THE CHEMISTRY OF BLEACHING AND POST-COLOR FORMATION IN KRAFT PULPS

Göran Gellerstedt
Department of Fibre and Polymer Technology, Royal Institute of Technology, KTH, SE-100 44 Stockholm, Sweden
e-mail: ggell@pmt.kth.se

Abstract

In this review, the chemical structure of the residual lignin in softwood and hardwood is presented as far as we know it. With this knowledge as a starting point, the basic principles in bleaching of kraft pulp with bleaching agents such as chlorine dioxide, oxygen and hydrogen peroxide is discussed with an emphasis on differences between the behaviour of guaiacyl (softwood) and syringyl-guaiacyl (hardwood) lignin. The importance of other pulp constituents such as hexenuronic acid on the outcome of bleaching operations and various possibilities for removing this structure from the pulp is discussed. In the final part of the presentation, the post-color formation by storage or heat treatment in fully bleached chemical pulp is described and possible means of reducing this non-desirable effect are suggested.

Introduction

In chemical pulping, the cook has to be interrupted before all the lignin has been removed since; otherwise, the quality characteristics of the fibers as well as the pulp yield will deteriorate to unacceptable low levels. Thus, when the kraft cook reaches the final delignification phase, the rate of lignin dissolution slows down considerably and prolonged cooking will result in an increased degradation and dissolution of carbohydrates. At this point, the hydrolytic reactions resulting in depolymerization and dissolution of lignin cease and, in practice, further delignification and bleaching is done using oxidation chemistry. In this part of the pulp mill, the bleach plant, the small amount of residual lignin present in the fiber is removed in a series of alternating oxidative and extractive stages with the ultimate goal being a clean and white cellulosic fiber [1].

In the bleaching of chemical pulp, the oxidation reactions result in the formation of carboxyl groups in the lignin which under alkaline conditions will ionize and, thus, provide increased solubility. This simple reaction principle is not enough, however, to completely eliminate the lignin from the fibers and fragmentation reactions are also required in order to obtaining molecules that are small enough to penetrate out from the swollen net-work structure of the fiber wall. The bleaching kinetics is such that the initial very rapid decrease in lignin content usually is followed by a much slower delignification rate and, consequently, one oxidative/extractive stage is not enough to completely eliminate the lignin [2]. Another important but much less investigated lignin dissolution mechanism is the diffusion through the fiber wall [3]. For other reactive components present in the fibers such as hexenuronic acid and “non-lignin” structures, the behavior towards various bleaching agents is variable.

In the following, an overview of the structural features of the lignin present in unbleached pulps will be given followed by a general discussion about bleaching chemistry. Thereafter, some details on the behavior of different bleaching agents will be highlighted. Finally, the presence of reactive groups in fully bleached pulps and their importance for inducing secondary yellowing will be briefly mentioned.

Residual Lignin; Softwoods

The structure of the residual lignin, present in unbleached softwood kraft pulps, has been the subject of numerous studies but, still, our knowledge is far from complete. The most apparent feature of the unbleached pulp lignin is its heterogeneity with structural units that range from virtually native to highly degraded and resembling the dissolved. Thus, all the original coupling modes, except the 5-5-O-4 structures, between the phenyl-propane units can still be found in the residual lignin albeit in different relative proportions in comparison to the native lignin. Certain structures such as those of the β-5 and β-1 types are present as such but may also partially be present as the corresponding stilbene. A small amount of the original β-O-4 structures can be found as the corresponding enol ether structure in addition to intact β-O-4 structures. Some 10-20% of the latter are still present in the pulp [4].

In comparison to wood lignin, the content of free phenolic hydroxyl groups in the residual softwood kraft pulp lignin is much higher (25-35 units per 100 phenylpropane units) but, due to the structural heterogeneity, the average value may include a large range of different values [5]. During the kraft cook, many of the terminal hydroxymethyl groups are split off as formaldehyde and, although a portion of these may incorporate into the lignin through condensation reactions, the major part is found in the cooking liquor. The residual lignin also contains saturated carbons of the methylene type. The predominant origin of these is the native lignin which contains small amounts of certain reduced structures such as dihydroconiferyl alcohol and secoiso-lariciresinol. These will survive the kraft cook. In addition, extractives of the fatty acid type are incorporated into the residual lignin to some extent, by chemical linkages, thus providing further amounts of unreactive saturated structures [6]. Other features contributing to the difficulty in removing the last portion of lignin in kraft pulps is the presence of chemical linkages between lignin and carbohydrates. All the major polysaccharides in the fiber, viz. cellulose, xylan and glucomannan, have been found to be linked to lignin, probably with benzyl ether linkages being the predominant mode of coupling [7].

Residual lignin; Hardwoods

Different hardwoods such as birch and eucalyptus behave differently in kraft pulping due to the large differences in wood morphology and composition. Thus, eucalyptus gives a much faster delignification to a given kappa number resulting in a pulp lignin having a much higher residual content of β-O-4 structures as shown in Figure 1 [8] and Figure 2. Various analyses on isolated eucalyptus pulp lignins further confirm the general behavior of lignin during kraft pulping [9-12].

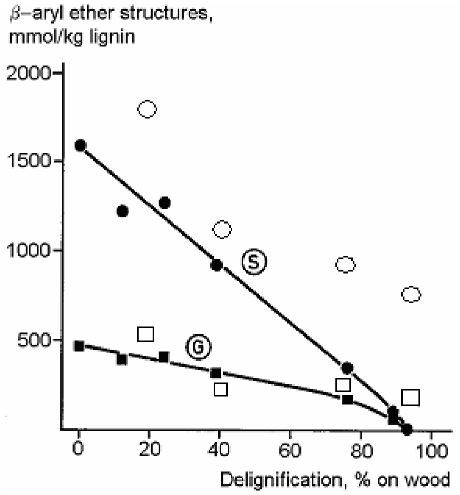


Figure 1. Remaining β-O-4 structures in birch pulp lignin, analysed as syringyl (S) and guaiacyl (G) structures separately. Unfilled values are from [9] for eucalyptus globulus kraft pulp.

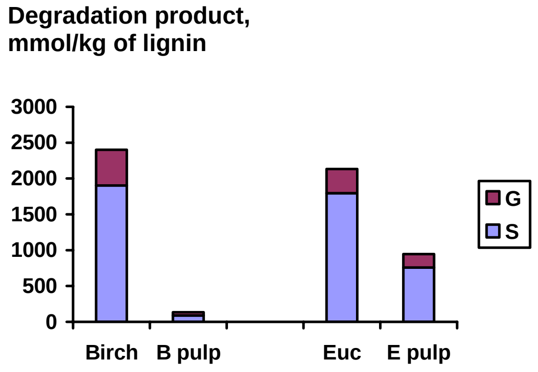


Figure 2. β-O-4 structures in birch and eucalyptus gl. wood and kraft pulps (Gellerstedt, unpublished).

As a consequence, bleaching of eucalyptus pulp with either TCF- or ECF-sequences should be expected to proceed with high efficiency [13-16]. The fast pulping rate for eucalyptus results also in a formation of hexenuronic acid which may increase with decreasing kappa number (Figure 3) [13], contrary to the behavior for softwood and for birch. The presence of large amounts of hexenuronic acid groups in the pulp will result in an increased consumption of bleaching chemicals such as chlorine dioxide or ozone. If present in the fully bleached pulp, hexenuronic acid groups will also contribute strongly to a high yellowing sensitivity of the pulp.

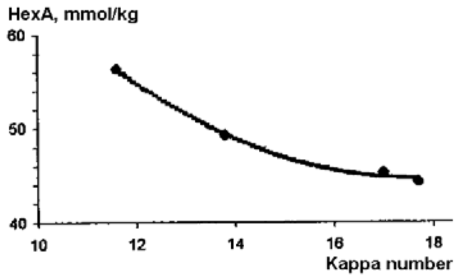


Figure 3. Formation of hexenuronic acid as a function of pulping time for eucalyptus globulus under otherwise constant conditions [13].

The Meaning of Kappa Number

For bleachable grades of pulp, the kraft cook is carried out to kappa numbers in the order of 25-35 for softwood and 15-20 for hardwood. The kappa number value includes, however, not only the amount of residual lignin but also other oxidizable structures present in the unbleached pulp [17]. The most important of these is hexenuronic acid which is attached to the xylan but other types of reactive structures/functional groups are also present and may, depending on pulping conditions and wood species, contribute several kappa units to the overall kappa number as exemplified in Table 1 [18]. The desirable brightness increase that is the objective of bleaching is, however, unequivocally related to the elimination of the lignin component as shown in Figure 4.

Table 1. Contributions to the kappa number from lignin, hexenuronic acid and "non-lignin" structures in various unbleached pulps [18].

Pulp type, Kappa number	Lignin (a)	HexA (a, b)	Non-lignin (a, c)
Pine kraft, 18.6	14.3	1.9	2.4
Pine soda/AQ, 18.9	16.8	0.3	1.8
Birch kraft, 13.6	6.5	4.5	2.6
Eucalyptus kraft, 17.2	9.0	7.4	0.8

a) calculated in Kappa number units
b) HexA = Hexenuronic acid
c) Non-lignin = non-specified but oxidizable structures

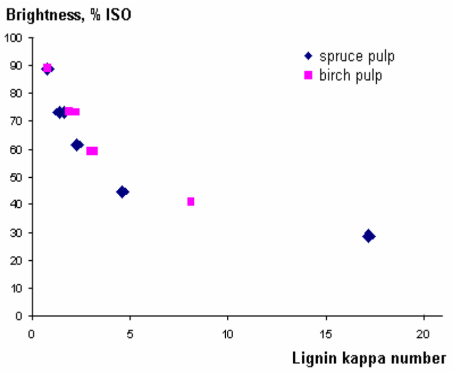


Figure 4. Brightness development for industrial kraft pulps as a function of the content of lignin, measured as lignin-related kappa number. Bleaching sequences: ODEQP (spruce) and OQ(OP)Q(PO) (birch).

Lignin-Carbohydrate Linkages

The presence of chemical linkages between lignin and polysaccharides in wood is well established. For kraft pulps, on the other hand, it is not until quite recently that unequivocal proof has been obtained for the presence of such linkages. By size exclusion chromatographic (SEC) analysis of unbleached kraft pulps from both pine and birch after dissolution in dimethylacetamide/lithium chloride (DMAC/LiCl), it was found that the UV-absorbing material (i.e. lignin) is connected to the high as well as the low molecular weight fraction of the polysaccharides. From birch kraft pulp, the curves shown in Figure 5 were obtained [19].

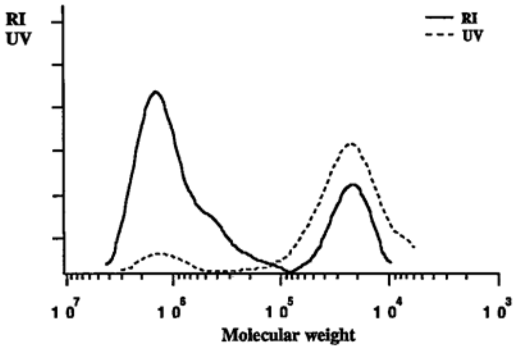


Figure 5. SEC-analysis of unbleached birch kraft pulp after dissolution in DMAC/LiCl. RI = refractive index; UV = ultraviolet detection [19].

By selective degradation of the cellulose portion of kraft pulp by endoglucanase treatment followed by swelling, alkaline extraction and pH-fractionation, a more detailed picture of the relative amounts of lignin linked to the various polysaccharides has also been obtained (Figure 6). Thus, almost all residual lignin present in a kraft pulp is chemically linked to the polysaccharides with the majority being linked to the hemicelluloses. These features are shown in Figure 6 for softwood pulp [20].

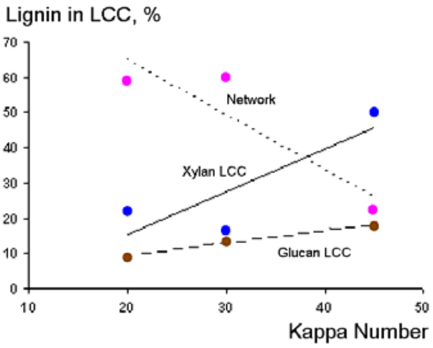


Figure 6. Amount of lignin chemically linked to glucan, xylan and glucomannan (network) respectively in softwood kraft pulps having different kappa numbers. The amount of non-linked lignin is ~10% of the total [20].

For hardwood pulps, the picture is not yet complete since a major portion of the residual lignin could not be made soluble by the action of endoglucanase alone on the cellulose. This may possibly be due to coverage of the fibres with xylan or lignin. In addition, a further portion of the lignin (as LCC) could not be isolated and is reported as "missing lignin" (Figure 7) [Gellerstedt, unpublished].

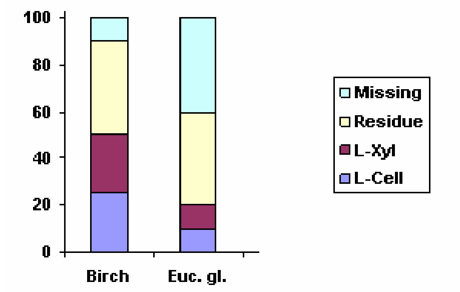
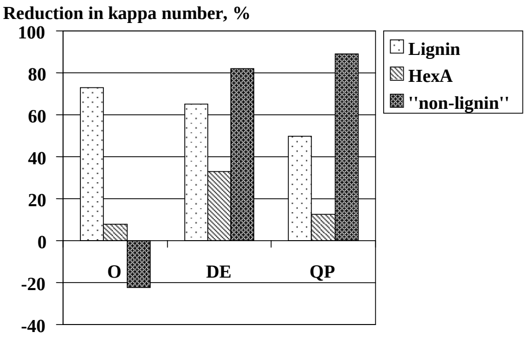


Figure 7. Distribution of lignin in birch and eucalyptus kraft pulps with kappa number ~16 (lignin-related kappa number = 4.0; 5.7) . Residue = remaining pulp after repeated treatment with endoglucanase. Missing = highly soluble lignin presumably linked to xylan.

Oxygen Delignification

After kraft pulping, the residual fiber lignin is structurally heterogeneous. Among the various structural units present, the free phenolic end-groups are, however, by far the most reactive towards electrophilic reagents. This is taken advantage of in the oxygen delignification stage which, when applied, proceeds directly after the pulping stage. In practice, typical reaction conditions can be 100 °C for 60 min and with an oxygen pressure of around 0.6 MPa corresponding to an oxygen charge of ~22 kg/tonne of pulp (for softwoods). The degree of delignification, measured as change of kappa number, is in the order of 25-55% depending on wood species and exact process conditions. The carbohydrate derived contribution to the kappa number is, however, not decreased during an oxygen stage and, consequently, for both softwood and hardwood, the dissolution of lignin is much greater than indicated by the kappa number reduction (Figure 8) [18].



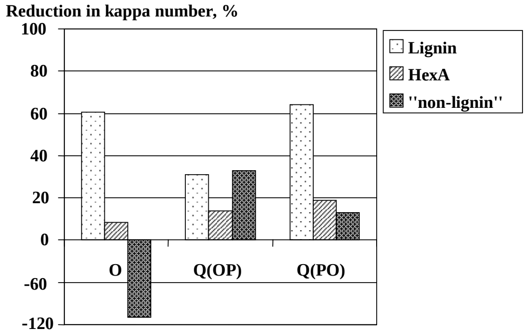


Figure 8. Successive changes in kappa number for industrial softwood (spruce/pine) (upper figure) and birch (lower figure) kraft pulps when bleached to full brightness [18].

For softwood, it has been shown that the rate of delignification in oxygen delignification proceeds in two phases, with the first being approximately 20 times faster than the second [21]. Both phases are, however, dependent on alkali concentration and oxygen pressure.

The reactions between phenolic structures related to lignin and oxygen has been studied in detail. In this work, the oxidation mechanism, the detailed degradation pathways as well as the reaction kinetics has been elucidated. The reactions of polymeric lignin have also been studied both with isolated lignin preparations and through chemical and spectroscopic analyses of dissolved and residual lignin after an oxygen stage [5]. The primary reaction step in the oxygenation of a phenolic structure is the slow electron transfer from the phenolate anion to oxygen with formation of a superoxide ion and a phenoxy radical. The phenoxy radical, stabilized by resonance, reacts with a second molecule of oxygen to form an organic peroxy radical which rapidly is reduced to a hydroperoxide or, alternatively, reacts directly with a superoxide ion. In subsequent steps, the organic hydroperoxide isomers will react further and the aromatic ring can be either degraded, or eliminated from the rest of the lignin macromolecule (Figure 9) [22].

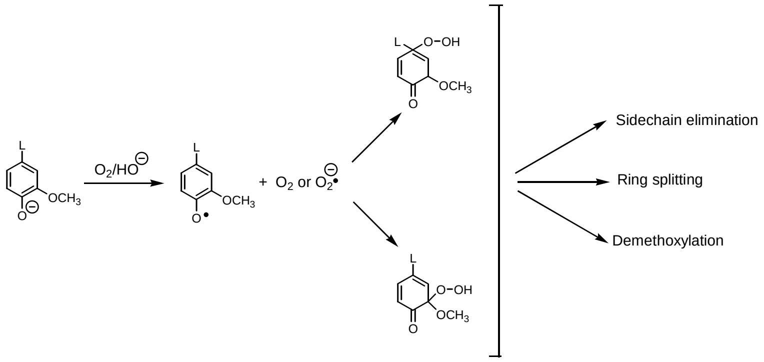


Figure 9. Reaction modes in the oxidation of phenolic end-groups in lignin during oxygen delignification.

Among the secondary reactions, the oxidative cleavage of the aromatic ring and formation of acidic groups must be regarded as the most important since that reaction will render the lignin more hydrophilic. A certain decrease of the molecular size of the lignin through side chain cleavage reactions may, however, also play a role since the oxidized lignin must be able to diffuse out of the fiber wall. Analysis by SEC of the dissolved lignin from an oxygen stage has revealed that the molecular size distribution is rather similar to the lignin dissolved in a kraft cook as shown in Figure 10.

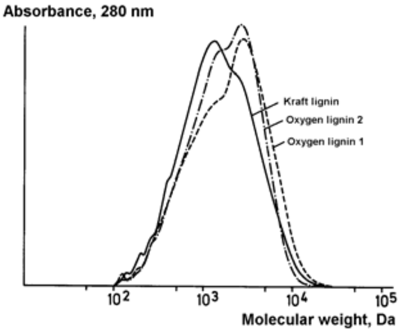


Figure 10. Size exclusion chromatography, SEC, of lignin dissolved from a softwood kraft cook and from different degrees of delignification (8 and 15 kappa No units) in a subsequent O-stage respectively.

The third reaction type, demethoxylation is also possible and from softwood, approximately 1.5 kg of methanol per tonne of pulp has been found in the oxygen stage effluent.

After pulping, the residual pulp lignin contains about 30 phenolic hydroxyl groups per 100 phenylpropane units. After a subsequent oxygen stage, this number is reduced to values around 10-15 in the fiber lignin. For the corresponding dissolved lignin in the oxygen stage, a surprisingly high number of phenolic hydroxyl groups are found (Figure 11). In addition, a large number of carboxyl groups are formed as a result of the oxidation of lignin. This apparent anomaly can be explained by assuming that the analytical value for phenols obtained for unbleached pulp lignin, in fact is a mean value covering a broad range of values with a substantial portion being much higher than the average. A lignin fraction with a high content of phenols can be assumed to be the most reactive and preferentially removed. In addition, a certain formation of new phenolic hydroxyl groups in lignin during the course of an oxygen stage cannot be excluded, e.g. by cleavage of aryl ether linkages.

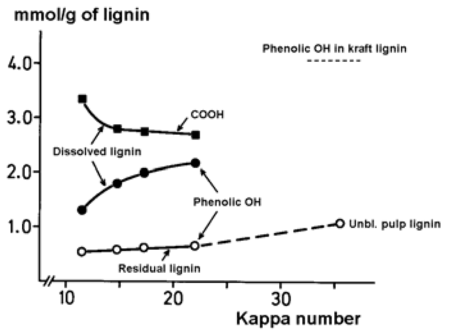


Figure 11. Amounts of carboxyl groups and phenolic hydroxyl groups in lignins after kraft pulping and oxygen delignification respectively.

The fact that a rather large viscosity loss in the pulp takes place during an oxygen stage has been regarded as a serious drawback and has been a major reason for the slow rate of introduction of oxygen stages in the industry despite the advantage of using an easily available cost efficient and environmentally friendly oxidant. The reduction of the degree of polymerisation of cellulose (i.e. the viscosity loss) is due to an oxidation of one or more of the hydroxyl groups located along the cellulose chain. Thereby, a carbonyl group is created and, due to the alkaline conditions, an elimination reaction occurs resulting in a cleavage of the chain into two shorter units (Figure 12). One of these will have a newly formed reducing end group but thanks to the oxidative conditions, the peeling reaction will not take place to any noticeable extent. In this reaction type, end-groups of the hexenuronic acid type can be formed in addition to those already present in the xylan. Furthermore, 6-aldehydo cellulose, the first oxidation product, may also be present.

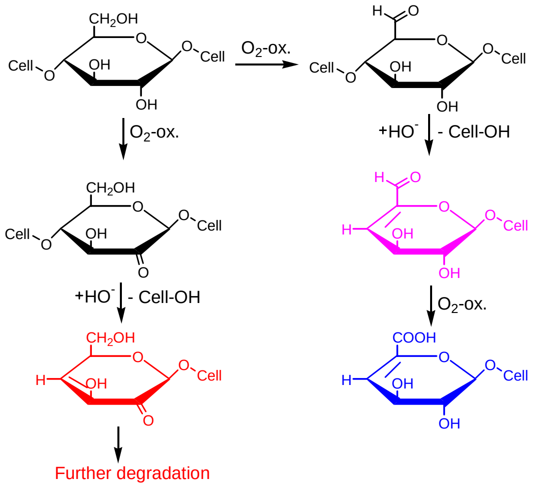


Figure 12. Major carbohydrate reactions in the O-stage resulting in the cleavage of a cellulose chain.

In order to determine the possible contribution from such structures to the overall amount of oxidized structures in the carbohydrate fraction of kraft pulps, the methanolysis method has been optimized and applied to spruce/pine and birch pulps respectively. By combining a direct analysis of glucuronic acid units present in the pulp with a second analysis after a preceding oxidation with cupric sulfate, all oxidized groups were analysed. Thereby, a complete determination of these groups could be achieved and their relative amounts monitored as the bleaching of the pulps progressed. The results are shown in Figure 13. In particular, a PO-stage seems to be prone to giving oxidized groups in the cellulose [23].

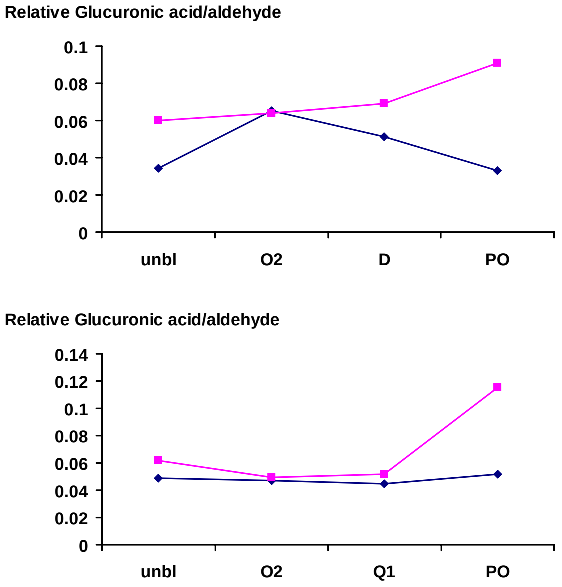


Figure 13. Relative amounts of glucuronic acid (blue) and glucuronaldehyde units present in kraft pulps from spruce/pine (upper) and birch (lower) after various bleaching stages. Squares = sum of acid and aldehyde units, diamonds = acids [23].

The comprehensive dissolution of lignin in the oxygen stage is not accompanied by a similar large decrease in the kappa number of the pulp. The most important reason for this discrepancy can be found in the fact that the oxygen stage is not able to degrade hexenuronic acid units originally present in the pulp after the kraft cook. In addition, a further formation may take place as shown above. A minor dissolution of xylan seems, however, also to take place in the oxygen stage and this might result in a slight decrease of hexenuronic acid groups. Therefore, the overall decrease in kappa number can be in the order of ~50% for softwood and ~30% for hardwood pulps.

Two examples of the changes in kappa number taking place when going from unbleached to oxygen delignified pulp are shown in Table 2. Here, it is quite obvious that the kappa number alone does not at all give information about the degree of delignification (cf. Figure 8). In industrial operation, on the other hand, the kappa number is a very suitable parameter for process analysis.

Table 2. Changes in the contribution to kappa number from lignin, HexA and other non-lignin structures after an O-stage of spruce/pine and birch pulps respectively.

Pulp	Kappa No	Lignin (a)	HexA (a, b)	Non-lignin (a, c)
Spruce, unbl	22.5	17.2	1.3	4.0
Spruce, O-stage	10.7	4.6	1.2	4.9
Birch, unbl	13.8	8.1	4.7	1.0
Birch, O-stage	9.6	3.2	4.3	2.1

a) calculated in Kappa number units
b) HexA = Hexenuronic acid
c) Nonlignin = non-specified but oxidizable structures

The lignin remaining in the fibers after the oxygen stage has a somewhat different chemical structure in comparison to the lignin in wood. Thus, the cleavage of β-O-4 structures that takes place during the kraft cook is reflected in lower values for this type of structure also in the residual oxygen delignified pulp lignin. An apparent increase of such structures after the oxygen stage in comparison to the value in unbleached pulp is, however, observed. Therefore, a large inhomogeneity in the structure of the residual lignin after the cook must again be assumed and it seems obvious that once the accessible portions of the lignin have been removed by the oxygen oxidation, the remaining part again becomes structurally more like the wood lignin (Table 3).

Other structural changes in lignin in the O-stage seem to include a certain preferential oxidation of simple guaiacyl end-groups. Thereby, and in analogy with kinetic data, an accumulation of biphenyl (5-5') structures can be found in the residual lignin. As expected, the residual lignin also contains an increased amount of carboxyl groups.

All residual (softwood) kraft pulp lignin after the O-stage has been found to be linked to polysaccharides (LCC structures) albeit in different proportions as compared to the unbleached pulp. Thus, the xylan-linked lignin which contributes some 20% of the residual lignin after the cook is strongly reduced in the O-stage with a decrease that is proportional to the extent of delignification (Figure 14) [20].

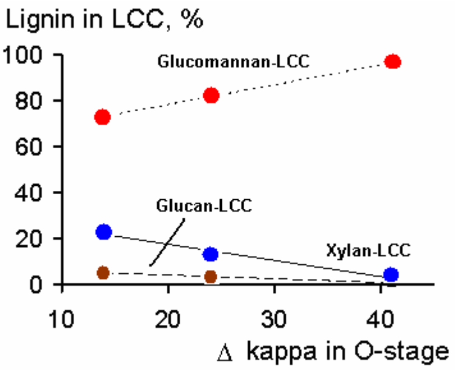


Figure 14. Amount of lignin linked to glucan, xylan and glucomannan respectively in softwood kraft pulp after an O-stage at different degrees of delignification.

For the glucan-linked lignin, a similar trend is found but at lower lignin contents. The major contribution to the heterogeneity of the lignin after pulping thus seems to originate from these two types of LCC. The major portion of the residual lignin after the cook is linked predominantly to glucomannan ("network") with the amount of lignin being at least 50% of the total (cf. Figure 6).

Table 3. Frequency of various linkage types in (softwood) lignin from wood, unbleached and oxygen delignified kraft pulp.

Lignin sample	β-O-4	β-5	β–β	5-5	4-O-5
		NMR-data[a)]		Oxidative degr.[b)]	
Wood lignin	48	12	3.5	10	5
Kraft pulp lignin, kappa 30-35	10	5	2	12	7
O-stage pulp lignin, kappa 9-11	18	8	2	13	4

[a)] NMR-data on isolated lignin samples
[b)] Oxidative degradation on wood and pulp samples (includes only phenolic structures)

After a subsequent oxygen stage, this value increases further and 80-90% of all residual pulp lignin seems to be linked in this type of network structure having a strong structural resemblance to the native lignin-glucomannan LCC in wood.

From these results, it can be concluded that the lignin-xylan LCC after softwood pulping contains most of the phenolic lignin units whereas most of the remaining β-O-4 structures are located in the lignin-glucomannan LCC.

Chlorine Dioxide Bleaching Chemistry

At present, chlorine dioxide constitutes the most important bleaching agent for chemical pulps. The gradual replacement of elemental chlorine with chlorine dioxide in the industry has been driven by the concern that bleaching effluents originating from chlorine bleaching contains harmful chlorinated substances. With chlorine dioxide, the residual lignin in chemical pulps is efficiently oxidized and degraded although chlorination also occurs to a limited extent. In a combined bleach plant effluent based on chlorine dioxide bleaching, the efficient dechlorination of lignin taking place in alkaline conditions results, however, in very low values for the residual amount of organically bound chlorine (AOX).

The reactions of lignin with chlorine dioxide have been thoroughly investigated both with lignin model compounds and by analyses of the structure of residual lignin using chemical and spectroscopic methods. Furthermore, a large number of low molecular weight compounds have been identified in bleaching liquors with special emphasis put on the presence of chlorinated compounds [5].

Chlorine dioxide itself has an unpaired electron and its major reaction with pulp lignin is through an electron transfer reaction from the aromatic rings with formation of chlorite ion. Phenols as well as phenol ethers react with about the same rate of reaction whereas phenolate ions show a reactivity which is around 10^6 times higher [24]. Therefore, despite the fact that the bleaching with chlorine dioxide is carried out under acidic conditions, the free phenolic units in lignin react much faster than the etherified (Figure 15) [25]. On oxidation, the aromatic ring in lignin is rapidly degraded with formation of muconic acid and quinone structures as predominant end products as shown in Figure 16.

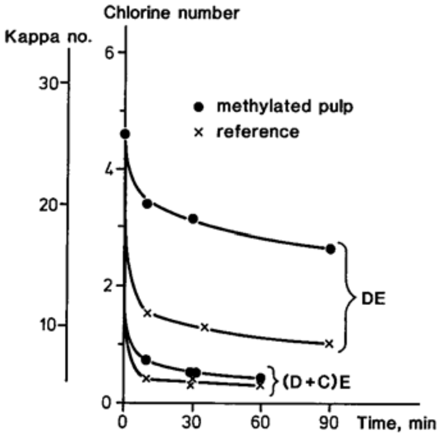


Figure 15. Bleaching of softwood kraft pulp with chlorine dioxide in the presence/absence of chlorine. Effect of pre-methylating phenolic hydroxyl groups [25].

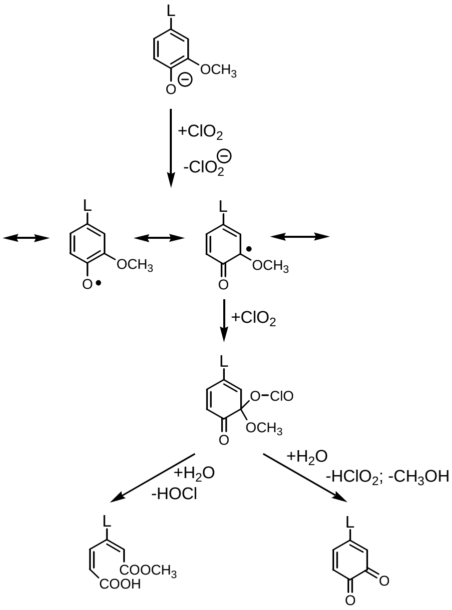


Figure 16. Reactions between a phenolic lignin structure and chlorine dioxide.

The rapid development of new bleaching technologies, taking place since the early 1990s, has resulted not only in TCF-bleaching but also in bleaching sequences in which part of the chlorine dioxide charge has been replaced by hydrogen peroxide. In addition, more powerful O- and P-stages have been introduced. The complete substitution of chlorine with chlorine dioxide that has taken place has also resulted in far less acidic bleaching liquors and, consequently, also in lesser risk of getting acid hydrolysis in the polysaccharides during the course of bleaching. At the same time, however, the ability of removing hexenuronic acid groups from the pulp during bleaching has decreased. This is illustrated in Table 4 which shows some typical pulp quality data from bleaching of softwood kraft pulp.

Table 4. Changes in brightness, viscosity and kappa number for a softwood kraft pulp after an O-stage and subsequent ECF-bleaching. Kappa number = sum of lignin, hexenuronic acid and "non-lignin" structures.

Pulp sample	Brightness, % ISO	Viscosity, dm^3/kg	Kappa Number	Lignin[a]	HexA[a, b]	Non-lignin[a, c]
after O-stage	44.7	910	10.7	4.6	1.2	4.9
after ODE	73.3	850	3.3	1.6	0.8	0.9
after ODEQP	88.8	800	1.6	0.8	0.7	0.1

[a] calculated in Kappa number units
[b] HexA = hexenuronic acid
[c] Non-lignin = unspecified but oxidizable structures

The oxidation of pulp with chlorine dioxide is carried out at a temperature of around 65-75 °C and with a reaction time of 30-45 min. The pH is in the order of 2-3. The initial consumption of chlorine dioxide by the pulp is very fast and within a matter of seconds, the concentration of chlorine dioxide has been reduced to a considerable extent. At the same time, a formation of chloride, chlorite and chlorate ions starts to take place (Figure 17) [26]. Whereas chlorite ions may still participate in the overall reactions of pulp lignin, the formation of chlorate is undesirable since this ion is inert and cannot contribute to any further pulp reactions. In addition, the chlorate ion is biologically active and may cause environmental problems.

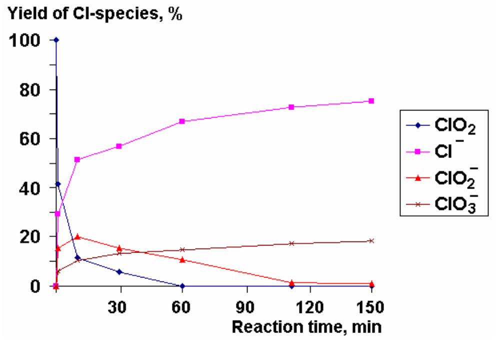


Figure 17. Formation of inorganic species during bleaching of unbleached softwood kraft pulp with chlorine dioxide [26].

By addition of sulfamic acid to the bleaching liquor as a scavenger for hypochlorous acid/chlorine (Figure 18, Reaction 1), it has been shown that chlorine dioxide bleaching of kraft pulp results in the formation of a substantial amount of methanol which occurs in parallel with the dissolution of lignin. Furthermore, by using a kraft pulp having all phenolic hydroxyl groups blocked by methylation prior to reaction with chlorine dioxide, the presence of sulfamic acid was shown to prevent virtually all reactions and the pulp kappa number remained almost unaffected. Pulp bleaching with chlorine dioxide in the presence of sulfamic acid will also give a complete suppression of the formation of chlorate. These observations are in line with the view that i) methanol is formed directly from the oxidation with chlorine dioxide (and subsequent hydrolysis), ii) under the conditions of technical bleaching, non-phenolic lignin structures do not react to any noticeable extent and iii) hypochlorous acid and/or chlorine is involved in the formation of chlorate according to Figure 18, Reaction (2) and (3).

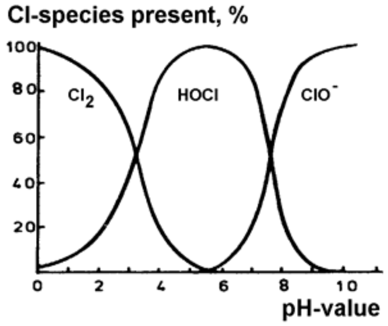
$$H_2N\text{-}SO_3^{\ominus} + HOCl \longrightarrow HClN\text{-}SO_3^{\ominus} + H_2O \qquad (1)$$

$$HOCl + ClO_2^{\ominus} \longrightarrow ClO_3^{\ominus} + Cl^{\ominus} + H^{\oplus} \qquad (2)$$

$$Cl_2 + ClO_2^{\ominus} + H_2O \longrightarrow ClO_3^{\ominus} + 2Cl^{\ominus} + 2H^{\oplus} \qquad (3)$$

Figure 18. Reactions between hypochlorous acid/chlorine and sulfamic acid (1) or chlorite (2, 3) respectively.

The presence of sulfamic acid in a D-stage has also been shown to decrease the amount of delignification which can be obtained for a given set of reaction conditions. Therefore, from a bleaching point of view, the formation of the highly reactive hypochlorous acid is advantageous/necessary since all types of aromatic structures will become oxidized. On the other hand, the presence of the hypochlorous acid/chlorine system in the bleaching liquor will also induce a certain degree of chlorination of the lignin. Of these two species, elemental chlorine is, however, a far more powerful chlorination agent than hypochlorous acid. Since, in aqueous solution, an equilibrium exists between hypochlorous acid, hypochlorite and chlorine as given by Figure 19, even rather small changes in the pH-value prevailing in the D-stage will affect the amount of chlorinated lignin that is formed.



$$Cl_2 + H_2O \rightleftharpoons HOCl + Cl^{\ominus} + H^{\oplus} \quad (pK_1 = 3.4)$$

$$HOCl + H_2O \rightleftharpoons ClO^{\ominus} + H_3O^{\oplus} \quad (pK_2 = 7.5)$$

Figure 19. Chlorine species present in aqueous solution at different pH-values.

By isolating the remaining pulp lignin after each stage in a complete softwood pulp bleaching sequence and analysis of the methoxyl content, the successive oxidation of the lignin could be followed as depicted in Figure 20. A corresponding trend in the ratio carbon/oxygen was also found with values ranging from 3.45 (unbleached pulp lignin) to 1.43 (fully bleached pulp lignin). In the first chlorine dioxide stage (D_0-stage), a certain chlorination of the lignin accompanies the oxidation as shown in Figure 20. Later in the bleaching sequence, a substantial portion of this lignin-bound chlorine is removed and for fully bleached softwood pulps, a residual amount of organically bound chlorine of ~50-100 ppm can be found after ECF-bleaching [27]. The corresponding dissolved high molecular weight material, predominantly lignin, from such a bleaching sequence contains ~10 chlorine/1000 carbon atoms.

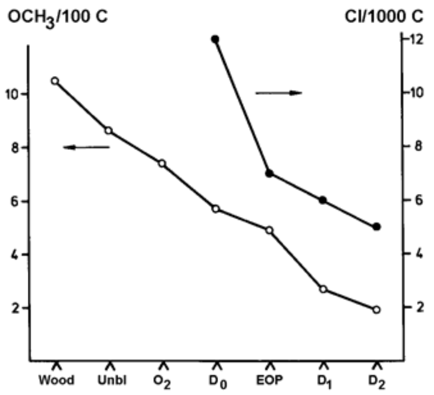


Figure 20. Changes in methoxyl and chlorine content in the residual lignin of industrial pine kraft pulp when going from wood to fully bleached pulp.

The detrimental effects on pulp quality, e.g. brightness stability that can be caused by the presence of hexenuronic acid groups have resulted in a further development of bleaching technology. Thus, the fact that hexenuronic acid is sensitive to acidic conditions has prompted some mills to introduce a specific hydrolytic stage which can be done either as an isolated stage (A-stage) or as part of a prolonged chlorine dioxide stage carried out at high temperature. In either case, the objective is to achieve a selective hydrolytic degradation of hexenuronic acid groups as depicted in Figure 21.

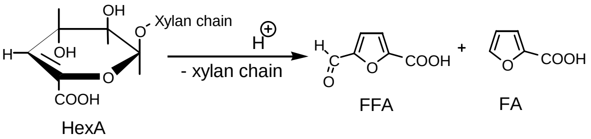


Figure 21. Acidic hydrolysis of hexenuronic acid (HexA) with formation of 5-formylfuroic acid (FFA) and furoic acid (FA).

In particular for hardwood pulps with their much higher content of hexenuronic acid as compared to softwood pulps, this is an important development. Recently, it was shown that a long D-stage at high temperature was able to remove almost all (90%) hexenuronic acid from a eucalyptus pulp. As long as chlorine dioxide was still present in the system, the rapid delignification was accompanied by a fast removal of hexenuronic acid due to the presence of hypochlorous acid. Once, the delignification ceased, the remaining low amount of active chlorine species present in the system were found to promote a further rather slow oxidation of hexenuronic acid as shown in Figure 22. During the conditions employed, a further 30% of hexenuronic acid was removed by hydrolysis. By contrast, normal D-stage bleaching conditions gave a lower total removal of hexenuronic acid, almost exclusively by oxidation (Table 5) [28].

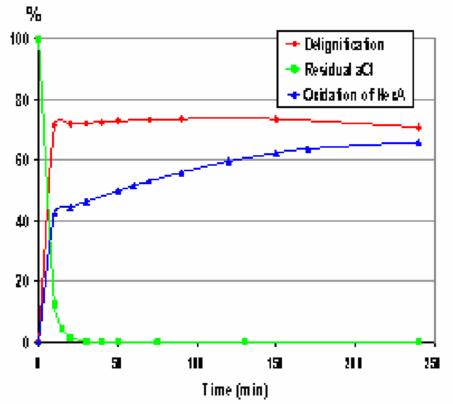


Figure 22. Oxidative removal of lignin and hexenuronic acid in DE bleaching of oxygen delignified eucalyptus kraft pulp.

Table 5. Comparison of the efficiency of hexenuronic acid removal in ECF-bleaching of eucalyptus pulp. D_0 = pH 3, 60 °C, 45 min; D_{ht} = pH 3, 90 °C, 240 min.

Stage	HexA removal, mmol/kg			Visc. ml/g	Brightness % ISO
	Tot	Hydrol.	Ox		
-		0 (67)$^{a)}$		1041	58.5
D_0	36	0.4	36	935	79
D_{ht}	60	22	38	857	74
D_0(EO)DD	55			912	90.1
D_{ht}(EO)DD	66			830	90.5

$^{a)}$ Original value in pulp after the O-stage

Bleaching with Hydrogen Peroxide

Hydrogen peroxide in alkaline media has been used since a long time for the bleaching of mechanical pulp. Here, it is required that only the chromophoric structures present in the pulp are removed but virtually without any loss of pulp yield and, consequently, rather moderate reaction conditions must be chosen (~60-80 °C). The bleaching liquor must also contain sodium silicate in order to stabilize the peroxide and to provide a buffering capacity to the bleaching system.

The same type of bleaching conditions, applied on a kraft pulp, will, however, only give a limited brightness increase and in order to get an efficient bleaching, the lignin must also be removed. Therefore, a temperature around 100 °C must be used and for reasons of chemical recovery, the silicate should be omitted. This type of bleaching requires a pulp in which virtually all types of transition metal ions have been eliminated and it has been found that a pre-treatment stage of the pulp with a chelating agent, EDTA or DTPA, under specified conditions must be carried out (Q-stage).

Analysis of pulps which had been subjected to alkaline peroxide bleaching after a Q-stage, performed at different pH-values and temperatures, showed that a high temperature (~90 °C), a pH around 4-6 and one hour reaction time was required in the Q-stage in order to get an efficient utilization of the peroxide and a preserved pulp viscosity. It has also been shown that these conditions result in a very efficient removal of transition metal ions while, at the same time, magnesium ions are retained in the pulp.

In pulp bleaching, the preservation of the bleaching agent, hydrogen peroxide, is of utmost importance since, otherwise, the degradation products, viz. oxygen and water, will provide a very inefficient bleaching system. Despite the removal of almost all of the transition metal ions present in the pulp, a certain decomposition of hydrogen peroxide through spontaneous and/or metal catalysed reactions is unavoidable, however. These reactions will result in the formation of oxygen and water via the intermediate formation of hydroxyl and superoxide radicals.

The radical species present in a peroxide stage will contribute to the oxidation of lignin but also to a certain oxidation of the polysaccharides. The latter oxidation will give rise to a further drop of pulp viscosity and, for a peroxide-based bleaching sequence, a loss of some 50-200 units (dm^3/kg) can be encountered depending on the conditions in the stage(s).

The fact that the residual pulp lignin after an oxygen stage has "regained" a chemical structure which has a resemblance to the native structure in wood, i.e. with a comparatively high amount of β-O-4 structures, will facilitate an oxidative degradation by alkaline hydrogen peroxide [29]. The high temperature required (~100 °C) in a peroxide stage results in formation of a quinone methide from phenolic benzyl alcohol structures. Thereby, a nucleophilic addition of a peroxy anion is made possible and, in subsequent reaction steps, a lignin side chain cleavage and fragmentation may occur. The reaction is shown in Figure 23.

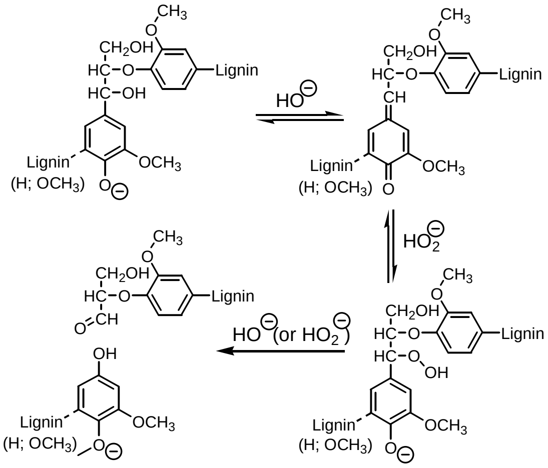


Figure 23. Reaction sequence for the cleavage of a phenolic β-O-4 structure in lignin with alkaline hydrogen peroxide.

The degree of delignification encountered in a peroxide stage can be substantial (cf Figure 8) and it is accompanied by a considerable brightness increase of the pulp. The latter effect is in part due to the removal of lignin but also to the direct brightening effect exerted by alkaline hydrogen peroxide.

The two types of reactions encountered in a peroxide stage, viz. general lignin oxidation and brightening (chromophore elimination), have been further supported by experiments with isolated lignin samples. Thus, it has been shown that the slow consumption of phenolic lignin structures is accompanied by a formation of carboxyl groups throughout the reaction. Simultaneously, a gradual consumption of hydrogen peroxide takes place. The direct brightening effect on the lignin, on the other hand, is fast but far from complete (Figure 24).

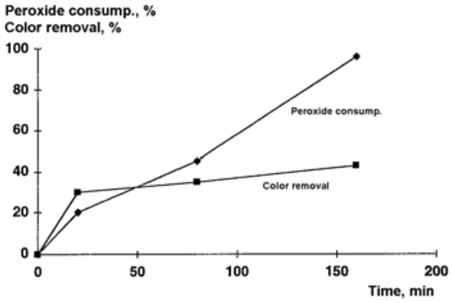


Figure 24. Alkaline hydrogen peroxide oxidation of lignin showing the gradual consumption of hydrogen peroxide and the fast removal of color.

Table 6. Changes in brightness, viscosity and kappa number for a birch kraft pulp after an O-stage and subsequent bleaching in a peroxide-based sequence. Kappa number = sum of lignin, hexenuronic acid and "non-lignin" structures.

Pulp sample	Brightness, % ISO	Viscosity, dm^3/kg	Kappa Number	Lignin[a]	HexA[a, b]	Non-lignin[a, c]
after O-stage	59.1	920	9.6	3.2	4.3	2.1
after OQ(OP)	73.3	850	7.3	2.2	3.7	1.4
after OQ(OP)Q(PO)	89.0	710	4.6	0.8	3.0	0.8

[a] calculated in Kappa number units
[b] HexA = hexenuronic acid
[c] Non-lignin = unspecified but oxidizable structures

Although the exact structure of the chromophoric groups present in the pulp lignin after pulping and oxygen delignification is virtually unknown, it can be assumed that quinones may contribute to the most reactive portion of these.

In analogy to an O-stage, alkaline hydrogen peroxide is not able to degrade hexenuronic acid groups. Therefore, bleaching sequences only based on oxygen and hydrogen peroxide will result in fully bleached pulps in which the remaining amount of hexenuronic acid may contribute a substantial portion of the final kappa number. One example is shown in Table 6.

Post-Yellowing Chemistry

Fully bleached kraft pulps contain less than 1% lignin (<50 mmol aromatic groups/kg pulp) and have brightness values about or above 90% ISO. In addition to the oxidative breakdown of lignin, the conditions prevailing during bleaching are, however, also able to introduce oxidized groups in the polysaccharides as exemplified in Figure 12. In addition, hexenuronic acid groups are present in most kraft pulps although the amount will vary with wood species and pulping conditions. It has been found that hardwood pulps (in particular) are prone to discoloration caused by heat treatment, an effect which also can be found on storage of bleached pulp bales. Furthermore, a profound effect of pH has been demonstrated with a maximum in yellowing occurring around pH=4.5. The yellowing that may take place in a pulp bale is illustrated in Figure 25 for birch pulp and, here, it is obvious that the remaining moisture in the bale is sufficient for inducing a dramatic yellowing effect at comparatively mild conditions.

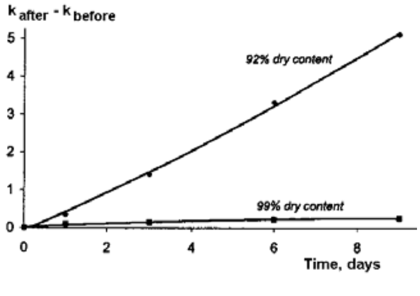


Figure 25. Yellowing at 60 °C of bleached birch kraft pulp at two different moisture contents.

Recently, it could be shown that, irrespective of pulp type and bleaching sequence, a clear correlation was obtained if the yellowing tendency (pc-number) was plotted against the content of hexenuronic acid groups present in the pulp. This effect is illustrated in Figure 26 for three different pulp types, viz. bleached spruce, birch and eucalyptus pulps respectively [30].

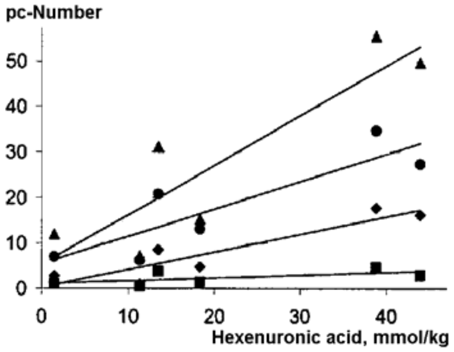


Figure 26. Post-color number for bleached pulps (spruce, birch, eucalyptus) on heat-induced yellowing for 2-9 days at 70 °C, pH=4.5 and 92% dryness [30].

The fact that oxidized carbohydrate structures such as uronic acids and various keto-sugars are unstable when exposed to acidic conditions has been known since a long time. It has also been shown that a common degradation product, reductic acid, is formed as an unstable and reactive product (Figure 27) [31, 32]. In later work, the importance of oxidized carbohydrates for the heat-induced yellowing as well as the high reactivity of reductic acid was further demonstrated in simple experiments when filter paper was impregnated with such compounds and exposed to heat treatment as shown in Table 7 [33].

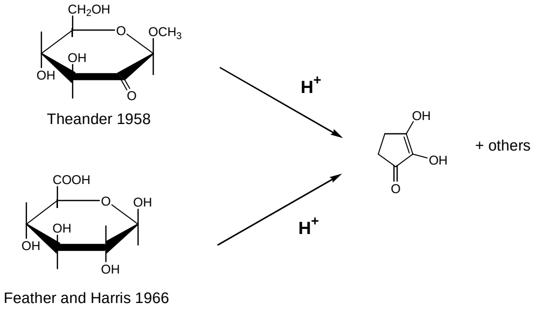


Figure 27. Formation of reductic acid on acidic treatment of oxidized sugar structures.

Table 7. Brightness of filter paper, impregnated with various compounds, after treatment at 80 °C for 16 h at 80% Rh [33].

Added Compound	Brightness, %
None	86.8
Cellobiose	83.5
Glucuronic acid	37.4
3-keto-methyl-β-glucoside	37.4
Reductic acid	19.4

Accelerated heat-induced yellowing of bleached kraft pulp under weakly acidic conditions results in the formation of reductic acid in addition to furoic acid and 5-formylfuroic acid (see Figure 21) [30]. Among the degradation products from hexenuronic acid, reductic acid as well as 5-formylfuroic acid were found to give rise to rapid yellowing. A further enhancement of the color formation could be induced by addition of a small amount of ferrous ion. Based on these observations, a reaction scheme for color formation in bleached kraft pulps as shown in Figure 28 has been formulated [34].

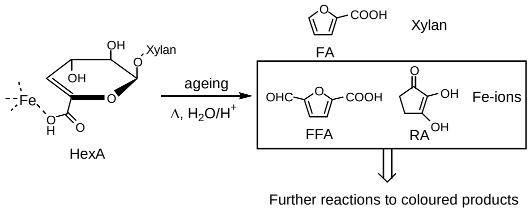


Figure 28. Reaction scheme for the formation of yellowing products in bleached chemical pulps.

There are several methods by which the heat-induced yellowing of kraft pulps can be surpressed or eliminated, the most common today including an acidic stage in the bleaching sequence as discussed above [35, 36]. Other options could be to cool down the pulp before baling since temperature has been shown to play an important role, to add radical scavenging compound(s) to the bleached pulp or to adjust the pH-value in the pulp prior to baling.

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