



*Institute of Paper Science and Technology
Atlanta, Georgia*

IPST Technical Paper Series Number 875

Evaluation of Hexenuronic Acids in U.S. Kraft Pulps

F.S. Chakar, L. Allison, T.J. McDonough,
A.J. Ragauskas, and U.S. Sezgi

August 2000

Submitted to
Sixth European Workshop on Lignocellulosics and Pulp
Bordeaux, France
September 3-6, 2000

Copyright® 2000 by the Institute of Paper Science and Technology

For Members Only

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 50 member companies. The purpose of the Institute is fulfilled through four missions, which are:

- to provide a 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 damages 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.

EVALUATION OF HEXENURONIC ACIDS IN U.S. KRAFT PULPS

F.S. Chakar, L. Allison, T.J. McDonough, and A.J. Ragauskas
Institute of Paper Science and Technology, Atlanta, GA, USA

Umit S. Sezgi
GL&V-Impco-Jones, 150 Burke Street, Nashua, NH, USA

ABSTRACT

The studies by Buchert et al. (1) have established the importance of hexenuronic acids to kraft bleaching operations. Although the contribution of hexenuronic acids to Northern European pulps has been extensively reported, the content of hexenuronic acids in U.S. commercial operations has not been as well documented. This study examined the contribution of hexenuronic acids to commercial U.S. SW and HW kraft pulping and bleaching operations. Based on a mild acid hydrolysis procedure, the content of hexenuronic acids contributed 33-67% to the kappa number of commercial HW kraft pulps, whereas for SW kraft mill pulps, the hexenuronic acids contributed only 5-12% of the pulp kappa number.

I. INTRODUCTION

The formation of hexenuronic acids during kraft pulping conditions was initially postulated by Clayton (2). These classical studies were directed at investigating the degradation of hardwood 4-*O*-methyl-D-glucuronoxylans under aqueous alkali conditions at 170°C. Johansson and Samuelson (3) employed 2-*O*-(4-*O*-methyl- α -D-glucopyranosyluronic acid)-D-xylitol as a model compound to provide evidence for the formation of hexenuronic acids upon treatment with alkali at elevated temperatures. Subsequent studies by Simkovi et al. (4) provided spectroscopic data that alkaline degradation of L-arabino-(4-*O*-methyl-D-glucurono)-D-xylan involved the elimination of 4-*O*-methyl-D-glucuronic acid residues yielding, in part, hexenuronic acid. Despite these early studies, the importance of hexenuronic acids to pulp bleaching studies was not fully appreciated until the research results reported by Buchert et al. (5). Subsequent to these reports, it became readily apparent that hexenuronic acids contributed to pulp bleachability (6, 7), influenced the retention of nonprocess elements in kraft pulps (8, 9), contributed to the formation of oxalic acids during ozone bleaching (10), and impacted pulp brightness values (11). Accompanying these investigations, were significant improvements in the methodology for detecting and removing hexenuronic acids from kraft pulps (12).

Despite these advances, the contribution of hexenuronic acids to SW and HW kraft pulping operations in the U.S. has been a largely unreported issue. Past studies by Hanna et al. (13) and Senior et al. (14) have indicated that laboratory cooks of North American wood sources can yield pulps that have hexenuronic acids contributing 10-40% to the pulp kappa number. The present study surveyed the contribution of hexenuronic acids to the pulp kappa number of several U.S. pulping operations.

II. EXPERIMENTAL

Materials. All pulps were acquired from commercial U.S. HW and SW kraft pulping operations. The pulps were extensively washed with deionized water until the filtrate was pH neutral and colorless. Laboratory cooks were prepared from wood chips that originated from a single sweetgum tree.

Kraft pulping. Laboratory kraft pulps were prepared in accordance with standard laboratory conventional batch and RDH cooking procedures. Conventional kraft pulps were prepared employing an H-factor of 1,800-800. The H-factor for the RDH pulps varied from 1,000-200.

Hexenuronic acid analysis. The presence of hexenuronic acids in kraft pulps was evaluated indirectly using a modified literature method. In brief, the pulps were placed in a pH 3 formic acid/sodium formate buffer solution yielding a final consistency of 5%. The mixtures were refluxed for 2 and 5 hours. The treated pulps were filtered, washed, and analyzed for kappa number in accordance with TAPPI Standard Method T236-cm85. Kappa number measurements were performed in duplicate and typically these values differed by less than 2%. In selected cases, the initial acid hydrolysis effluents were analyzed for 2-furoic acid using standard UV/Vis methods (6).

III. RESULTS AND DISCUSSION

The contribution of hexenuronic acids to the measured kappa number of several commercial pulps has been reported in the literature. Typically, the contribution of hexenuronic acids to HW kraft pulps has been found to be approximately 30–35% of the pulp kappa number for northern Scandinavian pulp mills (5). For SW kraft pulps, the northern Scandinavian pulp mills yield fibers that contain 10% hexenuronic acid based on kappa number analysis (15). Allison et al. (16) have reported comparable values for commercial SW kraft pulp mills employing Radiata pine as a fiber source. This paper examined the level of hexenuronic acids from U.S. kraft pulp mill operations. A total of 14 pulps were examined for hexenuronic acid content. In each case, the pulps were refluxed in pH 3 buffered solution for 2 and 5 hours and pulp kappa number was determined. The results of this analysis are summarized in Table 1.

Table 1. Contribution of Hexenuronic Acid to Kappa Number of Commercial U.S. Kraft Pulps.

Pulp	Kappa #			Pulp	Kappa #		
	Brownstock	2 h A ¹	5 h A		Brownstock	2 h A	5 h A
HW Kraft	10.5	6.3	4.9	HW Kraft	14.1	10.5	8.1
“	11.6	11.0	8.2	“	11.6	6.7	5.4
“	13.6	9.5	9.1	“	14.2	9.8	7.5
“	13.4	9.6	8.3	“	13.5	10.0	8.2
Post O2	10.6	7.3	5.9	“	11.4	5.6	-
Post O2	8.5	2.8	-				
SW Kraft				SW Kraft			
“	21.5	21.5	20.4	“	23.7	21.4	21.1
“	30.0	27.4	26.4				

¹ Refluxed pulp in pH 3 buffered solution for 2 or 5 hours.

The industrial HW kraft pulps exhibited varying responses to an A-stage treatment with reductions in kappa number varying from 67–33%. Undoubtedly, this is due in part to the different HW sources and different cooking technologies employed at the various mills. Commercial SW kraft pulps were found to have substantially reduced amounts of hexenuronic acids contributing to the pulp kappa number. These results are consistent with literature results, although in general many of the HW pulps exhibited exceptionally high levels of hexenuronic acids contributing to the pulp kappa number.

To further explore the formation of hexenuronic acids as a function of kraft cooking technologies, a series of laboratory cooks was performed from a common HW source employing conventional and simulated RDH pulping conditions. The pulps from these cooks were then analyzed for their response to an A-stage. Figure 1 summarizes the results of these studies. For both the RDH and conventional cooks, the contribution of hexenuronic acids to the kappa increases as delignification is extended to approximately kappa 13. Extending delignification reduces the level of hexenuronic acids presumably due to a slow degradation occurring during the cook. Analysis of the effluents for 2-furoic acid, by UV/Vis, confirmed the kappa number trends observed after mild acid hydrolysis (see Figure 2).

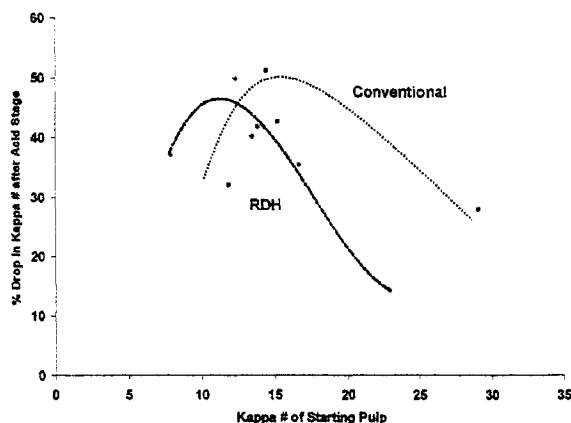


Figure 1. Contribution of hexenuronic acids to pulp kappa number for laboratory kraft cooks.

The data in Figures 1 and 2 suggest that the extent of delignification is one of the most significant factors contributing towards the hexenuronic acid content for batch-cooked pulps.

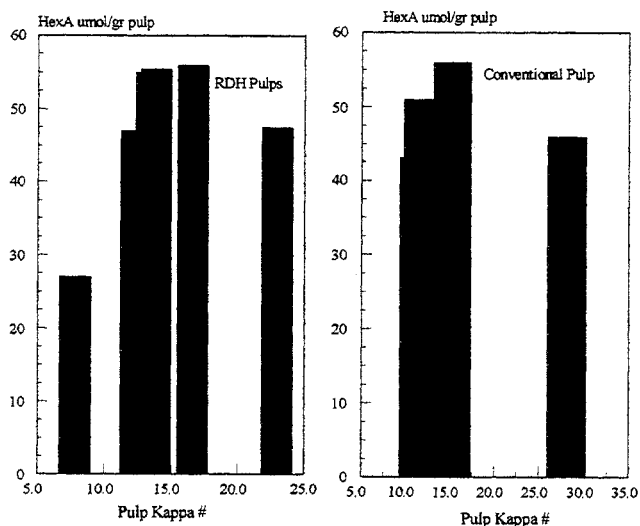


Figure 2. Concentration of hexenuronic acids in µmol/gr pulp

IV. CONCLUSIONS

The results presented in this report demonstrate the importance of hexenuronic acids to U.S. HW pulp bleaching operations. For some HW pulping operations, hexenuronic acids appear to be the dominant component contributing to the kappa number. In these cases, a substantial component of pulping operations is being directed at removing these unsaturated sugars and not lignin. The well-documented ability of an A-stage to selectively remove hexenuronic acids in kraft pulps provides a significant opportunity to reduce the operating and capital costs associated with bleaching such pulps.

V. ACKNOWLEDGMENTS

The authors wish to thank the member companies of IPST and the Department of Energy (Project #: DE-FC07-96ID13442) for their support of this research. This manuscript was prepared, in part, with the support of the U.S. Department of Energy (DOE) Cooperative Agreement No. DE-FC07-96ID13442. However, any opinions, findings, conclusions, or recommendations expressed herein are those of the author(s) and do not necessarily reflect the views of DOE. Portions of this work were used by F.S.C. as partial fulfillment of the requirements for the Ph.D. degree at the Institute of Paper Science and Technology.

VI. REFERENCES

1. Buchert, J.; Teleman, A.; Harjunpää, V.; Tenkanen, M.; Viikari, L.; Vuorinen, T., Effect of cooking and bleaching on the surface chemistry of conventional pine [*Pinus*] kraft pulp. Proceedings of 3rd EWLP, August 28-31, Stockholm, pp.16-19 (1994).
2. Clayton, D.W., The alkaline degradation of some hardwood 4-*O*-methyl-D-gluconoxylans, *Svensk Papperstidning* 28(4):115-124 (1963).
3. Johansson, M.H.; Samuelson, O., Epimerization and degradation of 2-*O*-(4-*O*-methyl- α -D-glucopyranosyluronic acid)-D-xylitol, *Carbohydr. Res.* 54: 295-299 (1977).
4. Simkovic, I.; Alfoldi, J.; Matulova, M., A ¹³C NMR study of the alkaline degradation products of polysaccharides, *Carbohydr. Res.* 152:137-141 (1986).
5. Buchert, J.; Tenkanen, M.; Ek, M.; Teleman, A.; Viikari, L.; Vuorinen, T., Effects of pulping and bleaching on pulp carbohydrates and technical properties. Proceedings of IPBC, April 14-18, Washington, D.C., book 1, pp.39-42 (1996).

6. Vuorinen, T.; Buchert, J.; Teleman, A.; Tenkanen, M.; Fagerström, P., Selective hydrolysis of hexenuronic acid groups and its application in ECF and TCF bleaching of kraft pulps. Proceedings of IPBC, April 14-18, Washington, D.C., book 1, pp.43-52 (1996).
7. Vuorinen, T.; Fagerström, P.; Räsänen, E.; Vikkula, A.; Henricson, K.; Teleman, A., Selective hydrolysis of hexenuronic acid groups opens new possibilities for development of bleaching processes. Proceedings of 9th ISWPC, June 9-12, Montreal, pp.M4-1-M4-4 (1997).
8. Presley, J.; Hill, R.; Chauveheid, E.; Devenyns, J., New metals-control technique improves bleaching performance, *J. Pulp Paper Sci.* 71(10):129-131 (1997).
9. Devenyns, J.; Chauveheid, E., Uronic acids and metals control. Proceedings of 9th ISWPC, June 9-12, Montreal, pp.M5-1-M5-4 (1997).
10. Nilvebrant, N.; Reimann, A., Xylan as a source for oxalic acid during ozone bleaching. Proceedings of 4th EWLP, September 8-11, Stresa, pp.485-491 (1996).
11. Vuorinen, T.; Fagerström, P.; Buchert, J.; Tenkanen, M.; Teleman, A., Selective hydrolysis of hexenuronic acid groups and its application in ECF and TCF bleaching of kraft pulps, *J Pulp Paper Sci.* 25(5):155-162 (1999).
12. Tenkanen, M.; Gellerstedt, G.; Vuorinen, T.; Teleman, A.; Perttula, M.; Li, J.; Buchert, J., Determination of hexenuronic acid in softwood kraft pulps by three different methods. *J. Pulp Paper Sci.* 25(9):306-311 (1999).
13. Hanna, R.J.; Fisher, J.J.; Krohn, M.J.; Goyal, G.C.; Packwood, R.E.; Ragauskas, A.J., Differences in bleaching and refining response of displacement batch hardwood and softwood caused by pulping conditions and structure of residual lignin. Proceedings of IPBC, June 1-5, Helsinki, book 1, pp.323-328 (1998).
14. Senior, D.J.; Oldroyd, D.L.; Fleming, B.I.; Ragauskas, A.J.; Zawadzki, M., High-Yield pulping and bleaching strategy for aspen kraft pulps. Proceedings of IPBC, June 1-5, Helsinki, book 1, pp.49-60 (1998).
15. Bergnor-Gidnert, E.; Tomani, P. E.; Dahlman, O., Influence on pulp quality of conditions during the removal of hexenuronic acids, *Nordic Pulp Paper Research Journal* 13(4):310-316 (1998).
16. Allison, R. W.; Timonen, O.; McGrouther, K.G.; Suckling, I.D., Hexenuronic acid in kraft pulps from radiata pine, *Appita J.* 52(6): 448-453 (1999).