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Influence of the carbohydrate composition on the molecular weight distribution of kraft pulps

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Abstract

The molecular weight distribution (MWD) of hardwood kraft pulps and softwood kraft pulps dissolved in lithium chloride/*N*,*N*-dimethylacetamide (LiCl/DMAc) have a different shape. Two fairly well separated distributions of hardwood kraft pulps are obtained by size exclusion chromatography whereas the MWDs of softwood kraft pulp is more complex. Since these two pulps contain different types of hemicelluloses, the neutral carbohydrate composition of different cuts of the MWDs was examined.

The results indicate that the two distributions observed for hardwood kraft pulps originate from cellulose and xylan, respectively. In contrast, the hemicellulose of softwood kraft pulps elute over the entire molecular weight range. The carbohydrate analysis of the collected fractions shows that glucose is the major component in all fractions. The relative concentration of mannose decreases during elution, i.e. with decreasing molecular weight (*M*) whereas galactose, xylose and arabinose increases during elution, i.e. with decreasing *M*. The coelution of cellulose and glucomannan may be due to association properties, which gradually decrease with increasing amount of galactose substituents. The difference in elution behaviour between hardwood and softwood kraft pulp xylans may be due to different amounts of glucuronic acid groups and/or how these groups are distributed along the main chain. It is thus more difficult to interpret differences in the MWDs of softwood kraft pulps than of hardwood kraft pulps.

Keywords: Kraft pulps; Cellulose; Molecular weight distribution; Hemicellulose; Lithium chloride/*N*,*N*-dimethylacetamide

1. Introduction

Cellulose, hemicellulose and lignin are the major polymer constituents in wood. While cellulose consists solely of β-D-glucan, with an average degree of polymerisation (DP) of around 10 000 (Sjöström, 1993a), the hemicelluloses are heterogeneous polysaccharides. The principal hemicellulose component in hardwoods is *O*-acetyl-4-*O*-methylglucurono-β-D-xylan, glucuronoxylan (Sjöström, 1993a). To the partially acetylated xylan backbone, α-D-glucuronic groups are linked with a frequency of one to ten xylose units. A small amount of β-D-glucomannan is also present in hardwoods having a glucose-to-mannose ratio of 1:1–1:2. The major hemicellulose in softwoods is galactoglucomannans. The partially acetylated β-D-glucomannan is divided in two types depending on amount of α-D-galactose substituents. For the low galactose type the galactose:glucose:mannose ratio is around 0.1:1:4 and for the high galactose portion the ratio is around 1:1:3. The softwood β-D-xylan is on an average substituted with two α-D-glucuronic and one α-L-arabinose per 10 xylose units. According to Sjöström (1993a), the DP of hemicelluloses isolated from softwood is around 100 and for hardwood hemicelluloses the DP is around 200.

Lignin is a heterogeneous polymer composed of various phenylpropane units (for a detailed description the reader is referred to Sjöström, 1993b). Around 90% of the lignin is removed during kraft pulping; the overall pulp yield is around 53 and 47% for birchwood and pinewood, respectively (Sjöström, 1993c). Around half of the birchwood hemicelluloses and 64% of the pinewood hemicelluloses are dissolved in the process liquor and around 10% of the cellulose is lost as well. The remaining hemicelluloses are deacetylated and partially degraded.

The polysaccharides in pulp, particularly cellulose, have a limited solubility in common solvents. However, cellulose can be dissolved, for example, as a metal complex in alkaline solutions, as a derivative or directly, e.g. in cadoxen, a solution of cadmiumoxide in aqueous ethylenediamine, or in lithium chloride/*N*,*N*-dimethylacetamide (LiCl/DMAc).

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Table 1
Characteristics of the investigated pulps

Designation	Sample	Viscosity (dm^3/kg)	Kappa number[a]	Brightness (%)
HP	Unbleached HWKP	1130	15	–
BHP	Bleached HWKP	816	–	88
SP	Unbleached SWKP	950	18	–
BSP	Bleached SWKP	610	–	86

[a] Amount of oxidizable structures.

The viscosity of a pulp sample dissolved in cuprietyldiamine (CED) is commonly used to estimate the degree of degradation of the pulp. A more detailed characterisation of the constituent polymers is obtained by size exclusion chromatography (SEC). This technique is commonly used for characterisation of polymers with respect to molecular weight distribution (MWD) and average molecular weights (*M*). To study the MWD by SEC, pulp samples can be carbanilated and dissolved in tetrahydrofuran (THF). There are, however, several disadvantages with this procedure: (i) the MWD of pulp lignin derived from unbleached samples cannot be determined because samples have to be delignified prior to derivatisation (Schroeder & Haigh, 1979); (ii) low molecular weight cellulose may be lost because methanol precipitation is used (Wood, Connor & Hill, 1986); (iii) loss of hemicellulose, which has a lower molecular weight than cellulose, may occur because the precipitation procedure has been optimised for cellulose (Evans, Wearne & Wallis, 1989).

A commonly used solvent for SEC characterisations of wood pulps is LiCl/DMAc. This solvent has been used to characterise the MWD of birch wood kraft pulp (Kennedy, Rivera, White, Lloyd & Warner, 1990; Westermark & Gustafsson, 1994). One disadvantage of using LiCl/DMAc is the limited solubility of softwood kraft pulps (Karlsson & Westermark, 1994; Sjöholm, Gustafsson, Pettersson & Colmsjo, 1997). The degree of solubility depends on the amount of lignin in the sample but even fully bleached pulps are not completely soluble (Sjöholm et al., 1997). After dissolution of an unbleached softwood kraft pulp, a gel-like residue can be isolated by ultracentrifugation. The residue was found to consist of a higher relative amount of mannan and lignin as compared with the original pulp sample (Sjöholm et al., 1997). Nevertheless, the solvent has also been used for SEC characterisations of softwood kraft pulps (Karlsson & Westermark, 1994; Silva & Laver, 1997).

SEC characterisations of wood pulps are commonly evaluated based upon the MWDs. The elution profiles, i.e. the MWDs of hardwood pulps is generally different compared to those of softwood pulps. By using differential refractive index detection, two distributions can be discerned in the SEC chromatogram of a hardwood kraft pulp, whereas the MWD of softwood pulps consists of several unresolved distributions. Hitherto, the carbohydrate compositions of the MWD of wood pulps dissolved in LiCl/DMAc have not been determined. However, xylan has indirectly been associated with the low molecular weight fraction of hardwood kraft pulp (Karlsson, 1997**)**.

In order to improve the interpretation of the MWDs of wood pulps dissolved in LiCl/DMAc it is important to determine the carbohydrate composition in the different elution volumes. In the present study the carbohydrate composition in the different elution volumes of hardwood and softwood kraft pulps are examined and the influence of the carbohydrate composition on the MWD profiles are discussed.

2. Experimental

2.1. Materials

All chemicals were of analytical grade. Lithium chloride (LiCl) (Merck, Darmstadt, Germany) was divided into small portions and stored in a desiccator over phosphorous pentoxide. Once withdrawn from the desiccator, a desired amount of salt was weighed and then immediately added to *N*,*N*-dimethylacetamide (DMAc) (Sigma–Aldrich, Gillingham, UK) which was filtered prior to use. Dissolution of the salt was carried out under vacuum, with cautious heating and continuous stirring for about 30 minutes. Eight percent (w/v) LiCl/DMAc was stored at + 4°C, while a fresh solution of 0.5% (w/v) LiCl/DMAc was used as the mobile phase.

Industrially produced kraft pulps were used: two hardwood (HWKP) and two softwood kraft pulps (SWKP), see Table 1. One of the HWKPs (HP) and one of the SWKPs (SP) were unbleached. The other pulps were both delignified by oxygen and bleached by ozone (BHP) and chlorine dioxide (BSP), respectively.

2.2. Chemical analysis

The viscosity of pulps dissolved in cupridiethylenediamine (CED) was determined according to SCAN-CM 15:88 (1988). Kappa number, which was determined according to SCAN-C 1:77 (1977), was used to estimate the amount of lignin in unbleached pulps. Brightness of the bleached pulps was measured according to SCAN-C11:75 (1975). The neutral carbohydrate composition of the pulps was determined after extraction with dichloromethane and acid hydrolysis (Theander & Westerlund, 1986). After reduction, the corresponding alditols were

Table 2
Recovery (%) of carbohydrate analysis and relative monosaccharide composition (%) of pulps

Pulp[a]	Recovery	Glc	Xyl	Ara	Man	Gal
HP	97.0	73.2	26	0.1	0.4	0.3
BHP	89.4	74.7	25	0.1	0.5	0.2
SP	91.8	84.8	7.5	0.7	6.6	0.5
BSP	98.2	84.9	7.4	0.8	6.6	0.4

[a] See Table 1 for abbreviations.

acetylated and analysed by gas chromatography using 2-deoxy-galactose as an internal standard. Separation was performed on a fused silica column DB-1 (J&W Scientific). The injector temperature was 260°C and the temperature of the detector 290°C. Helium was used as a carrier gas, flow 1.85 ml/min, split ratio 1:20. The temperature program was 160°C for 2 min, followed by a temperature increase of 2°C/min up to a final temperature of 250°C.

To obtain the neutral composition of pulp samples fractionated by SEC, the DMAc was removed by vacuum evaporation at room temperature. A small portion of deionized water was added to dissolve the salt followed by addition of concentrated sulphuric acid to a final concentration of 72%. This solution was left to stand at 30°C for 30 min. Acid hydrolysis was then performed at 125°C, 1.4 bar for 60 min. The monosaccharide composition of the hydrolysate was determined as described above.

2.3. Sample dissolution

Pulps were thoroughly washed with deionized water and were activated in deionized water at + 4°C for 1 h. Excess water was removed and the pulps were solvent-exchanged three times with methanol and then three times with DMAc with an intermediate equilibration of the pulp for 30 min. Eight percent LiCl/DMAc was added to give a concentration of 0.8% with respect to the pulp. The sample solution was allowed to stand for five days at + 4°C. The pulps were then diluted with DMAc to a final concentration of 0.5% with respect to LiCl and 0.05% with respect to the pulp. In order to remove any undissolved material and dust, the final solutions were centrifuged at 87 000*g* for 30 min.

2.4. Size exclusion chromatography

Pulps were characterized on a SEC system consisting of an automatic sampler, AS-4000A (Hitachi), with an L-6200A pump (Hitachi), an ultraviolet (UV) detector, L4250 (Hitachi) and a refractive index detector, RI-71 (Shodex). The injection volume was 100 and 200μl when fractions were collected. In order to obtain sufficient amount of the sample to determine the carbohydrate composition of the fractions, eight repeated injections were made. The separations were performed at 80°C with 0.5% LiCl/DMAc at a flow rate of 1 ml/min on four 20 μm Mixed-A columns (Polymer Laboratories) proceeded by a guard column (Polymer Laboratories). Pullulan standards 853k, 380k, 186k, 100k, 48k, 23.7k, 12.2k, 5.8k and 738 Da (Polymer Laboratories), were used to calibrate the columns. The linear coefficient of determination (r^2) between the M_p of the standards and time was 0.995. Data acquisition and calculations were carried out with PL Caliber (Polymer Laboratories).

The lignin content in the unbleached pulp samples was detected at 295 nm. This is not a specific absorption wavelength for lignin but was chosen since the DMAc portion of the mobile phase (LiCl/DMAc) has a UV cutoff at 268 nm.

3. Results and discussion

The relative composition of neutral monosaccharides of the pulps is shown in Table 2. The large amounts of xylose detected are typical for hardwood pulps. The industrial process commonly alternates between using hardwood and softwood, which explains the small amount of arabinose and galactose in the hardwood pulp. The relative large amount

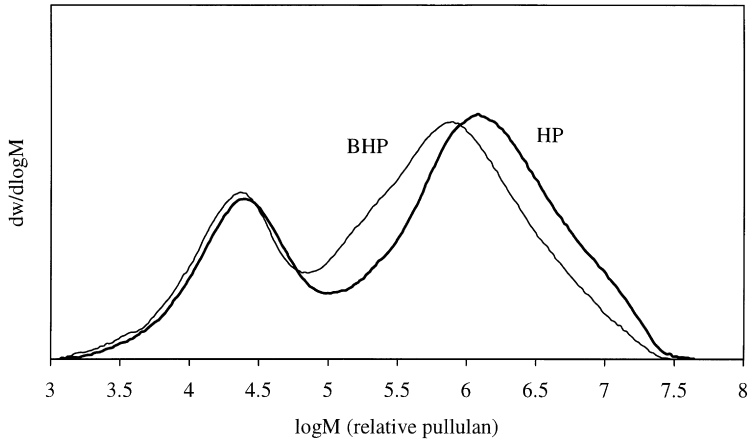

Fig. 1. Molecular weight distribution of unbleached (HP) and bleached (BHP) hardwood kraft pulp. Size-exclusion chromatography was performed at 80°C on PL Mixed A columns using 0.5% LiCl/DMAc as the mobile phase and a refractive index detector.

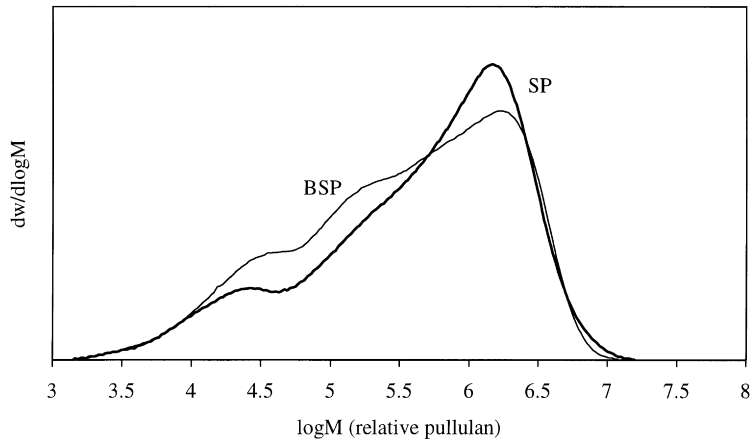

Fig. 2. Molecular weight distribution of unbleached (SP) and bleached (BSP) softwood kraft pulp. Chromatographic conditions as in Fig. 1.

of mannose in the softwood pulps reflects the galactoglucomannan content of these samples. As expected, the result shows that the relative neutral carbohydrate composition of wood kraft pulps is hardly affected by bleaching.

3.1. Molecular weight distributions

The hardwood kraft pulps were completely soluble in LiCl/DMAc. In contrast, 63% of the SP and 92% of the BSP were dissolved. There is a clear difference in the MWD profiles between hardwood kraft pulps and softwood kraft pulps dissolved in LiCl/DMAc. The MWDs obtained by refractive index (RI) detection of HP and BHP is shown in Fig. 1; and of SP and BSP in Fig. 2. The SEC of hardwood pulps gives two fairly well separated distributions that continue far into the high molecular weight region. In contrast, the MWDs of softwood pulps seems to be composed of several unresolved distributions. After bleaching the molecular weight (M) of hardwood pulp is shifted towards lower M, Fig. 1.

The MWD of the bleached softwood kraft pulp (BSP) is redistributed compared with the corresponding unbleached sample (SP), Fig. 2. The MWD in the high molecular weight range of BSP is suppressed and has a more accentuated middle fraction compared with the MWD of SP. In a previous report it was shown that the dissolved portion of unbleached softwood kraft pulps is not representative of the pulp (Sjöholm et al., 1997) and thus it is not possible to conduct a detailed comparison between SP and BSP. However, bleaching does not change the characteristic differences in the MWDs between hardwood and softwood kraft pulps.

Although differently accentuated, the UV-absorbing components of the unbleached kraft pulps are separated into two distributions, Fig. 3. The removal of lignin during bleaching leads to a depletion of the UV absorbing components for both pulp types, although the shapes of the chromatograms obtained by the RI detector is not changed. Thus, the reason for the different MWD profiles between hardwood and softwood kraft pulps obtained with the RI detector, seems to be caused by differences in hemicellulose composition rather than the composition of the pulp lignin.

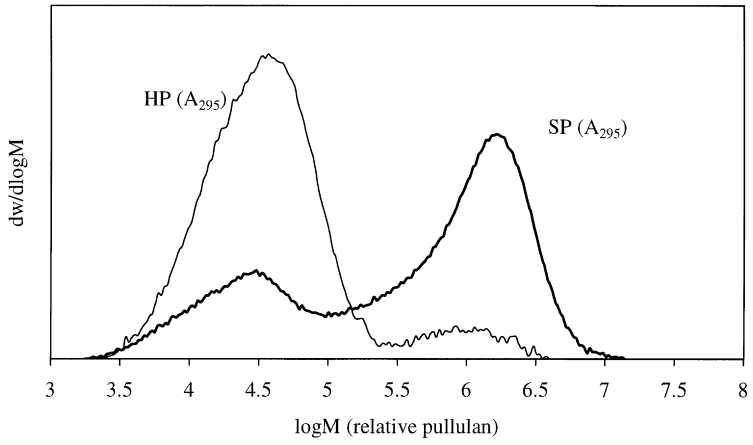

Fig. 3. Molecular weight distribution of UV-absorbing components of unbleached hardwood (HP) and softwood (SP) kraft pulp. Size-exclusion chromatography was performed at 80°C on PL Mixed A columns using 0.5% LiCl/DMAc as the mobile phase. The absorbance was measured at 295 nm.

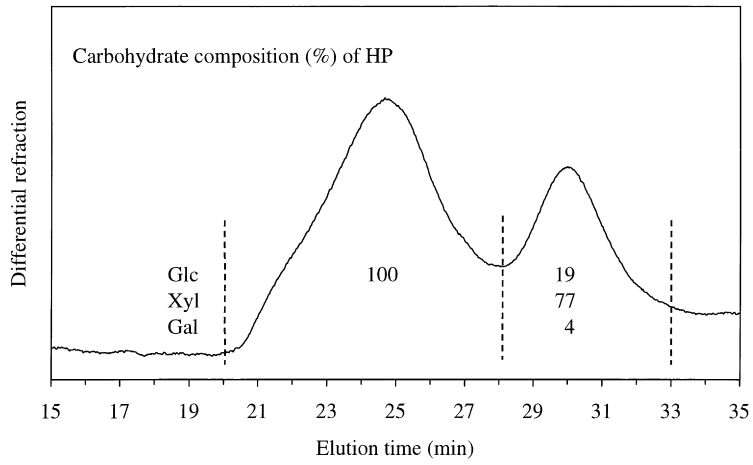

Fig. 4. Chromatogram showing the relative carbohydrate composition (%) in different elution volumes of unbleached hardwood kraft pulp (HP). Chromatographic conditions as in Fig. 1.

3.2. Carbohydrate composition in different elution volumes

The neutral carbohydrate composition in different molecular weight ranges of one hardwood and one softwood kraft pulp sample were determined, Figs. 4 and 5. Two fractions were collected for the HP sample, Fig. 4. Since bleaching improves the solubility of softwood pulp in LiCl/DMAc, the bleached softwood kraft pulp (BSP) was used in order to increase the amount of sample available for carbohydrate determinations. The undissolved fraction of the sample was determined by gravimetric analysis. The chromatogram shown in Fig. 5 represents around 92% of the BSP sample and shows the elution times of the three fractions collected. The overall recovery of the carbohydrate analysis for the fractions collected from the HP sample was 62 and 84% for the BSP sample (Figs. 4 and 5).

In Fig. 4 the relative carbohydrate composition of the fractions of HP are shown. The high molecular weight distribution was found to consist solely of glucose whereas for the low molecular weight fraction xylose and a small amount of galactose were also detected. Although the acid monosaccharide content was not determined, the carbohydrate analysis of the fractions suggests that the high and low molecular distributions of HP consist of cellulose and glucouronoxylan, respectively.

The carbohydrate composition of the three distributions of the BSP sample was more complex. In Fig. 5 the relative monosaccharide composition in each elution fraction is shown. Glucose was the major monosaccharide in all fractions, although it is not the most abundant monosaccharide of softwood hemicelluloses. The other monosaccharides identified indicate that the hemicelluloses of BSP elute over the entire elution range. In the highest molecular weight fraction, i.e. the fraction that elutes first, the largest relative amount of mannose was found. In the intermediate and in the lowest molecular weight fraction, xylose was the most abundant monomer in addition to glucose.

The molecular weights, relative to pullulan, of the two distributions of the hardwood kraft pulps, agree fairly well with the DP of hardwood glucuronoxylan and cellulose,

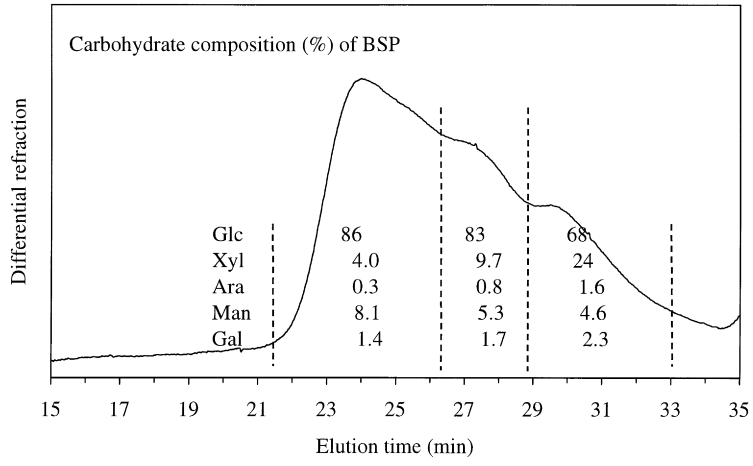

Fig. 5. Chromatogram showing the relative carbohydrate composition (%) in different elution volumes of bleached softwood kraft pulp (BSP). Chromatographic conditions as in Fig. 1.

respectively (Sjöström, 1993a). According to Sjöström (1993a) the DP of softwood hemicellulose is around half the DP of hardwood hemicellulose and far lower than the DP of wood cellulose. This implies that the xylose, arabinose, mannose and galactose identified in the two highest molecular weight fractions of the softwood kraft pulp do not reflect the true molecular weight distributions of hemicellulose.

The principal hemicellulose in softwood, galactoglucomannan, is considered to be of two main types (see above), either of a low or a high galactose content: the former often referred to as glucomannan. Glucomannan has been proposed to be associated with the cellulose in the fibre wall (Salmén & Olsson, 1998). In solution, glucomannans have also been reported to have a high affinity for cellulose (Iwata, Indrarti & Azuma, 1998; Whitney, Brigham, Darke, Reid & Gidley, 1998). If the co-elution of cellulose and glucomannan in our study is because to this type of association this then would account for LiCl/DMAc not being able to disrupt these associations. Furthermore, it has been suggested that cellulose acts as a template for unsubstituted mannan segments which may allow glucomannan to partly adopt a "cellulosic conformation" (Whitney et al., 1998). The amount (Dea, Morris, Rees, Welsh, Barnes & Price, 1977) and distribution of galactosyl substituents (Dea, Clark & Wallis, 1986) influence associations involving galactoglucomannans. Large amounts of galactose substituents and low frequency of unsubstituted portions in the galactoglucomannan would be expected to significantly hinder these associations. In the present study, galactose was found in all fractions but the relative amount increased with decreasing molecular weight. This may thus indicate that galactose groups in the galactoglucomannan aggravate association with cellulose.

Arabinoglucuronoxylan is the second most abundant hemicellulose in softwood. Interestingly, xylan was detected in all fractions of the BSP sample but the relative amount increased with increasing elution volume. This was also true for arabinose, which illustrates its connection to xylan in the softwood pulp. Furthermore, the arabinose: xylose ratio is about the same in all fractions.

The reason for the different elution behaviour of the xylan portion of the hardwood and softwood kraft samples is not clear. The difference may be due to higher amounts of glucurono-substituents in the hardwood kraft pulp compared with the bleached softwood kraft pulp. Also the distribution of substituents, i.e. block or even, may aggrevate formation of associations. The glucuronic content has not been determined for the pulp samples in the present study, and no report concerning the distribution of glucuronic groups along the xylan backbone in hardwood and softwood kraft pulps has been published. In birch wood samples the glucuronic groups have been reported to be randomly (Havlicek & Samuelson, 1972) or irregularly (Rosell & Svensson, 1975; Lindquist & Dahlman, 1998) distributed along the xylan backbone.

The high degree of substitution and randomly distributed substituents in the hardwood pulp sample would aggrevate associations and may explain the elution profile obtained for HP xylan. For softwood xylan, the glucuronic substituents have been proposed to be irregularly distributed (Shimizu, Hashi & Sakurai, 1978; Comtat & Joseleau, 1981) on the main chain, some located in close vicinity of each other. This distribution pattern was also reported for arabinose substituents (Comtat & Joseleau, 1981). In contrast, Lindquist and Dahlman (1998) reported that the glucuronic acid groups in a sample isolated from a thermomecanically produced pulp of spruce were uniformly distributed along the xylan chain.

It is also possible that there exist different types of xylans in softwood kraft pulps with different substitution patterns which may be able to associate to some extent with cellulose and/or glucomannan.

Thus, the major portion of softwood xylan and galactoglucomannan appears to belong to the low molecular weight fraction whereas the glucomannan and xylan with a low degree of substitution elutes together with cellulose in LiCl/DMAc. The results indicate that the degree of substitution is continuously increased for components eluted at the end. However, the influence of the acid groups on the shape of the MWD needs to be further studied.

4. Conclusion

The complex elution SEC profile of softwood kraft pulps depends on the hemicellulose portion, which was found to elute over the entire molecular weight range. The neutral monosaccharide composition implies that associations between galactoglucomannan and cellulose increase with decreasing amount of galactose. Similarly, a minor part of the softwood kraft pulp xylan presumably having a lower degree of substitution co-elutes with cellulose (and glucomannan). Although the arabinose:xylose ratio is about the same in all of the studied fractions, the xylan gradually elutes later and the relative amount becomes highest in the low molecular weight region. One explanation for this behaviour may be that the amount of glucuronic groups increases as the molecular weight decreases. However, this suggestion needs to be confirmed in future studies since the distribution of acid substituents have not been studied in this report. In contrast to softwood kraft pulps, the hemicellulose (mainly xylan) and cellulose of hardwood kraft pulps are fairly well separated. Thus, the xylan in hardwood and softwood kraft pulps differs in elution behaviour. The softwood and hardwood xylan, consists both of glucuronic substituents. One explanation for this difference in the elution behaviour may depend on the amount and/or how these substituents are distributed along the xylan backbone.

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