

Characterization of Residual Lignin in Kraft Pulps (1996)

A Dissertation by Peter M. Froass

Abstract: Conventional kraft pulps were produced from loblolly pine wood chips with kappa numbers 28, 18, and 13. Simulated EMCC kraft pulps having similar kappa numbers were also produced from the same wood chips. Residual lignins in these pulps and kraft lignins from black liquor samples extracted during these cooks were isolated and structurally characterized by advanced NMR spectroscopic techniques. Results from these analyses showed that residual lignin structure is quite different in these various kappa number pulps. The lower kappa number residual lignins had lower contents of aliphatic hydroxyl groups and -O-4 structures and higher contents of phenolic hydroxyl groups, carboxylic acid groups, and condensed structures compared to higher kappa number residual lignins. Comparisons between conventional and EMCC residual lignins with similar kappa numbers showed that conventional residual lignins had slightly lower contents of -O-4 structures and slightly higher contents of condensed structures. These differences may help in explaining the improved delignification selectivity of EMCC kraft pulping because residual lignins with higher contents of -O-4 structures and lower contents of condensed structures would be more reactive under pulping conditions. Isolated residual lignins treated under kraft pulping conditions showed that residual lignin is still reactive under pulping conditions as additional aryl ether fragmentation was observed.

Kraft lignin isolated from black liquor extracted early during the cook had higher phenolic contents, lower -O-4 contents, and higher contents of condensed structures compared to kraft lignins isolated from black liquors extracted later during the cook. Comparisons between the conventional and EMCC kraft lignins extracted at similar extents of delignification showed that conventional kraft lignins had higher contents of phenolic groups, lower contents of -O-4 structures, and lower contents of condensed structures. These differences have been explained in terms of kraft delignification chemistry and the different process variables used in conventional and modified kraft pulping.

The bleachability of these pulps was measured by bleaching the pulps in a D(EO) sequence and calculating the consumption of ClO₂ per unit kappa number drop over this partial delignification sequence. The results showed that the lower kappa number pulps were more difficult to delignify than the higher kappa number pulps which seems to be directly related to the structure and reactivity of the unbleached residual lignin. The lower kappa residual lignin compared to the higher kappa residual lignin had a lower content of aryl ether linkages and a higher content of condensed structures, which may be the cause for the different reactivity of these lignins. Experiments in which the isolated residual lignins were reacted in homogeneous solutions with similar charges of ClO₂ showed that higher kappa residual lignins were more reactive toward ClO₂ as evidenced from the greater introduction of carboxylic acid groups. The introduction of such groups would increase the water solubility of the lignin enhancing its dissolution.

Residual lignins were isolated from ClO₂ bleached and alkaline-extracted pulps and dissolved lignins isolated from the alkaline extraction effluents and characterized by NMR techniques to provide greater insights into the chemical mechanisms causing the oxidation and dissolution of residual lignin during

ClO₂ bleaching. Results from this analysis found that lignin is oxidized by chlorinedioxide, resulting in demethylation, the loss of phenolic groups, and the formation of significant quantities of carboxylic acids and methyl ester functional groups. During an alkaline extraction, an additional increase in the carboxylic acid content was observed, which was suggested to be due to the saponification of methyl ester groups. The further increase in carboxylic acid groups during the alkaline extraction enhances the solubility of the lignin during the alkaline extraction. The phenolic content of the lignin was found to decrease during the alkaline extraction as a result of such groups being oxidized by air (oxygen). This oxidation was found not to result in the formation of carboxylic acids. Reinforcing the alkaline extraction stage with oxygen resulted in a minor but noticeable increase in the carboxylic acid content compared to an alkaline extraction without oxygen reinforcement, suggesting that an intense treatment with oxygen can introduce carboxylic acid groups into the lignin.