Origin of carbohydrates dissolved during oxygen delignification of birch and pine kraft pulp

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SUMMARY: Pine and birch kraft pulps were treated under oxygen delignification conditions and reference alkaline conditions. The structures of the dissolved polysaccharides were determined using methylation analysis. During oxygen delignification of pine pulp, polysaccharides have previously been shown to dissolve together with lignin in the form of lignin-carbohydrate complexes. Their structures included 1,4-linked xylan, 1,3(,6)-linked and 1.4-linked galactan and 1,5-linked arabinan. In this work, notable amounts of a 1,3-linked glucan also dissolved. For the first time it was shown that this compound is present in bleaching effluents from alkaline stages and that it is probably associated with lignin in significant amounts. Contrary to the common interpretation, the glucose-containing polysaccharide in the pine pulp effluent was thus this 1,3-linked glucan and not cellulose. Oxygen delignification of the birch pulp removed mainly xylan, but also traces of arabinan, 1,3-linked galactan and 1,4-linked glucan.

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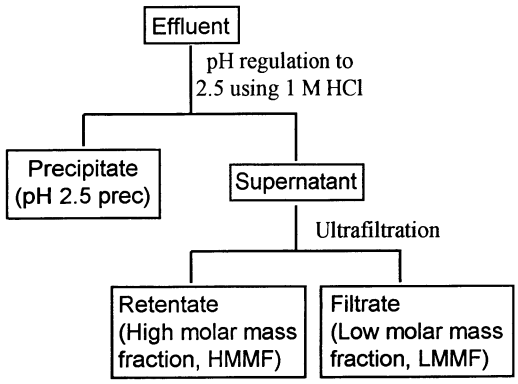
α Oxygen delignification is attractive for both economic and environmental reasons, and is therefore widely used, especially in Scandinavian fiber lines (Tench, Harper 1987). However, problems with its selectivity remain unsolved. A practical limit is therefore about 50% delignification.

More detailed knowledge of fiber morphology and the interactions between the fiber components lignin, cellulose and the different hemicelluloses may help in the search for ways of improving selectivity.

Residual lignin may be trapped in amorphous regions in proximity to, or even linked to, hemicelluloses or cellulose. It is probable that cellulose and/or hemicelluloses are at least partly bound to lignin, which would explain the difficulty of achieving selective delignification.

The theory of "tie molecules" has been introduced into wood chemistry as a result of research on primary cell walls. It is suggested that these molecules connect cellulose microfibrils to each other (Albersheim 1975). The role of xyloglucans – referred to as hemicelluloses or pectic compounds – in this connection has been verified (Fry 1989). Next to hemicelluloses, amorphous regions of cellulose microfibrils may act as tie molecules between crystalline regions, as described for synthetic polymers (Encyclopedia of Polymer Science and Engineering 1987). A network of connected cellulose microfibrils or crystalline regions of cellulose would be expected to be elastic, and this may be essential for good mechanical properties.

Degradation and dissolution of these tie molecules would lead to a decrease in fiber strength, and dissolved carbohydrates were therefore subjected to detailed analysis. Another aim was to find out whether specific polysaccharide structures are removed together with lignin.



Scheme 1. Principle of the ultrafiltration.

Materials and methods

Oxygen delignification

Conventional laboratory-cooked kraft pine PK (*Pinus silvestris*, kappa 29, viscosity 1 226 ml/g) and birch pulp BK (*Betula pendula/pubescens*, kappa 18, viscosity 1 319 ml/g) were treated in rotating reactors (1l) in an air bath (30 min heating up + 60 min at reaction temperature). The pulp treatment conditions were 9% consistency, 100°C, 3% NaOH, 0.2% $MgSO_4$ and 8 bar oxygen or nitrogen pressure in the oxygen and reference treatments, respectively (PKO, PKE, BKO and BKE).

Work-up procedure

The pulp suspensions were filtered through a plastic wire. Both pulps and filtrates were collected.

For the ultrafiltration, the pH of the filtrates was adjusted to 2.5 and the filtrates centrifuged after standing overnight. The precipitate was freeze-dried after repeated washing with pH 2.5 water (pH 2.5 prec). Ultrafiltration of the supernatant was performed using a Prep/Scale TFF cartridge (polyethersulfone, membrane size 0.09 m^2, Millipore, USA) with a cut-off value corresponding to a nominal mass limit of 10 kDa. The retentate (high molar mass fraction, HMMF) was washed with water adjusted to pH 2.5 and freeze-dried. (Liukko, Poppius-Levlin 1999) The fractionation of the effluents is shown in Scheme 1.

Analysis

Total organic carbon (TOC) (SFS-EN 1484), kappa number (ISO 302), viscosity (SCAN-CM 15) and ISO brightness (ISO 2470) were determined according to standard procedures. Lignin content was calculated by dividing the UV absorbance at 280 nm by 20 l/g cm (Tamminen, Hortling 1999). Carbohydrate content and composition were deter-

mined using acid hydrolysis and high performance anion exchange chromatography with pulse amperometric detection (HPAEC/PAD) or acid methanolysis and gas chromatography coupled with mass spectrometer (GC/MS) as described earlier (Hausalo 1995; Laine et al. 1999). Methylation analysis was performed using a modification of the method of Ciucane and Kerek (1984) and acid methanolysis (Laine et al. 2002): About 20 mg ground sodium hydroxide and 100 µL methyl iodide were added to 3–5 mg HMMF sample in 500 µL dimethylsulfoxide (DMSO). The sample was kept for 30 min in an ultrasonic bath at room temperature. Distilled water was added to the sample and the water phase was extracted with dichloromethane. The organic phase was extracted three times with distilled water, dried and evaporated. After the methylation, acid methanolysis was performed (Sundberg et al. 1996). After that the samples were silylated with 250 µL N,O-bis(trimethylsilyl)trifluoroacetamide containing 5% trimethylchlorosilane and the samples were analysed by GC/MS. About 1 µL of silylated sample was injected via a split injector (HP7863 Series Injector/Autosampler, 260°C, split ratio 1:50) into a 30 m/0.25 mm HP-5 column (film thickness 0.25 µm) in an HP6890 Series GC System with an HP5973 Series Mass Selective Detector. The temperature program was 100°C (2 min) – 4°C/min – 220°C (2 min) – 15°C/min – 300°C (2 min). The carrier gas was helium (1 mL/min, constant flow). The detector conditions were 70 eV, 40–600 amu. The retention times and mass spectra of the methylated and/or silylated monosaccharides were confirmed by comparison with earlier results of model compounds.

Results and discussion

Bleaching

Pine and birch kraft pulps were oxygen delignified under typical conditions. Reference alkaline treatments were performed. The effects of the pulp treatments are shown in *Table 1*.

Composition of the bleaching effluent

The degree of delignification and the selectivity of the stages were evaluated from the amount of TOC and the amount of dissolved lignin and carbohydrates. The contribution from carbohydrates and lignin to TOC was calculated. The content of carbon was estimated to be 60% and 44% in lignin and carbohydrates, respectively. In addition, some contribution to TOC remained unexplained, probably mainly originating from low molar mass acids and non-aromatic lignin degradation products (*Fig. 1*). In particular for the birch pulp effluents, also wood extractives contribute to the unidentified TOC. The unidentified TOC decreases the reliability of the evaluation of selectivity based on effluent analysis.

Table 1. *Properties of the treated pulps.*

	Kappa number	Brightness (%)	Viscosity (ml/g)
PKE	25	27.6	1 250
PKO	12	36.2	990
BKE	14	32.9	1 270
BKO	10	45.8	1 100

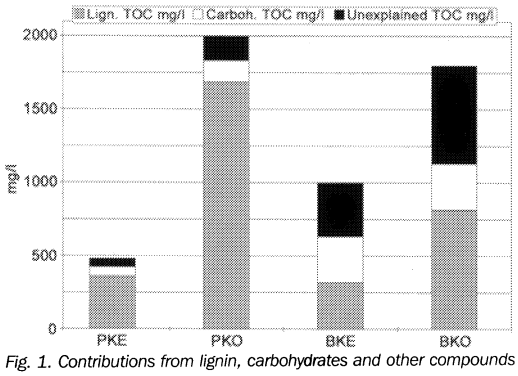


Fig. 1. Contributions from lignin, carbohydrates and other compounds to total organic carbon (TOC).

As expected, far more organic compounds dissolved during oxygen delignification than during the alkaline treatment. This was much more pronounced for the pine pulp than the birch pulps. Most of the compounds dissolved during the pine pulp treatments were lignin and carbohydrates (approximately 90%), with only a little TOC originating from other compounds. The ratio of dissolved lignin (mg/l) to dissolved carbohydrates (mg/l) was 8.3 and 4.1 for the O and the E stage, respectively. Thus, the selectivity of the oxygen delignification was much better than that of the alkaline treatment. For the birch pulp treatments, less of the TOC was explained by dissolved carbohydrates and lignin (about 63%). This low value is roughly in agreement with a study of the oxygen stage of birch kraft pulp at a mill (Ristolainen, Alén 1998). The ratio of the amount of dissolved lignin to that of dissolved carbohydrates was 1.9 and 0.7 for the O and E stage, respectively. Again, the O stage was more selective, although the selectivity was poor compared to the pine treatments.

Carbohydrate composition of the effluents

The compositions of the dissolved carbohydrates are shown in *Table 2*. For the pine pulp, the dissolved carbohydrates were mainly composed of xylose, glucose and galactose. The total amount of all monosaccharide units in dissolved carbohydrates was higher in the O stage than in the E stage, approximately twice as much for arabinose, glucose, xylose and mannose, but over three times as much for galactose. This confirmed the results of earlier studies (Hortling et al. 1998).

Bleaching dissolved mostly xylose from the birch pulp in both treatments. The O stage produced more carbohydrates composed of arabinose and galactose than the E stage. The presence of carbohydrates containing arabinose and galactose in birch pulp effluents has been reported earlier (Ristolainen, Alen 1998) and this was confirmed here. The

Table 2. *Carbohydrate content and composition in effluents from the bleaching stages.*

mg/l	Ara	Gal	Glc	Xyl	Man	Rha	total
PKE	13	25	29	77	5.2	+	149
PKO	30	85	51	130	12	+	308
BKE	4	12	27	460	+	+	503
BKO	12	19	22	590	+	+	643

Table 3. Distribution of the carbohydrates into the different fractions during ultrafiltration, % of recovered carbohydrates.

	pH 2.5 prec	HMMF	LMMF
PKE	47%	23%	29%
PKO	7%	54%	40%
BKE	70%	19%	10%
BKO	36%	43%	22%

Table 4. Carbohydrate content and composition in the HMMF of the effluents determined after acid methanolysis (calculated as mg/l of original effluent).

	Ara	Gal	Glc	Xyl	Man	Rha	MeGlcA	GlcA
PKE	4.4	10	6.9	35	1.2	0.3	0.4	1.1
PKO	23	64	33	118	6.6	0.7	1.3	1.9
BKE	1.5	9.0	6.5	147	0.8	0.6	11	1.1
BKO	7.0	16	10.0	434	1.4	1.6	30	1.8

difference between the O and E stages was not as great as for the pine pulps.

The carbohydrate composition of the effluents showed that the treatment, particularly oxygen delignification, affected the dissolution of those carbohydrates that are present in only small amounts in the pulp. For example, the ratio of galactose to xylose in pine wood (*Pinus sylvestris*) has been reported to be 0.25 (Fengel, Wegener 1983), while in the effluent from PKO it is 0.65. This finding, together with the known crucial role of galactose in residual lignin-carbohydrate complexes (Hortling et al. 1998), prompted us to analyze the polymeric structure of the corresponding dissolved material.

Fractionation of the effluents

The bulk of the carbohydrates from the E stages was found to be precipitated at pH 2.5 for both the birch and pine pulp effluents (*Table 3*). For the O stage, most of the carbohydrates were in the HMMF.

The distribution is probably due to the fact that at least part of the carbohydrate fraction is bound to lignin. The lignin is not hydrophilic after the alkaline treatment and thus precipitated at pH 2.5 with the attached carbohydrates. The O stage renders lignin more hydrophilic and thus the lignin and carbohydrates stay in solution at pH 2.5. Some of the carbohydrates present in the HMMF may naturally be present as polysaccharides without linkages to lignin. The different monosaccharide building blocks of the oligo/polysaccharides were distributed in a similar way, the exception being galactose of the birch effluents, which was found to more than 60% in the HMMF.

Polysaccharides present in effluents

The content and composition of the carbohydrates in the HMMF were determined using acid methanolysis (*Table 4*). This method enabled the determination of uronic acids (except hexenuronic acid), the common neutral monosaccharides and small amounts of rhamnose and fucose. In agreement with the results shown above, xylose was the major building block of the dissolved polysaccharides from the O stage of pine pulp, but galactose, glucose and arabinose were present in considerable amounts, too. Methyl glucuronic acid (MeGlcA) was present in the birch pulp effluents (part of the birch xylan). However, the proportion of MeGlcA in the pine xylan of the effluents was much lower. All effluents also contained some glucuronic acid and rhamnose. In addition, galacturonic acid was detected in the effluents from the E stages (approximately 0.3 mg/l) and traces of fucose (<0.1 mg/l) were found in all effluents, indicating preferential dissolution of trace polysaccharides from the pulps.

The polysaccharides in the HMMF were analyzed using methylation analysis (*Table 5*). The method has been used for example for analysis of hemicellulose samples in black liquor (Vikkula et al. 1997; Laine et al. 1999) and delivers information on the linkages between the structural units of the polysaccharides. However, no information on the anomeric configuration (α or β) of the units is obtained.

The structure of the dissolved xylan from pine pulp was as expected: mainly linear 1,4-linked with substituents (arabinose and MeGlcA or hexenuronic acid (HexA)) at positions 3 and 2. Only 10% of the 2-substitution was explained by substitution with MeGlcA. The frequency of 2-substitution in birch xylan was about 10%, of which MeGlcA accounted for approximately 50%. Some 3-substitution was also observed in the birch xylan, although it is normally not substituted in that position. The missing substituent in the xylans at position 2 or 3 could be HexA or linkages to lignin.

Arabinose was mostly present as non-reducing end groups (part of pine xylan). However, oxygen treatment also dissolved 1,5-arabinan from both pine and birch pulps.

Only 1,3-galactan was leached out by alkali for both pulps. In the case of birch pulp, it was partly substituted at position 6. Oxygen delignification induced dissolution of 1,4-linked galactan from pine pulp together with substituted 1,3-galactan. This supports earlier findings that selective degradation of 1,4-linked galactan would enhance delignification (Tamminen et al. 1999). No effect of oxygen on dissolved galactan structures was found for the birch pulp.

The glucose units in the pine samples were mainly from a 1,3-linked glucan (*Fig. 2*). 1,3-linked glucan has been found in traces in the hemicelluloses of spruce kraft black liquor and residual lignin-carbohydrate complexes of spruce kraft pulp (Laine et al. 1999). Its presence in residual lignin samples showed that it is linked to lignin. This glucan was even more abundant in the oxygen delignification eff-

Table 5. Distribution of structural units in the polysaccharides present in the HMMF. The positions of substitution are indicated (mol% of identified units, T=terminal, non-reducing end).

	xylose					arabinose		galactose				glucose		mannose
substitution	T	4	2	2,4	3,4	T	5	T	3	3,6	4	3	4	4
PKE	–	70.5	–	8.2	7.5	3.9	–	–	4.8	–	–	5.1	–	–
PKO	–	55.6	–	6.5	4.5	2.5	1.4	1.5	6.2	2.4	7.5	9.4	1.5	1.1
BKE	3.3	83.3	0.3	9.1	1.5	0.2	0.1	–	0.3	0.5	–	–	1.4	–
BKO	3.5	82.3	0.3	9.8	1.7	0.1	0.4	–	0.4	0.5	–	0.1	0.8	–

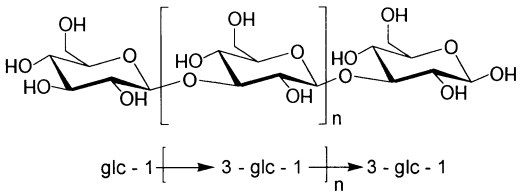


Fig. 2. Structure of the main glucose-containing polysaccharide (1,3-glucan) in the pine effluents. The probable anomeric configuration (β) is shown.

luent than in the effluent from the alkaline treatment. Its origin is probably laricinan, reported as a non-cellulosic 1,3-β-linked glucan in the compression wood of several softwood species and a trace component in normal softwood. The distribution of laricinan in the fiber wall is not known. However, as it can easily be extracted from delignified wood with dilute alkali, it has been suggested that there are no strong interactions between laricinan and cellulose microfibrils (Timell 1986). When this suggestion is combined with our finding that this glucan is dissolved along with lignin in the E and O stages, it can be concluded that the glucan is bound to lignin, as suggested earlier for galactan and xylan in pine pulp (Hortling et al. 1998).

The usual interpretation that glucose-containing dissolved carbohydrates originate from cellulose has thus been proven to be wrong for the pine pulp effluents. In the birch pulp effluents, only traces of 1,3-glucan were seen, the main glucan component being 1,4-linked. The absence of 4,6-linked glucose units (building blocks of xyloglucan) indicated that no xyloglucan was present neither in the pine nor in the birch pulp effluents.

Conclusions

The composition and structure of the carbohydrate material dissolving during alkaline or oxygen delignification treatments indicated that trace polysaccharides from the pulp are preferentially dissolved. Methylation analysis of the samples revealed that 1,3-linked glucan, 1,3(,6)-linked and 1,4-linked galactan, and 1,5-linked arabinan together with the main component xylan have been dissolved from the pine pulps. These components were probably linked to lignin, as has been shown earlier by analysis of isolated lignin-carbohydrate complexes (Laine et al. 1999). The glucose found in the effluent of the pine pulp was thus not from cellulose but most probably from the 1,3-linked glucan laricinan. The presence of this type of glucan in bleaching effluents has not been reported earlier. For the birch pulps, the situation was different. Most of the carbohydrates that dissolved together with lignin in the E and O stages were xylan of typical structure. The presence of 3,4-linked xylose units was surprising, because no substituent was expected in this position of birch xylan. This may indicate bonds to lignin. Only traces of 1,3-linked glucan were found in the birch effluents. Instead, small amounts of 1,4-linked glucan were present in the effluent. This glucan may be degraded cellulose or, more likely, non-cellulosic 1,4-β-glucan.

The dissolution of carbohydrates bound to lignin is a significant cause of yield losses in oxygen delignification. Cleavage of the lignin-carbohydrate (LC) bonds would thus increase the selectivity of this stage. The detailed knowledge of the polysaccharide structures participating in the LC bonds revealed in this work will help in the development of suitable activating treatments. ✿

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