ACID TREATMENT APPLIED TO PORTUGUESE EUCALYPTUS GLOBULUS KRAFT PULPS BEFORE BLEACHING: EFFECT ON QUALITY AND ON HEXENURONIC ACIDS AND METALS CONTENTS.

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During kraft pulping, uronic acids (which are side groups linked to the xylan chain) are partially converted to hexenuronic acids (HexA). Although HexA is also destroyed throughout the cooking, its residual amount depends on wood species and on cooking parameters. In the case of eucalypt kraft pulps produced in the range of industrial cooking conditions the HexA content is quite high - 45 to 60 mmol/kg pulp (Pedroso and Carvalho 2003). This content is sufficient to provoke some harmful effects on the pulp bleaching and on brightness stability due to the unsaturated structure of this acid. In fact, during the bleaching process, the remaining HexA reacts with electrophilic chemicals (ozone, chlorine dioxide, chlorine and peracetic acid), increasing their consumption without the corresponding improvement in brightness. Although unreactive in the alkaline peroxide stage, the HexA bind damaging transition metal ions like manganese (II) which catalyses the decomposition of peroxide. Thus, previous pulp treatment with expensive and environmental non friendly complexing agents, such as EDTA or DTPA, is usually employed. It has also been found that HexA groups contribute to the pulp kappa number. In fact, as much as 5 kappa number units of eucalypt unbleached pulps could be due to HexA contribution (Pedroso and Carvalho 2003). The HexA content in pulps could be reduced selectively by implementing a mild acid treatment prior to the bleaching process (A stage) as HexA is converted to soluble acids and aldehyde (Furtado et al. 2001). For some mills an acid stage can contribute to close the filtrate cycle (Bouchard et al. 1995; Silva et al. 2002).

The aim of this work was to study the impact of an acid pre-treatment to Portuguese Eucalyptus globulus kraft pulps on their metals, HexA, lignin and pentosan contents, and on yield, kappa number and viscosity. The unbleached pulps (kappa number 18, viscosity 1410 dm3/kg), produced in the laboratory, were treated with sulphuric acid, pH 3, 3.5 and 4, at 90 and 95°C, during 1 to 3h. The pulps were characterized following standard procedures except for HexA, which was quantified by the UV spectroscopy of the solution resulting from the HexA hydrolysis with mercuric chloride-sodium acetate mixture (Pedroso and Carvalho 2003). The influence of an A stage on the consumption of chlorine dioxide was also studied and is a subject of another paper (Barroca and Carvalho, 2003).

The influence of acid hydrolysis on kappa number, HexA and residual lignin content are illustrated in Figures 1 to 3. The acid hydrolysis of the E. globulus kraft pulp used in this work provided a significant reduction of kappa number, between 2.2 (at pH 3, 90°C, 3h) and 4.8 (at pH 3, 95°C, 3h) units. The kappa reduction is mainly due to the HexA hydrolysis: about 50% and 90% of this acid, respectively, was reduced at the mentioned conditions. Simultaneously, a maximum of 20% of the residual lignin was removed. The hydrolysis rate increased with increasing time, temperature and acidity, but minor changes were verified above 2 h of treatment. A statistical analysis of all data indicated that temperature is the main factor for kappa number reduction, while the three parameters are almost equally significant for HexA reduction in the ranges studied. The simultaneous evolution of kappa number and HexA content can be translated by the equation HexA= 9.53 K - 115 (R2=0,934). Thus, about 10 mmol HexA/kg pulp contribute to one kappa number unit, similar to other results already published (Gellerstedt and Li 1996). The HexA removal diminishes the pulp affinity to metal ions and allows their dissolution as can be seen in Figure 4. Thereby the selectivity of a subsequent oxygen or peroxide bleaching would increase. Nevertheless, while removing transition metals, the acid treatment also removes the alkali-earth metals associated with the pulp. Although not fully accepted, it has been stated that the latter, especially magnesium, help to control peroxide decomposition and prevent cellulose depolymerization. At pH 3 and 90°C, the removal of metal ions was slightly efficient: 20% of Fe, 50% of Mn, 25% of Cu and 59% of Mg were removed. However, at the hardest conditions (pH 3 and 95°C) 80% of Fe, 98% of Mn, 85% of Cu and 99.5% of Mg were removed. Minimal degradation and little loss of polysaccharides would be desirable to preserve pulp quality and yield. In fact, the viscosity is maintained at 90°C for the studied ranges of time and pH, as shown in Figure 5, but half of the initial viscosity value was obtained in the hardest conditions. Additionally, pentosan content varied between 0.5 to 2 percentage units for 90 and 95°C, respectively - Figure 5.

It can be concluded that the introduction of an acid stage in a bleaching sequence of E. globulus kraft pulps, selectively remove HexA without decreasing the viscosity if the operating conditions are properly selected. In fact, at pH 3 and 90°C, about 50% of the original amount of HexA was removed while the viscosity was maintained. However, the acid treatment conditions for high metal ions removal are the same as for HexA removal. At these conditions the selectivity towards viscosity is low. Moreover, the acid treatment removes all the metal ions unselectively which could be a disadvantaged with respect to Mg ion. Therefore, the optimum conditions for an

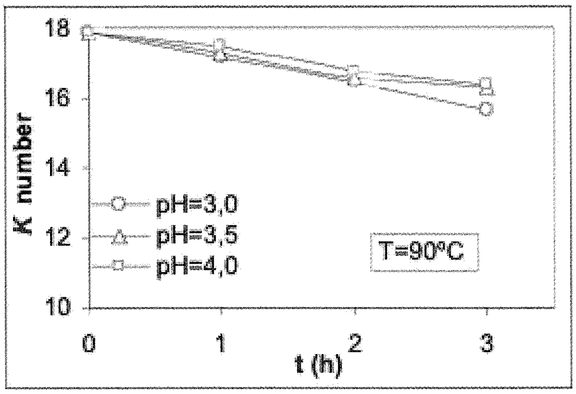

Figure 1. Evolution of K number with reaction time.

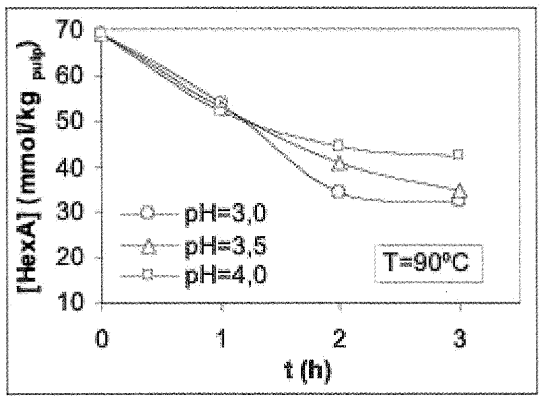

Figure 2. Evolution of HexA with reaction time.

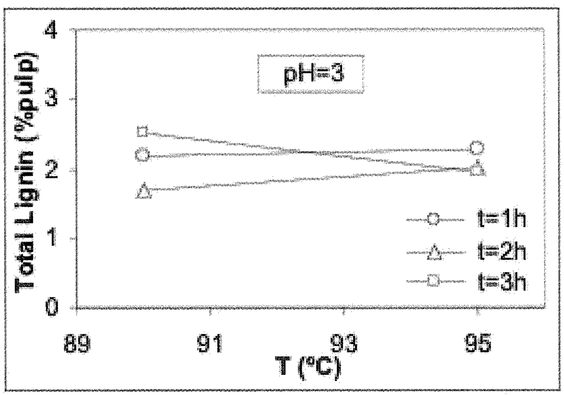

Figure 3. Effect of temperature on the content of pulp lignin.

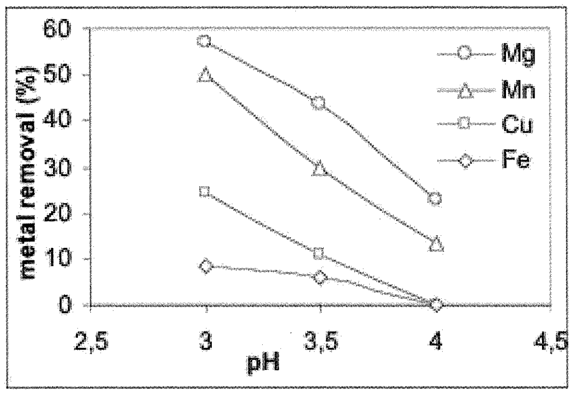

Figure 4. Effect of pH on metal removal (%) after 2h at T= 90°C.

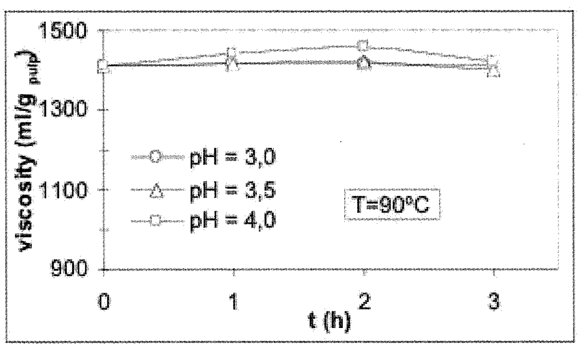

Figure 5. Evolution of viscosity with reaction time.

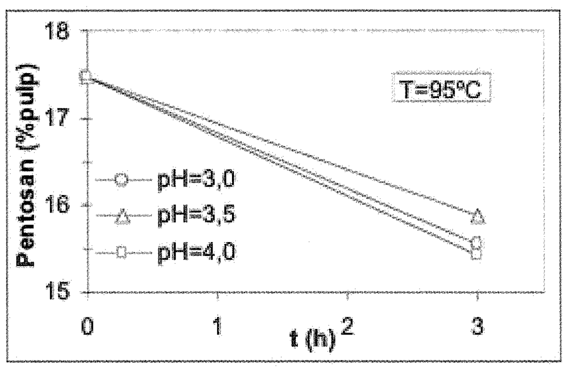

Figure 6 -Evolution of pentosan content with reaction time

acid treatment result from the compromise between the reduction on pulp quality and the removal of metals and hexenuronic acids.

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