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Abstract

The goal of this thesis was to determine the origin of the yield loss of kraft pulps in each bleaching stage in an Elemental Chlorine Free (ECF) bleaching sequence, including oxygen delignification (O), acid hydrolysis (A), chlorine dioxide bleaching (D), alkaline extraction with oxidative reinforcement (Ep) and peroxide bleaching (P). The literature review was elaborated on reactions of different pulps components, namely lignin, carbohydrates and hexenuronic acid (HexA), with bleaching chemicals, with emphasis on carbohydrates degradation. Effects of bleaching conditions on pulp yield loss were also considered.

Laboratory bleaching experiments (O-D₀+Ep-D₁-P) of softwood kraft pulps (85% pine, 15% spruce) provided by a Finnish pulp mill were done at the conditions similar to those used at the supplying mill. For each stage, pre- and post-bleached pulps were analysed for HexA content, viscosity and kappa number. Bleaching effluents were analysed for Total Organic Carbon (TOC) and lignin contents. Yield losses during bleaching were 2.4, 2.8, 0.6 and 0.5% for O-, D₀+Ep-, D₁- and P-stages, respectively. Combined yield losses of lignin and HexA were translated into kappa number reduction, which was close to the change in measured kappa numbers. Significant carbohydrate degradation was observed in Ep- and P-stages due to the wash-away of Mg²⁺ ions.

Keywords**Kraft pulp, yield loss, bleaching, lignin, hexenuronic acid, carbohydrate**

FOREWORD

This Master's thesis has been carried out from 01.05.2013 – 31.10.2013 under Professor Tapani Vuorinen's supervision as a part of MIB project in the Wood Chemistry research group at the Department of Forest Products technology, School of Chemical Technology, Aalto University.

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Le Huy Quang

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1. TOC of bleaching effluents
2. Lignin content and lignin contributions to TOC of bleaching effluents
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1 INTRODUCTION

Nowadays, Elemental Chlorine Free, i.e. ECF, bleaching is the dominant sequence to bleach and brighten kraft pulps, where chlorine dioxide substitutes elemental chlorine to be the work horse of the sequence (Suess et al. 1998). Unlike what was done previously, kraft cook is now stopped earlier, at higher kappa number, followed by an oxygen delignification (O) stage which is more selective towards lignin removal (Sixta et al. 2006). Oxygen delignified pulp can also be subjected to a mild acid hydrolysis (A) treatment (recommended for hardwood pulp) for selective removal of hexenuronic acid (HexA) and washing out of transition metal ions (Vuorinen et al. 1999). Then comes the chlorine dioxide (D) stages, separated by alkaline extraction (E) stages, e.g. in a typical sequence as DEDED, where residual lignin structures are oxidized and solubilized. Recently, alkaline extraction stages are oxidatively reinforced with oxygen and hydrogen peroxide for better extraction and brightening performance while limiting brightness reversion effects. It was also confirmed that replacement of the final E stage by a hydrogen peroxide (P) stage is beneficial for the pulp's brightness and the reduction of chlorine dioxide charge (Sixta et al. 2006 and Suess et al. 2010).

The ultimate purpose of pulp bleaching is to selectively degrade and dissolve residual lignin structures, which cannot be effectively removed by kraft cooking without significantly affecting pulp's properties, yielding brightened pulp containing trace amount of chromophoric structures suitable for subsequent processes (such as paper-making or dissolving pulps refining). The cost of bleaching is an important factor in evaluation of chemical pulp production; it is comprised of not only the costs of bleaching chemicals utilized but also the pulp yield loss (Suess et al. 1998). During bleaching, yield loss is ideally expected to originate from the removal of only lignin. However, due to the complex nature of the fiber structures and low selectivity of bleaching chemicals, carbohydrates are also attacked during the process, leading to the unnecessary yield loss, which should be avoided. Therefore, in order to maximize

the profitability of a bleaching plant, the origin of pulp yield loss, i.e. reactions of main pulp's components (such as lignin, carbohydrates and HexA) with bleaching chemicals during each bleaching stages and its correlation with process parameters during each stage in a bleaching sequence must be carefully studied. That is the objective of this thesis.

Despite being an important issue, "pulp yield loss in bleaching" has not been receiving much attention, proven by the lack of literature on the topic. Conventionally pulp yield loss is determined by gravimetric methods, which is unreliable, even in laboratory scale, due to the small yield loss in bleaching (typically less than 1 - 2% for each stage), and impossible to perform in larger scale (Rööst et al. 2001). Earlier, Suess et al. (1998) correlated the chemical oxygen demand (COD) of bleaching effluent with pulp yield loss. However, the oxidative performance of bleaching chemical is not fully under control, i.e. dissolved materials in effluents can be oxidized to different extent, making the generalization of COD – yield hard to accomplished. A better tool, total organic carbon (TOC), can be used with higher reliability to COD, as TOC is directly related to the amount of dissolved organic material (i.e. lignin, carbohydrates) in the effluents, regardless of their oxidation stage (Rööst et al. 2001). In this thesis work, estimation of pulp yield loss was performed by TOC determination, supported by dissolved lignin quantification (by UV photospectrometry) and pulp's HexA content quantification.

The literature study on origin of pulp yield loss in chemical pulp bleaching, together with experimental data, can be implied to an existing pulping simulation program.

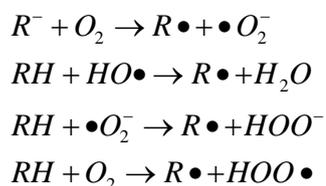
PART 1

LITERATURE REVIEW

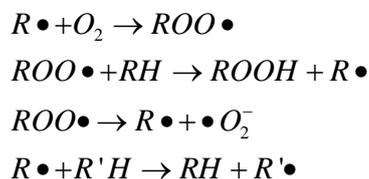
2.1 Reactions of pulp components in oxygen delignification

Reactions of lignin

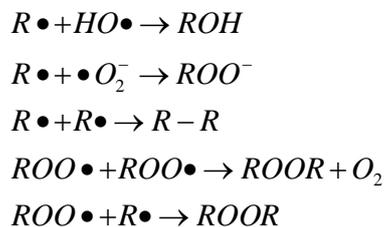
Residual lignin is oxidized by oxygen and reacts with a wide range of intermediate radicals formed in the oxygen-alkaline system (such as hydroxyl radicals, superoxide anion radicals) via a chained-process called autoxidation, comprising of three stages: initiation, propagation and termination which is shown below in equations 1, 2 and 3 (Gierer 1985, Gratzl 1992 and Sixta et al. 2006).



Equation 1. Initiation (adapted from Sixta et al. 2006).



Equation 2. Propagation (adapted from Sixta et al. 2006).



Equation 3. Termination - Recombination (adapted from Sixta et al. 2006).

Where: R is the activated lignin substrate, particularly phenolate structures.

Oxygen delignification proceeds with different pathways, falling into four main categories, proposed by Kuitunen et al. (2011), in which the two first set of reactions contribute the most to lignin fragmentation during the process:

- Reactions involving phenolates and phenoxy radicals (phenolic structures)
- Reactions involving aliphatic side-chains (phenolic and non-phenolic structures)
- Reactions involving chromophoric structures
- Degradation of aliphatic organic compounds

Lignin oxidation in oxygen-alkali environment starts with ionization of phenolic lignin structures into phenolate ions, followed by the attack of oxygen, forming phenoxy radical and superoxide radical, non-phenolic lignin can also be converted to phenoxy radical but with much slower rate (Gratzl 1990 and Sixta et al. 2006). According to Gratzl (1990), lignin depolymerization then proceeds via different routes which are shown in Figure 2, leading to the formation of different degradation products: *para*-quinone (route a), *ortho*-quinone (route b), muconic acid (route c, main pathway) or products from side chain cleavage (route d).

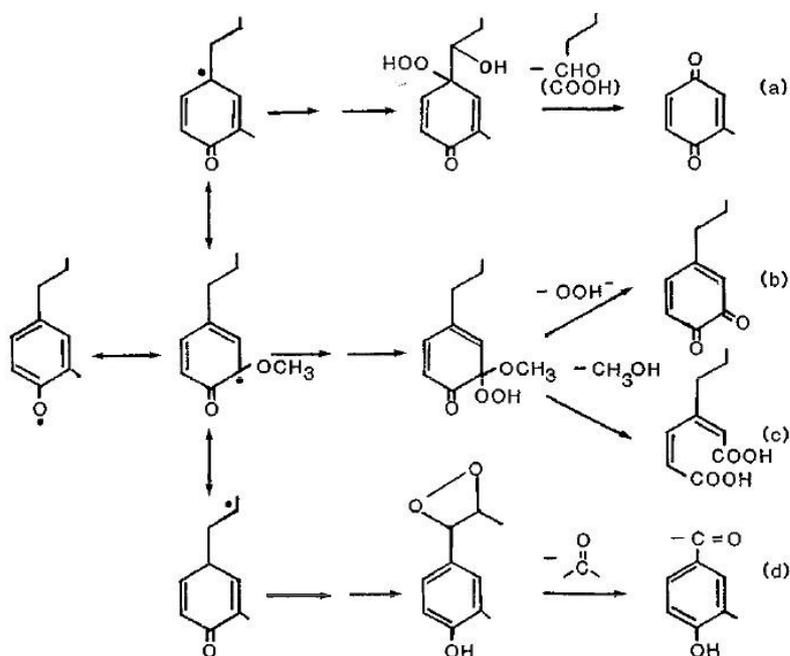


Figure 2. Oxidation of lignin structure (adapted from Gratzl 1990).

Reactions of carbohydrates

The most reactive structures in pulp's carbohydrates are reducing end-groups, which are prone to peeling reactions, contributing to carbohydrates depolymerization and pulp yield loss (Gratzl 1990 and Sixta et al. 2006). Under oxygen-alkali environment, classical alkaline peeling, to which the pulp is subjected during pulping, leading to the formation of isosaccharinic and lactic acids, is depressed, and carbohydrates are instead end-wise degraded into 3,4-dihydroxybutyric acid, glycolic acid, 3-deoxy-pentonic acid, formic acid and glyceric acid (Malinen 1975, Theander 1975). Malinen et al. (1973) found that, for hydrocellulose, stabilization of reducing end-groups by formation of aldonic acid groups is low, as a consequence, peeling results in a loss of 10 – 50 sugar units depending on reaction conditions. Peeling reactions are shown in Figure 3, and they are applicable not only to cellulose but to pulp's hemicelluloses such as xylan and glucomannan. Nevertheless, stabilized end-groups can be degraded at elevated temperature and subsequently subjected to peeling (Sixta et al. 2006).

R = Polysaccharide chain

R₁ = -H for xylan

- 23 Xylose end-group
- 25 Xylulose end-group
- 26 4-Deoxy-2,3-pentodiulose
- 27 Xyloisosaccharinic acid
- 28 2-Deoxy-glyceric acid
- 29 Glycolic acid
- 30 Dihydroxyacetone and glycolaldehyd
- 31 Methyl glyoxyl
- 32 Lactic acid
- 33 Glycolic acid
- 34 Formic acid
- 35 Glyceric acid

R₁ = -CH₂OH for cellulose / glucomannan

- 23 Glucose end-group
- 24 Mannose end-group
- 25 Fructose end-group
- 26 4-Deoxy-D-glycero-2,3-hexodiulose
- 27 Isosaccharinic acid
- 28 3,4-Dihydroxybutyric acid
- 29 Glycolic acid
- 30 Dihydroxyacetone and glyceraldehyd
- 31 Methyl glyoxyl
- 32 Lactic acid
- 33 Glycolic acid
- 34 Formic acid
- 35 Glyceric acid

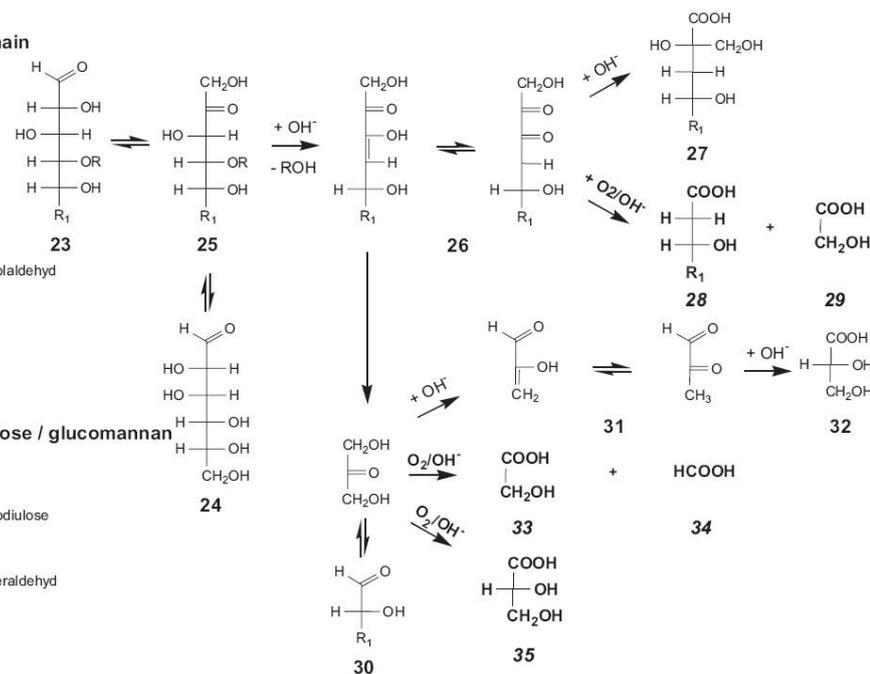


Figure 3. Polysaccharides peeling during alkaline and oxidative alkaline conditions (adapted from Sixta et al. 2006, redrawn from Malinen 1975).

Similar to carbohydrate degradation in pulping, besides end-wise degradation, polysaccharides are also subjected to random cleavage in the oxidative alkali environment. Theander (1981), Gratzl (1990) and Gierer (1997) proposed the mechanism for random cleavage of polysaccharides in oxygen/alkali conditions (illustrated in Figure 4) as following: the process starts with an oxidation of alcohol groups at C2 or C3, which can only be realized by hydroxyl radical ($\bullet\text{OH}$) with its high oxidation potential. It is followed by oxygenation of the resultant carbon-centered radical and elimination of superoxide anion radical, forming a ketone at the corresponding carbon (structure 2 and 3, Figure 4), which allows the subsequent cleavage of glycosidic bond by β -elimination, thus decreasing the polysaccharide's degree of polymerization (DP). Cleaved cellulose chain then undergoes benzilic acid rearrangement (B.A.R) to a carboxy-furanoside structure (structure 5 in Figure 4).

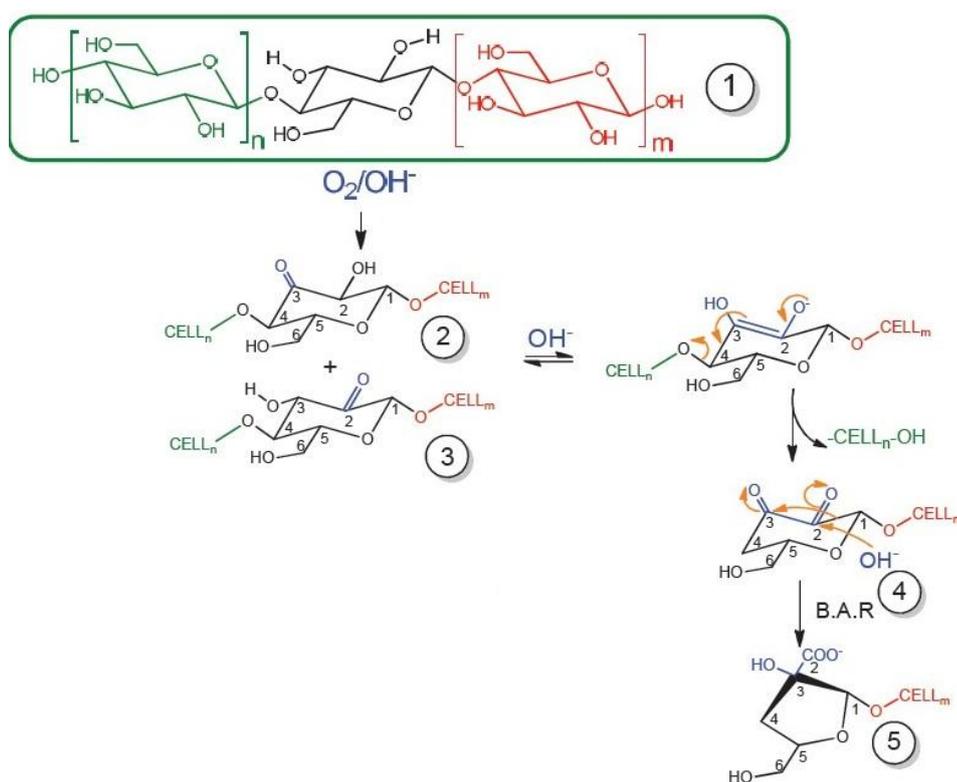


Figure 4. Mechanism for oxidative cleavage of cellulose (structure 1) initiated by hydroxyl radicals (adapted from Theander 1981).

2.2 Pulp yield loss during oxygen delignification

Effect of temperature

Oxygen delignification of kraft pulp requires a temperature above 80°C for a reasonable rate of reaction, and a low temperature during the initial phase of about 5 – 10 minutes is beneficial for the selectivity, *i.e.* less carbohydrate degradation (Sixta et al. 2006). As polysaccharide chain scission's activation energy is slightly higher than those of lignin degradation reactions, increasing the temperature would be detrimental to the carbohydrate yield (Olm 1979 and Iribarne et al. 1997). Furthermore, high temperature (*e.g.* well above 110°C) would induce the homolytic decomposition of peroxide, forming hydroxyl radicals, an extremely reactive species with poor selectivity (Sixta et al. 2006). Therefore, a temperature of 120°C would be the practical upper limit for oxygen delignification without sacrifice of the pulp quality (Kleppe 1972).

Effect of alkali charge

Ionization of lignin's phenol to phenolate is a prerequisite in lignin degradation, therefore starting pH of oxygen delignification must be higher than lignin's pK_a value, about 10.5 – 11 (Chang et al. 1973). A drop of pH below that level would negatively impact the lignin extraction due to lignin precipitation while too high alkali charge would accelerate cellulose chain scission, thus lower the selectivity and pulp yield (Sixta et al. 2006 and Suess et al. 2010).

Effect of consistency and oxygen charge – oxygen pressure

Mass transfer of oxygen is the limiting factor in the system. Higher consistency means less diffusion distance and higher alkali concentration (at a given alkali charge), resulting in an increased delignification rate (Elton et al 1980). Oxygen charge should not be either too low (insufficient oxidation) or too high (formation of big gas bubbles and channeling), higher oxygen pressure leads to better oxygen mass

transfer from the gas phase to liquid phase (reaction medium) and then solid phase, *i.e.* the fiber wall (Sixta et al. 2006 and Suess et al. 2010).

Effect of transition metal ions

The selectivity of oxygen delignification is impaired by the presence of transition metal ions such as copper, manganese, iron and cobalt. Those transition metals catalyze the homolytic decomposition of the peroxides formed during oxygen delignification (*e.g.* Fenton reaction), giving rise to the highly reactive hydroxyl radicals, as shown in Figure 5, thus promoting cellulose degradation (Manouchehri et al. 1973). Addition of a small amount of magnesium (*ca.* 2 – 3 kg/ton pulp) was found to give protective effect on the carbohydrates during oxygen delignification, which was explained by Reitberger et al. (2001) as following:

- The co-precipitation of transition metal ions with magnesium hydroxide/carbonate stabilize the peroxides against catalytic decomposition leading to the presence of hydroxyl radicals
- The formation of Mg-cellulose complexes, shielding the cellulose against hydroxyl radicals' attack

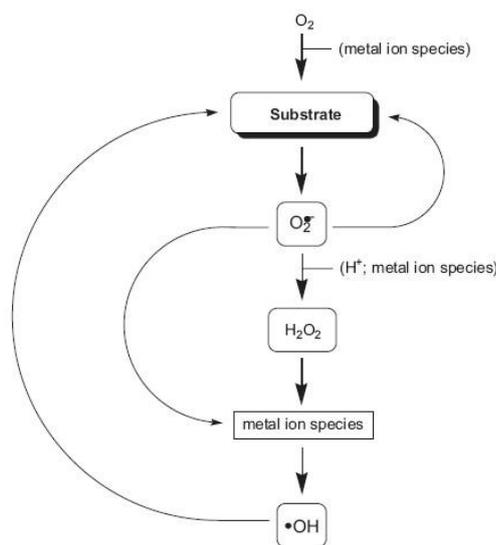


Figure 5. Catalysis by transition metal ions in the oxygen reduction (Adapted from Sixta et al. 2006, which is redrawn from Reitberger et al. 2001).

3 HOT ACID HYDROLYSIS (A-STAGE)

3.1 Reactions of pulp components during hot acid hydrolysis

Reactions of carbohydrates

During kraft pulping, a major part of the 4-O-methylglucuronic acid groups in native xylan (especially in hardwood) undergoes methanol elimination, forming 4-deoxy-4-hexenuronic acid groups (Figure 6), which are hereafter shortly called HexA (Teleman et al 1995). HexA was found to be stable in oxidative alkaline environment but, due to their unsaturated nature, prone to attack by electrophiles such as chlorine dioxide, ozone, peracids, chlorine, leading to loss of bleaching chemicals (Buchert et al. 1995, Vuorinen et al. 1999, van Heiningen et al. 2008 and Andrew 2009). Vuorinen et al. found that a mild acid hydrolysis at elevated temperature is an effective way to remove HexA in pulp by degradation into soluble products such as formic acid, 2-furancarboxylic acid and 5-formyl-2-furancarboxylic acid (Figure 6). Later on, Andrew et al. (2009) confirmed that 95% of HexA from eucalyptus pulp can be removed under treatment at pH 3.5, temperature 110°C for 120 minutes.

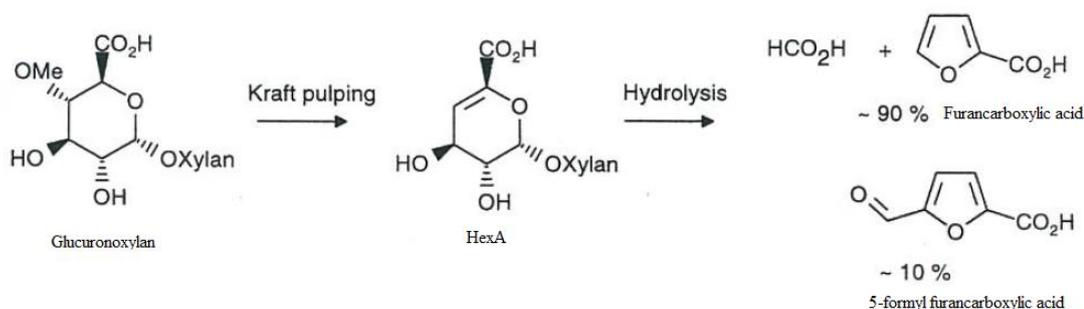


Figure 6. Formation of HexA and its conversion into furanic carboxylic acid during hot acid hydrolysis (Adapted from Vuorinen et al. 1999).

Glucose and xylose contents in pulp was found to be resistant to acid hydrolysis, but pulp viscosity significantly dropped (due to glycosidic bond cleavage in acidic

conditions), especially at higher temperature and elongated hydrolysis time, as an example, treatment at 125°C for 3 hours decreases pulp viscosity to one-fourth of that of oxygen delignified pulp (Andrew et al. 2009).

Reactions of lignin

Andrew et al. (2009) found that mild hot acid hydrolysis helped to reduce the lignin content in pulp down to about 1.0 – 1.2% on pulp (from about 1.7 % on oxygen delignified pulp), and a further increase in temperature and reaction time did not reduce the lignin content further. This experimental observation is explained by the cleavage of lignin's internal ether linkages and, more important, the linkages between residual lignin and carbohydrates in lignin-carbohydrate complexes (LCC), including ester bonds, benzyl ether bonds and phenyl glycosidic linkages, leading to a small soluble lignin fraction (Hosoya et al. 1993 and Ikeda et al. 1997).

Removal of metal ions

Transition metal ions, especially manganese (II), are effectively removed during a hot acid treatment similar to a chelation stage with EDTA and DTPA, and much better than in a normal acid washing step (Vuorinen et al. 1999). Vuorinen et al. also pointed out one slight drawback of the hot acid hydrolysis: a substantial amount of magnesium (added during oxygen delignification), which determine the success of subsequent peroxide bleaching stage, is removed in this step.

3.2 Pulp yield loss during hot acid hydrolysis

Besides pH (2.5 – 3.5), temperature and treatment time are the two most important parameters in the hot acid treatment. Suess (2010) and Clavijo et al. (2012) gave clear insight about the effects of these two parameters on yield loss: Increasing temperature up to 120°C leads to HexA removal with faster rate and to a greater extent, beyond

that level, HexA removal is almost the same but pulp degradation is much greater. Prolonged exposure to acidic conditions has similar effect on pulp quality. The initial rapid decrease of kappa number (representing HexA and partly lignin removal) slows down after about 120 minutes, beyond that, the amount of dissolved organic compound, measured by COD, increase rapidly, implying carbohydrates' degradation. Andrew et al. (2009) suggested a compromise for HexA removal and pulp yield preservation for hot acid hydrolysis of eucalyptus pulp with the conditions: pH 3.5, temperature 95°C and treatment time 180 minutes.

4 CHLORINE DIOXIDE BLEACHING (D-STAGE)

The pressure of elimination the use of chlorine in bleaching has shifted chlorine dioxide (ClO_2) from an additive to the chlorine bleaching stage (C-stage) to the work horse of Elemental Chlorine Free (ECF) bleaching, the most popular bleaching sequence nowadays (Sixta et al. 2006 and Suess et al. 2010). Unlike the oxygen/alkali in oxygen delignification, chlorine dioxide is a selective bleaching chemical, *i.e.* mainly targets at lignin, leaving the polyoses almost intact, even at elevated temperature such as 70 – 90°C (Lachenal et al. 2000), which make ClO_2 even better than chlorine, which functions well only at low temperature (Suess et al. 2010).

During D-stage, chlorine dioxide undergoes different conversions, leading to all the possible oxidation states of chlorine (Kolar et al. 1996). The reaction scheme of chlorine dioxide is shown in Figure 7. Chlorine dioxide is converted to chlorite ion (ClO_2^-) in the initial bleaching by hydrogen abstraction from a phenol group (pathway 1), chlorine dioxide can react to form hypochlorous acid, HOCl (pathway 2), which is in equilibrium with chlorine (pathway 3). HOCl and Cl_2 react with lignin yielding chlorinated organic compounds and chlorate ions, ClO_3^- (pathway 4 to 8). Chlorine dioxide can be regenerated by the reactions in pathway 9 and 10. The formation of

Cl_2O_2 , which subsequently reacts very fast with ClO_2^- , from HClO_2 and HOCl was not included in the scheme proposed by Kolar et al. (1996).

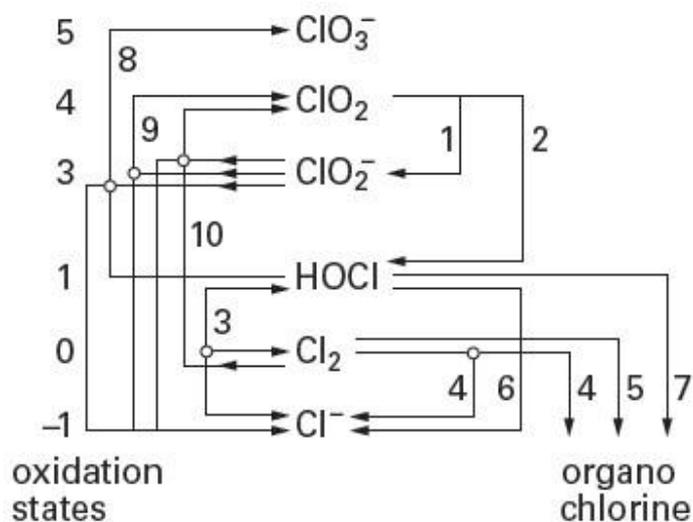


Figure 7. Reactions of chlorine dioxide during D-stage, the intersection points (\circ) indicate equilibrium between both compounds (Adapted from Kolar et al. 1996).

4.1 Reactions of pulp components in chlorine dioxide bleaching

Reactions of lignin

Initial steps of delignification with ClO_2 are shown in Figure 8. Unlike oxygen delignification, both phenolic and non-phenolic lignin structures are attacked by ClO_2 , yielding activated radicals which are subsequently subjected to degradation.

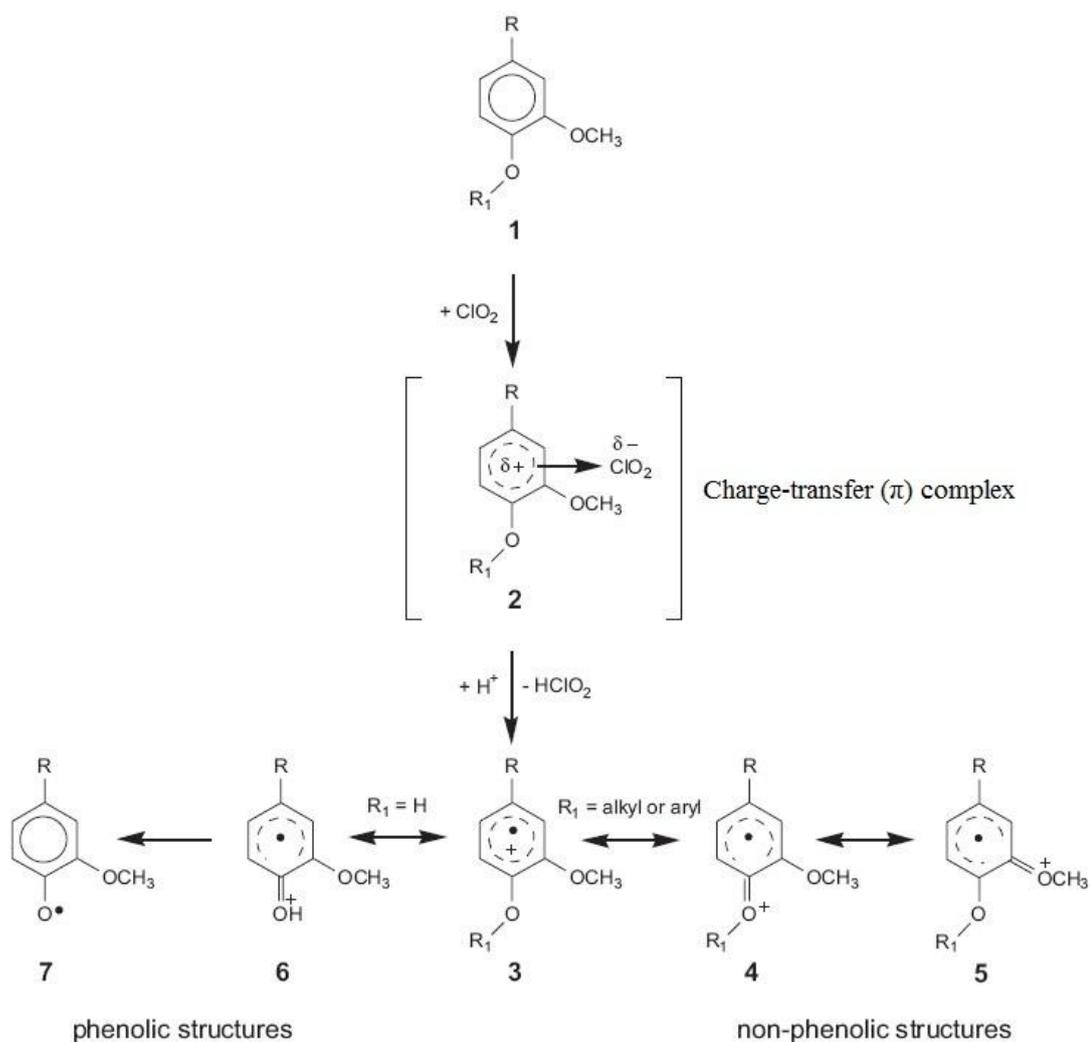


Figure 8. Initiation of chlorine dioxide bleaching (Adapted from Brage et al. 1991).

Brage et al. studied the continuation of the initial steps with creosol (representing the phenolic structures of residual lignin) and creosol methyl ether (the non-phenolic ones) as model compounds. The reaction mechanisms are given in Figures 9 and 10. The introduction of hydrophilic groups such as phenolic groups or carboxylic acid in muconic acid-like structures makes the residual lignin prone to solubilization in the subsequent alkaline extraction stage (Berry 1996).

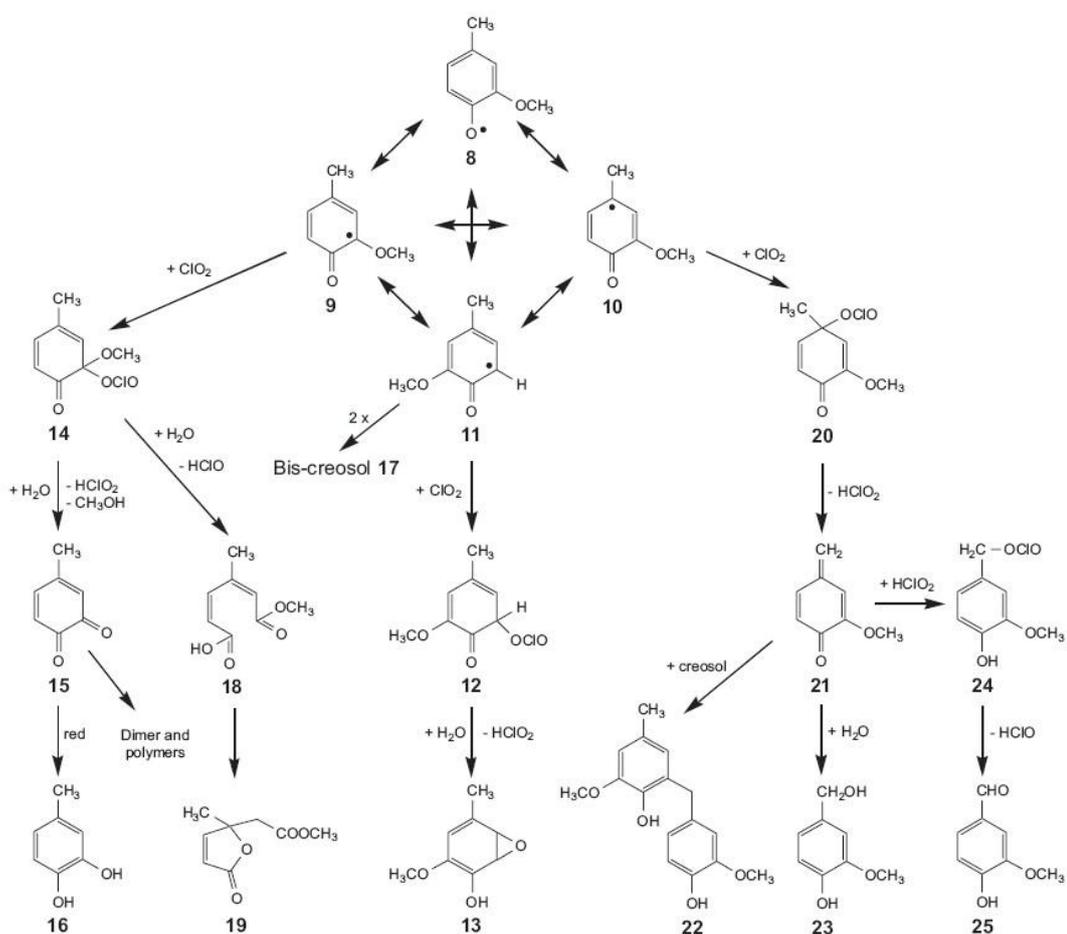


Figure 9. Reaction of phenolic lignin structure in D-stage (adapted from Brage et al. 1991).

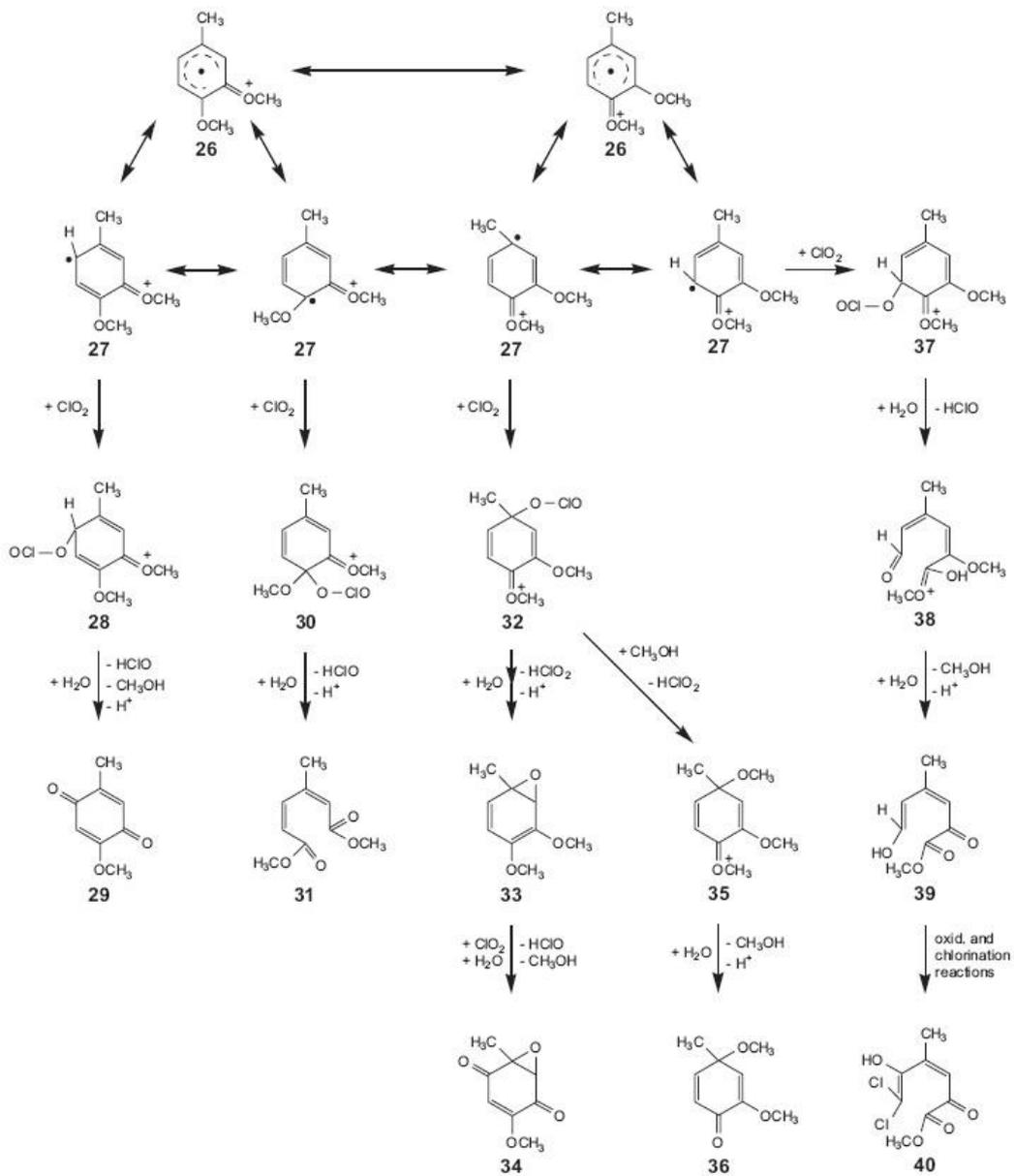


Figure 10. Reaction of non-phenolic lignin structure in D-stage (adapted from Brage et al. 1991).

Reactions of hexenuronic acid groups

Unsaturated structure of HexA is prone to attack by different active chlorine species such as Cl_2 , HOCl , and HClO_2 (ClO_2 does not react with HexA), forming dissolved halogenated compounds (AOX) which is removed by subsequent extraction (Juutilainen et al. 1999 and Costa et al. 2007). The main chlorinated products from HexA in this stage are tetraric acid, pentaric acid, 2-chloro-2-deoxypentaric acid and 3-deoxy-3,3-dichloro-2-oxohexaric acid (Tarvo et al. 2010).

Reactions of carbohydrates

As mentioned earlier, carbohydrates are not likely to be attacked by the selective bleaching chemical ClO_2 . However, under the acidic conditions during ClO_2 stage, especially D_0 , carbohydrates are subjected to glycosidic bond hydrolysis (Sjöström 1993), thus resulting in yield loss and reduction of intrinsic viscosity.

Chlorous acid (HClO_2), an active chlorine species evolved during ClO_2 bleaching, was found to be able to oxidize aldehyde structures (equation 4), including that of glucose, at slow rate, ca. $3 \times 10^{-3} \text{ M}^{-1}\text{s}^{-1}$ (Lehtimaa et al. 2010). Under the same mechanism, cellulose with reducing end-groups can be oxidized, at much lower rate than that of glucose, thus becoming more hydrophilic.



Reactions of residual extractives

Chlorine dioxide readily reacts with unsaturated sterols and fatty acids yielding unsaturated unchlorinated product (Jansson et al. 1995 and Freie et al. 2003). However, the amount of extractives in pulp after cooking is small and insignificantly contributes to the yield loss, so it can be omitted.

4.2 Pulp yield loss during chlorine dioxide bleaching

Normally, the yield loss in D-stages is small as only thoroughly oxidized lignin is readily water-soluble at acidic pH, partly oxidized lignin with higher molecular weight becomes soluble only at high pH and higher temperature than the one used in D-stages, requiring a subsequent extraction stage (E-stage) for effective delignification (Suess et al. 2010). Therefore, in practice, the yield losses of chlorine dioxide stage and the following extraction stage are combined. Though most of the yield loss occurs during the latter stage, the performance of lignin oxidation during chlorine dioxide bleaching is decisive for extraction performance.

pH is an important factor in bleaching with ClO_2 . A too high pH (> 5) gives rise to the useless chlorate ion which would be wasted (Rapson 1963). At the end of the first ClO_2 stage (D_0), pH must be as low as 2.5 – 3.5 (Suess et al. 2010) to ensure effective removal of residual lignin and HexA. Therefore, H_2SO_4 is added in the first chlorine dioxide bleaching to ensure low end pH; for the later D-stages (D_1 and D_2), acidic environment caused by ClO_2 is already enough. Elevated temperature (over 70°C) is favorable for fast ClO_2 consumption and effective removal of residual lignin structures.

5 ALKALINE EXTRACTION (E-STAGE)

As mentioned in the yield of chlorine dioxide bleaching section, the acidic conditions during D-stages is unsuitable for solubilization of partly oxidized lignin. Therefore, a subsequent alkaline stage is needed to facilitate the dissociation of acidic and phenolic groups in oxidized lignin, thus increasing its hydrophobicity and finally be solubilized and extracted (Dence et al. 1996). Furthermore, alkaline treatment swells the pulp, thus improving accessibility to the oxidized and degraded cell wall components (Sixta et al. 2006). Nowadays, the alkaline extraction stages are often

reinforced with oxidative chemicals, oxygen or/and hydrogen peroxide in order to improve the kappa number reduction, brightness and brightness stability (Suess et al. 2010).

In this thesis, the extraction stage after D₀ bleaching is reinforced with hydrogen peroxide addition, so the E_p stage is mainly discussed in this section. In such alkaline condition of an extraction stage (pH >12), hydrogen peroxide exists in the solution as hydroperoxy anion ($\text{H}_2\text{O}_2 + \text{OH}^- \leftrightarrow \text{HOO}^- + \text{H}_2\text{O}$). At elevated temperature, with the presence of trace of transition metal ions, homolytic cleavage occurs yielding the reactive hydroxyl radicals.

5.1 Reactions of pulp components in alkaline extraction reinforced with H₂O₂

Reactions of lignin and chromophoric structures

Most of the lignin coming from the previous D-stage (structure shown in Figures 9 and 10) dissolves very fast by dissociation into sodium salt of carboxylic acid ($\text{RCOO}^- \text{Na}^+$) or phenolic group ($\text{RO}^- \text{Na}^+$), facilitated by the high pH of the stage; less oxidized and higher molecular weight lignin dissolve more slowly in a leaching reaction (Berry 1996). Besides, muconic acid esters (structure 18 and 31 in Figures 9 and 10) are hydrolyzed by OH^- , forming the more soluble sodium salt of muconic acid (Kuitunen et al. 2011).

Hydroperoxy anion is a strong nucleophile which attacks quinoid structures (chromophores), which are formed during chlorine dioxide bleaching (structure 15, 21, 29, 34) leading to soluble degradation products, and eliminate lignin side-chain enone structures (Gierer et al. 1975 and Gierer 1982). The reaction mechanisms are illustrated in Figure 12, section 5.1.

Reactions of carbohydrates

In alkali media, polysaccharides are subjected to peeling and random chain scission with the mechanisms similar to those happening in other alkali-based process in pulping and bleaching, but, in a lesser extent due to the substantially lower alkali charge and lower temperature in comparison to kraft cook and oxygen delignification (Sixta et al. 2006). The more important polyoses degradation is caused by the extremely reactive hydroxyl radical ($\bullet\text{OH}$) generated from homolytic cleavage of H_2O_2 (Basta et al. 1992).

Reaction of halogenated compounds

Chlorinated aliphatic compounds generated during the preceding D-stage are subjected to nucleophile substitution of Cl^- by OH^- , which helps reduce the residual halogenated compounds content in bleached pulp (Suess et al. 2000 and Suess et al. 2010).

5.2 Pulp yield loss during alkaline extraction

The oxidized pulp components are subjected to solubilization in alkaline medium, making E_p -stage the stage where the most pulp yield loss occurs during the whole bleaching sequence. Temperature, alkali charge, hydrogen peroxide charge and also transition metal ions have great impacts on the yield.

Effect of transition metal ions

The effect of transition metal ions is similar to that in oxygen delignification: decomposition of H_2O_2 to the harmful hydroxyl radicals which degrade cellulose.

Effect of alkali charge

Too high alkali charge would trigger carbohydrate degradation while too low would reduce the extraction performance. An alkali charge of 15 – 17.5 kg NaOH/ton of bone dry pulp give the best performance for softwood pulp (Suess et al. 2000). No visible positive effect is achieved with higher alkali input. The demand is lower for hardwood pulp (Suess et al. 2010).

Effect of temperature

Due to the lability of H_2O_2 , E_p stage is sensitive to temperature, which is illustrated in Figure 11. Extraction is practically performed at 70-80°C; higher temperature does not add visible positive result in lignin and chromophore removal but significantly degrade the pulp quality, yielding more carbohydrate loss (Basta et al 1992)

Effect of H_2O_2 addition

The addition of peroxide and temperature are closely connected. The number of lignin's sites potentially reacting with H_2O_2 is limited, therefore, at lower temperature, a large amount of peroxide is not readily consumes. Therefore, increasing peroxide charge is accompanied by a raise of temperature, also leading to the threat of carbohydrate degradation (Suess et al. 2000). The effect of hydrogen peroxide charge is shown in Figure 11. Suess et al. (2006) proposed that, an addition of 0.25% hydrogen peroxide, at about 70°C is enough for a good delignification, high brightness pulp and low cellulose degradation.

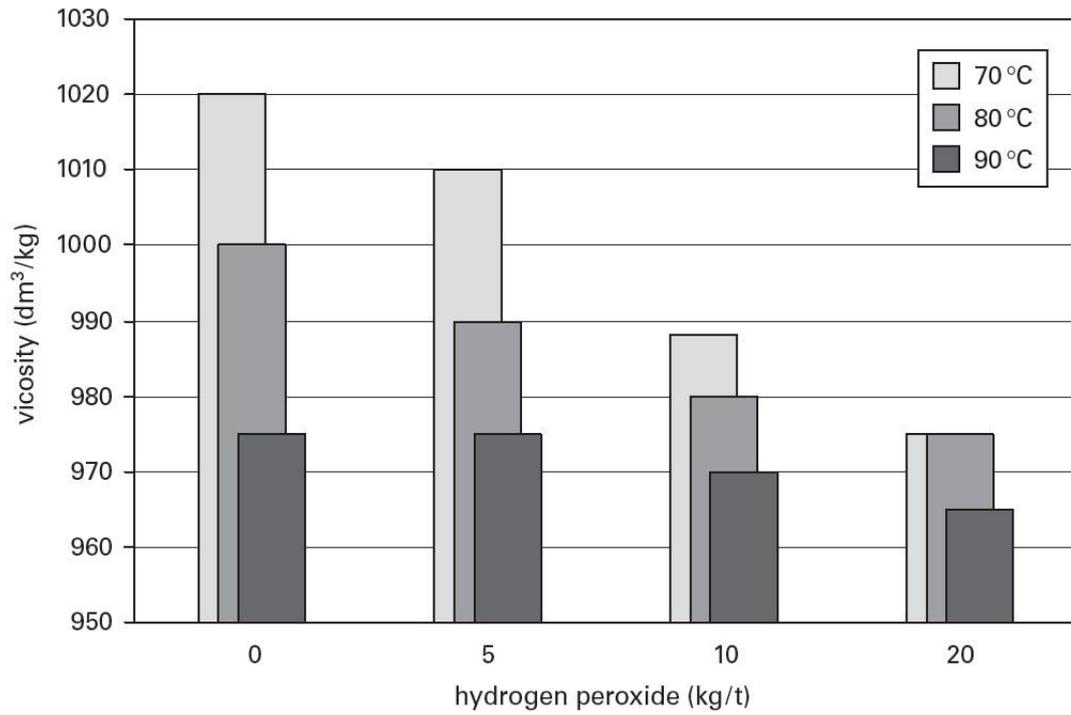


Figure 11. Effect of H₂O₂ addition and temperature in E_p stage (Adapted from Basta et al. 1992).

6 HYDROGEN PEROXIDE BLEACHING (P-STAGE)

Hydrogen peroxide is employed as the final brightening stage in ECF bleaching, substituting the traditional D₂ stage in the effort of reducing the use of chlorinated compound in bleaching. The chemistry of this stage is very similar to that of the alkaline extraction, which was discussed previously.

Residual lignin's enone structures in the side chain and residual chromophoric quinonoid structures are attacked by the hydroperoxy anions generated from the dissociation of hydrogen peroxide in alkali media (Gierer et al. 1975 and Gierer 1982). Reaction mechanisms are shown in Figure 12. Degradation of cellulose due to alkaline peeling occurs in a lesser extent but degradation due to oxidative cleavage by •OH is larger, because of higher H₂O₂ charge. Magnesium sulfate can be added to suppress the formation of hydroxyl radical, thus protecting the carbohydrates, with the mechanism similar to that in oxygen delignification (Suess et al. 2000).

In P-stage, temperature is usually slightly higher than in alkaline extraction reinforced with H₂O₂ in order to facilitate the consumption of H₂O₂, but, again, not too high to avoid the risk of increase the carbohydrate yield loss.

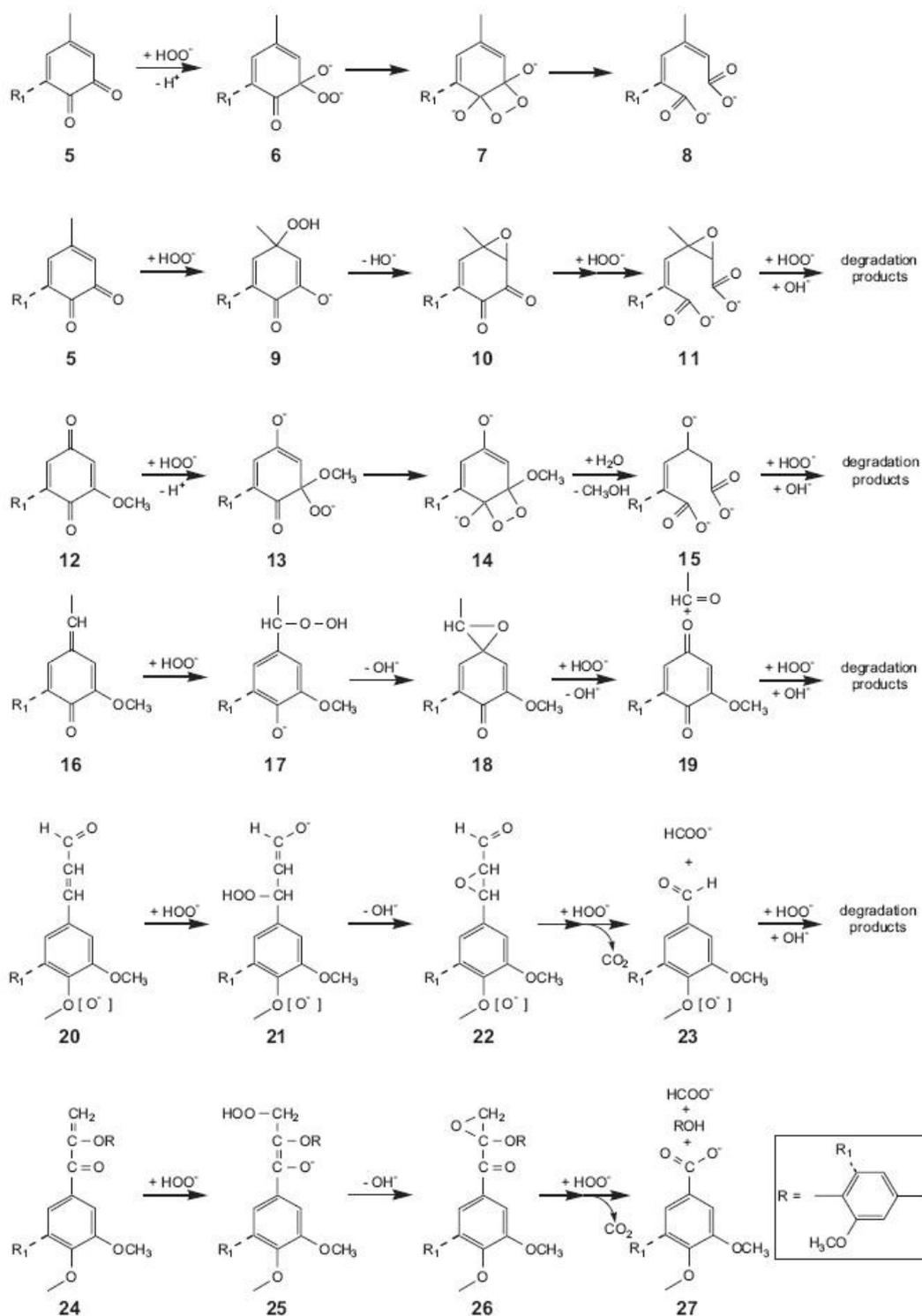


Figure 12. Reaction of lignin and chromophores with hydroperoxide anions (Adapted from Gierer et al. 1975 and Gierer 1982).

PART 2

EXPERIMENTAL STUDY

7 MATERIALS, METHODS AND CALCULATIONS

7.1 Pulp supply and bleaching sequence

The pulps used in the bleaching experiments were supplied by a Finnish softwood kraft pulp mill (shortly called mill A hereafter), they were produced from 85% pine and 15% spruce wood chips. Bleaching was performed in the same sequence and conditions as those of mill A: O-D₀-E_p-D₁-P. Pulps were taken from different points in the fiber-line including post-kraft cook, post-oxygen delignification, post-alkaline extraction, and post-D₁ pulps.

Pulps were delivered in an intensively washed state. Each of the pulps was subjected to the next bleaching stage in the sequence mentioned above. D₀ and E_p stages were combined, *i.e.* post-oxygen delignification was first subjected to D₀ bleaching, and then E_p bleaching; effluents from those two stages were combined.

Oxygen delignification (O-stage)

Oxygen delignification experiments were done in two-liter bombs heated in an air bath. About 100 bone-dry (b.d.) grams of post-kraft cook pulp (from mill A) was equally divided into three bombs, with chemical charge (on pulp basis) of 1.8% NaOH and 0.2% MgSO₄, oxygen pressure was 6 bar. Oxygen delignification was performed at 90°C at 10% consistency for 90 minutes, mixing was done automatically by rotation of bombs in the air bath.

After the reaction, the pulp and effluent were collected. The pulp was washed thoroughly with deionized water until the filtrate was clear, then centrifuged and stored for further analysis. The experiment was repeated three times.

First chlorine dioxide bleaching stage (D₀-stage)

D₀ bleaching was done in PE plastic bag heated in a water bath. About 50 b.d. g of post-oxygen delignification pulp (from mill A) was bleached with chemical charge (on pulp basis) of 3% active chlorine (from ClO₂) and 0.36% H₂SO₄. D₀-stage was performed at 55°C at 10% consistency for 15 minutes, mixing was done manually every 5 minutes. After the reaction, the pulp and effluent were collected. The pulp was washed with 1 liter of deionized water for three times, and then centrifuged. Dry matter content of the D₀ bleached pulp was quickly determined by drying under infrared lamp for calculation of the amount of water needed in subsequent E_p stage. The experiment was repeated three times.

Alkaline extraction reinforced with hydrogen peroxide (E_p-stage)

Pulp obtained from D₀-bleaching mentioned above (originally 50 b.d. g) was used in this stage. This stage was done in plastic bag heated in a water bath, with chemical charge (on pulp basis) of 1.7% NaOH and 0.4% H₂O₂. E_p-stage was performed at 76°C for 70 minutes, mixing was done manually every 10 minutes. After the reaction, the pulp and effluent were collected. The pulp was thoroughly washed with deionized water until clear filtrate, then centrifuged and stored for further analysis. 250 ml of D₀-stage effluent and 250 ml of E_p-stage effluent were combined (to make 500 ml D₀+E_p effluent) and stored for further analysis. The experiment was repeated three times.

Second chlorine dioxide bleaching stage (D₁-stage)

D₀ bleaching was done in PE plastic bag heated in a water bath. About 50 b.d. g of post-alkaline extraction pulp was bleached with chemical charge (on pulp basis) of 1.5% active chlorine (from ClO₂). D₁-stage was performed at 77°C at 10% consistency for 155 minutes, mixing was done manually every 15 minutes. After the

reaction, the pulp and effluent were collected. The pulp was thoroughly washed with deionized water until clear filtrate, then centrifuged and stored for further analysis. The experiment was repeated for three times.

Peroxide bleaching stage (P-stage)

P bleaching was done in PE plastic bag heated in a water bath. About 50 b.d. g of post-D₁ bleaching pulp (from mill A) was bleached with chemical charge (on pulp basis) of 0.6% NaOH and 0.8% H₂O₂. P-stage was performed at 80°C at 10% consistency for 70 minutes, mixing was done manually every 10 minutes. After the reaction, the pulp and effluent were collected. The pulp was thoroughly washed with deionized water until clear filtrate, then centrifuged and stored for further analysis. The experiment was repeated for three times.

7.2 Bleached pulp analyses

For each stage, pre- and post-bleached pulps were analyzed for hexenuronic acid content, kappa number and viscosity, each analysis was done in duplicate.

Hexenuronic acid quantification

HexA content of pulp was determined by the procedure proposed by Tenkanen et al. 1999. In brief, about 2 b.d. g of pulp was hydrolyzed in an autoclaved at 110°C for 60 minutes, at pH about 3.5 maintained by sodium formate – formic acid buffer. After hydrolysis, the hydrolyzate was collected. The pulp was washed with distilled water and filtered; the filtrate was combined with the hydrolyzate and diluted to 1 L. Diluted hydrolyzate was analyzed by UV spectrophotometry (Shimadzu UV-2550) for 2-furoic acid at 245 nm with baseline correction at 480 nm. UV spectrum of the blank solution (made from sodium buffer) was subtracted from the samples' spectra. The amount of HexA, c, (in meq/kg pulp) is calculated by equation 5.

$$c = \frac{A_{245} - A_{480}}{8.7 \times m} \quad (5)$$

Where: A_{245} , A_{480} are the absorbance at 245 and 480 nm respectively
 m [kg] is the dry weight of the pulp

Kappa number and intrinsic viscosity measurement

Kappa number of the pulp was measured according to SCAN-C 1:00 standard. Intrinsic viscosity of the pulp in cupriethylenediamine solution was measured according to SCAN-CM 15:99 standard.

7.3 Effluent analyses

Effluent from each bleaching stage was analyzed for dissolved lignin content by UV spectrophotometry and Total Organic Carbon (TOC).

Total Organic Carbon determination

TOC of the effluents was measured by the instrument Shimadzu TOC-control V according to EN 1484 standard. TOC results are given on effluent basis, as g/L.

Dissolved lignin content

Dissolved lignin in the effluents was quantified by UV spectrophotometry (Shimadzu UV-2550). The dissolved lignin content (in g/L) can be calculated from equation 6.

$$Lignin \left[\frac{g}{L} \right] = \frac{Abs \times DF}{\epsilon} \quad (6)$$

Where Abs is the absorbance at 205 or 280 nm
 DF is the dilution factor
 ϵ [L/g.cm] is the extinction coefficient

For acidic sample (effluent from D₁-stage), the absorbance was measured at 205 nm with the extinction coefficient of 110 L/g.cm (TAPPI useful method 250). For alkaline and neutral samples (effluent from O-stage, D₀+E_p-stage and P-stage), the absorbance was measured at 280 nm with the extinction coefficient of 24.6 L/g.cm (Nörström 1970, Fengel et al. 1981 and Alén et al. 1988).

7.4 Calculation for TOC contribution of pulp components

The total TOC on pulp basis was calculated by equation 7.

$$TOC(Total) \left[\frac{g}{kg \text{ pulp}} \right] = \frac{TOC(Total) \left[\frac{g}{L} \right] \times V_{effluent} [L]}{m_{pulp} [kg \text{ pulp}]} \quad (7)$$

Where: $V_{effluent}$ [L] is the total volume of effluent, which is assumed to be equal to the total volume of water in the system before bleaching
 m_{pulp} [kg] is the bone dry weight of pulp used in bleaching

Lignin contribution to TOC

The average molecular weight of oxidized (soluble) lignin structure is assumed to be 190 g/mol for a phenylpropane (C₉) unit. Therefore, the TOC contribution (on effluent basis) of lignin in each stage can be calculated by equation 8. The average molecular weight of 190 g/mol is a commonly used value in calculation for soluble lignin structures, without any reference, thus the accuracy of equation 8 can be improved by searching the literature for the average molecular weight and structure of oxidized lignin for each bleaching stage. For each phenyl propane (C₉) unit, there is an average of about 0.9 methoxyl group attached, the carbon content of lignin is assumed to be 9.9 C per phenyl propane unit.

$$TOC(lignin) \left[\frac{g}{L} \right] = \frac{Lignin \left[\frac{g}{L} \right] \times 9.9 \times 12 \left[\frac{g}{mol} \right]}{190 \left[\frac{g}{mol} \right]} \quad (8)$$

The contribution of dissolved lignin to TOC on pulp basis is calculated by equation 9.

$$TOC(lignin) \left[\frac{g}{kg \text{ pulp}} \right] = \frac{TOC(lignin) \left[\frac{g}{L} \right] \times V_{effluent} [L]}{m_{pulp} [kg \text{ pulp}]} \quad (9)$$

Where: $V_{effluent}$ [L] is the total volume of effluent, which is assumed to be equal to the total volume of water in the system before bleaching
 m_{pulp} [kg] is the bone dry weight of pulp used in bleaching

HexA contribution to TOC

The contribution of hexenuronic acid (with 6 carbons in a molecule) to TOC (on pulp basis) is calculated from the change in HexA content in the pre- and post-bleached pulp, as shown in equation 10.

$$TOC(HexA) \left[\frac{g}{kg \text{ pulp}} \right] = \Delta HexA \left[\frac{mol}{kg \text{ pulp}} \right] \times 6 \times 12 \left[\frac{g}{mol} \right] \quad (10)$$

Where: $\Delta HexA$ [mol/kg pulp] is the change in HexA content

Carbohydrates contribution to TOC

The contribution of carbohydrates (cellulose and hemicelluloses) to TOC (on pulp basis) is determined by subtraction the contribution of lignin and HexA from the total TOC, as shown in equation 11.

$$TOC(carbohydr.) \left[\frac{g}{kg \text{ pulp}} \right] = TOC(Total) - TOC(lignin) - TOC(HexA) \left[\frac{g}{kg \text{ pulp}} \right] \quad (11)$$

7.5 Calculation for pulp yield loss

Componential pulp yield loss (of lignin, hexenuronic acid and carbohydrate) is calculated from the TOC contribution of each pulp component by using equation 12.

$$Yield \ loss \left[\frac{g}{kg \text{ pulp}} \right] = \frac{M \left[\frac{g}{mol} \right]}{C \ content \left[\frac{g}{mol} \right]} \times TOC \left[\frac{g}{kg \text{ pulp}} \right] \quad (12)$$

Where: M [g/mol] is the average molecular weight of one unit structure of the pulp component

C content [g/mol] is the carbon content of one unit structure of the pulp component

The average molecular weights and carbon contents of the pulp's lignin, hexenuronic acid and carbohydrates are given in Table 1.

The structure of residual lignin in pulp is assumed to be nearly unchanged (Gellerstedt et al. 1989, Gellerstedt et al. 1997 and Suess et al. 1998), i.e. the structure and molecular weight are very near to those of native lignin. As the pulps were made from 85% pine and 15% spruce, the average molecular weight of lignin (ca. 185 g/mol) was calculated from those of pine's enzymatically liberated lignin, $C_9H_{8.5}O_{2.6}(OCH_3)_{0.86}$ (Pillow et al. 1935) and spruce's Brauns' native lignin, $C_9H_{8.7}O_{2.6}(OCH_3)_{0.9}$ (Brink et al. 1961, Brink et al. 1962).

During hydrolysis, xylan-O-HexA structure is cleaved at the O-HexA bond, and one hydrogen will replace HexA, forming -OH group. Therefore, molecular weight of one

HexA unit was calculated from the structure shown in Figure 6, minus 1 g/mol, resulting in 158 g/mol. Carbohydrate loss was assumed to be from cellulose, the molecular weight is taken from that of anhydroglucose unit of 162 g/mol.

Table 1. Average molecular weight and carbon content of pulp's main components.

Pulp Component	M g/mol	C content g/mol
Lignin:	185	119
HexA:	158	72
Cellulose:	162	72

7.6 Kappa number reduction contribution of lignin and HexA removal

According to Vuorinen et al. (1999) and Clavijo et al. (2012), the average reduction of about every 9.5 meq HexA/kg pulp is equivalent to the reduction of 1 kappa unit. For lignin, the average reduction of about every 1.5 g lignin/ kg pulp is equivalent to the reduction of 1 kappa unit (Genco et al. 2000, Rööst 2001 and Suess et al. 2010). The contribution of lignin and HexA in pulp's kappa number reduction can be calculated using equation 13 and 14.

$$\Delta k_{\text{lignin}} = \frac{\Delta \text{lignin} \left[\frac{\text{g}}{\text{kg pulp}} \right]}{1.5 \left[\frac{\text{g}}{\text{kg pulp}} \right]} \quad (13)$$

$$\Delta k_{\text{HexA}} = \frac{\Delta \text{HexA} \left[\frac{\text{meq}}{\text{kg pulp}} \right]}{9.5 \left[\frac{\text{meq}}{\text{kg pulp}} \right]} \quad (14)$$

8 RESULTS AND DISCUSSION

8.1 Pulp yield loss in laboratory bleaching experiments

The average dissolved lignin contents of the effluents and TOC contribution of lignin are shown in Table 2 (full experimental results can be found in APPENDIX 2)

Table 2. Lignin content in each bleaching effluent and TOC contribution of lignin.

Bleaching stage	Lignin content [g/L]	TOC (lignin) [g/L]	TOC (lignin) [g/kg pulp]
O	1.63 ± 0.03	1017 ± 19	11.3 ± 0.21
D ₀ + E _p	0.49 ± 0.07	304 ± 41	5.5 ± 0.73
D ₁	0.112 ± 0.002	70.1 ± 1.4	0.63 ± 0.013
P	0.033 ± 0.003	20.8 ± 1.6	0.19 ± 0.014

HexA content of pre- and post-bleached pulp, changes in HexA content and HexA contribution in TOC of each bleaching stage's effluent, are shown in Table 3 (full experimental results of pulp's HexA content can be found in APPENDIX 3).

Table 3. HexA content of pre- and post-bleached pulp, change in HexA content during the bleaching stages and contribution of HexA to bleaching effluent's TOC.

Bleaching stage	HexA content [mmol/kg pulp]			TOC (HexA) [g/kg pulp]
	pre-bleached pulp	post-bleached pulp	ΔHexA	
O	23.2	22.7 ± 0.29	0.5 ± 0.29	0.034 ± 0.021
D ₀ + E _p	27.4	9.7 ± 0.19	17.8 ± 0.19	1.279 ± 0.014
D ₁	9.7	3.3 ± 0.17	6.3 ± 0.17	0.457 ± 0.012
P	6.6	6.0 ± 0.09	0.5 ± 0.09	0.039 ± 0.006

Table 4 summarizes the effluents' total and componential TOC values for each bleaching stage. Pulp yield losses are shown in Table 5 and visualized in Figure 13.

Table 4. TOC contributions of lignin, HexA and carbohydrate, on pulp basis.

Bleaching stage	Total g/kg pulp	Lignin g/kg pulp	HexA g/kg pulp	Carbohydrate g/kg pulp
O	14.0 ± 0.4	11.3 ± 0.21	0.034 ± 0.021	2.6 ± 0.45
D ₀ + E _p	15.4 ± 1.2	5.5 ± 0.73	1.279 ± 0.014	8.6 ± 1.40
D1	3.0 ± 0.06	0.63 ± 0.013	0.457 ± 0.012	2.0 ± 0.06
P	2.1 ± 0.04	0.19 ± 0.014	0.039 ± 0.006	1.9 ± 0.04

Table 5. The losses of pulp component and the total yield loss during bleaching

Bleaching stage	Lignin g/kg pulp	HexA g/kg pulp	Carbohydrate g/kg pulp	Total g/kg pulp	Yield loss %
O	17.6 ± 0.3	0.1 ± 0.05	5.9 ± 1.0	23.6 ± 1.1	2.4
D ₀ + E _p	8.5 ± 1.1	2.8 ± 0.03	19.4 ± 3.0	30.7 ± 3.2	3.1
D1	1.0 ± 0.02	1.0 ± 0.03	4.4 ± 0.1	6.4 ± 0.1	0.6
P	0.3 ± 0.02	0.1 ± 0.01	4.3 ± 0.1	4.7 ± 0.1	0.5

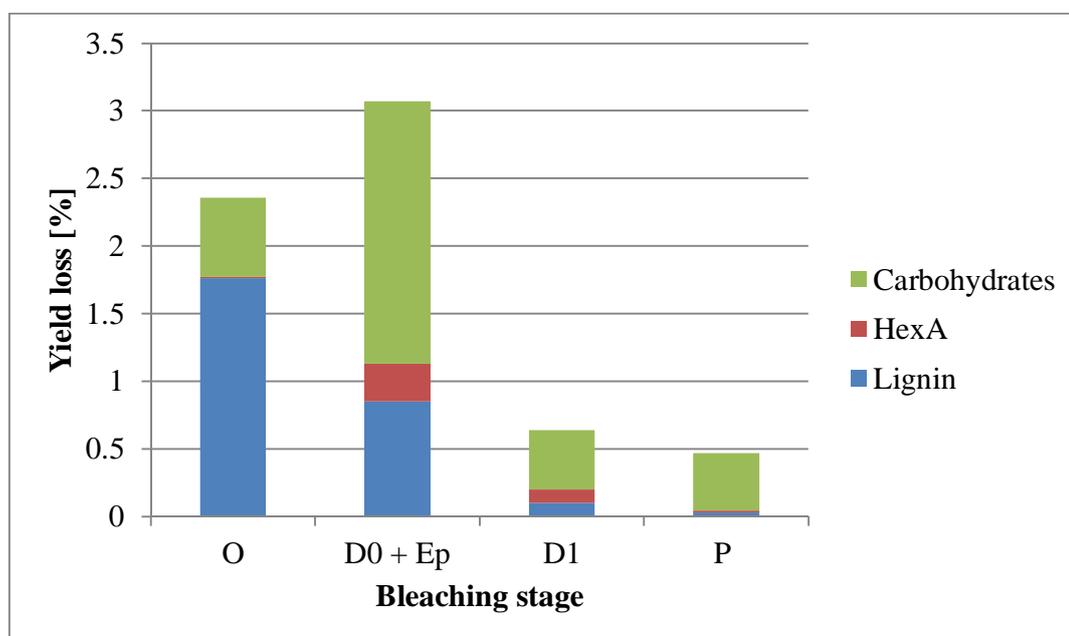


Figure 13. Pulp yield loss in laboratory bleachings (error bars omitted for simplicity).

Changes in pulps' viscosity and kappa number during the bleaching stages in this experiment are summarized in Table 6.

Table 6. Changes in viscosity and kappa number of pulp during laboratory oxygen delignification, D₀+E_p, D₁ and P stages.

Bleaching stage	kappa number, κ			viscosity, η [ml/g]		
	before	after	$\Delta\kappa$	before	after	$\Delta\eta$
O	25.7	13.5	12.2	1044	927	117
D ₀ + E _p	15	3.6	11.4	1009	976	32
D ₁	3.1	1.6	1.5	953	923	30
P	2.1	1.9	0.2	936	858	77

The losses of lignin and HexA in pulp during each bleaching stage are translated into kappa number reduction and compared to the measured value, which are shown in Table 7.

The pulp yield loss in oxygen delignification stage was at a reasonable magnitude, about 70% of the loss originated from lignin removal, which is comparable to the results obtained by Ala-Kaila et al. (2002a), who determined the pulp yield loss in a continuous industrial two-stage oxygen delignification process. With the process parameters of 85°C, 6 bar O₂, 0.14% NaOH, 0.25% MgSO₄, which are quite similar to those of this work, the yield loss was found to be about 2.4%, in which the losses of lignin and carbohydrates were 15.14 and 2.54 g/kg pulp, respectively. The loss of lignin in Ala-Kaila's work was in the same range as in this study but carbohydrate loss was lower, which can be explained by slightly lower process temperature, lower alkali charge and higher Mg²⁺ charge. The contribution of lignin and HexA removal to pulp's kappa number reduction is consistent to the measured kappa value (see Table 7).

In D_0+E_p stage, most of the pulp's HexA was removed. Remarkably, significant loss of carbohydrates (ca. 2% on pulp) occurred, comprising 65% of the pulp yield loss in this stage, which is too high. However, the drop in pulp viscosity after D_0+E_p stage was small (from 1008 ml/g to 976 ml/g, i.e. about 32 ml/g, see Table 6), suggesting that the removal of carbohydrate proceeded mainly via the peeling mechanism, as with this end-wise degradation mode, a large number of glucose units can be peeled from cellulose chains but the degree of polymerization changes very little, resulting in small drop of pulp's intrinsic viscosity. If random oxidative cleavage of cellulose were to be the main degradation mode, pulp's intrinsic viscosity would drop more, for example in oxygen delignification experiment, the loss of carbohydrates was about 0.8% but pulp's intrinsic viscosity dropped by more than 120 ml/g (see Table 6). There is also inconsistency in the kappa number reduction obtained from direct measurement ($\Delta\kappa = 11.4$) and from calculation of lignin and HexA removals ($\Delta\kappa = 7.6$), see Table 7. The difference of 3.8 kappa unit can be assigned to the amount of lignin fully degraded to smaller molecules, which was not included in the UV-absorption at 280 nm. Therefore, the componential yield loss in D_0+E_p stage can be recalculated, taking in to account that an addition of 3.8 kappa unit is from lignin loss, equivalent to 5.7 g lignin/kg b.d. pulp (1.5 g lignin/kg pulp \sim 1 kappa unit), HexA loss stays the same. The corrected componential yield losses in D_0+E_p stage are: 14.2 g lignin/kg pulp, 2.8 g HexA/ kg pulp and 11.2 g carbohydrate/kg pulp, making the total pulp yield loss 2.8% in this stage.

In D_1 stage, more HexA was removed, lignin was oxidized modestly (about 0.1% on pulp) but carbohydrate loss was high, comprising ca. 70% of the yield loss (0.65%) of this stage. The contribution of lignin and HexA removal to pulp's kappa number reduction is consistent with the measured kappa value (see Table 7).

In the final brightening P stage, removal of lignin and HexA was low. Yield loss was mainly from the loss of carbohydrates which can be explained by the lack of magnesium ions in the bleaching system, due to intensive washing of oxygen

delignified pulps for transportation from mill A. Without Mg^{2+} , carbohydrates were not protected from oxidative attack of $\bullet OH$, evolved from H_2O_2 , catalyzed by the transition metal ions. The contribution of lignin and HexA removal to pulp's kappa number reduction is consistent with the measured kappa value (see Table 7).

Table 7. Comparison of kappa number reduction between measurement and calculation from changes in pulp's lignin and HexA content (assumption: each 1.5 g lignin/kg pulp or 9.5 meq HexA/kg pulp equivalent to 1 kappa unit).

Bleaching stage	$\Delta\kappa$			
	Lignin	Hex A	Total	From κ measurement
O	11.8	0.1	11.9	<i>12.2</i>
D ₀ + E _p	5.7	1.9	7.6	<i>11.4</i>
D ₁	0.7	0.7	1.4	<i>1.5</i>
P	0.2	0.1	0.3	<i>0.2</i>

8.2 Sources of errors

A major source of error in this experiment is the heterogeneity of pulps. The pulps were delivered from mill A in bags of 5 – 7 kg, dry matter content 30 – 35%, from which only 100 or 50 g (dry) was taken to be bleached, and for the analysis (HexA, kappa and viscosity), the amount is even smaller (1 – 5 g dry). Thus, it is difficult to get representative samples.

The deviation in yield loss of D₀+E_p stage was big, more than 10%. This can be explained by the fact that D₀ phase was done in so short time, only 15 minutes, and the repeatability of the plastic-bag bleaching system is not good at this time frame. As a consequence, the results deviated quite much from each other.

The yield of laboratory bleaching is generally higher than that in industrial scale due to the fact that in industrial bleaching, the effluents are often recirculated back to the

previous stages for washing purpose, leading to the re-adsorption of dissolved material on the pulp, thus narrowing the yield loss.

8.3 Simulation of pulp yield loss in bleaching

There have been many efforts in simulation the chemical pulping process. However, the pulp yield loss in bleaching has not been seriously considered, even though that is important for evaluation of the process' profitability. Pulp yield loss determination in a simulation environment can be accomplished by taking into account all the reactions of pulp's components with bleaching chemicals in each stage leading to their solubilization. Kinetics of those reactions should also be included, which is not discussed here as it is far beyond the scope of this thesis. The reactions related to yield loss are shown below:

Oxygen delignification (O):

- HexA should be assumed to be unreactive while simulating the O-stage, thus do not contribute to the yield loss.
- Phenolic lignin is solubilized through the oxidation of phenoxy radicals to: muconic acid, quinone, aldehyde in the side chain (as in Figure 2). This requires the phenolic lignin fraction in pulp to be specified.
- Carbohydrates with reducing end-groups are subjected to peeling; the effect of stabilization should also be taken into account. Carbohydrates are oxidized and cleaved into smaller fractions under the attack of hydroxyl radical (as in Figure 3 and 4).

Acid hydrolysis (A):

- HexA is hydrolyzed into 2-furancarboxylic acid and 5-formyl-2-furancarboxylic acid (as in Figure 6).
- Lignin is cleaved from carbohydrates in LCC, this requires the defining of LCC and their content in pulp in the simulation.

- Carbohydrates are subjected to hydrolysis, yield loss might be small, but the degree in cellulose's DP needs to be followed.

Chlorine dioxide bleaching (D) and alkaline extraction (E_p):

- HexA reacts with Cl_2 , HOCl and $HClO_2$, and is then removed by alkali extraction
- Residual lignin (both phenolic and non-phenolic) undergoes reactions shown in Figures 9 and 10, and is then extracted in the subsequent E_p stage. The forced dissolution of unreacted lignin by adsorption of hydrophilic lignin, as discussed by Tarvo et al. (2010) should also be included in the simulation.
- Carbohydrates' DP is affected by acidic hydrolysis, reducing end-groups are oxidized by $HClO_2$, making short enough cellulose chains prone to dissolution.

Hydrogen peroxide bleaching (P):

- Residual lignin's chromophoric quinonoid and enone structures react with HOO^- (as in Figure 11).
- Carbohydrates are randomly cleaved by hydroxyl radicals.

9 CONCLUSION

The reactions of pulp's main components (lignin, carbohydrates and HexA) with bleaching chemicals, leading to yield loss (solubilization of material) in different bleaching stages, including O, A, D, E_p and P, were discussed. The bleaching conditions affecting pulp yield loss were also considered.

Componential pulp yield losses in each stage of an ECF bleaching sequence of softwood kraft pulp were successfully determined using TOC of the effluents supported by analysis of bleaching effluents' dissolved lignin content and bleached pulps' HexA content. The pulp yield losses were 2.6, 3.0, 0.7 and 0.5% for the O, D₀+E_p, D₁ and P stages, respectively. Quantification of dissolved lignin in bleaching effluents might give significant error due to the degradation of lignin into smaller structure, especially in the first chlorine dioxide stage where high charge of active chlorine is applied. That error can be corrected by comparison the reductions in pulp's lignin and HexA contents with changes in pulp's kappa number, using the coefficients found in literature.

Generally, the pulp yield losses were in the right magnitude and the changes in pulp's lignin and HexA content were reasonable translated into kappa number reduction, except for the D₀+E_p stage, where the correction just mentioned above needed to be applied.

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APPENDIX 1

TOC of bleaching effluents of the bleaching effluents: O, D₀+E_p, D₁ and P.

Bleaching stage	Effluent	TOC mg/L	TOC average mg/L
O	I	1294.0	1255 ± 37
	II	1205.0	
	III	1265.0	
D ₀ + E _p	I	945.3	855 ± 64
	II	801.8	
	III	818.7	
D ₁	I	331.3	337 ± 7
	II	346.7	
	III	333.3	
P	I	242.8	236 ± 5
	II	232.8	
	III	233.5	

APPENDIX 2

Dissolved lignin content and lignin contribution to TOC of the bleaching effluents: O, D₀+E_p, D₁ and P (each bleaching was done three times, each bleaching effluent was analyzed in duplicate).

Stage	Sample	Absorption	DF	Lignin content g/L	TOC mg/L	TOC average mg/L
O	Ia	0.408	100	1.659	1037	1017 ± 19
	Ib	0.409	100	1.663	1040	
	IIa	0.387	100	1.573	984	
	IIb	0.396	100	1.610	1007	
	IIIa	0.4	100	1.626	1017	
	IIIb	0.4	100	1.626	1017	
D ₀ + E _p	Ia	0.283	50	0.575	360	304 ± 41
	Ib	0.285	50	0.579	362	
	IIa	0.211	50	0.429	268	
	IIb	0.212	50	0.431	269	
	IIIa	0.222	50	0.451	282	
	IIIb	0.222	50	0.451	282	
D ₁	Ia	0.622	20	0.113	70.7	70.1 ± 1.4
	Ib	0.637	20	0.116	72.4	
	IIa	0.609	20	0.111	69.2	
	IIb	0.6	20	0.109	68.2	
	IIIa	0.624	20	0.113	70.9	
	IIIb	0.608	20	0.111	69.1	
P	Ia	0.453	2	0.037	23.0	20.8 ± 1.6
	Ib	0.454	2	0.037	23.1	
	IIa	0.384	2	0.031	19.5	
	IIb	0.383	2	0.031	19.5	
	IIIa	0.393	2	0.032	20.0	
	IIIb	0.391	2	0.032	19.9	

HexA contents of the pulps supplied by mill A (HexA quantification was done in duplicate).

Pulp	HexA (meq/kg pulp)		
	a	b	average
After kraft cook	23.1	23.2	23.2
After O	27.9	27.0	27.4
After D ₀ + E _p	9.7	9.7	9.7
After D ₁	6.7	6.4	6.6
After P	4.4	4.7	4.5

HexA contents of bleached pulps (Each pulp from mill A was bleached by the subsequent stage, repeated 3 times, HexA quantification was done in duplicate). There were problems in measuring the HexA content of P-bleached pulps, two samples were thus discarded.

Pulp	HexA (meq/kg pulp)						
	Ia	Ib	Iia	Iib	IIa	IIb	average
O-delignified	23.0	23.2	22.5	22.4	22.5	22.6	22.7 ± 0.3
D ₀ +E _p -bleached	9.3	9.7	9.6	9.8	9.8	9.9	9.7 ± 0.2
D ₁ -bleached	3.2	3.3	3.2	3.2	3.7	3.3	3.3 ± 0.2
P-bleached	6.1	N/A	6.1	5.9	6.0	N/A	6.0 ± 0.1