On the Origin of Cellulose Depolymerization During Ozone Treatment of Hardwood Kraft Pulp

Frédéric Pouyet,* Christine Chirat, and Dominique Lachenal

An oxygen-delignified eucalypt pulp (*Eucalyptus grandis x Eucalyptus urophylla* hybrid) was provided by a Brazilian pulp mill. It was treated with chlorite to remove lignin, or by a long acidolysis stage to remove most of the hexenuronic acid groups (HexA) followed by a chlorite treatment to remove the lignin. Three pulp samples were treated with increasing ozone charges (up to 2% on pulp) at high consistency and room temperature. The pulp containing no lignin but all of the HexA appeared to be the most affected by the ozone treatment. This indicated that the reaction of ozone with HexA generates radicals, which then react with cellulose, leading to depolymerization. It also indicated that lignin captures some of these radicals. ESR spectroscopy confirmed that hydroxyl radicals are formed when ozone reacts with maleic acid, which can be considered a HexA model compound. These findings open the way to the improvement of chlorine-free bleaching sequences containing ozone stages.

Keywords: Ozone; Pulp bleaching; Hexenuronic acid; Cellulose depolymerisation; Radicals; ESR spectroscopy

Contact information: Grenoble INP-Pagora, The International School of Paper Print Media and Biomaterials, 461 rue de la papeterie – CS 10065, 38402 St Martin d'Hères Cedex, France;
** Corresponding author: frederic.pouyet@grenoble-inp.org*

INTRODUCTION

Ozone bleaching was implemented on an industrial scale for the first time in 1992 (Nutt *et al.* 1993). Since then, more than 20 bleaching lines containing an ozone stage (Z) have been installed in chemical pulp mills to reduce the consumption of or to eliminate the use of chlorine dioxide and other chlorinated reagents that contribute to effluent load and adsorbable organic halides (AOX). Most of the totally chlorine-free bleaching (TCF) sequences developed so far have implemented an ozone stage, as ozone is by far the most powerful chlorine-free oxidant available. However, there are some drawbacks to its use, such as a decrease in the degree of polymerization (DP) of the cellulose (Rautonen *et al.* 1996; Ragnar *et al.* 1999a), or an increase in the carbonyl content (Chandra and Gratzl 1985), which might lead to further depolymerization during subsequent alkaline stages. These carbonyl groups can also lead to lower brightness stability (Sjöström and Eriksson 1968; Chirat and De la Chapelle 1999).

Various mechanisms are described in the literature to explain the depolymerization of cellulose by ozone. Some refer to a direct addition of ozone to the cellulose (Godsay and Pearce 1985), while other references suggest that the degradation is mainly due to the generation of secondary radicals (Ragnar *et al.* 1999a; Kang *et al.* 1995) during the reaction of ozone with some specific structures of the lignin, such as phenols. Although more seldom invoked, the production of radicals from peroxide generated when ozone reacts on carbon-carbon double bonds has also been proposed (Chirat and Lachenal 1997).

High brightness can be achieved by TCF sequences using oxygen and peroxide combined with ozone or, to a lower extent, with peracids. Moreover, more severe environmental regulations regarding effluent quality might lead someday to a higher use of ozone in elemental chlorine-free (ECF) sequences. For these reasons, it is of high interest to know the conditions under which the degradation of cellulose by ozone is minimized.

The purpose of this paper is to determine the causes of cellulose degradation of a kraft hardwood pulp, containing both lignin and hexenuronic acids (HexA), when treated with ozone. In this study, pulps of various compositions were treated with increasing amounts of ozone. The ozonation of some pulp model compounds was followed by ESR spectroscopy to complete this investigation. The new results reported may pave the way for improved selectivity of TCF sequences.

EXPERIMENTAL

Pulps

Oxygen-delignified (kappa 9.3) and fully-bleached eucalypt kraft pulps (*Eucalyptus grandis x Eucalyptus urophylla* hybrid) were provided by a Brazilian pulp mill (Table 1). Two other pulps were prepared from this oxygen-delignified pulp by applying either a chlorite treatment (holocellulose procedure) to remove the lignin, or both a long hot acid stage (A stage) to remove most of the HexA and a chlorite treatment, respectively referred to as lignin-free pulp and HexA- and lignin-free pulp in this paper.

Table 1. Pulp Samples

Pulp	DP_v	HexA content (μeq/g)
Kraft+O	1630	71.7
Lignin-free	1630	48.2
HexA- and lignin-free	1420	<6

Operating Conditions and Standards

The conditions used for the bleaching stages composing the sequences are listed in Table 2. The reagents were applied on an oven-dried basis to the pulp.

Table 2. Conditions Used During Bleaching Stages

	pH	T (°C)	Consistency (%)	Time (h)	Reagents
Z_x	2.5	25	40	n/a	H_2SO_4 O_3 (x%)
Long A	3	90	10	7	H_2SO_4

Prior to the ozone treatment, the pulp was acidified to pH 2.5 with sulfuric acid at a consistency of 1% and then filtered to thicken it. The filtered pulp was centrifuged to reach a consistency of 40%, and then fluffed. The ozonation was then performed in a rotating spherical reactor. The quantity of ozone is expressed as the percentage of ozone charge on an oven-dried basis.

For the other stage, the temperature was controlled using a thermostated bath, with the reactions taking place in polyethylene bags. The following procedures were used for pulp characterization: viscosity (ISO 5351/ 1-1981), reported in terms of DP (DP_v) calculated from viscosity values using the following formula (Sihtola *et al.* 1963).

$$DP_v = (0.75\ (954 \log \eta - 325))^{1.105} \quad (1)$$

The hexenuronic acid (HexA) content was measured according to a procedure described by Chai and Zhu (1999).

ESR Spectroscopy Experiments

Ozonations of two model compounds were followed by ESR spectroscopy. Acetovanillone (Aldrich-Europe) was used as a model for residual lignin after oxygen delignification, and (*cis*) maleic acid (Aldrich, 99%) was used as a model for HexA.

X-band ESR spectra were recorded at room temperature with a Bruker EMX Plus spectrometer equipped with a ER-4102ST Bruker cavity. It was operating at 9.8 GHz. Samples were analyzed in a water flat cell at room temperature. Hydroxyl radicals generated in the medium were trapped with 5,5-dimethyl-pyrrolidine-1-oxyl (DMPO, Sigma-Aldrich, 99%) as the stable radical (DMPO-OH), which can be detected with an ESR spectrometer.

Ozonated water was prepared by bubbling ozone gas, generated by an ozone generator, in water at pH 2.5 (H_2SO_4) for 90 min. An average concentration of 0.02 g/L was reached. A 2-mL water solution of DMPO (and model) was prepared separately. The necessary volume of ozonated water was added to the latter solution, depending on the conditions. The analysis was performed immediately after mixing. The pH of the resulting solution was not substantially changed by this dilution.

RESULTS AND DISCUSSION

Effect of Ozone on Various Pulps

Pulps of various compositions were treated with increasing charges of ozone, and the DP_v of cellulose was measured after ozonation treatment.

Ozone on HexA- and lignin-free pulp

Figure 1 shows the action of ozone on a pulp containing essentially cellulose and HexA-free hemicelluloses (HexA- and lignin-free pulp in Table 1). The corresponding results for the starting oxygen-delignified kraft pulp (referred to as Kraft+O) are also shown.

The degradation of the HexA- and lignin-free pulp was much slower than that of the Kraft+O starting pulp. This result was expected and is in accordance with the fact that radicals are produced when ozone reacts with lignin. This observation confirms that carbohydrates are not readily oxidized by ozone, as even if all the ozone is available for carbohydrate oxidation, cellulose depolymerization does not occur as quickly as with lignin and HexA. This result was confirmed in another study (Pouyet *et al.* 2013) where it was shown that fewer carbonyl groups were formed on the cellulose during ozonation of a HexA- and lignin-free pulp.

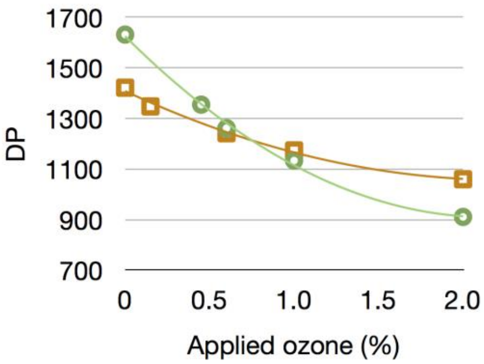

Fig. 1. *DP_v versus* ozone charge for HexA- and lignin-free pulp (squares) in comparison with the behavior of the oxygen-delignified pulp (circles)

Ozone on a lignin-free pulp

According to the literature, ozone reacts heavily with HexA (Ventorim *et al.* 2008). This reaction should not produce radicals (Ragnar *et al.* 1999a). Therefore, the DP_v of a pulp that does not contain lignin but does contain HexA should vary, as in the case of HexA- and lignin-free pulp, or even less, as HexA should consume some ozone.

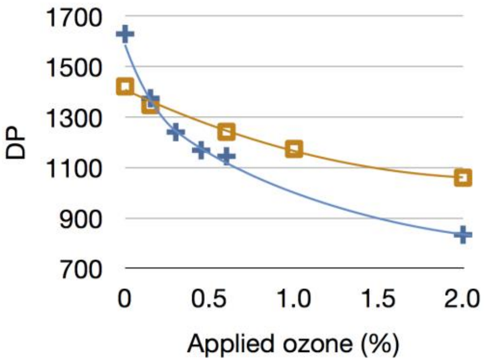

Fig. 2. DP_v of a HexA- and lignin-free pulp (squares) and of a lignin-free pulp (crosses) at various ozone charges

As seen in Fig. 2, there was a severe DP_v loss in the case of the lignin-free pulp. This decrease was higher than in the case of the HexA- and lignin-free pulp. Considering only the first 0.3% of applied ozone in Fig. 2, the starting DP_v was higher in the case of the lignin-free pulp and reached the same level as the DP_v of the other pulp. Because the reactivity of ozone was much higher with double bonds than with polysaccharides, and considering the quantity of HexA that was actually degraded (around 50 µeq/g pulp), the amount of ozone left to react with the cellulose at this application level for the lignin-free pulp must have been very low (*i.e.*, less than 0.1%, according to a rough calculation, supposing that 1 mole of ozone reacts with one mole of HexA). This should not lead to any significant decrease of the DP_v of cellulose; however, there were more than 200 DP units lost. This observation demonstrated that the reaction of the ozone with the HexA was the source of most of the DP_v decrease. There is definitely a cause-effect relationship between the reaction of HexA with ozone and the depolymerization. One possible explanation could be the generation of radicals.

Figure 3 compares the DP_v for both the starting Kraft+oxygen delignified pulp (Kraft+O) and the lignin-free pulp as a function of ozone treatment charge.

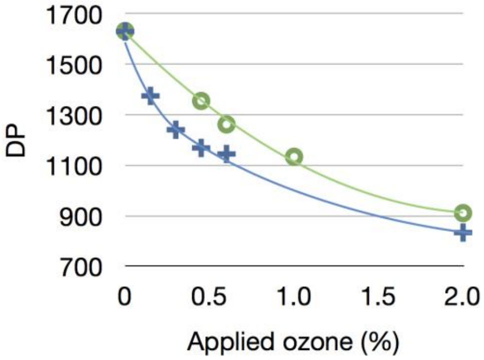

Fig. 3. DP_v of a lignin-free pulp (crosses) and a Kraft+O pulp (circles) at various ozone charges

By comparing these two curves, it was clear that the Kraft+O pulp was not degraded as much as the lignin-free pulp at low ozone charges. Earlier, it was shown that the reaction of ozone with HexA led to a higher amount of cellulose depolymerization. It is well documented that the reaction of ozone with lignin leads to additional cellulose depolymerization (Kang *et al.* 1995; Magara *et al.* 1996). As a consequence, a pulp containing both compounds should be more degraded during ozonation, which was not the case. Therefore, in the case of the starting pulp, fewer radicals reacted with cellulose, possibly because they reacted with lignin instead (Ek *et al.* 1989).

Detection of OH Radical during Ozonation of Models

The formation of hydroxyl radicals when ozone reacts with lignin has been well documented (Ragnar *et al.* 1999a; Kang *et al.* 1995), and several techniques are available to detect their presence (Reitberger and Gierer 1988; Chirat and Lachenal 1997). ESR spectroscopy was chosen in this work. It is common to add 5,5-dimethyl-pyrrolidine-1-oxyl (DMPO) for ESR spectroscopy. DMPO forms a rather stable radical (DMPO-OH) that can be detected (Finkelstein *et al.* 1980).

Acetovanillone was chosen as a model for the free phenolic groups present in lignin after oxygen delignification. Although this model is certainly less reactive toward oxidation than other compounds, such as guaiacol (Eriksson and Gierer 1985), it should react with ozone under the conditions used in this study. Maleic acid, which mimics a key functional group of HexA (*i.e.*, a carboxyl group conjugated to a carbon-carbon double bond), was used as a representative HexA model.

DMPO-OH radicals formed by addition of the hydroxyl radical onto DMPO were detected at room temperature in ozonated water (0.020 g/L) containing DMPO. Figure 4 illustrates a typical ESR signal indicating the existence of DMPO-OH radicals (4 peaks, g-factor = 2.003).

In the first experiment, ozone (as ozonated water) was added to a medium containing only DMPO (2×10^{-7} moles of ozone and 1×10^{-4} moles of DMPO). No radical signal was initially detected when ozone was added to the DMPO-only solution. However, a small signal was registered after a certain period of reaction (more than a few minutes). Under these conditions, ozone would be only slowly turned into radicals. It was anticipated that when the models were present, ozone would react first with the phenolic structures or the double bonds before self-decomposing. In addition, in most of the experiments, the amount of ozone would be lower than the amount of model compound. As a consequence, these compounds will consume most of the ozone. If a signal is registered, then it can be concluded that it comes from the reaction of ozone with the compound rather than from ozone self-decomposition.

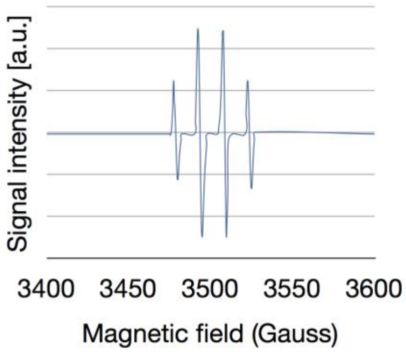

Fig. 4. Typical ESR signal of DMPO-OH radical

In a second experiment, ozone was added to a solution containing acetovanillone and DMPO (2 x 10^{-7} moles of ozone, 2 x 10^{-6} moles of phenol, and 1 x 10^{-4} moles of DMPO). In this case, a signal was registered. This confirmed that ozone produced OH radicals when it reacted with a phenolic compound, as has been reported in the literature (Han *et al*. 1998).

In a third experiment, ozone was added to a solution containing maleic acid and DMPO (2 x 10^{-7} moles of ozone, 3 x 10^{-6} moles of maleic acid, and 1 x 10^{-4} moles of DMPO). The results shown in Fig. 5 indicate that OH radicals were generated when ozone reacted with maleic acid. The corresponding spectrum without maleic acid is also given for comparison. One more experiment was carried out with a lower amount of maleic acid (2 x 10^{-7} moles of ozone, 1 x 10^{-7} moles of maleic acid, and 1 x 10^{-4} moles of DMPO). The signal observed with this last experiment showed the generation of radicals, the concentrations of which were higher than that of ozone alone with DMPO, but lower than the earlier experiment with higher maleic acid content. As a consequence, the amount of radicals generated when ozone reacted with maleic acid seemed to be linked to the concentration of maleic acid.

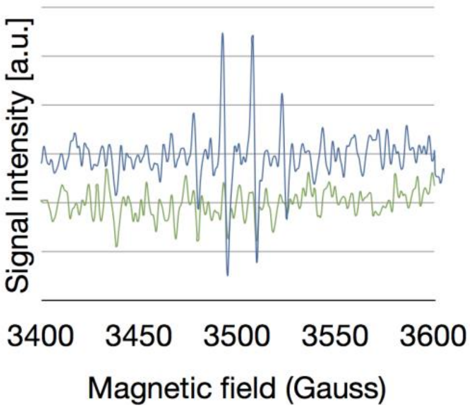

Fig. 5. ESR signals obtained with DMPO for ozone (in green) and ozone and maleic acid (in blue)

This result was not expected because the ozonolysis of carbon-carbon double bonds by the Criegee mechanism does not generate OH radicals (Criegee 1957). Two hypotheses might explain this observation. One is related to the generation of hydrogen peroxide by the reaction of ozone with a carbon-carbon double bond. The resulting peroxide could be catalytically decomposed into radicals due to the presence of transition metal ions in the reaction medium, which cannot be totally excluded. The other possible explanation is that there is an electrophilic action of ozone on carbon-carbon double bonds leading to the formation of the ozonide radical, $O_3^{\bullet-}$, which would then decompose to a hydroxyl radical after protonation; such a reaction mechanism has already been proposed to occur with phenol ozonation (Ragnar *et al.* 1999b). In addition, the formation of OH radicals has been described to occur during gas-phase alkene ozonolysis (Anglada *et al.* 2002) and recently reported to occur during the ozonation of electron-rich moieties in an aqueous medium (Audenaert *et al.* 2013).

Practical Consequences

The previous results indicated that the majority of cellulose depolymerization during ozone bleaching is likely due to the presence of lignin and HexA. The effect of lignin was known, contrary to that of HexA. According to the preliminary ESR study of maleic acid ozonolysis, OH radicals are potentially formed when ozone reacts with carbon-carbon double bonds of the type found in maleic acid.

Therefore, the way to minimize cellulose degradation during ozone delignification would be to avoid the presence of such carbon-carbon double bonds in the medium as much as possible. Actually, these double bonds may have two origins: the HexA and the muconic acid derivatives resulting from the ozonolysis of phenolic groups in lignin. In fact, the latter can also be modeled by maleic acid.

A first approach would be to eliminate the HexA before ozone treatment. A hot acidolysis stage (A) with H_2SO_4 is currently performed in conventional elemental chlorine-free bleaching (ECF) to eliminate part of the HexA. The purpose of an A stage in this example is to save some chlorine dioxide, which would otherwise react with the HexA. Results shown in Table 3, obtained with the Kraft+O pulp, show that the application of the A stage before a Z stage leads to a higher DP_v, which cannot be explained if HexA is not the origin of cellulose depolymerization (in these experiments, an extraction stage with caustic soda (E) was performed after Z). In typical A stages, only about 50% of the HexA is removed. Developing a more efficient A stage would certainly be even more beneficial to the preservation of cellulose DP_v.

Table 3. Ozone Bleaching Strategies to Minimize Cellulose Depolymerization

Treatment	Ozone charge % on pulp	Brightness %	DP_v
None	-	51.0	1630
A	-	54.7	1510
ZE_2	0.8	67.5	1050
AZE_2	0.8	82.1	1170
ZE_2	0.6	64.4	1180
ZE_1ZE_1	0.3 + 0.3	73.1	1340

E_2 stage: 2% NaOH, 70°C, 1h, 10% consistency. E_1 stage: 1% NaOH
A stage: pH 3, 90°C, 2h, 10% consistency (HexA after A: 34 µeq/g)

A second approach would be to eliminate the muconic acid derivatives once they are formed, which would be rather difficult. One way is to split the ZE process into multiple stages (*e.g.*, ZEZE) at the same overall ozone charge. This type of sequence has already been proposed (Allison 1982). The results presented in Table 3 show that this arrangement is not only more efficient in terms of delignification but is also less harmful to the cellulose. Again, this result is easily explained if the muconic acid derivatives generate radicals when reacting with ozone. Combining these two approaches could be the basis of the development of high-performance TCF bleaching sequences.

CONCLUSIONS

1. When a Z stage bleaching treatment was carried out on an oxygen-delignified eucalypt pulp, cellulose depolymerization occurred. However, if the lignin was removed and the HexA was left, the amount of depolymerization was even more severe.
2. The reaction of ozone with the HexA is the origin of some cellulose depolymerization.
3. It is proposed that the reaction of ozone with the carbon-carbon double bond of HexA generates radicals. A portion of these radicals would be captured by the lignin.
4. ESR spectroscopy confirms that OH radicals are formed when ozone reacts with a lignin model (acetovanillone), which is already well-documented in the literature. However, ESR spectroscopy also confirms that OH radicals are generated when ozone reacts with a HexA model (maleic acid).
5. The muconic acid groups, formed from the reaction of ozone with lignin, have structural similarities to HexA and to maleic acid; these groups also might be the origin of radical formation during Z-stage treatment.
6. TCF bleaching sequences that include an extensive HexA removal stage coupled to several (ZE) phases should be of interest because they would minimize the occurrence of radicals from ozone reactions with unsaturated species.

ACKNOWLEDGEMENTS

The authors would like to thank the “TGE Réseau National de RPE Interdisciplinaire”, Grant FR-CNRS 3443. More specifically, the authors acknowledge the assistance of Florian Molton and Carole Duboc (Molecular Chemistry Department, Université Joseph Fourier, Grenoble) in the ESR spectroscopy analysis.

REFERENCES CITED

Allison, R. W. (1982). “Efficient ozone and peroxide bleaching of alkaline pulps from *Pinus radiata*,” *Appita* 36(1), 42-1982.

Anglada, J. M., Aplincourt, P., Bofill, J. M., and Cremer, D. (2002). "Atmospheric formation of OH radicals and H_2O_2 from alkene ozonolysis under humid conditions," *Chemphyschem* 3(2), 215-221.

Audenaert, W. T. M., Vandierendonck, D., Van Hulle, S. W. H., and Nopens, I. (2013). "Comparison of ozone and $HO^\bullet$ induced conversion of effluent organic matter (EfOM) using ozonation and UV/H_2O_2 treatment," *Water Res.* 47(7), 2387-2398.

Chai, X. S., and Zhu, J. Y. (1999). "A simple and rapid method to determine hexenuronic acid groups in chemical pulps," *J. Pulp Paper Sci.* 27(5), 165-170.

Chandra, S., and Gratzl, J. S. (1985). "Kinetics of carbohydrate and lignin degradation and formation of carbonyl and carboxyl groups in low consistency ozonation of softwood pulps," *1985 International Pulp Bleaching Conference,* Quebec, Canada, 27-35.

Chirat, C., and De la Chapelle, V. (1999). "Heat-and light-induced brightness reversion of bleached chemical pulps," *J. Pulp Paper Sci.* 25(6), 201-205.

Chirat, C., and Lachenal, D. (1997). "Effect of hydroxyl radicals on cellulose and pulp and their occurrence during ozone bleaching," *Holzforschung* 51(2), 147-154.

Criegee, R. (1957). "The course of ozonization of unsaturated compounds," *Record of Chemical Progress* 18(2), 111-120.

Ek, M., Gierer, J., Jansbo, K., and Reitberger, T. (1989). "Study on the selectivity of bleaching with oxygen-containing species," *Holzforschung* 43(6), 391-396.

Eriksson, T., and Gierer, J. (1985). "Relative rates of ozonation of lignin model compounds," *3rd International Symposium on Wood and Pulping Chemistry,* Vancouver, Canada, August, 29-30.

Finkelstein, E., Rosen, G., and Rauckman, E. (1980). "Spin trapping of superoxide and hydroxyl radicals: Practical aspects," *Arch. Biochem. Biophys.* 200(1), 1-16.

Godsay, H. P., and Pearce, E. M. (1985). "Mechanism of inhibition & retardation of ozone-lignocelllulose reactions," *TAPPI Pulping Conference,* Hollywood, Florida, USA, 245-262.

Han, S.-K., Ichikawa, K., and Utsumi, H. (1998). "Quantitative analysis for the enhancement of hydroxyl radical generation by phenols during ozonation of water," *Water Res.* 32(11), 3261-3266.

Kang, G., Zhang, Y., Ni, Y., and Van Heiningen, A. R. P. (1995). "Influence of lignins on the degradation of cellulose during ozone treatment," *J. Wood Chem. Technol.* 15(4), 413-430.

Magara, K., Ikeda, T., Tomimura, Y., and Hosoya, S. (1996). "Accelerated degradation of cellulose in the presence of lignin during ozone bleaching," *1994 International Pulp Bleaching Conference,* Washington D.C., USA, 553-558.

Nutt, W. E., Griggs, B. F., Eachus, S. W., and Pikulin, M. A. (1993). "Developing an ozone bleaching process," *Tappi J.* 76(3), 115-213.

Pouyet, F., Chirat, C., Potthast, A., and Lachenal, D. (2013). "Formation of carbonyl groups on cellulose during ozone treatment of pulp. Practical consequences for pulp bleaching", *17th International Symposium on Wood, Fiber and Pulping Chemistry* (*ISWFPC*), Vancouver, Canada.

Ragnar, M., Eriksson, T., and Reitberger, T. (1999a). "Radical formation in ozone reactions with lignin and carbohydrate model compounds," *Holzforschung* 53(3), 292-298.

Ragnar, M., Eriksson, T., Reitberger, T., and Brandt, P. (1999b). "A new mechanism in the ozone reaction with lignin like structures," *Holzforschung* 53(4), 423-428.

Reitberger, T., and Gierer, J. (1988). "Chemiluminescence as a means to study the role of hydroxyl radicals in oxidative processes," *Holzforschung* 42(6), 351-356.
Sihtola, H., Kyrklund, B., Laamanen, L., and Palenius, I. (1963). "Comparison and conversion of viscosity and DP-values determined by different methods," *Paperi ja Puu* 45(4a), 225-232.
Sjöström, E., and Eriksson, E. (1968). "The influence of carboxyl and carbonyl groups on the brightness stability of bleached pulps," *TAPPI J.* 51(1), 16-24.
Ventorim, G., Colodette, J., de Fatima Gomes, A., and da Silva, L. (2008). "Reaction rates of lignin and hexenuronic acids with chlorine dioxine, ozone, and sulfuric acid," *Wood and Fiber Science* 40(2), 190-201.

Article submitted: June 26, 2013; Peer review completed: August 21, 2013; Revised version received: August 26, 2013; Accepted: August 27, 2013; Published: August 29, 2013.