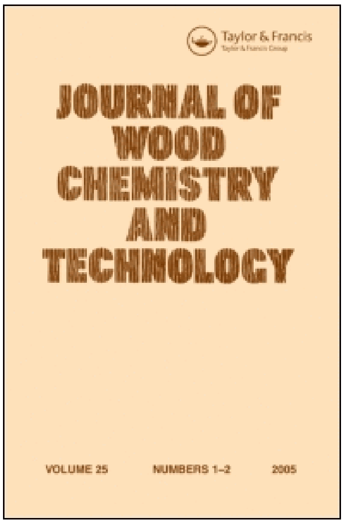

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Use of a Nitrogen-Centered Peroxide Activator to Increase the Chromophore Removal Potential of Peroxide-Lignin Model Compound Study

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Abstract: The kinetics of reaction of a lignin model compound, acetovanillone (4′-hydroxy-3′-methoxyacetophenone), in tetraacetylethylenediamine (TAED)/H_2O_2 and peroxide-alone systems were investigated. The oxidation of acetovanillone followed first-order kinetics in both systems. In the TAED-peroxide system, the first-order rate constant, k, was 0.34 min^{-1} with a half-life, $t_{1/2}$, of 2 min, compared to k of 0.0035 min^{-1} and $t_{1/2}$ of 220 min in the peroxide-alone system. Thus, TAED/H_2O_2 oxidized acetovanillone about one hundred times faster than peroxide alone. The results of the study explain why, when using TAED/H_2O_2 to bleach TMP softwood pulp, the initial pH should be about 11 for increased production of peroxyacetic acid, and the final pH should be about 7 to minimize decomposition and increase bleaching efficiency and reactivity.

Keywords: Acetovanillone, tetraacetylethylenediamine, TAED, hydrogen peroxide, lignin model, activators, peroxyacetic acid

INTRODUCTION

Hydrogen peroxide has been used as a bleaching agent for mechanical pulps for many years. Alkaline hydrogen peroxide can be used to bleach

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lignin-rich pulps to brightness levels of 80–83% ISO without substantial delignification.

Often the first approach in investigating a process or chemical reaction mechanism is kinetic studies. Wright and Abbot[1,2] have proposed two distinct categories of chromophores that are eliminated through first-order processes, rather than the higher order reactions suggested in previous kinetic analyses. Their models[1,2] predict a maximum in the rate of bleaching in the range pH 11–12, whereas previous models imply that the rate of chromophore elimination increases continuously with increasing hydroxide ion concentration.

Xu[3] has proposed a kinetic model for peroxide brightening of Canadian black spruce groundwood pulp. The model suggests: (1) the bleaching rate is first-order with respect to the peroxide concentration; (2) the rate will become independent of peroxide concentration if the [H_2O_2] increases above a certain level; (3) under constant conditions and very low consistency, the bleaching rate either remains unchanged or increases with higher consistency at the same chemical concentration; (4) in a medium or high consistency process, where the H_2O_2 concentration and pH are not controlled, the bleaching rate will decrease at higher consistency with the same bleaching chemical concentrations; and (5) in terms of bleaching efficiency, higher consistency is generally expected to be more efficient. In a two-stage bleaching process, the temperature effect is greater in the first phase and less important in the second phase of the first stage, whereas the opposite is observed for the second stage.[4]

The literature contains numerous recent studies of ways to activate hydrogen peroxide for mechanical pulp bleaching.[5–8] Recently, tetraacetylethylenediamine (TAED) has been shown to be an interesting peroxide activator. It contains nitrogen-bound acetyl groups, which are able to react with the nucleophilic hydroperoxy anion to yield peroxyacetic acid (PAA, Figure 1) *in situ*, thereby increasing the brightening potential of the peroxide.[9] Under alkaline conditions (pH 9–10) TAED reacts with peroxide rapidly. Depending on the pH of the bleaching stage, TAED will react with peroxide to produce either peroxyacetic or the peroxyacetate anion. Both species are known to be stronger oxidants than hydrogen peroxide. Edwards[10] and Hauthal et al.[11] have shown that peroxyacetic acid is a more active bleaching agent than peroxide, having an oxidative power 10^5 times that of peroxide.[12]

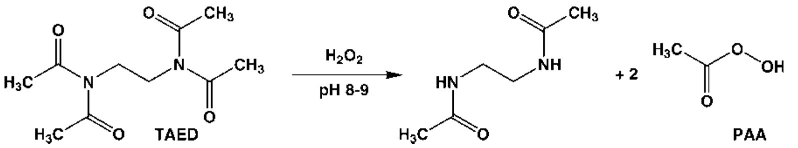

Figure 1. Reaction of TAED with hydrogen peroxide under alkaline conditions.

Leduc et al.[5] have shown that the use of TAED with the peroxide offers a means to improve the thermomechanical pulp brightness significantly in a conventional bleaching tower. They observed that the activator used in the peroxyacetic bleaching liquor gave a higher brightness than peroxyacetic acid alone. Davies and co-workers[13] have investigated the hydrolysis of TAED and its kinetics. They found that TAED formed triacetylethylenediamine and diacetylethylenediamine consecutively during reaction with water and H_2O_2. Their kinetic model is based on three variables: pH, temperature, and nucleophile concentration.

A kinetic model built by Coucharrière et al.[14] to predict the generation of PAA during the reaction between TAED and hydrogen peroxide (perhydrolysis) shows that mathematical modeling is a useful tool, not only to predict the generation rate of PAA but also optimal operating conditions. Strumila and Rapson[15] studied the products of peroxyacetic oxidation of simple lignin model compounds. The order of decreasing reactivity with peroxyacetic acid is:

$$\text{methoxyhydroquinone} > \text{acetovanillone} > \text{2-methoxy-4-acetoxyphenol} \quad (1)$$

In this study we analyzed the kinetics of chromophore elimination during TAED/H_2O_2 reaction with acetovanillone (Figure 2).

EXPERIMENTAL

Materials and Methods

Acetovanillone (98%, 4′-Hydroxy-3′-methoxyacetophenone, Figure 2) was from Aldrich Chemical. Hydrogen peroxide (30%) and sodium hydroxide (99.99%) were from Anachemia. Tetraacetylethylenediamine (TAED) was a granular material specifically formulated for application in pulp bleaching.

UV-visible spectra were recorded on a Varian Cary 3 spectrophotometer. Acetovanillone concentrations were determined from the absorbances at 309 nm and 343 nm.

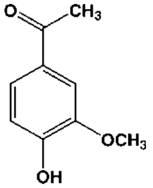

Figure 2. Acetovanillone (4′-Hydroxy-3′-methoxyacetophenone).

Peroxyacetic acid and hydrogen peroxide concentrations were measured at various reaction times using an iodometric titration. Sulfuric acid, an excess of potassium iodide, and ammonium molybdate were added to aliquots of the reaction solution. The liberated iodine was then titrated with sodium thiosulfate using starch indicator.

Experimental Conditions

Acetovanillone was dissolved in deionized water (0.12 mmol/L), to which appropriate amounts of NaOH were added to obtain various pH levels. A water bath was used to maintain the reaction temperature. The initial peroxide concentration was 12 mmol/L for the peroxide-only system. TAED was added at a molar ratio of 0.5 (6 mmol/L) for the peroxide-TAED system.

RESULTS AND DISCUSSION

UV-visible absorption spectra of acetovanillone at various pHs are shown in Figure 3. Because of its pK_a value of 7.81,[16–18] ionization of the phenolic hydroxyl group of acetovanillone is strongly pH dependant. This is especially evident for the pH values located close to the pK_a, for examples at 7.7 and 7.8. For TAED/H_2O_2 bleaching, the pH values dropped during the bleaching reaction. Thus, the wavelength used to measure the acetovanillone concentration had to be chosen carefully, to be essentially independent of pH. As can be seen from the absorption curves for acetovanillone

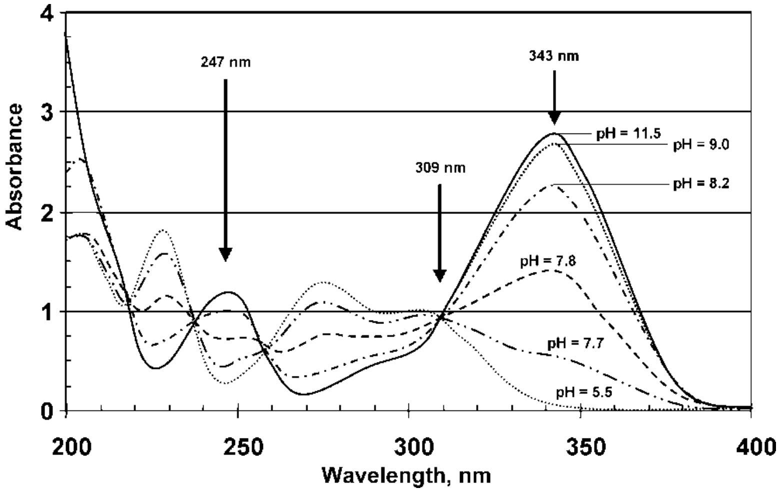

Figure 3. Effect of pH on the UV-visible absorption spectra of acetovanillone.

(Figure 3), once the pH of the solution exceeds 10.5, the absorbance at 343 nm is essentially constant. As long as the pH of the reaction system was higher than 10.5, the absorbance at 343 nm could be used to measure the concentration of the acetovanillone. There is also an isobestic point at 309 nm, at which the absorbance is independent of the pH. This could also be used to measure the concentration of acetovanillone, but the absorption coefficient is 2.8 times lower than the absorption coefficient at 343 nm, as shown in Figure 4.

Oxidation Kinetics

For low acetovanillone concentrations, the oxidation reaction followed first-order kinetics with respect to acetovanillone.

$$\ln C = -kt + \ln C_0 \tag{2}$$

where C is the concentration of acetovanillone, C_0 is the initial concentration of acetovanillone, r is the reaction rate, k is the first-order rate constant, and t is the reaction time.

Concentration versus time curves for reactions of acetovanillone in the peroxide-alone system and the TAED/H_2O_2 system are presented in Figure 5. The rate constant, k, for the TAED assisted system ($0.34\,\text{min}^{-1}$) was two orders of magnitude higher than the peroxide-alone system ($0.0035\,\text{min}^{-1}$), that is, the reaction proceeded 100 times faster in the presence of TAED, with half-lives, $t_{1/2}$, of 2 and 220 min for TAED/H_2O_2 and peroxide-alone, respectively.

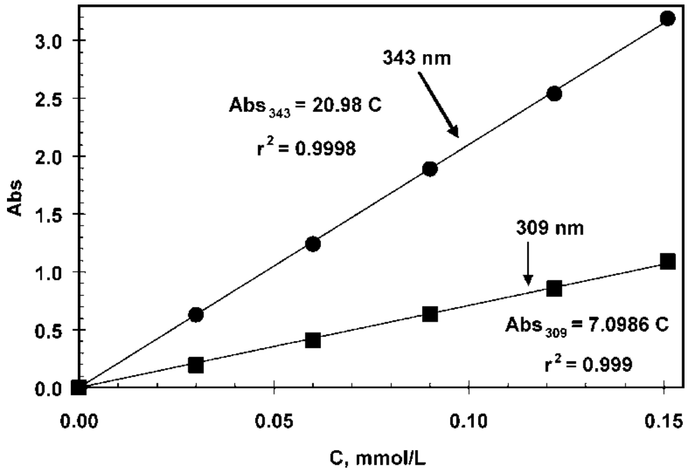

Figure 4. Absorbance of acetovanillone solutions at 309 nm and 343 nm, pH 11.5.

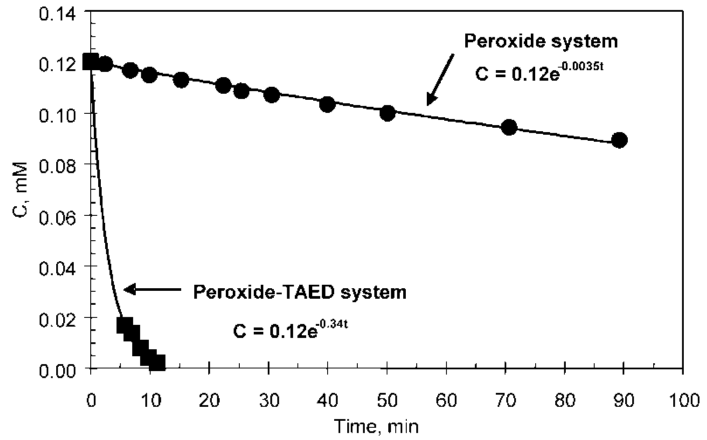

Figure 5. Reaction of acetovanillone with peroxide (60°C, pH: 11.0–11.5) and TAED/H_2O_2 (60°C, pH: 7.9–8.3, TAED molar ratio 0.5).

pH Effect

The pH dependence of the rate constant, *k*, of the reaction of acetovanillone with TAED/H_2O_2 at 60°C is shown in Figure 6. Additional data is presented in Table 1. A maximum is observed around pH 8.2. Thus, the optimal pH range is between 8 and 9. According to Hofmann[19] the maximum rate of decomposition of peroxyacetic acid occurs at pH 8.3, which corresponds to the pK_a of peroxyacetic acid. It is also the point of maximum bleaching activity of

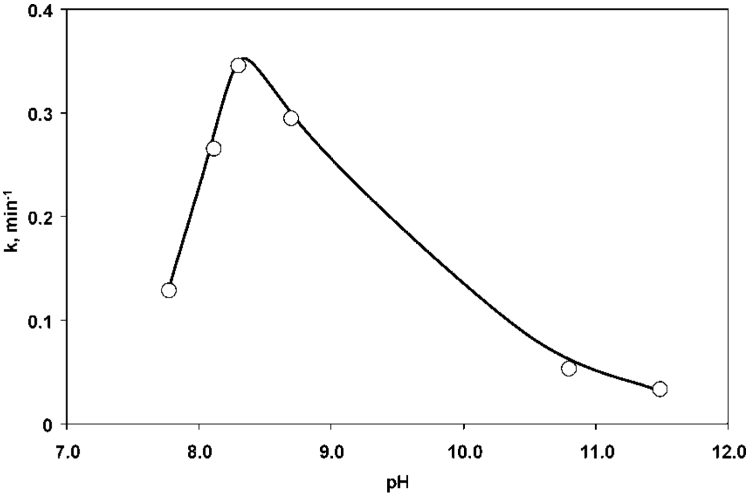

Figure 6. pH dependence of the rate constant for reaction of acetovanillone with TAED/H_2O_2 at 60°C.

Table 1. Reactions of acetovanillone with TAED/H_2O_2.[a]

	Temperature, °C		
NaOH, mmol/L	22	40	60
2			
k, min^{-1}	0.03	0.07	0.13
$t_{1/2}$, min	23.1	9.9	5.3
Initial pH	8.1	8.0	7.8
7			
k, min^{-1}	0.04	0.13	0.35
$t_{1/2}$, min	17.3	5.3	2.0
Initial pH	8.7	8.6	8.2
14			
k, min^{-1}	0.007	0.02	0.05
$t_{1/2}$, min	99.1	34.7	13.9
Initial pH	10.9	10.7	10.7

[a] H_2O_2 concentration, 12 mM; TAED concentration, 6 mM.

systems containing both bleaching activators and sodium perborate. Because of this, it has been suggested that singlet oxygen must play a decisive role in the activated bleaching of textiles during the washing process.

We believe that singlet oxygen also plays an important role in the oxidation of our model compound. If so, it means that the reaction takes place between one peroxyacid anion and one molecule of the neutral peroxyacid. It indicates that peroxyacid anion is not the major oxidizing species eliminating chromophores in bleaching TMP softwood pulp.

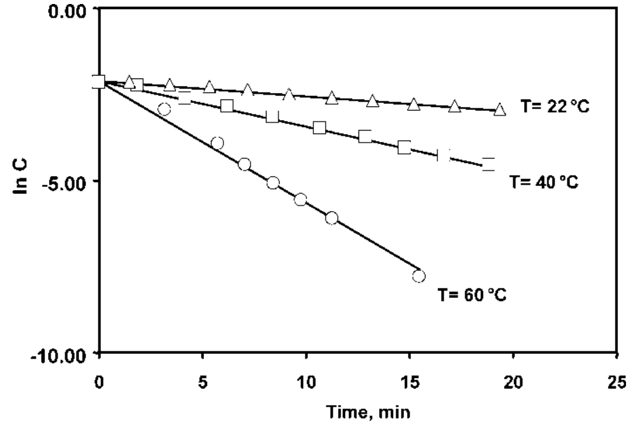

Figure 7. Effect of temperature on the reaction of acetovanillone with TAED/H_2O_2: 7 mM NaOH, 12 mM H_2O_2, 6 mM TAED.

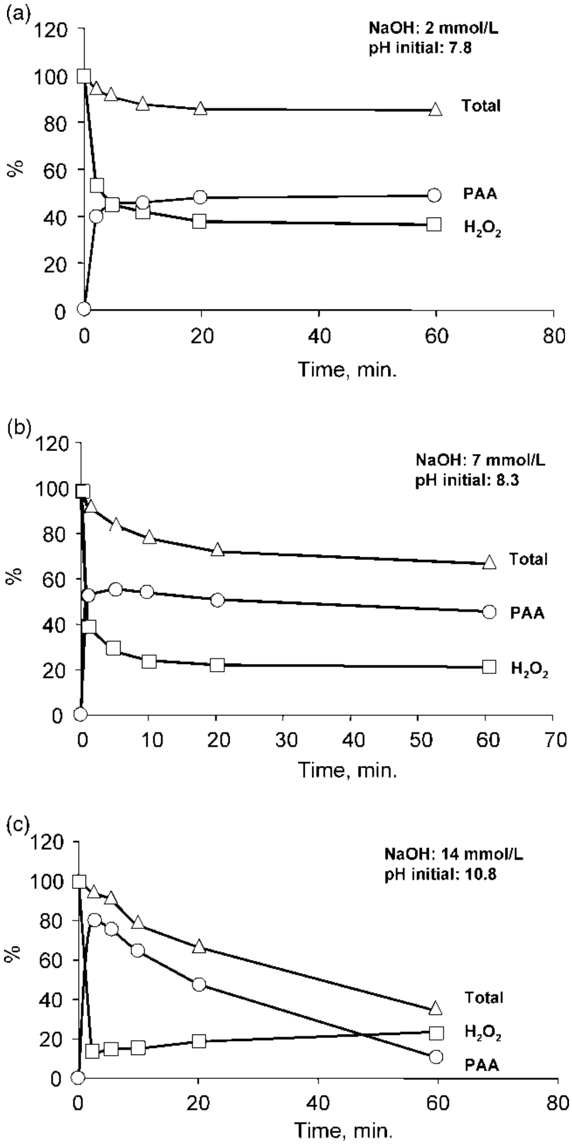

Figure 8. Reaction of TAED with hydrogen peroxide at 60°C at various pHs: (a) pH 7.8, (b) pH 8.3, and (c) pH 10.8. Initial concentrations: acetovanillone, 0.12 mM; H_2O_2, 12 mM; and TAED, 6 mM.

Effect of Temperature

Figure 7, and additional data in Table 1, show that the rate of reaction of acetovanillone with TAED/H_2O_2 increases with increasing temperature.

With the standard TAED/H_2O_2 concentrations and a NaOH concentration of 7 mmol/L there was a 133% increase in the rate constant (*k*) as the temperature was increased from 22 to 40°C and a further 169% increase when going from 40 to 60°C. The results are, in general, consistent with observations in TAED/H_2O_2 bleaching of mechanical pulp.[5]

Formation of Peroxyacetic Acid

Figures 8a–c show the reactions of TAED with hydrogen peroxide to form peroxyacetic acid at various pHs at 60°C. Two phases were observed in the reaction. During the first phase (1 to 2 min), peroxyacetic is produced immediately. The second phase is dominated by the consumption of the oxidants (PAA and H_2O_2). We also observed that both the rate of peroxyacetic acid formation and consumption of the oxidants increased with the alkalinity of the medium.

Thus, a starting bleaching pH around 11 resulted in a high production rate of peroxyacetic acid. As the pH dropped, decomposition of peroxyacetic acid was minimized, an improvement in its bleaching reactivity was observed as the optimal pH range was approached.

CONCLUSIONS

The oxidation of acetovanillone followed first-order kinetics for both peroxide-alone and TAED/H_2O_2 oxidizing systems. The rate constant, *k*, for the TAED assisted system ($0.34\,\mathrm{min}^{-1}$) was two orders of magnitude higher than the peroxide-alone system ($0.0035\,\mathrm{min}^{-1}$), which results in a reaction that proceeds 100 times faster in the presence of TAED, with $t_{1/2}$ of 2 and 220 min for TAED/H_2O_2 and peroxide-alone bleaching systems, respectively.

It appears that there is an optimum pH range to achieve a maximum rate constant of acetovanillone bleaching reaction with TAED/H_2O_2 system. This value is about pH 8.2, which corresponds to the pK_a of peroxyacetic acid.

Singlet oxygen may play a role in the oxidative reaction of acetovanillone, and peroxyacetic anion may not be the major oxidizing species eliminating chromophores bleaching of TMP softwood pulp.

The rate of peroxyacetic acid formation in the TAED/H_2O_2 system increases with increasing alkalinity of the medium during the beginning of the reaction. Consumption of the total also increases with increasing alkalinity of the medium.

A higher pH is required at the start of the reaction: to increase production of peroxyacetic acid, while a much lower pH is required in the second phase to minimize decomposition of the peroxyacetic acid and improve its bleaching efficiency.

REFERENCES

1. Abbot, J.; Wright, P.J. Kinetic phenomena during alkaline peroxide bleaching. Appita J. **1992**, *45* (5), 332–335.
2. Wright, P.J.; Abbot, P.J. Kinetics models for peroxide bleaching under alkaline conditions, Part 1. One and two chromophores models. J. Wood Chem. Technol. **1991**, *11* (3), 349–371.
3. Xu, E.C. H_2O_2 bleaching of mechanical pulps. Part I: kinetics and mechanism. J. Pulp Paper Sci. **2000**, *26* (3), 367–376.
4. Xu, E.C. H_2O_2 bleaching of mechanical pulps. Part II: pH and temperature. J. Pulp Paper Sci. **2000**, *26* (11), 407–413.
5. Leduc, C.; Montillet, C.; Daneault, C. Activator for the peroxide bleaching of mechanical pulp. Appita J. **1998**, *51* (4), 306–311.
6. Sain, M.M.; Daneault, C.; Parenteau, M. Bleach activation of thermomechanical pulp. Can. J. Chem. Eng. **1997**, *75*, J362–J369.
7. Leduc, C.; Sain, M.M.; Daneault, C. Use of new oxidizing agents (peroxide-activated peroxide-perborate) for the bleaching of mechanical pulp. Pulp Pap. Can. **2001**, *102* (1), 34–38.
8. Leduc, C.; Sain, M.M.; Daneault, C.; Lanouette, R.; Valade, J.L. Peroxide-activated peroxide-sodium perborate; which one to use and where to add it in the bleaching of mechanical pulp. *Procceding 1997 Tappi Pulping Conference*, San Francisco, Book 1, 1997, 471–476.
9. Cround, V.B.; Mathews, A.J. TAED.A new activator for the peroxide bleaching of pulp. *Proceedings of 1996 Intl. Non-Chlorine Bleaching Conference*, Orlando, USA, 1996; paper 3–4.
10. Edwards, J.O. *Peroxide Reaction Mechanism*; Wiley Insterscience: New York, 1962.
11. Hauthal, H.G.; Schmidt, H.; Scholz, H.J.; Hofmann, J.; Pritzkow, W. Studies concerning the mechanism of bleaching activation. Tenside Surf. Det. **1990**, *27* (3), 187.
12. Strukul, G. Catalytic oxidations with hydrogen peroxide as oxidant. In *Activation of Hydrogen Peroxide by Organic Compounds*; Kluwer Academic Publishers: Dordrecht/Boston/London, 1992; Chapter 3, 45–95.
13. Davies, D.M.; Deary, M.E. Kinetics of hydrolysis and prehydrolysis of tetraacetylethylenediamine, a peroxide bleach activator. J. Chem. Soc. Perkin Trans. **1991**, *2* (10), 1549–1552.
14. Coucharrière, C.; Mortha, G.; Lachenal; Briois, L.; Larnicol, P. Rationalization of the use of TAED during activated peroxide delignification and bleaching. Part 1: kinetic model. J. Pulp Paper Sci. **2002**, *28* (10), 332–340.
15. Strumila, G.; Rapson, H. Reaction products of neutral peracetic acid oxidation of model lignin phenols. Pulp Paper Can. **1975**, *76* (9), 74–78.
16. Ragnar, M. pK_a-values of lignin-related phenols. Available at http://w1.541.telia.com/~u54104246/kemi/pka.htm.
17. Jones, R.A.Y. *Physical and Mechanistic Organic Chemistry*; Press, C.U., Ed.; Cambridge Texts in Chemistry and Biochemistry: Cambridge, 1979.
18. Ragnar, M.; Lindgren, C.T.; Nilvebrant, N.O. pK_a-values of guaiacyl and syringyl phenols related to lignin. J. Wood Chem. Technol. **2000**, *20* (3), 277–305.
19. Hofmann, J.; Just, G.; Pritzkow, W.; Schmidt, H. Bleaching activators and the mechanism of bleaching activation. J. Prakt. Chem. **1992**, *334*, 293.