

# Fundamentals and characteristics of modern hardwood pulp bleaching

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## **Abstract**

Modern hardwood kraft pulp lines utilize chlorine dioxide, ozone, oxygen and hydrogen peroxide as bleaching chemicals. Unbleached hardwood kraft pulps contain typically equal amounts of residual lignin and hexenuronic acid. The bleaching sequences are planned to operate at minimal running costs while keeping the impact on environment low and the quality of pulp high. In this paper the chemistry of modern pulp bleaching is reviewed with links to characteristics of the bleaching.

## **Introduction**

Understanding and practices in bleaching of hardwood kraft pulps have changed a lot since 1994 when the discovery of hexenuronic acid (HexA) in kraft pulps was presented for public (1). Soon after the discovery it was shown that elimination of HexA with an acid treatment significantly decreased the chemical consumption in ECF and TCF bleaching of hardwood kraft pulps (2). Today the hot acid treatment has become a common practice in new hardwood ECF bleaching lines.

AOX of the mill effluent is one of the key parameters that the mills need to follow to meet the limits set by authorities. Many changes in the bleaching sequences have led to decreasing AOX levels and undetectable amounts of dioxins that dominated bleaching research still in 1980'ies (3). The debate on dioxins led also to the introduction of TCF bleaching sequences with ozone, oxygen and hydrogen peroxide as sole bleaching chemicals.

The expected victory of TCF bleaching has not yet been realized for several reasons. Although some hardwood pulp mills operate successfully their TCF plants, there are some features in the bleaching chemistry that may make the TCF lines more difficult to run smoothly and to produce pulps with the highest quality. In this paper we want to report on some observations on bleaching of hardwood kraft pulps, largely based on previously published literature.

## **Residual structures in bleached pulps**

Traditionally the bleaching result is analyzed as the brightness and kappa number (consumption of permanganate) of the pulp. Although the brightness is, by definition, proportional to the chromophore content of the pulp, the brightness stability may vary greatly depending on the chemical composition of the pulp (4). A high brightness stability can only be obtained, although is not necessarily reached, when the residual lignin and HexA contents are low. Therefore, any bleaching sequence should be systematically planned to reach this target together with the high brightness. Because of its unspecificity the kappa number determination does not alone give enough information for systematic development of bleaching sequences (5).

In addition to the residual lignin and HexA, especially the oxidized structures of polysaccharides, organically bound chlorine, residual extractives and transition metal compounds have claimed to be responsible for the brightness reversion.

Recently there have been some developments in analytical wood chemistry that have made it much easier to analyze traces of residual structures in bleached pulps in details. By UV resonance Raman spectroscopy (UVRRS) it is possible to follow how the amount of unsaturated structures in pulp decreases as the bleaching proceeds (Fig. 1) (6). The UVRR spectra reveal to major bands at wavenumbers  $\sim 1600$  and  $1650\text{ cm}^{-1}$ . After analyzing spectra of various extractives (7,8), lignin model compounds (9,10), quinones, muconic acids, oxidized structures of cellulose (11), HexA etc., it seems very clear that the band at  $\sim 1600\text{ cm}^{-1}$  originates solely from aromatic structures.

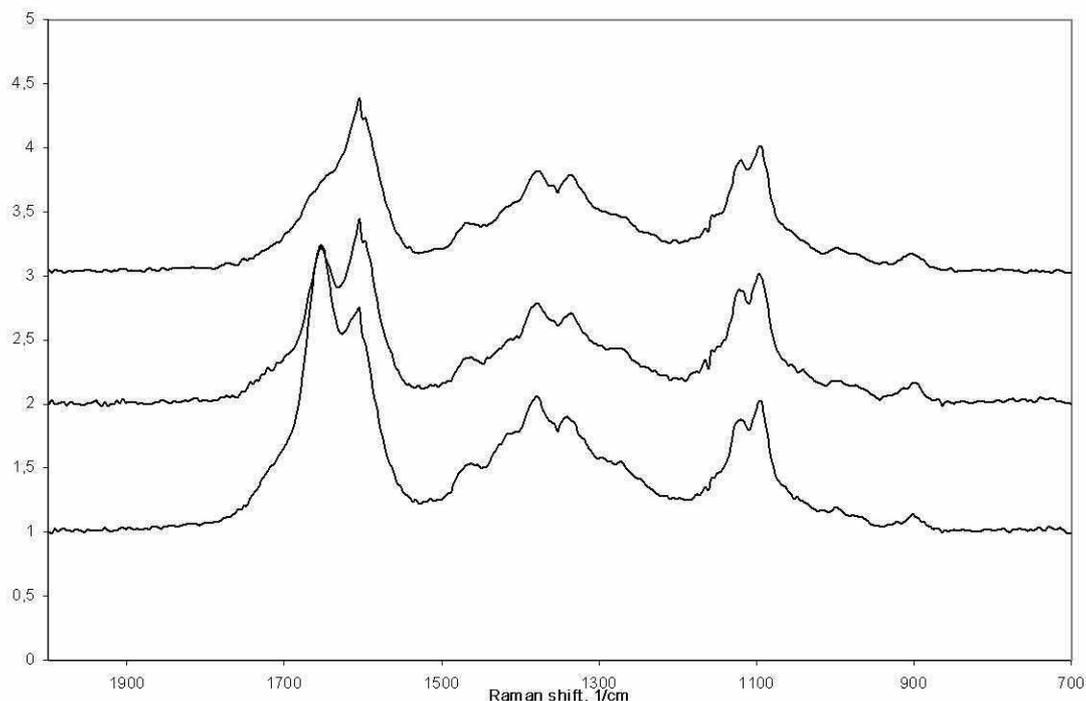


Figure 1. UVRR spectra of fully bleached eucalyptus pulps applied for different bleaching sequences. The band at  $\sim 1600\text{ cm}^{-1}$  originates from aromatic lignin residues while the band/shoulder at  $\sim 1650\text{ cm}^{-1}$  is caused by HexA and oxidized, non-aromatic lignin. The other bands are mainly unenhanced cellulose signals.

The band at  $\sim 1650\text{ cm}^{-1}$  could have contributions from unsaturated structures conjugated to aromatic lignin units, oxidation products of the aromatic ring, unsaturated extractives and even oxidized cellulose. The signal from HexA is, however, dominating and therefore the band can generally be used as indicative for the content of HexA. This is illustrated by how UVRR spectrum of a hardwood kraft pulp changes during conditions of an A-stage planned for the selective hydrolysis of HexA (Fig. 2).

### Organically bound chlorine

Chlorine dioxide is a strong one-electron oxidant. It reacts rapidly with compounds that yield, through abstraction of an electron, stable radicals. Such radicals can be formed from phenolic and benzylic structures of lignin. On the other hand chlorine dioxide does not react with HexA (12). The reaction of chlorine dioxide with 2-furoic acid, a degradation product of HexA, is also very slow (13). As a non-electrophile chlorine dioxide is unable to chlorinate organic molecules

directly. It is, however, well known that hypochlorous acid is formed through decomposition of inorganic and organic chlorites that are the reduction products of chlorine dioxide (14).

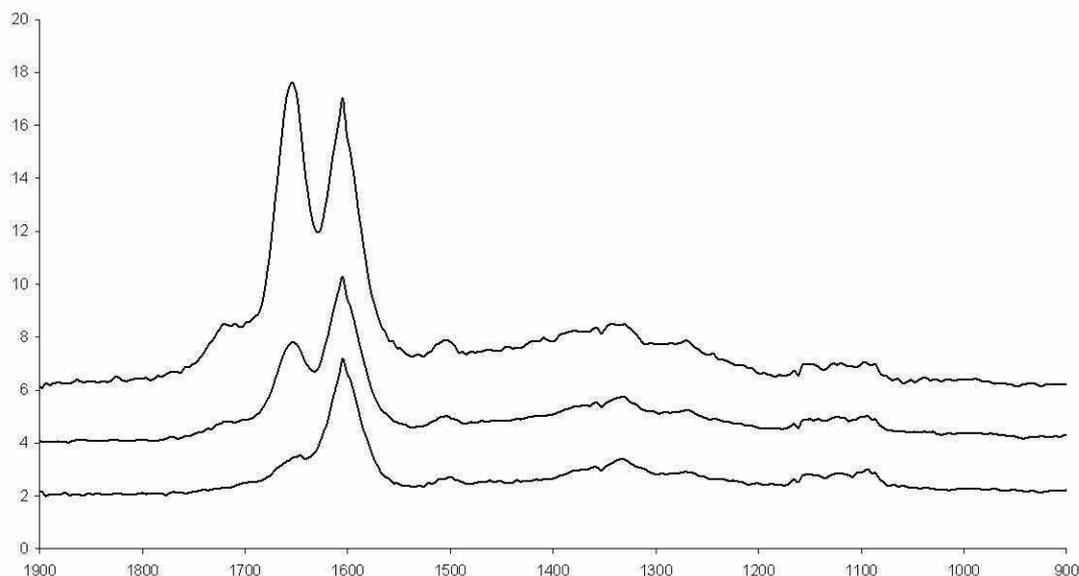


Figure 2. UVRR spectra of oxygen delignified eucalyptus kraft pulps treated for 1, 2 or 5 h, reading down, at pH 3.5 at 95 °C. The decline in the intensity of the  $\sim 1650\text{ cm}^{-1}$  band shows that it mainly originated from HexA.

If a kraft pulp is treated with chlorine dioxide at a high pH (end pH > 6), all chlorine dioxide is consumed rapidly whereas  $\sim 40\%$  of the active chlorine remains unreacted (12). This amount of active chlorine represents inorganic chlorite that is practically stable at the high pH. Because only traces of chlorate are formed at high pH, the primary reactions could be explained as follows. Chlorine dioxide oxidizes phenols to phenoxy radicals and is reduced to chlorite ion. An equivalent amount of chlorine dioxide adds rapidly to the phenoxy radicals forming organic chlorites. These are then decomposed to *o*- and *p*-quinones and muconic acids depending on where the organic chlorite group is located (14). An equimolar amount of hypochlorite ion is simultaneously liberated.

Hypochlorous acid forms rapidly an equilibrium with chlorine (15). The molar ratio of these two active chemicals depends mainly on pH and the concentration of chloride ion. In organic chemistry both chlorine and hypochlorous acid are known as chlorinating agents. On the other hand it has been shown that, in water, hypochlorous acid does not chlorinate *p*-xylene, or, if it does, it does it very slowly (16). On the contrary, chlorine reacts with *p*-xylene rapidly (at least  $10^4$  times faster than does hypochlorous acid).

HexA is converted in chlorine dioxide bleaching to various chlorinated and oxygenated dicarboxylic acids (17). The formation of all these acids can be explained by an initial electrophilic addition of chlorine or hypochlorous acid to HexA. At the low pH of a  $D_0$ -stage (pH 2-3) the products are largely chlorinated while the less acidic  $D_1$ - and  $D_2$ -stages (pH 4-5) yield mostly non-chlorinated acids.

The extent of aromatic substitution of lignin by chlorine depends also on pH and, interestingly, on the concentration of chloride ion. Thus, the content of polychlorinated degradation products of lignin was remarkably decreased when the pH of chlorine bleaching was increased and its chloride concentration was controlled (18).

Alkyl chlorides are hydrolyzed slowly in water (19). The hydrolysis, that follows the S<sub>N</sub>2 mechanism, is not catalyzed by acid but is catalyzed by alkali. Under acidic conditions the uncatalyzed reaction is faster than the alkali-catalyzed hydrolysis. Therefore the preferred generation of oxygenated degradation products of HexA in D<sub>1</sub>- and D<sub>2</sub>-stages cannot be explained by possible hydrolysis of originally formed chlorinated degradation products. Thus it seems probable that hypochlorous acid actually does hydroxylate HexA and aromatic lignin in aqueous media.

The equilibrium between hypochlorous acid and chlorine is defined by Eq. 1. The magnitude of the equilibrium constant (K) is  $1 \times 10^{-3} \text{ M}^2$  in the temperature range of chlorine dioxide bleaching (60-90 °C) (15). The calculated molar ratio of hypochlorous acid and chlorine ( $[\text{HOCl}]/[\text{Cl}_2]$ ) varies from ~10 in D<sub>0</sub>-stage (filtrate pH 2.5, 0.05-0.1 M Cl) to ~10<sup>-3</sup> in D<sub>1</sub>- and D<sub>2</sub>-stages (filtrate pH 4.5, 0.02-0.05 M Cl).

$$(1) \quad K = [\text{HOCl}][\text{H}_3\text{O}^+][\text{Cl}^-]/[\text{Cl}_2]$$

With the assumption that hypochlorous acid hydroxylates, but does not chlorinate unsaturated structures, the relative rate of chlorination would be directly proportional to the the concentrations of hydronium and chloride ions (Eq. 2).

$$(2) \quad \text{Rate}_{\text{Cl}}/\text{Rate}_{\text{OH}} = [\text{H}_3\text{O}^+][\text{Cl}^-]/K$$

The experimental data on the chlorination and hydroxylation of HexA does not completely fit to this equation although it clearly shows the trend (17). One reason for the deviation could be chlorination *via* organic hypochlorites that are formed as equilibrium products of hydroxyl group carrying organic substances and hypochlorous acid. Actually it has been observed that the hypochlorites of phenols undergo a regiospecific *o*-chlorination, which refers to an entropy assisted intermolecular substitution reaction (20). Analogously, HexA could partly be chlorinated through a hypochlorite of the COOH group.

The oxidation (D-stage) products of HexA are all dicarboxylic acids (17). One of the carboxylic acid groups is formed through oxidation of the C-1 aldehyde that is liberated through hydrolysis of the already attacked HexA. The oxidation could be brought either by hypochlorous or chlorous acid (21). In the latter case, hypochlorous acid would be formed as a byproduct.

The third step in the oxidation of HexA includes a carbon-carbon chain cleavage between C-4 and C-5 or between C-5 and C-6 or electrophilic displacement at C-4. The cleavage reactions are analogous with the oxidation of aldehydes – both hypochlorous and chlorous acid are able to cleave the bonds.

### Competing oxidation of HexA and lignin

At a high pH (final pH 6.7) of an abnormal D-stage ~ 60 % of the active chlorine was rapidly consumed; 40 % in primary and secondary reaction of lignin with chlorine dioxide and 20 % in reactions of hypochlorous acid with lignin or HexA (12). Thus, at least in the beginning, lignin is oxidized more extensively than HexA. On the other hand, every attack of hypochlorous acid on HexA leads to its elimination. All further oxidations of the already liberated HexA residues could, in principle, be caused by chlorous acid. The average HexA content of hardwood kraft pulps is ~ 60 mmol/kg (2). If all of this HexA would consume an equimolar amount hypochlorous acid, its need as active chlorine would be ~ 4 kg/t. Another extreme possibility is that HexA consumes three equivalents of hypochlorous acid without participation of chlorous acid. In this case the consumption of HOCl would be ~ 13 kg/t, expressed as active chlorine. The observed consumption of active chlorine by HexA is somewhat higher (2).

We have found that in 'normal' chlorine dioxide bleaching of birch kraft pulps lignin and HexA are relatively removed at equal relative rates (17). The ratio of the rate constants could, however, depend on the bleachability of the pulp.

Ozone oxidizes HexA via two routes. One route involves a decarboxylation step while the other one is producing oxalic acid (17). Generally, the oxidation products of HexA by ozone are carboxylic acid, aldehydes and their derivatives. Ozone removes HexA and lignin at similar relative rates, probably because the reaction rates are limited by the diffusion rate of ozone into the cell wall.

### **Competing oxidation of dissolved and residual cell wall structures**

Because of its high oxidation power ozone prefers to react with dissolved unsaturated organic substances over the less accessible cell wall components. Thus, e.g. a hypothetical A/Z prebleaching step does not bleach hardwood kraft pulps because furancarboxylic acids, the major degradation products of HexA, react rapidly with ozone (17).

Chlorine dioxide is practically unreactive towards 2-furancarboxylic acid which, however, reacts rapidly with hypochlorous acid (13). In A/D-stage chlorine dioxide starts to react with lignin that is mainly present in the cell wall. The hypochlorous acid formed in situ reacts rapidly with the residual lignin or HexA. If the bleaching chemical is rapidly mixed with the pulp, the reaction of hypochlorous acid with 2-furancarboxylic acid does not take place (17). Overcharging of chlorine dioxide may eat the reactive sites of the cell wall to an extent that allows the competing reactions by the furancarboxylic acids to take place (13).

### **Observations on bleaching sequences**

Modern bleaching sequences should meet at least the following criteria: (1) the environmental impact should be low, (2) the bleaching costs should be low, (3) the bleaching line should operate smoothly, (4) the strength of the pulp should be high and (5) its brightness stability should be high. The discussion on the environmental impact is still quite often focused on organically bound chlorine although the dioxin concentrations of ECF bleaching effluents are immeasurable. The major factors affecting the formation of chlorinated organic compounds are the charge of chlorine dioxide, pH and chloride concentration. The bleaching costs can be minimized best by removing HexA from the pulp prior to bleaching with the actual bleaching chemicals. In ECF bleaching the hydrolytic step of removing HexA can be combined directly with a D-stage without losing little or no of the bleaching result. The A-stage can be favorably combined with ozone bleaching if an intermediate washing step is used. Without the A-stage ozone bleaching can easily form scalings of calcium oxalate. The strength of hardwood kraft pulps is quite difficult to destroy although long delays at high temperatures and low pH (< 3) may cause problems. High brightness stability can be obtained only when residual lignin and HexA contents are low.

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### **References**

1. J. Buchert, A. Teleman, V. Harjunpää, M. Tenkanen, L. Viikari and T. Vuorinen, 3rd European Workshop on Lignocellulosics and Pulp, Stockholm, 1994, 16-19.

2. T. Vuorinen, J. Buchert, A. Teleman, M. Tenkanen and P. Fagerström, International Pulp Bleaching Conference, Washington D.C., 1996, TAPPI Proceedings, 43-51.
3. R. Berry, In: C. W. Dence and D. W. Reeve (eds.), Pulp Bleaching – Principles and Practice, TAPPI, Atlanta, 1996, 801-820.
4. I. Forsskähl, In: P. Stenius (ed.), Forest Products Chemistry, Fapet, Helsinki, 2000, 279-332.
5. J. Li, O. Sevastyanova and G. Gellerstedt, J. Pulp Pap. Sci. 28 (2002) 262-266.
6. M. Halttunen, J. Vyörykkä, B. Hortling, T. Tamminen, D. Batchelder, A. Zimmermann and T. Vuorinen, Holzforschung 55(2001) 631–638.
7. M. Nuopponen, S. Willför, A.-S. Jääskeläinen, A. Sundberg and T. Vuorinen, Spectrochim. Acta, Part A 60 (2004) 2953–2961.
8. M. Nuopponen, S. Willför, A.-S. Jääskeläinen and T. Vuorinen, Spectrochim. Acta, Part A 60 (2004) 2963–2968.
9. A.-M. Saariaho, A.-S. Jääskeläinen, M. Nuopponen and T. Vuorinen, Appl. Spectrosc. 57 (2003) 58–66.
10. A.-M. Saariaho, D. S. Argyropoulos, A.-S. Jääskeläinen and T. Vuorinen, Vibr. Spectrosc. 37 (2005) 111–121.
11. A. Potthast, T. Rosenau, P. Kosma, A.-M. Saariaho and T. Vuorinen, Cellulose 12 (2005) 43–50.
12. S. Juutilainen, A. Vilpponen, O. Pikka, T. Vuorinen and K. Henricson, TAPPI Pulping Conference, Orlando, 1999, Vol. 2, 645-651.
13. K. Toikka, L. Pekkanen, A.-S. Jääskeläinen, T. Vuorinen, J. Vehmaa and O. Pikka, International Pulp Bleaching Conference, Stockholm, 2005, Poster presentations, 259–261.
14. Y. Ni, X. Shen and A. R. P. van Heiningen, J. Wood Chem. Technol. 14 (1994) 243-262.
15. R. E. Connick and Y.-T. Chia, The J. Am. Chem. Soc. 81 (1959) 1280-1284.
16. E. A. Voudrias and M. Reinhard, Environ. Sci. Technol. 22 (1988) 1049-1056.
17. T. Vuorinen, P. Fagerström, E. Räsänen, A. Vikkula, K. Henricson and A. Teleman, International Symposium on Wood and Pulping Chemistry, Montreal, 1997, Preprints, M4, 1-4.
18. R. G. Hise, Tappi J. 72 (1989):12, 121-126.
19. P. M. Jeffers, L. M. Ward, L. M. Woytowitch and N. L. Wolfe, Environ. Sci. Technol. 23 (1989) 965-969.
20. M. Anbar and D. Ginsburg, Chem. Rev. 54 (1954) 925-958.
21. E. Dalcanale and F. Montanari, J. Org. Chem. 51 (1986) 567-569.