The Fate of Hexenuronic Acid Groups During Kraft Pulping of Hardwoods

X.S. Chai, Q. Luo, S.-H. Yoon, and J.Y. Zhu

April 2000

Submitted to
Journal of Pulp and Paper Science
INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY
PURPOSE AND MISSIONS

The Institute of Paper Science and Technology is an independent graduate school, research organization, and information center for science and technology mainly concerned with manufacture and uses of pulp, paper, paperboard, and other forest products and byproducts. Established in 1929 as the Institute of Paper Chemistry, the Institute provides research and information services to the wood, fiber, and allied industries in a unique partnership between education and business. The Institute is supported by 51 North American companies. The purpose of the Institute is fulfilled through four missions, which are:

- to provide multidisciplinary graduate education to students who advance the science and technology of the industry and who rise into leadership positions within the industry;
- to conduct and foster research that creates knowledge to satisfy the technological needs of the industry;
- to provide the information, expertise, and interactive learning that enables customers to improve job knowledge and business performance;
- to aggressively seek out technological opportunities and facilitate the transfer and implementation of those technologies in collaboration with industry partners.

ACCREDITATION

The Institute of Paper Science and Technology is accredited by the Commission on Colleges of the Southern Association of Colleges and Schools to award the Master of Science and Doctor of Philosophy degrees.

NOTICE AND DISCLAIMER

The Institute of Paper Science and Technology (IPST) has provided a high standard of professional service and has put forth its best efforts within the time and funds available for this project. The information and conclusions are advisory and are intended only for internal use by any company who may receive this report. Each company must decide for itself the best approach to solving any problems it may have and how, or whether, this reported information should be considered in its approach.

IPST does not recommend particular products, procedures, materials, or service. These are included only in the interest of completeness within a laboratory context and budgetary constraint. Actual products, materials, and services used may differ and are peculiar to the operations of each company.

In no event shall IPST or its employees and agents have any obligation or liability for damages including, but not limited to, consequential damage arising out of or in connection with any company's use of or inability to use the reported information. IPST provides no warranty or guaranty of results.

The Institute of Paper Science and Technology assures equal opportunity to all qualified persons without regard to race, color, religion, sex, national origin, age, disability, marital status, or Vietnam era veterans status in the admission to, participation in, treatment of, or employment in the programs and activities which the Institute operates.
The Fate of Hexenuronic Acid Groups during Kraft Pulping of Hardwoods

X.S. Chai, Q. Luo§, S.-H. Yoon†, and J.Y. Zhu*

Institute of Paper Science and Technology
500 10th Street, N.W., Atlanta, GA 30318
(404) 894-5310, (404) 894-5752(FAX), Junyong.Zhu@ipst.edu

ABSTRACT

Detailed characterizations of hexenuronic acid (HexA) content in five North American hardwood (aspen, basswood, birch, maple, and sweetgum) pulps obtained from laboratory conventional kraft pulping processes were 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, very different from the HexA content found in the softwood pulps. The study revealed that the variations in wood species contributed not only to the HexA content but also to the time-dependent HexA content profile in corresponding pulps. The study provided detailed data of HexA contribution to the pulp kappa number for the five hardwoods investigated. The study also provided detailed data on kappa reduction through HexA hydrolysis for practical applications. Finally, it was found that the HexA content in pulps linearly correlates with kappa reductions through HexA hydrolysis, and the slope of the linear correlations may vary with wood species.

Key words: Hexenuronic acid; xylans; kraft; hardwood; pulping; kappa number; alkali.

§ Permanent address: State Key Lab of Pulp and Paper Engineering, South China University of Technology, Guangzhou, China.
†Permanent address: Korea Minting and Security Printing Corporation, Buyeo Paper Mill, 17 Yeomchang-ri, Buyeo-eup, Chungnam, 323-800 Korea
* Author to whom correspondence should be addressed
INTRODUCTION

The formation of hexenuronic acid groups (HexA) during alkaline wood pulping has recently been a concern in the pulp and paper industry because of its detrimental effects on bleaching operations, such as increased bleaching chemical consumption, bonding with transition metals, and reduced pulp brightness ceiling. It is well known that the HexA in pulp are formed during alkaline pulping through the alkali-catalyzed reactions of elimination of methoxy groups in hemicellulose of xylans. The fundamental reaction chemistry of HexA formation during alkaline pulping was established by Clayton [1]. Because the alkali-catalyzed methanol elimination reaction occurs very rapidly, the formation of HexA is very fast in the early stage of pulping. This fact has been confirmed by the Finnish researchers [2] and the present authors [3, 4]. In a recent study [4], we found that the maximum formation rate of HexA during pulping is proportional to the initial effective alkali (EA) concentration in the cooking liquors, and the faster formation of HexA will lead to greater loss of HexA in pulps in the late stage of the cook. Furthermore, we found that the HexA in pulps correlates very well with the consumed alkali for a given wood species (loblolly pine), independent of the pulping conditions, which means that HexA in a pulp can be estimated by determining the amount of alkali consumed at the end of the cooking.

Hardwood has a higher hemicellulose content than softwood. Buchert et al. [2] and Gellerstedt and Li [5] 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 operations of hardwood pulps. Therefore, it is of great interest and importance to study the fate of HexA in the hardwood
pulping process. This study reports the fate of HexA during conventional kraft pulping of several North American hardwood species. The objectives of the study are to obtain HexA content in various hardwood pulps, and to provide detailed data of the contribution of HexA content to pulp kappa number for practical applications.

EXPERIMENTAL

Pulping

All the 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, bass, birch, maple, and sweetgum) were used in each cook. The cooking liquor-to-wood chip ratio was 4.0 L/kg. Conventional kraft pulping was conducted. The active alkali charge AA (as Na₂O) was maintained at 16% on wood for all the pulping processes. The sulfidity was S = 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 200-mesh screen. Pulp pads were then prepared in a handsheet machine for the measurement of pulp yields, kappa numbers, and HexA. The pulp kappa number, yield and chemical strength of the cooking liquor, such as EA and sulfidity, were measured according to the standard TAPPI test methods [6].
**Measurement of HexA in Chemical Pulps**

A simple, rapid, and reliable HexA measurement method we developed previously [7] was used in this study. The method has been described elsewhere [3, 4, 7]. 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 HgCl₂ hydrolysis solution of 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 in the vial was obtained by hand shaking. The vial was then heated for 30 minutes in a water bath within a temperature range of 60-70°C. After the solution was 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) in a wavelength range of 250 to 300 nm.

**Measurement of Kappa Number**

The kappa number of the original pulps from the pulping experiments were measured using the standard TAPPI kappa test method [6]. A pulp sample size of a minimum of 1 gram is required when the TAPPI test method (titration based) for kappa number determination 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 human random operation errors that tend to produce inconsistent results, not suitable for computing kappa reductions of only about 3-5 units after the hydrolysis reactions and for comparisons of the kappa reductions among various pulp samples. The spectrophotometric kappa test technique [8, 9] through direct permanganate measurements (or the Chai-Zhu kappa
test method) that we developed can eliminate the random human operating errors and provides rapid, reliable, and accurate kappa measurements with a very small pulp sample size of below 0.1 gram. Therefore, the Chai-Zhu method described in detail in our previous studies [8, 9] was employed to determine the kappa number reduction before and after HexA hydrolysis in this study.

RESULTS AND DISCUSSIONS

Time-dependent HexA Formation and Degradation during Kraft Pulping

Figure 1 shows the HexA content in the pulps as a function of pulping time in conventional kraft pulping of maple (a hardwood) with a sulfidity of 30%. For comparison purposes, Figure 1 also plotted the HexA data [4] as a function of pulping time in kraft pulping of loblolly pine (a softwood). The results indicate that the HexA contents in the maple and loblolly pine pulps both increase rapidly with the increase of pulping time due to rapid methoxyl group elimination from the hemicellulose according to Clayton [11]. The results also indicate that the overall HexA formation rate is higher in kraft pulping of loblolly pine than that in pulping of maple. Furthermore, the HexA degradation is much faster in kraft pulping of loblolly pine than that in kraft pulping of maple. The HexA content in maple pulps continues to increase until much later in the pulping process (one hour after the pulping temperature reached 170°C). To explain this difference, Figure 1 shows EA concentrations during these two kraft pulping processes. The data indicate that more alkali is consumed by the neutralization reactions during kraft pulping of maple, which, perhaps, causes a lower overall HexA formation rate and a lower rate of the subsequent HexA degradation reaction because the HexA formation rate is proportional to the EA concentration, based on the formation mechanism proposed by Clayton.
The degradation of HexA is also only a function of the amount of the alkali consumed according to the HexA content measured in loblolly pine pulps that we presented previously [4]. Another factor that contributes to the difference of HexA in hardwood pulps from that in softwood pulps is that hardwoods generally have a much higher hemicellulose (responsible for HexA formation) content [10], therefore, it will need a longer cooking time to achieve complete elimination of methoxyl groups from the hemicellulose.

Figure 2 shows the HexA contents measured from kraft pulps of other US hardwood species as a function of pulping time. The data clearly indicate that the maximum HexA content and time-dependent HexA content in pulp vary significantly among various hardwood species. The maximum overall HexA formation rate was found during kraft pulping of birch and basswood, while the minimum overall HexA formation rate was found during kraft pulping of aspen. The overall formation rates of HexA during kraft pulping of maple and sweetgum are about the same. The HexA formation characteristics during kraft pulping of aspen are different from those of the other hardwoods. The maximum amount of HexA was formed about when the pulping temperature reached 170°C, which is similar to the results obtained during kraft pulping of loblolly pine (a softwood) [4]. Furthermore, the HexA content remained at a constant level once the maximum level is achieved for the remainder of the pulping process, indicating the amount formed is equal to that degraded. Overall, the time-dependent HexA content during pulping of hardwood is very different from that during pulping of softwood. Unlike softwood pulping, during hardwood pulping, HexA content increases as pulping proceeds and significant degradation of HexA was not observed during most of the pulping process. The closest case to softwood pulping is the pulping of aspen, where HexA content maintains a fairly constant value once the maximum level is attained.
Relationship of HexA Content in Pulp with Kappa Number

Figure 3 shows the relationship between HexA content and kappa number during kraft pulping of hardwoods. The results show that HexA content increases rapidly with the reduction of kappa number (or delignification), which is just opposite to what occurs in kraft pulping of softwood [4]. The decrease of HexA content was observed only in maple and aspen pulps with very low kappa numbers (below 10). Furthermore, the slope of the HexA-kappa curve increases as delignification continues in the later stage of pulping (except for aspen), indicating HexA formation is much faster than kappa reduction in the later stage of kraft pulping of hardwoods, which is simply due to the fact that delignification enters the residual lignin removal phase. Any extended cooking process will significantly increase HexA content in the pulp, which will result in higher consumption of bleaching chemicals in bleaching operations. As we discussed previously, both the lower alkali concentration in the hardwood pulping liquors and the higher hemicellulose content in hardwoods contributed 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.

Buchert et al. [2] and Li and Gellerstedt [11] reported that HexA can contribute as high as 50% to kappa number of several northern Scandinavian kraft pulps. Their results were obtained by measuring the pulp kappa number before and after acidic hydrolysis of the pulp. In this study, we used a mercuric chloride-sodium acetate solution [7] to hydrolyze HexA. Compared with acidic hydrolysis, this hydrolysis method is highly selective, efficient, and 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 [8,9] that
reduced the random errors in the traditional titremetric 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) in five kraft pulping processes under same conditions but terminated at different pulping times. The results indicate that the relative kappa reduction increases with pulping time. At pulping time of 140 minutes, corresponding to original pulp kappa number of 10, 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 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 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 only can achieve a very small kappa number reduction and increases the amount of HexA formation significantly, which causes an increase in the consumption of bleaching chemicals in bleaching plant operations. Therefore, the data presented in Fig. 5 has practical importance for bleach plant operations. 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 of the relationship between kappa reduction and kappa number among the various wood species.
Figure 6 shows the relationship between measured HexA content and kappa reduction through hydrolysis. The results provide quantitative information of the HexA contribution to pulp kappa number (for the five hardwoods) discussed in the previous paragraph. Again, the results from the maple pulps 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 [5], i.e., one unit of kappa number equals 11.6 μg HexA in pulps, and those by Ikeda et al. [12]. 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 of the relationship between kappa reduction and kappa number among the various wood species.

CONCLUSIONS

We conducted detailed characterizations of HexA content in five North American hardwood (aspen, basswood, birch, maple, and sweetgum) pulps obtained from laboratory conventional kraft pulping processes. The results indicate that the HexA content in hardwood pulps increased after the temperature reached the final cooking temperature (170°C) and did not decrease until later in the pulping process at kappa number of about 10, which is very different from the HexA content found the softwood (loblolly pine) pulps as we 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 stage of the pulping by the neutralization reactions during the hardwood kraft pulping, which results in a slow HexA formation reaction, and to the fact that hardwood has more 4-O-methylglucuronoxylan content (another reactant to
form HexA). It was found that the variations in wood species contributed not only to the HexA content but also to the time-dependent HexA content profile in corresponding pulps, which is perhaps due to the variations of the 4-O-methylglucuronoxylan content and the wood structure. The study provided detailed data of HexA contribution to the 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 for practical applications. Finally, it was found that the HexA content in pulps linearly correlates with kappa reductions through HexA hydrolysis and the slope of the linear correlations may vary with wood species.

ACKNOWLEDGEMENT

This research was supported by the United States Department of Energy (Grant No. DE-FC07-96ID13438). The authors would like to acknowledge Dr. Jian Li of the Institute of Paper Science and Technology for helping us in the design of the pulping processes.
REFERENCES


List of Figures

Fig. 1 Comparisons of time-dependent HexA content in pulps and alkali concentrations in pulping liquors during conventional kraft pulping of southern pine and maple.

Fig. 2 Comparisons of time-dependent HexA in pulps during conventional kraft pulping of five North American hardwoods.

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

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

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

Fig. 6 The correlation between HexA content in pulps and the kappa number reduction through hydrolysis treatment.
Fig. 1

HexA EA

T = 170°C

Loblolly Pine

Maple

Fig. 2

[Graph showing pulping time vs. HexA (μg/g-ODW) and EA (g/L as Na₂) for various species, including Aspen, Basswood, Birch, Maple, and Sweetgum.]