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Abies Wood Delignification by Acetic Acid – Hydrogen Peroxide Mixture under the Action of TiO₂ Catalysts and UV Irradiation

Boris N. Kuznetsov^{a,b*}, Svetlana A. Kuznetsova^{a,b},
Vladimir G. Danilov^a and Olga V. Yatsenkova^a

^a Institute of Chemistry and Chemical Technology SB RAS,
42 K. Marx st. Krasnoyarsk, 660049 Russia

^b Siberian Federal University,
79 Svobodny, Krasnoyarsk, 660041 Russia ¹

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The present paper describes the influence of TiO₂ catalyst and of UV pretreatment of reaction mixture “abies sawdust-CH₃COOH-H₂O₂-catalysts TiO₂” on the yield and composition of cellulosic product. The significant increase of the delignification activity as a result by the use of photochemical pretreatment of reaction mixture with TiO₂ catalyst was established. Optimum parameters of abies wood delignification resulting in the high yield of cellulosic product with low residual lignin content has been selected.

Keywords: abies wood, oxidative delignification, TiO₂ catalyst, UV irradiation, cellulosic products yield and composition.

Introduction

New methods of wood delignification in organic solvents use sulphur-free reagents and they allow to utilize the side-products from lignin and hemicelluloses into valuable chemicals and also to reduce the energy expenses in solvent re-using as compared to conventional pulping processes [1-2]. Molecular oxygen, hydrogen peroxide, ozone are used as ecology pure delignification reagents in the presence of different catalysts [3-7]. In our previous study the intensive oxidation of wood-lignin was detected in acetic acid/hydrogen peroxide mixture in the presence of sulphuric acid catalyst [8]. It is well known that

UV irradiation promotes the destruction of wood lignin in a higher degree than that of cellulose. Therefore the application of photochemical pretreatment has prospects in wood pulping and bleaching [9].

TiO₂ is the most used photocatalyst [10]. When TiO₂ is irradiated with wavelength greater than 390 nm electron-hole pairs are generated. The latter promotes the hydroxyl radicals formation in the presence of water [11]. It was shown recently [8] that TiO₂ catalyses the delignification of abies wood in CH₃COOH/H₂O₂ mixture.

This paper describes some regularities of abies-wood delignification by CH₃COOH/H₂O₂

* Corresponding author E-mail address: bnk@icct.ru

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mixture under the action of TiO_2 catalyst and UV pretreatment of pulp.

Experimental

Air dry aspen-wood (*Populus tremula* L.) harvested in suburb of Krasnoyarsk city was used as the initial raw material. The chemical composition of aspen-wood (% wt.): 46.3 cellulose, 21.8 lignin, 24.5 hemicelluloses, 7.8 extractive substances. Wood sawdust with the average particle size 2-5 mm was used in delignification experiments.

The delignification mixture 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).

The industrially produced TiO_2 powder (GOST 9808-84) with an average particle size of about 10 nm, phase composition: rutile 92 %, anatase 8 % and with the BET surface 3 m²/g was applied as a catalyst.

Before the start of delignification process the reaction mixture (wood pulp) containing 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 wood pulp was carried out in a metal shaking reactor of 200 cm³ 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

Kinetic curves of the lignin isolation from UV irradiation pulp look like curves for treated wood pulp [7]. The shape of these curves indicates the heterogeneous composition and non-uniform accessibility of wood lignin.

The optimal parameters of abies-wood catalytic delignification by $\text{CH}_3\text{COOH}/\text{H}_2\text{O}_2$ mixture resulting in an acceptable yield of cellulosic product with low content of residual lignin were selected.

Fig. 1 demonstrates the influence of temperature of abies wood pulping on the residual lignin content and cellulosic product yield in the presence of TiO_2 catalyst.

According to obtained results the optimal delignification temperature is 120-130°C and time of pulping 2-3 hours. At these conditions the cellulosic products with low content of lignin (2.7-0.8%) were obtained. The yield of cellulosic product with low lignin content was increased with the decrease of TiO_2 concentration to 0.5% wt. (Table 1).

The residual lignin content in cellulosic products was increased at the further growth of the delignification temperature. This fact can be explained by the intensification of condensation reactions in the pulping liquor with the formation of so-called “pseudo-lignin” at temperatures higher 120 °C [9]. Delignification properties of pulping liquor can be improved by optimizing the concentrations of CH_3COOH , H_2O_2 and liquor ratio.

The increase of H_2O_2 concentration in reaction mixture from 1.5% to 8.2% promotes the lignin removal from wood (Fig. 2). Residual lignin is practically absent in cellulosic product obtained at H_2O_2 concentrations 6.4% and delignification time 2 h. But the higher duration of the pulping process reduces significantly the cellulosic product yield.

The comparison of the efficiency of different methods of wood delignification (Fig. 3) show that

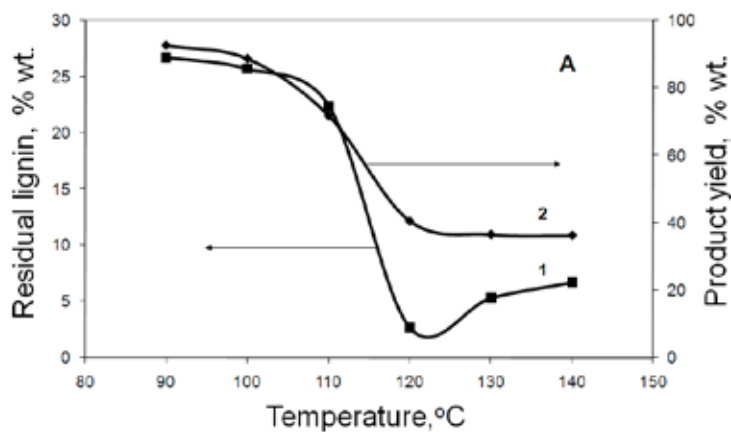


Fig.1. Influence of delignification temperature on the residual lignin content (1) and on the yield of cellulosic product (2) from abies wood (liquid/wood ratio 15, process time 3 h, CH_3COOH 23.6 % wt., H_2O_2 6.4 % wt., TiO_2 0.5 % wt.)

Table 1. Influence of TiO_2 concentration and time of abies wood delignification at 130°C on the yield and composition of cellulosic product (CH_3COOH 24.5% and H_2O_2 6.4%, liquor ratio 15)

Parameters	TiO_2 catalyst concentration, % wt. on a.d.w.							
	0.5		1.0		1.5		2.0	
	2 h	3 h	2 h	3 h	2 h	3 h	2 h	3 h
Yield of cellulosic product, %*	53.6	48.4	42.6	39.8	40.1	35.8	36.5	34.0
Product composition, %**:								
cellulose	83.5	89.5	84.7	83.9	78.1	86.9	84.6	87.9
lignin	4.4	0.8	4.5	1.8	12.0	7.2	5.3	4.8

* relative to mass of a.d.wood; ** relative to mass of a.d. product

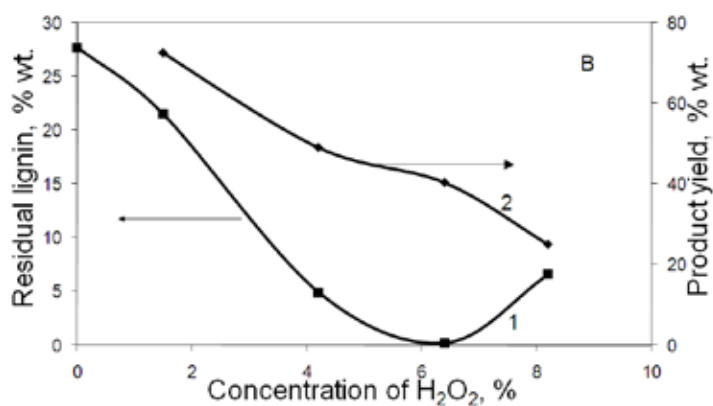


Fig. 2. Influence of H_2O_2 concentration on the residual lignin content (1) and on the yield of cellulosic products (2) from abies wood pulp (liquid/wood ratio 15, CH_3COOH 23.6 % wt., H_2O_2 6.4 % wt., TiO_2 0.5 % wt., process time 2 h)

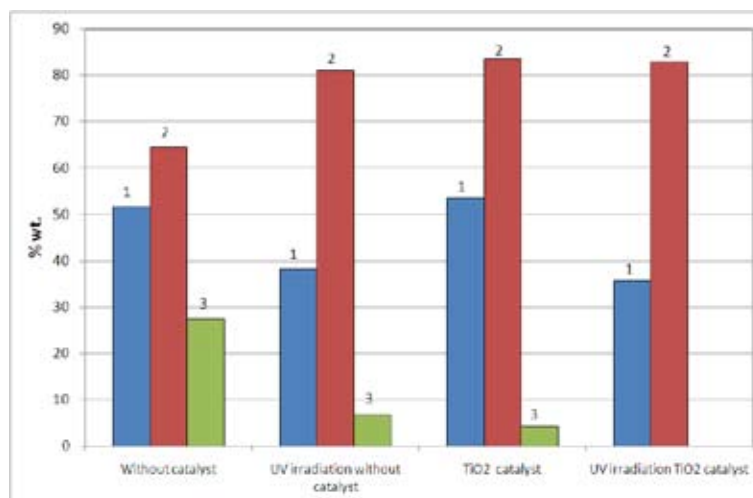


Fig. 3. The comparison of different methods of abies wood delignification in acetic acid – hydrogen peroxide mixture (130 °C, 2 h, CH₃COOH 23.6 % wt., H₂O₂ 6.4 % wt., TiO₂ 0.5 % wt., liquid/wood ratio 15). Cellulosic product yield on a.d.wood (1), cellulose (2) and lignin (3) content in the product

the combined action of UV irradiation and TiO₂ catalyst allow to produce the chemically pure cellulose containing no residual lignin. But the UV pretreatment reduces the yield of cellulosic product up to 35.7 % wt.

It was found that liquid/wood ratio value influences considerably on the yield of cellulosic product from UV-activated pulp and on residual lignin content in the product (Table 2). Diffusion limitations at liquid/wood ratio 7.5 restrict the dissolution of lignin destruction fragments and the cellulosic product with high yield (to 62.9 % wt.) and with residual lignin content 16.5-15.6 % wt. was obtained. 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 reasons explaining the promoting action of UV-irradiation on wood pulping process. Chromoform centers of lignin are able to absorb UV-irradiation at region 200-400 nm and then the photo excited

groups of lignin can easily react with active oxygen species [8]. Besides, the UV-irradiation promotes the photolysis of hydrogen peroxide with the formation of hydroxyl radicals HO•, peroxyradicals HOO• and other active oxygen species. The same can make the TiO₂ catalysts under UV-irradiation [7]. These radical species are considered as the most active in reactions of lignin destructions: in the rupture of C-C bonds of alifatic chains, splitting of alkyl-aryl bonds and in demethoxylation reactions [10].

Taking these data into account the promoting action of UV pretreatment of the mixture “wood sawdust – acetic acid – hydrogen peroxide – water – TiO₂” at the further process of the pulp delignification can be explained by the intensification of reactions of •OH and •OOH radicals generation. These radicals are formed during the photolysis of H₂O₂ or H₂O molecules on the surface of photocatalyst TiO₂ with participation of electron-hole pairs [7]. Since the hydrogen peroxide molecules are more reactive than that of water they should play the important role in hydroxyl radical and peroxyradicals generation on UV-irradiated TiO₂. As it is known,

Table 2. The influence of pulping liquor ratio on the yield and composition of cellulosic product obtained from photochemically activated abies wood (temperature 130°C, CH₃COOH 23.6 % wt., H₂O₂ 6.4 % wt., TiO₂ 0.5 % wt.)

Liquor ratio	Process time, h	Cellulosic product yield, %*	Composition of cellulosic product, % wt. **	
			cellulose	lignin
7,5	2	62,9	67,5	16,5
7,5	3	59,5	70,3	15,6
7,5***	3	55,6	59,6	29,8
10	2	60,3	72,2	6,8
10	3	59,4	76,3	5,8
10***	3	54,3	69,4	22,0
15	2	43,5	82,9	0,3
15***	2	53,6	83,5	4,4
15	3	40,3	85,7	0
20	3	42,0	85,1	0

* relative to a.d.wood.; ** relative to a.d. cellulosic product; *** without of UV activation.

these radical species can accelerate the oxidative destruction of lignin to low molecular mass soluble products [10]. In the case of suspended TiO₂ catalyst the active radicals can diffuse through the liquid reaction medium 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 •OH radicals generated in a pulp at the combined action of UV irradiation and TiO₂ catalyst promotes the oxidative destruction not only lignin, but also hemicelluloses and amorphous part of cellulose. This results in the reduced yield of cellulosic product (Table 3).

The removal of amorphous cellulose increases the content of crystalline cellulose in the cellulosic products of wood delignification. Permolecular structure of cellulosic products was studied by X-ray diffraction and FTIR methods. The main characteristics of cellulosic product obtaining by 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 producing from wood include the steps of wood delignification, bleaching and mild hydrolysis [12]. The suggested approach based on catalytic delignification of UV pretreated pulp in acetic acid – hydrogen peroxide mixture allow to produce MCC by one-step process without the use of ecology dangerous delignification and bleaching agents and sulphuric acid.

Conclusion

The influence of conditions of abies wood delignification in CH₃COOH/H₂O₂ medium (temperature, TiO₂ catalyst concentration, composition of reaction mixture, UV-pre-treatment, liquor ratio and process time) on the yield and composition of cellulosic product was established. The most pronounced intensification of delignification process was observed under combined action of TiO₂ catalyst and photochemical pre-treatment of reaction mixture. The optimum operating parameters of catalytic delignification process supplying the production of cellulosic

product with acceptable yield and demanded properties were selected. They allow to obtain the conventional cellulosic product (yield 60.3-59.4%) with lignin content 6.8-5.8% and pure cellulose (yield 42.0-40.3%) with lignin content less 0.04%.

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