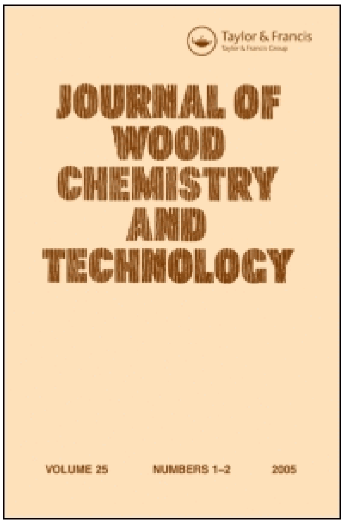

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POLYSACCHARIDES DISSOLVED FROM NORWAY SPRUCE IN THERMOMECHANICAL PULPING AND PEROXIDE BLEACHING

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ABSTRACT

Methanolysis, followed by GC analysis, was used to determine the amount and composition of sugar units comprising the carbohydrates present in water samples from unbleached and peroxide bleached thermomechanical pulp (TMP). Circulation experiments were carried out in the laboratory to simulate white water system closure in mechanical pulp mills. Water samples from simulated "closed" water systems were fractionated to determine the composition of the neutral and anionic polysaccharides released from the TMP samples. Decreasing fresh water consumption from 100 to 10 m^3/t, for both unbleached and peroxide bleached TMP, had little influence on the overall sugar composition of the carbohydrates in the water samples.

Alkaline peroxide bleaching resulted in substantial changes in the sugar composition of the carbohydrates comprising the dissolved and colloidal substances (DCS) in the water samples. The polysaccharides released from unbleached TMP were comprised of neutral (88%) and anionic (12%) polysaccharides. The neutral polysaccharides were mostly *O*-acetyl-galactoglucomannans and the anionic polysaccharides were mostly arabinogalactans. The galactoglucomannans, partially acetylated when dissolved in the unbleached suspension, were deacetylated by the alkaline conditions of peroxide bleaching, thereby causing their substantial adsorption onto the TMP fibers. The anionic arabinogalactans probably originated from heartwood present in the TMP furnish. About half of the dissolved polysaccharides present after peroxide bleaching were neutral, probably comprised mostly of galactoglucomannans. Anionic galacturonans and arabino-(4-*O*-methylglucurono)xylans were released from the pulp in peroxide bleaching. Anionic arabinogalactans were also present after alkaline peroxide bleaching.

INTRODUCTION

Dissolved and colloidal substances (DCS) originating from the wood raw material can be carried with the pulp into the wet end of the paper machine where they may interfere with papermaking operations. Both ionic and nonionic interactions may be responsible for the detrimental effects DCS have on papermaking[1-5]. Such "detrimental substances" have been defined as the total amount of anionic oligomers and polymers and nonionic hydrocolloids[1]. Apart from their potentially detrimental effects, DCS released from wood in mechanical pulping and bleaching operations represent a potential yield loss and effluent load. Due to stiffening environmental regulations, mills are being forced to take measures to further reduce their fresh water consumption. Closure of mill water systems has led to increased runnability problems associated with "detrimental substances", also commonly referred to as "anionic trash".

Anionic hemicelluloses and lignin originating from the wood raw material are believed to act as "detrimental substances" in papermaking. Pine wood xylan[6-8] and lignin sulfonate[8,9] have been shown to complex with cationic papermaking polymers. It is believed that such complexation can affect the performance of cationic retention/drainage aids[10]. However, it is not clear whether xylans or anionic lignins are present in typical mechanical pulp suspensions. It is of long term interest to characterize the DCS released in mechanical pulping in order to better understand their behavior in papermaking processes. This may lead to new strategies for managing the effects of DCS in highly closed papermaking systems. The purpose of this study was to determine the types of dissolved wood polysaccharides present in unbleached and peroxide bleached thermomechanical pulp suspensions of Norway spruce.

EXPERIMENTAL

Preparation of DCS Samples

Norway spruce (*Picea abies*) thermomechanical pulp (TMP) was sampled from a pulp mill in southern Finland. The pulp, at 29% consistency, was stored at -24°C until used in the circulation experiments described in Figure 1. Distilled water was used to dilute the fresh pulp to 10% consistency. The pulp was then bleached at 60°C for 90

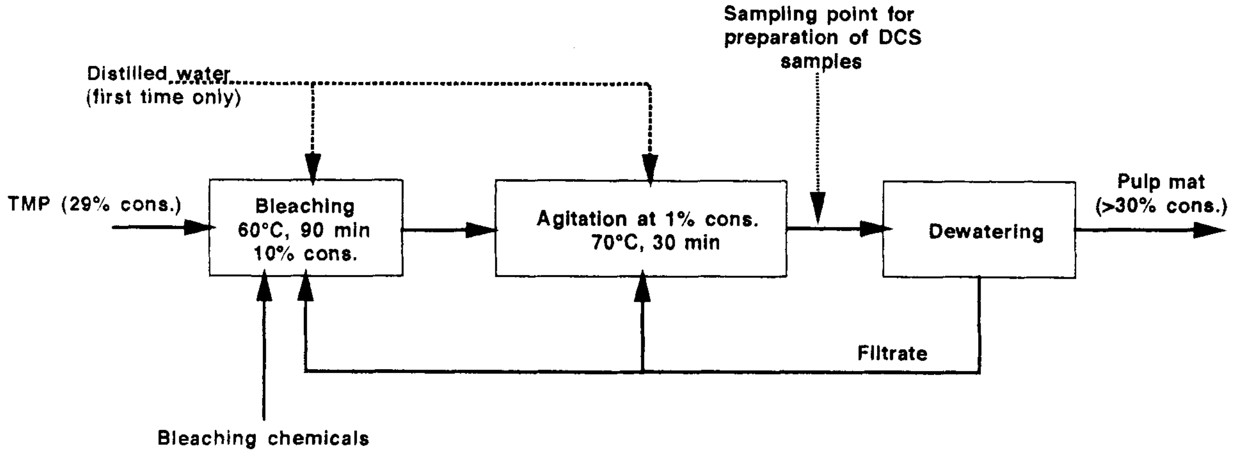

FIGURE 1. General diagram depicting the circulation experiments carried out to obtain DCS samples from "open" and "closed" water systems.

min using 3% peroxide on o.d. pulp[11]. After bleaching, the pulp was acidified with SO_2 water and further diluted to 1% consistency with distilled water. For studies with unbleached pulp, the same procedure was used with the exception that no bleaching chemicals were added. The final suspension was thoroughly agitated for 30 min at 70°C to remove pulp latency and reach a constant level of organic DCS released from the pulp. A suspension sample was then taken and centrifuged[11] in order to obtain a DCS sample representing an "open" pulp mill water system (100 m^3/t specific water consumption).

The suspension was then vacuum-dewatered using a 150 mesh wire, resulting in the formation of a 25-cm diameter pulp mat with a dry basis weight of about 150 g/m^2. Additional water was removed from the mat by pressing, resulting in a final mat consistency of 30-35%. All of the water was collected for reuse in the subsequent circulation. From this point on, no fresh water was added to the system except the small amount comprising the added bleaching chemicals and fresh TMP. The amount of fresh TMP added to the system was determined by the amount of filtrate recovered from the preceding circulation. No effort was made to prevent the buildup of fines in the circulation water. The concentration of fines was ignored when calculating the amount of fresh TMP to add to the system. The intention was to maintain agitation consistency at 1% based on the fresh TMP added to the system.

Specific water consumption was determined for each circulation by dividing the total amount of fresh water added during the course of circulations, including water added with the fresh TMP or bleaching chemicals, by the total amount of fresh TMP (dry basis) used in the circulations. Circulations were carried out until specific water consumption reached about 10 m^3/t, representing a pulp mill with a "closed" water system. For unbleached TMP, 17 circulations were required. For bleached TMP, 3 additional circulations were required to compensate for the small amount of fresh water introduced with the bleaching chemicals.

Analysis of Carbohydrates in DCS Samples

Carbohydrates were analyzed by subjecting freeze-dried DCS samples (volume chosen to correspond to about 0.2 mg of carbohydrates) to methanolysis in 2M HCl in methanol (2 mL) at 100°C for 3 h, followed by neutralization with pyridine (50 μL), addition of internal standard (0.1 mg sorbitol in 1 mL methanol) and overnight silylation with hexamethyldisilazane (170 μL) and trimethylchlorosilane (70μL) at room temperature. The resulting silylated methyl glycosides (from pentoses and hexoses) and methyl glycoside methyl esters (from hexuronic acids) were analyzed by gas chromatography[12]. Concentrations of the original sugar units comprising the DCS samples were calculated based on correction factors determined for arabinose (Ara), xylose (Xyl), mannose (Man), galactose (Gal), glucose (Glc), glucuronic acid (GlcA) and galacturonic acid (GalA).

Fractionation of Neutral and Anionic Polysaccharides

The DCS samples (10 mL) from the unbleached and bleached TMP suspensions ("closed" system) were filtered through 0.1 μm filters to prepare samples of dissolved substances (DS) as reported previously[11]. A Hewlett Packard Model 1090A liquid chromatograph with a DAD detector was used for liquid chromatography. The general techniques used to fractionate the DS samples were adopted from well-known separation methods used in biotechnical applications. As in a previous method developed at this department[13], anionic exchange was considered a key step in the fractionation in order to separate neutral and anionic polysaccharides. It was necessary to first remove interfering hydrophobic substances and salts in order to properly carry out ion exchange chromatography (IEC).

Hydrophobic interaction chromatography (HIC) was used to remove hydrophobic substances from the DS samples by passing the samples (6X0.5 mL) through a Phenyl Superose HR 5/5 column (Pharmacia LKB Biotechnology AB, Sweden). A 2-mL sample loop was loaded with 1M $(NH_4)_2HPO_4$ prior to loading the 0.5-mL sample. This salt solution was used to enhance the hydrophobic interactions between the dissolved hydrophobic substances and the stationary phase of the column[14], maximizing the separation of hydrophobic substances from the hydrophilic substances. A flow rate of 0.5 mL/min was used and the eluent was distilled and deionized water (Milli-Q™ grade). The hydrophilic substances were the first 3 mL passing through the column (giving a total of 18 mL). Methanol was then used to elute the hydrophobic substances from the column (which were not subjected to further analysis). The column was re-equilibrated with water for 5 min prior to the next sample injection.

The low-molar-mass substances (including the added ammonium phosphate) were then separated from the hydrophilic substances by gel permeation chromatography (GPC) using a Fast Desalting Column HR 10/10 (Pharmacia, Sweden). The flow rate was 2 mL/min and the eluent was 20 mM NaCl. The samples were injected (14X1 mL) using a 2-mL sample loop and the desalted fraction was the first 5 mL passing through the column (giving a total of 42 mL). The low-molar-mass substances were not subjected to analysis. The approximate minimum molar mass of the recovered fraction was 10^3.

Finally, the resulting neutral and anionic hydrophilic wood polymers (mostly polysaccharides) were fractionated with IEC using a Mono Q HR 5/5 column (Pharmacia, Sweden) equilibrated with 20 mM NaCl at a flow rate of 1 mL/min. A 50-mL sample loop (Superloop, Pharmacia, Sweden) was used to apply 20 mL of the desalted sample onto the anion-exchange column. The neutral substances passing through the column were collected in the first 22 mL of eluate. The anionic substances were then eluted from the column by increasing the salt concentration of the eluent from 20 mM to 1 M over 10 min and 10 1-mL fractions were collected (arbitrarily designated samples A-J). The column was re-equilibrated with 20 mM NaCl for 5 min prior to the next sample application. The DCS samples, DS samples, desalted hydrophilic samples (from HIC and GPC), neutral hydrophilic polymeric samples (passing through IEC), and the anionic hydrophilic polymeric samples (each individual fraction) were analyzed for carbohydrates.

Extraction of Norway Spruce Wood Meal with Water

Fresh Norway spruce wood was cut into 2-cm thick discs (samples used in another study; tree B[15]). The diameter of the 40-year-old stem was 10 cm. The heartwood/sapwood boundary occurred at the 20th growth ring (5.5 cm diameter). The bark was peeled away from the disc and the innermost 15 growth rings were splintered and designated as heartwood. The sapwood sample was taken from growth rings 28-30. The heartwood and sapwood splinters were freeze-dried, ground in a Cyclo-Tec mill, and Soxhlet extracted with dichloromethane for 24 h to remove lipophilic components from the wood meal. The extracted meals were then dried and suspended in distilled water (1% consistency) and agitated for 3 h at 60°C prior to DCS sampling[11]. The resulting DCS sample was analyzed for carbohydrates and mono- and disaccharides as described previously[11].

RESULTS AND DISCUSSION

Alkaline peroxide bleaching of TMP resulted in a significant change in the concentration and composition of sugar units comprising the carbohydrates in the DCS samples (Figure 2). The major effects of bleaching were the decrease in mannose and glucose concentration and the increase in galacturonic acid concentration. These results were in agreement with our earlier findings[11]. Comparing Figures 2 a and b, it is evident that carbohydrate composition remained essentially constant throughout the circulation experiments. This suggests that no selective enrichment or sorption occurred for the dissolved carbohydrates. The DCS samples representing the "closed" water system (Figure 2 b), about 10 times more concentrated than the samples from the "open" system, where fractionated using liquid chromatography in order to better understand the composition of the dissolved carbohydrates.

Polysaccharide Fractionation

Dissolved substances (DS) were sampled by filtration of the original "closed" system DCS samples. The filtration step resulted in a 13% and 16% decrease in carbohydrates for the unbleached and bleached DCS samples, respectively. In agreement with earlier findings[11], the results show that carbohydrates were likely present in the colloidal fraction, either adsorbed onto or incorporated into the colloidal particles. Colloidal lipophilic extractives are the most abundant colloidal substances present in DCS samples from unbleached and peroxide bleached TMP[11]. Also, it has been observed that DCS samples contain fibrous colloidal substances, also referred to as "micro-fines"[16,17].

Mannose-containing carbohydrates were least affected by the filtration step showing less than 5% retention on the filter. For unbleached DCS, nearly all of the other sugar units decreased in concentration by about 20-30% due to the filtration. For both unbleached and bleached DCS samples, the concentration of glucose-containing carbohydrates decreased 25% due to the filtration. This may be due to the retention of "micro-fines", possibly partially degradable by methanolysis, or starch granules, known to be present in spruce bark[18,19] and the sapwood of softwoods. For bleached DCS, almost 30% of the galacturonic acid-containing substances were retained by filtration. It has been shown that the addition of small amounts of calcium chloride can

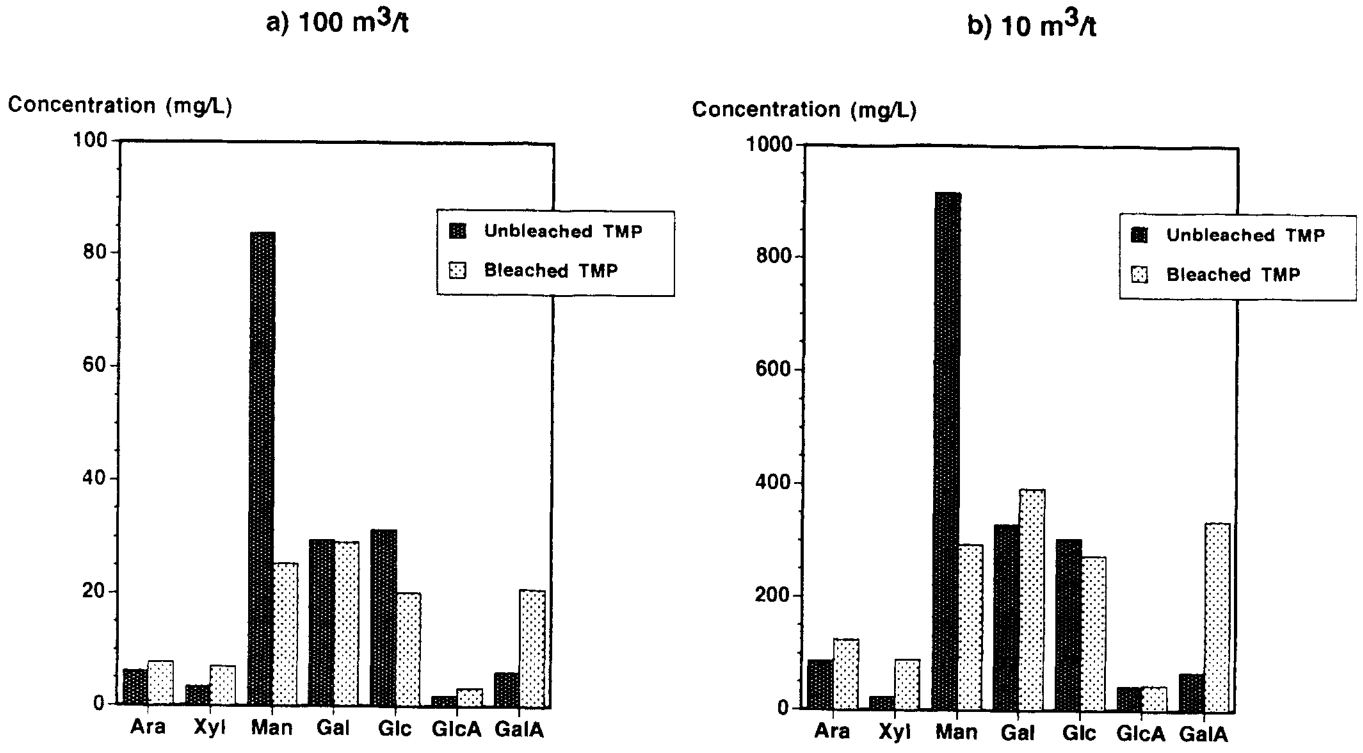

FIGURE 2. Concentration of sugar units comprising carbohydrates in DCS samples from unbleached and bleached TMP; a) 100 m^3/t specific water consumption ("open" system), b) 10 m^3/t specific water consumption ("closed" system).

effectively flocculate the galacturonic acid-containing carbohydrates and colloidal particulate material present in peroxide bleached DCS samples[20]. Perhaps such aggregation took place due to the presence of calcium or other metal ions in the "closed" system suspension, resulting in the retention of the colloidal aggregates upon filtration of the DCS sample.

After removing hydrophobic substances and low-molar-mass substances, including interfering salts, the samples were then fractionated using IEC. There were significant differences in the composition of the polysaccharides for the unbleached and bleached samples (Figure 3). In general, anionic polysaccharides were more predominant after peroxide bleaching than before peroxide bleaching. For dissolved polysaccharides from both unbleached and bleached TMP, all of the measurable uronic acids were retained by the anion exchange column (Figure 3). The presence of neutral sugar units in the anionic fraction can be explained by their chemical linkage with the uronic acid units.

O-acetyl-galactoglucomannans

The large amount of mannose comprising the neutral polysaccharides from the unbleached TMP (Figure 3 a) strongly suggests the presence of galactoglucomannans. Alkaline treatment of DCS samples from unbleached TMP resulted in the formation of acetic acid[16,17]. Therefore, it is probable that the galactoglucomannans in unbleached suspensions exist as their native *O*-acetyl-galactoglucomannans. Glucomannans have also been reported to be present in the warm water extracts of Norway spruce refiner pulps[21] and stone groundwood[22]. Assuming *O*-acetyl-galactoglucomannans comprise about 16% of wood[23], mannose represents about 10% of wood. Therefore, from the mannose concentration presented in Figure 2 b, about 10% of the original *O*-acetyl-galactoglucomannans may have been released from the wood in thermomechanical pulping.

It has been reported that *O*-acetyl-galactoglucomannans lose their water solubility when their acetyl groups are removed by alkaline treatment[24]. The resulting deacetylated galactoglucomannan may adsorb onto accessible cellulosic surfaces[24,25]. The decrease in mannose and glucose concentration in the DCS samples, due to alkaline peroxide bleaching (Figure 2 a and b), can probably be attributed to this deacetylation/adsorption behavior.

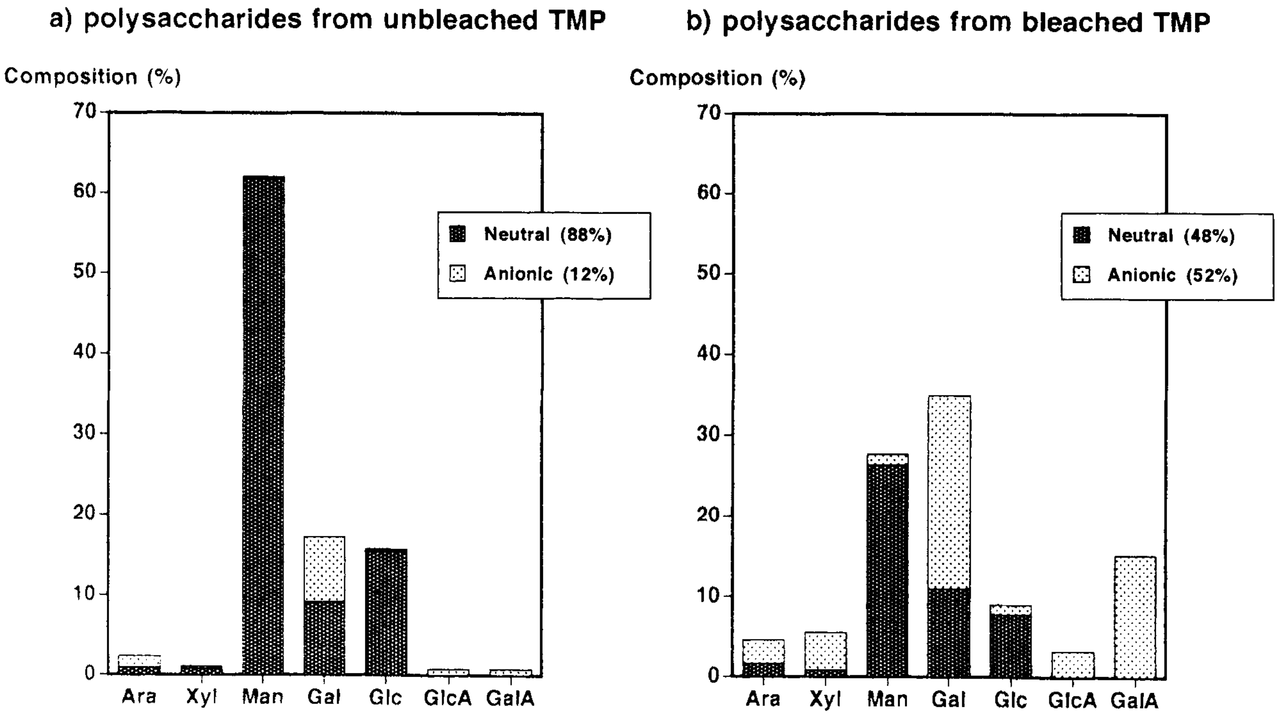

FIGURE 3. Overall composition of sugar units comprising neutral and anionic polysaccharides dissolved from a) unbleached TMP and b) bleached TMP.

There are typically two types of galactoglucomannans in softwoods. Their approximate Man:Glc:Gal ratios are 4:1:0.1 and 3:1:1, respectively[26]. The ratio of Man:Glc:Gal in the neutral polysaccharide fraction from the unbleached TMP was about 4:1:0.6 (Figure 3 a). After peroxide bleaching, the ratio changed to 3.4:1:1.4 (Figure 3 b). From this data it cannot be concluded that these neutral fractions were comprised solely of galactoglucomannans. However, the values tend to agree with the literature values for the two different typical galactoglucomannan fractions[26]. Perhaps some of the galactose present in these fractions originated from neutral polysaccharides such as galactans or arabinogalactans.

Arabino-(4-*O*-methylglucurono)xylans

Xylose is the major sugar unit comprising the anionic arabino-(4-*O*-methylglucurono)xylans, the second most abundant hemicelluloses in softwoods[23]. It is evident that these anionic polysaccharides were not substantially dissolved in thermomechanical pulping. However, in agreement with previous results[22], alkaline peroxide bleaching apparently resulted in the dissolution of small amounts of arabino-(4-*O*-methylglucurono)xylans (Figure 3 b).

Pectic substances

To learn more about the composition of the anionic polysaccharides, individual anionic fractions were analyzed. Only the first five of the ten fractions collected contained measurable amounts of carbohydrates. Figure 4 shows the relative sugar compositions of the anionic polysaccharides from unbleached and bleached TMP. Pectic substances are comprised primarily of galacturonic acid, however, other neutral sugar units such as galactose, arabinose, and rhamnose can also be present[27]. Galacturonans, galactans, arabinans, and arabinogalactans can all be considered as examples of pectic substances[27].

It is evident that galacturonans, also referred to as polygalacturonic acids, are released from the TMP in peroxide bleaching (fractions D and E in Figure 4 b). Pectic substances have also been identified in the spent liquor from peroxide bleached spruce groundwood pulp[28]. Because of the predominance of galacturonic acid, galactose, and arabinose units, it is likely that most of the anionic polysaccharides in both the

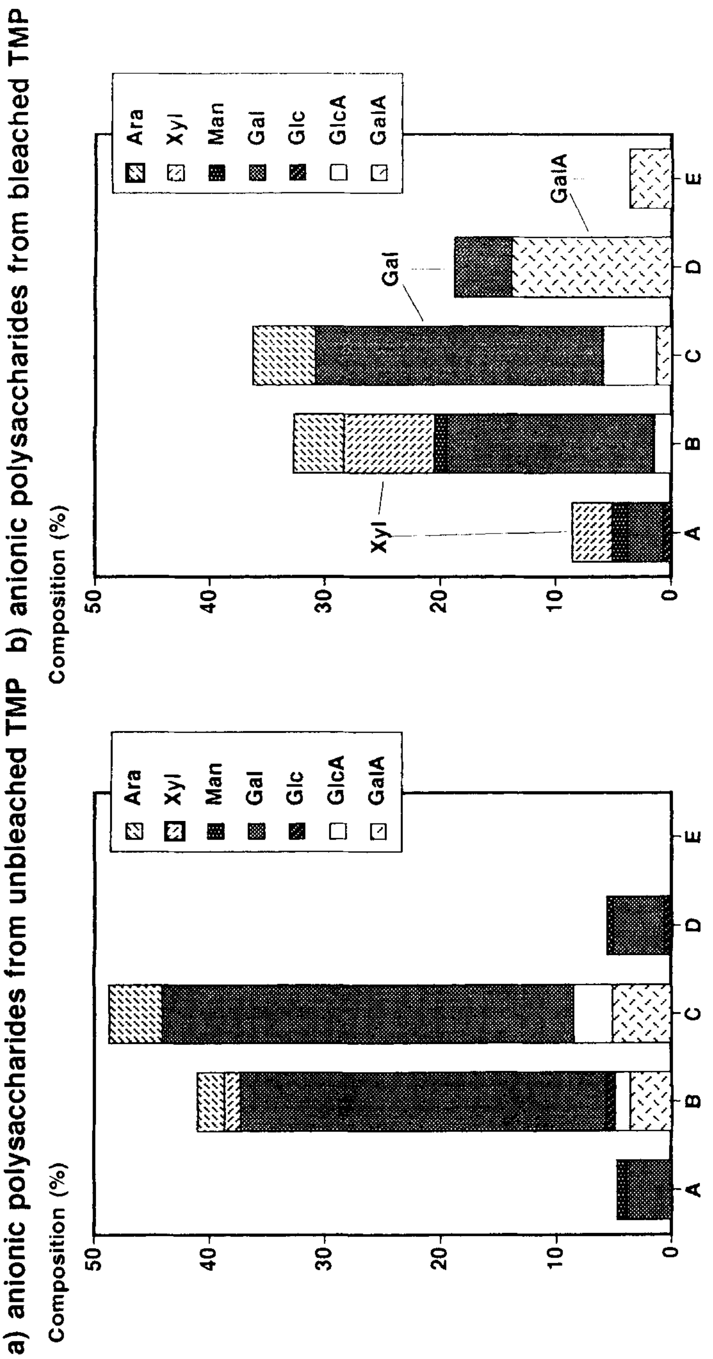

FIGURE 4. Composition of sugar units in anionic polysaccharide fractions from a) unbleached TMP and b) bleached TMP.

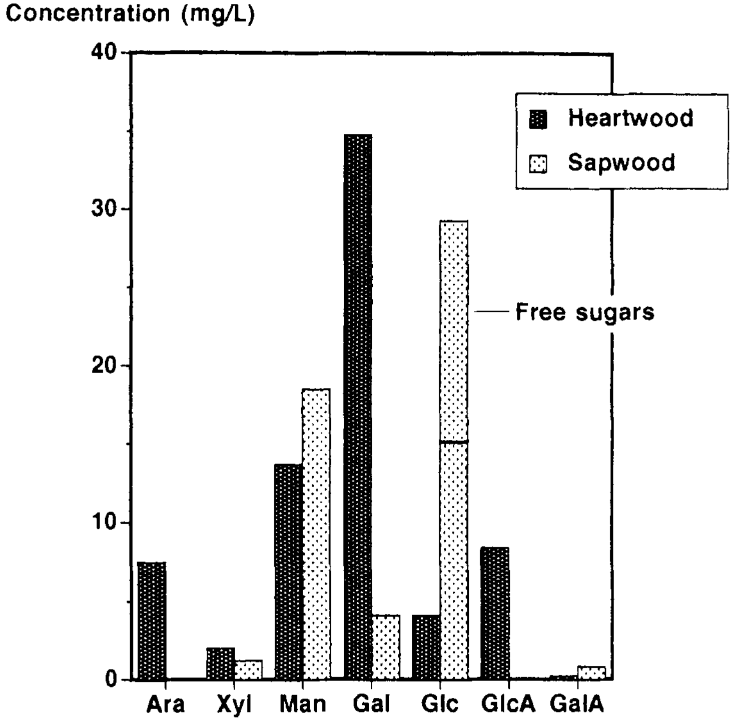

FIGURE 5. Concentration of sugar units comprising carbohydrates in water extracts of dichloromethane-extracted Norway spruce wood meal samples.

unbleached and bleached samples originated from pectic substances. The exception to this would be the presence of arabino-(4-*O*-methylglucurono)xylans released in peroxide bleaching as indicated by the xylose in fractions A and B (Figure 4 b).

Larch wood arabinogalactans are known to contain small amounts of glucuronic acid[26]. Therefore, the presence of glucuronic acid (GlcA) in the anionic polysaccharide fractions may suggest the presence of arabinogalactans. Analysis of the Norway spruce heartwood and sapwood water extracts revealed substantial differences in their respective sugar compositions (Figure 5). In agreement with the literature[26,29], arabinogalactans were apparently dissolved from the heartwood sample as indicated by the presence of galactose, arabinose, and glucuronic acid units. A similar water-soluble

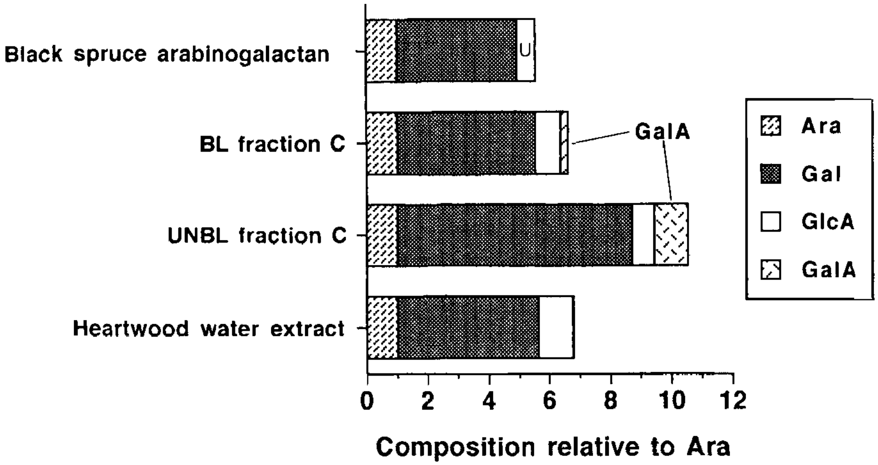

FIGURE 6. Comparison of the sugar compositions of Norway spruce heartwood water extract, unbleached TMP anionic polysaccharides (UNBL fraction C), bleached TMP anionic polysaccharides (BL fraction C), and Black spruce arabinogalactan (U=unspecified uronic acid)[30]. Compositions are calculated relative to arabinose.

polysaccharide containing galactose, arabinose, and uronic acid has been isolated from Black spruce[30].

Figure 6 presents a comparison of the sugar compositions of the Norway spruce heartwood water extract, the major anionic polysaccharide fractions (fraction C) from the unbleached and bleached DCS samples, and the data reported[30] for the Black spruce water-soluble polysaccharide. There is general agreement between the different data, with the exception that additional galactose- and galacturonic acid-containing polysaccharides were present in fraction C of the anionic polysaccharides from unbleached TMP. This may be explained by the presence of Norway spruce compression wood galactans, known to contain 13% galacturonic acid units[31]. Also, it is possible that partially methylated pectic substances, containing galacturonic acid and galactose, comprised part of this fraction. It is uncertain why the change in composition of the two anionic polysaccharide fractions occurred in peroxide bleaching. If partially methylated pectic substances were present, alkaline conditions would likely demethylate and/or degrade these substances[27], possibly leading to changes in the composition of the anionic polysaccharide fractions. The anionic polysaccharides from unbleached TMP should be isolated in order to further study their chemical nature.

It appears as though arabinogalactans were the most prevalent anionic polysaccharides present in the DCS samples from unbleached and peroxide bleached TMP. However, for peroxide bleached TMP suspensions, the highest concentration of anionic sugar units were attributed to the galacturonans. The anionic xylans, arabinogalactans, and galacturonans may very well act as "anionic trash" in papermaking systems utilizing mechanical pulp. Therefore, it is important that these polysaccharides be isolated from wood, or mechanical pulp suspensions, so that their interactions with cationic papermaking polymers and other papermaking additives can be studied.

CONCLUSIONS

The major polysaccharides dissolved from Norway spruce wood in thermomechanical pulping are the *O*-acetyl-galactoglucomannans. Peroxide bleaching causes substantial changes in the composition of the carbohydrates dissolved from mechanical pulp. Deacetylation of the *O*-acetyl-galactoglucomannans in alkaline peroxide bleaching results in substantial adsorption of galactoglucomannans onto the pulp. Furthermore, anionic xylans and galacturonans are released from the pulp in peroxide bleaching. Anionic arabinogalactans are present in unbleached and peroxide bleached mechanical pulp suspensions and probably originate from heartwood present in the wood raw material.

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