

# Kinetic studies and optimization of abies wood fractionation by hydrogen peroxide under mild conditions with TiO<sub>2</sub> catalyst

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**Abstract** The kinetic study of abies wood delignification by H<sub>2</sub>O<sub>2</sub> in the medium acetic acid–water was first carried out in the presence of TiO<sub>2</sub> catalyst under mild conditions: temperatures 70–100 °C, atmospheric pressure. The oxidative delignification process is described satisfactory by the first order equation in all temperature range. The rate constants varied between 0.80 and 12.3 × 10<sup>-3</sup> min<sup>-1</sup> and the activation energy was near 81 ± 0.21 kJ mol<sup>-1</sup>. The optimal parameters of the delignification process, providing the effective fractionation of abies wood on microcrystalline cellulose and soluble lignin, were established by experimental and numerical methods.

**Keywords** Abies wood · Oxidative fractionation · Hydrogen peroxide · TiO<sub>2</sub> catalyst · Kinetics · Optimization

## Introduction

The manufacture of cellulose by sulfate and sulfite pulping is the most developed direction of chemical wood processing [1, 2]. These industrial pulping processes are based on the application of harmful and corrosive sulfur and chlorine-containing delignification reagents. Advanced processes of organosolv delignification, where organic and water–organic solvents are used, can become an alternative to the traditional pulping methods [3–5]. The most promising solvents, free from sulfur

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and chlorine, are organic acids (acetic and formic acids), alcohols (methanol, ethanol, butanol), acetone and other low-toxic organic compounds [6–9]. Organosolv methods of delignification causes less environmental damage and they are less energy-intensive, as compared to existing pulping processes.

The processes of organosolv delignification in the presence of environmentally safe oxidants, like oxygen and hydrogen peroxide [10–12], has drawn a lot of attention. The new organosolv processes do not always allow obtaining cellulose quality, required for its further chemical processing. However, they can be successfully used for the wood fractionation on cellulose and soluble lignin for the purpose of their further processing to chemicals and biofuels. It has been shown that some catalysts are able to intensify the processes of organosolv delignification [13, 14].

Some complexes of the transition metals, for example so-called polyoxometalates, can promote the processes of pulp and wood delignification by oxygen [15, 16]. However, the practical use of these catalysts is complicated by their high cost and the complexity of regeneration for reuse.

Sulfuric acid can act as a catalyst of wood oxidative delignification by  $\text{H}_2\text{O}_2$  in acetic acid–water solvent [17]. But  $\text{H}_2\text{SO}_4$  promotes the hydrolysis of polysaccharides decreasing the yield of cellulosic product. Besides,  $\text{H}_2\text{SO}_4$  catalyst has such technological disadvantages as high toxicity and corrosion activity.

More technologically convenient solid  $\text{TiO}_2$  can catalyze an oxidative delignification of the wood by  $\text{H}_2\text{O}_2$  at 120–130 °C and elevated pressure [18, 19]. Advantages of  $\text{TiO}_2$  application, as delignification catalyst, are stipulated by the absence of corrosion activity and toxicity, availability, low cost and lack of need for its regeneration. It is important to note that the catalytic properties of  $\text{TiO}_2$ -based materials are sensitive to the method of their producing [20].

The different side reactions of low molecular mass products condensation with the formation of so-called “pseudo-lignin” [21] take place in the wood delignification processes at elevated temperatures. The contribution of condensation reactions can be reduced by acceleration the diffusion of lignin depolymerization products from the wood particles into solution.

In a previous paper [22], the authors have shown that the use of small particles of wood (sawdust), high liquid to wood ratio (LWR) and intensive mixing of reaction solution, allow to reduce externally diffusion limitations and to provide in the presence of 2%  $\text{H}_2\text{SO}_4$  catalyst a high rate of aspen wood delignification by  $\text{H}_2\text{O}_2$  under mild conditions (70–100 °C, atmospheric pressure).

The present work demonstrates a possibility of successful replacement the  $\text{H}_2\text{SO}_4$  catalyst on non-toxic and non-corrosive solid  $\text{TiO}_2$  catalyst in the oxidative fractionation of abies wood on cellulose and soluble lignin under mild conditions. The kinetic study of abies wood sawdust delignification in the medium “ $\text{H}_2\text{O}_2$ – $\text{CH}_3\text{COOH}$ – $\text{H}_2\text{O}$ – $\text{TiO}_2$  catalyst” at temperatures 70–100 °C, atmospheric pressure and under vigorous agitation was accomplished. By experimental and computational methods the optimal process conditions providing a high yield of quality cellulosic product, were determined.

## Experimental

Air dry sawdust (fraction 2–5 mm) of abies wood (*Abies sibirica* L.), harvested in the forest area near Krasnoyarsk city, has been used as an initial raw material. The chemical composition of abies wood (wt% on abs. dry wood): cellulose—45.7, lignin—25.3, hemicelluloses—17.7, extractive substances—6.2, ash—0.5.

The delignification solution was composed of the “chemically pure” acetic acid (GOST 61-75), “medical grade” hydrogen peroxide (GOST 177-88) and distilled water (GOST 6709-72). All chemical reagents were purchased at the CJSC “Khimreactivsnab” (Russia).

Commercial TiO<sub>2</sub> (GOST 9808-84) in rutil modification with an average particle size of about 10 microns and BET surface area 3 m<sup>2</sup>/g was used as the delignification catalyst.

Delignification of wood sawdust was carried out using 250 cm<sup>3</sup> glass reactor equipped with mechanical stirrer, reflux condenser and thermometer. Abies wood sawdust (10 g) was placed into the glass reactor. Then, a mixture of glacial acetic acid (98 wt%), hydrogen peroxide (32 wt%), distilled water and TiO<sub>2</sub> was added. The reaction mixture was vigorously stirred (700 rpm) under selected temperature (70–100 °C) for duration of 1–5 h. Composition of the reaction mixture was varied in the following range: hydrogen peroxide 3–7 wt%, acetic acid 20–35 wt%, liquid/wood ratio (LWR) –10 to 15. The concentration of TiO<sub>2</sub> catalyst was kept at 1 wt% in all experiments. The solid product was separated under vacuum using a Buchner funnel, followed by washing with distilled water and drying at 105 °C until constant weight.

Such parameters as the residual lignin content and hemicelluloses content in cellulosic product were used to evaluate the delignification activity of TiO<sub>2</sub> catalyst.

The cellulosic product yield was estimated by gravimetric method and calculated as follows:

$$Y = (m/m_o) \times 100 \quad (1)$$

Here  $Y$  is the yield of cellulosic product, wt%,  $m$  is the mass of abs. dry cellulosic product, g,  $m_o$  is the mass of abs. dry wood, g.

The contents of cellulose, lignin and hemicelluloses were defined by chemical methods, generally accepted in wood chemistry [23].

X-ray diffraction analysis was carried out with the use of PANalytical X'Pert Pro diffractometer with Cu K<sub>α</sub> source ( $\lambda = 0.154$  nm) in the  $2\theta$  range 5–70° and scanning step width of 0.01°/scan. The cellulose samples were analyzed by the powder method in cuvette with 2.5 cm diameter. The crystallinity index (CI) was calculated from the ratio of the height between the intensity of the crystalline peak ( $I_{002} - I_{AM}$ ) and the total intensity ( $I_{002}$ ) after the subtraction of the background signal [24]:  $CI = (I_{002} - I_{AM}) / I_{002}$ , where  $I_{002}$  is the height of the 002 peak ( $I_{002}$ );  $I_{AM}$  is the height of the minimum between the 002 and the 101 peaks.

FTIR spectra were recorded with Bruker Tensor—27 wavenumbers in the range 4000–400 cm<sup>-1</sup> in transmission mode. Samples of cellulose (4 mg for each) were

prepared in tablet with matrix KBr. Spectral data were processed by OPUS/YR program (version 2.2).

Solid state  $^{13}\text{C}$  CP/MAS spectra were recorded with the use of Bruker Avance III spectrometer, operating at 150.9 MHz  $^{13}\text{C}$  resonance frequency. Samples were packed in 3.2 mm rotors and spun at 7.5 kHz. All spectra were acquired at room temperature (25 °C). Acquisition parameters were set as follows: acquisition time 0.33 ms, crosspolarization contact time 3 ms, 4096 accumulated scans with repetition interval 5 s. Chemical shifts were referenced relative to adamantane as external standard (methylene at  $\delta^{13}\text{C} = 29.5$  ppm). Acquired free induction decays were multiplied with exponential window function with 25 Hz line broadening before Fourier transformation.

## Result and discussion

To optimize the process of abies wood delignification, the influence of reaction conditions (temperature, concentrations of acetic acid and hydrogen peroxide, liquid/wood ratio, time) on the yield and composition of cellulosic product was studied.

The effect of  $\text{TiO}_2$  concentration on the process of peroxide delignification of wood at elevated temperatures (120–140 °C) was early studied by authors [18]. It was found that the optimal concentration of  $\text{TiO}_2$  catalyst providing the rather high yield of cellulosic product with low content of residual lignin corresponds to 1%  $\text{TiO}_2$  on the weight of absolutely dry wood. For this reason, the concentration of  $\text{TiO}_2$  1 wt% was used in the study of abies wood peroxide delignification under mild conditions (70–100 °C).

The impact of  $\text{H}_2\text{O}_2$  and  $\text{CH}_3\text{COOH}$  concentration on the yield and composition of cellulosic products obtained by abies wood delignification with 1%  $\text{TiO}_2$  catalyst was investigated at the fixed temperature, LWR and time.

The increase of  $\text{H}_2\text{O}_2$  concentration in the reaction mixture from 3 to 5 wt% significantly reduces the content of residual lignin and hemicelluloses in the cellulosic product (Table 1). But at the same time, the yield of cellulosic products is

**Table 1** Impact of  $\text{H}_2\text{O}_2$  concentration on the yield and composition of cellulosic products obtained by abies wood delignification at 100 °C,  $\text{CH}_3\text{COOH}$ -30 wt%, LWR-15, time-4 h

Concentration of $\text{H}_2\text{O}_2$ , wt%	Yield of cellulosic product* (wt%)	Composition of cellulosic product** (wt%)		
		Cellulose	Lignin	Hemicelluloses
3	69.7	73.0	15.4	11.1
4	56.5	88.7	3.9	7.9
5	55.0	93.2	2.1	4.4
7	52.6	94.1	1.8	3.8

\* On abs. dry wood

\*\* On abs. dry cellulosic product

decreased from 69.7 to 52.6 wt% The same regularities were observed with the increase of acetic acid concentration (Table 2).

Acetic acid was used in the reaction mixture to facilitate the dissolution of the products of lignin oxidative depolymerization. When the concentration of CH<sub>3</sub>COOH in the reaction medium is less than 20 wt%, the obtained cellulosic product has a high content of residual lignin.

The rather high LWR (10–15) was used in the experiments in order to reduce the external diffusion limitations. The increase of LWR from 10 to 15 only slightly affects the yield of cellulosic product but reduces the content of residual lignin from 2.8 to 1.1 wt% and that of hemicelluloses-from 5.9 to 4.8 wt% (Fig. 1).

The kinetic study of abies wood delignification by H<sub>2</sub>O<sub>2</sub> was accomplished in the temperature range of 70–100 °C. The variation of lignin concentration in the cellulosic product was used for calculating the rate constants of delignification process. A nonlinear fitting method was used for the processing of the kinetic data [25].

It was found that the process of oxidative delignification of abies wood by H<sub>2</sub>O<sub>2</sub> in the presence of TiO<sub>2</sub> catalyst is described satisfactory by the first order equation:

$$c = c_0 \exp^{-kt} \tag{2}$$

Here *c* is the concentration of lignin in the cellulosic product, wt%; *c*<sub>0</sub> is the concentration of lignin in abies wood, wt%; *k* is the reaction rate constant, min<sup>-1</sup>; *t* is the time, min (Fig. 2).

The calculated rate constants of abies wood oxidative delignification with catalyst TiO<sub>2</sub> are presented in Table 3.

The value of activation energy of abies wood oxidative delignification process was determined using temperature dependence of the rate constants in Arrhenius coordinates (Fig. 3). The rather high value of activation energy (81 ± 0.21 kJ mol<sup>-1</sup>) points to the absence of significant of external diffusion limitations at the used conditions of abies wood oxidative delignification with TiO<sub>2</sub> catalyst.

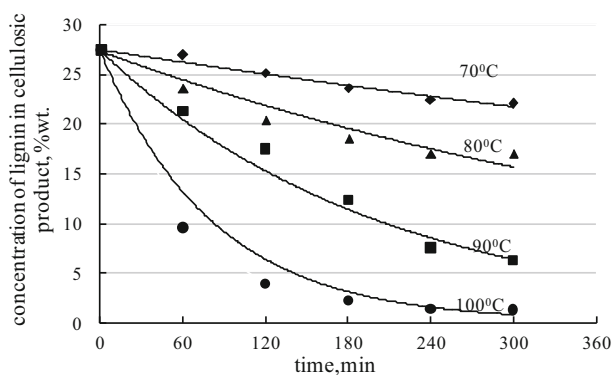
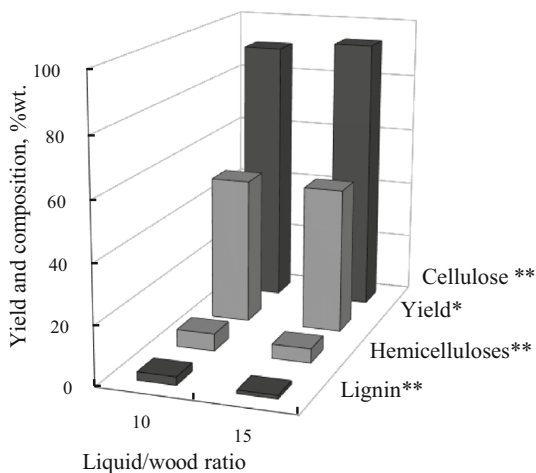
**Table 2** Impact of CH<sub>3</sub>COOH concentration on the yield and composition of cellulosic products obtained by abies wood delignification at 100 °C, H<sub>2</sub>O<sub>2</sub>-6 wt%, LWR-15, time-4 h

Concentration of CH <sub>3</sub> COOH, wt%	Yield of cellulosic product* (wt%)	Composition of cellulosic product** (wt%)		
		Cellulose	Lignin	Hemicelluloses
20	58.9	83.2	9.5	6.9
25	55.2	90.2	3.2	6.2
30	52.6	91.6	2.3	5.7
35	52.0	93.7	2.2	3.7

\* On abs. dry wood

\*\* On abs. dry cellulosic product

**Fig. 1** Influence of liquid/wood ratio on the yield and composition of cellulosic products from abies wood: temperature—100 °C; CH<sub>3</sub>COOH—30 wt%; H<sub>2</sub>O<sub>2</sub>—6 wt%; time—4 h. Asterisk on abs. dry wood, double asterisk on abs. dry cellulose product

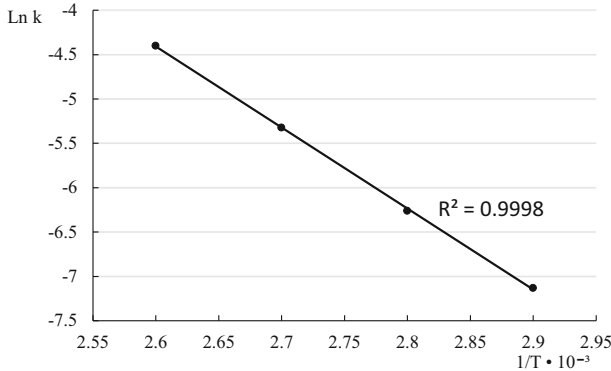


**Fig. 2** The time dependence of lignin concentration in cellulosic products obtained by abies wood oxidative delignification in the presence of 1 wt% TiO<sub>2</sub> catalyst (H<sub>2</sub>O<sub>2</sub>—6 wt%, CH<sub>3</sub>COOH—30 % wt., LWR—15)

**Table 3** Rate constants of abies wood delignification process (delignification conditions are the same as in Fig. 2)

Temperature, °C	K × 10 <sup>-3</sup> (min <sup>-1</sup> )	R <sup>2</sup>
70	0.8 ± 0.19	0.96
80	1.9 ± 0.05	0.91
90	4.9 ± 0.10	0.97
100	12.3 ± 0.64	0.89

The numerical optimization of the abies wood oxidative delignification process with TiO<sub>2</sub> catalyst was carried out with the Statigraphic application software, according to earlier described procedure [26]. The main purpose of the analysis was to find conditions for the most complete removal of lignin from wood, while maintaining a sufficiently high yield of cellulosic product.



**Fig. 3** Temperature dependence of rate constants of abies wood oxidative delignification process with TiO<sub>2</sub> catalyst (CH<sub>3</sub>COOH—30 wt%, H<sub>2</sub>O<sub>2</sub>—6 wt%, LWR = 15, time—4 h)

As independent variables, the following factors have been selected: X<sub>1</sub> is the the H<sub>2</sub>O<sub>2</sub> concentration in reaction solution, wt%; X<sub>2</sub> is the liquid to wood ratio. The other process parameters were fixed: temperature 100 °C, concentration of acetic acid 30 wt%; TiO<sub>2</sub> 1 wt%, time 4 h.

The following output parameters for optimization were selected: Y<sub>1</sub> is the the cellulosic product yield, wt%; Y<sub>2</sub> is the the cellulose content in the product, wt%; Y<sub>3</sub> is the lignin content in the product, wt%

Optimization was performed with the use of generalized parameter of optimization (W<sub>a</sub>), which was calculated using the following equation:

$$W_a = \frac{\sum_{j=1}^p \delta_j d_j}{\sum_{j=1}^p \delta_j}$$

Here  $\delta$  is the weight of the output parameter  $0 \leq \delta_j \leq 1$ ;  $d_j$  is the private utility function, which was calculated using the following equation:

$$d_j = \frac{\varphi_o(x) - y_j^{(-)}}{y_j^{(+)} - y_j^{(-)}}$$

Here  $\varphi_o(x)$  is the response of output parameter at the point X;  $y_j^{(+)}$  and  $y_j^{(-)}$  are the best and worst values of the output parameters, within the studied region.

Table 4 presents the data of conditions and results of experiments for the calculation of generalized parameter of optimization. When choosing weights  $\delta$ , it was assumed that the residual lignin content is the most important parameter for assessing the quality of cellulosic product. For this reason, this parameter got the weight equal to 1. The weights of such parameters as yield of cellulosic product and cellulose content in the product were choosing equal 0.5.

**Table 4** Matrix for planning of the experiments of abies wood delignification, the results of dispersion analysis, the utility functions and the generalized parameter of optimization

Experimental number	X <sub>1</sub>	X <sub>2</sub>	Y <sub>1</sub>	Y <sub>2</sub>	Y <sub>3</sub>	d <sub>1</sub>	d <sub>2</sub>	d <sub>3</sub>	W <sub>a</sub>
1	2	5	76.8	71.0	21.8	1	0	0	0.25
2	4	5	72.6	73.6	19.2	0.858	0.126	0.126	0.309
3	6	5	63.8	78.9	13.9	0.560	0.385	0.385	0.428
4	2	10	64.9	76.4	16.4	0.597	0.263	0.263	0.346
5	4	10	51.2	87.6	5.2	0.135	0.809	0.809	0.640
6	6	10	47.7	89.1	3.7	0.017	0.883	0.882	0.666
7	2	15	56.6	84.3	8.8	0.317	0.648	0.634	0.558
8	4	15	49.9	90.3	2.5	0.091	0.941	0.941	0.728
9	6	15	47.2	91.5	1.3	0	1	1	0.75
Y <sup>(-)</sup>			47.2	71.0	21.8				
Y <sup>(+)</sup>			76.8	91.5	1.3				
δ			0.5	0.5	1				

The results of analysis of the influence of the main factors on the generalized parameter of optimization  $W_a$  are given in Table 5.

F-ratio variances (F ratio) and the level of significance (P value) characterize the contribution of each factor in the outcome of the process. The contribution of the factor is more significant when the F ratio is greater and the significance level (P value) is smaller.

The analysis of variances showed that the effect of both factors  $X_1$  and  $X_2$  on the generalized parameter of optimization is statistically significant (P value less than 0.05 and the confidence level is above 95%).

As a result of mathematical processing the following regression equation was obtained:

$$W_a = 0.5990 + 0.115X_1 + 0.1748X_2 - 0.0593 X_1^2 + 0.0035X_1X_2 - 0.0468X_2^2$$

The response surface of the generalized parameter of optimization is presented in Fig. 4.

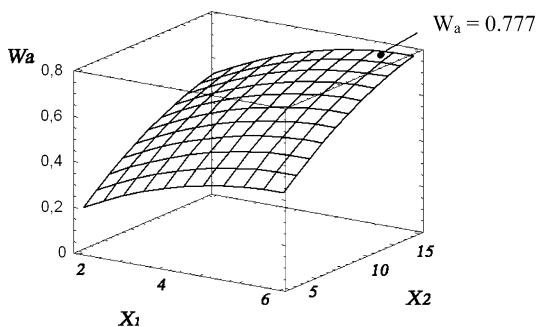
It was found that the generalized parameter of abies wood oxidative delignification process optimization is set to 0.777. This compiles with the following optimal

**Table 5** Analysis of variances for  $W_a$ 

Dispersion source	Sum of squares	df	F-ratio	P value
A:X1	0.07935	1	15.60	0.0289
B:X2	0.1834	1	36.07	0.0092
AA	0.00704	1	1.38	0.3242
AB	0.000049	1	0.01	0.9280
BB	0.004386	1	0.86	0.4215



**Fig. 4** Response surface of the generalized parameter ( $W_a$ ) of the optimization of abies wood delignification with  $\text{TiO}_2$  catalyst:  $X_1$  is the initial concentration of  $\text{H}_2\text{O}_2$ ,  $X_2$  is the liquid to wood ratio

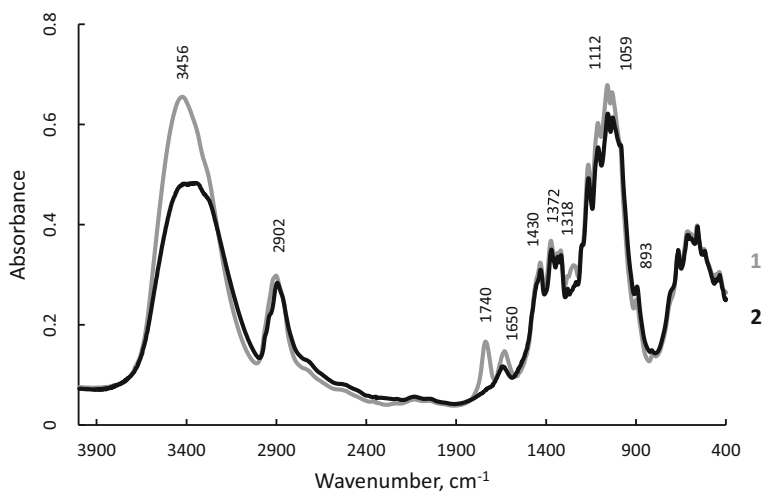


parameters of delignification process: temperature  $100\text{ }^\circ\text{C}$ , concentrations in reaction solution of  $\text{H}_2\text{O}_2$  5.9 wt% and of  $\text{CH}_3\text{COOH}$  30 wt%, LWR 15, duration 4 h.

The cellulosic product obtained by oxidative delignification of abies wood at optimal parameters was studied by XRD, FTIR and  $^{13}\text{C}$  NMR methods.

The FTIR spectra of cellulosic product from abies wood and the commercial sample of MCC Vivapur are very similar (Fig. 5).

Both samples have an absorption bands attributed to microcrystalline cellulose [27, 28]. The absence of the cellulosic product from abies wood the peaks in the spectrum in the range  $1509\text{--}1609\text{ cm}^{-1}$ , which would correspond to  $\text{C}=\text{C}$  aromatic skeletal vibrations, indicates the removal of lignin from the cellulosic product. The absorption band, which corresponds to either the acetyl or uronic ester groups of hemicelluloses, normally appears in the region  $1700\text{--}1740\text{ cm}^{-1}$  [29]. The presence of this band in the spectrum of cellulosic product from abies wood indicates that some part of hemicelluloses was not removed during abies wood delignification with  $\text{H}_2\text{O}_2$  at  $100\text{ }^\circ\text{C}$ .



**Fig. 5** FTIR spectra of cellulosic product from abies wood (1) and of commercial MCC Vivapur (2)

The absorption peak at  $1430\text{ cm}^{-1}$  corresponds to the  $\text{CH}_2$  bending vibration that is attributed to the “crystallinity band” in the cellulose [30]. The band at  $893\text{ cm}^{-1}$  was attributed to the C–O–C stretching vibration of  $\beta$ -(1 $\rightarrow$ 4)-glycosidic linkages of cellulose, which was considered as an “amorphous band” in the cellulose [30]. The ratio of peak areas  $A_{1430}/A_{893}$  was proposed as sensible to cellulose type I crystallinity [31]. Practically, the same values of this ratio for cellulose from abies wood (1.13) and for commercial MCC Vivapur (1.12) indicate the similar structures for both samples.

According to X-ray diffraction data, the cellulose from abies wood and the commercial MCC Vivapur have a crystal lattice typical for cellulose I [32] and the crystallinity indexes 0.70–0.75 (Fig. 6).

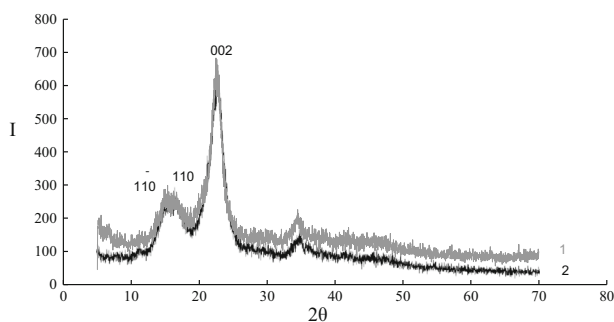
In order to compare the structure of cellulosic product from abies wood and MCC Vivapur 101, the  $^{13}\text{C}$  CP-MAS NMR solid state analysis was performed. The resonance lines in abies wood cellulosic product and MCC Vivapur 101 were almost similar (Fig. 7). Both spectra have resonance lines which indicate the presence of crystalline and amorphous forms of cellulose. Spectra were assigned after deconvolution procedure conducted on Bruker Topspin 3 software. Component line shapes were restricted to Gaussian form. Initial chemical shifts of peaks were set and assigned according to data from Wikberg and Maunu [33].

Peaks have been assigned based on the literature data [33, 34] and are displayed on the Table 6.

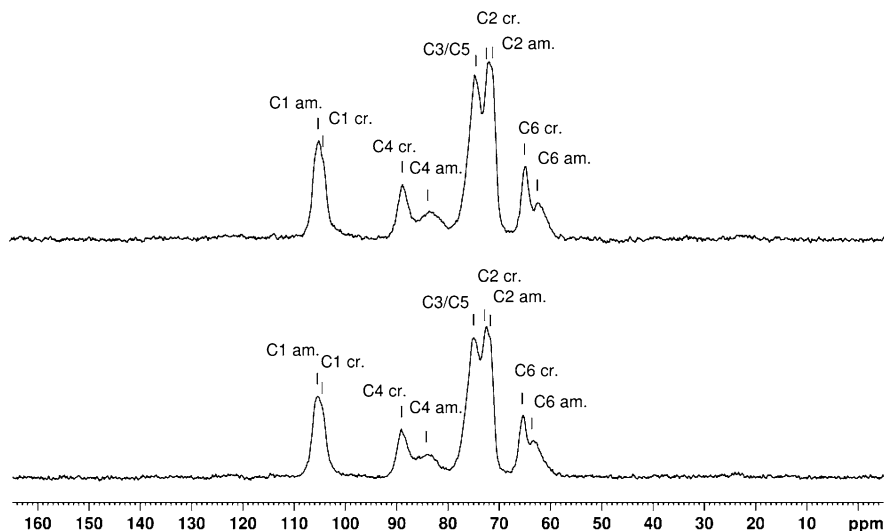
The similar kinetic parameters of peroxide delignification of aspen wood [22], birch wood [35] and abies wood in the presence of  $\text{H}_2\text{SO}_4$  and  $\text{TiO}_2$  catalysts (the first order equations, the comparable values of activation energies  $82\text{--}91\text{ kJ mol}^{-1}$ ) point to the identical mechanism of delignification of these wood species.

The deep oxidation of lignin with the disclosure of aromatic rings takes place in the process of wood peroxide delignification. The main final products of lignin degradation by hydrogen peroxide are dicarbonic acids (maleic, fumaric, oxalic acids), acetic and formic acids [36].

Hydrogen peroxide can interact with organic acids with the formation of peroxyacids:



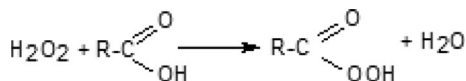
**Fig. 6** X-ray diffraction patterns of cellulose from abies wood (1) and of the commercial MCC Vivapur (2)



**Fig. 7** Solid state  $^{13}\text{C}$  CP-MAS NMR spectra of cellulosic product from abies wood (*top spectrum*) and of the commercial MCC Vivapur 101 (*bottom spectrum*)

**Table 6** Signal assignments for  $^{13}\text{C}$  CP-MAS spectra of cellulose

Chemical shift (ppm)	Assignment
104.5	C-1 of crystalline cellulose
89.1	C-4 of crystalline cellulose
84.2	C-4 of amorphous cellulose
71.7–75.1	C-2/C-3/C-5 of cellulose
65.7	C-6 of crystalline cellulose
63.4	C-6 of amorphous cellulose

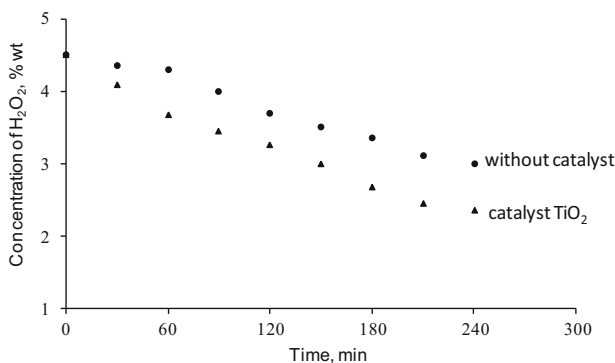


Peroxyacids are strong electrophilic oxidizers:

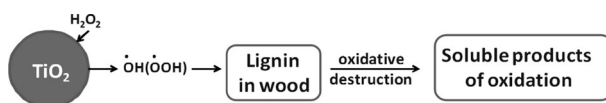


Both the peroxyacids and  $\text{H}_2\text{O}_2$  can generate the hydroxyl ( $\cdot\text{OH}$ ) and peroxide ( $\cdot\text{OOH}$ ) radicals. Therefore, lignin oxidation in acetic acid medium can be carried out via radical and electrophilic mechanisms [36].

$\text{TiO}_2$  can promote the destruction of lignin fragments via the indirect catalysis route, which includes the formation of hydroxyl and peroxide radicals from  $\text{H}_2\text{O}_2$  on the  $\text{TiO}_2$  surface and their diffusion to wood particles [37]:



**Fig. 8** Dynamics of H<sub>2</sub>O<sub>2</sub> decomposition at 100 °C in the medium “H<sub>2</sub>O<sub>2</sub>–CH<sub>3</sub>COOH–H<sub>2</sub>O” in the presence of TiO<sub>2</sub>



To confirm the proposed mechanism, the dynamics of H<sub>2</sub>O<sub>2</sub> decomposition in the medium “H<sub>2</sub>O<sub>2</sub>–CH<sub>3</sub>COOH–H<sub>2</sub>O” in the presence of TiO<sub>2</sub> catalyst was studied (Fig. 8). It was found that the catalyst TiO<sub>2</sub> promotes the decomposition of hydrogen peroxide in acetic acid–water medium.

## Conclusion

The reduction of diffusion limitations by reducing the size of abies wood particles and the use of intensive agitation of the reaction mixture allowed to decrease the temperature of wood delignification by H<sub>2</sub>O<sub>2</sub> with TiO<sub>2</sub> catalyst and to provide an effective fractionation of wood on microcrystalline cellulose and soluble lignin at mild conditions.

The kinetic study of abies wood delignification by H<sub>2</sub>O<sub>2</sub> in the medium acetic acid–water was first studied in the presence of TiO<sub>2</sub> catalyst under mild conditions: temperatures 70–100 °C, atmospheric pressure. The oxidative delignification process is described satisfactory by the first order equation in all temperature range.

The rate constants are varied between 0.80 and  $2.3 \times 10^{-3} \text{ min}^{-1}$  and the activation energy is near  $81 \text{ kJ mol}^{-1}$ .

By experimental and numerical optimization the parameters of delignification process providing a high yield (53.3 wt%) of quality cellulosic product were established: temperature 100 °C, concentration of H<sub>2</sub>O<sub>2</sub> 5.9 wt%, of CH<sub>3</sub>COOH 30 wt%, LWR 15, duration 4 h.

According to XRD, FTIR and <sup>13</sup>C CP-MAS NMR data, the cellulose obtained by abies wood oxidative delignification with 1 wt% TiO<sub>2</sub> catalyst has the structure of microcrystalline cellulose.

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