

# CONTRIBUTION OF OXIDIZABLE STRUCTURES OF DIFFERENT ORIGIN TO KAPPA NUMBER AND BRIGHTNESS OF *EUCALYPTUS GLOBULUS* KRAFT PULP

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## ABSTRACT

The contribution of different oxidizable structures to kappa number (KN) and brightness of well-delignified unbleached *E. globulus* industrial kraft pulp has been investigated. It was found that 61.0% of KN is a contribution from residual lignin (7.2 from 11.8 KN units), 28.0% from HexA (3.3 KN units), 5.5% from extractives (0.6 KN units) and 5.5% from poorly soluble black liquor compounds adsorbed on pulp. The brightness of unbleached pulps is primarily determined by lignin chromophore structures, followed by tannin type extractives. Diffuse reflectance UV-vis and EPR spectroscopies were suggested to be complementary techniques for the study of chromophore structures in unbleached pulps.

## INTRODUCTION

Kappa number (KN) is a basic parameter of pulp widely used in industry as a technologic control parameter and in laboratory as an index related to the residual lignin content. Formally KN reflects the number of potassium permanganate oxidation equivalents consumed in reaction with pulp under strictly defined acidic conditions and it is attributed essentially to the presence of lignin, which reacts much faster with  $\text{KMnO}_4$  than polysaccharides [1]. However, during last decade, it has been demonstrated that non-lignin oxidizable structures contribute strongly to KN as well, showing, sometimes, comparable to the residual lignin contribution [2, 3]. These non-lignin structures are mainly assigned to hexeneuronic acid (HexA) residues and to other unknown carbohydrate-derived unsaturated moieties [4]. The contribution of lignin and non-lignin oxidizable structures to KN values varies remarkably, depending on the origin of unbleached pulps (softwood or hardwood, pulping method). This knowledge is crucial to understand the correctness of applying KN for the description of pulp bleaching behaviour with different bleaching reagents. The input of different pulp components (residual lignin, polysaccharides and extractives) to KN, brightness and brightness reversion of unbleached/partially-bleached

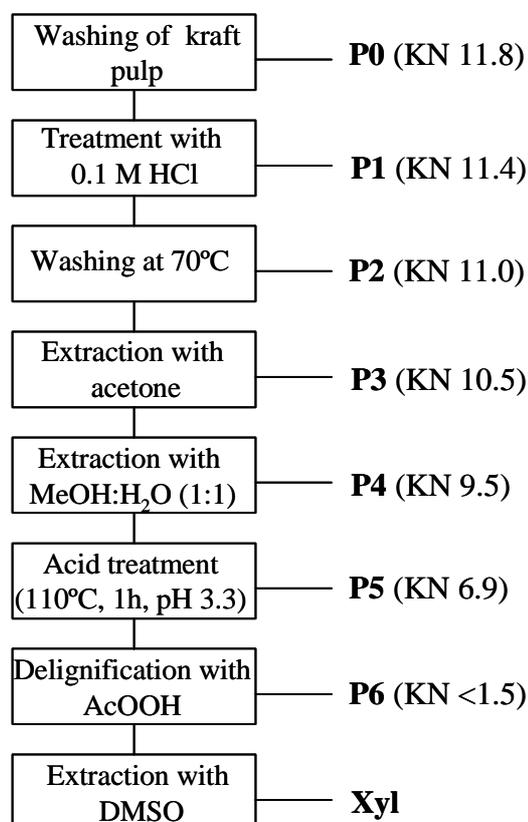
pulps are topics of intensive studies in the area, aiming to provide new bleaching strategies [4-6].

The contribution of different components of *E. globulus* unbleached kraft pulp to its KN and brightness was never studied before and was the goal of this study.

## EXPERIMENTAL

### Materials

Industrial unbleached *E. globulus* kraft pulp from PORTUCEL (Cacia, Portugal) was exhaustively washed with distilled water, according to common mill practice, until pH 6.5-7.0 of washing filtrate (pulp **P0**, KN 11.8) and used for the multi-stage fractionation in order to estimate the contribution of different pulp components to its KN (Figure 1). **P0** was treated with 0.1 N HCl (pulp-to-liquid ratio 50) at room temperature during 12h resulting pulp **P1** (adapted from T 237 om-93). Such a treatment was used to eliminate transition metal ions coordinating a part of black liquor lignin and its derivatives. These were removed after **P1** treatment at 70°C during 1h (pulp-to-liquid ratio 50) resulting pulp **P2**. The latter pulp, after



**Figure 1.** Fractionation scheme of different oxidizable structures in unbleached eucalypt kraft pulp.

air drying, was extracted with acetone (Soxhlet extraction) during 6h according to T 204 om-88 to eliminate lipophilic extractives (pulp **P3**) followed by the extraction with MeOH/H<sub>2</sub>O (1:1, v/v) (refluxing during 1h) to eliminate polyphenolic compounds (pulp **P4**). Pulp **P4** was acid-treated at 110°C in formate buffer at pH 3.3 during 1h to remove HexA residues (pulp **P5**) [2]. Pulp **P5** was delignified with excess of peracetic acid (90°C, 30 min, 5% AcOOH, liquid-to-wood ratio 50) to remove residual lignin (pulp **P6**) [7].

## Analyses

The KN of all pulps (**P0-P6**) was determined manually according to the TAPPI standard T 236 cm-85. The brightness and brightness reversion (dry method) were assessed according to ISO standards (3688/1977 and 5630-1/1991, respectively). Consecutive kraft pulp treatments were also monitored by EPR and diffuse reflectance UV spectroscopy. ESR spectra (X band) were run on a Bruker ESP 300E spectrometer at 9.75 GHz (293 K, 1.2 mW microwave power, and attenuation of 10 dB). Pulp samples were analysed as 3-mm diameter pressed pellets (13±0.3 mg). The values of *g*-factor were estimated based on spectrometer calibration with “strong pitch” standard. Diffuse Reflectance spectra of pulp pellets (11-mm diameter) were registered on a Shimadzu UV2100 spectrophotometer (0.1 nm resolution). Organic extracts from **P3** and **P4** were characterised by GC-MS as TMS-derivatives [8]. Glucuronoxylan was extracted from **P6** with DMSO and characterised by <sup>1</sup>H NMR as described previously [7]. The contents of HexA and residual lignin in pulp samples were determined spectrophotometrically in cadoxen solution [9].

## RESULTS AND DISCUSSION

### Fractionation of different oxidizable groups

The fractionation results of different oxidizable groups in *E. globulus* kraft pulp are presented in Figure 1. As could be expected, residual lignin and HexA residues were the major contributors to KN, because 9.5 from 11.8 units remained in pulp after the removal of water- and organic solvent-soluble components contributed of 2.3 KN units. In order to better understand the origin of extractable components, these were investigated in more details. Water-soluble compounds were essentially the components of aromatic origin from black liquor (UV and <sup>1</sup>H NMR analyses of dry residue). These compounds were adsorbed on pulp in the form of poorly soluble salts (apparently, Ca and Mg phenolates and carboxylates). After pulp washing at 70°C 2-furoic acid was found in the aqueous extract in notable and 5-formyl furoic acid in minor amounts. These are typical products of HexA degradation under acidic conditions [2] formed during acidic pulp washing even under mild conditions (confirmed by HexA determination in pulp before and after the acid

washing). The estimated contribution of HexA residues to water-soluble material was 0.2 from 0.8 KN units, taken into consideration that 10 meq/kg of HexA in pulp correspond to 0.86 KN units [3]. The GC-MS analysis of acetone and methanol-water extracts also revealed 2-furoic acid as the major low molecular weight product. It was estimated that 0.2 from 0.5 KN units reduction in pulp after acetone extraction and 0.6 from 1.0 KN unit reduction after methanol-water extraction was due to HexA residues degradation. Hence, 1.0 from 2.3 KN units removed after extraction of demineralised pulp with cold and hot water and with organic solvents belongs to HexA degradation products. Although the pulp demineralisation under acidic conditions was rather efficient (almost twice when compared to the treatment with chelating agents) the partial degradation of HexA residues clearly complicated the estimation of water- and organic solvent-soluble components contribution to pulp KN.

### Oxidizable structures of extractives

The potential contribution of different compounds of acetone and aqueous methanol extracts to kraft pulp KN has been evaluated. The most abundant compounds from about 50 identified in acetone extract (0.18% on o.d. pulp) are presented in Table 1. Besides 2-furoic acid, benzoic and ellagic acids were suggested to be the major contributors to pulp KN. Ellagic acid, the most abundant component in acetone extract, was never detected before in significant amounts [8]. The main reason for this may be the presence of ellagic acid in the form of poorly soluble metal complexes

**Table 1.** Major acetone extractives from *E. globulus* unbleached kraft pulp (mg/100g).

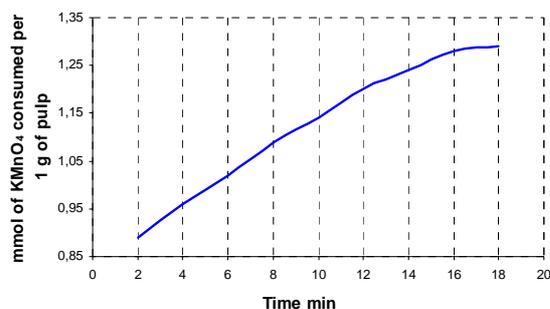
Compound	Content
Propionic acid	1.27
2-furoic acid	8.20
Benzoic acid	2.36
Glycerol	0.82
1-Tetradecene	1.33
1-Hexadecene	1.73
Azelaic acid	1.36
Palmitic acid	1.62
1-Octadecanol	0.66
Stearic acid	0.60
Docosanoic acid	1.56
Tetracosanoic acid	2.64
22-Hydroxydocosanoic acid	0.96
Hexacosanoic acid	2.57
24-Hydroxytetracosanoic acid	2.06
Ellagic acid	6.04
β-Sitosterol	5.53
β-Sitostanol	1.07

with calcium or with magnesium that was difficult to remove from pulp with organic solvent without preliminary pulp demineralization. A significant part of aqueous methanol extract (0.30% on o.d. pulp) was composed of tannins as revealed by  $^1\text{H}$  NMR analysis. Among the low molecular weight compounds identified by GC-MS, sugars derivatives, glycerol, ellagic and 2-furoic acids were the most abundant.

### Contribution of HexA and lignin to kappa number

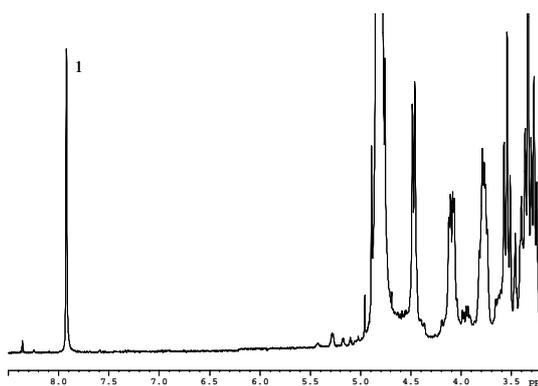
Based on UV-spectroscopy analysis of **P4** and **P5** in cadoxen solution it was suggested that only 2.3 from 2.6 KN units (Figure 1) responded to HexA residues removed from pulp during acidic treatment. The remaining 0.3 KN units were assigned to lignin degradation products (some of phenolics in the chloroform extract were detected by GC-MS). The amount of HexA residues directly found in **P0** (43.0 meq/kg of pulp) together with the sum of HexA residues estimated based on KN decrease after acidic treatment of **P4** and the contribution of HexA residues degraded in acidic washing of **P0** to 2-furoic acid found in aqueous and organic extracts (totally 37.9 meq/kg of pulp), showed a clear misbalance. This fact was tentatively assigned to the incomplete reaction of HexA with  $\text{KMnO}_4$  solution. The analysis of pulp residue after KN determination in cadoxen solution showed that about 15% of HexA residues and about 20% of residual lignin remained intact. This can be understood as a consequence of non-uniform delignification of pulp fibres during kraft pulping, when residual lignin and HexA residues in less cooked fibres react in smaller extent than in more cooked ones for the same oxidation period (10 min)  $\text{KMnO}_4$  in agreement with kinetic rules (50% consumption of oxidizing reagent) and, probably, also due to the diffusion problems. This is demonstrated in Figure 2 below showing the  $\text{KMnO}_4$  consumption during KN determination. It is clear that after 10 min some amounts of oxidised structures (about 15 %) are still not oxidized.

According to UV-spectroscopy analysis of **P6** in cadoxen solution, this pulp practically did not contain the residual lignin (<0.1%) and the consumption of



**Figure 2.** Kinetics of  $\text{KMnO}_4$  consumption during KN determination.

$\text{KMnO}_4$  could be explained also by the presence of unsaturated structures in polysaccharides partially oxidised with excess of  $\text{AcOOH}$ . In fact, glucuronoxylan isolated from **P6** by DMSO extraction showed a strong resonance at 7.9 ppm in  $^1\text{H}$  NMR spectrum (Figure 3) indicating the presence of unsaturated moieties. Regarding these results KN in **P5** was assigned exclusively to residual lignin. Hence, 61.0% of KN in the well delignified eucalypt kraft pulp was attributed to residual lignin (7.2 KN units), 28.0% to HexA (3.3 KN units), 5.5% to extractives of different origin (0.6 KN units) and 5.5% to black liquor compounds bound on pulp and difficult to remove without pulp demineralization.



**Figure 3.** Fragment of  $^1\text{H}$  NMR spectrum of glucuronoxylan isolated from **P6** ( $\text{D}_2\text{O}$ ,  $25^\circ\text{C}$ ).

### Contribution of different oxidizable structures to pulp brightness

The determination of kraft pulp brightness after isolation of different fractions oxidizable with  $\text{KMnO}_4$  allowed the evaluation of their relative contribution to this parameter in initial pulp. Simultaneously, the determination of brightness reversion permitted some conclusions regarding the importance of different oxidizable structures to deteriorate the former pulp characteristic. Data of Table 2 clearly shows that pulp brightness was essentially determined by lignin

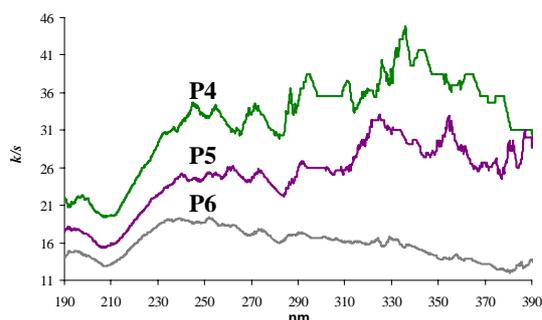
**Table 2.** Results on pulp brightness (% ISO) determination.

Pulp	Brightness	Brightness reversion
<b>P0</b>	42.3	0.8
<b>P1</b>	43.7	1.8
<b>P2</b>	43.9	1.6
<b>P3</b>	45.2	2.3
<b>P4</b>	45.9	2.0
<b>P5</b>	46.2	1.6
<b>P6</b>	90.3	9.2

chromophore structures followed by extractive compounds presumably of tannins origin. The contribution of adsorbed black liquor components was less important.

The results on brightness reversion of **P0-P5** were rather inconclusive. Unexpectedly, after the stepwise removal of transition metal ions, HexA residues and polyphenolic extractives the brightness reversion of unbleached pulp did not decrease progressively. A very significant brightness reversion of bleached pulp (**P6**) was observed, which can be explained by the formation of new chromophoric structures from oxidized polysaccharide moieties. Glucuronoxylan is responsible for this behaviour, at least partially, since the former contains notable amounts of unsaturated moieties (Figure 3). The formation of significant amounts of oxidized structures in glucuronoxylan was demonstrated previously in reactions with  $O_3$ ,  $O_2$ ,  $H_2O_2$ , and  $ClO_2$  [10]. The importance of different unsaturated structures in pulp polysaccharides for the pulp brightness reversion was highlighted previously by several researches [6, 11]. Therefore, unsaturated structures in polysaccharides formed during pulp oxidative delignification (not of HexA origin) are suspected for the pulp brightness reversion.

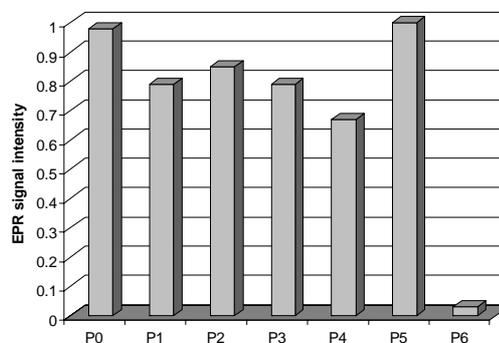
The monitoring of oxidizable structures fractionation in pulp employing diffuse reflectance UV spectroscopy did not show significant differences for pulps **P0-P4**. However, after hot acidic treatment, a notable decrease of absorption ( $k/s$ ) at 230, 245 and 255 nm was observed in **P5** and tentatively assigned to the removal of HexA residues and its degradation products from **P4** (Figure 4). The decrease of  $k/s$  at 275 and 290 nm and simultaneous increase of absorption at 320, 355, 380 and 390 nm indicated that residual lignin also suffered structural changes during hot acidic treatment resulting in new structures with conjugated double bonds.



**Figure 4.** Diffuse reflectance UV spectra of pulps.

In order to establish some correlations between the removal of chromophore structures and paramagnetic activity of pulp, **P0-P6** samples were submitted to EPR analysis. EPR spectra of all samples (**P0-P6**) revealed very similar patterns, i.e. singlets with

hyperfine splitting constant of about 14 G and  $g$  factor of 2.0031. Such EPR spectra features in lignocellulosic materials are normally assigned to free organic radicals (including of semi-quinone type) stabilized by double bond systems [12]. The relative intensities of EPR spectra are shown in Figure 5.



**Figure 5.** Relative intensity of EPR signals in pulps.

The demineralization of pulp (**P1**) favoured the decrease of residual lignin paramagnetic activity probably due to the diminishing of stabilization/formation of free radicals in lignin by transition metal cations [13]. The correlation between the brightness increase, when removing the extractives of polyphenolic origin (Table 2), and simultaneous decrease of EPR signal in **P3** and **P4** (Figure 5) evidenced the eventual paramagnetic activity of chromophore structures from tannins. The remarkable increase of EPR signal observed for **P5** after hot acidic treatment may be related to structural changes of the residual lignin as suggested from diffuse reflectance UV spectra (Figure 4). Previously, the analysis of residual lignin in eucalypt kraft pulp by  $KMnO_4$  oxidation showed its condensation during hot acidic treatment under similar conditions [14]. The increase of paramagnetic activity detected in **P5** can be explained by improved radical stability in residual lignin with higher conjugation degree of aromatic groups, i.e. system with easier delocalisation of impair electron.

## CONCLUSIONS

The results of this study showed that even in well-delignified unbleached industrial *E. globulus* industrial kraft pulp the residual lignin is the major contributor to pulp KN and brightness. Polyphenolic type extractives and black liquor components adsorbed on pulp represent the second important source of pulp colour. Due to possible incomplete reaction of residual lignin and HexA residues with  $KMnO_4$  during KN determination, calculations on the “true” residual lignin in pulp based on KN and HexA content

(corrected  $KN = KN - 0.086 * [HexA]$ ) may be underestimated. This underestimation is especially significant for the pulps with low KN and of high HexA content. Results on the brightness reversion of unbleached eucalypt kraft pulp did not allow the discrimination of some specific oxidizable structures responsible for this behaviour. It was proposed, however, that oxidised structures in glucuronoxylan, formed during oxidative delignification, might be partially responsible for the brightness reversion of oxidised eucalypt pulp. Techniques of diffuse reflectance UV-Vis and EPR spectroscopy showed their potential providing important additional information on the chromophore structures in unbleached pulps.

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