

ABOUT GLUCURONOXYLAN EFFECT ON THE HORNIFICATION OF *E. GLOBULUS* BLEACHED PULPS

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ABSTRACT

The effect of 4-*O*-methylglucuronoxylan (GX) on the hornification of bleached kraft and acid sulphite *Eucalyptus globulus* chemical pulps has been investigated. Almost straight-line dependence of kraft pulp hornification from GX content was explained through the diminishing of fibrils aggregation and better accessibility of amorphous cellulose regions to water in GX enriched pulps. The higher hornification of sulphite than kraft pulp was assigned to lower GX content in the former and to unfavourable rearrangement of cellulose molecules in crystalline and amorphous regions during acid sulphite pulping.

INTRODUCTION

Hornification is one of the fundamental concepts in pulp and paper science and could be defined as a set of physico-chemical phenomena occurring during pulp drying.^[1,2] The former term is directly associated with limited pulp swelling in water caused by rearrangement of cellulose molecules in fibrils and interfibril aggregation in virgin (never-dried) pulp leading to the fibre stiffening, surface collapse and shrinkage. In a significant degree these structural changes are irreversible, i.e. initial swelling properties are not restored after fibre re-wetting and beating.^[1,2] Hornification is responsible for the drastic decrease in papermaking properties of chemical pulps and recycled fibres.^[3] Different factors such as wood fibre origin (gymnosperms or angiosperms), pulping method, fibre biometrics, chemical environment of the stock (cations composition) and the amount of non-cellulosic concomitants (hemicelluloses, lignin and extractives) affect pulp ability to hornification.^[1-4]

Particular attention was paid to the impact of hemicelluloses on hornification of chemical pulps. Thus the effect of 4-*O*-methylglucuronoxylan (GX) could be understood through its determinant role as a holder of carboxyl groups,^[5] which have a significant influence on the pulp hornification.^[6, 7] Carboxyl groups can promote (being in H⁺ form) or decrease (being in cationic form) the hornification extent.^[6, 7] It has been also proposed that formation of lactone

bridges between uronic moieties of GX and cellulose hydroxyls favours the aggregation of cellulose microfibrils and is a part of the hornification mechanism.^[8, 9] At the same time, as reported, both acidic (such as GX) and neutral hemicelluloses (such as glucomanans) prevent the pulp hornification via diminishing of interfibril aggregation in fibres.^[10, 11] Hence, the role of hemicelluloses in the swelling behaviour of dried pulp is rather ambiguous. Particularly, the effect of glucuronoxylan (GX) on the hornification of eucalypt pulps is unknown.

In this work the relationship between GX abundance in *Eucalyptus globulus* kraft and acid sulphite pulps and their hornification during industrial drying process was evaluated. The structural changes in cellulose were elucidated in relationship to GX occurrence. The hornification features of eucalypt kraft and acid sulphite pulps were compared.

EXPERIMENTAL

Materials

Industrial never-dried and dried on airborne pulp drier (10% humidity) *Eucalyptus globulus* bleached kraft (KP) and acid sulphite (ASP) pulps were supplied by PORTUCEL and CAIMA pulp companies (Portugal), respectively. Kraft pulp was bleached to 90% ISO by DEDED sequence and sulphite pulp was bleached to 89% ISO by EOP-P sequence. The chemical (Table 1) and biometric (Table 2) characteristics of pulps are presented below.

Table 1 - Results on chemical analyses of eucalypt pulps.

Pulp	Intrinsic viscosity cm ³ /g	α -cellulose %	Pentosans content %	Lignin content %	COOH groups content, mmol/100g
Kraft	1000	78.8	17.1	0.15	11
Acid sulphite	1100	91.3	6.0	1.10	9

Table 2 - Biometric characteristics of eucalypt pulps.

Pulp	Fibre length (L _w) mm	Coarseness mg/m	Fines %
Kraft	0.66	0.074	7.5
Acid sulphite	0.61	0.077	10.6

Extraction of xylans

Partial removal of GX from pulps was carried out by extraction with 10% KOH under nitrogen atmosphere (0.01% NaBH₄) during 30-180 min.^[13] After pulp washing with distilled water to neutral pH the former was dried as handsheets of ~1mm thickness at 130-

140°C in an oven with forced air circulation to ~7% humidity thus simulating industrial pulp drying.

Dilute acid hydrolysis

The dilute acid (10% H₂SO₄) hydrolysis of pulps was carried out under reflux during 3.0-4.5 h. The intrinsic viscosity in CED and DP of cellulose was determined according to SCAN-CM 15:88. The hydrolysis rate constant (K_H) of amorphous cellulose in intercrystalline space was determined using values of cellulose DP before (DP₀) and after the hydrolysis to levelling-off DP (DP_t):^[14] $1/DP_t - 1/DP_0 = K_H * t$ (t- hydrolysis time to reach the levelling-off DP).

Analyses

The degree of pulp hornification was determined based on Water Retention Value (WRV)^[15] of never-dried (WRV₀) and dried (WRV₁) pulps according to Weise^[11].

$$\text{Hornification, \%} = \frac{(\text{WRV}_0 - \text{WRV}_1)}{\text{WRV}_0} * 100 \quad (1)$$

X-ray diffraction scattering analysis of pulps was carried out on a Philipps X Pert MPD diffractometer using Cu-K_α source (λ = 0.154 nm) in the 2θ range 2-40° and scanning step width of 0.02°/scan. Pulps were analysed as textured samples. Pulp pellets of 1.2 cm diameter and about 1 mm thickness were prepared by pressing (50 MPa). Each analysis was repeated in triplicate. The phone scattering was subtracted from pulp diffraction diagram. The crystalline reflections and amorphous halo were defined according to recommendations published previously.^[16] The degree of cellulose crystallinity (DC₀) was calculated as:

$$\text{DC}_0, \% = I_{\text{cr}} / (I_{\text{cr}} + I_{\text{am}}) * 100 \quad (2)$$

where I_{cr} and I_{am} are the scattering intensities from crystalline and amorphous regions of cellulose, respectively.

The degree of crystallinity (DC) corrected for the presence of non-cellulosic components in pulp was calculated as follow:^[16]

$$\text{DC, \%} = \text{DC}_0 * (1 + 0.3(1/w-1)) \quad (3)$$

where **w** is the relative proportion of cellulose in pulp. The average width of crystallite in 002 lattice plane was determined from Scherer equation taking into account the crystallite defects:^[16]

$$L_{002}, \text{ nm} = [(\beta_{002} \cos \theta_{002} / \lambda)^2 - (\delta_L / d_L)^2]^{-1/2} \quad (4)$$

where β₀₀₂ is a width on the middle height of 002 reflection, rad; θ₀₀₂ - is the maximum of 002 reflection, rad; λ - wavelength of X-ray source (0.154 nm); δ_L and d_L are parameters related to the lattice distortion perpendicular to 002 plane direction (0.05) and the distance between 002 lattice planes (0.395 nm), respectively.

¹³C solid-state Cross Polarization-Magic Angle Spinning Nuclear Magnetic Resonance (¹³C CP-MAS NMR) spectra were registered on a Bruker Avance 400 spectrometer. Samples (pulp of ~50% humidity) were packed into a zirconia's rotor sealed with Kel-F™ caps and spun at 7 kHz. Acquisition parameters were as follows: 90° proton pulse of 4μs width, contact time 2 ms, and pulse delay of 4 s. Number of scans varied between 20000 and 30000. The crystallinity index (CrI) was determined from areas of the crystalline (A_{86-92 ppm}) and amorphous (A_{79-86 ppm}) C-4 signals in cellulose:^[17]

$$\text{CrI, \%} = A_{86-92 \text{ ppm}} / (A_{86-92 \text{ ppm}} + A_{79-86 \text{ ppm}}) * 100 \quad (5)$$

The strength properties of pulps were assessed according to ISO standard procedures

RESULTS AND DISCUSSION

Effect of hornification on pulp strength properties

Eucalyptus globulus bleached airborne dried (convectonal drying) kraft (KP) and acid sulphite (ASP) pulps showed rather distinct degrees of the hornification, 48% and 29%, respectively. The hornification of KP decreased to 21% after beating to 30°SR indicating a partial recuperation of its swelling in water. In the case of ASP the beating effect was unclear because of a strong fibre shortening (the fraction of fines reached approx. of 30%) that gave rise to artificial WRV increase of beaten pulp. Visually beaten ASP fibres were less fibrillated and swollen than KP fibres. The conversion of both pulps to sodium form did not change significantly the main hornification features.

It is interesting to note that the drying machinery have a notable influence on the hornification of bleached pulp. Thus the hornification degree of airborne dried kraft pulp (KP) was remarkably lower (29%) than that of roll dried (contact drying) kraft pulp (KP1) (37%). The swelling recuperation of the later after beating to 30°SR was also rather moderate (25% of hornification for KP1 against 21% for KP).

Overall, the degree of pulps hornification correlated to their strength dropping after drying (Figure 1). This was especially remarkable in the case of unbeaten ASP showing the loss of tensile strength and burst resistance almost to 50%. The restoring of mechanical properties after beating was much more pronounced

for KP than for ASP. Hence, both pulps suffered a notable deterioration in strength properties after

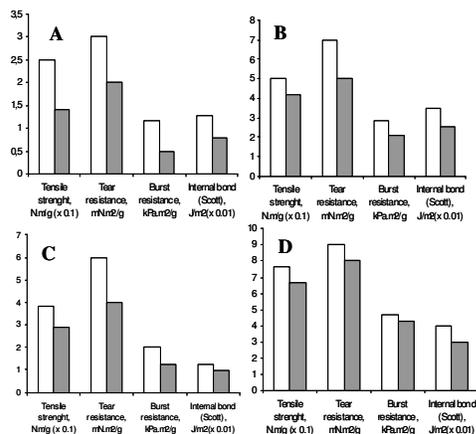


Figure 1 - Strength properties of unbeaten (A,C) and beaten to 30 °SR (B,D) sulphite (A,B) and kraft (C,D) bleached pulps before (clear bars) and after (dark bars) drying.

drying, which was more accentuated for ASP than for KP.

The kraft pulp dried on roll dryer (KP1) showed in general slightly lower (5-10%) mechanical strength when compared to that of pulp dried on airborne dryer after beating to 30°SR. The most significant decrease was noted for the burst resistance (about 15%).

Effect of glucuronoxylan on pulps hornification

A significant difference in hornification of KP and ASP can not be explained by their fibre biometrics, intrinsic viscosity or by the amount of carboxyl groups, which were very similar (Table 1, 2). The amount of GX, expressed as pentosans content, was the only component in pulps that varied significantly and is suspected to affect the pulp swelling behaviour after drying. In order to verify the importance of GX content on pulp hornification, KP was extracted with 10% KOH solution for different time periods aiming to produce a series of pulps with gradually decreased amounts of GX. All pulps, extracted of KP series and ASP, were dried in the laboratory to approx. 7% humidity.

Data presented in Figure 2 show almost straight-line dependence of kraft pulp hornification with GX content, i.e. GX plays a determinant protecting role against hornification. However, for the same GX level (about 6%) the hornification degree of ASP was almost 50% higher than that of KP (Figure 2). This fact indicates that other structural features in pulp, besides GX abundance, affected the fibre swelling after drying. One of these features may be the difference in chemical structure of GX and its occurrence in KP and ASP fibres.

Another reason could be the difference in cellulose supramolecular structure of two pulps and the

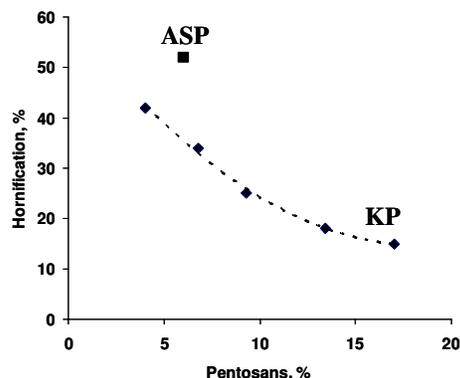


Figure 2 - Effect of pentosans content on the hornification of unbeaten kraft pulps (KP series). Hornification degree of ASP is depicted to compare with that of KP series.

structural changes occurred during pulp drying. Both possible causes were evaluated.

The GX structures in KP and ASP showed certain diversity (Table 3). Thus, GX in KP possess a high molecular weight and poor ramification with uronic moieties and acetyl groups. In contrast, GX in ASP has relatively small molecular weight and is highly ramified with uronic moieties. These structural features explain the similar amount of carboxyl groups in KP and ASP at rather different GX content in pulps (Table 1).

Table 3 - Structural features of *E. globulus* heteroxylans in wood and pulps.

Structural Fragment*	Relative abundance (per 100 Xylp units)		
	Wood xylan	KP xylan	ASP xylan
Xyl	45	91	88
Xyl-3Ac	24	1	2
Xyl-2Ac	15	5	4
Xyl-2,3Ac	6	1	trace
Xyl-3Ac-2GlcA	10	2	7
MeGlcA	7	2	9
MeGlcA-2Gal	3	2	trace
M _w , kDa	36.0	24.0	8.1

* The designations for the fragments are as follows: →4)-β-D-Xylp-(1→ (Xyl); →4)[3-O-Ac]-β-D-Xylp-(1→ (Xyl-3Ac); →4)[2-O-Ac]-β-D-Xylp-(1→ (Xyl-2Ac); →4)[3-O-Ac][2-O-Ac]-β-D-Xylp-(1→ (Xyl-2,3Ac); →4)[4-O-Me-α-D-GlcA-(1→2)][3-O-Ac]-β-D-Xylp-(1→ (Xyl-3Ac-2GlcA); 4-O-Me-α-D-GlcA-(1→ (MeGlcA); →2)-4-O-Me-α-D-GlcA-(1→ (MeGlcA-2Gal).

It can be speculated that, due to highlighted structural features, GX in KP is strongly bounded to cellulose fibril surface (especially over crystalline regions) and covers larger fibril areas than in ASP. This gives benefits to KP since promote better swelling of dried fibres due to existing of hydrophilic GX layer on the fibril surface facilitating water attraction and preventing strong interaction between crystalline regions of adjacent fibrils.

The concentration of GX on the fibre surface in chemical kraft pulps is usually higher than on the surface of fibres pulped by acid sulphite cooking.^[19] This should also contribute to better swelling of dried KP than of ASP due to easier fibre separation in suspension and higher contact area with water.

Changes in cellulose structure during drying

According to prevalent opinion cellulose suffers structural changes during pulp drying.^[1,20] Particularly, the degree of cellulose crystallinity (DC) is always slightly increased. A partial cocrystallization of crystallites in adjacent fibrils was proposed as part of hornification mechanism.^[20, 21] Aiming to evaluate the changes in cellulose of eucalypt pulps during industrial drying process these were analysed by wide-angle X-ray diffraction scattering, solid-state ¹³C NMR and diluted acid hydrolysis (Table 4).

X-ray diffraction (XRD) analysis confirmed the increase of cellulose DC during drying of KP and ASP. These data were coherent with results obtained by ¹³C CP-MAS NMR. However, the cocrystallization of crystallites in fibrils was not confirmed since their average widths in 002 plane (L_{002}) were practically the same before and after drying (Table 4). This also indicates that the observed increase in DC cannot be explained by ordering of paracrystalline cellulose on the crystallite surface as sometimes commented.^[8]

It is important to note that L_{002} of KP was about 15% larger than that of ASL and about 30% larger than in wood (L_{002} in wood cellulose was of 4.0 nm as assessed from XRD analysis of extractives-free sawdust). The increment of average width of crystallites originates from their partial cocrystallization during wood pulping and is an inherent property of cellulose.^[22] This phenomenon is associated with junction of crystalline domains in adjacent fibrils, whose surfaces are appropriately

Table 4 -Cellulose structural analysis in *E. globulus* industrial pulps.

Pulp	DC/CrI (%)	L_{002} , (nm)	Levelling-off $[\eta]$, (cm ³ /g)	K_H *10 ⁵ (min ⁻¹)
KP n/d	68.7/59.7	5.8	105	2.0
KP	70.2/60.4	5.6	111	1.8
ASP n/d	67.2/56.3	4.9	113	1.6
ASP	68.1/57.7	5.0	125	1.2

n/d means never-dried pulp.

oriented and free off non-cellulosic components. The plasticizing properties of reaction medium influence the degree of cocrystallization being ordered depending the pulping origin as follows: kraft > soda > neutral sulphite \approx acid sulphite > acid organosolv.^[22] Therefore, our results confirm previously published observations that partial cocrystallization is much more pronounced during kraft pulping than during acid sulphite process.

Following the commonly accepted fringed-micellar theory postulating that crystalline regions in fibril alternate with less ordered amorphous regions^[23] it is possible to assess the changes in cellulose longitudinal crystallite size during pulp drying via the hydrolysis of amorphous counterpart with diluted strong mineral acid (10% H₂SO₄). The hydrolysis rate constant (K_H) also provides an idea about the density of molecular package in amorphous regions.^[13] The small increase in levelling-off intrinsic viscosity of both pulps after drying indicates the increase of molecular order in amorphous regions or even their partial recrystallization (Table 4). The last could explain a small increase of cellulose DC during pulp drying. These features were less pronounced for KP than for ASP.

Data of Table 4 allows the conclusion that cellulose chains in amorphous regions of never-dried KP are less ordered than those in ASP. This is certainly a consequence of different pulping media applied (alkalinity is better than acidity to promote a loosening of cellulose chains in amorphous regions) and possibly reflects a GX structural intervention when cellulose chains in amorphous regions are embedded in GX matrix preventing their strong intermolecular interaction. In the last case GX should play a role of spacer preserving cellulose ordering when drying. Evidence was provided from structural analysis of cellulose in pulps with different GX content (Table 5). As the amount of GX in KP decreased the constant of hydrolysis rate to levelling-off DP (K_H) of cellulose diminished. Simultaneously, DC of cellulose gradually increased with progressive GX removal from pulp indicating probable partial recrystallization of amorphous cellulose regions abutting to crystalline

Table 5 – Results on cellulose structural analyses in kraft pulps with different GX content.*

Xylan content in kraft pulp, (%)	DC, (± 0.3%)	K_H , *10 ⁵ (min ⁻¹)	Hornification, (± 2%)	Stiffness, kN/m
17.1	69.5	1.4	15	198
9.3	71.8	0.9	25	243
6.8	-	0.7	34	270
4.0	72.1	0.6	42	288

*- pulps with different GX content were obtained from KP by extraction with 10% KOH. All pulps were dried under laboratory conditions.

zones. Hence, the lack of GX increased the molecular order in amorphous regions during drying diminishing their accessibility to water molecules under pulp re-wetting thus enhancing pulp hornification. As a consequence the flexibility and plasticity of fibres decreased dramatically leading to their stiffening after drying (Table 5).

The influence of GX on cellulose structural changes during pulp drying was additionally confirmed by ^{13}C CP-MAS NMR (Table 6). The latter technique also permits the estimation of average lateral fibril aggregate dimensions. This can be done by determining the relative integral intensity of water accessible and total (accessible and inaccessible) fibril surfaces based on a simple approximation that aggregates have square cross-sections.^[11] As can be seen from data of Table 6, the diminishing of GX content in KP increased the statistical dimensions of fibril aggregates. This confirms the positive effect of GX on the prevention of excessive aggregation of fibrils during pulp drying.

Table 6 - Results on cellulose analyses in kraft pulps employing ^{13}C CP-MAS NMR.*

Xylan content in KP, (%)	CrI, ($\pm 0.4\%$)	Average lateral fibril aggregate dimension, (± 1 nm)
17.1	62.8	14
9.3	63.5	16
4.0	65.5	19

*- pulps with different GX content were obtained from KP by extraction with 10% KOH. All pulps were dried under laboratory conditions

CONCLUSIONS

Results of the present work allow some propositions concerning the role of GX in pulp hornification. As almost all GX in bleached pulps occurs in the interfibrillar space of secondary wall, their influence on the fibril-fibril interaction during drying is of great importance.^[24] Thus GX physically impede the strong bounding of adjacent fibrils during water removal from interfibrillar cavities. In this way GX control the extent of fibrils aggregation in pulp. These features are schematically depicted in Figure 3. Due to the hydrophilic nature, GX favour re-wetting of dried fibres partially restoring fibre swelling capacity and diminishing pulp hornification.^[1-3]

In the case of KP, where GX envelops fibrils extensively, their aggregation upon drying is less pronounced (pathway A, Fig. 3) than in ASP containing rather small amounts of GX (pathway B, Fig. 3) thus diminishing hornification. The structure and molecular weight can also contribute to the mode of GX interaction with fibrils and is a good challenge for the future investigations.

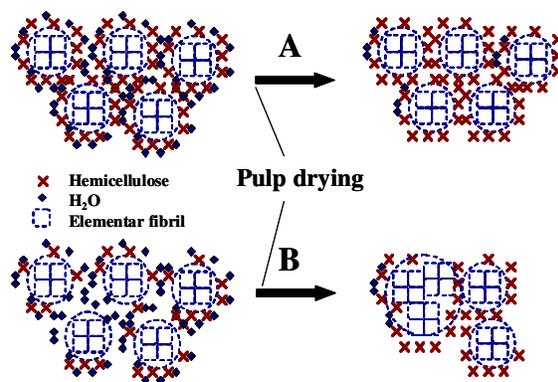


Figure 3 - Schematic representation of cellulose fibrils aggregation during pulp drying.

The larger average width of cellulose crystallites in KP when compared to ASP implies a lower specific surface of fibrils in KP that reduce their ability to aggregation. In this context a higher cocrystallization of cellulose crystallites during kraft pulping than in acid sulphite process is beneficial regarding pulp hornification.

GX affects the structural changes of cellulose during pulp drying hindering the rearrangement of cellulose molecules in amorphous zones and preserving them from tighter package or even from partial recrystallization. This improves cellulose accessibility at re-wetting. As a consequence, fibres become less stiffen and better swollen in water. Such a GX effect that avoids the strong consolidation of amorphous cellulose during pulp drying may be of the same importance as the GX protection role against fibrils aggregation and contribute to the diminishing of pulp hornification. The molecular package of cellulose in amorphous regions of ASP is tighter than that of KP and these regions suffer a greater subsequent ordering (or even recrystallization) during drying. This is one of the reasons why at the same level of GX content ASP exhibited higher hornification than KP.

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