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Role of Hemicelluloses in the Formation of Chromophores During Heat Treatment of Bleached Chemical Pulps

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Summary: The heat-induced colour formation of TCF- and ECF-bleached chemical pulps has been investigated. Partial hydrolysis of the pulps and analysis of the carboxyl content of the pulps and hydrolysed matter were carried out. It was found that the yellowing tendency of the pulps corresponds to the content of hydrolysable substances. The hydrolysis leads to a considerable removal of the carboxyl groups in the case of hardwood pulps. Differences between softwood and hardwood pulps are discussed in terms of their hemicellulose content. The yellowed pulps were extracted and the extracts were analysed by different NMR and mass spectrometric techniques. Structures of low molecular products were elucidated and the routes of their formation were proposed. The results suggest that the yellowing proceeds in two main steps, i.e. decay of unstable polysaccharide chains such as hemicelluloses to low molecular carbohydrate compounds that subsequently undergo dehydration and condensation reactions to form coloured products.

Keywords: bleached pulps; chromophore structures; hemicelluloses; thermal yellowing

Introduction

Cellulosic fibre materials such as bleached wood pulp or paper come into contact with heated surfaces or high temperature reaction media during their production or processing, e.g. in drying or bleaching lines as well as in gluing devices or hot presses for the manufacture of laminated boards. At the contact surfaces, these materials are exposed to temperatures above 100 °C. The heat induces thermal processes which usually lead to non-beneficial effects such as yellowing, discolouration, or unpleasant odour. Chlorine-free bleached pulps are particularly sensitive to high-temperature reactions caused by their relatively high content of oxidized groups and short carbohydrate chains [1–3]. Two main steps of the yellowing process can be distinguished. The first one is the thermal decay of polysaccharide chains to deliver short chain products or sugar monomers. Here, a different role of carbonyl and carboxylic groups was found [4,5]. In addition, the high temperatures lead to oxidation of the cellulose surface [6], thus suggesting that oxygen radicals are involved. The participation of free radicals was then proven by chemiluminescence measurements during artificial aging in the temperature range up to 200 °C [7–9]. Chain cleavage proceeds also by hydrolytic pathways at lower pH or as peeling-like reactions in the presence of alkali.

The intrinsic acid content of the pulps, the humidity as well as oxidizing agents such as transition metal ions act as additional factors.

The formation of pulp chromophores requires the presence of low-molecular carbohydrate structures. These may stem from oxidized cellulose molecules as well as hemicellulose residues which remain on the pulps even after strong alkaline

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treatment [10]. Probably, even monomeric precursors are required. Transformation reactions already start at 120 °C, if catalysts are used. In the case of all pentoses or hexoses investigated, furan derivatives were formed. They appeared in the reaction mixture as intermediates giving rise to the formation of oligomers or polymers. Besides these substances, products with 3 or 4 carbon atoms were found. Among them were hydroxy acetone, hydroxy propionic acid, or hydroxy butyric acid. In alkaline solutions, minor amounts of phenolic compounds were formed, probably by condensation of the above mentioned decomposition products of sugar [11–13].

However, the formation and chemical characteristics of the coloured products produced during heat-induced yellowing of bleached pulps and papers made from those pulps have been investigated quite rarely. Granström and Gellerstedt [14] reported on chromophoric structures found in aqueous extracts of thermally yellowed TCF pulps. Among these structures various saturated and unsaturated dicarboxylic compounds, lactones, as well as furancarboxylic acid have been identified. However, it is unlikely that they contribute to the yellow-brownish colour that is obtained when TCF-bleached pulps are heated. Even though it was shown that the addition of 5-hydroxymethyl furfural to filter paper leads to a strong discolouration of the paper sample [15], the structures of the colour forming compounds have not yet been elucidated except in the work done by Rosenau et al. [16]. It was shown that so-called ''Theander-products'' are formed that can be isolated by a special procedure using the BF_3-acetic acid complex. So far, the origin of the chromophores has not been fully proven. Therefore, the structure of additional chromophores as well as their sources should be studied in connection with the different thermal stability of hemicelluloses and cellulose. For this, an attempt was made to extract at least part of the coloured matter formed during heat treatment of bleached pulps and investigate the structures of some of the compounds found within the extracts. In addition, some pathways of colour forming reactions should be discussed in the light of the structures found.

Materials and Methods

The TCF bleached pulp samples from soft and hardwood were provided by Metsä Botnia Oy (Finland). Some of them were commercial products which originated from different pulp producers. These samples were used without further bleaching or other treatment.

The conditions of the heating experiments are indicated in the respective parts of the discussion.

In order to produce sufficient amounts of chromophores, the heating was carried out for 24 h at 140 °C in an 100 ml laboratory autoclave which was placed into an oil bath. The reaction medium was air at ambient pressure. There was no special adjustment of the moisture content during the heat treatments. Methanol extraction was realized in a Soxhlet extractor for 6 hours. It was followed by vacuum evaporation of the extracts at room temperature. The dry residues of the extracts were re-dissolved in the corresponding solvents for subsequent NMR measurements.

Partial acid hydrolysis was carried out for 2 h at 95 °C. 1 g of the pulp was weighed into a round bottle flask and 250 ml of 2 N hydrochloric acid were added. After stopping the reaction, the residue was filtered with a glass filter and washed thoroughly with distilled water. The hydrolytic mass loss was determined after drying at 105 °C.

The determination of the carboxyl content was carried out in two steps – a pre-treatment step and the titration procedure. For the pre-treatment, 3 g of the pulp sample were twofold soaked with 0.5 l of a 0.1 N solution of hydrochloric acid for 1 h each, and subsequently filtered. After the second treatment, the filtered pulp was five times suspended in 200 ml of deionised water which was previously saturated with carbon dioxide, and subsequently filtered.

The electric conductivity of the water used did not exceed 0.05 μS/cm. After the last filtration, no chloride ions were found in the filtrate. Finally, the pulp was washed with degassed water.

For the titration, the pulp was once more filtered and suspended in 0.5 l of a 1 mM solution of sodium chloride in degassed water, followed by stirring of the suspension in a nitrogen atmosphere. The titration was made with an aqueous solution of 0.1 N sodium hydroxide which was added in portions of 0.1 ml each. After the addition of a portion, one had to wait 3 min before the next 0.1 ml would be added. The titration curve was obtained by measuring the electric conductivity.

For the enzymatic treatment, 5 g of the pulp was suspended in 300 ml of a citrate buffer (pH 4.9) containing 450 U of *Trichoderma viride* xylanase (Sigma). The suspension was 60 h shaken at 35 °C. Subsequently, it was filtered and the pulp was washed thoroughly with deionised water. After drying at 60 °C, the pulp was weighed.

The carbohydrate monomers (Fluka) were used as purchased without further purification. These compounds were added to the filter paper from their aqueous solutions. The paper samples were previously extracted with a mixture of acetone and water (1:1).

The brightness of the pulp sheets was determined by means of a Shimadzu UVPC 2101 equipped with a device for diffuse reflectance measurements. The yellowing intensity was characterized by the yellowing factor YF described by equation 1.

$$\mathrm{YF} = \frac{R_0 - R}{R_0} \times 100\% \qquad (1)$$

where R_0 and R are the diffuse reflexion indexes at 457 nm before and after heat treatment.

The ^{1}H- and ^{13}C- as well as HMQC measurements of the pulp extracts were carried out with a 500 MHz NMR spectrometer (Bruker). For GC-MS, a Hewlett-Packard G 1530A system equipped with a quadrupol mass detector MSD 5973, was used. MALDI-TOF measurements were made with a Shimadzu MALDI 2 (MALDI-TOF, N_2-laser 337 nm/6 mW, puls duration 3 ns, 3/20 kV AV).

Results and Discussion

Structural Sources of Chromophores

In Table 1, the properties of the investigated pulps are demonstrated. The birch TCF and ECF as well as eucalyptus kraft pulps contain the highest amount of carboxyl groups.

Heating of fully bleached ECF and TCF pulps at 130 °C in air caused an intensive loss in brightness. The birch pulp undergo strongest yellowing effect. This is shown in Table 2.

The maximum of the difference spectra of the samples before and after heating was at approximately 450–460 nm, i.e. the spectral range where the brightness index as well as YF were measured. Hence, colour formation strongly influences the brightness of the pulps. The shape of the spectra did not vary in the temperature range between 120 °C and 160 °C thus indicating that the nature of the chromophores has not considerably changed when the temperature increased. However, a significantly

Table 1.
Degree of polymerisation (DP) and content of functional groups of non-treated commercial pulps.

No.	Sample	DP	Carboxyl content, μmol/g	Carbonyl content, μmol/g
1	Hardwood kraft ECF	1208	40,0	26,5
2	Mixed hardwood kraft ECF	845	29,0	15,7
3	Birch kraft TCF	974	85,5	11,3
4	Eucalyptus kraft ECF	978	67,2	17,8
5	Pine kraft TCF	672	43,3	15,2
8	Birch kraft ECF	997	57,6	16,5

Table 2.
Yellowing factors of various TCF or ECF bleached pulps before (column A) and after (column B) enzymatic removal of xylan. Column C: difference B-A as a measure of the stabilising effect of xylanase treatment.

No.	Sample	YF, %		ΔYF, %
		A	B	B-A
1	Hardwood kraft ECF	19,9	17,0	−2,9
2	Mixed hardwood kraft ECF	12,7	11,8	−0,9
3	Birch kraft TCF	30,2	25,1	−5,1
4	Eucalyptus kraft ECF	17,7	15,6	−2,1
5	Pine kraft TCF	19,5	17,3	−2,2
6	Birch kraft ECF	26,6	21,0	−5,6

higher amount of coloured substances was formed at the higher temperature.

The greater part of the coloured material could be removed from the pulps by extraction with methanol. Evaporation of the extract had to proceed at room temperature in vacuum, otherwise polymerisation occurred. The dissolving strength of solvents with lower polarity such as cyclohexane or methylene chloride was insufficient. This can be explained by the low swelling ability of these solvents towards the polysaccharides as well as the polar character of the chromophores.

After extraction, the pulps remained weakly coloured. It was therefore assumed that chromophores might also be formed within the polyose or cellulose chains or at least be linked to these chains. Attempts to isolate those structures by treatment of the pulps with hydrolysing enzymes and subsequent extraction failed. Use of the extraction method suggested by Rosenau et al. [16,17] did neither lead to completely colourless carbohydrate residues. Analysis of the extract gave evidence to the formation of condensation products of furfural. The aromatic compounds described in these works could not been detected. This might be due to the different heating conditions, since these products were detected when carbohydrates were treated under alkaline conditions [11–13].

Previous research did not convincingly provide an answer to the question which of the constituents of the holocellulose do mainly contribute to the formation of coloured substances. It is, however, well known that high amounts of acidic groups lead to increased thermal yellowing [1,3]. Since hemicelluloses are regularly furnished with carboxylic groups, it had to be elucidated whether their removal from the pulps would stabilise their brightness.

Softwood contains less hemicelluloses of the xylan type (approx. 3–6%) than hardwood (approx. 17–20%) [18]. Hemicelluloses of hardwood contain approx. 4–6% of 4-methyl-glucuronic acid units as well as 4% of additional acetyl groups attached to xylan whereas in softwoods the content of glucuronic acid and acetyl groups is lower (2–5% and 1.2–1.6% respectively). If hemicelluloses of the mannan type are also taken into consideration, hardwoods contain the fourfold amount of acidic groups than softwood species. Hoffmann and Patt investigated the xylan contents of pulps made from spruce and beech by selective delignification with $NaClO_3$. They found 9.5% for spruce and 35,8% for the beech pulp [19] with respect to the overall hemicellulose. When these pulps were subsequently treated with magnesium bisulphite to a holocellulose yield of approx. 60%, the xylan contents decreased to 7.9 for spruce and 27.7% for beech. The alternative treatment with 0.5% NaOH to a comparable pulp yield lowered the xylan content to 6.8% and 21.4% respectively.

Bachner et al. [20] investigated the distribution of hemicelluloses in different layers of the cell wall of unbleached pulps. They found the xylan content of pine kraft pulp to be 8.8%, whereas spruce sulphite pulp contained 6.5%. This shows that the differences between sulphate and sulphite pulps are conserved under pulping and bleaching conditions although the absolute contents are decreasing.

The mild acid hydrolysis by 2n HCl caused a considerable loss of matter which was by almost four times higher for birch TCF than for the pine TCF. The ratio of the removed acidic components by dilute hydrochloric acid was higher by a factor of 4.4 for birch compared to pine (Table 3). Although a considerable part of the

Table 3.
Changes in ECF bleached hardwood and softwood pulps caused by partial acidic hydrolysis. For comparison, the mass loss during xylanase treatment is given.

Sample	Mass loss by hydrolysis, %	Content of acidic groups in the non-dissolved residue, % of starting material	Removed part of acidic components, % of starting material	Mass loss by xylanase treatment, %
Birch	24.1	9	21.8	20.5
Pine	6.4	23	4.9	1.7

dissolved matter may come from the cellulose, this ratio demonstrates that most of the acidic groups were removed by dissolution of the hemicelluloses.

The treatment with xylanase caused a remarkable mass decrease of the birch sample, as well, whereas the pine pulp was only weakly affected (Table 2). The partially hydrolysed pulps underwent a lower yellowing than the starting material (Table 1). The stabilising effect is higher for the birch pulp than for the pine pulp. This agrees with the differences in the loss of substance during the hydrolysis. Thus, it can be concluded that the components removable by gentle hydrolytic procedures form a considerable part of chromophore precursors. Among them, xylan type hemicelluloses play a remarkable role as source of chromophores.

Investigations of the Chemical Structure of Chromophores

HPLC measurements showed that the coloured solutions obtained by methanol extraction of heated pulps contained a mixture of numerous low-molecular compounds at low concentration. To elucidate some of the chromophoric structures, it was necessary to use a combination of different measuring techniques.

The ^{1}H NMR spectrum of the extract of birch ECF pulp shows a group of signals in the 0.5–2.5 ppm region connected with protons $-CH_3$, or $-CH_2-$, and $-CH-$ moieties (Figure 1). The strong peaks between 2 and 2.5 ppm stem from protons of CH_2- or CH_3- groups linked to $-C{=}C-$ or $-C{=}O$ double bonds. Protons of CH_x connected with –O– provide a less intensive but distinct group of signals between 3.0 and 4.3 ppm, which are mainly related to carbohydrate structures. The presence of minor amounts of aromatics or heteroaromatics is confirmed by weak signals from 6.5 to 9 ppm. The presence of lignin aromatics cannot be excluded. Aldehyde protons are indicated by a weak single peak at 9.8 ppm.

The ^{13}C NMR spectrum shows indications of CH_x- (30 ppm (weak), 40 ppm (multiplett, strong)), aromatic systems (127 ppm, very weak), carboxylic groups 166 ppm (medium), and carbonyl groups 185 ppm (very weak) and 197 ppm (very weak), too.

The extracts were subsequently silylated and analysed by GC-MS. Except for a number of rearrangement products of the silylating agent, various compounds could be observed that were obviously products of the thermal decay of carbohydrates, i.e. furan carboxylic acid (7.8 min), glycerol (11.5 min), succinic and/or malonic acid (12.3 min). In addition, the extract contained at least two different hexose monomers (20.5 and 26.3 min). The measurement suffered from the low solubility of most of the compounds, thus it could not be excluded that some structures were not covered by this method.

MALDI-TOF-MS is suitable to record molecules of low volatility. In addition, in the course of its deposition on the sample holder, the sample may be concentrated by repeated dropping and evaporation of its solution on the same spot. This makes the method worthy when only low concentrations of a compound are formed. The mass spectrum of the birch sample indicates that different mono- and disaccharide structures were liberated from the pulp during heating (Figure 2).

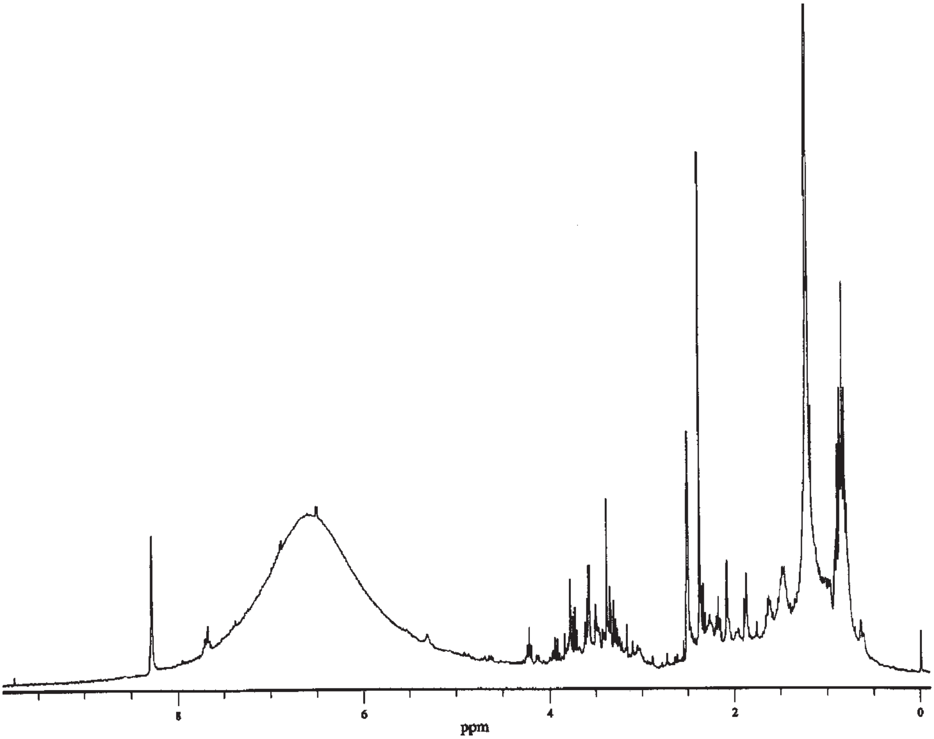


Figure 1.
^{1}H-NMR spectrum of a methanol extract of a heated TCF bleached birch kraft pulp after vacuum drying and re-dissolution in D_6-DMSO in presence of small amounts of CD_3COOD.

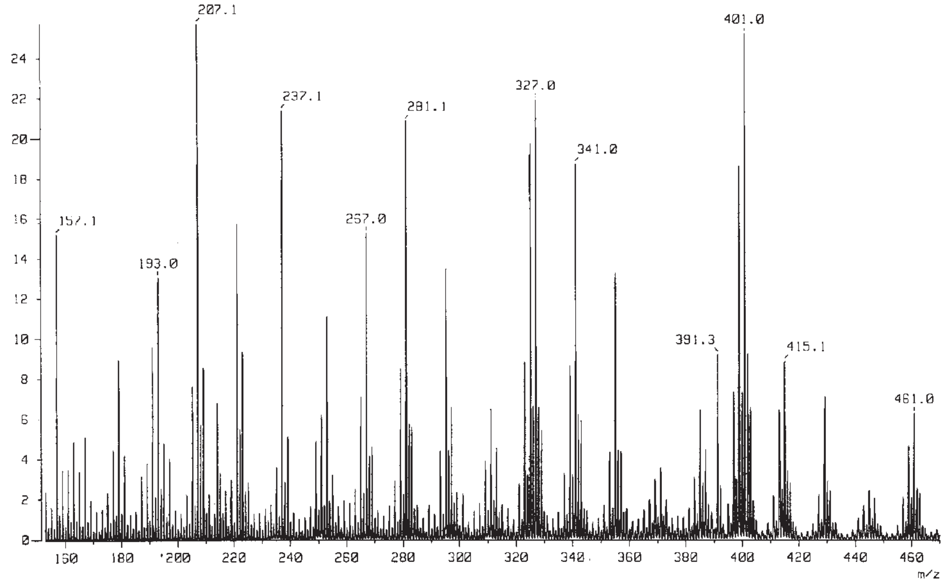


Figure 2.
MALDI-TOF mass spectrum of a methanol extract of heated TCF bleached birch kraft pulp.

In addition to small amounts of glucose (m/z 180), 4-methoxy glucuronic acid (m/z 207) as well as hexenuronic acid (m/z 176) were detected. The signal peaks at 281 and 341 were assigned to xylobiose and cellobiose, respectively.

Further peaks originate from products formed by thermal conversion of monosaccharides. The signal with m/z 193 stems from an condensation product of furan-2-aldehyde, whereas the one at m/z 252 is caused by the dimerisation product of 5-hydroxymethyl furan-2-aldehyde.

In addition, there is a signal at m/z 221 with the adjacent peaks 222 and 223. A compound with a molecular mass of 222 g/mol can be formed during the thermal treatment of hexoses as a condensation product of 5-hydroxymethyl-2-furan aldehyde and reductic acid (1) (Figure 3). Reductic acid is easily formed from monosaccharides, especially from hexuronic acids by heating [21]. The reaction pathway leading to structure 1 is also shown in Figure 3.

The condensation of 5-hydroxy-furan-2-aldehyde with a dehydration product of glucose forms compound 2 (Figure 4). Its occurrence in combination with Maillard-type products has also been described in [21]. A peak with the appropriate m/z value 251 is also present in the spectrum.

Studies with Carbohydrate Monomers

The oxidation of polysaccharides during the bleaching processes leads to a number of oxidised hexose or pentose structures [22]. The occurrence of those structures such as aldehydes, ketones or carboxylic acids in cellulose or polyoses acts as starting point for chain scissions. In addition, peeling reactions from the newly formed chain ends lead to the formation of monomeric sugar acids. These are, among others, important sources of chromophores. To elucidate whether there are differences in the colour forming behaviour of monosaccharides with different chemical structures, filter paper was soaked with aqueous solutions of glucose, gluconolactone, and glucuronic acid, dried at room temperature and subsequently heated. The treatment with high temperatures led to weak yellowing in the case of glucose and gluconolactone. Figure 5 demonstrates that the brightness loss of paper treated with these substances is comparable to or slightly stronger than that of the untreated one. In contrast, glucuronic acid is converted to a dark brown product decreasing the brightness value considerably.

This reflects the reactivity of the different sugar monomers. It is obvious that, in particular, the free carboxylic groups give rise to formation of coloured matter. As

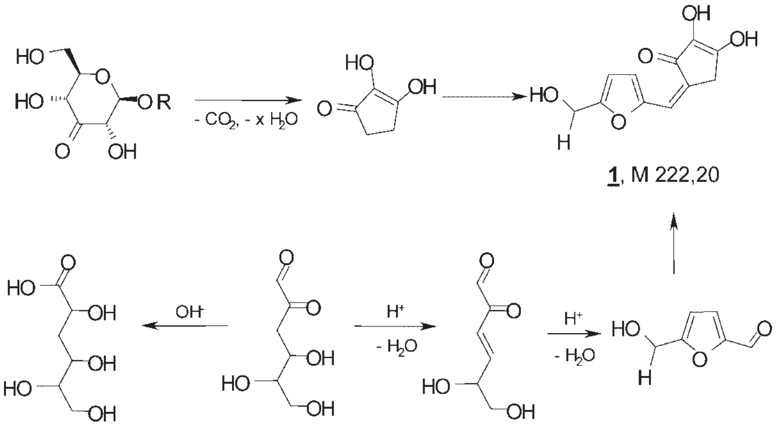
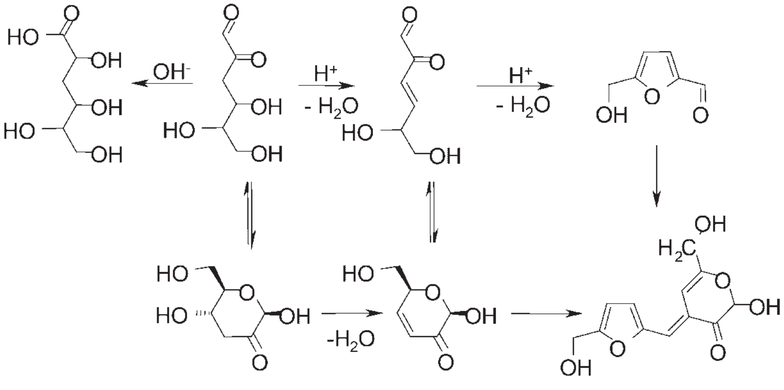


Figure 3.
Reaction scheme of the formation of compound 1.



2, M 251

Figure 4.
Reaction scheme of the formation of compound **2**.

was already mentioned, Theander and Nelson [21] described the formation of reductic acid from glucuronic acid. The acidic conditions provided by the presence of high amounts of acidic components in the pulp may lead to an additional degradation of the cellulose chains, thus producing more monosaccharids which are then transformed into chromophores. It is well known that 5-hydroxymethyl furan-2-aldehyde is formed from hexoses under acidic conditions in high yield. Its condensation to respective polymers also requires an acidic environment.

Conclusion

The heat-induced yellowing of TCF- or ECF bleached kraft pulps is associated with the presence of thermally less stable

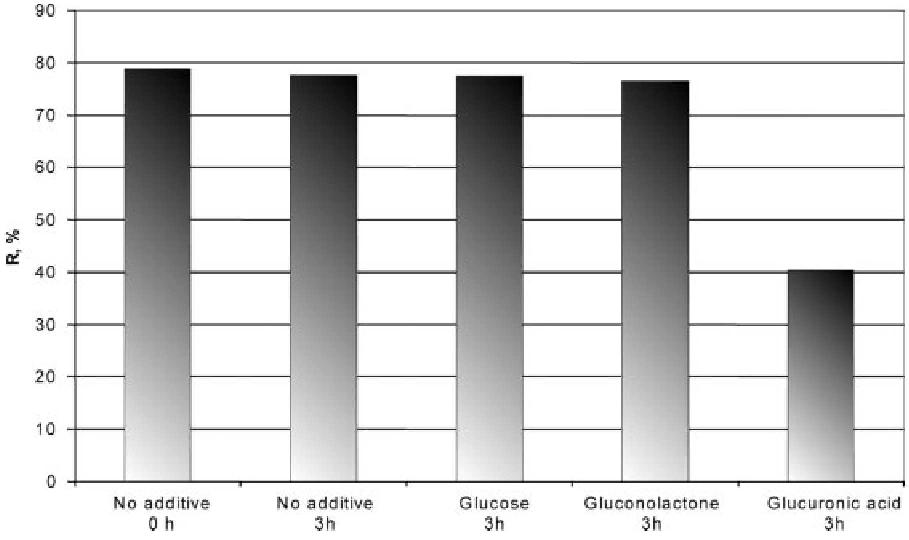


Figure 5.
Brightness of a filter paper sheet with adsorbed monosaccharide derivatives after heat treatment at 130 °C. The concentration of the adsorbed compounds was 3% (w/w).

polysaccharide components. They are represented first of all by hemicelluloses, though partial oxidation and degradation of the cellulose can also contribute to their appearance. In hardwood pulps, these substances contain the major part of oxidized groups such as carboxyl with respect to the whole pulp. They are considered to be the main source of low molecular precursors which give rise to the formation of dehydration products such as hydroxymethyl furaldehyde or reductic acid. In addition to phenolic compounds, the so-called ''Theander's products'', the condensation of these substances leads to the formation of chromophores. Among the monosaccharides, the glucuronic acid exhibits the highest reactivity with respect to chromophore formation. It is obvious that the removal of the readily degradable pulp components contributes strongly to the stabilisation of the pulps. At present state there are too few data to make a differentiation between ECF and TCF pulps neither between sulphate and sulphite pulps in terms of their hemicellulose content and composition. However, it could be shown that acid hydrolyses removes large parts of the acidic groups from the hardwood pulps, whereas most of the carboxyl groups of the softwood pulp remain in the pulp. The stabilisation effect is therefore higher for hardwood pulps at higher initial yellowing. The challenge is now to find conditions by which these compounds can be removed or deactivated without further oxidation and degradation of the cellulose.

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