

## **Elucidating the Formation and Chemistry of Chromophores during Kraft Pulping (2004)**

**A Dissertation by Thomas J. Dyer**

Abstract: Research efforts in the pulp and paper industry have focused on tailoring unit operations and product properties to environmental regulations and changing market demands. Over the past several years, growing concerns over the use of chlorine and chlorine-containing chemicals have forced the pulp and paper industry to tailor bleaching processes to have minimal impact on the environment. Wood utilization practices have also come to the research forefront as the availability of and accessibility to inexpensive fibers will diminish in the long run. More recently, research efforts have focused on tailoring fiber properties to specific end uses. A considerable amount of attention has been given to developing methods to adapt pulp fiber strength and surface properties for this cause. However, pulp production utilizing the kraft pulping process addresses many of the physical strength properties that are of concern. Despite this, one area that has not received a considerable amount of attention has been tailoring optical properties to specific end uses. The production of dark colored pulps from the kraft pulping process has been a problem since the inception of this technology in 1879 by C.F. Dahl.

This research project was consequential in furthering the fundamental knowledge of chromophore formation during kraft pulping. In this research, a method was developed to obtain the chromophore content of lignocellulosic materials based on the dilution pulp method. This measurement is known as the total visible absorption of the material and is based on the absorption coefficient. A second method was developed and shown to be commensurate in measuring the chromophore content of lignocellulosic materials. This method is known as the chromophore index and is based on the Kubelka-Munk remission function. These methods showed that the brightness is not a suitable measure of the chromophore content of lignocellulosic materials.

Kraft pulping experiments were carried out at varying levels of effective alkali, sulfidity, and maximum cooking temperature utilizing a central composite design with the goal of determining the importance of these variables on the chromophore content of kraft pulps. The effective alkali and sulfidity were statistically significant while the maximum cooking temperature was not statistically significant at the 95% confidence level. A low EA, high sulfidity condition resulted in a high pulp chromophore index while a high EA, low sulfidity condition resulted in a low pulp chromophore index. Hexenuronic acids may have a role in chromophore formation, but there was no clear relationship with the pulp chromophore index in this study. Although carbohydrates may contribute to the chromophore index, this was not surprising since their contribution to the overall chromophore development during kraft pulping is presumably small. The extractives had a significant impact on the pulp chromophore index. However, their contribution to the overall chromophoric content of the kraft pulps used in this study is likely small.

Further investigation elucidated the mechanism of chromophore formation and removal during kraft pulping. A series of high and low chromophore index pulps with varying lignin contents (3-22%) were examined and found to vary greatly in both the hexenuronic and carboxylic acid group content, indicating that these pulps varied drastically in physical and chemical properties. Chromophores were removed at a faster rate for kraft pulps produced under a high EA, low sulfidity condition than for a low

EA, high sulfidity condition. The amount of sodium hydroxide consumed during the kraft cook was found to be linearly related to the pulp chromophore index. The chemistry of chromophore formation is likely related to the chemistry of the initial phase of kraft pulping. Lower energy (longer wavelength) chromophores were formed in pulps produced from low EA, high sulfidity conditions when compared to those from high EA, low sulfidity conditions.

Potential chromophores in kraft pulps were examined through advanced NMR and UV/vis techniques. This study also provided the first direct evidence that residual lignin is responsible for the majority of the chromophoric properties of unbleached kraft pulps. The results of this research showed that quinones, catechols, biphenyls, and carbonyl functionalities contribute to the chromophore content of kraft pulps. In addition, substituents on these chromophores can have a detrimental impact on the final chromophoric properties of unbleached kraft pulps.

The influence of transition and alkaline earth metals on the chromophore content of unbleached kraft pulps was also examined. A cold acid treatment was performed to liberate metal cations and retain hexenuronic acids. This study indicated that the pulp chromophore index decreased significantly as a result of metals removal. The cold acid treatment did not remove all of the chromophores in the unbleached pulps, indicating that functionalities other than metals are responsible for more than 50% of the color of unbleached kraft pulps at a 30 kappa number. A mechanism for the formation of the chromophores removed by the cold acid treatment was proposed. The majority of the loss in chromophore index was accounted for by the loss in three different alkaline earth metals. Acid and chelation treatments on wood chips were also investigated as possible means to eliminate metal cations before kraft pulping. These studies indicated that a chelation treatment was more effective at removing metals than an acid treatment at the same temperature. These results also indicated that metals removal prior to kraft pulping can have a significant impact on the chromophoric properties of unbleached kraft pulps.

The influence of certain pulping additives on the chromophoric properties of unbleached kraft pulps was also investigated. The chromophoric properties of polysulfide (PS), anthraquinone (AQ), PS/AQ and normal kraft pulps were examined. The data suggested that PS pulps had a lower chromophore index than the other pulps in this study. The residual and dissolved kraft lignins were isolated and characterized employing advanced NMR and differential ionization UV/vis spectroscopy. Differential ionization UV/vis spectroscopy indicated an increased amount of conjugated and unconjugated phenolics in the dissolved kraft lignins, with PS/AQ dissolved kraft lignin having the greatest concentration of conjugated and unconjugated phenolics, followed by PS, AQ and conventional kraft dissolved lignin. The differential ionization UV/vis spectra were also utilized to characterize some of the chromophores present in residual and dissolved kraft lignins. The data suggested that phenolic  $\alpha$ -carbonyl structures correlated well with the chromophore index of the four pulps investigated and may be a critical factor in determining the overall color or color differences between conventional kraft, polysulfide, anthraquinone, and PS/AQ kraft pulps.

Methods were also investigated for their feasibility in reducing or eliminating the chromophore content of wood. This research utilized a laccase pretreatment of wood chips to destroy possible chromophoric

and leucochromophoric structures prior to kraft pulping. These studies were the first of their kind in demonstrating the potential of laccase-mediator systems as a pretreatment to improve kraft pulping properties. The 1-hydroxybenzotriazole bio-pretreatments had the greatest impact on kraft pulping, enhancing delignification while concomitantly increasing pulping yield. These pretreatments also improved the chromophoric properties of the unbleached kraft pulps relative to the conventional kraft pulp.

Additional studies were performed utilizing several oxidative and reductive chemistries used to eliminate the chromophoric and leucochromophoric structures prior to kraft pulping. These studies showed that alkaline hydrogen peroxide, sodium borohydride, and chelation pretreatments effectively reduced the pulp chromophore index. Mechanisms behind each pretreatment were proposed. Different pulping conditions yielded different responses to these pretreatments. Generally, the low effective alkali, high sulfidity conditions yielded a better response to the pretreatments than a high effective alkali, low sulfidity condition. This is perhaps due to the higher metals content and enrichment of hydroxyl-substituted carbonyl structures in the low effective alkali, high sulfidity pulping conditions. Multiple pretreatments decreased the chromophore index to a greater extent than a single pretreatment. However, the extent of this reduction was dependent on the pulping condition, with the low effective alkali, high sulfidity pulps having the greatest response to the multiple pretreatments. Overall, these pretreatments may provide further insight into the causes for chromophore formation during kraft pulping.