On the importance of oxidizable structures in bleached kraft pulps

Olena Sevastyanova

Doctoral Thesis

Supervisors: Professor Göran Gellerstedt
Dr. Jiebing Li

Royal Institute of Technology
Department of Fibre and Polymer Technology
Division of Wood Chemistry and Pulp Technology

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ABSTRACT

After cooking, kraft pulps always contain not only residual lignin but also significant amounts of hexenuronic acid and other non-lignin structures oxidizable by permanganate under the standard kappa number determination conditions. These here referred to as false lignin. Like ordinary lignin, the false lignin also consumes bleaching chemicals, thus increasing both the production costs and the environmental impact of bleach plant effluents. The false lignin also has an effect on pulp properties such as brightness stability. This necessitates the development of efficient experimental routines for the determination of false lignin in different types of unbleached and bleached kraft pulps, together with studies of its formation, chemical behaviour, and ultimate fate.

The main aim of this work has been to establish a method for the quantification of various types of oxidizable structures in bleached kraft pulps and to study their impact on pulp quality, particularly, on the brightness stability of pulps bleached in elemental-chlorine-free (ECF) and a totally-chlorine-free (TCF) processes.

Part of this research deals with the relationship between the kappa number and the lignin content in the case of partly oxidized lignins. Spruce and birch kraft pulps processed according to the ODEQP and OQ(OP)Q(PO) bleaching sequences, respectively, have been analyzed. It has been found that the oxidation equivalent of the residual lignin decreases with increasing degree of oxidation along each bleaching sequence. This finding has been further supported by experiments with a number of model compounds. The Ox-Dem kappa number method has been shown to be an accurate means of determining the residual lignin content and of monitoring the efficiency of lignin removal along different bleaching sequences. It has been demonstrated that the kappa number can always be fractioned into partial contributions, the first of which comes from the residual lignin and is measured by the Ox-Dem kappa number, and the second from the false lignin and is given by the difference between the standard kappa number and the Ox-Dem kappa number. The effect of false lignin on the pulp kappa number is most pronounced in unbleached and oxygen-delignified kraft pulps.

The extractability of residual and false lignin in different solvents has been investigated. The changes that occurred in the kappa number following different extraction steps have been compared with corresponding changes in the chemical composition and the conclusion has been drawn that the hemicellulose component of a kraft pulp is a major source of non-lignin structures contributing to the kappa number.

The influence on the brightness stability of various oxidizable structures, viz.: residual lignin, hexenuronic acid and other non-lignin structures, in spruce, birch and eucalyptus kraft pulps bleached in ECF and TCF type processes was studied. It was demonstrated that the selective removal of all false lignin structures significantly improves the brightness stability. The degree of yellowing was found to be proportional to the content of HexA groups in pulps. It has been shown that 2-furancarboxylic acid, 5-formyl-2-furancarboxylic acid and reductic acid are formed during the course of thermal yellowing. The influence of two bleaching sequences, D0(EP)D1 (ECF-type) and Q1(OP)Q2(PO) (TCF)-type, on the content of different oxidizable structures in eucalyptus kraft pulp was studied in relation to the brightness stability of the pulp. It was shown by kappa number fractionation that pulp bleached to full brightness with ECF- and TCF-type sequences contains different amounts of HexA. The most significant discoloration was observed in the case of TCF-bleached pulp having an especially high content of HexA.

The mechanism of the moist (8 % moisture) thermal yellowing of fully bleached kraft pulps was further studied using dissolving pulp impregnated with a set of model compounds representing the most likely HexA degradation products, viz. as 2-furancarboxylic acid (FA), 5-formyl-2-furancarboxylic acid (FFA) and reductic acid (RA), either alone or in combination with Fe(II) or Fe(III) ions. It was found that the latter two acids take part in reactions leading to colour formation whereas 2-furancarboxylic acid does not. The effect of iron ions on the colour formation appears to vary with their oxidation state. The brightness loss caused by either FFA or RA, present in an amounts similar to the content of HexA in industrial pulps, was of the same order of magnitude as that observed in industrial pulps aged under the same conditions. Based on these findings, it is suggested that the overall mechanism of moist thermal yellowing involves several stages, including the degradation of hexenuronic acid and the formation of reactive precursors, such as 5-formyl-2-furancarboxylic acid and reductic acid. The presence of ferrous ions further enhances the discoloration.

KEYWORDS: bleached pulps, betula, eucalyptus, 5-formyl-2-furancarboxylic acid, 2-furancarboxylic acid, hexenuronic acid, kappa number, kraft pulps, oxidation equivalents, permanganate consumption, picea, reaction mechanism, reductic acid, thermal yellowing.
List of publications


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1 INTRODUCTION

1.1 Wood fibre

Wood fibres are composed of organic polymers, including cellulose, hemicelluloses and lignin, which form a complex, highly ordered material with distinctive structural and mechanical properties (see, e.g., Parham 1969).

Cellulose is the main strength-bearing component of the fibre. Approximately 40–45% of the dry substance in most wood species is cellulose. The cellulose is a straight-chain, unbranched, hydrophilic polysaccharide composed of repeating β-D-glucopyranose monomer units which are linked together via (1-4)-glycosidic bonds. The average degree of polymerisation (DP) in wood is considered to be about 10,000. Cellulose has a strong tendency to form intra- and intermolecular hydrogen bonds, which stiffen the straight chain and promote aggregation into a crystalline structure (Fengel and Wegener 1989, Sjöström 1993a). It has been established that, in wood, cellulose forms lattices with ordered regions and also regions where the lattice is slightly disturbed and has a lower degree of order, the latter being referred to as “amorphous cellulose”. However, the state of order can probably not be divided only into crystalline and amorphous parts; several degrees of intermediate or semicrystalline order also exist.

Hemicelluloses form a matrix which penetrates and encases the cellulose framework. The presence of hemicelluloses is believed to regulate the pattern of aggregation of cellulose in wood (Atalla 1995). In contrast to cellulose, hemicelluloses are heteropolysaccharides. Hemicelluloses have a lower DP, typically in the range of only 50–300 (Parham 1996, Sears et al. 1978), possess side groups on the chain molecule, and are essentially amorphous. Hemicelluloses are very hydrophilic and play a major role in the ability of the fibre to absorb water.

In wood, hemicelluloses account for 20 to 30% of the dry substance. The composition and structure of the hemicelluloses in softwood differ in a characteristic way from those in hardwood. There are also considerable differences in the hemicellulose content and composition between stem, branches, roots, and bark.
The principal hemicelluloses in softwood are galactoglucomannans (about 20%) and arabinoglucuronoxylan (5–10%). The backbone of galactoglucomannans is a linear or slightly branched chain built up of (1–4)-linked β-D-glucopyranose and β-D-mannopyranose units. The α-D-galactopyranose residue is linked as a single-unit side chain to the framework by (1–6)-bonds. An important structural feature is that the hydroxyl groups at the C2 and C3 positions in the chain units are partially substituted by O-acetyl groups, on the average one group per 3–4 hexose units. Arabinoglucuronoxylan is composed of a framework containing (1–4)-linked β-D-xylopyranose units which are partially substituted at C2 by 4-O-methyl-α-D-glucuronic acid groups, on the average two residues per ten xylose units. In addition, the framework contains α-L-arabinofuranose units.

The main hemicellulose in hardwood is glucuronoxylan: O-acetyl-4-O-methylglucurono-β-D-xylan. Depending on the hardwood species, the xylan content varies within the range of 15–30%. Besides xylan, hardwoods contain 2–5% of a glucomannan which is composed of β-D-glucopyranose and β-D-mannopyranose units linked by (1–4)-bonds.

Lignin is produced by maturing cells and permeates the fibre walls and the intercellular regions (middle lamellae) rendering the wood tissue rigid and cohesive. In wood, lignin makes up approximately 20–30% of the dry substance and is second in natural abundance only to cellulose. From a chemical viewpoint, lignin is an amorphous cross-linked irregular network biopolymer, arising from the co-polymerisation of three phenylpropanoid monomers, viz.: coniferyl, sinapyl and p-coumaryl alcohols (Fig.1).

Lignin from almost all softwoods (guaiacyl lignin) is largely a polymerization product of coniferyl alcohol, whereas lignin from hardwoods (guaiacyl-syringyl lignin) is a copolymer of coniferyl and sinapyl alcohols with the monomer ratio ranging from 4:1 to 1:2 (Sjöström 1993b). The cross-linking is effected via fairly stable covalent bonds, such as C-C bonds and ether bonds, and less stable hydrogen bonds.
The primary wall as well as the middle lamella also contains considerable amounts of pectic materials, e.g. polygalacturonic acid and its methylated analogues.

It has been proposed that covalent bonds between lignin and carbohydrates (LC-bonds) can exist in wood (Björkman 1957) although there is considerable ambiguity about their types and number. Recently, Lawoko (2005) has shown that lignin is linked through covalent bonds to all the major polysaccharides in the woody cell wall, viz: to arabinoglucuronoxylan, galactoglucomannan, glucomannan, and cellulose. He also concluded that the lignin polymer cross-links various polysaccharides to each other forming a lignin-carbohydrates network in wood.

In addition to the major chemical components already mentioned, wood contains small quantities of various extraneous, low molecular weight organic materials, normally referred to as “extractives” or “pitch”, and inorganic material. The inorganic material is of little importance for the papermaking fibres but it may be a serious problem for instance in the chemical recovery system in a closed pulp mill or in bleaching. The extractives, on the other hand, cause serious disturbances in papermaking, in spite of their usually low content in wood.

The average chemical compositions of different wood species are shown in Table 1.
**Table 1.** Chemical composition of different wood species (after E. Sjöström (1993c)). All values are given as % of the dry wood weight.

<table>
<thead>
<tr>
<th>Main chemical components</th>
<th>Wood species</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Spruce (<em>Picea abies</em>)</td>
</tr>
<tr>
<td></td>
<td>Blue gum (<em>Eucalyptus globulus</em>)</td>
</tr>
<tr>
<td></td>
<td>Birch (<em>Betula papyrifera</em>)</td>
</tr>
<tr>
<td>Cellulose</td>
<td>41.7</td>
</tr>
<tr>
<td>Glucomannan</td>
<td>16.3</td>
</tr>
<tr>
<td>Xylan</td>
<td>8.6</td>
</tr>
<tr>
<td>Other carbohydrates</td>
<td>3.4</td>
</tr>
<tr>
<td>Lignin</td>
<td>27.4</td>
</tr>
<tr>
<td>Extractives</td>
<td>1.7</td>
</tr>
</tbody>
</table>

1.2 Wood pulping

Pulp produced from wood is the predominant raw material for papermaking. The main purpose of wood pulping is to liberate the fibres. This can be accomplished either chemically or mechanically or by combining these two types of treatment. Depending on the process involved, the common commercial pulps can be grouped into chemical, semichemical, and mechanical.

Chemical pulping is a process in which lignin is removed so completely that the wood fibres are easily liberated on discharge from the digester or at most after a mild mechanical treatment. The kraft process was invented in 1879 (Dahl 1884) and is today the dominant global process for the production of chemical pulp. Its advantages compared to other pulping processes are the high pulp strength and the well developed recovery process. In the digester, the wood chips are brought into contact with the cooking liquor (an aqueous solution of NaOH and Na₂S). The chips are impregnated with the cooking liquor and heated to a temperature of 150 to 170°C. Such a vigorous treatment cleaves ether bonds, bringing about depolymerization of lignin. Due to a lack of selectivity at high degrees of delignification, the process has to be interrupted after approximately 90% removal of lignin. After that, the pulp is treated in more selective chemical environments in a bleaching plant.

The purpose of bleaching is to reach an acceptable brightness level and to improve the cleanliness of the pulp by removing extractives and other contaminants, including
inorganic impurities and bark residues. To accomplish this task, the residual lignin needs either to be removed from the pulp or, alternatively, to be freed from strongly light-absorbing chromophoric groups. Bleaching can be used to produce semi-bleached grades with a brightness of 60–70% and fully-bleached pulps with a brightness of about 90%. Lignin-removing bleaching is predominantly carried out in a multi-stage process with oxidative stages normally combined with at least one alkaline extraction stage. Hardwood pulps generally require fewer bleaching stages than softwood pulps.

Elemental-chlorine-free (ECF) and totally-chlorine-free (TCF) processes are the major types of bleaching process used in the modern industry. The ECF process is based on chlorine dioxide stages (D) followed by alkaline extraction stages (E). Chlorine dioxide is known to react with all types of aromatic rings, readily with phenolic and slowly with non-phenolic structures (Brage et al. 1991).

The TCF process uses chelating stages (Q) to decrease the metal content of the pulp followed by bleaching stages containing oxygen-based chemicals such as hydrogen peroxide (P), peracetic acid (Paa) and ozone (Z). Hydrogen peroxide is known to react chiefly with phenolic structures through side chain cleavage reactions (Heuts and Gellerstedt 1998).

1.3 Chemical changes in pulp during kraft cooking and bleaching

The main goal of chemical pulping is delignification. Delignification in the kraft process occurs mainly through the depolymerization and dissolution of lignin fragments. Depolymerization of lignin goes through the cleavage of ether linkages, whereas the carbon-to-carbon linkages are essentially kept intact. Cleavage of ether linkages, promoted by both hydroxyl and hydrogen sulphide ions, also results in an increasing hydrophilicity of the lignin because of the liberation of phenolic hydroxyl groups. The degraded lignin is dissolved in the cooking liquor as sodium phenolates, with the last (thirane) structure losing sulphur on heating (Gierer 1970). Main reactions of phenolic β-aryl ether structures during kraft pulping are shown in Figure 2.
Kraft pulp fibres are brown because of the formation of chromophoric groups during pulping. These groups may be present in both lignin and carbohydrates although lignin is assumed to be the predominant contributor. Although the exact structures of the chromophores involved are not known with certainty, it is reasonable to assume that double bonds conjugated with aromatic rings, quinones and quinone methides play a predominant role as colour contributors (Dence 1992).

After kraft cooking, the pulp is subjected to oxygen delignification. The main lignin reactions in this oxygen stage involve phenolic structures. In an alkaline environment, the phenolic structures are ionized and form phenoxy and superoxide anion-radicals as a result of electron transfer from phenolate ions to molecular oxygen (Kratzl et al. 1974, Gierer and Imsgard 1977). Further reactions between the substrate and the oxygen species lead to side-chain elimination, ring-opening reactions and demethoxylation (Ljunggren 1986). Hydrogen peroxide and hydroxyl radicals are formed in secondary reactions and they then take part in the lignin depolymerization as well as in carbohydrate degradation reactions.

In contrast to kraft cook, lignin-removing bleaching promotes the dissolution of lignin primarily through the introduction of carboxyl groups into the lignin structure. Accordingly, trace amounts of residual lignin found in bleached kraft pulp normally have a high content of carboxyl groups.

A large body of data concerning the reactivity of lignin towards various bleaching agents is available in the literature (Dence and Reeve 1996). The major reaction with oxygen and chlorine dioxide is believed to be the oxidative opening of the phenolic aromatic rings.
leading to the formation of a muconic acid structure (Fricko et al. 1980, Brage et al. 1991). A similar reaction may take place with ozone, but in this case the oxidative power is so great that further oxidation of the intermediate product will readily occur (Eriksson and Gierer 1985). In peroxide bleaching, two major reaction routes can be envisaged, viz.: (i) the elimination of chromophore structures containing conjugated double bonds and (ii) the oxidation of benzyl alcohol groups (Kadla et al. 1997, Heuts and Gellerstedt 1998). All such reactions result in a modified lignin structure with partly oxidized aromatic rings (Fig. 3):

![Oxidation products of lignin](image)

**FIGURE 3.** Possible products from the oxidation of lignin.

During the pulping, a significant part of the carbohydrates is also removed from the wood simultaneously with the dissolution of lignin. Cellulose is dissolved to some extent in the kraft process, primarily through end-group peeling reactions. The typical cellulose yield for chemical kraft pulps is about 90%, as reported by Sjöström (1993d). Some dissolution of cellulose is brought about by cellulose chain shredding due to alkaline hydrolysis, with the DP level decreasing to about 1,000 to 1,500 in bleached kraft pulps (cf. SCAN-C15:62) or even lower under unsuitable process conditions. The rate of these reactions is directly dependent on the temperature.

Hemicelluloses are degraded more extensively in the pulping process due to their low degree of polymerization and amorphous state. Only the most resistant hemicelluloses,
glucomannan and xylan, are partly preserved in the pulp, xylan being the dominant hemicellulose type found in hardwood kraft pulps. Glucomannan is more susceptible to kraft cooking and, because of its high degradability, most of it is removed already at the beginning of the process. Conversely, xylan proves to be more resistant under alkaline pulping conditions. An appreciable portion of the lost xylan is actually not degraded but dissolves in the cooking liquor as a polysaccharide. Xylan dissolution is strongly affected by the concentration of hydroxy ions, and this can be used to regulate the xylan dissolution kinetics (Sjöström 1977).

Of considerable importance are the acidic groups on xylan, mainly 4-O-methyl-glucuronic acid residues, which are believed to be largely preserved during the kraft cook, albeit in an altered form as 4-deoxy-4-hexenuronic acid (HexA) (Johansson and Samuelsson 1977, Teleman et al. 1995, Jacobs et al. 2001). The amount of HexA depends on the cooking conditions. It has been shown that increased alkalinity, temperature and cooking time reduce the amount of HexA in unbleached pine kraft pulp (Gustavsson and Al-Dajani 2000). It has been reported that a large proportion of these groups is removed by bleaching with chlorine or chlorine dioxide. At the same time, TCF-bleaching with peroxide seems to leave a considerable proportion of the acid groups intact (Buchert et al. 1995, Bergnor-Gidnert et al. 1998).

Numerous experiments with model compounds (D-glucose, D-xylose, cellobiose) have revealed that, under certain conditions, oxidative changes may occur at the anhydroglucose unit in cellulose. Here, ketone, aldehyde or carboxyl groups can be introduced into the same glucose unit or into different units along the cellulose chain (Rapson and Spinner 1979). It has also been demonstrated that it is possible to generate a crude mixture of different cyclic enols and phenolic compounds by treatment of sugars with sodium hydroxide at an elevated temperature (Forsskåhl et al. 1976). This latter observation suggests conclusively that both cooking and bleaching can affect the content and structure of polysaccharides in kraft pulps. Carboxylic groups introduced during bleaching affect several pulp properties, such as swelling and brightness (Sjöström and Eriksson 1968, Scallan 1983).
1.4 Residual lignin content and kappa number determination

The removal of lignin from the pulp is the primary target of cooking and bleaching. The most common measure of the amount of residual lignin content in pulp is the pulp kappa number. Kappa number determinations are performed routinely to monitor the efficiency of the delignification process and to estimate bleaching chemicals requirements.

The kappa number is defined as the number of millilitres of a 20 mM potassium permanganate solution consumed by one gram of moisture-free pulp under the standardized conditions specified in SCAN-C 1:00. In this standard it is assumed that the permanganate consumption is directly proportional to the amount of lignin present in the pulp.

Permanganate is consumed in the oxidation of the aromatic rings in lignin. Structural peculiarities of guaiacyl and guaiacyl-syringyl lignins lead to an average consumption of 11.6 equivalents of KMnO$_4$ per phenylpropane unit. This can be used for the quantitative determination of lignin. Provided that the conditions specified by the standard are maintained, permanganate reacts predominantly with lignin and the presence of carbohydrates does not hinder the determination.

Lately, however, it has been realized that the relationship between the kappa number and the actual lignin content of pulps is not as straightforward as one might expect, and that the relationship varies depending on the wood species and the pulping process. There are instances where the kappa number miscounts the lignin content. It has, for example, been reported that, when the history of the pulp includes certain types of oxidative treatment, as in the case of bleached kraft pulps, the lignin content tends to be overestimated (Dence 1992). The present standard permits the analysis of semi-bleached pulps obtained in yields under 60% and the kappa number remains in common use in both industrial and academic laboratories.

1.5 False lignin and its contribution to the kappa number

After cooking, kraft pulps always contain not only residual lignin but also significant amount of hexenuronic acid (HexA) and other non-lignin structures containing double
bonds and/or carbonyl groups (Li and Gellerstedt 1998). Collectively, they are referred to as false lignin because they behave in a manner similar to lignin in the kappa number test.

In a comprehensive study by Li (1999), the specific permanganate consumption by various carbohydrates and aliphatic structures was measured and it was found that aliphatic structures containing a free aldehyde group, a double bond and an α,β-unsaturated carbonyl group or an α-keto-carboxylic acid group all consume permanganate under the conditions used in the kappa number determination. Therefore, it is logical to expect that the presence of analogous structures derived from polysaccharides modified during pulp cooking and bleaching can significantly affect the pulp kappa number.

These structures not only consume bleaching chemicals, as does the residual lignin itself, but they also may affect many vital pulp properties such as brightness stability. This motivates continuing efforts to understand the mechanism whereby false lignin is formed, to study its chemical properties, and to develop reliable quantification methods. The first steps in this direction were taken by Li (1999), where the contribution of the false lignin to the pulp kappa number was determined for several types of unbleached chemical pulps.

1.6 Fractionation of pulp kappa number in unbleached kraft pulps

1.6.1 Kappa number fraction due to residual lignin

The kappa number contribution of residual lignin can easily be estimated, provided that the Klason lignin content (TAPPI test Method T222 om-83) and the oxidation equivalent of lignin are known (Li and Gellerstedt 1998).

Alternatively, the contribution due to true lignin can be measured directly using a modified procedure (Li 1999), according to which the pulp sample is initially freed from interfering structures, such as HexA, carbonyl groups and double bonds. In this case, the pulp is first treated with mercury acetate, Hg(OAc)₂, which selectively reacts with olefin double bonds forming oxymercurated adducts. At this stage HexA groups are selectively removed from pulp. Sodium borhydride, NaBH₄, is then used to reduce the
oxymercurated structures. Any carbonyl groups present are also reduced to alcohols (Fig.4).

(i) Oxymercuration

(ii) Demercuration

**FIGURE 4.** Reaction scheme for the oxymercuration-demercuration treatment.

Pulp pretreated in this way is then subjected to the standard kappa number determination. The kappa number so obtained, hereafter referred to as the Ox-Dem kappa number, has been found to represent the true residual lignin.

### 1.6.2 Kappa number fraction due to HexA

Several well-established methods are available for the quantitative determination of HexA in kraft pulps. Two of the methods are based on the UV-spectroscopic or chromatographic determination of furan carboxylic acids formed from HexA on hydrolysis by acids (Vuorinen et al. 1999, Jiang et al. 2001).

An alternative method involves the selective hydrolysis of HexA with mercury acetate, followed by oxidation of the hydrolysis product, 4-deoxy-5-oxo-1-threo-hexenuronic acid, with periodate to give β-formyl pyruvic acid, and condensation of the latter with thiobarbituric acid to obtain a coloured form suitable for HPLC separation and detection (Gellerstedt and Li 1996). The reaction sequence is shown in Fig.5:
The condensation product containing a conjugated system of π-electrons has a purple colour with an intensive absorption at about 549 nm and suitable for a direct UV-analysis.

It has also been proposed to use enzymes which operate under very mild conditions instead of acids to hydrolyse the pulp polysaccharides to mono- and oligosaccharides and to quantify HexA-substituted oligosaccharides in the enzymatic hydrolysate by means of high-performance anion-exchange chromatography (HPAEC) (Tenkanen et al. 1995) and capillary electrophoresis (Dahlman et al. 1997).

After the HexA content in pulp has been determined, its contribution to the pulp kappa number can be calculated using the molar oxidation equivalent of 8.6. A quantity of 11.6 μmol HexA in 1g pulp corresponds approximately to 1 kappa number unit. Principal sub-processes involved in the reaction between HexA and acidic permanganate are depicted in Fig. 6 (Li and Gellerstedt 1997):

**FIGURE 5.** Reaction sequence for the HexA analysis.

**FIGURE 6.** Reaction scheme for the oxidation of HexA by the acidic permanganate solution.
1.6.3 **Kappa number fraction due to other non-lignin structures**

When the contents of residual lignin and HexA have been quantified and the corresponding partial contributions to the pulp kappa number calculated, the remaining contribution due to other non-lignin structures can be determined as the difference between the total kappa number and the combined contribution from residual lignin and HexA,

\[
\kappa_{\text{other}} = \kappa_{\text{total}} - (\kappa_{\text{lignin}} + \kappa_{\text{HexA}})
\]

The pulp kappa number is thus fractioned into three components, each corresponding to a specific oxidizable species.

1.7 **Bleached kraft pulps as the objective of the present study**

Theoretically, for both bleached and unbleached pulps, the kappa number can be expressed as the sum of the individual contributions of various permanganate-oxidizable species, including lignin, HexA and the other non-lignin structures, but the pattern of the individual contributions may be different in the two cases because of chemical changes occurring in the pulp during oxygen delignification and bleaching.

This may provide a basis for the quantitative analysis of the chemical composition of bleached kraft pulps after different oxidative treatments. Such information is very useful for a better understanding of the mechanism of bleaching and the optimization of bleaching process.

1.7.1 **Brightness stability of fully bleached kraft pulps**

Brightness and brightness stability are important quality parameters of fully bleached chemical pulps. Therefore, the tendency for fully bleached kraft pulps to lose brightness on storage or when exposed to heat represents a serious problem.

Previously, it has been reported that in bleached kraft pulps the ageing reactions are predominantly related to the transformation of polysaccharides (Chirat and De la Chapelle 1999, Forsskåhl et al. 2000, Granström et al. 2001), an important role being played by the bleaching sequence (Croon et al 1966, Tran 2002, Eiras and Colodette 2005).
In the case of bleached birch pulps, the problem was early recognized and it was suggested that chlorinated extractives present in pulp may slowly release hydrochloric acid on storage. The increased acidity in the pulp would then induce hydrolysis and further conversion of polysaccharides into coloured products (Croon et al. 1966).

More severe environmental regulations initiated a worldwide trend towards the broader use of ECF and TCF technologies for the bleaching of kraft pulps. However, the chlorine-free bleaching does not eliminate the mentioned problems since ECF- and TCF-bleached pulps are also susceptible to thermal yellowing; TCF-bleached pulps are generally less stable to the heat than ECF-bleached pulps. The presence of chlorinated pulp components is negligible or absent in this case and, so far, no mechanism for the thermal yellowing of the modern pulps has been presented.

1.7.2 Specifications of the testing methods

In order to estimate the brightness stability of industrial pulps, accelerated yellowing experiments are usually conducted in the laboratory. Apart from the temperature, the most important external factors influencing the thermal yellowing of bleached chemical pulps are the humidity and the acidity of the pulps (Granström et al. 2001). This means that the experimental conditions may have a strong influence on the final result.

In one of the standard methods, Tappi UM 200, the brightness stability of a pulp is evaluated by keeping the pulp in an oven at 105°C for 4 hours. Under such conditions, chemical reactions requiring water will not take place, and hence, the simulation of e.g. pulp storage will be poor.

The degradation of cellulose is very sensitive to moisture. In order to be representative of natural conditions it is desirable that in an accelerated ageing atmosphere paper should have the same moisture content as in a natural ageing atmosphere. For this reason, after studying the ageing of many papers under different conditions of temperature and relative humidity, 80 °C and 65 % relative humidity have been selected in standard method ISO 5630-3:1996. The ageing time is between 24 and 144 hours. In another test method, Tappi T 260, the pulp sample is kept above boiling water for 2 hours. This method should also
give a good correlation to actual ageing but it suffers from the fact that water-soluble
discoloration products may escape detection. Nor will reversion reactions requiring a
longer time be included in this case.

Simple and convenient laboratory method for the simulation of pulp storage has been
presented by Granström et al (2001). In their work, handsheets of bleached pulp having a
dryness of 92% were produced at a slightly acidic pH and placed in sealed double
polyethylene bags. The bags were placed in a water bath and kept there at the desired
temperature for the chosen length of time.

1.7.3 Factors influencing the brightness stability of fully bleached kraft pulp

From a chemical point of view, the heat-induced yellowing of a bleached chemical pulp is
an extraordinarily complex process, influenced by a large number of interacting factors.
The thermal yellowing of chemical pulps has been reported to be influenced by the
chemical composition of the pulp, i.e. the contents of lignin, hemicellulose, metal ions,
and carbonyl and carboxyl groups (Jappe and Kaustinen 1959, Czepiel 1960, Kleinert and
Marraccini 1966, Rapson and Hakim 1957, Sjöström and Eriksson 1968, Chirat and De la
pH and high humidity accelerate the yellowing (Granström et al. 2001).

Recently, thermal yellowing has been related to the content of hexenuronic acid
(Vuorinen et al. 1999, Tenkanen et al. 2002), pulps with a high HexA content being less
stable to heat treatment. It has also been demonstrated that the brightness reversion of
birch pulp is accompanied by a progressive degradation of hexenuronic acid groups and
that compounds imparting colour to the pulp are to a great extent soluble in water. The
water-soluble fraction of colour contains metal ions together with various low-molecular
fragments (Granström et al 2002).

According to model studies, another possible cause of the thermal yellowing could be
furan compounds such as 2-furanaldehyde (furfural) and 5-hydroxymethylfurfural
(Forsskåhl et al. 2000, Beyer et al. 1999). These may form as the result of hydrolysis of
polysaccharides to sugars and their further transformation via dehydration and cyclization
reaction. Furan dimers and tetramers were, for example, found as the major products
formed during the thermal ageing of a TCF-bleached softwood sulfite pulp (Beyer et al. 1999). In other model experiments, it has been shown, however, that, although hydroxymethylfurfural and furfural may act as colour precursors, other carbohydrate-derived products such as glucuronic acid and, in particular, reductic acid are much more active in yellowing reactions (Theander and Nelson 1988).

Transition metal ions, such as Fe$^{2+}$, Fe$^{3+}$, Cu$^{2+}$ or Mn$^{2+}$, present in bleached pulps in trace amounts, have been associated with a faster brightness loss (Czepiel 1960, Presley et al. 1997, Beyer et al. 1999, Forsskål 2000), but their exact role in the colour formation is not yet known. One feasible explanation is that the metal ions are retained in the pulp due to complexation with carboxy, oxo-carboxy, and especially HexA groups, which are all good chelating agents. During the thermal yellowing reactions, involving a successive degradation of HexA, the chelated metal ions become liberated but they may recombine with reaction products from HexA. Indirect support for this hypothesis comes from the fact that, if the metal ions are removed from pulp without destroying HexA, for example by warm acidic treatment, improved brightness stability is attained, even though the yellowing tendency is not fully eliminated (Granström et al. 2001, Granström et al. 2002). An alternative explanation of the role of metal ions in the thermal yellowing reactions is that they act as Lewis acids, simply accelerating the hydrolysis of polysaccharides, and/or as oxidation catalysts.

1.8 Aims of the present research

The main aim of this work has been to establish the method for quantification of various oxidizable structures, including residual lignin, HexA and other non-lignin structures, in bleached kraft pulps and to study their impact on the pulp brightness and brightness stability. Specific sub-tasks addressed in this study include:

- To establish the Ox-Dem kappa number method as a tool for the quantification of residual lignin in bleached kraft pulps;
- To study the formation, chemical structure and bleaching response of residual and false lignin (HexA and other non-lignin oxidizable structures) by applying the
kappa number fractionation to bleached kraft pulps of different origin taken from different steps of ECF- and TCF-type bleaching sequences;

- To investigate the influence of various oxidizable structures (residual lignin and false lignin) on the brightness and brightness stability of fully bleached chemical pulps;
- To investigate the influence of ECF- and TCF-bleaching on the content of various oxidizable structures in kraft pulps in relation to their brightness stability;
- To explain the mechanism of moist thermal yellowing in bleached kraft pulps based on the studies with industrial pulps and on the studies with the model compounds representing the degradation products of the carbohydrates.
2 EXPERIMENTAL

2.1 Materials

2.1.1 Pulp samples for the kappa number fractionation

Samples of industrial spruce (Picea abies) and birch (Betula papyrifera) kraft pulps of unbleached, oxygen-delignified, and bleached types, taken after each stage in the ODEQP and OQ(OP)Q(PO) sequences respectively were obtained from a Swedish mill. The pulps were sampled at pertinent positions along the process run at time intervals corresponding to the retention times required for each stage. Two samples were taken from each position, mixed and homogenized, thoroughly washed with deionized water, and finally air-dried.

2.1.2 Fully bleached pulp samples for the studies of thermal stability

Samples of fully bleached spruce (Picea abies) and birch (Betula papyrifera) pulps from TCF- and ECF-bleaching sequences were obtained from a Swedish mill. The two spruce pulp samples, hereafter denoted "spruce ECF-1" and "spruce ECF-2", were collected at different times from an ECF bleaching sequence where chlorine dioxide and hydrogen peroxide was used as bleaching chemicals; with a hydrogen peroxide final stage. Two birch samples, denoted "birch ECF-1" and "birch TCF-2", were obtained from ECF and TCF sequences, respectively; in the latter case, hydrogen peroxide was used as a bleaching agent.

Fully bleached eucalyptus (Eucalyptus globulus) pulps from ECF bleaching sequences were taken from a Brazilian mill. The major difference between the “eucalyptus ECF-1” and “eucalyptus ECF-2” samples was in the final bleaching stage, where chlorine dioxide (D) was used for ECF-1 and hydrogen peroxide (P) for ECF-2.

Dissolving pulp from a Swedish mill was lignin-free and extractives-free (acetone) and contained 5.5% hemicellulose.
2.1.3 Pulp samples for the laboratory bleaching

Oxygen delignified hardwood kraft pulp with kappa number 10.4 was received from the mill and stored in a cold room (5 °C). The pulp was used without further washing. The wood species of the pulp was *Eucalyptus globulus* from South America.

2.1.4 Model compounds

Reductic acid, *2,3-Dihydroxy-2-cyclopenten-1-one*, was prepared according to Feather and Harris (1966) with some modifications. The solution of pectin in sulphuric acid was kept in an autoclave at 120°C for 6 hours. The final product, reductic acid, was recrystallized from ethyl acetate.

*trans*-Muconic acid and 2-furancarboxylic acid (FA) were commercial products of analytical grade obtained from Sigma. 5-formyl-2-furancarboxylic acid (FFA) was obtained from TCI Europe.

2.2 Methods

2.2.1 Isolation of residual lignin

The pulp was first freed from extractives by acetone extraction, and then treated with 0.1M HCl in 82:18 v/v dioxane-water solution at 3% pulp consistency at the reflux temperature for 2 hours. The pulp was then filtered and the material collected on the filter rinsed with 82:18 v/v dioxane-water. The filtrate was evaporated at a reduced pressure to remove dioxane. Small doses of water were added repeatedly to keep the solution volume constant and thus prevent any increase in acidity while the dioxane was being removed. Precipitated lignin was then separated by centrifugation, washed with ice-cold water, freeze-dried, and finally re-extracted with pentane overnight in order to remove retained extractives (Gellerstedt et al. 1994). Based on the Klason lignin reduction, the yield of isolated lignin was about 50%.
2.2.2 Peroxide oxidation of isolated lignins

Residual lignins isolated from oxygen-delignified spruce and birch pulps as described above were oxidized by hydrogen peroxide at 80°C for 1 hour according to Gärtner and Gellerstedt (2000). About 60% of the lignin could be recovered after the peroxide treatment, whereas the remainder was degraded into water-soluble fragments.

2.2.3 Extraction of hemicellulose

The first extraction step consisted of extracting 10 grams of air-dried extractives-free pulp with 300 ml of dimethylsulphoxide (DMSO) at room temperature for 24 hours. Subsequently, the DMSO extract was filtered and dissolved hemicelluloses were precipitated by the addition of 1200 ml of ethanol, acidified by acetic acid to pH 4.5.

In the second extraction step, the DMSO-extracted sample was further extracted with 300 ml of 5% aqueous potassium hydroxide solution for 24 hours. The alkaline extract was acidified with acetic acid to pH 4.5 and dissolved hemicelluloses were precipitated by the addition of 1200 ml of ethanol as in the previous case.

The precipitates from both the extraction steps were thoroughly washed 6 times with aqueous ethanol (70 vol. %), 3 times with acetone, and twice with ether, and thereafter air-dried.

2.2.4 Bleaching

Bleaching was done in polyethylene bags placed in a water bath. The starting amount of eucalyptus pulp for each bleaching was 100 g d.w. The conditions for each bleaching sequence are shown in Table 2.

After each oxidation stage in the TCF- and ECF- bleaching sequences, 10 g of pulp was withdrawn and analysed with respect to the contents of lignin, HexA and other oxidizable structures. The brightness and viscosity were also monitored along each bleaching sequence.
2.2.5 Impregnation of dissolving pulp with model compounds

Handsheets of dissolving pulp with a grammage of ~70 g/m² were prepared according to SCAN-CN 26:99, except for pH adjustment and addition of EDTA as in SCAN-CN 11:95. Subsequently, these were impregnated with either of the compounds FA, FFA or RA, dissolved in ethanol, at amounts of 28.9, 34.7 and 30.1µmol/g pulp respectively. In experiments with metal ions present at the same time, these were added as aqueous solutions of either FeCl₃·6H₂O or FeSO₄·7H₂O to give 111 and 122 mg/kg of pulp, as Fe(III) and Fe(II), respectively. The doped paper sheets were kept for 24 hours in a conditioning room (23°C, 50% humidity) to reach equilibrium (8 % moisture content) before being subjected to accelerated ageing.

2.2.6 Accelerated ageing of pulp samples

Accelerated ageing of pulp handsheets with a grammage of 70 g/m² and a moisture content of 8 % was carried out in sealed double polyethylene bags in a water bath at 70°C.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Charge</th>
<th>pH</th>
<th>Temperature (°C)</th>
<th>Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>ECF-bleaching:</strong>&lt;br&gt;D₀(EP)D</td>
<td>0.2 x kappa number a Cl</td>
<td>2-3</td>
<td>60</td>
<td>45</td>
</tr>
<tr>
<td>(EP)</td>
<td>0.3 % H₂O₂&lt;br&gt;1.5% NaOH, 0.2% MgSO₄</td>
<td>11</td>
<td>70</td>
<td>60</td>
</tr>
<tr>
<td><strong>TCF-bleaching:</strong>&lt;br&gt;Q₁(OP)Q₂(PO)</td>
<td>0.5-1.0-1.5 % a Cl</td>
<td>4-5</td>
<td>70</td>
<td>120</td>
</tr>
<tr>
<td>Q₁, Q₂</td>
<td>0.2 % EDTA&lt;br&gt;1.12% H₂SO₄</td>
<td>4-5</td>
<td>70</td>
<td>60</td>
</tr>
<tr>
<td>(OP)</td>
<td>0.5 % H₂O₂&lt;br&gt;1.0% NaOH&lt;br&gt;0.3% MgSO₄</td>
<td>11</td>
<td>105</td>
<td>60</td>
</tr>
<tr>
<td>(PO)₁,₀&lt;br&gt;(PO)₂,₀&lt;br&gt;(PO)₃,₀</td>
<td>1.0–2.0–3.0 % H₂O₂&lt;br&gt;1% NaOH&lt;br&gt;0.3% MgSO₄</td>
<td>11</td>
<td>110</td>
<td>120</td>
</tr>
</tbody>
</table>
with residence times from 2 to 9 days. The pH-value of each handsheet was adjusted to pH=4.5 with sulphuric acid in the low consistency solution prior to the sheet-making.

2.3 Analytical determinations

2.3.1 Oxidation equivalents

Isolated lignins and a number of model compounds were subjected to oxidation with permanganate under the same conditions as in the standard kappa number determination. The amount of permanganate consumed was determined using inverse titration, whereby the excess permanganate was first reduced by adding potassium iodide and the iodine released was then titrated with sodium thiosulphate. The consumption values obtained were converted into oxidation equivalents assuming that the following reduction half-reaction takes place in an acidic environment,

\[
\text{MnO}_4^- + 8\text{H}^+ + 5e^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}
\]

where \(e^-\) stands for an electron supplied by the reducing reagent.

Under practical conditions, it should be noted that, due to kinetic factors and the low selectivity of permanganate as an oxidant, the oxidation of many organic compounds will hardly obey a stoichiometric equation, and hence, non-integral values of oxidation equivalent are not uncommon.

In the case of lignins, the oxidation equivalent is counted per phenylpropane unit and the final result has to be normalized to 50% consumption in order to permit a comparison with the kappa number.

2.3.2 Kappa number, Ox-Dem kappa number, Klason lignin, and viscosity

The standard and Ox-Dem kappa numbers for pulps were determined according to the SCAN-C1:00 standard and a procedure described by Li and Gellerstedt (2002), respectively.
The Klason lignin content was determined according to the TAPPI Test Method T222 om-83 (1983). The viscosity of the pulps was measured according to SCAN-test method CM 15:99.

2.3.3  $^{31}$P-NMR analysis of lignin

After preliminary derivatization of isolated lignins with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane, $^{31}$P-NMR analysis with a 90-degree pulse angle, an inverse gated proton decoupling and a delay time of 10 seconds was used for the identification and quantification of hydroxyl and carboxyl groups (Granata and Argyropoulos 1995).

2.3.4  Molecular weight distribution by GPC

Gel permeation chromatography (GPC) of lignin was carried out at 25°C using a Waters system with a series of 3 Styrage columns (1000Å, 500Å, 100Å). As a mobile phase, a 90:10 v/v dioxane/water mixture was used. The flow rate was 0.6 mL/min. The UV-absorption at $\lambda = 280$ nm was determined.

2.3.5  HexA analysis

The HexA content of pulps was determined using the method described by Gellerstedt and Li (1996; see also Section 1.6.2).

2.3.6  Carbohydrate analysis by gas chromatography

The carbohydrate content of the pulps was determined by converting the monosaccharides contained in filtrates from the Klason lignin analysis into corresponding alditol acetates and analysing the latter by gas chromatography (Theander and Westerlund 1986). The GC analysis was carried out using a Hewlett-Packard 6890 instrument equipped with a BPX 70 column (12m, 0.32 mm, 0.25 μm film thickness). Split injection was used. The injector was kept at 230°C and the detector at 250°C. The oven temperature was 215°C. Helium was used as the carrier gas; the flow rate was 0.9 ml/min.
2.3.7 Brightness

Standard 70 g/m² laboratory sheets were prepared from pulp samples after adjustment of pH to 4.5. The reflectance of sheets was measured according to the two-background method (SCAN-Forsk 1976) before and after yellowing using a Varian UV-Vis-spectrophotometer equipped with an integrating sphere. The reflectance values at 457 nm were reported as the brightness (%). The brightness loss (units) was expressed as the difference between the brightness before ageing and the brightness after ageing.

ISO brightness was determined according to ISO 2470 standard method.

2.3.8 Analysis of 2-furancarboxylic acid (FA), 5-formyl-2-furancarboxylic (FFA) acid and reductic acid (RA) by GC/MS and HPLC

FFA, FA and RA were detected by ethanol extraction of aged pulp samples followed by evaporation, trimethylsilylation and GC-FID or GC/MS analysis using a DB-5MS column with a temperature program from 100°C to 160°C at a rate of 5°C/min. The FA and FFA formed during the thermal ageing were quantified by a HPLC method. A Waters system with two Waters 510 pumps, a Waters 717 plus Autosampler, a Waters Model 996 photodiode array detector and a Millenium 32 software for operation control and data processing were used. Approximately 30 mg of pulp sample was extracted with deionised water for 24 hours. After filtration, the aqueous extracts were injected into the HPLC system using benzoic acid as internal standard. The separation was carried out on an ODS column (HICHROM H5ODS-3519) with a size of 4.6x150 mm. An isocratic mobile phase of water–acetonitrile (70:30 v/v) was used with a flow-rate of 1 mL/min. Detection was by UV absorption.
3 CHEMICAL TRANSFORMATIONS OF RESIDUAL LIGNIN DURING BLEACHING (PAPER I)

3.1 Structural changes in lignin during oxidative treatment

Since lignin is of major interest in the kappa number determination, chemical changes in the lignin structure as a result of oxidative treatments have been a primary concern. In particular, the changes in the hydroxyl and carboxyl group contents and in the molecular size were monitored using $^{31}$P NMR and GPC analysis, respectively (see Section 2.3).

Both oxygen delignification and peroxide bleaching have been shown to have a significant effect on the hydroxyl and carboxyl group contents of the treated lignins, with the number of phenolic hydroxyl groups steadily decreasing and the number of carboxyl groups increasing during the course of the treatment. A minor decrease could also be seen in the content of aliphatic hydroxyl groups (see Table 3).

<table>
<thead>
<tr>
<th>TABLE 3. Contents of hydroxyl and carboxyl groups in isolated kraft lignins before and after oxidative treatment.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lignin sample</td>
</tr>
<tr>
<td>Spruce kraft residual lignin</td>
</tr>
<tr>
<td>– unbleached</td>
</tr>
<tr>
<td>– O$_2$-delignified</td>
</tr>
<tr>
<td>– OP-oxidized</td>
</tr>
<tr>
<td>Birch kraft residual lignin</td>
</tr>
<tr>
<td>– unbleached</td>
</tr>
<tr>
<td>– O$_2$-delignified</td>
</tr>
<tr>
<td>– OP-oxidized</td>
</tr>
</tbody>
</table>

These observations suggest conclusively that the aromatic rings of lignin containing phenolic hydroxyl groups undergo a partial degradation in the oxygen stage, followed by further oxidation in the peroxide stage. As a result, new structures containing carboxyl groups emerge.
It is interesting that, despite the significant changes in the chemical structure of the oxidized lignins, their molecular weight distribution remains almost unaffected, as shown in Figure 7.

![Figure 7. GPC spectra of lignin isolated from unbleached kraft pulp (---); and of lignin isolated from O-delignified kraft pulp before (---) and after (-----) oxidation with alkaline hydrogen peroxide.](image)

The peroxide oxidation of the isolated O-stage lignin results in some yield loss due to the formation of water-soluble material, but it has no major effect on the molecular weight distribution of the remaining lignin. Both spruce and birch lignins give similar results, except that spruce lignins have somewhat broader distributions with a slightly shorter retention time, and thus a somewhat higher molecular weight.

### 3.2 Consumption of permanganate by oxidized lignin structures

The changes occurring in the lignin in an oxidative environment should lead to a decrease in the kappa number. This has been confirmed by measurements of permanganate consumption for model compounds representing the oxidized lignin species (see Table 4 and Fig.3). In all cases, the structures containing oxidized aromatic rings revealed consistently lower permanganate consumption values than two reference structures with intact aromatic rings.
### TABLE 4. Oxidation equivalents of the model compounds studied.

<table>
<thead>
<tr>
<th>Model compound</th>
<th>Structural significance in lignin</th>
<th>Molar oxidation equivalent</th>
</tr>
</thead>
<tbody>
<tr>
<td>trans-muconic acid</td>
<td>oxidized aromatic ring</td>
<td>10.8</td>
</tr>
<tr>
<td>(E)-2-methyl-2-butene-dioic acid*</td>
<td>“</td>
<td>9.2</td>
</tr>
<tr>
<td>2-furoic acid</td>
<td>“</td>
<td>4.2</td>
</tr>
<tr>
<td>α-ketoglutaric acid*</td>
<td>“</td>
<td>2.0</td>
</tr>
<tr>
<td>crotonaldehyde*</td>
<td>unspecific oxidation</td>
<td>7.7</td>
</tr>
<tr>
<td>DL-glyceric aldehyde*</td>
<td>“</td>
<td>2.4</td>
</tr>
<tr>
<td>DL-glyceric acid*</td>
<td>“</td>
<td>0.0</td>
</tr>
<tr>
<td>2-methoxyphenol*</td>
<td>unoxidized reference</td>
<td>15.3</td>
</tr>
<tr>
<td>2,6-dimethoxyphenol*</td>
<td>“</td>
<td>15.3</td>
</tr>
</tbody>
</table>

*After Li (1999)

The same tendency can be traced for isolated lignins subjected to oxygen delignification and peroxide oxidation: the permanganate consumption shows a steady decrease as a result of the lignin oxidation (see Fig. 8).

![Figure 8](image-url)

**FIGURE 8.** Influence of oxygen delignification and peroxide oxidation on the permanganate consumption by residual lignin

In Figure 8 the permanganate consumption is expressed as the volume of 20 mM KMnO₄ solution consumed per gram of lignin, since the phenylpropane unit can no longer be used.
as a structural block representing the lignin because of the rupture of some of the aromatic rings.

Unbleached spruce kraft lignins consume about 640 mL/g of permanganate, i.e. approximately 11.7 equivalents of KMnO$_4$ per phenylpropane unit. Oxygen delignification leads to a decrease of 17% in the oxidation equivalent of lignin, and the subsequent peroxide oxidation leads to a further decrease of 17%.

Unbleached birch kraft lignins consume about 470 mL/g of permanganate, i.e. 9.4 equivalents of KMnO$_4$ per phenylpropane unit. Oxygen delignification leads to a decrease of 28% in the oxidation equivalent of lignin, and the subsequent peroxide oxidation leads to a further decrease of 16%.

The results obtained provide a proof that birch kraft lignin is more susceptible to oxygen delignification than spruce kraft lignin, well in accord with the fact that syringyl units are more readily oxidized than guaiacyl units (Kratzl et al. 1974).

The fact that the overall permanganate consumption by birch kraft lignins is consistently lower than that by spruce kraft lignins can be attributed to a “contamination” of the isolated lignins by structures of carbohydrate origin, probably in the form of furfural polymers. This hypothesis is indirectly supported by reports that isolated lignins from birch kraft pulps have unusually low methoxyl group content (less than 9.5 per 100 carbons) (Gellerstedt et al. 1994).

3.3 Ox-Dem kappa number and oxidation equivalent of lignin

The contribution of the true residual lignin to the pulp kappa number can be estimated from the Klason lignin content, provided that the oxidation equivalent of lignin is known. Lignin from unbleached kraft pulps has an oxidation equivalent of about 11.6 per phenylpropane unit (Li and Gellerstedt 1998). However, the situation becomes more complex if bleaching is applied, since the partial oxidative degradation of lignin during bleaching decreases its oxidation equivalent. This means that an independent determination of the oxidation equivalent after each bleaching stage is necessary before the above method can be applied.
Another accurate method for the quantitative analysis of lignin in unbleached pulps is the determination of the Ox-Dem kappa number (see Section 2.4.2). Before extending this method to the case of bleached pulps, it was crucial to verify that the Ox-Dem treatment has no significant effect on the oxidation equivalent of oxidized lignin. The experimental data are summarized in Table 5.

The values obtained are in satisfactorily good agreement with each other, with the exception of the $\alpha$-keto-carboxylic acid which does not, however, give any significant contribution to the Ox-Dem value because of the low content of this type of structure in lignin.

The predominant lignin structures reacting with permanganate after Ox-Dem treatment are aromatic rings and, in the case of bleached pulps, conjugated carboxyl groups, presumably of the muconic acid type.

**TABLE 5.** Oxidation equivalents for isolated lignins and model compounds before and after Ox-Dem treatment.

<table>
<thead>
<tr>
<th>Lignins</th>
<th>Permanganate consumption [mL/g lignin]</th>
<th>Molar oxidation equivalent</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Regular</td>
<td>Ox-Dem</td>
</tr>
<tr>
<td>Spruce lignin</td>
<td></td>
<td></td>
</tr>
<tr>
<td>– unbleached</td>
<td>640</td>
<td>660</td>
</tr>
<tr>
<td>– O$_2$-delignified</td>
<td>530</td>
<td>540</td>
</tr>
<tr>
<td>– OP-oxidized</td>
<td>420</td>
<td>450</td>
</tr>
<tr>
<td>Birch lignin</td>
<td></td>
<td></td>
</tr>
<tr>
<td>– unbleached</td>
<td>470</td>
<td>470</td>
</tr>
<tr>
<td>– O$_2$-delignified</td>
<td>340</td>
<td>360</td>
</tr>
<tr>
<td>– OP-oxidized</td>
<td>265</td>
<td>290</td>
</tr>
<tr>
<td>Model compounds</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$trans$-muconic acid</td>
<td>10.8</td>
<td>11.5</td>
</tr>
<tr>
<td>(E)-2-methyl-2-butenedioic acid*</td>
<td>9.2</td>
<td>9.0</td>
</tr>
<tr>
<td>$\alpha$-ketoglutaric acid*</td>
<td>2.0</td>
<td>0.1</td>
</tr>
</tbody>
</table>

*After Li (1999).
3.4 Determination of Ox-Dem kappa number for bleached kraft pulps

To appreciate the practical significance of the application of the Ox-Dem kappa number method of assessing structural changes occurring in residual lignin during bleaching, two types of industrial pulp, a spruce pulp bleached with a ODEQP sequence and a birch pulp bleached with a OQ(OP)Q(PO) sequence, were subjected to the standard and Ox-Dem kappa number determinations and the results were compared (see Table 6). Both pulps had been produced in a Swedish mill and bleached to full brightness. In addition to the kappa number measurements, the Klason lignin content was also determined after each bleaching stage.

**TABLE 6.** Kappa number, Ox-Dem kappa number, and Klason lignin content for spruce and birch kraft pulps.

<table>
<thead>
<tr>
<th>Pulp sample</th>
<th>Standard kappa number</th>
<th>Ox-Dem kappa number</th>
<th>Klason lignin content [%]</th>
<th>KMnO₄ consumption [mL/g]*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spruce pulp</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>– unbleached</td>
<td>22.5</td>
<td>17.2</td>
<td>3.1</td>
<td>560</td>
</tr>
<tr>
<td>– O₂-delignified</td>
<td>10.7</td>
<td>4.6</td>
<td>1.0</td>
<td>460</td>
</tr>
<tr>
<td>– ODE</td>
<td>3.3</td>
<td>1.6</td>
<td>0.4</td>
<td>400</td>
</tr>
<tr>
<td>– ODEQP</td>
<td>1.6</td>
<td>0.8</td>
<td>0.3</td>
<td>270</td>
</tr>
<tr>
<td>Birch pulp</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>– unbleached</td>
<td>13.8</td>
<td>8.1</td>
<td>1.7</td>
<td>480</td>
</tr>
<tr>
<td>– O₂-delignified</td>
<td>9.6</td>
<td>3.2</td>
<td>0.8</td>
<td>400</td>
</tr>
<tr>
<td>– OQ(OP)</td>
<td>7.3</td>
<td>2.2</td>
<td>0.6</td>
<td>370</td>
</tr>
<tr>
<td>– OQ(OP)Q(PO)</td>
<td>4.6</td>
<td>0.8</td>
<td>0.3</td>
<td>270</td>
</tr>
</tbody>
</table>

*Obtained by dividing the permanganate consumption in the Ox-Dem method by the Klason lignin content.

Once again, a steady decrease in the permanganate consumption is observed in the sequence from unbleached to oxygen-delignified to fully bleached pulps. However, the absolute values differ considerably from those obtained for isolated lignins (cf. Table 5). This difference might be caused by a large error in the determination of the Klason lignin content for bleached pulps, or by certain structural differences between the Klason lignin and the residual lignin isolated by acid hydrolysis.
It should be emphasized that the Ox-Dem kappa number remains a valid characteristic of the lignin content, irrespective of pulp type. Indeed, as can be seen in Fig. 9, there is a linear correlation between the Ox-Dem kappa number and the Klason lignin content. Conversely, the standard kappa number may be strongly affected by the presence of false lignin, the error being especially large for fully bleached pulps (cf. Table 6). The slight deviation from linearity in Fig. 9 is explained by the decrease in the oxidation equivalent of lignin discussed previously.

The data in Table 6 show that the actual amounts of lignin remaining after the complete bleaching are quite similar in the two pulps despite the different bleaching sequences used. At the same time, the corresponding standard kappa number of the birch pulp is noticeably greater than that of the spruce pulp due to a higher HexA content. This agrees with finding that HexA is not affected by oxygen and peroxide bleaching but readily reacts with permanganate (Vuorinen et al. 1999, Tenkanen et al. 1999, Li and Gellerstedt 1997).
4 QUANTITY AND BLEACHING RESPONSE OF FALSE LIGNIN DURING ECF- AND TCF-BLEACHING (PAPER II)

4.1 Fractionation of kappa number for spruce and birch bleached kraft pulps

Fractionation of the pulp kappa number permits the changes in the amounts of residual lignin, HexA and other non-lignin structures to be monitored along a bleaching sequence.

The results of such a kappa number fractionation are shown for a number of bleached kraft pulps in Table 7; the contribution of residual lignin being determined as the Ox-Dem kappa number.

**TABLE 7.** Fractionation of the pulp kappa number for spruce and birch kraft pulps bleached according to the ODEQP and OQ(OP)Q(PO) sequences, respectively.

<table>
<thead>
<tr>
<th>Pulp type</th>
<th>Pulp kappa number</th>
<th>Kappa number contributions</th>
<th>False lignin</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Residual lignin</td>
<td>HexA</td>
</tr>
<tr>
<td>Spruce kraft pulp</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Unbleached</td>
<td>22.5</td>
<td>17.2</td>
<td>1.3</td>
</tr>
<tr>
<td>O\textsubscript{2}-delignified</td>
<td>10.7</td>
<td>4.6</td>
<td>1.2</td>
</tr>
<tr>
<td>OD-bleached</td>
<td>5.2</td>
<td>2.3</td>
<td>0.8</td>
</tr>
<tr>
<td>ODE-bleached</td>
<td>3.3</td>
<td>1.6</td>
<td>0.8</td>
</tr>
<tr>
<td>ODEQ-bleached</td>
<td>2.3</td>
<td>1.4</td>
<td>0.7</td>
</tr>
<tr>
<td>ODEQP-bleached</td>
<td>1.6</td>
<td>0.8</td>
<td>0.7</td>
</tr>
<tr>
<td>Birch kraft pulp</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>unbleached</td>
<td>13.8</td>
<td>8.1</td>
<td>4.7</td>
</tr>
<tr>
<td>O\textsubscript{2}-delignified</td>
<td>9.6</td>
<td>3.2</td>
<td>4.3</td>
</tr>
<tr>
<td>OQ-bleached</td>
<td>9.4</td>
<td>3.0</td>
<td>4.3</td>
</tr>
<tr>
<td>OQ(OP)-bleached</td>
<td>7.3</td>
<td>2.2</td>
<td>3.7</td>
</tr>
<tr>
<td>OQ(OP)Q-bleached</td>
<td>7.0</td>
<td>1.9</td>
<td>3.7</td>
</tr>
<tr>
<td>OQ(OP)Q(PO)-bleached</td>
<td>4.6</td>
<td>0.8</td>
<td>3.0</td>
</tr>
</tbody>
</table>
As can be seen in Table 7, HexA comes from the cooking stage and its amount decreases during the oxygen delignification and subsequent bleaching stages. It has been reported that the actual HexA content after each stage depends on the wood species and on the type of bleaching operation applied (Buchert et al. 1995, Teleman et al. 1995, Bergnor-Gidnert et al. 1998).

ECF-bleached spruce pulp contains a smaller amount of HexA than the TCF-bleached birch pulp, since most of the HexA is eliminated by chlorine dioxide bleaching.

In the bleached birch kraft pulp, HexA is the major contributor to the kappa number and its contribution remains significant throughout the bleaching sequence. This agrees with reports that HexA is resistant to oxygen or hydrogen peroxide treatment (Tenkanen et al. 1999, Ragnar 2001).

Other non-lignin structures are formed both during the cooking and during the subsequent oxygen-delignification of the pulp. In the case of the unbleached spruce kraft pulp, the contribution of these structures to the kappa number is about 4.0 kappa units, and it increases to 4.9 kappa units following the oxygen delignification. In the case of unbleached birch kraft pulp, the corresponding contribution is only about 1 kappa unit, and it increases to 2.1 kappa units following the oxygen delignification.

It should also be pointed out that, in comparison with the TCF bleaching sequence, the ECF bleaching sequence was more efficient in removing the other non-lignin structures consisting of carbonyl groups and/or double bonds.

4.2 **Bleaching response of false lignin in spruce and birch kraft pulps**

Since false lignin contains oxidizable structures, it can probably be attacked by many bleaching chemicals. By comparing the amount of false lignin before and after each bleaching stage, the efficiency of a given operation with respect to the removal of false lignin can be judged. Furthermore, by fractionation of the kappa number, further information can be obtained about differences in the bleaching response between true residual lignin and false lignin components, including HexA and other non-lignin structures.
The bleaching responses of lignin, HexA and other non-lignin structures, expressed as the percentage reduction in the respective kappa number fractions, are compared in Figure 10.

![Graphs showing percentage reduction in kappa number for lignin, HexA, and other structures](image)

**FIGURE 10.** Percentage reduction in the contents of residual lignin, HexA and other structures in spruce (a) and birch (b) kraft pulps bleached according to the ODEQP and OQ(OP)Q(PO) sequences, respectively.

In this figure, it can be seen that oxygen is quite an efficient delignification agent. Although the standard kappa numbers indicate only about 52 and 30% reduction for softwood and hardwood pulps, respectively, the actual degree of delignification is, in fact, as high as 73 and 60%, respectively. Further bleaching with either chlorine dioxide or hydrogen peroxide brings the amount of lignin down to approximately 0.8 kappa units for the fully bleached pulps.

The removal of lignin seems to be much more efficient in the softwood case, since both oxygen and chlorine dioxide oxidation led to a greater lignin removal than in the hardwood case in which two oxygen stages (the second with peroxide reinforcement) were employed. In the former case, a total amount of lignin corresponding to 15.6 kappa units was eliminated whereas from the birch pulp, only 5.9 kappa units of lignin were removed. This suggests that the softwood pulp can be subjected to a milder final peroxide bleaching stage than the hardwood pulp in order to reach full brightness.
The amounts of other non-lignin structures increase slightly during the oxygen delignification and then decrease again after the subsequent bleaching with either chlorine dioxide or hydrogen peroxide; the chlorine dioxide and subsequent extraction stages being the most efficient in removing the other structures.

Direct oxidative elimination of HexA does not appear to be possible with either oxygen or hydrogen peroxide. It is only in the chlorine dioxide stage that HexA can actually be oxidized (Bergnor-Gidnert et al. 1989), resulting in a noticeable decrease in the HexA/xylan ratio as shown in Fig. 11. The decrease in HexA content during the D-stage depends on the bleaching conditions (Törngren and Ragnar 2002).

In the other stages, only a moderate elimination of HexA is observed (Table 7). Such behaviour can probably be attributed to the extraction of a portion of the HexA-bound xylan under the alkaline conditions prevailing during the oxygen delignification or in the bleaching with hydrogen peroxide (Colodette et al. 2002). The deviation in the ratio of HexA to xylan from a constant in Fig.11 after these stages suggests that the distribution of HexA groups in the xylan chain is not homogeneous.

Figure 11. Changes in the HexA/xylose ratio along the ODEQP and OQ(OP)Q(PO) bleaching sequences for (a) spruce and (b) birch kraft pulps, respectively.
5 CHEMICAL STRUCTURE OF FALSE LIGNIN (PAPER III)

5.1 Extraction studies

Unbleached and especially oxygen-delignified pulps contain substantial amounts of false lignin, which can contribute 5-6 units to the pulp kappa number, with 4 to 5 units being contributed by the other non-lignin structures.

To shed some light on the chemical structure of different false lignin components, extraction studies were performed. Unbleached and oxygen-delignified spruce kraft pulps which contained the largest amounts of these structures were chosen for the extraction experiment. Since the hemicellulose component of kraft pulps was thought to be the major source of the false lignin structures, the work was focused on the extraction of xylan.

Successive extractions of the pulps with DMSO and 5% KOH were applied using a technique described by Sjöström and Enström (1967). In order to determine the yields of the different extraction steps and to quantify changes in the chemical composition of the pulp, both the extracted pulps and the extracts were analysed with regard to their sugar composition and Klason lignin content. The results are summarized in Table 8.

The chemical analysis of the extracts confirmed that xylan is extracted fairly specifically by both DMSO and KOH, only xylose and arabinose were detected by carbohydrate analysis. The low recovery of Klason lignin from the DMSO extracts can be explained by incomplete precipitation of the lignin by ethanol because of its high solubility in organic solvents.
**Table 8.** Extraction yields (per cent) of lignin and different sugars from pulp residues and extracts after successive extraction of unbleached and O₂-delignified kraft pulps with DMSO and 5% KOH.

<table>
<thead>
<tr>
<th></th>
<th>Unbleached kraft pulp</th>
<th>O₂-delignified kraft pulp</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Original pulp</td>
<td>Original pulp</td>
</tr>
<tr>
<td></td>
<td>Pulp residue</td>
<td>Pulp residue after</td>
</tr>
<tr>
<td></td>
<td>DMSO extraction</td>
<td>DMSO extraction</td>
</tr>
<tr>
<td></td>
<td>DMSO extract</td>
<td>KOH extraction</td>
</tr>
<tr>
<td></td>
<td>KOH extract</td>
<td></td>
</tr>
<tr>
<td>Recovered yield*</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Klason lignin**</td>
<td>3.0</td>
<td>2.6</td>
</tr>
<tr>
<td>Arabinose**</td>
<td>1.0</td>
<td>0.9</td>
</tr>
<tr>
<td>Xylose**</td>
<td>12.3</td>
<td>9.6</td>
</tr>
<tr>
<td>Mannose**</td>
<td>5.9</td>
<td>6.3</td>
</tr>
<tr>
<td>Galactose**</td>
<td>0.5</td>
<td>-</td>
</tr>
<tr>
<td>Glucose**</td>
<td>73.5</td>
<td>76.1</td>
</tr>
<tr>
<td>Total sugars**</td>
<td>93.2</td>
<td>92.9</td>
</tr>
</tbody>
</table>

* based on the original unextracted pulp;  
** based on the corresponding pulp residue or extract.

### 5.2 Effect of extraction on the kappa number

Changes in the kappa number and in the amounts of lignin and false lignin components in the course of DMSO/alkali extraction have also been quantified. The results are presented in Table 9.
TABLE 9. Amounts of different oxidizable structures in DMSO/alkali extracted kraft pulps and their contributions to the pulp kappa number.

<table>
<thead>
<tr>
<th>Spruce kraft pulp</th>
<th>Kappa number</th>
<th>Lignin</th>
<th>HexA</th>
<th>other structures</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Kappa number contribution</td>
<td>Klason lignin content (%)</td>
<td>KMnO₄ consumption (ml/g)</td>
</tr>
<tr>
<td>Unbleached (extractive-free)</td>
<td>21.8</td>
<td>17.2</td>
<td>3.0</td>
<td>570</td>
</tr>
<tr>
<td>Residue after DMSO extraction</td>
<td>18.7</td>
<td>15.4</td>
<td>2.8</td>
<td>550</td>
</tr>
<tr>
<td>Residue after DMSO+5%KOH</td>
<td>17.0</td>
<td>14.5</td>
<td>2.4</td>
<td>600</td>
</tr>
<tr>
<td>O₂-delignified (extractive-free)</td>
<td>10.2</td>
<td>4.8</td>
<td>1.0</td>
<td>480</td>
</tr>
<tr>
<td>Residue after DMSO extraction</td>
<td>8.3</td>
<td>4.5</td>
<td>0.86</td>
<td>520</td>
</tr>
<tr>
<td>Residue after DMSO+5%KOH</td>
<td>7.5</td>
<td>4.3</td>
<td>0.78</td>
<td>550</td>
</tr>
</tbody>
</table>

(a) Determined as the Ox-Dem kappa number;
(b) Calculated by dividing the permanganate consumption (in millilitres of 20 mM KMnO₄) measured according to the Ox-Dem kappa number method by the Klason lignin content (in grams);
(c) Based on the molar oxidation equivalent of 8.6 (Li and Gellerstedt 1997);
(d) Calculated as explained in Section 1.6.

As can be seen in this table, the oxidation equivalents of the residual lignin increase as result of the DMSO/alkali extraction of the pulp samples. This suggests that the oxidized lignin fraction, which has a lower oxidation equivalent, is preferentially removed by extraction. Such behavior agrees with the previous conclusion that oxidized lignin has a higher content of carboxylic groups and is more fragmented than the original lignin (see also Section 3). Both these factors render the oxidized lignin fraction more soluble.

Based on the data presented in Tables 8 and 9, the extraction yields of xylan, Klason lignin, and false lignin components have been calculated and summarized in Table 10.
TABLE 10. Comparative extraction yields of xylan, Klason lignin, HexA and the other structures.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Extraction yield (%)</th>
<th></th>
<th></th>
<th>Other non-lignin structures</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Xylan</td>
<td>Klason lignin</td>
<td>HexA</td>
</tr>
<tr>
<td>Unbleached / DMSO</td>
<td>24</td>
<td>16</td>
<td>32</td>
<td>17</td>
</tr>
<tr>
<td>Unbleached / KOH</td>
<td>30</td>
<td>13</td>
<td>21</td>
<td>25</td>
</tr>
<tr>
<td>O₂-delignified / DMSO</td>
<td>23</td>
<td>17</td>
<td>25</td>
<td>31</td>
</tr>
<tr>
<td>O₂-delignified / KOH</td>
<td>32</td>
<td>12</td>
<td>30</td>
<td>10</td>
</tr>
</tbody>
</table>

In both the unbleached and oxygen-delignified kraft pulps, about 24% of the xylan contained in the pulp was extracted with DMSO and another 30% with potassium hydroxide. These extraction yields are close to those reported by Sjöström and Enström (1967) for pine kraft pulp.

The fact that DMSO/alkali extraction removes xylan and the other non-lignin structures in similar proportions also indicates that most of these other structures originate from the hemicellulose.

5.3 NMR- and UV-spectroscopic analysis of extracted species

Extracts from both the extraction steps described in the previous section were analyzed by NMR and UV-spectroscopy. The presence of HexA in the alkaline extracts was confirmed by the signals at 5.3 and 5.8 ppm in the ¹H NMR spectra (see Figure 12). At a higher resolution, some aromatic structures giving a broad signal in the 6.5 to 8.0 ppm region can also be detected.
FIGURE 12. $^1$H NMR spectra of alkaline extracts from (a) unbleached and (b) oxygen-delignified spruce kraft pulps.

The UV-spectra of both the DMSO and alkaline extracts from unbleached and oxygen-delignified pulps are shown in Figure 13. The absorbance maxima characteristic of HexA (at $\lambda = 235$ nm) and of lignin (at $\lambda = 280$ nm) are present.

The third region with a maximum at about 350 nm can also be distinguished, but since many aromatic and non-aromatic organic compounds with conjugated double bonds can absorb in this region, no assignment of this last peak has been made.
5.4 Chemical origin of the other non-lignin structures

As shown in the foregoing sections, a substantial fraction of the kappa number of bleached kraft pulps comes from other non-lignin structures, which represent a part of the false lignin. Although the exact composition of this part of the false lignin is as yet unknown, it probably represents a complex mixture of unsaturated compounds containing double bonds, and aldehyde and/or α-keto-carboxy groups as its structural fragments (Li and Gellerstedt 2002). Such structures are formed during the kraft cooking and during the oxygen-delignification stage. Due to the peeling of the polysaccharide chain under the alkaline conditions an aldehydic end group is formed after each cleavage of the glycosidic linkage. The termination of the peeling reaction involves a number of reaction steps where double bonds, carbonylic, and finally, carboxylic acid groups are formed as shown in Figure 14.

![Figure 14](image_url)

**Figure 14.** Termination of the peeling reaction in polysaccharides. R’ = polysaccharide chain, R = CH₂OH (cellulose and glucomannans) or H (xylan).

In the presence of oxygen during the oxygen-delignification stage carbonyl and carboxyl groups can be introduced into cellulose and hemicelluloses chains (Sjöström 1993e). The examples of the oxidized structures formed in monomeric sugar units are shown in Figure 15:

![Figure 15](image_url)

**Figure 15.** Examples of chemical structures formed in sugar unit by oxidative action of oxygen. R’, R” = polysaccharide chains, R = CH₂OH or H.
6 INFLUENCE OF RESIDUAL AND FALSE LIGNIN ON THE PULP BRIGHTNESS AND BRIGHTNESS STABILITY (PAPER II, IV)

Independent determinations of the standard kappa number, Ox-Dem kappa number, and HexA content make it possible to compare the different pulp properties with various oxidizable structures present in pulp. The present study was focused on the brightness and the brightness stability of ECF- and TCF- bleached chemical pulps.

6.1 Role of residual lignin

6.1.1 Influence on the brightness

The main purpose of bleaching is to increase the brightness of the pulp. Traditionally, any residual lignin remaining in pulp after the cooking and bleaching is considered to be detrimental to the brightness. Since the Ox-Dem kappa number proved to be a reliable method of determination of the residual lignin content in bleached pulps, the dependence of the pulp brightness on lignin content can be demonstrated by plotting the brightness against the Ox-Dem kappa number as shown in Figure 16 for spruce and birch kraft pulps (see Table 12 for the chemical composition). The correlation is fairly obvious and is independent on the pulp type.

![Figure 16. Brightness vs. Ox-Dem kappa number for spruce and birch kraft pulps bleached according to the ODEQP and Q(OP)Q(PO) sequence, respectively.](image-url)
Another example where kappa number fractionation gives a better explanation of pulp properties is shown in Table 11. Here six fully bleached pulp samples from different wood species are shown. All of them have brightness values of about 90, but the kappa number varies from 0.3 to 4.1. The Ox-Dem kappa number shows that all the pulp samples contained small amounts of residual lignin, accounting for no more than 0.6 kappa number units, which is in good agreement with the brightness values (88-94%).

**TABLE 11.** Brightness and chemical composition of fully bleached kraft pulp samples expressed in kappa number units.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Brightness %</th>
<th>Kappa number</th>
<th>Ox-Dem kappa number</th>
<th>Hexenuronic acid µmol/g</th>
<th>Other non-lignin structures*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spruce ECF-1</td>
<td>88</td>
<td>1.54</td>
<td>0.54</td>
<td>11.5</td>
<td>0.90</td>
</tr>
<tr>
<td>Spruce ECF-2</td>
<td>90</td>
<td>2.11</td>
<td>0.62</td>
<td>18.3</td>
<td>1.46</td>
</tr>
<tr>
<td>Birch ECF-1</td>
<td>91</td>
<td>4.12</td>
<td>0.56</td>
<td>43.9</td>
<td>3.51</td>
</tr>
<tr>
<td>Birch TCF-2</td>
<td>92</td>
<td>4.00</td>
<td>0.54</td>
<td>38.8</td>
<td>3.10</td>
</tr>
<tr>
<td>Eucalyptus ECF-1</td>
<td>94</td>
<td>0.34</td>
<td>0.33</td>
<td>1.5</td>
<td>0.01</td>
</tr>
<tr>
<td>Eucalyptus ECF-2</td>
<td>94</td>
<td>2.27</td>
<td>0.30</td>
<td>13.5</td>
<td>1.07</td>
</tr>
</tbody>
</table>

*Calculated as a difference between the kappa number and the summed contribution to the kappa number of residual lignin and HexA

The large differences in kappa number of the pulps, up to 3.78 kappa units, can be explained by the presence of HexA, with a high concentration especially in the birch samples. The contribution to the kappa number of other non-lignin structures was found to be quite small, not exceeding 1 kappa unit.

### 6.1.2 Influence on the brightness stability

The lignin content in a fully bleached chemical pulp is usually very low, but traditionally lignin is suspected of being a precursor in the formation of chromophores which lead to brightness reversion. It may also form complexes with metal ions and thus produce a more intense colour.
To study the influence of each type of oxidizable structures on the brightness stability of chemical pulps bleached with an ECF or TCF bleaching sequence, the accelerated ageing experiments described in Experimental (2.2.6) were performed with spruce, birch and eucalyptus pulps. In order to compare the degree of brightness reversion of kraft pulps with the contents of different oxidizable structures, the kappa number fractionation was performed for each type of pulp sample before the ageing. The results of this fractionations for all the samples are shown in Table 11.

When the pulp samples with 8% moisture content were kept at 70 °C and pH~ 4.5 for 9 days, a large drop in brightness was observed. Figure 17 shows brightness losses of the order of 20 - 40 brightness units for the various samples. The most severe brightness loss was observed for the birch pulp which contained the largest amount of HexA (Table 11).

![Figure 17](image)

**Figure 17.** Brightness of pulp sheets as a function of time on ageing at 70°C, pH=4.5, 8% moisture.

To clarify the role of residual lignin in thermal yellowing, the pulp was treated with a combination of mercury acetate and sodium borohydride (the Ox-Dem treatment) in order to selectively remove the HexA groups and other oxidizable structures of carbohydrate origin present in the pulp. After the Ox-Dem treatment, the brightness stability was significantly improved, as shown in Figure 18. All the pulp samples demonstrated good brightness stability during the first 7 days of accelerated ageing, suggesting that the residual lignin under these conditions did not play a significant role in the formation of
colour. This conclusion is further strengthened by the fact that the brightness of the lignin-free dissolving pulp was similar to that of the other pulps (Fig. 18).

![Graph showing brightness over time for different types of pulp](image)

**FIGURE 18.** Brightness of pulp sheets as a function of time for dissolving pulp and for pulp samples after Ox-Dem treatment. Ageing conditions: 70°C, pH=4.5, 8 % moisture.

After 9 days of accelerated ageing, however, a significant drop in the brightness occurred in all the samples. The reason for this is unknown, but it may be due to a decomposition of native carbohydrate structures.

6.2 Role of false lignin in thermal yellowing of bleached kraft pulps

Even though HexA is colourless, its presence is detrimental to bleaching, since it increases the consumption of bleaching chemicals (Vuorinen et al. 1999, Ragnar 2000). At the same time, HexA and other non-lignin structures in pulps are expected to be sensitive to oxidative conditions such as those encountered during pulp storage in the presence of air and humidity, and many of them are also good complexing agents for metal ions. This means that both these components of false lignin are likely to be involved in the thermal yellowing of bleached pulp.
6.2.1 Correlation between HexA amount and brightness loss

Because of the small amounts of non-lignin structures present in the samples chosen for the present study (Table 12), it appears that the improved brightness stability of the Ox-Dem-treated samples shown in Fig. 16 was due to the removal of HexA. This was further investigated by plotting the brightness loss of the pulp as a function of the content of HexA in the pulp (Fig. 19). It can be seen that, for all the pulp samples, regardless of origin, there was a fairly good correlation between the brightness loss and the HexA content, which becomes more obvious with increasing ageing time.

**Figure 19.** The degree of thermal yellowing expressed as the brightness loss after 2, 5, 7 and 9 days of treatment (70°C, pH=4.5, 8 % moisture) plotted against the content of HexA before ageing in fully bleached spruce, birch and eucalyptus kraft pulps.

The dependence of the degree of thermal yellowing on the HexA content has been reported earlier for birch and pine kraft pulp and a decrease in the amount of HexA with ageing time was found (Granström et al. 2001, Granström et al. 2002, Tenkanen et al. 2002). Consequently, these results suggest that HexA plays a role as precursor in the formation of compounds which are subsequently involved in colour formation.
6.2.2  Role of HexA in the formation of reactive intermediates

To identify reactive intermediates, the aged pulp samples were extracted with ethanol, and the low-molecular weight products were analysed by GC/MS and GC-FID. In this analysis, 2-furancarboxylic (FA) and 5-formyl-2-furancarboxylic (FFA) acid, the two possible acid degradation products of HexA, were detected in significant amounts. Table 12 shows the successive degradation of HexA and the simultaneous formation of FA and FFA with time for all samples except the eucalyptus ECF-1 sample, which only contained a trace of HexA. It should be noticed that FA and FFA have been reported to be the products of severe acidic hydrolysis of HexA (Teleman et al. 1996).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ageing time (days)</th>
<th>HexA in pulp (µmol/g)</th>
<th>FA+FFA (µmol/g)</th>
<th>Missing HexA (µmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spruce ECF-1</td>
<td>0</td>
<td>11.5</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>11.2</td>
<td>0.1</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>10.1</td>
<td>0.2</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>7.9</td>
<td>0.5</td>
<td>3.1</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>4.3</td>
<td>3.9</td>
<td>3.3</td>
</tr>
<tr>
<td>Spruce ECF-2</td>
<td>0</td>
<td>18.3</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>13.3</td>
<td>0.6</td>
<td>4.4</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>11.0</td>
<td>1.5</td>
<td>5.8</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>6.0</td>
<td>2.3</td>
<td>10.0</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>4.6</td>
<td>3.3</td>
<td>10.4</td>
</tr>
<tr>
<td>Birch ECF-1</td>
<td>0</td>
<td>43.9</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>34.3</td>
<td>1.2</td>
<td>8.4</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>27.2</td>
<td>2.7</td>
<td>14.0</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>15.8</td>
<td>4.7</td>
<td>23.4</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>6.3</td>
<td>3.5</td>
<td>34.1</td>
</tr>
<tr>
<td>Birch TCF-2</td>
<td>0</td>
<td>38.8</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>31.3</td>
<td>1.3</td>
<td>6.2</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>19.0</td>
<td>1.9</td>
<td>17.9</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>13.2</td>
<td>3.8</td>
<td>21.8</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>7.5</td>
<td>4.8</td>
<td>26.5</td>
</tr>
<tr>
<td>Eucalyptus ECF-2</td>
<td>0</td>
<td>13.5</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>12.9</td>
<td>0.5</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>11.6</td>
<td>1.1</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>6.6</td>
<td>1.8</td>
<td>5.1</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>3.9</td>
<td>3.1</td>
<td>6.5</td>
</tr>
</tbody>
</table>
If FA and FFA were the final products of HexA decomposition, the molar sum of the amounts of FFA, FA and remaining HexA would be equal to the original content of HexA. As shown in Table 12, Figure 20 (birch ECF-1) and Figure 21 (eucalyptus ECF-2) this is not the case, and there is large and increasing difference between the
amount of HexA present in the original sample and the cumulative amount of the furoic acids and HexA found after ageing. This difference is denoted “missing HexA”.

The amount of missing HexA was found to be proportional to the brightness loss for all pulp samples (Fig. 22), which suggests that a part of the FA and FFA formed may participate in further reactions leading to the formation of colour in the pulp samples.

![Graph](image-url)

**Figure 22.** The brightness loss for fully bleached kraft pulps after different ageing time plotted against the missing HexA (see Fig.19 and 20).

The absence of a universal linear correlation for all the samples may be explained by other differences in pulp composition, not related to the HexA content, for example, different contents of metal ions. In the case of the eucalyptus ECF-2 samples the contribution from the other non-lignin structures can be important, since their amount is comparable to the content of HexA (see Table 11).
7 INFLUENCE OF THE BLEACHING SEQUENCE ON THE BRIGHTNESS STABILITY OF BLEACHED KRAFT PULPS (PAPER V)

7.1 Influence of TCF- and ECF- bleaching on the chemical composition of eucalyptus kraft pulp

Using the kappa number fractionation method as an analytical tool, the influence of bleaching chemicals on the chemical composition of different pulps can be compared and related to the pulp properties.

In the present study, D₀(EP)D₁ (ECF-type) and Q₁(OP)Q₂(PO) (TCF-type) bleaching sequences were applied to an oxygen-delignified eucalyptus kraft pulp with kappa number of 10.4 (see Experimental 2.2.4). The influence of the two types of bleaching on the content of different oxidizable structures in the eucalyptus kraft pulp was studied in relation to the brightness stability of the pulp. The choice of bleaching sequences was intended to give two fully bleached pulp samples of similar brightness but considerably different contents of HexA groups.

To estimate the changes in the chemical composition of pulp introduced by different bleaching chemicals, the kappa number fractionation was performed for the O₂-delignified pulp sample and for the samples after each oxidative stage in both bleaching sequences. The data are summarized in Table 13.

As can be seen in Table 13, HexA was the only non-lignin contributor to the kappa number and its amount was the highest in the unbleached pulp. The D₀(EP)D bleaching effectively reduced the amounts of residual lignin and HexA in the pulp. In the D₀ stage, the removal of lignin was more efficient than the removal of HexA; the amount of residual lignin decreased by approximately 80%, whereas the amount of HexA decreased by only 46%. The second D-stage proved to be much more effective in removing HexA, especially at a higher chlorine dioxide charge. During this stage, the amount of residual lignin remained almost unchanged.
TABLE 13. Kappa number fractionation, brightness and viscosity for unbleached eucalyptus kraft pulp and for pulp samples bleached according to D_0(EP)D and Q_1(OP)Q_2(PO) bleaching sequences.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Kappa number</th>
<th>Lignin* Kappa number units</th>
<th>HexA, kappa number units</th>
<th>Brightness (%)</th>
<th>Viscosity (dm^3/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O_2-delignified</td>
<td>10.4</td>
<td>3.3</td>
<td>7.1</td>
<td>59</td>
<td>926</td>
</tr>
<tr>
<td>ECF-D_0(EP)</td>
<td>4.5</td>
<td>0.7</td>
<td>3.8</td>
<td>86</td>
<td>872</td>
</tr>
<tr>
<td>ECF-D (0.5)</td>
<td>3.1</td>
<td>0.7</td>
<td>2.4</td>
<td>91</td>
<td>866</td>
</tr>
<tr>
<td>ECF-D (1.0)</td>
<td>2.3</td>
<td>0.7</td>
<td>1.6</td>
<td>91</td>
<td>874</td>
</tr>
<tr>
<td>ECF-D (1.5)</td>
<td>1.4</td>
<td>0.5</td>
<td>0.9</td>
<td>92</td>
<td>876</td>
</tr>
<tr>
<td>TCF-Q_1(OP)</td>
<td>8.8</td>
<td>2.6</td>
<td>6.2</td>
<td>77</td>
<td>895</td>
</tr>
<tr>
<td>TCF-Q_2(PO) (1.0)</td>
<td>7.9</td>
<td>2.0</td>
<td>5.9</td>
<td>86</td>
<td>844</td>
</tr>
<tr>
<td>TCF-Q_2(PO) (2.0)</td>
<td>7.0</td>
<td>1.1</td>
<td>5.9</td>
<td>88</td>
<td>789</td>
</tr>
<tr>
<td>TCF-Q_2(PO) (3.0)</td>
<td>6.8</td>
<td>1.0</td>
<td>5.8</td>
<td>89</td>
<td>733</td>
</tr>
</tbody>
</table>

* Measured by Ox-Dem kappa number method

TCF-bleaching, as expected, was inefficient with respect to the removal of HexA. Small changes in the amount of HexA can be attributed to the partial dissolution of xylan. The (OP) stage had only a limited effect on both the lignin and the HexA: 22% of lignin and 13% of HexA, respectively, were removed. The increased charge of peroxide from 1.0 % to 2.0 % in the second (PO) stage led to the removal of 67% lignin, but only 19% of HexA was removed at the same time. A further increase in the charge of peroxide did not give noticeable effect on the lignin or HexA contents, but viscosity dropped significantly.

7.2 Accelerated ageing of the laboratory bleached pulps

According to our hypothesis, the presence of HexA should have a great impact on the brightness stability of the ECF- or TCF-bleached chemical pulps. In order to test this hypothesis, samples ECF-D (1.5) and TCF-(PO) (3.0) with the lowest possible content of lignin and the highest brightness (see Table 13) were selected for studies of the thermal yellowing under conditions described above. Brightness decreases are compared in Figure 23.
Accelerated ageing of the pulp samples led to a large loss in brightness. Discoloration was especially rapid during the first three days and levelled out after approximately one week. The most significant discoloration was observed in the sample from the TCF sequence having a high content of HexA. After three days, the drop in brightness of the TCF-bleached sample was 30 units compared to 15 units for the ECF-bleached sample. A similar relationship between the brightness loss values was maintained after 10 days of ageing: 46 units loss for the TCF- and 26 units loss for the ECF-bleached sample.

7.3 Thermal yellowing and HexA decomposition

The decrease in the amount of HexA with ageing time and the simultaneous formation of 2-furancarboxylic (FA) and 5-formyl-2-furancarboxylic (FFA) acids was quantified for the eucalyptus pulp samples studied. Results are shown in Figure 24 and Figure 25.
As can been seen in Figures 24 and 25, the amount of HexA in the pulp samples decreases during the course of ageing, and, simultaneously, FA and FFA are generated. The amount of “missing HexA” increases as the discoloration proceeds.
In the case of both the pulp samples, the brightness loss, expressed as the difference between the brightness values before and after the ageing test, was found to be proportional to the amount of missing HexA (see Fig. 26). Once again, this led us to conclude that the HexA plays a role as precursor in the formation of colour in pulp during the ageing.

**FIGURE 26.** Relation between the amount of missing HexA and the brightness loss for eucalyptus kraft samples bleached according to ECF- and TCF-bleaching sequences.
The formation of reactive intermediates from HexA

The dependence on temperature, humidity and acidity of the degree of thermal yellowing of bleached chemical pulps suggests that hydrolytic reactions are involved. It has also been known for a long time that under such conditions polysaccharides can undergo partial hydrolysis to form small amounts of monosaccharides which subsequently further react to give a variety of low molecular weight products. Glucuronic acid yielded furfural, 2-furancarboxylic acid and reductic acid in addition to several aromatic compounds (Popoff and Theander 1972). Under more strongly acidic conditions, uronic acids have been shown to be converted into furfural, 5-formyl-2-furancarboxylic acid and reductic acid (Feather and Harris 1966), and reductic acid has also been obtained from oxidized sugars such as methyl β-D-2(or 3)-oxo-glucopyranoside (Theander 1958).

Kraft pulping leads to the formation of hexenuronic acid groups by the elimination of methanol from the original 4-O-methyl-glucuronic acid groups attached as side groups to the xylan of softwood as well as of hardwood (Buchert et al. 1995). In most ECF- and TCF-bleaching sequences, the HexA-groups survive, at least in part, and consequently almost all bleached kraft pulps contain some residual HexA-groups. As shown in the previous sections, a substantial portion of the HexA-groups originally present in the pulp was eliminated in the course of accelerated ageing of bleached kraft pulp. The degree of yellowing was found to be correlated with the concentration of HexA, but no similar correlation with the lignin content could be obtained. The amount of residual lignin was always found to be low and of a similar amount, irrespective of pulp type and bleaching sequence.

Attempts to establish a mass balance for HexA after the yellowing reaction afforded two degradation products, viz. 2-furancarboxylic acid (FA) and 5-formyl-2-furancarboxylic acid (FFA), in addition to the remaining HexA. The total amounts of the products identified were, however, much lower than the original amount of HexA in the bleached
pulp. It was concluded that this discrepancy was due to the formation of coloured reaction products, accounting for the “missing HexA”.

An alternative explanation of the missing HexA could be the existence of parallel reaction pathways leading to products even more reactive than those already mentioned. Reductic acid, which may be formed in the hydrolysis of carbohydrates, has been shown to be highly reactive under accelerated ageing conditions and to lead to a high degree of discoloration of cellulosic samples (Popoff and Theander 1972, Theander and Nelson 1988). In order further to test the hypothesis that reductic acid can be formed on heat treatment of the pulp samples, the aged samples were extracted with ethanol, and the GC-MS analysis of the extracts did indeed reveal the presence of reductic acid together with other low-molecular weight compounds formed during the ageing.

![Mass spectrum at 70 eV of reductic acid (as trimethylsilyl ether derivative).](image)

**Figure 27.** Mass spectrum at 70 eV of reductic acid (as trimethylsilyl ether derivative).

Figure 27 shows the mass spectrum of reductic acid, obtained from the ethanol extract of the birch ECF-1 sample aged for 7 days. This assignment was confirmed by comparison of the spectrum with that of the synthetic compound.

Chemically, all these three products, 2-furancarboxylic acid, 5-formyl-2-furancarboxylic acid and reductic acid, may be formed from HexA, as shown in Figure 28.
FIGURE 28. Reaction routes for the formation of 2-furancarboxylic acid (FA), 5-formyl-2-furancarboxylic acid (FFA) and reductic acid (RA) from hexenuronic acid under acidic conditions.
8.2 The chemical behaviour of HexA degradation products

To clarify the role of each of these three HexA degradation products in the formation of colour during ageing, handsheets of dissolving pulp containing the individual compounds, with and without ferrous or ferric ions, were prepared and the brightness was measured. As can be seen in Table 14, neither FA nor FFA caused any reduction in the initial brightness compared to the reference pulp alone. RA, on the other hand, could not be synthesized in an absolutely pure form (~15% of pectin impurities according to NMR data) and the solution in ethanol had a pale yellow colour which gave an immediate brightness drop of 6 brightness units when it was added to the pulp.

**TABLE 14.** Brightness values after different periods of thermal ageing (70°C) for the dissolving pulp doped with FA, FFA, RA and with mixtures of these compounds with Fe(II) or Fe(III) ions.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Brightness, %</th>
<th>Brightness after ageing, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ISO 2 days</td>
<td>5 days</td>
</tr>
<tr>
<td>Dissolving pulp</td>
<td>94</td>
<td>89</td>
</tr>
<tr>
<td>Fe(II)-doped</td>
<td>83</td>
<td>78</td>
</tr>
<tr>
<td>Fe(III)-doped</td>
<td>89</td>
<td>87</td>
</tr>
<tr>
<td>FA-doped</td>
<td>94</td>
<td>91</td>
</tr>
<tr>
<td>FA+Fe(II)-doped</td>
<td>87</td>
<td>74</td>
</tr>
<tr>
<td>FA+Fe(III)-doped</td>
<td>84</td>
<td>83</td>
</tr>
<tr>
<td>FFA-doped</td>
<td>94</td>
<td>71</td>
</tr>
<tr>
<td>FFA+Fe(II)-doped</td>
<td>83</td>
<td>60</td>
</tr>
<tr>
<td>FFA+Fe(III)-doped</td>
<td>86</td>
<td>70</td>
</tr>
<tr>
<td>RA-doped</td>
<td>88</td>
<td>55</td>
</tr>
<tr>
<td>RA+Fe(II)-doped</td>
<td>57</td>
<td>37</td>
</tr>
<tr>
<td>RA+Fe(III)-doped</td>
<td>84</td>
<td>65</td>
</tr>
</tbody>
</table>

On thermal ageing, using HexA-free dissolving pulp as well as fully bleached spruce and birch kraft pulps as references, large differences between the effects of the various additives emerged. Whereas FA did not accelerate the yellowing of the pulp to any
significant degree beyond that of the dissolving pulp reference, both FFA and RA gave a rapid and comprehensive yellowing reaction (Fig. 29).

**Figure 29.** Brightness loss as a function of ageing time for fully bleached spruce and birch pulps as well as for bleached dissolving pulp doped with the model compounds: FA, FFA and RA.

The kinetics of colour formation were, however, different from that of the two kraft pulps with a more rapid initial decrease in brightness followed by a stabilization, whereas the reference pulps showed a continuous decrease in brightness. These differences indicate that there is a rate-limiting step in the yellowing process during which the colour precursors such as FFA and RA are generated. The difference in yellowing tendency between the two pulp samples should reflect the differences in the amounts of HexA present (Table 11). In the birch pulp, the initial amount of HexA was around 38 µmol/g which was similar to the amounts of FA, FFA or RA added (ca. 30 µmol/g). The similarities in the degree of yellowing after 6-7 days further support the view that FFA and/or RA are to a major degree are responsible for the colour formation.

### 8.3 Thermal yellowing in the presence of Fe ions

As shown in Table 14, the additions of ferrous and ferric ions (~110-120 ppm) to the dissolving pulp caused an immediate brightness drop of about 10 and 5 units respectively. The simultaneous presence of either FA or FFA did not change these values to any large...
extent. The presence of RA, on the other hand, gave together with ferrous ion a brightness drop of almost 40 units during the drying time in the conditioning room (see Experimental 2.2.5). On thermal ageing of the various hand sheets for 2, 5 and 7 days, almost all the further brightness reduction took place during the first two days. The combination of either FFA or RA with ferrous ions gave the highest degree of discoloration, although the effect of added Fe(II) may have been obscured e.g. by the initial presence of Fe in the dissolving pulp (2 ppm) or by easy oxidation of Fe(II) to Fe(III) by oxygen (Fig. 30).

![Figure 30](image)

**Figure 30.** Brightness loss for dissolving pulp doped with FA, FFA or RA respectively in combination with either Fe(II) or Fe(III) after 2 days of thermal ageing.

### 8.4 The mechanism of thermal yellowing

Based on these results, the most important mechanism for the thermal yellowing of bleached chemical pulps can be suggested as shown in Figure 31. In a fully bleached pulp, the pH is usually slightly acidic due either to a final D-stage in the process or to acidification of the pulp following a P-stage. On drying and baling of the pulp, a high temperature at a pulp dryness of ca. 90% is maintained. Despite the fact that, on storage, the temperature gradually drops to ambient, a mechanism involving a slow release of HexA followed by its further conversion to FA, FFA and RA seems reasonable. In the complete absence of Fe-ions, the yellowing process can be expected to proceed at a very slow rate, but in normal pulp manufacture this situation does not exist. Therefore, the location, availability and oxidation state of the trace amounts (typically ~10 ppm or less)
of Fe-ions present in the pulp will be decisive for the degree and rate of the yellowing reaction.

On accelerated yellowing in the laboratory, the above reactions take place much more rapidly and with increased accessibility to Fe-ions. Therefore, very high degrees of brightness reversion can be obtained with a drop of 40-50 units in brightness of bleached pulp after about one week. Under such conditions, the presence of FFA and, in particular, RA in the pulp is only transient whereas FA, having a much higher stability, can still be found (cf. Granström et al. 2002). It can be assumed that the FFA and RA are in part degraded into colourless products, and several of the low molecular weight organic acids found in an aqueous extract of aged pulp by Granström et al. (2002) may have this origin. Some of the FFA and RA may, however, participate in colour-forming reactions, as shown in Figure 31.

[Figure 31. Reaction scheme for the thermal yellowing of bleached chemical pulps.]
9 CONCLUSIONS

- The structure of residual lignin is altered by bleaching. As a consequence, a substantial decrease in its oxidation equivalent is observed. Apart from residual lignin, some non-lignin oxidizable structures are generated in the course of kraft cooking and oxygen delignification. This limits usability of the standard kappa number test. In contrast, the Ox-Dem kappa number method proved to be an accurate way of determining the residual lignin content in bleached kraft pulps and of monitoring the efficiency of lignin removal along different bleaching sequences;

- The kappa number in unbleached and bleached kraft pulps is always represented by the sum of partial contributions, one due to lignin and the other due to the so-called “false lignin”. The false lignin is comprised of HexA and other non-lignin structures containing carbonyl groups and/or double bonds, oxidizable by permanganate under the standard kappa number determination conditions.

- The effect of false lignin on the pulp kappa number is especially pronounced in the case of unbleached and oxygen-delignified kraft pulps. Removal of false lignin from pulp seems to be more efficient in ECF-type bleaching than in TCF-type bleaching;

- The other non-lignin structures are, so far, the least studied component of false lignin. The available data suggest that these structures are probably formed by various oxidation, elimination, condensation and molecular rearrangement reactions occurring during the cooking and oxygen delignification stages, and that they are chemically related to carbohydrates;

- The brightness stability of the fully bleached chemical pulps is related to the content of the false lignin in these pulps. The hexenuronic acid groups present in pulp xylan apparently play a dominant role in the moist thermal yellowing. It is suggested that the mechanism of colour formation involves several stages, including acid-induced degradation of HexA to reactive intermediates such as 2-furancarboxylic, 5-formyl-2-furancarboxylic acid and reductic acid. The formation of the latter two compounds seems to be the rate-determining step in the yellowing process. The presence of ferrous ions further enhances the discoloration.
REFERENCES


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