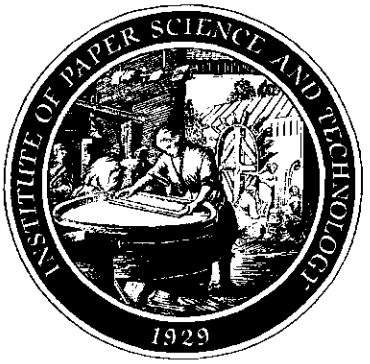

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THE FATE OF HEXENURONIC ACID GROUPS DURING KRAFT PULPING OF HARDWOODS

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ABSTRACT

Detailed characterization of hexenuronic acid (HexA) content in five North American hardwood pulps (aspen, basswood, birch, maple, and sweetgum) obtained from laboratory conventional kraft pulping processes was conducted in this study. The results indicate that the HexA content in hardwood pulps continued to increase with delignification and did not decrease until much later in the pulping process. The variations in wood species contributed not only to the HexA content but also to the time-dependent HexA content profile. The HexA contribution to the pulp kappa number for the five hardwoods was investigated. It was found that the HexA content of pulps linearly correlates with kappa reduction through HexA hydrolysis, and that the slope of the linear correlations may vary with wood species.

INTRODUCTION

Hexenuronic acid groups (HexA) formed during alkaline wood pulping have attracted great attention recently because of their effect on bleaching operations, such as increased consumption of bleach chemicals, bonding with transition metals, and reduced ceiling of pulp brightness. Although the fundamental reaction chemistry of HexA formation through the alkali-catalyzed reactions of 4-O-Me-Glucuronic acid groups with hydroxide ions was established by Clayton [1] in the 1960s, the formation of HexA in kraft pulping was revealed by Buchert et al. [2] only recently. Because the alkali-catalyzed methanol elimination reaction occurs very rapidly, the formation of HexA is very fast in the early stages of pulping, as discovered by Buchert et al. [2]. This fact was confirmed by the present authors [3, 4]. A number of studies have reported that the HexA content in pulp is affected by the pulping process [5-7]. Limited studies have also reported on the effect of pulping parameters on the HexA formation [2, 8]. In a recent study [4], we found that the maximum formation rate of HexA during pulping of loblolly pine is proportional to the initial EA concentration in the cooking liquor, and the faster formation of HexA will lead to a greater loss of HexA in pulps in the later stages of the cook. Furthermore, we found that the HexA content of pulp correlates very well with the alkali consumed for a given wood species (loblolly pine), independent of the pulping process, which means that HexA content of a pulp can be estimated by determining the amount of alkali consumed at the end of the cooking.

Gellerstedt and Li [9] reported that birch pulp (unbleached) has much higher HexA content compared to equivalent unbleached pine pulps, which means that more bleaching chemicals will be consumed by the HexA (not lignin) during the bleaching of hardwood pulps. Therefore, it is of great interest and importance to study HexA content in hardwood pulps. This study reports the fate of HexA during conventional kraft pulping of five North American hardwood species. The objectives of the study were to determine the HexA content of various hardwood pulps and to provide detailed data on the contribution of HexA content to pulp kappa number for bleach operations.

EXPERIMENTAL

Pulping

All pulping experiments were conducted using eight rotating bomb digesters. The volume of each bomb digester was 500 mL. Fifty grams of oven-dry wood chips of five North American hardwoods (aspen, basswood, birch, maple, and sweetgum) were used in each cook. The ratio of cooking liquor-to-wood chips was 3.7 L/kg. Conventional kraft pulping was conducted. The active alkali charge AA (as Na_2O) was maintained at 16% on wood for all pulping processes. The sulfidity was 30% to achieve the desired kappa number. For each set of pulping conditions selected, cooking temperature was ramped from a room temperature of 23°C to 170°C in 70 minutes or at a rate of 2.1°C per minute, then maintained at 170°C to continue delignification. The pulping processes in different digesters were terminated at different pulping times to obtain the rate of formation of HexA. At the end of each cook, the pulp was completely disintegrated in a laboratory blender and thoroughly washed with tap water in a basket with a 200-mesh screen. Pulp pads were then prepared in a handsheet machine for the measurement of pulp yield, kappa number, and HexA content. The pulp kappa number, yield, and chemical strength of the cooking liquor, such as EA and sulfidity, were measured according to standard TAPPI test methods [10].

Measurement of HexA in Chemical Pulps

A simple, rapid, and reliable HexA measurement method we developed previously [11] was used. Approximately 0.05 gram of air-dried pulp handsheet with a known moisture content was accurately weighed and put into a 20-mL vial with 10 mL of $HgCl_2$ hydrolysis solution containing 22 mmol/L (0.6%) mercuric chloride and 0.7% sodium acetate. The mixture was sealed in the vial by a septum. Good mixing of the chemicals was obtained by hand shaking. The vial was then heated for 30 minutes in a water bath in a temperature of about 60-70°C. After the solution had cooled to room temperature, UV absorption measurements of the filtered solution were conducted in a 10-mm path length silica cell using a commercial spectrophotometer (UV-8453, Hewlett-Packard) over a wavelength range of 250 to 300 nm.

Measurement of Kappa Number

The kappa number of the original pulps from the pulping experiments was measured using the standard TAPPI kappa test method [10]. A pulp sample size of a minimum of 1 gram is required when the TAPPI test method (titration-based) is employed. It would take about 500 mL of hydrolysis solution for removal of HexA in just a single pulp sample of 1 gram in each hydrolysis experiment using the present hydrolysis technique, which would be impractical. Furthermore, the TAPPI kappa test method suffers from the random human operation errors that tend to produce inconsistent results and is not suitable for computing kappa reductions of only about 3-5 units after the hydrolysis reactions and for comparing kappa reduction among various pulp samples. The spectrophotometric kappa test technique [12, 13] through direct permanganate measurements (or the Chai-Zhu kappa test method) that we developed can eliminate random human operating errors and provides rapid, reliable, and accurate kappa measurements with a very small pulp sample size of less than 0.1 gram. Therefore, the Chai-Zhu method described in our previous studies [12, 13] was employed to determine the kappa number before and after HexA hydrolysis in this study.

RESULTS AND DISCUSSION

Time-dependent HexA Formation and Degradation during Kraft Pulping

Figure 1 shows the HexA content of the pulps as a function of pulping time in conventional kraft pulping of maple (a hardwood). For comparison purposes, Figure 1 also plots the HexA data [4] as a function of pulping time in kraft pulping of loblolly pine (a softwood). The pulping conditions of loblolly pine were active alkali charge of 18%, sulfidity of 30%, and ratio of cooking liquor to wood chips of 4.0 L/kg, only slightly different from those for all hardwood pulping described in the experimental section previously. The results indicate that the HexA content of the maple and loblolly pine pulps both increase rapidly with pulping time. The overall HexA formation rate is higher in kraft pulping of loblolly pine than in pulping of maple. Furthermore, the HexA degradation starts earlier in pulping of loblolly pine than in maple. The HexA content of pine pulp started to decrease about 20 minutes after the pulping temperature reached 170°C, while the HexA content of maple pulp continued to increase until much later in the pulping process, about one hour after the pulping temperature reached 170°C, and the kappa number was about 11. Because the pulp will not cook to such a low kappa number in mill practice, the decrease in HexA content of pulp with pulping time will not be observed. To explain the difference in the HexA content profiles, Figure 1 shows the EA concentration during these two kraft pulping processes. The data indicate that more alkali is consumed by neutralization reactions during kraft pulping of maple, which, perhaps, causes a lower overall HexA formation rate because the HexA formation rate is proportional to the EA concentration, based on the formation mechanism proposed by Clayton [1]. Our experimental data reported previously [4] indicate that the formation of HexA is only a function of the amount of alkali consumed.

Figure 2 shows the measured HexA content of kraft pulps from other US hardwood species as a function of pulping time. The data clearly indicate that the maximum HexA content and the profile of time-dependent HexA content of pulp vary significantly among the various hardwood species. The overall formation rates of HexA are about the same for maple and sweetgum. The maximum overall HexA formation rate was found during pulping of birch and basswood, while the minimum overall HexA formation rate was found in the pulping of aspen. The HexA content of aspen pulp achieved a maximum value about 20 minutes after the pulping temperature reached 170°C and then leveled off. The maximum HexA content of aspen pulp is much lower than that of other pulps. Overall, the profile of time-dependent HexA content of hardwood pulp is different from that of softwood pulp. During hardwood pulping, the HexA content increases as pulping proceeds and significant degradation of HexA is not observed during most of the pulping process. The wood structure may contribute to this difference.

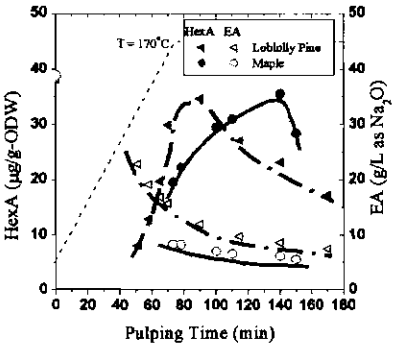

Fig. 1 Time-dependent HexA in pulps and EA in the pulping liquor during conventional kraft pulping .

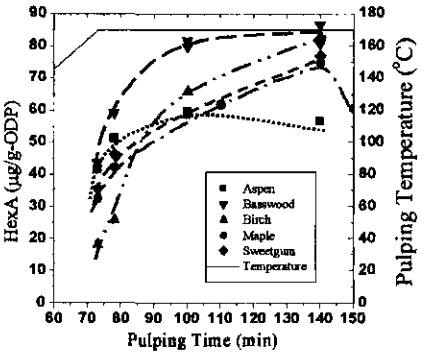

Fig. 2 Time-dependent HexA of pulps from conventional kraft pulping of five North American hardwoods.

Relationship of HexA in Pulp with the Kappa Number

Figure 3 shows the relationship between the HexA content and the kappa number during kraft pulping of hardwoods. The results show that the HexA content increases rapidly with the reduction of kappa number (or

delignification), which is just the opposite of what occurs in kraft pulping of softwood [4]. A decrease in HexA content was observed only in maple and aspen pulps with very low kappa numbers (about 10). Because pulp will not cook to kappa number 10 in mill practice, reduction of HexA content of pulp will not be observed. Furthermore, the slope of the HexA-kappa curve increases as delignification continues, indicating that HexA formation is much faster than kappa reduction in the later stages of the kraft pulping of hardwoods because delignification enters the residual-lignin removal phase. Any extended cooking process will significantly increase the HexA content of the pulp, especially for birch, as shown in the figure, which will result in higher consumption of bleaching chemicals. As discussed previously, the lower alkali concentration in hardwood pulping liquors contributes to the difference in the HexA-kappa relationship between softwoods and hardwoods. Because hardwood pulps have a lower kappa number (or lignin content) than softwood pulps for an equivalent grade of pulp, the HexA contribution to the kappa number will be much more significant for hardwoods than for softwoods.

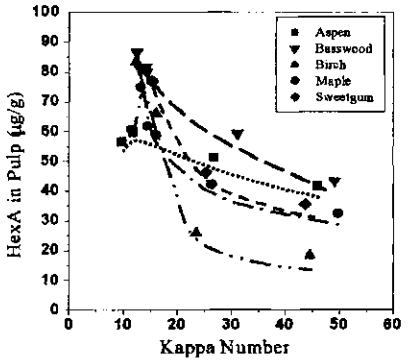

Fig. 3 The relationship between HexA content of pulps and the corresponding pulp kappa numbers for five North American hardwoods.

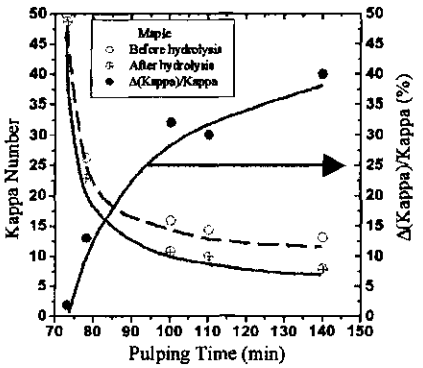

Fig. 4 Kappa number reduction through hydrolysis for the maple pulps obtained at different cooking times.

Buchert et al. [2] and Li and Gellerstedt [15] reported that HexA can contribute as much as 50% to the kappa number of several northern Scandinavian kraft pulps. Their results were obtained by measuring the kappa number before and after acidic hydrolysis of the pulp. In this study, we used a mercuric chloride-sodium acetate solution [11] to hydrolyze HexA. Compared with acidic hydrolysis, this method is highly selective, efficient, and is conducted in a neutral pH medium. Thus, the loss of lignins and other carbohydrates from pulp during the hydrolysis pretreatment can be minimized. We used the Chai-Zhu kappa test method [12, 13] that reduces the random errors in the traditional titrametric kappa method to determine the kappa number before and after pulp hydrolysis. Figure 4 shows the time-dependent kappa numbers of five maple pulps (before and after the HexA hydrolysis) cooked under the same conditions; however, the pulping process was terminated at different pulping times. The results indicate that the relative kappa reduction increases with pulping time. The relative kappa reduction is defined as the difference in the measured pulp kappa numbers before and after hydrolysis, Δ(Kappa), divided by the kappa number before hydrolysis. At a pulping time of 140 minutes, corresponding to an original pulp kappa number of 13, the kappa reduction is about 40% after hydrolysis.

Figure 5 shows the relative kappa reduction after hydrolysis as a function of pulp kappa number. The results from the maple pulps were plotted along with those from the other four hardwood pulps. The dash-dot curve was drawn based on the maple pulps only. The results indicate that the relative reduction was less than 10% for pulps with kappa numbers above 40. However, the relative kappa reduction increases rapidly with the reduction of kappa number (or increased delignification). The relative reduction is about 50% at a kappa number of about 10 for the five wood species studied. Because the hydrolysis of HexA is directly responsible for the kappa reduction, the results indicate that the contribution of HexA to pulp kappa number is significant at relatively low kappa numbers (below 20 for hardwoods). Furthermore, the results suggest that continued delignification at low kappa numbers is not desirable because it can achieve only a very small kappa number reduction relative to the amount of HexA formation. It should be pointed out that the data scatter from the dash-dot curve (drawn from the maple data set) is due to two factors: the measurement uncertainty, especially in kappa reduction measurements, and the true variation in the relationship between kappa reduction and kappa number among the various wood species.

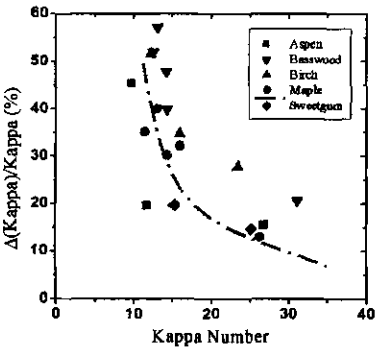

Fig. 5 The correlation between the relative kappa number reduction through hydrolysis and the pulp kappa number for five North American hardwood pulps.

Figure 6 shows the relationship between measured HexA content and kappa reduction through hydrolysis. The results provide quantitative information on the HexA contribution to pulp kappa number (for the five hardwoods) discussed in the previous paragraph. Again, the results from the maple pulp were plotted along with the other four hardwood pulps. The dash-dot line was the least-squares fitted line using the maple pulp data by forcing the fitting through the origin of the coordinate system. The slope of 13.7 of the least-squares line is close to the value reported by Li and Gellerstedt [9], i.e., one unit of kappa number equals 11.6 μg HexA in pulps, and values reported by Ikeda et al. [16]. Again, the data scatter from the dash-dot line (least-squares fitting using the maple data set) is due to two factors: the measurement uncertainty, especially in kappa reduction measurements, and the true variation in the relationship between kappa reduction and kappa number among the various wood species.

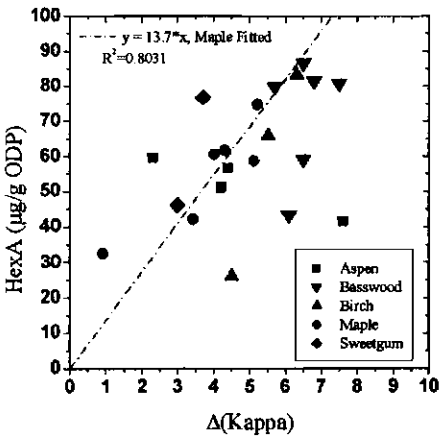

Fig. 6 The correlation between HexA content of pulps and the kappa number reduction through hydrolysis.

CONCLUSION

We conducted detailed characterizations of HexA content of five North American hardwood (aspen, basswood, birch, maple, and sweetgum) pulps obtained from a laboratory conventional kraft pulping process. The results indicate that the HexA content of hardwood pulps increased after the temperature reached the final cooking temperature (170°C) and did not decrease until much later in the pulping process at kappa number of about 10, which is very different from the HexA content found for softwood (loblolly pine) pulps as reported previously [4]. This difference can be attributed to the fact that a significant amount of alkali (EA, the reactant to form HexA) had been consumed in the early stages of hardwood kraft pulping by neutralization reactions, which results in slow HexA formation. It was found that the wood species contributed not only to variations in the HexA content but also to the profile of time-dependent HexA content of the corresponding pulp, which is perhaps due to variations in the 4-O-methylglucuronoxylan content and the wood structure. The study provided detailed data on the HexA contribution to pulp kappa number for the five hardwoods investigated. The HexA contribution to kappa is less than 10% for pulps with kappa numbers greater than 40; however, the contribution can be as high as 50% for pulps with kappa number of about 10. The study also provided detailed data on kappa reduction through HexA hydrolysis. Finally, the study showed that the HexA content of pulp correlates linearly with kappa reduction through HexA hydrolysis, and that the slope of the correlations varies with wood species.

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