ABSTRACT

This thesis originated from the interest in bleaching eucalyptus kraft pulp with clean technologies (*i.e.* by using environmentally benign methods). It was a response to existing widespread environmental concern with the polluting effects of the chemicals typically used to bleach paper pulp and also to the strategic interest in using eucalyptus wood in Spain. To this end, we assessed the potential of new enzymatic systems for efficiently delignifying and bleaching this type of pulp.

The work conducted for this purpose falls within the framework of the pulp bleaching research line of the Paper and Graphic Speciality laboratory of the Textile and Paper Engineering Department of the Polytechnical University of Catalonia concerned with the application of Biotechnology to pulp bleaching.

In this work, we focused on the use of xylanases for improved bleaching in ECF and TCF sequences, and also on the use of laccases in combination with appropriate mediators as pulp bleaching and delignifying agents. Also, the high contents in hexenuronic acids (HexA) of eucalyptus kraft pulp, and their significance to the bleaching process, prompted us to study changes in these components during the different treatments.

The study was started by screening various new and commercial xylanases for performance in order to identify the most efficient enzymes with a view to improving bleaching results. To this end, the enzymes were used in XD, XP and XDP sequences, the resulting pulp samples being characterized in terms of kappa number, brightness, viscosity and HexA contents, and the effluents from the X stages being analysed by thin-layer chromatography. Based on the results, the commercial xylanase X_C and the new xylanase X_G were the most efficient in boosting bleaching. The most efficient new xylanase is a member of the 11 families of glycosyl hydrolases. Also, xylanase X_J (family 5) had only slight effects on pulp and all new xylanases (families 5, 10 and 11) efficiently reduced the HexA contents.

In a second series of tests, the best commercial and new xylanase (X_C and X_G) were used in a complete ECF bleaching sequence ($XDEopD_1$). The scientific interest of using a new xylanase from family 5 for the first time led us to employ it in the whole bleaching sequence as well. X_J was used both alone and in combination with X_G. Based on the results, an X pretreatment improves pulp properties and saves chlorine dioxide. Moreover, the xylanases have no adverse effect on the physical properties of the resulting paper.

At a later stage, a laccase-HBT system (L) was applied to the pulp in order to optimize the conditions of the L stage as regards kappa number and brightness, and also to determine whether the xylanase pretreatment would boost the effect of L and affect HexA contents, lignin and viscosity. A low mediator dose and a short treatment time were found to provide pulp with good properties. The L treatment reduced not only the lignin content, but also the HexA content of the pulp; on the other hand, viscosity was scarcely affected and sterols were removed during the treatment. Moreover, the X pretreatment boosted the effect of the laccase-mediator system in removing HexA from the pulp. The results confirmed the need to subject the pulp to alkaline extraction after L.

We then compared the efficiency of NHA and HBT as mediators for laccase. In addition to being more inexpensive and potentially less environmentally harmful than HBT, NHA reacts in a reversible manner and is as efficient as HBT in delignifying pulp. We also tested a research of natural mediators produced from *Pycnoporous cinnabarinus* growing on pine wood. In addition, we used tyrosinase for the first time to bleach pulp and found further research to be needed in order to confirm its potential biotechnological use. This test series was conducted at the "National Institute of Agronomic Research" (INRA) in Marseille (France).

Finally, the significance of changes in HexA during the bleaching process and the way they were removed by the different chemicals and enzyme treatments used is discussed. As found in this work, the HexA content of eucalyptus pulp is correlated with its kappa number.