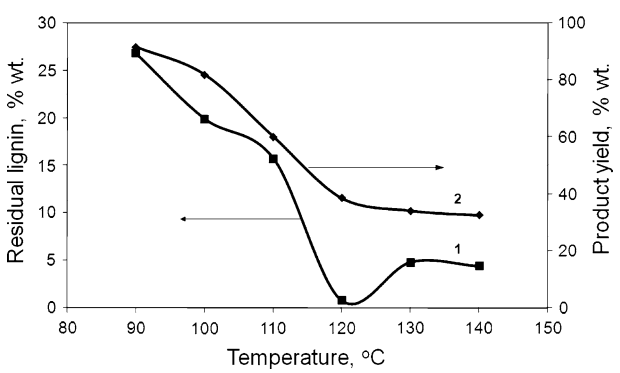

Fig. 1 Influence of delignification temperature on the residual lignin content (1) and on the yield of cellulosic product (2) from activated abies wood (liquid/wood ratio 15, process time 3 h, CH_3COOH 23.6 wt%, H_2O_2 6.4 wt%, TiO_2 0.5 wt%)

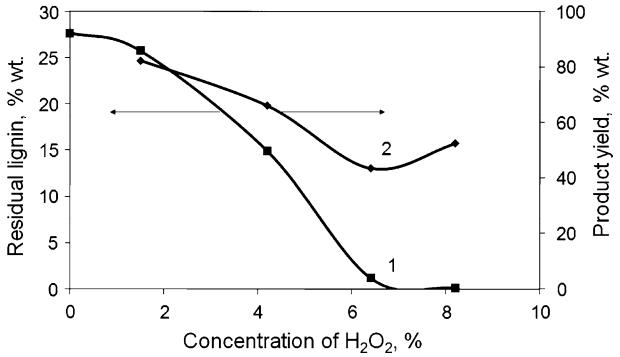

Fig. 2 Influence of H_2O_2 concentration on the residual lignin content (1) and on the yield of cellulosic products (2) from photochemically activated abies wood pulp (liquid/wood ratio 15, CH_3COOH 23.6 wt%, H_2O_2 6.4 wt%, TiO_2 0.5 wt%, process time 2 h)

absent in the cellulosic product obtained at H_2O_2 concentrations 6.4% and delignification time 2 h. However, the longer duration of the pulping process reduces significantly the cellulosic product yield.

It was found that liquid/wood ratio value effects considerably on the cellulosic product yield and on the residual lignin content in the product from the delignification of UV-activated wood (Table 2). Diffusion limitations at liquid/wood ratio 7.5 restricting the dissolution of lignin degradation fragments results in obtaining high yields (up to 62.9 wt%) of cellulosic product with the residual lignin content of 16.5–15.6 wt%. The higher liquid/wood ratios improve the mass transfer conditions. Therefore, the cellulosic products with residual lignin content 6.8–5.8 wt% were obtained at liquid/wood ratio 10. The higher liquid/wood ratios (15–20) allow to produce the pure cellulose containing no residual lignin.

There are a few possible interpretations for the promoting action of UV-irradiation on wood pulping process. Chromoform centers in lignin are able

Table 2 Influence of liquid/wood ratio on the yield and composition of cellulosic products obtained from photochemically activated abies wood pulp

Liquid/wood ratio	Process time (h)	Cellulosic product yield (%)[a]	Cellulosic product composition (wt%)[b]	
			Cellulose	Lignin
7.5	2	62.9	67.5	16.5
7.5	3	59.5	70.3	15.6
10	2	60.3	72.2	6.8
10	3	59.4	76.3	5.8
15	2	43.5	82.9	0.3
15	3	40.3	85.7	0
20	3	42.0	85.1	0

Temperature 130 °C, CH_3COOH 23.6 wt%, H_2O_2 6.4 wt%, TiO_2 0.5 wt%, UV-activation time 10 min

[a] Relative to a.d. wood

[b] Relative to a.d product

to absorb UV-irradiation at region 200–400 nm and then photoexcited groups in lignin can easily react with active oxygen species [8]. In addition, the UV-irradiation promotes the photolysis of hydrogen peroxide and water with the formation of hydroxyl radicals ($^{\bullet}$OH), peroxyl radicals ($^{\bullet}$OOH) and other active oxygen species. They can be produced with TiO_2 catalysts under UV-irradiation [7]. These radical species are considered as the most active in the lignin degradation reactions: in the cleavage of C–C bonds in aliphatic side-chains, alkyl–aryl bonds and *O*-demethoxylation reactions [10].

Taking these data into account, the promoting action of UV-pretreatment of the mixture "wood sawdust–acetic acid–hydrogen peroxide–water–TiO_2" at the further process of delignification can be interpreted by the intensification of reactions of $^{\bullet}$OH radicals generation. In the case of suspended TiO_2 catalyst, the active radicals can diffuse through the pulping liquor to wood particles, resulting in the oxidative destruction of lignin.

Besides, the hydroxyl radicals can cleave any glycosidic linkage in the carbohydrate chains [11]. Therefore, the excess concentration of $^{\bullet}$OH radicals generated in a pulp liquor at the combined action of UV irradiation and TiO_2 catalyst promotes the oxidative degradation of not only lignin, but also hemicelluloses and amorphous part of cellulose, resulting in the reduced yield of cellulosic product (Table 2).

The removal of amorphous cellulose increases the content of crystalline cellulose in the cellulosic products of wood delignification. The structure of cellulosic products was studied by γ-ray diffraction and FTIR methods. The major characteristics of cellulosic product obtained by the catalytic delignification of UV-pretreated abies wood correspond to characteristics of microcrystalline cellulose (MCC) [12]. This cellulosic product has the lattice of cellulose I, crystallinity index 0.71, polymerization degree 240.

The known methods of MCC production from wood include the steps of wood delignification, bleaching and mild hydrolysis [12]. The suggested approach on the basis of the catalytic delignification of UV-pretreated wood in acetic acid–hydrogen peroxide medium allows producing the MCC by one-step process without the use of ecology dangerous delignification and bleaching agents and sulfuric acid.

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