Recent Hypotheses for Brightness Reversion of Hardwood Pulps

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The thermal brightness revision of chemical pulps, notably hardwood pulps bleached in an ECF- or TCF-sequence, is a technical problem that sometimes can be severe. In order to obtain information about the underlaying chemistry, an industrial TCF-bleached pulp has been exposed to an accelerated ageing procedure in the laboratory. By variation of ageing conditions, several parameters of importance for the yellowing reactions to occur have been identified. By extraction of aged pulp, an aqueous extract containing most of the colored components was isolated. This extract has been analysed by GC-MS thus revealing a series of low molecular weight organic acids as major reaction products. So far, no colored component has been identified, however.

Introduction

Bleached chemical pulps contain very little residual lignin. Recent work has shown that for both softwood and hardwood pulps bleached to full brightness with ECF- or TCF sequences, the amount of remaining pulp lignin is in the order of 0.8 kappa number units[1]. The contribution from other oxidizable structures can, however, be substantial resulting in much higher overall kappa numbers of fully bleached pulps, notably in hardwood pulps.

The thermal ageing of bleached kraft pulps has been the subject of a considerable amount of research and already in the 1960's it was recognized that hardwood (birch) pulps showed a higher yellowing tendency as compared to softwood pulps. A major reason for this behaviour was thought to be the formation of chlorinated extractives formed in the first chlorine stage of the bleaching sequence. On storage, it was demonstrated that hydrochloric acid was released from the pulp, thus causing a hydrolysis of polysaccharides and further conversion of the degradation products into colored products[2]. Furthermore, the ageing of cellulose has been shown to be influenced by the presence of moisture[3]. Both the loss of cellulose DP and the brightness loss were found to be greater when the heat treatment was done in a moist atmosphere. A similar work in which also the influence of metal ions was investigated confirmed that the amount of moisture influenced the degree of brightness reversion on heat treatment[4].

The chemistry of conversion of simple carbohydrate structures on heat treatment under acid conditions has been the subject of comprehensive studies. Already some 40 years ago[5, 6], it was demonstrated that oxidized sugars like 2-(or 3-)keto-methyl-β-D-glucoside or glucuronic acid are degraded in the presence of acid to form reductic acid together with several other products (Figure 1). Further work under more well-defined acidic conditions revealed a series of conversion products from simple sugars on heat treatment as shown in Figure 2[7].

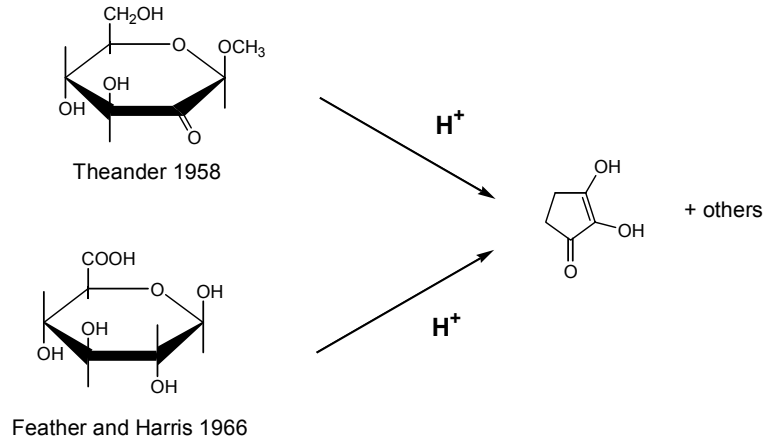


Figure 1. Conversion of oxidized sugar structures into reductic acid on treatment with acid.

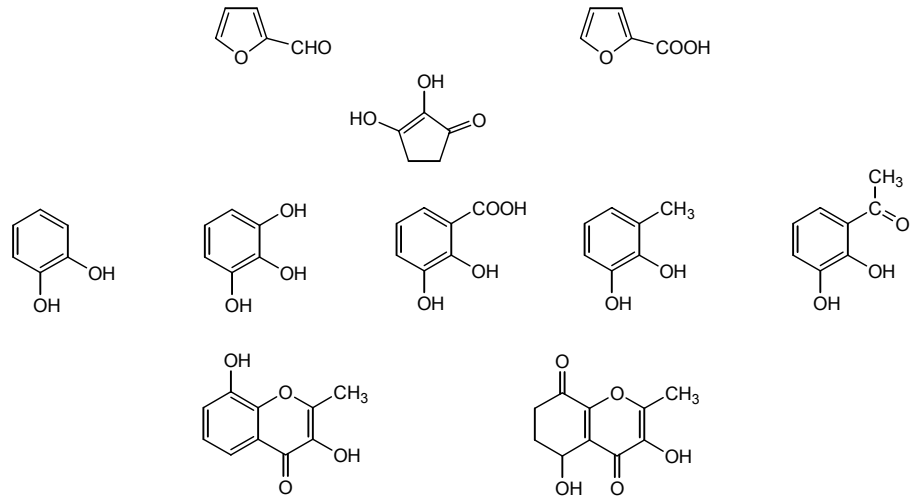


Figure 2. Products, formed after treatment of glucuronic acid in water at pH=3.5-4.5 and 96 ^{o}C for 4h.

Several of these products are sensitive to oxidative conditions such as those encountered when pulp is stored in the presence of air and humidity and many are also good complexing agents for metal ions. Thus, a variety of chemical structures are theoretically possible as being the course of thermal post-yellowing in bleached chemical pulps. Some of these have been tested in order to find out their tendency to introduce color under accelerated ageing conditions of bleached chemical pulp. These results are presented in Table 1 where it can be seen that oxidized carbohydrates as well as reductic acid are especially prone to give discoloration[8].

Table 1. Accelerated ageing of filter paper impregnated with various model compounds. Conditions: 80% rel. humidity, pH=5.5, 80 °C, 16 h.

Added compound	Brightness, %
None	86.8
Cellobiose	83.5
Hydroxymethyl-furfural	74.3
Glucuronic acid	37.4
3-keto-methyl-β-D-glucoside	37.4
Reductic acid	19.4

Some 10 years ago, it was demonstrated that the 4-OMe-glucuronic acid groups attached to the xylan in both softwood and hardwood to a great extent are converted into unsaturated hexenuronic acid (HexA) groups during the course of a kraft cook[9]. The reaction is outlined in Figure 3. In the subsequent bleaching operation, the HexA-groups were found to be completely or partly retained in the pulp depending on the bleaching chemicals employed[1, 10]. Furthermore, it was found that on bleaching of softwood as well as of hardwood, the degree of thermal yellowing was high after bleaching with ECF- or TCF-sequences[11]. The yellowing could, however, be substantially reduced if the pulp was pretreated with xylanase prior to the heat treatment thus supporting the view that HexA might be actively involved in the yellowing reactions (Figure 4).

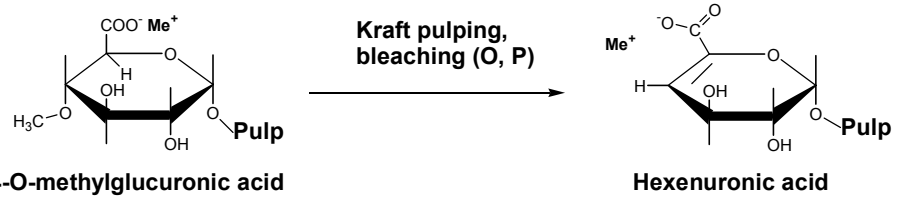


Figure 3. Formation of hexenuronic acid (HexA) from 4-OMe-glucuronic acid units in xylan on kraft cooking. The stability of HexA under alkaline conditions results in residual amount in bleached pulps.

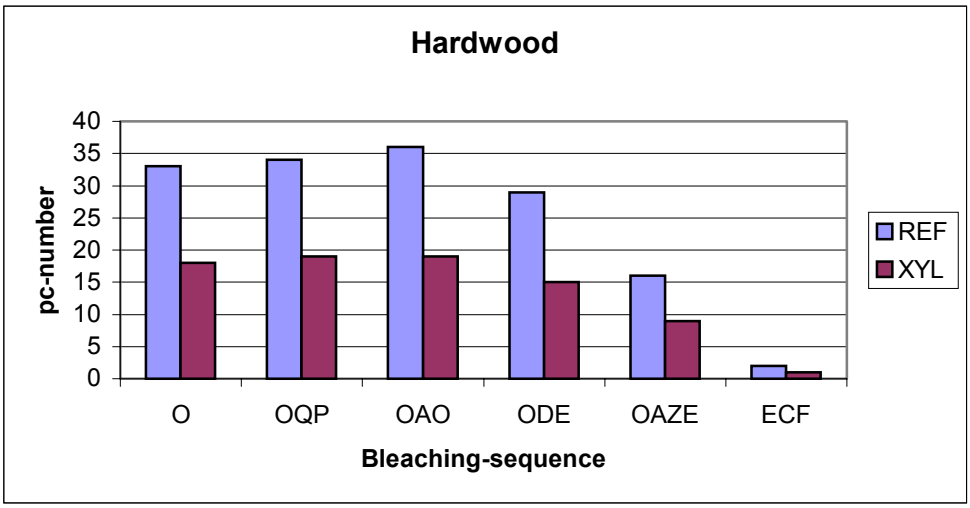


Figure 4. Yellowing tendency (pc-number) on thermal ageing of bleached birch pulps with/without prior treatment with xylanase (XYL).

In the present work, attempts have been made to further investigate the chemistry encountered when bleached chemical hardwood (birch) pulps are subjected to heat treatment in the absence of light. The conditions for maximum yellowing as well as the influence of transition metal ions have been investigated. The degree of yellowing was also analysed as a function of the amount of HexA present in the pulp. Furthermore, a major portion of the colored component(s) have been isolated and subjected to chemical analysis by gas chromatography and mass spectrometry. Correlations between the low molecular weight products obtained from aged pulp and from aged HexA attached to xylan have been sought.

Experimental

Pulp Samples

A commercial birch kraft pulp was used in most experiments. The bleaching was done in the sequence OQPQ(PO). The brightness of the pulp was 90.3% ISO.

Hexenuronic acid, HexA

The content of HexA in pulp samples was determined according to a published method developed at the Royal Institute of Technology[12].

Accelerated ageing of pulp samples

The procedures described in Refs 13 and 14 were followed.

Preparation of water extracts from aged pulp samples

Dried pulp (~92% dry content) was aged for various lengths of time. Subsequently, the sample was impregnated with 1.25 mL of pure water per gram of pulp and placed in a sealed polyethylene bag over-night, thus allowing the water to distribute evenly in the sample. By applying a pressure of 0.5 MPa on the sample, the water was pressed out to yield an aqueous pulp extract.

Separation of products present in aqueous extracts

After purification of aqueous pulp extracts by either TLC or anion exchange resin chromatography, the resulting solutions were freeze-dried and silylated. Further analysis was done by GC-MS on an Rtx-5 column. The program was 80 ^{o}C for 1 min followed by a temperature rise of 10 ^{o}C/min to a final temperature of 250 ^{o}C which was kept for 3 min. The MS instrument was operated in the EI mode at 70 eV.

Results and Discussion

On treatment of pulp samples at an elevated temperature under conditions ressembling those encountered during pulp storage, a large drop in brightness could be observed. The yellowing tendency was found to have an optimum at pH-values around pH=4.5 and, depending on the temperature, could reach brightness loss values of around 20-40 units after approximately one week (Figure 5). In analogy to the heat-induced yellowing of mechanical pulps, it was found that the content of moisture in the pulp played an important role and large differences in yellowing tendency was found for completely dry pulps and for pulps at e.g. 92% dry content. Whereas the former did not yellow at all, the latter gave the results shown in Figure 5. This result also confirms the old data described above.

Another feature of the aged pulp samples was the fact that a considerable amount of the color could be removed by a simple washing with water, thus indicating the formation of low molecular weight

material (Figure 6). The fact that some of the color seems to be more strongly retained in the fibers indicates, however, also that more than one reaction mode may be operative. Alternatively, the colored compound(s) are successively becoming attached to the fibers by some secondary reaction as the ageing reactions proceed.

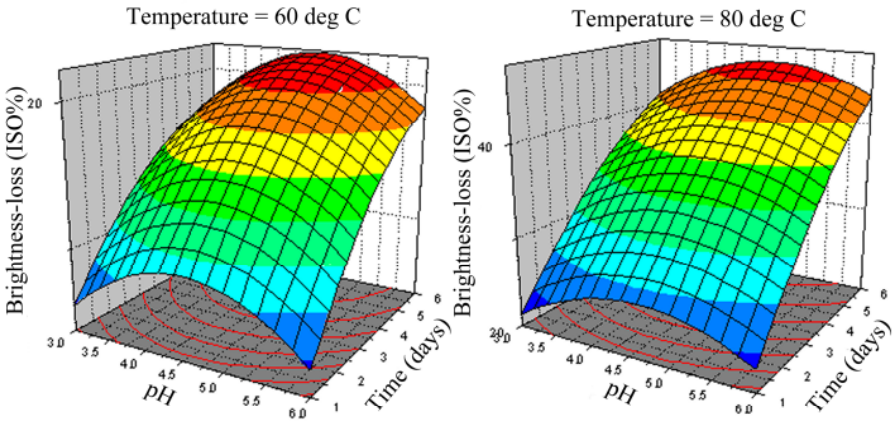


Figure 5. Heat-induced yellowing of bleached birch kraft pulp at two different temperatures and at 92% dryness. Influence of time and pH-value in the sheet.

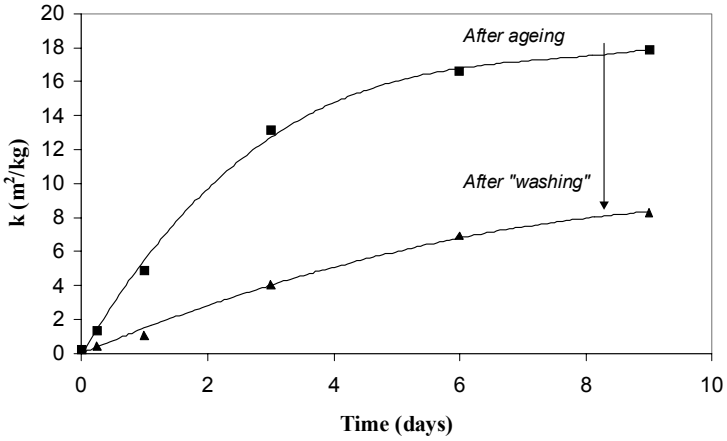


Figure 6. Light absorption coefficient (k) at 457 nm of pulp as a function of ageing time at 80 °C at 92% dryness. The effect of washing the pulp with water is shown by the arrow.

On some of the aged pulp samples, the formation of color was analysed by UV-Vis spectroscopy of the pulp sheets. As shown in Figure 7, the discoloration was found to gradually increase as the severity of the treatment increased. A certain increase in the spectra at 280 nm was clearly discernible, thus indicating, in accordance with the discussion above, that a formation of aromatic structures may have taken place. The predominant feature of the spectra is, however, the large increase in absorption that can be seen over almost the entire wavelength region from around 250 to 700 nm. Obviously, a much more complex reaction pattern is directing the total formation of color than just a formation of aromatics.

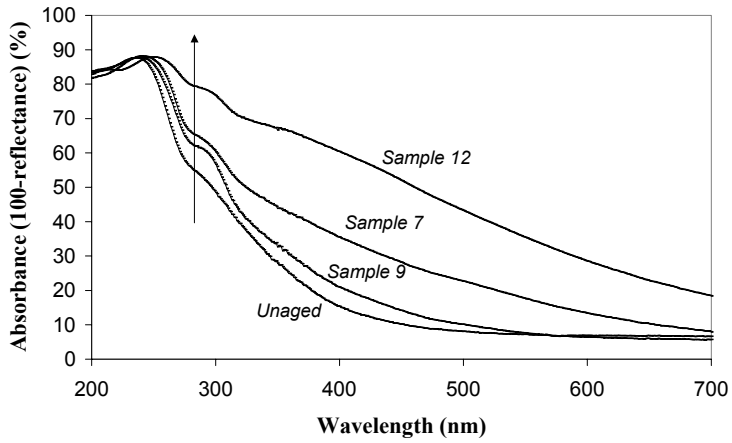


Figure 7. Light absorption of bleached birch kraft pulp samples after heat treatment for various lengths of time at 92% dryness. The arrow indicates the absorbance at 280 nm.

The behaviour of pulps on heat treatment, described in Figure 4, indicates that hexenuronic acid (HexA) may play an important role in the yellowing reactions. Therefore, the concentration of HexA in pulp was followed as a function of heat treatment time. As shown in Figure 8, a substantial loss of HexA could be noticed which followed the degree of yellowing.

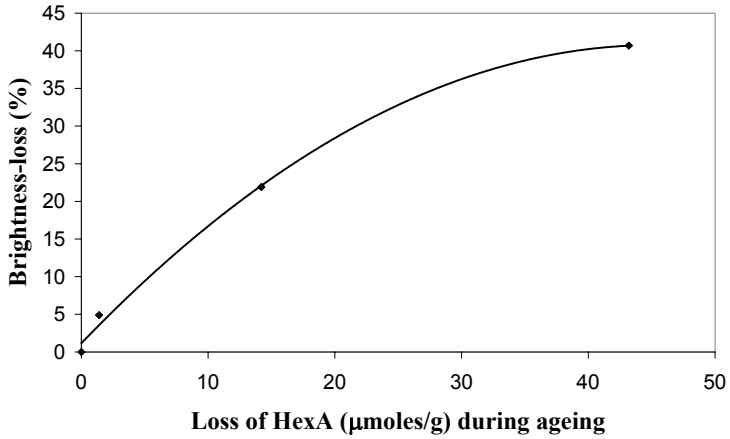


Figure 8. The consumption of HexA on heat-induced ageing at 92% dryness of bleached birch kraft pulps.

Further attempts to correlate the concentration of HexA in the pulp with the ageing tendency was done by prior partial removal of HexA before the heat treatment was carried out. Two different modes of HexA elimination were tried, viz an acid hydrolysis and an ozone treatment. In both cases, the concentration of HexA in the pulp was lowered substantially and, as a result, the yellowing tendency was also lowered. In neither of the experimental approaches could, however, a clear correlation between the remaining HexA in the pulp and the yellowing tendency be obtained. This is exemplified in Figure 9 which shows that the acid hydrolysis of the pulp was able to reduce the amount of HexA by ~80%. The corresponding decrease in yellowing was only reduced by less than 50%, however.

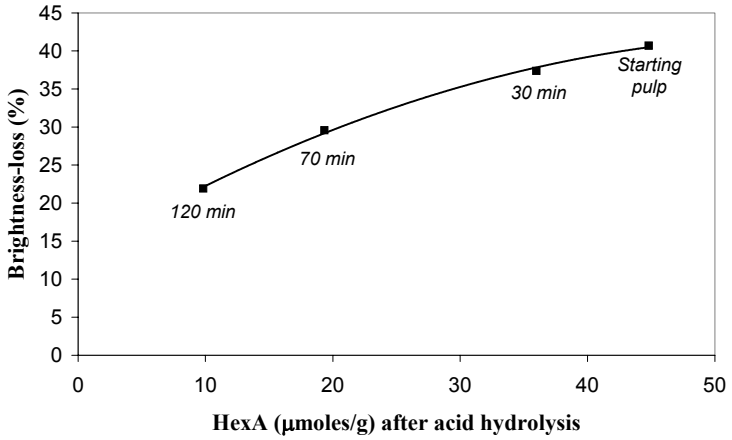


Figure 9. Brightness loss of pulp sheets containing various amounts of HexA. The HexA was removed by acid hydrolysis at 100 °C and pH=2.1 for various lengths of time. Ageing at 92% dryness, 80 °C, pH=4.5 and 6 days.

The bleached birch pulp used in this work was found to contain very small amounts of residual transition metal ions, viz. 2.1 ppm of iron and <0.5 ppm of copper and manganese. In an attempt to identify the role of transition metal ions, present at these levels, for the heat-induced ageing, pulp sheets were impregnated with either water, iron (II) or iron (III) and subjected to ageing at 92% dryness for 20 hours at 70 °C. The results are shown in Table 2 where it can be seen that only iron (II) gave a clearly discernible effect on the degree of color formation.

Table 2. Brightness reversion by added iron (~2 ppm) on heat-induced yellowing of bleached birch pulp.

Sample treatment	Brightness	Brightness loss
None	90.3	8.4
Water	90.1	8.9
2.3 ppm iron (II)	90.2	12.5
2.3 ppm iron (III)	90.3	9.4

In order further to identify the role of metal ions, a mild acidic washing of a pulp sample was performed such that the content of HexA was not affected. For each sample, the amount of removed iron was analysed and the sample subjected to heat-induced yellowing for 1 or 4 days respectively at 70 °C. As can be seen in Figure 10, a noticable reduction in the degree of brightness loss was obtained which was linearly related to the amount of iron that was removed from the pulp. All pulp samples showed, however, still a considerable yellowing, possibly related to the remaining amounts of iron in the pulps.

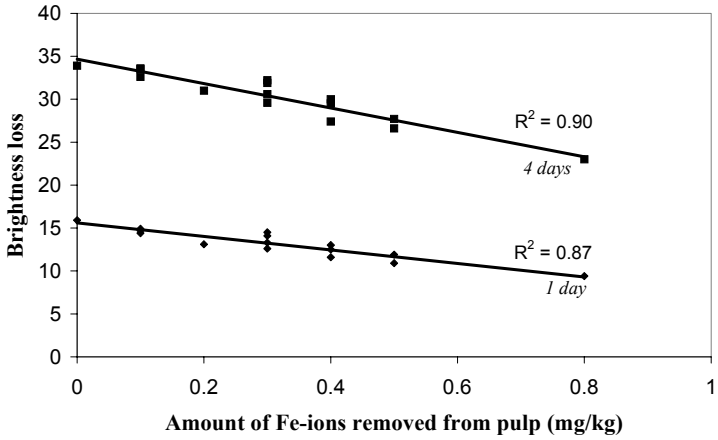


Figure 10. Yellowing tendency after 1 and 4 days of pulp samples after partial removal of iron from the pulp by mild acidic washing.

The fact that a substantial portion of the color-giving material formed on ageing is water soluble was used for a more thorough analytical investigation. For this purpose, a pulp sample was aged for 12 days at 80 °C. Both the unaged and the aged pulp were subjected to a comprehensive analytical scheme as outlined in Figure 11.

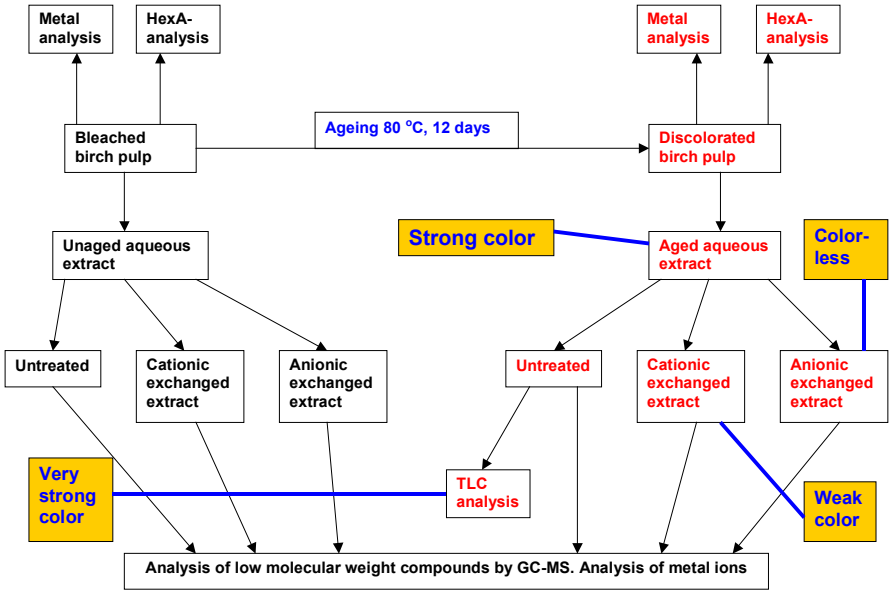
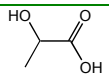
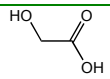
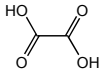
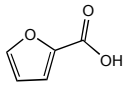
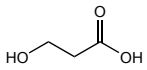
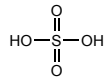
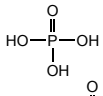
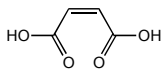
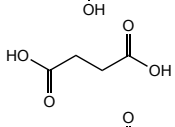
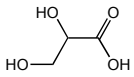
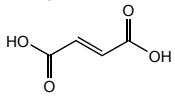
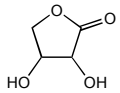
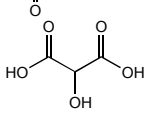
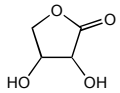
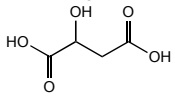
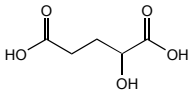
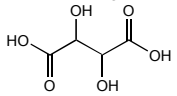
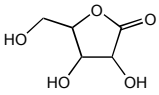
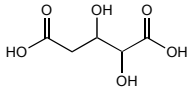


Figure 11. Analytical scheme used for the detailed investigation of pulp and aqueous extract before/after heat treatment for 12 days at 80 °C.

As seen in the figure, the aged aqueous extract was strongly colored with the colored components being further concentrated by TLC resulting in a dark brown extract. In the aged extract, a substantial portion of the iron, originally present in the pulp, was found with a simultaneous decrease in the amount remaining in the pulp. By GC-MS analysis of the various aqueous extracts shown in Figure 11, a total of 29 low molecular weight compounds were identified. For the purpose of comparison, a similar ageing of a HexA-containing xylan was also conducted. These analyses revealed that the presence of color in an

extract was related to certain compounds in the mixture. Furthermore, the degradation of HexA-xylan gave rise to the same compounds (with one exception). The results are shown in Table 3.

Table 3. Compounds identified after GC-MS analysis of aqueous extracts from unaged/aged bleached birch kraft pulp. Names in bold refer to compounds related to color. Numbers in bold refer to compounds obtained from an aqueous extract after ageing of a xylan-HexA product.

No.	Analyte	Chemical Structure	No.	Analyte	Chemical Structure
1	**2-hydroxy propanoic acid (lactic)**		**2**	**2-hydroxy acetic acid (glycolic)**	
3	**ethane-1,2-dioic acid (oxalic)**		4	2-furan-carboxylic acid	
5	3-hydroxy propanoic acid		6	sulfuric acid	
7	Phosphoric acid		8	2-butenedioic acid (maleic)	
9	**2-butanedioic acid (succinic)**		10	2,3-dihydroxy propanoic acid	
11	**2-butenedioic acid (fumaric)**		12	3,4-dihydroxy-2-furanone	
13	2-hydroxy propanedioic acid		14	3,4-dihydroxy-2-furanone	
15	**2-hydroxy butanedioic acid (malic)**		16	Pentose	
17	Pentose		**18**	**2-hydroxy pentanedioic acid**	
19	Pentose		20	2,3-dihydroxy butanedioic acid (tartaric)	
21	Xylonic acid lactone		22	2,3-dihydroxy pentanedioic acid	
23	Pentose		24	Pentose	
25	Hexose		26	Hexose	
27	Hexose		28	Pentose	
29	Hexose				

The overall results obtained indicate that HexA is involved in the color-forming reactions since the pH-optimum for ageing is much higher than that required for elimination of HexA from the pulp. The fact that HexA is degraded during ageing and that a lower amount of HexA in the pulp gives rise to a lower degree of yellowing are supportive of this view. Furthermore, the degradation of HexA is accompanied by a release of transition metal ions, notably iron. Other experiments indicated that iron (II) may contribute to the formation of color. In the chemical analysis no colored products were detected, however, only a number of aliphatic acids and some sugars and sugar-derived products. Although HexA seems to be involved in the ageing reactions, additional experiments are therefore necessary in order to clearly define the origin of color. Only then will it be possible to find ways of eliminating the heat-induced discoloration of chemical pulps.

Conclusions

The thermal brightness reversion of bleached chemical birch pulp can give rise to a large loss of brightness. This loss is influenced by the amount of water in the pulp, the temperature, the storage time and the pH of the pulp sheet. A high degree of brightness reversion was found at a dryness level of 92%, a temperature of 60 ^{o}C or higher and a pH=4-5. On storage, trace amounts of iron are released from the pulp together with organic degradation products which, predominantly, seem to originate from carbohydrates. The brightness reversion is accompanied by a successive degradation of hexenuronic acid groups and indications have been found that this degradation plays an active role in the discoloration reactions.

References

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