

# REACTIVITY OF HEXENURONIC ACID IN BLEACHING OF EUCALYPTUS KRAFT PULPS

Tapani Vuorinen<sup>1\*</sup>, Immanuel Adorjan<sup>2</sup>, Anna-Stiina Jääskeläinen<sup>2</sup>, Tuula Lehtimaa<sup>3</sup>, Katri Toikka<sup>3</sup>, Zhen Zhou<sup>3</sup>

<sup>1</sup>Professor, <sup>2</sup>Senior Scientist, <sup>3</sup>Doctoral Student, \*Laboratory of Forest Products Chemistry, Helsinki University of Technology (TKK), P.O. Box 6300, FI-02015 Espoo, Finland

## ABSTRACT

Bleached Eucalyptus kraft pulps form the fastest growing global source of virgin papermaking fibers. Modern Eucalyptus pulp bleaching lines are designed to produce pulps of high brightness and brightness stability with minimal consumption of bleaching chemicals. In most cases a mildly acidic stage is included to hydrolyze most of the uncolored hexenuronic acid that would otherwise consume bleaching chemicals and/or give rise to thermal discoloration.

In this paper alternative ways of bleaching Eucalyptus kraft pulps are reviewed with special emphasis on the fate of hexenuronic acid. The review is complemented with recent data (obtained by UV resonance Raman spectroscopy) on relative reaction rates of residual lignin and hexenuronic acid through complete bleaching sequences.

The complex reaction mechanisms in ECF bleaching sequences are analyzed through kinetic data from competing and/or consecutive model reactions of hexenuronic acid and lignin. The various active chlorine compounds, chlorine dioxide, chlorite and hypochlorous acid, differ largely on their reactivity towards the two substrates. Therefore the chemistries of hexenuronic acid and lignin in pulp bleaching are interdependent.

The paper ends up with a conclusion how hexenuronic acid reacts under various bleaching conditions and how its reactivity is related with the amount and type of residual lignin and/or various dissolved compounds that might be present in the bleaching filtrates. The information provided can be used in planning of bleaching sequences. The chemistry alone is not enough to rank between alternative bleaching sequences as they may differ from each other in respect of several incommensurable features.

**Keywords:** bleaching, chlorine dioxide, chlorite, ECF, eucalyptus, hexenuronic acid, hypochlorous acid, kraft pulp, lignin.

## INTRODUCTION

Bleached Eucalyptus kraft pulps form the fastest growing global source of virgin papermaking fibers. Modern Eucalyptus pulp bleaching lines are designed to produce pulps of high brightness and brightness stability with minimal consumption of bleaching chemicals. Because unbleached Eucalyptus kraft pulps contain typically large amounts of hexenuronic acid, its contribution to bleachability and quality of pulp has been studied widely.

Although several authors have failed to find a correlation between the hexenuronic acid content and brightness instability of Eucalyptus kraft pulps, there is no reason to believe why these pulps would differ from other kraft pulps in which a linear relationship has been reported (Björklund and Germgård 2005, Sevastyanova et al. 2006). Obviously the discrepancy is due to the different testing methods applied. The degradation of hexenuronic acid depends on the water content of the pulp and therefore the correlation cannot be observed with the standard method that applies a dry atmosphere.

Because of its definitive contribution to brightness instability, hexenuronic acid rich Eucalyptus kraft pulps, although bright, cannot obviously be considered as high quality pulps. Several approaches have been suggested to reduce the hexenuronic acid content prior to or during the initial bleaching. Bleaching sequences starting with a mild acid hydrolysis (Vuorinen et al. 1999) or a long chlorine dioxide stage at high temperature (Lachenal and Chirat 1998) are mostly applied in Eucalyptus kraft pulp mills. In both options hexenuronic acid is partly destroyed through hydrolytic cleavage by water (Forsström et al. 2005).

The reactivity of oxidizing bleaching chemicals towards hexenuronic acid varies depending mostly on the chemical nature of the oxidant. Electrophilic oxidants, such as ozone (Bokström and Wennerström 2001, Lopes da Silva and Pereira Ramos 2002) and peroxymonosulfuric acid (Petit-Breuilh et al. 2003), have been suggested as alternatives to reduce the hexenuronic acid content of Eucalyptus kraft pulps.

Our research group has carried out extensive studies on the reaction mechanisms and kinetics of Eucalyptus kraft pulp bleaching with several bleaching chemicals and sequences. This paper summarizes some of these results with reference to earlier publications. The findings on the reaction mechanisms are based largely on model experiments with simple substrates such as a monomeric hexenuronic acid derivative, benzene derivatives, furan derivatives and simple mono- and dicarboxylic acids. The discussion is limited here to ECF bleaching sequences and stages within them.

## EXPERIMENTAL

### Pulp bleaching

An industrial oxygen delignified eucalyptus kraft pulp (kappa number 10.5, hexenuronic acid content 68 mmol/kg, ISO brightness 63.4 %) was used in all bleaching experiments. The bleaching sequences studied included DEDD, Z/DED and A/DED. All the bleaching stages were carried out in well mixed reactors at 10 % pulp consistency.

In the DEDD sequence the active chlorine charge was 25, 30 or 35 kg/t of pulp. The kappa factor in the  $D_0$  stage was varied independently on the total active chlorine charge. The applied kappa factors were 0.11, 0.15 and 0.19. The target conditions for the stages were:  $D_0$ : 60 °C, 30 min, initial pH 3; E: 70 °C, 60 min, final pH 10.5;  $D_1$ : 75 °C, 120 min, initial pH 4;  $D_2$ : 75 °C, 180 min, initial pH 4.

The Z/DED sequences applied a 0.35 % charge of ozone (60 °C, 12 min, initial pH 3) while the addition of active chlorine in the Z/D stage was 1.5, 5.5 or 9.5 kg/t of pulp. The total charge of active chlorine was varied independently on Z/D charge. The applied total active chlorine charges were 15, 20 and 25 kg/t of pulp. The conditions of the E and  $D_1$  stages were otherwise equal to those applied in the DEDD sequences.

The A/D stage was carried out at 95 °C using an initial pH of 3.5. The delay of the A-stage was 120 min while the /D delay was varied (2, 5 or 10 min). The kappa factor of the A/D stage was 0.05, 0.07, 0.09, 0.11 or 0.15. The active chlorine charge of the  $D_1$  stage was 15, 18 or 20 kg/t of pulp. The conditions of the E and  $D_1$  stages were otherwise equal to those applied in the DEDD sequences.

### Chemical analyses

The pulps were tested after washing for kappa number and brightness. The contents of aromatic lignin and hexenuronic acid were evaluated by UV resonance Raman (UVR) spectroscopy (Saariaho et al. 2003). The residual active chlorine was quantified by titration.

## RESULTS AND DISCUSSION

### Reaction mechanisms and kinetics

Traditionally the mechanism of chlorine dioxide bleaching is considered very complicated (Reeve 1996). In addition to chlorine dioxide, at least chlorate, chlorite, hypochlorite, chloride and chlorine are formed and are present in the bleaching reactions. Organic chlorine compounds, both soluble (AOX) and insoluble (OX), are formed. Chlorine dioxide is a one-

electron oxidant (radical) that prefers to react with non-radical structures that can form stable radicals through a one-electron abstraction. This means that chlorine dioxide reacts easily with phenolic lignin structures while the reactions with non-phenolic lignin and hexenuronic acid are very slow (Behrooz Eshkiki et al. 2006). The initial oxidation step of chlorine dioxide with phenols produces an equimolar amount of chlorite. The phenoxy radical formed couples readily with another equivalent of chlorine dioxide and the coupling products are rapidly converted to oxidized lignin structures (quinones or muconic acids) while hypochlorite is liberated (Vuorinen et al. 2005).

The decomposition of hexenuronic acid in chlorine dioxide bleaching is caused by hypochlorous acid or its equilibrium product chlorine. According to our studies hypochlorous acid reacts faster with hexenuronic ( $k = 400 \text{ M}^{-1}\text{s}^{-1}$  at 25 °C) (Adorjan et al. 2006) than with lignin-like benzene derivatives ( $k = 40 \text{ M}^{-1}\text{s}^{-1}$  at 25 °C) (Zhou et al. 2007) which again are much more reactive than 2-furoic acid ( $k = 0.2 \text{ M}^{-1}\text{s}^{-1}$  at 25 °C) (Toikka et al. 2005). In addition, hypochlorous acid reacts very fast with oxalic acid ( $k = 2 \text{ M}^{-1}\text{s}^{-1}$  at 25 °C), somewhat slower with formic acid ( $k = 0.2 \text{ M}^{-1}\text{s}^{-1}$  at 25 °C) and much slower with hydroxycarboxylic acids (Zhou et al. 2006). The reaction with oxalic acid is almost as fast as the formation of acetyl hypochlorite from acetic acid ( $k = 4.5 \text{ M}^{-1}\text{s}^{-1}$  at 25 °C) (Jia et al. 2000). Moreover, hypochlorous acid can even oxidize alcoholic groups in cellulose (or hemicelluloses) (Zhou et al. 2006) and any aldehydes that may be present e.g. as oxidation products of hexenuronic acid. At least the oxidation of formaldehyde by hypochlorous acid is a very fast reaction ( $k = 65,000 \text{ M}^{-1}\text{s}^{-1}$  at 25 °C) (Chinake et al. 1998).

### Analysis of Eucalyptus kraft pulp bleaching

If Eucalyptus kraft pulp is bleached with pure chlorine dioxide (no hypochlorous acid initially present), the first reaction will be conversion of phenolic lignin structures to quinones and/or muconic acid structures. Two equivalents of chlorine dioxide are consumed while one equivalent of chlorous acid and another equivalent of hypochlorous acid are formed. The lignin contents of oxygen delignified eucalyptus kraft pulps are low, typically < 1 % of pulp. The pulp used in this study contained ~ 0.6 % lignin that equals to ~ 30 mmol of phenylpropane units/kg of pulp. This is a low value in comparison with the typical charges of chlorine dioxide in DEDD bleaching. The chlorine dioxide charges applied in this study were 140, 170 and 200 mmol/kg of pulp. With the largest  $D_0$  kappa factors a part of the chlorine dioxide (5-15 mmol/kg) remained unreacted. The UVR spectra indicated practically zero aromatic lignin content after the prebleaching (DE). Further bleaching had very minor effect on the residual aromatic signal. The residual content of hexenuronic acid after the DE prebleaching

was significant. These findings confirm that the oxidation routes of lignin and hexenuronic acid work, in part, separately. If the residual lignin content gets too low in comparison with the hexenuronic acid content, this cannot be reduced any more due to the block of conversion of chlorine dioxide to hypochlorous acid.

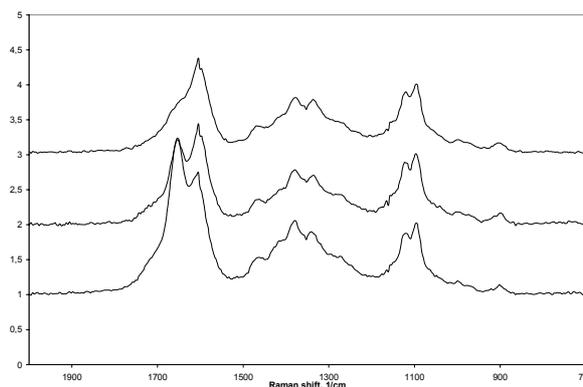
In principle, the hypochlorous acid formed in oxidation of lignin can add electrophilically to an equimolar amount of hexenuronic acid. The (~ ten times) higher reactivity of hexenuronic acid over the aromatic lignin structures should favor this reaction route. The covalent addition product is liberated from the xylan polymer through two hydrolytic steps. Formally the liberated aldehyde (uronic acid derivative) could react with the equimolar amount of chlorous acid, formed in oxidation of phenolic lignin, forming the corresponding carboxylic acid (aldaric acid derivative) and an equimolar amount of hypochlorous acid. Finally this may react with the aldaric acid derivative through cleavage of the C4-C5 or the C5-C6 bond or through chlorination of C4 (Vuorinen et al. 1997). Because the content of hexenuronic acid (68 mmol/kg) was equal to or lower than the consumption of chlorine dioxide in the D<sub>0</sub> stage (65-100 mmol/kg), one could expect close to complete oxidation of hexenuronic acid.

In another limiting case the hexenuronic acid derived aldehydes would be oxidized only by hypochlorous acid instead of chlorous acid which is 10<sup>2</sup>-10<sup>3</sup> times less reactive (than hypochlorous acid) under the conditions of D<sub>0</sub> bleaching (Chinake et al. 1998). In this case the amount of chlorine dioxide consumed (65-100 mmol/kg) could oxidize only 20-30 mmol/kg of hexenuronic acid. Although this amount may be close to the actual one (Forsström et al. 2005), the net of competing reactions is certainly much more complicated. For example, a reaction between hypochlorous acid and chlorite, will eventually lead to their composition to chlorate and chloride ions or regeneration of chlorine dioxide. Although the rate of this reaction has been claimed to be relatively slow ( $k = 1.6 \text{ M}^{-1}\text{s}^{-1}$  at 25 °C), a catalysis by carboxylic acids may fasten the reaction remarkably. Still the rate would be limited by the formation of the intermediate acyl hypochlorite (Jia et al. 2000).

It is quite interesting that the electrophilic peracetic acid prefers to react with hexenuronic acid rather than with lignin (Heikkilä et al. 1998). Similarly persulfuric acid has been reported as a chemical to suppress the hexenuronic acid content of eucalyptus kraft pulps (Petit-Breuilh et al. 2003). These findings are in line with our observation on that the electrophilic hypochlorous acid reacts faster with hexenuronic acid than aromatic lignin structures. Through the extensive oxidation by chlorine dioxide (65-100 mmol/kg) the aromatic lignin (30 mmol/kg) must be extensively modified. Therefore we are still missing the important

information on the relative reaction rate of the oxidized lignin structures.

In comparison with the sequence DEDD, the Z/DED sequence produced a pulp with a reduced hexenuronic acid content (Figure 1). The amount of ozone applied (70 mmol/kg) corresponded to the content of hexenuronic acid in the unbleached pulp (68 mmol/kg). The selectivity of ozone is, however, limited by its high reactivity that may lead to diffusion controlled reaction kinetics. In support of this, oxidation reactions of olefins by ozone have been reported to be very fast (Shafikov et al. 2005). For example, the second order rate constant for the ozonation of allyl alcohol is 200,000 M<sup>-1</sup>s<sup>-1</sup> at 25 °C.



**Figure 1.** UVRR spectra of Eucalyptus kraft pulps bleached with sequences DEDD (down), Z/DED (middle) and A/DED (top). The total active chlorine charges were: DEDD, 30 kg/t; Z/DED, 20 kg/t + 3.5 kg O<sub>3</sub>/t; A/DED, 30 kg/t.

The A/DED sequence led expectedly to the lowest residual hexenuronic acid content (Figure 1). The removal of hexenuronic acid did not substantially affect the oxidation of lignin. The /D stage destroyed the aromatic structure of the residual lignin more extensively than reduced the hexenuronic acid content.

The acid hydrolysis of hexenuronic acid produces mainly 2-furoic and formic acid as the products (Teleman et al. 1996). These compounds are quite unreactive relative to hexenuronic acid (10<sup>3</sup> times more reactive at 25 °C) and aromatic lignin (10<sup>2</sup> times more reactive at 25 °C).

## CONCLUSIONS

Electrophilic bleaching chemicals react faster with hexenuronic acid than with aromatic lignin. Mild electrophiles, like peracetic acid and persulfuric acid, decrease the content of hexenuronic relative to residual lignin. Extremely powerful electrophiles, at least ozone, partly lose their selectivity towards hexenuronic acid due to a diffusion control. A similar diffusion control could exist under extreme conditions

(low pH, high chloride concentration) of chlorine dioxide bleaching where the faster reactions of chlorine could dominate over the slower analogues by hypochlorous acid. Under milder conditions, oxidation by pure chlorine dioxide prefers to attack aromatic lignin rather than hexenuronic acid. Many mills, however, produce chlorine dioxide with varying contents of chlorine/hypochlorous acid. Therefore, the chlorine dioxide bleaching reactions of these mills show less selectivity towards residual lignin.

Although the chemistry of bleaching might not be as obscure as some of the earlier reviews have indicated, the complexity of the partial reactions makes it extremely difficult to understand their overall effects. Obviously there is need for a full computational simulation package that can bind together the kinetics and equilibria of chemical reactions and mass transfer (Kuitunen et al. 2005).

## ACKNOWLEDGMENT

This work has been funded through The National Technology Agency (TEKES) in Finland and by a consortium of forest cluster companies (Andritz, Kemira, Metsä-Botnia, Pöyry, Stora Enso).

## REFERENCES

Adorjan, I., Jääskeläinen, A.-S.; Zhou, Z.; Vuorinen, T., Synthesis and application of the HexA model methyl 4-deoxy- $\beta$ -L-*threo*-hex-4-enopyranosiduronic acid, **9th European Workshop on Lignocellulosics and Pulp**, Vienna, Austria, August 27–30, 2006, *Advances in Chemistry and Processing of Lignocellulosics*, pp. 138–141.

Behrooz Eshkiki, R.; Mortha, G.; Lachenal, D., A new fast and quantitative method for the titration of free phenolic hydroxyl groups in cellulosic pulps, **9th European Workshop on Lignocellulosics and Pulp**, Vienna, Austria, Aug. 27-30, 2006, CD-ROM.

Bokström, M.; Wennerström, M., Bleaching: ozone comes of age, **Pulp Pap. Eur.** 6(5): 16-21 (2001).

Chinake, C. R.; Olojo, O.; Simoyi, R. H., Oxidation of formaldehyde by chlorite in basic and slightly acidic media, **J. Phys. Chem. A** (102): 606-611 (1998).

Forsström, A.; Gellerstedt, G.; Jour, P.; Li, J., On selective removal of hexenuronic acid (HexA) by oxidative bleaching of eucalyptus oxygen-delignified kraft pulp, **2005 International Pulp Bleaching Conference**, Stockholm, Sweden, June 14–16, 2005, *Proceedings*, pp. 309-312.

Björklund, M.; Germgård, U., Effect of cooking conditions on ECF bleaching and brightness reversion of birch kraft pulps, **Tappi J.** 4 (7): 16-22 (2005).

Heikkilä, M.; Räsänen, E.; Stenberg, H.; Vuorinen, T., Competing electrophilic and nucleophilic reactions of peracids, **1998 International Pulp Bleaching Conference**, Helsinki, Finland, June 15, 1998, *Proceedings, Book 1, Oral Presentations*, 139-144.

Jia, Z.; Margerum, D. W.; Francisco, J. S., General-acid-catalyzed reactions of hypochlorous acid and acetyl hypochlorite with chlorite ion, **Inorg. Chem.** (39): 2614-2620 (2000).

Kuitunen, S.; Tarvo, V.; Lehtimaa, T.; Aittamaa, J., Fundamental modelling of pulp bleaching, **59th Appita Annual Conference and Exhibition incorporating the 13th ISWFPC** (International Symposium on Wood, Fibre and Pulping Chemistry), Auckland, New Zealand, May 16–19, 2005, *Proceedings, Volume 2, 13th ISWFPC Sessions - Oral papers*, pp. 257-264.

Lachenal, D.; Chirat, C., High temperature ClO<sub>2</sub> bleaching of kraft pulp, **1998 International Pulp Bleaching Conference**, Helsinki, Finland, June 15, 1998, *Proceedings, Book 1, Oral Presentations*, 95-98.

Lopes da Silva, E.; Pereira Ramos, L., Effect of OQ(OP)(ZQ)(PO) bleaching sequence on chemical composition of kraft pulps, **Papel** 63 (5): 67-74 (2002).

Petit-Breuilh, X.; Melo, R.; Zaror, C., Environmental implications of hexenuronic acid removal from Eucalyptus globulus kraft pulp using peroxymonosulphuric acid, **36th Pulp and Paper Annual Congress**, Sao Paulo, Brazil, Oct. 13-16, 2003, CD-ROM.

Reeve, D. W., Chlorine dioxide in delignification. In: Dence, C. W.; Reeve, D. W. (Eds.), **Pulp Bleaching – Principles and Practice**, TAPPI, Atlanta 1996, 261-290.

Saariaho, A.-M.; Hortling, B.; Jääskeläinen, A.-S.; Tamminen, T.; Vuorinen, T., Simultaneous quantification of residual lignin and hexenuronic acid from chemical pulps with UV resonance Raman spectroscopy and multivariate calibration, **J. Pulp Paper Sci.** 29: 363–370 (2003).

Safikov, N. Ya.; Zimin, Yu. S.; Gerchikov, A. Ya.; Komissarov, V. D., Kinetics of ozone-olefin reactions in aqueous solutions, **Kinet. Catal.** 46: 873-876 (2005).

Sevastyanova, O.; Li, J.; Gellerstedt, G., Influence of various oxidizable structures on the brightness stability of fully bleached chemical pulps, **Nord. Pulp Paper Res. J.** 21: 49-53 (2006).

Teleman, A.; Hausalo, T.; Tenkanen, M.; Vuorinen, T., Identification of the acidic degradation products of hexenuronic acid by NMR spectroscopy, **Carbohydr. Res.** 280: 197-208 (1996).

Toikka, K.; Pekkanen, L.; Jääskeläinen, A.-S.; Vuorinen, T.; Vehmaa J.; Pikka, O., Efficient chlorine dioxide bleaching of eucalyptus kraft pulp in laboratory scale, **2005 International Pulp Bleaching Conference**, Stockholm, Sweden, June 14–16, 2005, Proceedings, Poster presentations, pp. 259–261.

Vuorinen, T.; Fagerström, P.; Räsänen, E.; Vikkula, A.; Henricson, K.; Teleman, A., Selective hydrolysis of hexenuronic acid groups opens new possibilities for development of bleaching processes, **International Symposium on Wood and Pulping Chemistry**, Montreal, June 9-12, 1997, Preprints, M4, 1-4.

Vuorinen, T.; Fagerström, P.; Buchert, J.; Tenkanen, M.; Teleman, A., Selective hydrolysis of hexenuronic acid groups and its application in ECF and TCF bleaching of kraft pulps, **J. Pulp Paper Sci.** 25: 155-162 (1999).

Vuorinen, T.; Jääskeläinen, A.-S.; Lehtimaa, T.; Toikka, K.; Zhou, Z., Fundamentals and characteristics of modern hardwood pulp bleaching, ABTCP-PI 2005: **38th Pulp and Paper International Congress and Exhibition**, Sao Paulo, Brazil, Oct. 17–20, 2005, CD-ROM.

Zhou, Z.; Jääskeläinen, A.-S.; Adorjan, I.; Vuorinen, T., Mechanisms and kinetics: Oxidation of cellulose and carboxylic acids by hypochlorous acid, **9th European Workshop on Lignocellulosics and Pulp**, Vienna, Austria, August 27–30, 2006, Advances in Chemistry and Processing of Lignocellulosics, pp. 91–94.

Zhou, Z.; Jääskeläinen, A.-S.; Vuorinen, T.; Unpublished results, Helsinki University of Technology, 2007.