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Bis(*o*-phenanthroline)copper-catalysed oxidation of lignin model compounds for oxygen bleaching of pulp

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Abstract

The selectivity of the water-soluble and highly active catalyst bis(*o*-phenanthroline)Cu in the oxygen bleaching of pulp was explored in model compound studies. The experiments were carried out under reaction conditions typical for industrial oxygen bleaching (90 °C, pH 12, $p(O_2)$ 8 bar). The generation of hydrogen peroxide was an essential step in the oxidation of the lignin model compounds, veratryl alcohol and 2,2′-biphenol. Unfortunately, bis(*o*-phenanthroline)Cu also catalysed the depolymerisation of the carbohydrate model compound, dextran, both with oxygen and with hydrogen peroxide. The results explain well the inadequate selectivity of bis(*o*-phenanthroline)Cu in the oxygen bleaching of pulp.

Keywords: Catalytic oxidation; Activity; Selectivity; Model compound; Oxygen; Hydrogen peroxide

1. Introduction

In response to the toxic and mutagenic properties of chlorine and chlorine dioxide, totally chlorine-free (TCF) bleaching sequences based on oxygen, ozone and hydrogen peroxide have recently been developed for pulp bleaching. Among the TCF bleaching oxidants, molecular oxygen (O_2) is a particularly attractive alternative, not only for environmental reasons but because of the lower chemical costs. The complex oxidation process that occurs in oxygen bleaching includes chain reactions involving a variety of organic species derived from both lignin and carbohydrates. Selectivity, expressed as the ratio of the attack on lignin to attack on carbohydrates, is far lower in oxygen bleaching than in bleaching with chlorine chemicals [1]. Attempts have been made to improve the selectivity by adding water-soluble catalysts, such as polyoxometalates, metalloporphyrins, cobalt-Schiff bases and copper-diimines [2–17]. Despite the promising results achieved in the catalytic oxidation of lignin compounds [3–10], the activity and selectivity of the catalysts proposed for oxygen bleaching of pulp have not been sufficient to encourage the industrialisation of these processes [4,9–17].

In addition to high activity and good selectivity, an easy synthesis and a simple structure are advantageous for an industrially important bleaching catalyst. In aqueous alkaline medium, copper coordinates with certain nitrogen-containing ligands (L), such as *o*-phenanthroline and 2,2′-bipyridine, forming CuL_2^{2+} complexes [18]. These Cu-diimine complexes have an ability to form active species both with oxygen [19] and with hydrogen peroxide [20]. In view of this ability, the complexes have been studied in the oxygen [10,12–14], and also in the hydrogen peroxide [14,21–22] bleaching of pulp. In a previous study [10], we found that the Cu-diimine complexes bis(*o*-phenanthroline)Cu and bis(2,2′-bipyridine)Cu-catalysed not only the oxidation of the lignin model compounds with oxygen but also the depolymerisation of the carbohydrate model compound, dextran. Results we obtained in the oxygen bleaching of softwood pulp were in accordance with the model compound studies; Cu-diimines effectively lowered the lignin content of pulp, but they also tended to damage the cellulose fibres [10]. Similar results in the bis(*o*-phenanthroline)Cu-catalysed oxygen bleaching of pulp were obtained by Germer [12,13] and more recently by Argyropoulos et al. [14].

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According to Messner et al. [22], the low selectivity also limits the use of this otherwise effective catalyst in hydrogen peroxide bleaching. Since hydrogen peroxide is generated under alkaline oxygen bleaching conditions both in the presence [9] and in the absence [23–25] of the catalyst, the damage to the cellulose fibres observed in the oxygen delignification of pulp might also be explained by the reactions of the generated hydrogen peroxide. In our study with Co-sulphosalen, the selectivity of the delignification reactions was clearly improved by the addition of phenylglyoxalic acid, a reagent that rapidly reacted with the generated hydrogen peroxide to form the distinctly unreactive product benzoic acid [9]. The reaction to benzoic acid eliminated the unwanted reaction of hydrogen peroxide leading to depolymerisation of the carbohydrate model compound, dextran. The purpose of the present study was to investigate the source of the damage to cellulose fibres in bis(*o*-phenanthroline)Cu-catalysed oxygen delignification and to improve the selectivity of the highly active Cu-diimine complexes in the oxygen bleaching of pulp.

2. Experimental

2.1. Materials

2,2′-Biphenol (99%), veratryl alcohol (3,4-dimethoxybenzyl alcohol, 96%) and dextran (1,6-α-D-glucan, average molecular weight 73 000 g/mol), which were used as model compounds, were purchased from Aldrich. Oxygen (AGA, 99.5%) was used as oxidant and the buffer solution (Merck Titrisol^{TM} ampoules) for pH 12 as solvent. The catalyst, bis(*o*-phenanthroline)copper, was formed in situ in the buffer solution from dinitrato(*o*-phenanthroline)copper(II) (Aldrich, 96%) and *o*-phenanthroline (Aldrich 99+%).

2.2. Procedure

All experiments were carried out in a semi-batch glass reactor (Büchi Miniclave, 200 ml) equipped with a magnetic stirrer and a mixing baffle. Buffered alkaline water (pH 12) and dextran (if used) were added to the reactor. The reactor was flushed two times and re-pressurised with oxygen. The reaction temperature (90 °C) was maintained with a water bath. Where lignin model compounds (or in some experiments just one of them) were used, they were dissolved in 5 mL of the buffer solution and pumped (PAM syringe pump) to the reactor. The reaction time was considered to begin when the catalyst, dissolved in 3 mL of the buffer solution, was pumped in. After reaction of 5, 30, 60 and 180 min, liquid samples were withdrawn from the still pressurised (8 bar) reactor. The reactions of the lignin model compounds were followed with a high performance liquid chromatograph (Agilent 1100 Series HPLC) and the depolymerisation of dextran with a capillary viscosimeter (Schott Geräte AVS 400).

The fate of the generated hydrogen peroxide was studied by adding an equimolar mixture of phenylglyoxalic acid and sodium hydroxide (in buffer solution) to the reactor. In the experiments with added hydrogen peroxide, 3 mL of an aqueous solution of hydrogen peroxide (containing H_2O_2 0.5 mol/L) was pumped to the pressurised reactor at the rate 0.1 mL/min during the first 30 min of the reaction. The experimental and analytical procedures are described in detail elsewhere [9].

2.3. Calculations

Conversions of the lignin model compounds were calculated on molar basis. The conversions of veratryl alcohol and 2,2′-biphenol referred to in this study are total conversions of the compounds.

The initial oxidation rates of veratryl alcohol were calculated, following the formation of veratryl aldehyde, from Eq. (1):

$$-r_{0,\text{ver.alc.}} = r_{0,\text{ver.ald.}} = \left(\frac{\mathrm{d}c(\text{veratryl aldehyde})}{\mathrm{d}t}\right)_{t=0} \tag{1}$$

in which d*c*(veratryl aldehyde)/d*t* was calculated by fitting to the data a second order polynomial equation presenting the concentration of veratryl aldehyde as a function of time and then calculating the derivative of the polynome at time zero.

The reaction order with respect to veratryl alcohol was determined using the method of initial rates [26]. We assume that the rate law can be presented in the form

$$-r_{0,\text{ver.alc.}} = kc^{a}_{0,\text{ver.alc.}} \tag{2}$$

The initial oxidation rates of 2,2′-biphenol were calculated from Eq. (3):

$$-r_{0,2,2'\text{-biphenol}} = -\left(\frac{\mathrm{d}c(2,2'\text{-biphenol})}{\mathrm{d}t}\right)_{t=0} \tag{3}$$

in which d*c*(2,2′-biphenol)/d*t* was calculated by fitting to the data a second order polynomial equation presenting the concentration of 2,2′-biphenol as a function of time and then calculating the derivative of the polynome at time zero.

The relative viscosity (η_r) was calculated from the flow times measured with the capillary viscosimeter with the use of Eq. (4),

$$\eta_r = \frac{t}{t_0} \tag{4}$$

where t is the flow time of the sample and t_0 the flow time of the solvent.

3. Results and discussion

3.1. Catalytic oxidation of veratryl alcohol with oxygen

In order to understand the details of the reactions catalysed by bis(*o*-phenanthroline)Cu, we began our studies with the non-phenolic lignin model compound, veratryl

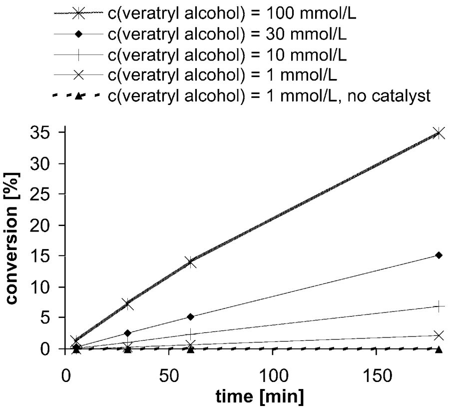

Fig. 1. Effect of the concentration of veratryl alcohol on its conversion (c_{cat} = 0.1 mmol/L, T = 90 °C, pH = 12, $p(O_2)$ = 8 bar).

alcohol (1–100 mmol/L). As shown in Fig. 1, the conversion increased rapidly with the initial concentration of the alcohol. From the mass balance, it could be deduced that the oxidation of veratryl alcohol to veratryl aldehyde was virtually the only reaction. However, in the presence of the highest concentration (100 mmol/L) of the alcohol, a trace amount of veratric acid was detected after reaction of 180 min. A preliminary kinetic study showed the order of the reaction with respect to veratryl alcohol to be 1.7 (slope, *a*, in Fig. 2). This confirms that the bis(*o*-phenanthroline)Cu-catalysed oxidation rate of veratryl alcohol strongly depends on the concentration of the alcohol.

3.2. Effects of 2,2′-biphenol and dextran on the catalytic oxidation of veratryl alcohol

Bis(*o*-phenanthroline)Cu (0.1 mmol/L) was also active in the oxidation of the phenolic model compound, 2,2′-biphenol. The initial oxidation rate of 2,2′-biphenol (1 mmol/L) was 6.4 × 10^{-4} mmol/(L min) in the absence of veratryl alcohol but only 3.9 × 10^{-4} mmol/(L min) in the simultaneous oxidation of these two lignin model compounds. In the simultaneous oxidation, the initial oxidation rate of veratryl alcohol (1 mmol/L) increased from the initial rate in the absence of 2,2′-biphenol 1.2 × 10^{-4} mmol/(L min) to 2.4 × 10^{-4} mmol/(L min). In the same way, the addition of the reactive phenolic model compound 2,4,6-trimethylphenol has been shown to increase the oxidation rate of veratryl alcohol [25].

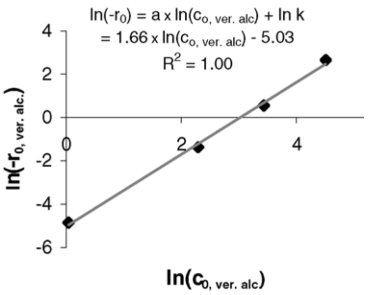

Fig. 2. Plot of ln(initial oxidation rate of veratryl alcohol) vs. ln(initial concentration of veratryl alcohol).

The addition of the carbohydrate model compound, dextran, dramatically increased the bis(*o*-phenanthroline)Cu-catalysed oxidation rate of veratryl alcohol. The initial oxidation rate of veratryl alcohol (1 mmol/L) in the presence of dextran (5 g/L) was 48 × 10^{-4} mmol/(L min). Unfortunately, bis(*o*-phenanthroline)Cu also catalysed the unwanted depolymerisation reaction of dextran.

3.3. Simultaneous oxidation of veratryl alcohol and 2, 2′-biphenol in the presence of dextran

In the simultaneous oxidation of the two lignin model compounds in the presence of bis(*o*-phenanthroline)Cu catalyst, 2,2′-biphenol was somewhat more reactive than veratryl alcohol in the presence of dextran (Fig. 3). The concentration of dextran affected the oxidation rates of the two lignin model compounds in the same way: rates were maximal when the concentration of dextran was 5 g/L. In the presence of the higher concentration (15 g/L) of dextran, complex formation between Cu^{2+} and dextran may have reduced the concentration of the active bis(*o*-phenanthroline)Cu complex [27].

The relative viscosities of the reaction mixture in the presence of the lignin model compounds (1.324, 1.168 and 1.138 after reaction of 5, 60 and 180 min, respectively) were lower than in their absence (1.333, 1.194 and 1.176 after reaction of 5, 60 and 180 min, respectively). This indicates that the depolymerisation of dextran was slower in the presence of the veratryl alcohol and 2,2′-biphenol than in their absence.

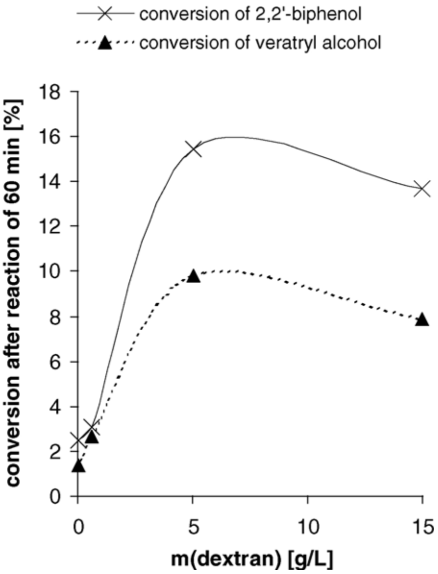

Fig. 3. Conversions of veratryl alcohol and 2,2′-biphenol after reaction of 60 min as a function of the concentration of dextran ($c_{0,\mathrm{ver.\ alc.}}$ = 1 mmol/L, $c_{0,2,2'\text{-biphenol}}$ = 1 mmol/L, c_{cat} = 0.1 mmol/L, T = 90 °C, pH = 12, $p(O_2)$ = 8 bar, pH 12).

Table 1
The formation of benzoic acid with 10 mmol/L phenylglyoxalic acid added to the reaction mixture ($c_{\text{cat}} = 0.1$ mmol/L, $T = 90\ ^\circ\text{C}$, pH 12, $p(O_2) = 8$ bar)

Lignin model compound	Carbohydrate model compound	$c_{0,\text{lignin model compound}}$ (mmol/L)	$c_{0,\text{carbohydrate model compound}}$ (g/L)	$-\Delta c_{60\text{ min, lignin model compound}}$ (mmol/L)	$c_{60\text{ min,benzoic acid}} = -\Delta c_{60\text{ min,phen. glyox. acid}}$ (mmol/L)
–	–	0	0	–	0.00
Veratryl alcohol	–	10	0	0.17	0.05
2,2′-Biphenol	–	10	0	0.15	0.13
Veratryl alcohol	–	90 (=15 g/L)	0	16.0	3.94
–	Dextran	0	15 g/L	–	4.66

3.4. Generation of hydrogen peroxide in the presence of lignin and carbohydrate model compounds

Several studies have shown that hydrogen peroxide is generated in the oxidation of lignin model compounds with oxygen [9,23–25]. We used phenylglyoxalic acid, which immediately reacts with hydrogen peroxide to form the highly unreactive product benzoic acid, to determine whether hydrogen peroxide was generated in the bis(*o*-phenanthroline)Cu-catalysed reactions [9,28]. As shown in Table 1, no benzoic acid was formed from phenylglyoxalic acid in the presence of bis(*o*-phenanthroline)Cu alone, but it was formed if any of the three model compounds was present as well (Table 1). This indicates that hydrogen peroxide is generated in the bis(*o*-phenanthroline)Cu-catalysed reactions of all three model compounds.

3.5. Effect of hydrogen peroxide on the catalytic reactions

The oxidation of veratryl alcohol was carried out in the presence of added hydrogen peroxide to determine whether hydrogen peroxide interferes the bis(*o*-phenanthroline)Cu-catalysed reactions. As shown in Fig. 4, the conversion after reaction of 30 min was 9.5% in the presence of the added hydrogen peroxide (15 mmol/L) and only 1.2% in its absence. In a non-catalytic experiment with added hydrogen peroxide, the conversion of veratryl alcohol after reaction of 30 min was only 0.3% (Fig. 4). In other words, bis(*o*-phenanthroline)Cu is required to activate the hydrogen peroxide for the oxidation of veratryl alcohol.

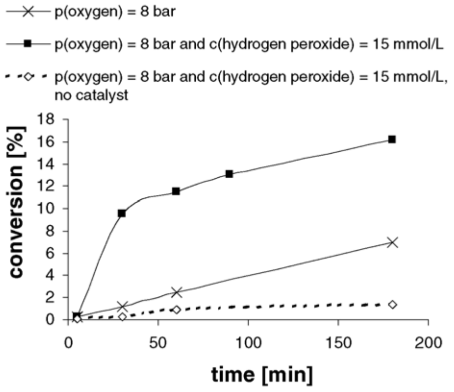

Fig. 4. Effect of hydrogen peroxide on the conversion of veratryl alcohol ($c_{0,\text{ver. alc.}} = 10$ mmol/L, $c_{\text{cat}} = 0.1$ mmol/L, $T = 90\ ^\circ\text{C}$).

Simultaneous oxidation of veratryl alcohol and 2,2′-biphenol in the presence of dextran and phenylglyoxalic acid (no hydrogen peroxide added) was carried out to determine more precisely the effect of generated hydrogen peroxide on the bis(*o*-phenanthroline)Cu-catalysed reactions. As shown in Fig. 5, the relative viscosity of the reaction mixture decreased even in the presence of high concentration (100 mmol/L) of phenylglyoxalic acid. From this we conclude that bis(*o*-phenanthroline)Cu catalyses the depolymerisation reaction of dextran with oxygen in the absence of hydrogen peroxide. (Hydrogen peroxide has been shown effectively to depolymerise dextran in the absence of any catalyst at room temperature [29].) The elimination of hydrogen peroxide with phenylglyoxalic acid dramatically lowered the conversions of the lignin compounds (especially 2,2′-biphenol), however, demonstrating the important role of hydrogen peroxide in the oxidation of the lignin compounds (Fig. 5).

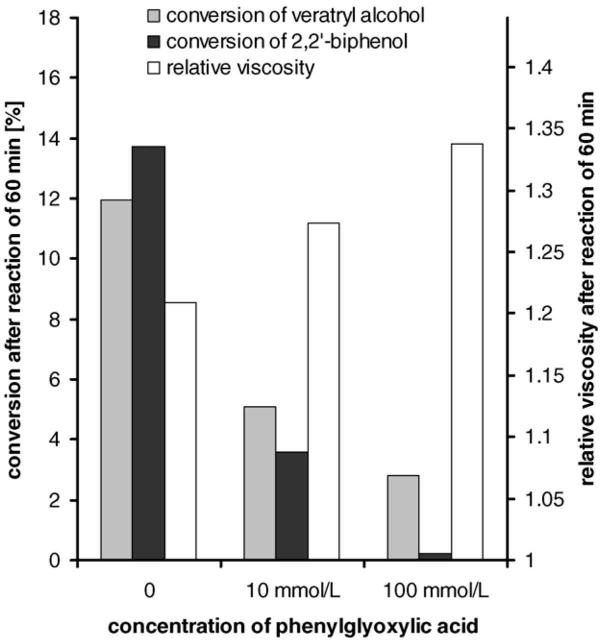

Fig. 5. Effect of phenylglyoxalic acid on the conversions of veratryl alcohol and 2,2′-biphenol and on the relative viscosity of the reaction mixture ($c_{0,\text{ver. alc.}} = 1$ mmol/L, $c_{0,2,2'\text{-biphenol}} = 1$ mmol/L, $c_{0,\text{dextran}} = 15$ g/L, $c_{\text{cat}} = 0.1$ mmol/L, $T = 90\ ^\circ\text{C}$, pH 12, $p(O_2) = 8$ bar). The optimum value of the relative viscosity of 1.44 has been determined using the reference sample containing 15 g of dextran in 1 L of buffer solution, pH 12.

As noted above, the bis(*o*-phenanthroline)Cu-catalysed reactions of all three model compounds generated hydrogen peroxide, and the hydrogen peroxide affected the rate of the reactions. The amounts of benzoic acid formed from phenylglyoxalic acid (Table 1) indicated that the reactions of 2,2′-biphenol and particularly of dextran generated more hydrogen peroxide than the reaction of veratryl alcohol. In the simultaneous oxidation of the two lignin model compounds, a part of the hydrogen peroxide generated in the oxidation of 2,2′-biphenol evidently reacted with veratryl alcohol. This increased the oxidation rate of veratryl alcohol while decreasing the oxidation rate of 2,2′-biphenol. Correspondingly, the increases in the oxidation rates of veratryl alcohol and 2,2′-biphenol in the presence of dextran (Fig. 3) evidently were the effect of the hydrogen peroxide generated in the reactions of dextran. Because the reactions of the lignin compounds consumed some of the generated hydrogen peroxide, the depolymerisation of dextran was slightly slower in the presence of the lignin model compounds than in their absence.

3.6. *Comparison of bis(o-phenanthroline)Cu and Co-sulphosalen catalysts*

The reaction kinetics with the bis(*o*-phenanthroline)Cu catalyst was found to be very different from the kinetics of the cobalt-sulphosalen-catalysed reaction. In our study with Co-sulphosalen [9], the oxidation of veratryl alcohol followed first order kinetics with respect to veratryl alcohol, in agreement with a reaction mechanism in which one veratryl alcohol molecule was oxidised per catalytic reaction cycle and hydrogen peroxide was generated in stoichiometric ratio 1:1. With bis(*o*-phenanthroline)Cu the reaction order with respect to veratryl alcohol was 1.7, indicating a reaction mechanism in which more than one veratryl alcohol molecule was oxidised per catalytic reaction cycle. Liu et al. [19] found Cu-diimine catalyst bis(2,2′-bipyridine)Cu to oxidise two benzyl alcohol molecules to benzyl aldehyde per catalytic reaction cycle in acetonitrile solution [19]. Unlike us, however, they found no evidence for the generation of hydrogen peroxide. The generation of hydrogen peroxide and its role in the reactions of bis(*o*-phenanthroline)Cu-catalysed oxidation of veratryl alcohol make our reaction mechanism considerably more complex than the mechanism derived by Liu et al. [19].

Both with bis(*o*-phenanthroline)Cu and with Co-sulphosalen [9], the generation of hydrogen peroxide in the presence of the three model compounds (veratryl alcohol, 2,2′-biphenol and dextran) affected the catalytic reactions. In the presence of either of the catalysts, the elimination of the generated hydrogen peroxide through addition of phenylglyoxalic acid to the reaction mixture suppressed the reaction rates of all model compounds. However, the relative viscosity of the reaction mixture decreased only when bis(*o*-phenanthroline)Cu was used as the catalyst. This means that, unlike Co-sulphosalen, bis(*o*-phenanthroline)Cu-catalysed the depolymerisation of the carbohydrate model compound dextran with oxygen as well as with hydrogen peroxide. Moreover, the oxidation rates of the lignin model compounds with bis(*o*-phenanthroline)Cu were much more dependent on the generation of hydrogen peroxide than the rates with Co-sulphosalen, which were only slightly lower in the absence than in the presence of the generated hydrogen peroxide [9]. The more abundant generation of hydrogen peroxide in the presence of dextran with bis(*o*-phenanthroline)Cu than with Co-sulphosalen as catalyst, and perhaps also the better ability of bis(*o*-phenanthroline)Cu to catalyse the oxidation of the lignin model compounds with the generated hydrogen peroxide, might also explain why the bis(*o*-phenanthroline)Cu-catalysed oxidation rates of the lignin model compounds increased with the concentration of dextran, whereas with Co-sulphosalen the rates were almost independent of it [9].

4. Conclusions

The aim of this study was to explore the selectivity of the highly active oxidation catalyst bis(*o*-phenanthroline)Cu in the oxygen bleaching of pulp. We found that the generation and reactions of hydrogen peroxide play a key role in the bis(*o*-phenanthroline)Cu-catalysed oxidation of the lignin model compounds veratryl alcohol and 2,2′-biphenol. Elimination of the generated hydrogen peroxide dramatically lowers the conversions of the lignin compounds. Unfortunately, bis(*o*-phenanthroline)Cu also catalyses the depolymerisation of the carbohydrate model compound dextran with both oxygen and hydrogen peroxide. A selective oxygen bleaching catalyst should catalyse only the oxidation of lignin compounds and not the depolymerisation of carbohydrate compound. From our results we infer that the selectivity in the oxygen bleaching process with the bis(*o*-phenanthroline)Cu catalyst would be even lower with the effect of hydrogen peroxide eliminated and that improving the selectivity of active Cu-diimine catalysts will be a challenging task.

Acknowledgements

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References

[1] J. Gullichsen, in: J. Gullichsen, C.-J. Fogelholm (Eds.), Chemical Pulping, Fapet Oy, Helsinki, 1999, p. 19, Chapter 12.
[2] T.J. Fullerton, S.P. Ahern, Tetrahedron Lett. 16 (1976) 139.

[3] S. Meguro, K. Sakai, H. Imamura, Mokuzai Gakkaishi 30 (1984) 1011.
[4] S. Meguro, H. Imamura, Mokuzai Gakkaishi 35 (1989) 261.
[5] W. Zhu, W.T. Ford, J. Mol. Catal. 78 (1993) 367.
[6] D.V. Evtuguin, A.I.D. Daniel, A.J.D. Silvestre, F.M.L. Amado, C. Pascoal Neto, J. Mol. Catal. A: Chem. 154 (2000) 217.
[7] D.V. Evtuguin, C. Pascoal Neto, H. Carapuca, J. Soares, Holzforschung 54 (2000) 511.
[8] V.O. Sippola, A.O.I. Krause, J. Mol. Catal. A: Chem. 194 (2003) 89.
[9] V. Sippola, O. Krause, T. Vuorinen, J. Wood Chem. Technol., in press.
[10] H. Korpi, P. Lahtinen, V. Sippola, O. Krause, M. Leskelä, T. Repo, Appl. Catal. A: Gen. 268 (2004) 199.
[11] T.J. Fullerton, S.P. Ahern, TAPPI 61 (12) (1978) 37.
[12] E.I. Germer, in: J.F. Kennedy, G.O. Phillips, P.A. Williams (Eds.), Ligno-cellulosics: Science, Technology, Development and Use, Ellis Horwood, New York, 1992, p. 227.
[13] E.I. Germer, TAPPI J. 78 (11) (1995) 121.
[14] D.S. Argyropoulos, M. Suchy, L. Akim, Ind. Eng. Chem. Res. 43 (2004) 1200.
[15] Y.-S. Perng, C.W. Oloman, P.A. Watson, B.R. James, TAPPI J. 77 (11) (1994) 119.
[16] D.V. Evtuguin, C. Pascoal Neto, J. Rocha, J.D. Pedrosa de Jesus, Appl. Catal. A 167 (1998) 123.
[17] D.V. Evtuguin, C. Pascoal Neto, J. Rocha, Holzforschung 54 (2000) 381.
[18] D.D. Perrin, V.S. Sharma, J. Inorg. Nucl. Chem. 28 (1966) 1271.
[19] X. Liu, A. Qiu, D.T. Sawyer, J. Am. Chem. Soc. 115 (1993) 3239.
[20] D.S. Sigman, A. Mazumder, D.M. Perrin, Chem. Rev. 93 (1993) 2295.
[21] T. Watanabe, K. Koller, K. Messner, in: Proceedings of the 7th International Conference on Biotechnology in the Pulp and Paper Industry, Vancouver, 16–19 June, 1998, p. B207.
[22] K. Messner, K. Koller, K. Fackler, E. Srebotnik, T. Watanabe, in: Proceedings of the 10th International Symposium on Wood Pulping Chemistry, Yokohama, Japan, 7–10 June, 1999, p. 550.
[23] J. Gierer, Holzforschung 51 (1997) 34.
[24] M. Yasumoto, Y. Matsumoto, A. Ishizu, J. Wood Chem. 16 (1996) 95.
[25] T. Yokoyama, Y. Matsumoto, G. Meshitsuka, J. Wood Chem. Technol. 19 (1999) 187.
[26] H.S. Fogler, Elements of Chemical Reaction Engineering, 3rd ed. Prentice-Hall, New Jersey, 1999, p. 239.
[27] E. Norkus, J. Vaičiūnienė, T. Vuorinen, M. Heikkilä, Carbohyd. Polym. 50 (2002) 159.
[28] T. Vuorinen, Mechanism and kinetics of isomerization, degradation, and oxidation of reducing carbohydrates: reaction paths in alkaline solutions containing oxygen and 2-anthraquinonesulfonic acid, Doctoral Thesis, Helsinki University of Technology, Finland, 1988, 162 pp.
[29] I. Levi, E. Lozinski, Can. J. Biochem. Physiol. 33 (1955) 448.