

INFLUENCE OF THE BLEACHING SEQUENCE ON THE BRIGHTNESS STABILITY OF EUCALYPTUS KRAFT PULP

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ABSTRACT

In the present research the influence of two bleaching sequences, D₀(EP)D (ECF-type) and Q₁(OP)Q₂(PO (TCF-type), on the content of various oxidizable structures and metal ions in eucalyptus kraft pulp was studied in relation to the brightness stability of these pulps. It was shown that pulps bleached to full brightness with ECF- and TCF-type bleaching sequences contain differing amounts of oxidizable structures of carbohydrate origin, such as hexenuronic acid groups (HexA). These structures play a dominant role in the thermal yellowing of bleached kraft pulps and largely determine the yellowing kinetics. The most significant discoloration is observed for Q₁(OP)Q₂-bleached pulp having an especially high content of HexA. The discoloration does not appear to be related to the presence of metal ions in pulps. The correlation between the HexA and brightness stability of the bleached kraft pulps is due to the reactions where HexA acts as a precursor in the formation of colored compounds or intermediates which are then involved in the color formation. Furoic structures representing the main acid degradation products of HexA are suggested as the actual intermediates that cause yellowing by forming colored compounds.

INTRODUCTION

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 [1-3], an important role being played by the bleaching sequence [4-6].

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 colored products [4]. More severe environmental regulations initiated a worldwide trend towards the broader use of elemental-chlorine-free (ECF) and totally-chlorine-free (TCF) technologies for the bleaching of kraft pulps. However, the chlorine-free bleaching does not eliminate the mentioned problems since ECF- and TCF-type bleached pulps are also susceptible to thermal yellowing; TCF-bleached pulps are generally less stable to the heat than ECF-bleached pulps. This explains a growing interest to the problem of thermal yellowing in the connection with development and use of chlorine-free bleaching sequences.

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, hemicelluloses, metal ions, and carbonyl and carboxyl groups [1, 7-13]. High temperature, low pH and high humidity accelerate the yellowing [3].

Recently, thermal yellowing has been related to the content of hexenuronic acid [14,15], 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 color contains metal ions together with various low-molecular fragments [16].

Bleached chemical pulps contain very little residual lignin. Our recent work has shown that, for both softwood and hardwood pulps bleached to full brightness with ECF- or TCF-type sequences, the amount of residual lignin is of order of 0.8 kappa number units [17]. However, the amount of other oxidizable structures, including HexA and other unsaturated compounds containing carbonyl groups and double bonds, collectively known as "false

lignin”, can be substantial, sometimes corresponding to 3-4 kappa number units. As it has been shown in our previous work, it is these

structures which play the dominant role in the thermal yellowing of bleached kraft pulps and largely determine the yellowing kinetics [18].

TABLE 1. Conditions for the bleaching of eucalyptus kraft pulp according to D₀(EP)D and Q₁(OP)Q₂(PO) bleaching sequences.

Treatment	Charge	pH	Temperature (°C)	Time (min)
ECF-type bleaching:				
D₀(EP)D				
D ₀	0.2 x kappa number a Cl	2-3	60	45
(EP)	0.3 % H ₂ O ₂ 1.5% NaOH, 0.2% MgSO ₄	11	70	60
D	0.5-1.0-1.5 % a Cl	4-5	70	120
TCF-type bleaching:				
Q₁(OP)Q₂(PO)				
Q ₁ , Q ₂	0.2 % EDTA 1.12% H ₂ SO ₄	4-5	70	60
(OP)	0.5 % H ₂ O ₂ 1.0% NaOH 0.3% MgSO ₄	11	105	60
(PO) _{1.0} (PO) _{2.0} (PO) _{3.0}	1.0–2.0–3.0 % H ₂ O ₂ 1% NaOH 0.3% MgSO ₄	11	110	120

Transition metal ions, such as Fe²⁺, Fe³⁺, Cu²⁺ or Mn²⁺, present in bleached pulps in trace amounts, have been associated with a faster brightness loss [2,8,19-20], but their exact role in the color 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 [3, 16]. 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.

In our present research the influence of two bleaching sequences, of ECF- and TCF-types, on the content of various oxidizable structures and

metal ions in eucalyptus kraft pulps is studied in relation to the brightness stability of these pulps.

EXPERIMENTAL

Materials. 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 grandis* from South America.

Chlorine dioxide and hydrogen peroxide were commercial products of reagent grade. 2-furancarboxylic acid (FA) was a commercial products of analytical grade obtained from Sigma. 5-formyl-2-furancarboxylic acid (FFA) was obtained from TCI Europe.

Methods. 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 1.

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

Hand-sheets of dissolving pulp with a grammage of ~ 70 g/m² were prepared according to SCAN-CN 26:99. The acidity of solutions used for the hand sheet making was adjusted with sulfuric acid to pH 4.5-5.0. Accelerated thermal ageing was carried out with samples sealed in double polyethylene bags placed in a water bath at 70 °C for 3 to 10 days.

Analytical determinations. The following SCAN standard methods were used: SCAN-C 1:00 (Kappa number) and SCAN-CM 15:99 (Viscosity). The reflectance of sheets was measured according to the two-background method (SCAN-Forsk 1976) before and after thermal ageing 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.

The kappa number fractionation (contribution to kappa number from various oxidizable structures including lignin, HexA and other false lignin structures) was done according to Ref. [17]. The HexA content of pulps was determined according to Gellerstedt and Li [21]. FFA, FA were detected by ethanol extraction of aged pulp samples followed by evaporation, trimethylsilylation and 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 Millennium 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 (HICROM 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.

RESULTS AND DISCUSSION

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

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. The choice of bleaching sequences was intended to give two fully bleached pulp samples of similar brightness but considerably different contents of HexA groups. HexA groups in pulp xylan are known to behave differently depending on the bleaching chemicals applied. Thus, ECF-type bleaching with chlorine-containing chemicals largely removes HexA, whereas TCF-type bleaching with hydrogen peroxide preserves a considerable portion of it.

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. 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 2.

As can be seen in Table 2, 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 higher chlorine

TABLE 2. Kappa number fractionation, brightness and viscosity for unbleached eucalyptus kraft pulp and for pulp samples bleached according to D₀(EP)D and Q₁(OP)Q₂(PO) bleaching sequences.

Sample	Kappa number	Lignin* Kappa number units	HexA, kappa number units	Brightness (%)	Viscosity (dm ³ /kg)
O ₂ -delignified	10.4	3.3	7.1	59	926
ECF-D ₀ (EP)	4.5	0.7	3.8	86	872
ECF-D (0.5)	3.1	0.7	2.4	91	866
ECF-D (1.0)	2.3	0.7	1.6	91	874
ECF-D (1.5)	1.4	0.5	0.9	92	876
Q ₁ (OP)	8.8	2.6	6.2	77	895
Q ₂ (PO) (1.0)	7.9	2.0	5.9	86	844
Q ₂ (PO) (2.0)	7.0	1.1	5.9	88	789
Q ₂ (PO) (3.0)	6.8	1.0	5.8	89	733

*Measured by Ox-Dem kappa number method

TABLE 3. The content of metal ions in fully bleached eucalyptus pulp samples

Pulp sample	Metal ions, ppm					
	Fe	Mn	Cu	Mg	Ca	Al
D ₀ (EP)D	6.2	0.3	0.4	108	236	2.3
Q ₁ (OP)Q ₂ (PO)	7.2	0.6	0.4	511	372	1.7

dioxide charge. During this stage, the amount of residual lignin remained almost unchanged.

Q₁(OP)Q₂(PO)-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.

Determination of metal ions in pulp samples before the ageing showed that both samples contained similar amounts of potentially harmful metal ions, with an exception for Mn and Mg which contents were higher in the Q₁(OP)Q₂(PO)-bleached sample (see Table 3).

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 1) were selected for studies of the thermal yellowing under conditions described above. Brightness decreases are compared in Figure 1.

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 for the sample from the Q₁(OP)Q₂(PO) sequence having a high content of HexA. After three days, the drop in brightness of the Q₁(OP)Q₂(PO)-bleached sample was 30 units compared to 15 units for the D₀(EP)D-bleached sample. A similar relationship between the brightness losses

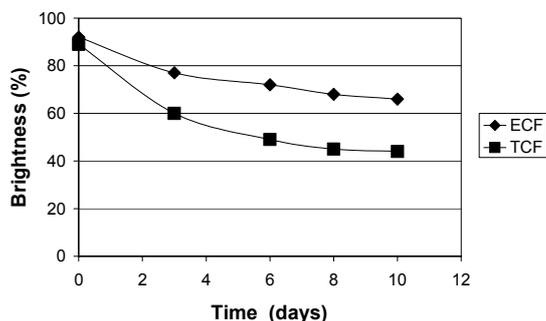


FIGURE 1. Brightness as a function of ageing time for the eucalyptus pulp samples bleached according to $Q_1(OP)Q_2(PO)$ (TCF-type) and $D_0(EP)D$ (ECF-type) bleaching sequences.

values was maintained after 10 days of ageing: 46 units loss for the TCF- and 26 units loss for the ECF- bleached sample.

Thermal yellowing and HexA decomposition

In our previous work, it was found that, during the course of accelerated ageing of industrially bleached kraft pulps, a substantial portion of HexA-groups originally present in the pulp were eliminated. The degree of yellowing was found to follow the content of HexA whereas no similar correlation with lignin content could be obtained [18]. The amount of residual lignin was always found to be low but of a similar amount, irrespective of pulp type and bleaching sequence. Since hexenuronic acid itself is a colorless structure, the correlation between the HexA content and the degree of yellowing of pulp can only be due to reactions where HexA acts as a precursor in the formation of colored compounds or intermediates which are then involved in color formation.

Attempts to establish a mass balance for HexA after the accelerated ageing of laboratory bleached eucalyptus pulps afforded two degradation products, viz. 2-furancarboxylic (FA) and 5-formyl-2-furancarboxylic (FFA) acids in addition to the remaining HexA (Fig.2 and Fig. 3).

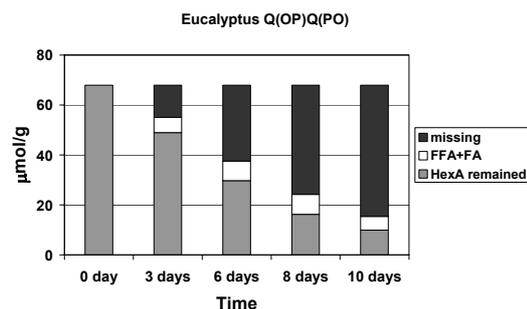


FIGURE 2. Changes in the contents of HexA, FA and FFA with ageing time for eucalyptus kraft pulp bleached according to the $Q_1(OP)Q_2(PO)$ bleaching sequence.

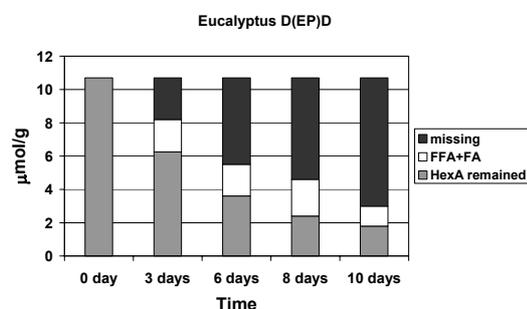


FIGURE 3. Changes in the contents of HexA, FA and FFA with ageing time for eucalyptus kraft pulp bleached according to the $D_0(EP)D$ bleaching sequence.

The total amounts of the products identified were, however, much lower than the original amount of HexA in fully bleached pulps. The discrepancy between the content of HexA in the original samples and the cumulative amount of formed furoic structures and HexA remaining in pulps, referred to as “missing HexA”, is increasing as the discoloration proceeds. For both pulp samples, the brightness loss was found to be proportional to the amount of “missing HexA” (see Fig.4), which suggests conclusively that a part of the FA and FFA formed may participate in further reactions leading to the formation of color in pulp samples.

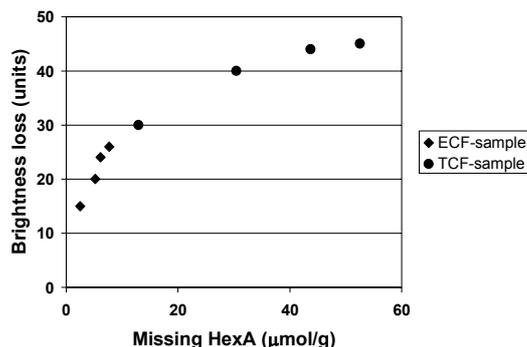


FIGURE 4. Relation between the amount of missing HexA and the brightness loss for eucalyptus kraft samples bleached according to $Q_1(OP)Q_2(PO)$ (TCF-type) and $D_0(EP)D$ (ECF-type) bleaching sequences.

CONCLUSIONS

1. During bleaching of eucalyptus kraft pulps, lignin is efficiently removed by either hydrogen peroxide or chlorine dioxide and only a small amount remains in the fully bleached pulps. Hexenuronic acid groups, on the other hand, are partly removed by a chlorine dioxide stage in the ECF-type bleaching sequence, but still present in fully bleached pulps. The bleaching sequence with a hydrogen peroxide (TCF-type) was not able to remove any significant amount of HexA.
2. The most significant discoloration on thermal ageing is observed for pulp bleached according to TCF-type bleaching sequence having an especially high content of hexenuronic acid groups. This does not appear to be related to the presence of metal ions in pulp.
3. The hexenuronic acid groups present in pulp xylan apparently play a dominant role in the brightness reversion of fully bleached eucalyptus kraft pulps on exposure to heat. The mechanism of color formation seems to involve several stages, including an acid-induced degradation of HexA with the formation of reactive compounds such as 2-furancarboxylic and 5-formyl-2-furancarboxylic acids. One of these or both take part in further reactions leading to the formation of color in the pulp.

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