2001 TAPPI JOURNAL PEER REVIEWED PAPER

CHARACTERIZATION OF CARBOXYLIC ACIDS DURING KRAFT AND SUPERBATCH PULPING

Johanna Buchert[1], Maija Tenkanen[1] And Tarja Tamminen[2]
1) VTT Biotechnology, P.O. Box 1500, FIN-02044 VTT, Finland
2) KCL, P.O. Box 70, FIN-02151 Espoo, Finland

Correspondence to: Johanna Buchert, fax: +358 9 4552103, e-mail: Johanna.Buchert@vtt.fi

Abstract

In this work the carboxylic acid profiles were followed during both conventional and Superbatch cooking. Different methods were used for the quantitative analysis of uronic acids, i.e. hexenuronic, 4-O-methyl glucuronic, 4-O-methyliduronic, galacturonic and glucuronic acid and the result obtained was compared to the conductometric titration. In the conventional pulp with kappa number of 24.2 uronic acids accounted for 52% of the total carboxylic groups as measured by conductometric titration hexenuronic acid being the major uronic acid. Due to the different alkaline profile during the Superbatch cooking the hexenuronic acids formed in the initial phase of the cook were almost completely degraded and as a result the Superbatch pulp contained significantly lower amounts of uronic acids, i.e. 25% of all carboxylic groups. By calculating the difference of the total amount of carboxylic groups and the measured amount of uronic acids and taking into account the formation of metasaccharinic acids it could be concluded that lignin bound acids were significant sources of charge in the unbleached pulps. In the conventional pulp the lignin bound carboxylic groups were estimated to account for 32% of the total acids, whereas in the Superbatch pulp the percentage was estimated to be even higher, *i.e.* 45% due to nearly complete degradation of HexA during the cooking.

Keywords: carboxylic groups, uronic acids, hexenuronic acid, carboxylic groups, kraft pulping, superbatch pulping

Introduction

Carboxylic groups in kraft pulps have impact on several technical properties such as swelling, paper technical properties, ion exchange with metal cations and consumption of certain bleaching chemicals (*1-5*).

The carboxylic groups in native wood are 4-O-methyl glucuronic acids (MeGlcA), galacturonic (GalA) and glucuronic acids (GlcA) being structural components of wood xylan and pectin (*6-8*). During kraft pulping the overall carboxylic group content but also to the chemical structure of the carboxylic acids is changed. Major changes are caused by the conversion of MeGlcA to

hexenuronic acid (HexA) via the intermediate product 4-O-methyliduronic acid (MeIdoA) (*9-11*). Acidic groups are also formed to lignin during the pulping process (*12-13*). In addition, end-group peeling of pulp carbohydrates is also known to result in formation of new carboxylic groups (*6*).

The formation and stability of HexA during pulping is known to be strongly affected by the pulping conditions, i.e. temperature and alkalinity (*9, 14-15*). Thus, pulps originating from different processes are reported to have different uronic acids profiles (*14*). In this work the carboxylic group profiles during kraft and Superbatch pulping were analyzed as a function of the cooking time using conductometric titration, total enzymatic hydrolysis combined to HPLC and acid methanolysis with subsequent gas chromatography.

Materials and methods

Pulps

Pinus sylvestris logs from Southern Finland were debarked and chipped in the field. The chips were dried and screened. The conventional cooking experiments were carried out at the Research Centre of Enso-Gutzeit Ltd as described previously (*9*). Superbatch cooking was carried out in the pilot scale unit at Western Laboratories Ltd. as described by Siistonen et al (*16*). Active alkali used in both cooking experiments was 18%. In the case of conventional pulping, eight experiments representing different stages of pulping were carried out. Similarly, in the case of Superbatch pulping, four experiments representing different stages of the pulping process were carried out (**Table 1**).

Pulping method	Cooking time, min	Temperature, °C	H-factor	Residual effective alkali, g/l	Kappa number	Yield %
Conventional	58	140	11	25.1	>50	77.4
	74	150	42	24.6	>50	73.5
	86	160	124	21.5	>50	67.5
	90	170	204	19.3	>50	63.0
	140	170	1007	9.5	45.7	50.4
	173	170	1500	7.8	27.6	48.0
	206	170	2001	5.6	26.0	47.4
	238	170	2517	4.7	24.2	46.6
Superbatch	40 [1)]	80	Nd	4.9	>50	93.3
	60 [2)]	155	Nd	8.1	>50	77.5
	107	170	370	25.0	41.7	48.6
	133	170	830	22.8	20.6	44.9
	199	170	1820	18.2	11.8	41.6

[1)] and [2)] refer to the samples withdrawn at the end of warm black liquor impregnation and hot black liquor pre-treatment, respectively (Siistonen et al 1999).

Table 1. Pulping parameters during conventional and Superbatch cooks. Active alkali was 18% on wood (as Na_2O).

Analyses

The carbohydrate composition of the pulps were analyzed by HPLC after acid hydrolysis according to Hausalo (*17*). The lignin content was analyzed after extraction with dichloromethane according to Browning (*18*). The xylan-bound uronic acids (MeGlcA, HexA, MeIdoA) in the pulps were analyzed by total enzymatic hydrolysis combined with HPLC as described by Tenkanen et al (*15*). Other uronic acids, *i.e.* galacturonic acid and glucuronic acids were analyzed by gas chromatography after methanolysis as described by Sundberg et al (*19*). The total amount of carboxylic groups in the pulp samples was analyzed by conductometric titration according to Katz et al (*20*).

Results

Comparison of the pulps obtained in kraft and Superbatch processes

Pine chips were cooked with conventional and Superbatch processes for different cooking times (1-4 hours). In the conventional cook, the alkaline concentration decreased to the end of the cook, whereas in the Superbatch-cook the alkaline concentration was increasing as the cook proceeded (Table 1). The different cooking conditions could be visualized in the chemical composition in the pulps (**Figure 1**). During the conventional cooking process, the xylan content was slightly increasing as the cook proceeded, whereas in the Superbatch cook the overall xylan content decreased indicating that no reprecipitation of solubilized xylan is occurring in the Superbatch process (Figure 1A). On the other hand the relative pulp glucomannan content throughout the Superbatch process was slightly higher than that in the conventional process (Figure 1B). The different cooking conditions were also visualized in the lower lignin and higher cellulose content in the Superbatch pulp as compared to the conventional pulp (**Table 2**).

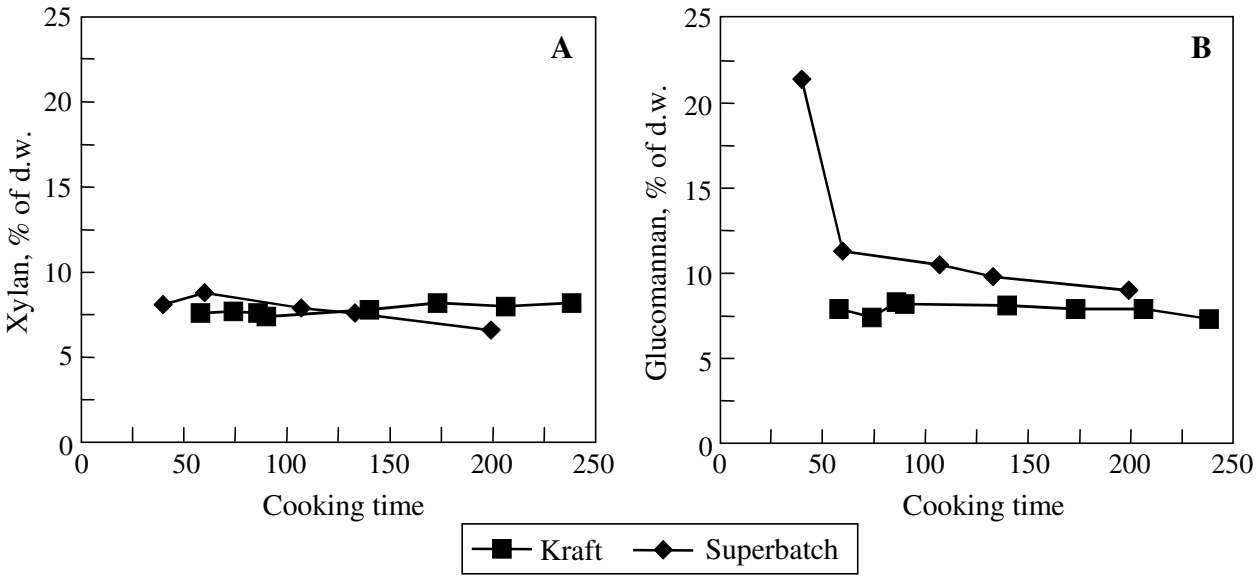

Figure 1. Comparison of the arabinoxylan (A) and galactoglucomannan (B) content of the pulps as a function of the cooking process. Galactoglucomannan has been calculated assuming mannose to glucose ratio of 4:1 (Sjöström 1993).

Pulp	Cooking time, min	Lignin, % of d.w.	Carbohydrate composition, % of d.w.					Total carbohydrates, % of d.w.
			Ara	Gal	Glc	Xyl	Man	
Conventional	58	27.2	1.5	1.1	48.4	6.1	5.4	62.5
	74	24.8	1.6	1.0	51.3	6.1	5.1	65.1
	86	20.6	1.4	0.9	55.0	6.2	5.9	69.4
	90	17.9	1.2	0.8	58.1	6.2	5.9	72.2
	140	6.5	0.9	0.6	69.6	6.9	6.0	84.0
	173	4.8	0.8	0.4	69.8	7.4	6.0	84.4
	206	3.5	0.7	0.4	72.0	7.3	6.0	86.4
	238	4.4	0.7	0.3	72.5	7.5	5.6	86.6
Superbatch	40	26.7	1.8	1.9	46.6	6.3	14.6	71.2
	60	25.0	1.8	1.3	53.6	7.0	7.5	71.2
	107	5.3	0.9	0.6	77.5	7.0	7.5	93.4
	133	2.5	0.7	0.3	83.8	7.0	7.1	98.8
	199	1.5	0.5	-	84.6	6.1	6.8	97.9

Table 2. Chemical composition of conventional pulps during cooking as analyzed by acid hydrolysis.

Effect of conventional pulping on uronic acid profile

In order to get profound understanding of the presence of different types of uronic acids during the cooking two different methods were used. The acidic components of pectins were analyzed by acid methanolysis and GC (*19*). For the analysis of xylan bound uronic acids, *i.e.* HexA, MeGlcA and MeIdoA, the pulp samples were hydrolyzed to mono- and oligosaccharides with a mixture of hemicellulolytic and cellulolytic enzymes, where after the composition of the solubilized fraction was analyzed by HPLC (*15*). As a result of the enzymatic solubilization, about 57-100% of the pulp d.w. was solubilized depending on the degree of delignification (results not shown).

In the conventional cook MeGlcA was the major acidic component in the first pulp sample after 58 min of cooking, and the concentration was 62 mmol/kg (**Figure 2A**). In the early phases of this conventional cook, pectin derived uronic acid, *i.e.* galacturonic acid could also be detected with the maximum amount of 9 mmol/kg. In addition to galacturonic acid, significant amount of glucuronic acid (GlcA) was detected with maximum concentration of 10 mmol/kg after 58 min of cooking. Native softwood is reported to contain less than 1% of galacturonans, which are mainly situated in the middle lamella and the tori of the bordered pit-membranes (*21*). A large portion of these galacturonic acid groups are methylated in native wood but complete demethylation of these groups is reported to occur at alkaline conditions (*7*). GlcA is reported to be a structural component of arabinogalactan (*8*).

The formation of HexA in the early phases of the kraft process was clearly observed as reported previously (*9*). After 74 minutes of cooking, the HexA content had increased from 5 mmol/kg to 21 mmol/kg and simultaneously also 9 mmol/kg of the intermediate product, *i.e.* MeIdoA was detected. When the maximum cooking temperature, i.e. 170^{o}C was reached after 90 min, the hexenuronic acid content in the pulp was 38 mmol/kg. Surprisingly, also in the highly delignified pulp samples a small amount of both the native MeGlcA group as well as its isomerization

product MeIdoA were detected indicating that part of the MeGlcA groups remained unreactive. The reason for this remains to be clarified but it seems possible that these remaining MeGlcA groups have been somehow sterically stabilized towards the isomerization reaction. After 74 minutes of cooking with the maximum HexA content of 40 mmol/kg, a clear degradation of HexA started without concomitant degradation of xylan thus resulting in final HexA content of 31 mol/kg (Figures 1A and 2A). Previously, when the structure of the surface xylan in the same pulps was analyzed by extensive xylanase treatment (about 30% of xylan analyzed) a even more substantial degradation of HexA was observed (*9*) indicating that the surface xylan accessible to xylanase treatment either contains lower amount of uronic acid side-groups or, alternatively, the formed HexA groups in the fibre surface are more easily further degraded in the alkaline conditions. One possibility of the lower overall substitution of the surface xylan is that it has reprecipitated to the fibers after solubilization and removal of the side groups during the cooking process.

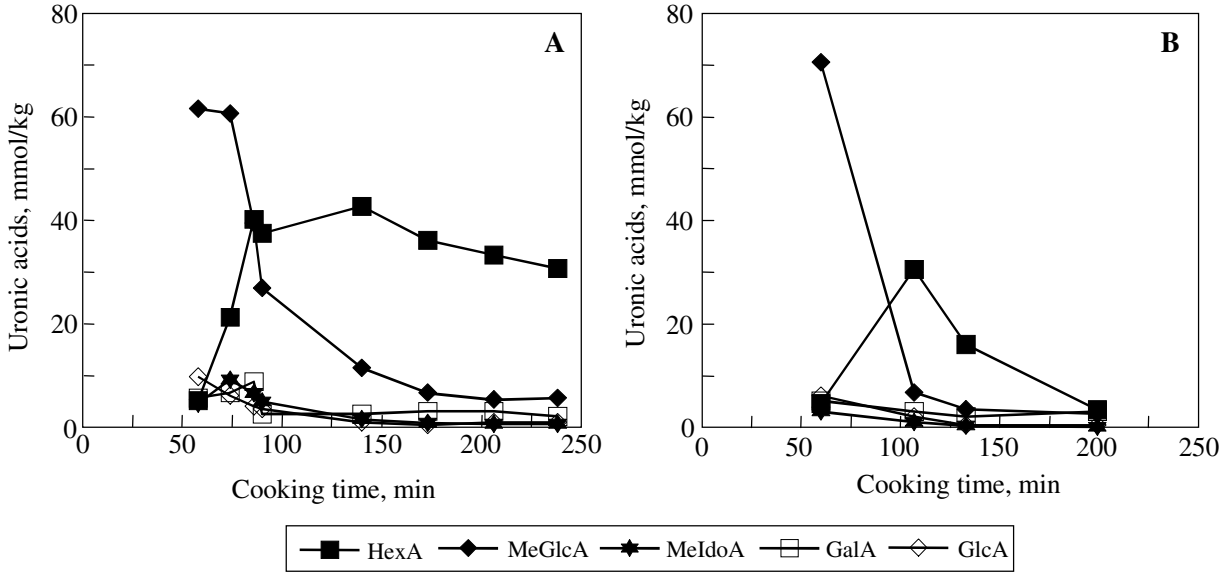

Figure 2. Uronic acid profile during (A) conventional kraft cooking and (B) Superbatch cooking.

In the final pulp with kappa number of 24.2 HexA accounted for 71% of the all uronic acids and MeGlcA and MeIdoA for 13% and 2%, respectively. Of the xylan-bound uronic acids, HexA accounted for 83%, MeGlcA for 15% and MeIdoA for 2% (Figure 2A). According to the total enzymatic hydrolysis the ratio of xylose to arabinose to uronic acids in the pulp with kappa number of 24.2 was 100:8.8:5.6, whereas the pulp with kappa number of 27.6 had a ratio of 100:10.3:6.5 (**Table 3**).

The total amount of carboxylic groups in the pulps were also analyzed by conductometric titration. The values obtained were significantly higher than the sum of all uronic acids detected by HPLC or methanolysis. For instance the total carboxylic acid content in the pulp with kappa number of 24.2 was 77 mmol/kg and the sum of all uronic acids (MeGlcA, MeIdoA, HexA, GlcA, GalA) was 40 mmol/kg (Figure 2A). Thus, the difference with these measurements was 37 mmol/kg. End-group peeling of pulp carbohydrates might contribute to the charge of the fibres

(*6*). It can be calculated that the metasaccharinic acids could contribute to ca. 12 mmol/kg of carboxylic groups assuming that the mean DP of pulp cellulose is 2300 and mean DP of hemicelluloses is 100 (*6*). According to Tenkanen et al (*15*) some minor additional potentially acidic peaks in the enzymatic hydrolyzate of kraft pulp can in fact be detected. In addition to carbohydrate bound carboxylic groups, the kraft pulp lignin has been reported to contain carboxylic groups (*12-13*). Assuming that metasaccharinic acids would contribute to 12 mol/kg, the amount of lignin bound acids would be as high as 25 mmol/kg, *i.e.* 32% of the carboxylic groups in the conventionally cooked kraft pulp. Previously, based on the potentiometric titration, the relative amount of non-uronic acid type of carboxylic groups has been estimated to be 20% in a similar type of unbleached pine kraft pulp (*22*).

Pulp	Kappa number	HexA	MeGlcA+ MeIdoA	Ara	Gal	Glc	Xyl	Man	Total carbohydrates analyzed, % of d.w.
Conventional	27.6	0.57	0.14	0.9	0.4	80.0	8.8	7.4	98.2
	26.0	0.53	0.11	0.8	0.4	80.0	8.9	8.9	99.6
	24.2	0.49	0.12	0.9	0.3	80.6	8.8	7.2	98.3
Superbatch	20.6	0.25	0.07	0.6	0.3	82.3	7.4	7.2	98.0
	11.8	0.06	0.05	0.4	0.2	87.1	6.5	7.0	101.4

Table 3. Total enzymatic hydrolysis of the conventional and Superbatch pulps. The values are expressed as % of d.w. (as anhydrosugars)

Effect of Superbatch cooking on uronic acid profile

The presence of different types of carboxylic groups in the Superbatch pulping process were analyzed using same techniques. The maximum amount of HexA detected was about 35 mmol/kg in pulp having kappa number of 41.7 with cooking time of 206 minutes (**Figure 2B**). When the cook proceeded, the amount of HexA present in the pulp was even more significantly decreased as compared to conventional cooking and thus the final pulp with kappa number of 11.8 contained only 3 mmol/kg of hexenuronic acids. The lower uronic acid content was also reflected in the total charge of the fibres as measured by conductometric titration (Figure 3B). When the carboxyl group content in conventional pulp and Superbatch pulp with respective kappa numbers of 24.2 and 20.6 were compared, it was found that the carboxyl group content was significantly lower in the Superbatch pulp, i.e. 46 mmol/kg vs.77 mmol/kg (**Figures 3A** and **3B**). The differences in the uronic acid profiles between the conventional kraft and Superbatch pulps were presumably caused by the higher residual alkalinity in the Superbatch pulping (Table 1). The high residual alkalinity causes both degradation of the formed HexA but also results in relatively lower xylan content in the Superbatch pulp as compared to conventional pulp (Figure 1A). When the side-group distribution of xylan in Superbatch pulps was calculated it was found to be less substituted with respect to both arabinose and uronic acids side groups as compared to the xylan in conventional kraft pulp (Table 3). Xylan in Superbatch pulps with kappa numbers of 11.8 and 20.6 had xylose:arabinose:uronic acid ratios of 100:6.1:1.3 and 100:8.4:3.6, respectively (Table 3).

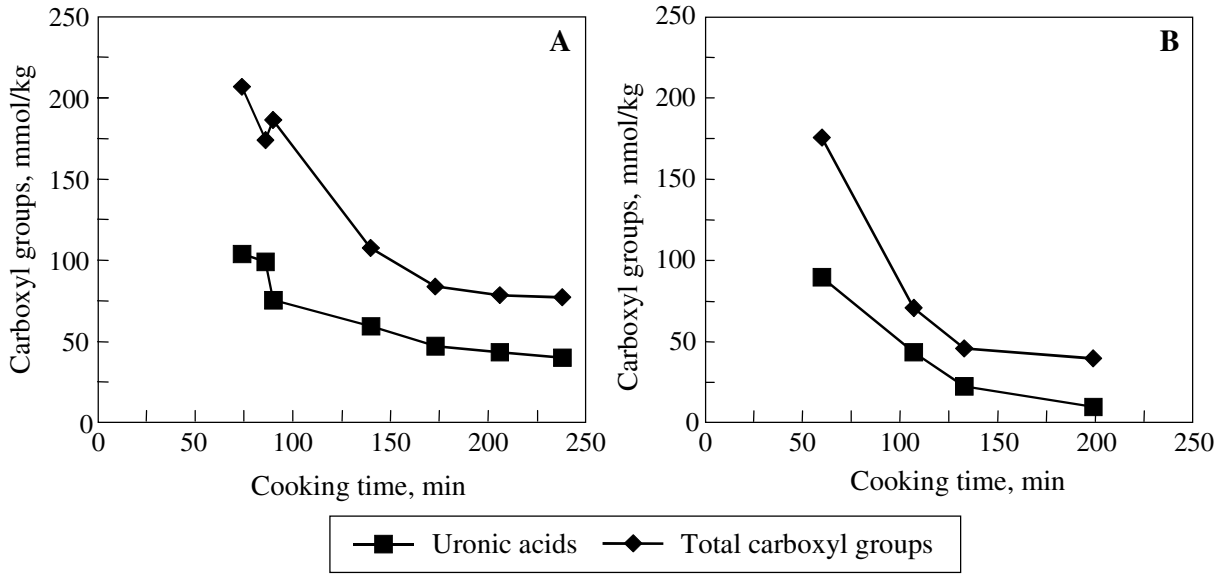

Figure 3. Carboxyl groups during (A) conventional and (B) Superbatch cooking analyzed by conductometric titration and total enzymatic hydrolysis/HPLC and methanolysis/GC. The amount of uronic acids is the sum of HexA, MeGlcA, MeIdoA, GalA and GluA.

When the amount of all uronic acids, i.e. 10 mmol/kg and the assumed metasaccharinic acids (12 mmol/kg) were subtracted from the total amount of carboxylic groups, i.e. 40 mmol/kg, it was found that the assumed lignin bound acids accounted for as much as 18 mmol/kg, *i.e.* 45% of all carboxylic groups. This higher percentage as compared to conventionally cooked kraft pulp is due to the degradation of HexA during the process thus changing the carboxylic group profile significantly. This different carboxylic group profiles in conventional kraft and Superbatch pulps may lead to different metal binding properties and subsequently to different requirements for chelator dosages in the bleaching stage.

Conclusions

The carboxylic acid profile in unbleached pulps was found to be strongly affected by cooking conditions. Superbatch cooking with high residual alkali resulted in significantly lower amounts of uronic acids, especially HexA than conventional cooking with different alkaline profile. In the conventional pulp about 83% of the uronic acids were hexenuronic acids. In both cases, also MeGlcA and MeIdoA were detected indicating incomplete conversion of methylglucuronic acids to hexenuronic acid groups. Lignin bound acids were found to be significant sources of charge in both Superbatch and conventional kraft pulps. In the conventional pulp the lignin bound carboxylic groups were estimated to account for 32% of the total acids, whereas in the Superbatch pulp the percentage was even higher, *i.e.* 45% due to nearly complete degradation of HexA during the cooking.

Acknowledgements

The authors thank Sebastian von Schoulz (Åbo Akademi University, Finland) for the methanolysis analyses, Tiina Leppänen and Kirsi Tuominen are thanked for excellent technical assistance and Marjukka Perttula for HPLC analyses. This work has mainly been financed by the Carbohydrate Research Programme of National Technology Agency of Finland (TEKES).

References

1. Scallan, A. M., *Tappi J*. 66(11): 73(1983).
2. Laine, J. and Stenius, P., *Paperi ja Puu* 79(4): 257(1997).
3. Sjöström, E. and Eriksson, E., *Tappi J*. 51(1): 16(1968). Buchert, J., Bergnor, E., Lindblad, G., Viikari, L. and Ek, M., *Tappi J*. 80(6): 165(1997).
4. Vuorinen, T., Fagerström, P., Buchert, J., Tenkanen, M. and Teleman, A., Selective hydrolysis of hexenuronic acid groups and its application in ECF and TCF bleaching of kraft pulps. *J. Pulp Pap. Sci*. 25(5): 155(1999).
5. Sjöström, E., *Wood Chemistry, Fundamentals and Applications*. 2nd ed., Academic Press, New York, 1993.
6. Holmbom, B., Pranovich, A. V., Sundberg, A. and Buchert, J., "Charged groups in wood and mechanical pulps", in *Pulp for Papermaking, Cellucon 98 Proceedings - 10th Int. Cellucon Conf.* (J. F. Kennedy, G. O. Phillips and P. A. Williams, Eds) Woodhead Publishing Ltd., UK, in press.
7. Willför, S. and Holmbom, B., "Isolation and characterization of water-soluble polysaccharides from Norway spruce and Scots pine". Submitted to *Wood Science and Technology.*
8. Buchert, J., Teleman, A., Harjunpää, V., Tenkanen, M., Viikari, L. and Vuorinen, T., *Tappi J*. 78(11): 125(1995).
9. Teleman, A., Harjunpää, V., Tenkanen, M., Buchert, J., Hausalo, T., Drakenberg, T. and Vuorinen, T., *Carbohydrate Res*. 272: 55(1995).
10. Teleman, A., Siika-aho, M., Sorsa, H., Buchert, J., Perttula, M., Hausalo, T. and Tenkanen, M., *Carbohydrate Res*. 293: 1(1996).
11. Froass, P. M., Ragauskas, A. J., McDonough, T. J. and Jiang, J., *Proc. 1996 Int. Pulp Bleaching Conf.,* Washington, D.C., 1996, Book 1, p.163.
12. Jiang, Z.-H. and Argyropoulos, D. S., *J. Pulp Pap. Sci*. 25(1): 25(1999).
13. Buchert, J., Tenkanen, M., Ek, M., Teleman, A., Viikari, L. and Vuorinen, T., *Proc. 1996 Int. Pulp Bleaching Conf*., Washington, D.C., 1996, p. 39.
14. Tenkanen, M., Gellerstedt, G., Vuorinen, T., Teleman, A., Perttula, M., Li, J. and Buchert, J., *J. Pulp Pap. Sci.* 25(9): 306(1999).
15. Siistonen, H., Svedman, M., Alén, R. and Tikka, P., *Paperi ja Puu* 81(5): 379(1999).
16. Hausalo, T., *8th Int. Symp. Wood and Pulping Chemistry*, Helsinki, Finland, 1995, Vol. 3, p. 131.
17. Browning, B. L., *Methods of Wood Chemistry*. Vol II, Interscience Publishers, New York, 1967, p. 785.
18. Sundberg, A., Sundberg, K., Lillandt, C. and Holmbom, B., *Nordic Pulp Paper Res. J*. 11(4): 216(1996).
19. Katz, S., Beatson, R. P. and Scallan, A. M., *Svensk Papperstidn*. 87(6): R48(1984).

20. Fengel, D. and Wegener, G., *Wood. Chemistry, Ultrastructure, Reactions*. Walter de Gruyter, Berlin, 1984.
21. Laine, J., Buchert, J., Viikari, L. and Stenius, P., *Holzforschung* 50(3): 208(1996).

Received: February 12, 1999
Accepted: August 25, 2000

This paper was accepted for abstracting and publication in the April 2001 issue of *TAPPI JOURNAL.*

TAPPI Website: www.tappi.org