

Quantitative Determination of Quinone Chromophore Changes During ECF Bleaching Kraft Pulp (1999)

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Abstract: Benzoquinone-lignin substructures have often been cited as important contributors to the color of lignocellulosic materials. Previously, model compound studies have suggested that these lignin substructures may figure predominantly in the chemistry of industrially important pulp bleaching processes, particularly chlorine dioxide (D) and oxidative alkaline extraction (E*). Unfortunately, the practical significance of these structure toward brightness development during pulp bleaching cannot be known a priori from model compound studies.

This study was focused on the development of a quantitative analytical methodology for the determination of quinone structures in isolated lignins. Lignin-quinone quantification was achieved by the development and application of a novel ³¹P-NMR spectroscopy-based methodology. Benzoquinone structures in isolated lignins were derivatized by trimethylphosphite and yielded aryldimethylphosphate ester adducts after controlled hydrolysis. The lignin-aryldimethylphosphate ester could readily be quantified by solution ³¹P-NMR spectroscopy using a triarylphosphate internal standard.

The developed methodology was applied toward the analysis of lignin-quinone introduction and removal during chlorine dioxide bleaching of kraft pulp. Chlorine dioxide bleaching was found to dramatically increase the quinone content of residual lignin. Lignin-quinone contents, of DE*DED pulps, correlated well with pulp brightness and brightness ceiling values indicating that these structures may negatively impact upon pulp brightness. An isolated lignin, treated in homogeneous solution with chlorine dioxide, revealed increased lignin-quinone formation with greater application of chlorine dioxide. The lignin-quinone content reached a maximum value of 0.30mmol/g lignin and further chlorine dioxide application did not alter the amount. The results are consistent with previous studies which indicated that quinone compounds are relatively stable toward further oxidation by chlorine dioxide.

Industrially, oxidative alkaline extraction often follows chlorine dioxide delignification of pulp. Benzoquinone contents of a series of lignins isolated at the oxidative alkaline extraction stage reveal that alkali alone causes a significant reduction of lignin-quinone content. Hydrogen peroxide and oxygen reinforcement of the alkaline extraction stage resulted in enhanced degradation of lignin-quinone structures.

A series of peracetic acid pretreated and oxygen delignified pulps (PaO) were prepared using both aggressive and standard oxygen delignification conditions. Regardless of the delignification conditions, the quinone contents of these pulps were uniformly low. These results suggest that lignin-quinone structures may not be a major chromophore influencing brightness development of PaO pulps.

The fundamental chemistry of trimethylphosphite derivatization was explored on a series of ortho- and para-benzoquinone model compounds. Both ortho- and para-benzoquinones were found to give dimethylphosphate ester isomers of the analogous catechol or hydroquinone structures. The phosphorus chemical shift of the aryldimethylphosphate, quinone adduct, occurred in the δ-2ppm

region. Generally, derivatization yield was found to be high, although thermally unstable quinones likely underwent partial degradation before complete derivatization.

Non-benzoquinone model compounds representing additional lignin functional groups were also studied. Notably, 3,4-dimethoxybenzyl alcohol was found to undergo transesterification with trimethylphosphite giving, after hydrolysis, hydrogen-phosphite adducts with phosphorus NMR signals in the $\delta 12$ ppm region. Derivatized lignin also gave products consistent with transesterification, although this side reaction did not interfere with quinone analysis. This study presents a practical and robust methodology for studying, previously poorly understood, lignin-quinone structures. The present methodology may contribute to an understanding of how to optimize brightness response of modern ECF bleaching sequences, by gaining fundamental knowledge about the chemistry of lignin-quinone structures. Understanding the nature of chromophoric lignin substructures is important if we are to selectively brighten pulp with greater efficiency.