Fundamental Delignification Chemistry of Laccase-Mediator Systems on High-Lignin-Content Kraft Pulps (2000)

A Dissertation by Fadi S. Chakar

Abstract: Research efforts in laccase biobleaching technologies have been ongoing for almost a decade. Interest in this field was strengthened when it was discovered that laccase, a lignolytic enzyme, in the presence of a mediator (LMS) could effectively delignify both softwood and hardwood kraft pulps with high selectivity. The two most studied mediators in laccase biobleaching are 2-2´ azinobis(3-ethylbenzthiazoline-6-sulfonate) (ABTS) and 1-hydroxybenzotriazole (HBT). The chemistry of these laccase-mediator systems (LMS) has been studied primarily on low-kappa pulps (kappa no. < 35). This research project, which was consequential in furthering the fundamental delignification chemistry of LMS on high-kappa kraft pulps employed a new generation of N-hydroxy mediators, more specifically, N-acetyl-N-phenylhydroxylamine (NHA) and violuric acid (VA). The application of LMS toward high-kappa kraft pulps is a feasible technology for improving pulping and bleaching yields.

Biobleaching treatments employing HBT, NHA and VA as mediators conclusively demonstrated that an LMS could effectively delignify high-lignin content kraft pulps with an initial kappa number greater than 70. In all LMS treatments, VA outperformed both NHA and HBT with respect to delignification. However, accompanying delignification was a loss in brightness, irrespective of which mediator was employed. Oxidative reinforcement of the alkaline extractions with oxygen, peroxide and oxygen peroxide was beneficial in countering this undesirable effect. These deleterious brightness trends were also observed when a kraft pulp (kappa no. 33.8), originating from the same wood source as the high-kappa kraft pulp, was subjected to LMS using HBT and NHA as mediators.

A two-step central composite experimental design illustrated the efficiency of an LMSNHA system, since most of the delignification occurred under one hour. This project also demonstrated that the delignification response of LMSVA treatments on high-kappa kraft pulps is comparable to oxygen delignification. Most noteworthy, however, LMSVA treatments outperformed oxygen delignification with respect to retention of end viscosity of pulps–another unique feature of LMS. Furthermore, gravimetric pulp yield measurements subsequent to LMS treatments were greater than 90%. Extensive 31P NMR characterization of residual lignins isolated from LMS treated kraft pulps revealed a substantial depletion of various lignin functional groups and showed that NHA and VA preferentially attack phenolic lignin moieties. However, these mediators exhibited differing selectivity toward lignin functional groups, despite the common N-OH moiety.

The brightness loss observed after LMS treatments was speculated to be due to the presence of quinonoid structures. This research presented some of the first spectroscopic data on the combined concentration of ortho and para quinones. Evidence for the formation of quinonoid structures during LMS was established. The trends also revealed a decrease in these compounds subsequent to alkaline extractions. This project also investigated the kismet of residual lignins first isolated and then treated with laccase and LMS. Spectral analysis revealed that the residual lignin incubated with only laccase was significantly modified. The depletion in functional groups followed similar trends to those observed in

the lignins isolated from LMS treated kraft pulps. The presence of mediators did not lead to any further lignin transformation, suggesting that in solution, the role of the mediator is secondary.