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# Carbohydrate content of black liquor and precipitated lignin at different ionic strengths in flow-through kraft cooking

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**Abstract:** The influence of sodium ion concentration  $[\text{Na}^+]$  on the dissolution of carbohydrates in black liquor (BL) during flow-through kraft cooking of Scots pine wood meal (*Pinus sylvestris*) was studied. Fractions of BL were collected at different times and the carbohydrate content of the various fractions was analysed. Lignin was precipitated from the BL by lowering the pH, and the carbohydrate content of the precipitated lignins ( $L_{\text{prec}}$ ) was also examined. The molecular weight distribution (MWD) of the  $L_{\text{prec}}$  samples was analysed. Xylose (Xyl) was found to be the most predominant sugar in BL aside from arabinose (Ara) and galactose (Gal), while the amounts of these sugars decreased with increasing levels of  $[\text{Na}^+]$  in the cooking liquor. The minor amounts of mannose (Man) found in BL was not influenced by the  $[\text{Na}^+]$ . The effects of NaCl and  $\text{Na}_2\text{CO}_3$  on the carbohydrate dissolution were similar, but slightly lower concentrations of Ara and Xyl were found in the case of NaCl application. All of the  $L_{\text{prec}}$  samples contained some carbohydrate residues, the contents of which increased with increasing cooking time and decreased with higher  $[\text{Na}^+]$ . It can be concluded that arabinoglucuronoxylan (AGX) along with arabinogalactans (AG) and arabinan, are covalently linked to lignin. The glucose (Glc) residue detected in  $L_{\text{prec}}$  may originate from 1,3- $\beta$ -glucan linked to lignin.

**Keywords:** black liquor, flow-through reactor, ionic strength, kraft cooking, precipitated lignin, sodium ion concentration, softwood

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## Introduction

In kraft pulping processes, the lignin moiety of wood is degraded and solubilised and this contributes to fibre separation in the course of the pulping procedure. The first step in delignification is the cleaving of lignins' aryl ether bonds (Gierer 1980). The actual rate of delignification is dependent on the desorption/solubilisation of the lignin and the mass transport of the solubilised lignin fragments leaving the fibre wall (Bogren et al. 2007; Brelid et al. 2011; Mattsson et al. 2017). The carbohydrate degradation occurring parallel to delignification influences the ultrastructure of the fibre wall and leads to consumption of hydroxide ions. A large part of the carbohydrate losses is due to the end-wise degradation (peeling) of the carbohydrate polymers beginning at the reducing end-groups of the chains (Sjöström 1977). Therefore, the majority of carbohydrate losses is not manifested by carbohydrates in the black liquor (BL). The pioneering work of Simonson (1963) shows that the (galacto)glucomannan (GGM) is virtually completely degraded during the pulping of pine wood (*Pinus sylvestris* L.). However, a part of the dissolved arabinoglucuronoxylan (AGX) retains its polymeric structure. It was also demonstrated that the xylan present in BL is linked to a large extent to the dissolved lignin and that part of the dissolved xylan is resorbed by the pulp in the course of a longer cooking time (Meller 1965). In BLs of pine, the following carbohydrates can be found apart from dissolved cellulose, GGM and AGX: minor amounts of arabinogalactans (AG), galactan, arabinan, other pectic materials and starch (Sjöström 1993). A substantial part of the carbohydrates in BL originates, in fact, from these minor constituents, while relatively high amounts of galactose (Gal) and arabinose (Ara) are detectable in BLs (Simonson 1963; Vikkula 1999; Niemelä et al. 2007). The Gal is from galactan, which has a backbone of  $\beta$ -(1,4)-linked Gal units partly substituted at the  $\text{C}_6$ -OH groups with galacturonic acid or from AG, where  $\beta$ -(1,3)-linked Gal units form the backbone (Laine and Tamminen 2002). Almost all of the Gal units in the backbone of pine AG are substituted at the  $\text{C}_6$ -OH groups with side chains containing units of Gal, Ara and glucuronic

acid (Willför et al. 2002). The Ara in softwood BLs originates from xylan, which contains Ara substituents, and also from AG (Simonson 1963; Vikkula 1999). Part of the Ara content may also originate from arabinan, which has a backbone consisting of  $\alpha$ -(1,5)-linked Ara units and  $\alpha$ -(1,3)-linked Ara units as side chains (Laine and Tamminen 2002; Luonteri et al. 2003). Analyses of lignin-carbohydrate complexes (LCCs) in BLs from pine indicate that more xylan and galactans are linked to the dissolved lignin than mannose (Man) and/or glucose (Glc) (Simonson 1963; Vikkula 1999; Niemelä et al. 2007). However, monosaccharide units detected after the acid hydrolysis of BLs may also originate from saccharinic acid galactoside residues formed during pulping. Niemelä (1989a,b) identified low molecular weight (MW) reaction products containing one Gal unit linked to different saccharinic acids in pine wood BLs. These are from GGM peeling reactions, when the  $\alpha$ -(1,6)-linked Gal substituents are set free from the glucomannan (GM) backbone as galactopyranosyl-saccharinic acids. The glycosidic bond between the Gal unit and the saccharinic acid stabilises the Gal part from alkali-promoted degradation. Alkaline treatments of AGs from larch leads to the formation of low MW carbohydrate residues originating from the side chains of the backbone (Young and Sarkanen 1977; Manley-Harris 1997; Ponder and Richards 1997). In this case, the side chains are also prevented from further alkaline peeling by the presence of a saccharinic acid as an end-group. Based on the structural similarities between AG from larch and pine (Willför et al. 2002), it can be assumed that the same type of side chain stabilisation may also occur during the kraft pulping of pine.

The behaviour of xylan during cooking has been extensively studied: the redistribution of dissolved xylan contributes to pulp yield increment and the xylan content has a great impact on the paper properties (Rydholm 1965; Schönberg et al. 2001). The extent of the xylan dissolution and its resorption from BLs to the pulp is different in the case of softwoods or hardwoods (Aurell 1965; Simonson 1971). Moreover, the alkali profile of the cook, the residual alkali at the end of the cook and the ionic strength of BLs are influential parameters (Aurell and Hartler 1965; Ribe et al. 2010; Jansson and Brännvall 2011). There are no studies available concerning the ionic strength on the desorption of xylan and other carbohydrates in the course of kraft pulping.

To fill this gap, the influence of ionic strength on the desorption of carbohydrates will be the focus of the present paper. Previous publications (Dang et al. 2013, 2014, 2016) reported on the impact of ionic strength, measured as sodium ion concentration, on kraft delignification

and carbohydrate retention. The kraft cooking trials of Scots pine wood meal were performed in a small-scale flow-through reactor as such a reactor minimises not only the resorption of lignin and xylan but also impedes the additional degradation of the dissolved lignin and carbohydrate fragments. In continuation of the quoted papers, the present paper addresses the carbohydrate analyses of the BLs and carbohydrates attached to the precipitated lignins ( $L_{\text{prec}}$ ).

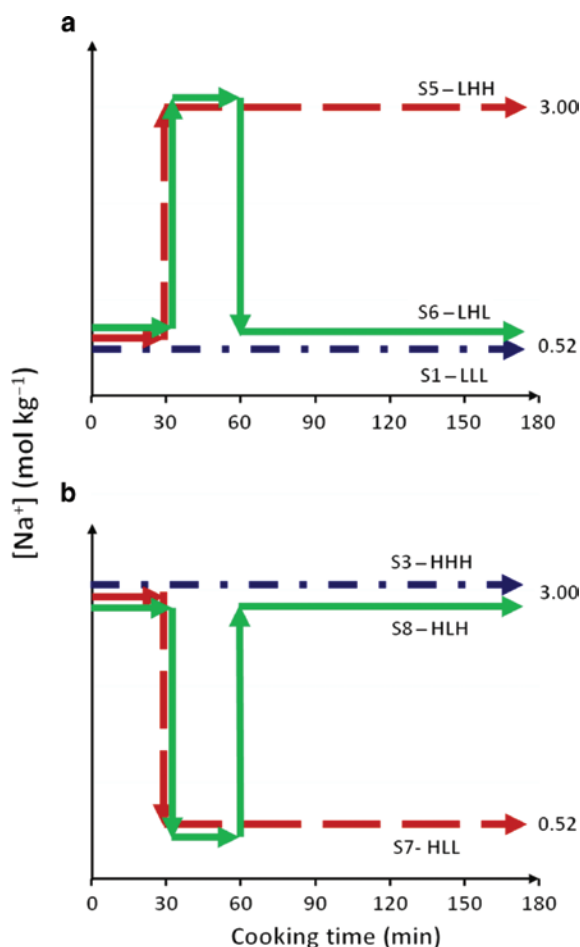
## Materials and methods

The kraft cooking experiments were carried out in a small-scale flow-through reactor (300 × 7.8 mm ID, SS) as described by Bogren et al. (2009). Sapwood meal of Scots pine (*P. sylvestris*) produced in a Wilely mill equipped with a sieve (<1 mm) was investigated. The wood meal was dried at room temperature (r.t.) prior to pulping to ensure a uniform moisture content (MC) of approx. 92% and its content of anhydrosugars (AHSs) was analysed (Table 1). Approximately 4 g (b.o. dry weight) wood meal was packed carefully into the reactor to ensure an even flow through the bed. Then, three to four free column volumes of cooking liquor were pumped through the reactor (impregnation) at r.t. before cooking began. The flow speed was 10 ml min<sup>-1</sup> during the first 12 min of cooking. It was then lowered to 8 ml min<sup>-1</sup> and 2.5 ml min<sup>-1</sup> after 22 min, respectively. Eight fractions of BL were collected as a function of cooking times: 0–10, 10–20, 20–40, 40–60, 60–90, 90–120, 120–150 and 150–180 min. All cooking experiments were performed at 158°C, which was reached after about 20 min from the starting temperature of 115°C. The cooking liquor was prepared from analytical grades of Na<sub>2</sub>S, Na<sub>2</sub>CO<sub>3</sub> and NaCl. The concentrations of the OH<sup>-</sup> and HS<sup>-</sup> ions were kept at 0.26 mol kg<sup>-1</sup> (b.o. solvent) in all trials.

Two types of experiments were performed: 1. The sodium ion concentration [Na<sup>+</sup>] was kept constant at three levels (0.52, 2.00, 3.00 mol kg<sup>-1</sup> b.o. solvent) during cooking by adding either Na<sub>2</sub>CO<sub>3</sub> or NaCl. 2. The [Na<sup>+</sup>] varied between 0.52 and 3.00 mol kg<sup>-1</sup> (b.o. solvent) during cooking and adjusted by the addition of Na<sub>2</sub>CO<sub>3</sub>. The [Na<sup>+</sup>] in this part was varied by employing two different routes (Figure 1a and b): it was changed at two different points during cooking, with the first taking place after 30 min and the second after 60 min. The experimental conditions are listed in Table 2. The estimation of experimental errors was based on duplicate experiments of the reference series S1-LLL. The pooled standard deviations of experiments were estimated to be 0.01% (b.o. wood) for xylose (Xyl) and Gal and 0.03% (b.o. wood) for Ara. All reagents used in this study were purchased from Sigma-Aldrich (Stockholm, Sweden) and used as received.

**Table 1:** Analyses of the anhydrosugars in acid hydrolysate of the pine wood meal (*Pinus sylvestris*).

(% Based on dry wood)					
Ara	Gal	Glc	Xyl	Man	Ara:Xyl ratio
0.98	1.29	44.3	4.5	12.6	0.22:1



**Figure 1:** Profiles of the concentration of sodium ions in the second part of the experiments.

L, low level of  $[\text{Na}^+] = 0.52 \text{ mol kg}^{-1}$  (b.o. solvent); H, high level of  $[\text{Na}^+] = 3.00 \text{ mol kg}^{-1}$  (b.o. solvent).

**Lignin precipitated from black liquors (BL):** The lignin was precipitated at a pH of 2.5 at r.t. Concentrated  $\text{H}_2\text{SO}_4$  (95–97% w/w) was added drop-wise to the BL until a pH of 2.5 was reached: the samples

**Table 2:** Cooking conditions used in the two parts of experiments.

Series	Initial composition ( $\text{mol kg}^{-1}$ ) <sup>a</sup>			Salt addition	Exch. time (min)	Exch. for $[\text{Na}^+]$ ( $\text{mol kg}^{-1}$ ) <sup>a</sup>
	$[\text{OH}^-]$	$[\text{HS}^-]$	$[\text{Na}^+]$			
$[\text{Na}^+]$ const						
S1 – LLL	0.26	0.26	0.52	No	–	–
S2 – MMM	0.26	0.26	2.00	$\text{Na}_2\text{CO}_3$	–	–
S3 – HHH	0.26	0.26	3.00	$\text{Na}_2\text{CO}_3$	–	–
S4 – HHH	0.26	0.26	3.00	NaCl	–	–
$[\text{Na}^+]$ varied						
S5 – LHH	0.26	0.26	0.52	$\text{Na}_2\text{CO}_3$	30	0.52→3.00
S6 – LHL	0.26	0.26	0.52	$\text{Na}_2\text{CO}_3$	30; 60	0.52→3.00→0.52
S7 – HLL	0.26	0.26	3.00	$\text{Na}_2\text{CO}_3$	30	3.00→0.52
S8 – HLH	0.26	0.26	3.00	$\text{Na}_2\text{CO}_3$	30; 60	3.00→0.52→3.00

<sup>a</sup>Based on solvent. L, Low level of  $[\text{Na}^+]$  ( $0.52 \text{ mol kg}^{-1}$ ); M, middle level of  $[\text{Na}^+]$  ( $2.00 \text{ mol kg}^{-1}$ ); H, high level of  $[\text{Na}^+]$  ( $3.00 \text{ mol kg}^{-1}$ ).

were agitated continuously and the pH was monitored. The resulting suspensions were then left overnight in a freezer at  $-18^\circ\text{C}$ . At r.t. again, the  $L_{\text{prec}}$  was collected by filtration on a glass filter, washed with approximately 100 ml of acidic water at a pH of 2.5 and then dried in a desiccator containing  $\text{P}_2\text{O}_5$  at  $50^\circ\text{C}$  for 24 h.

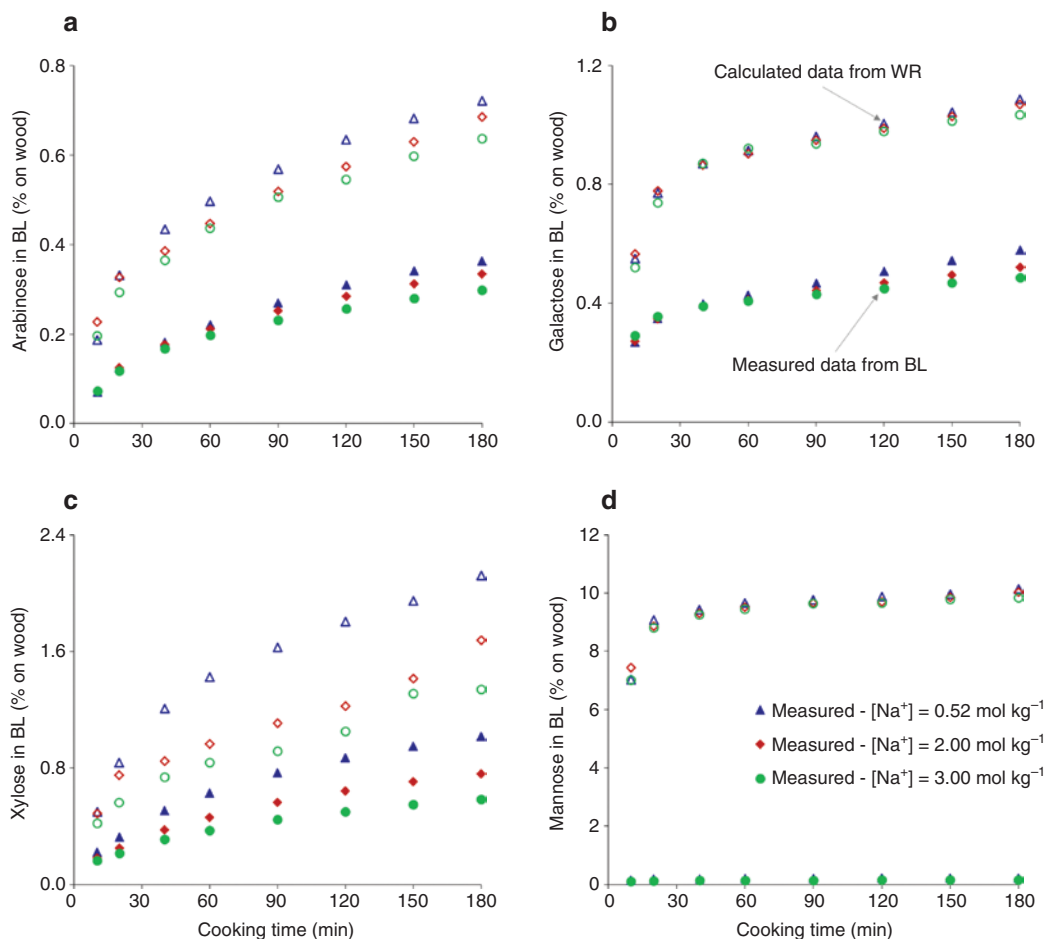
**Carbohydrate analysis:** The carbohydrates in the BLs and in the  $L_{\text{prec}}$  were subjected to acid hydrolysis (Theander and Westerlund 1986). The filtrate was diluted and fucose was added as an internal standard. High-performance anion exchange chromatography with pulse amperometric detection (HPAEC-PAD) was performed (gold reference electrode). Instrument: Dionex ICS-5000 HPLC system (Sunnyvale, CA, USA) equipped with Dionex CarboPac PA1 columns (guard column  $2 \times 50 \text{ mm}$ , pre-column  $2 \times 50 \text{ mm}$  and separation column  $2 \times 250 \text{ mm}$ ). The software Chromeleon 7 from Chromatography Data System (Vers. 7.1.0.898) was used.

**Molecular weight distribution (MWD):** The dried lignin samples were dissolved in dimethyl sulfoxide (DMSO) containing 10 mM LiBr, and the MWD was recorded by a GPC (PL-GPC 50 Plus Integrated instrument equipped with both refractive index (RI) and ultra violet (UV) detection, Polymer Laboratories, Varian Inc., Amherst, MA, USA). Two PolarGel-M columns ( $300 \times 7.5 \text{ mm}$ ) and a PolarGel-M guard column ( $50 \times 7.5 \text{ mm}$ ) were employed. DMSO containing 10 mM LiBr served as eluent with a flow rate of  $0.5 \text{ ml min}^{-1}$  ( $50^\circ\text{C}$ ). The calibration was performed by means of ten pullulan standards with MWs of 708, 375, 200, 107, 47.1, 21.1, 11.1, 5.9, 0.667 and 0.180 kDa. For data evaluation the Cirrus GPC (Vers. 3.2) software was used.

## Results and discussion

### Cumulative amount of AHSs in BL at a constant $[\text{Na}^+]$

The cumulative amount of AHSs in BLs at different sodium ion concentrations ( $[\text{Na}^+]$ ) (obtained via  $\text{Na}_2\text{CO}_3$  addition) is presented in Figure 2 (filled symbols). The



**Figure 2:** The effect of sodium ion concentration on the cumulative amount of anhydrosugars dissolved in black liquors during flow-through kraft cooking (filled symbols).

Calculated values of the amounts of anhydrosugars removed from the wood residue (WR) are also shown (open symbols).  $[\text{OH}^-] = 0.26 \text{ mol kg}^{-1}$  (b.o. solvent);  $[\text{HS}^-] = 0.26 \text{ mol kg}^{-1}$  (b.o. solvent);  $T = 158^\circ\text{C}$ .  $[\text{Na}^+]$  was controlled by the addition of  $\text{Na}_2\text{CO}_3$ .

calculated values based on measurements of the remaining amounts of AHSs in wood (assuming that all of AHSs in wood give rise to sugars) are also presented in Figure 2 with open symbols. These data were obtained by Dang et al. (2013) under exactly the same conditions as applied in the present paper.

There is a difference between the AHSs in the BL and those calculated from sugars remaining in the wood residues and this is due to the sugar loss in the course of the peeling reaction: a substantial part of the AHSs extracted from the wood must have been converted into other compounds, mainly into monomeric acids. The conversion rate of Ara, Xyl and Gal was approximately 50, 52 and 47%, respectively, after 180 min of cooking in series without added sodium salt ( $0.52 \text{ mol kg}^{-1} [\text{Na}^+]$  b.o. solvent), while approximately 98% of the extracted Man was converted. The results for both Man and Xyl are to be expected. The peeling reaction of Man containing GGM is very fast, as

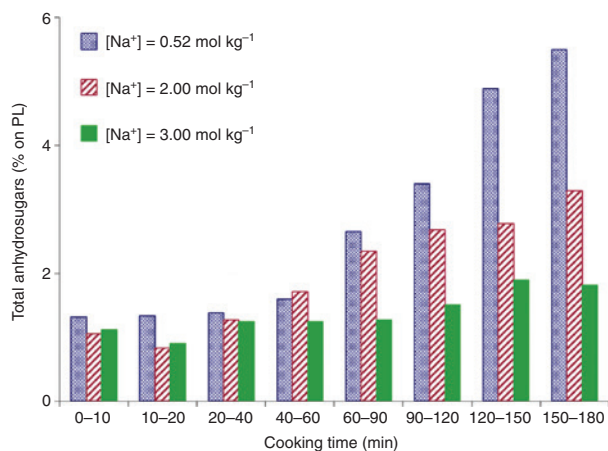
there are no substituents, which would hinder degradation, on the backbone of this hemicellulose. This means that the loss of GGM is due to chemical degradation rather than dissolution. In the case of Xyl containing AGX, the peeling reactions are impeded to a certain extent by Ara and methylglucuronic acid substituents. Thus, a substantial part of the AGX loss is not due to degradation: the missing part is dissolved in the cooking liquor in polymeric form (Sjöström 1993). The finding that the most predominant AHSs detected in BL are Xyl, Ara and Gal is in accordance with the literature data (Simonson 1963; Bhaskaran and Von Koeppen 1970; Vikkula 1999; Niemelä et al. 2007). As pointed out in the introduction, it can be assumed that the origin of the Xyl in BL is related to dissolved AGX, the Ara to dissolved AGX, AG and arabinan, and the Gal is from acid galactan and AG. The Gal detected in the BL after acid hydrolysis may also originate from galactopyranosyl-saccharinic acids formed during the peeling of GGM.

Small amounts of Glc were detected in BL: 0.10–0.15% (b.o. wood) after 180 min, (results not shown). Consistent with earlier findings, Glc is indicative of acid hydrolysis of starch (Simonson 1963) and 1,3-linked  $\beta$ -glucan (Laine and Tamminen 2002). Figure 2 also illustrates the influence of  $[\text{Na}^+]$  on the cumulative amount of AHSs dissolved in BL during flow-through kraft cooking. Obviously, Xyl decreased with increasing  $[\text{Na}^+]$  in the cooking liquors (Figure 2c), which is in agreement with the results of Jansson and Bränvall (2011). The corresponding data for Ara (Figure 2a) shows the same trend, although the relative impact of  $[\text{Na}^+]$  is less pronounced. The cumulative amount of Gal dissolved in BL decreased slightly at an elevated  $[\text{Na}^+]$  level (Figure 2b). Only a minor amount of Man was found in BL and no significant influence of the  $[\text{Na}^+]$  can be observed in this regard (Figure 2d). Corresponding experiments were also performed with NaCl instead of  $\text{Na}_2\text{CO}_3$  (see Supporting Materials, Figure S4). No difference was seen for Gal and Man, but a minor decrease in the contents of Ara and Xyl in BL was found in the case of NaCl as additive.

The results illustrated in Figure 2 imply that the dissolution of AGX is influenced substantially by the ionic strength. This is in accordance with previous findings, that the retention of AX in pulp is enhanced at higher ionic strengths (Dang et al. 2013, 2014). This is most likely because of the lower solubility of xylan at high ionic strength.

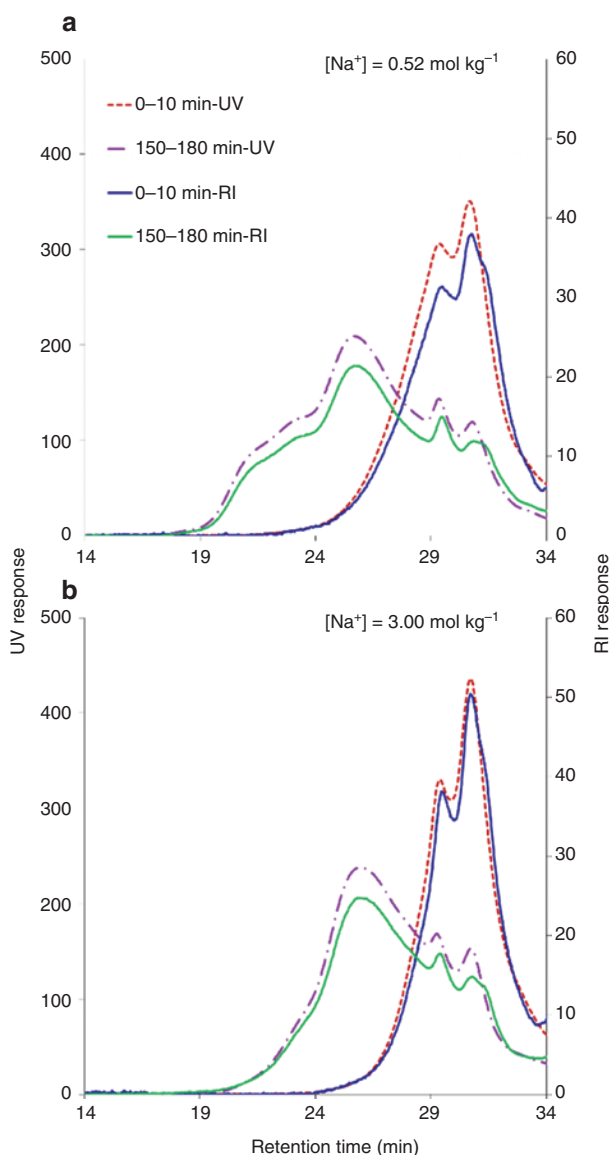
### Cumulative amount of AHSs in BL at varied $[\text{Na}^+]$

Figures S5–S7 (Supporting Materials) show the cumulative amount of Xyl, Ara and Gal, respectively, in BL obtained



**Figure 3:** Total content of anhydrosugars in the dissolved lignin precipitated from black liquors during flow-through kraft cooking.  $[\text{OH}^-] = 0.26 \text{ mol kg}^{-1}$  (b.o. solvent);  $[\text{HS}^-] = 0.26 \text{ mol kg}^{-1}$  (b.o. solvent);  $T = 158^\circ\text{C}$ .  $[\text{Na}^+]$  was controlled by the addition of  $\text{Na}_2\text{CO}_3$ .

with varying  $[\text{Na}^+]$  (Figure 1). The cumulative content of Xyl changed very instantaneously as a function of  $[\text{Na}^+]$  (Figure S2, Supporting Materials). Dang et al. (2014) made similar observations. Ara and Gal, on the other hand, show slightly different behaviour concerning the high and low  $[\text{Na}^+]$  at the beginning. This observation can be rationalised by the fact that Xyl originates only from AGX, i.e. only one kinetic pathway is involved, but the arising of Ara and Gal from several sources are governed by several kinetic pathways.



**Figure 4:** Chromatograms of four samples of dissolved lignin precipitated from BL during flow-through kraft cooking.  $[\text{OH}^-] = 0.26 \text{ mol kg}^{-1}$  (b.o. solvent);  $[\text{HS}^-] = 0.26 \text{ mol kg}^{-1}$  (b.o. solvent);  $T = 158^\circ\text{C}$ .  $[\text{Na}^+]$  was controlled by the addition of  $\text{Na}_2\text{CO}_3$ . The data has been base line corrected. The UV data (280 nm) was published very recently (Dang et al. 2016).

## MWD and carbohydrates in precipitated lignin ( $L_{\text{prec}}$ )

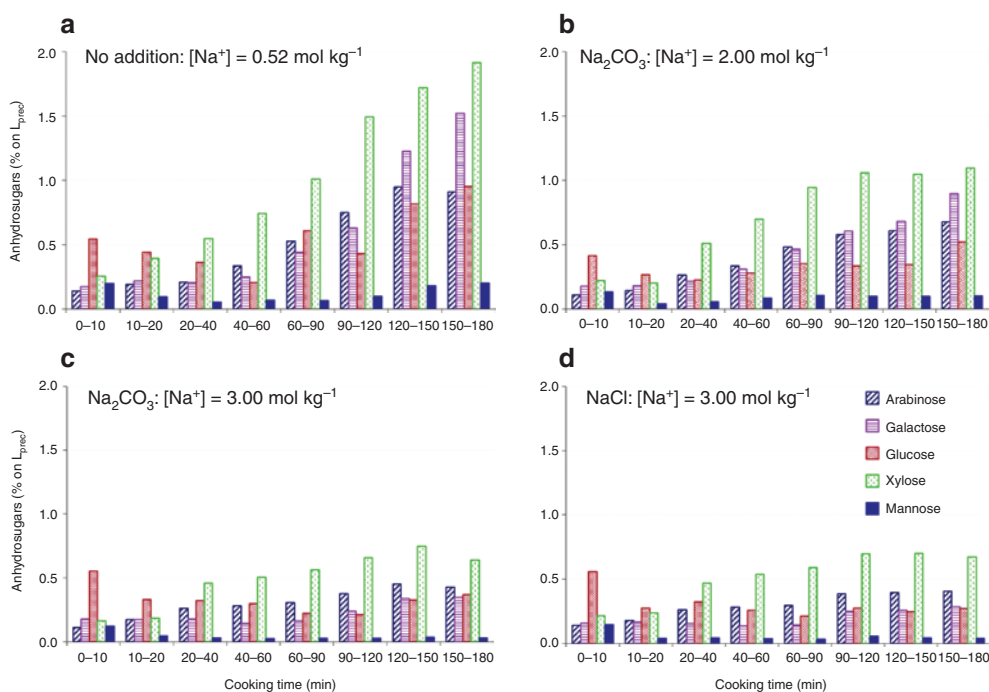
The pH of the BL samples obtained at different times was decreased to 2.5 after adding sulfuric acid, and most of the lignin in BL was precipitated. The carbohydrate content of the precipitates was analysed and four of the  $L_{\text{prec}}$  samples were subjected to GPC analysis. Figure 3 shows the total amount of Ara, Xyl, Gal, Glc and Man as a function of delignification time. Accordingly, the concentration of AHSs in  $L_{\text{prec}}$  increased with increasing cooking time, while it decreased with increasing  $[\text{Na}^+]$ .

The MWD profiles presented in Figure 4a and b are from the samples S1 and S3 with 0.52 and 3.00 mol  $\text{kg}^{-1}$   $[\text{Na}^+]$ , respectively. As is visible, the  $\text{UV}_{280\text{nm}}$  and RI response profiles are similar. The former is related to the lignin concentration, while the latter is related to the concentration of the total amount of dissolved material. However, the different UV and RI profiles are difficult to interpret because of the low carbohydrate content of the  $L_{\text{prec}}$  (around 5% at most, Figure 3). Nevertheless, carbohydrates and the lignin moieties elute from the column simultaneously, i.e. indicating the presence of LCCs. The literature reported on similar findings (Simonson 1963, 1969; Fengel and Przyklenk 1975; Eriksson and Lindgren 1977; Eriksson et al. 1980; Lawoko et al. 2005, 2006). Eriksson et al. (1980) suggested that all types of sugar units

can be linked to lignin. Lawoko et al. (2006) reported that lignin of spruce is linked through covalent linkages to all major polysaccharides, such as GGM, AGX, cellulose and pectin. Furthermore, the MW of  $L_{\text{prec}}$  increased with increasing cooking time and decreased at higher  $[\text{Na}^+]$ , as was already reported by Dang et al. (2016). Our findings are also in agreement with those of Zinoviyev et al. (2017).

The results presented in Figure 5 show that Ara, Xyl, Gal, Glc and Man are present in all  $L_{\text{prec}}$  samples with the dominance of Xyl. A minor amount of Man was also detected along with a rather high amount of Glc, particularly at the end of the reference series in the absence of a surplus of sodium salt (Figure 5a). Laine and Tamminen (2002) noted that 1,3-linked  $\beta$ -glucan was liberated from the fibres during alkali leaching of unbleached pine kraft pulp and concluded that this substance is associated with the dissolved lignin in BL. This interpretation may also be valid for the high Glc content in  $L_{\text{prec}}$  of the present study. The literature reports of similar findings: Niemelä et al. (2007) found that Xyl and Gal are dominating in the LCCs of pine BL; Balakshin et al. (2003) found that Xyl is the dominant sugar in precipitates from pine BL; Tamminen et al. (1995) showed that lignin isolated from pine BL is rich in Xyl, Gal, Ara and Glc.

The amounts of Xyl, Ara and Gal in the  $L_{\text{prec}}$  are increasing as a function of cooking time (Figure 5). A sugar yield decrement is visible at higher  $[\text{Na}^+]$  levels



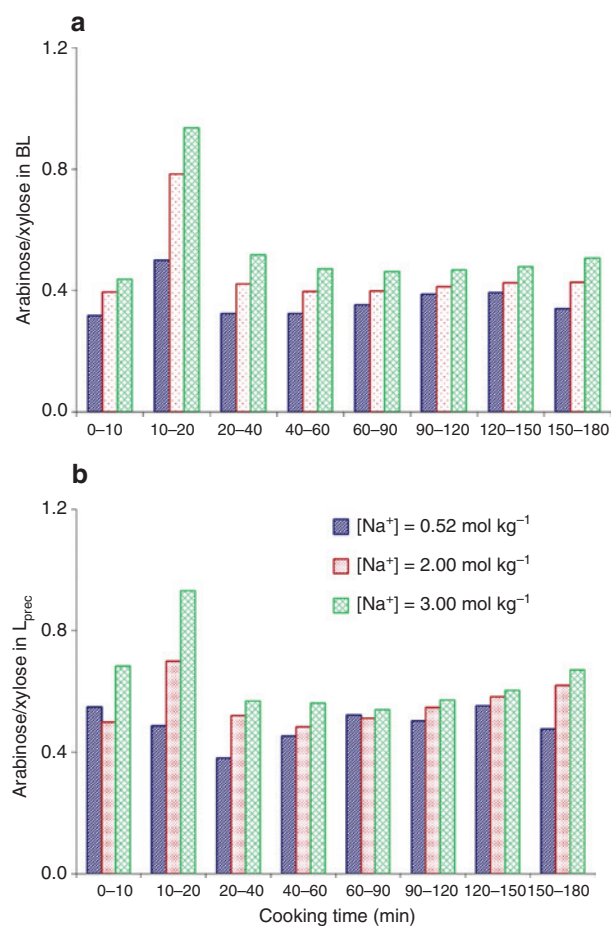
**Figure 5:** The effect of sodium ion concentration on the amount of anhydrosugars present in precipitated lignin during flow-through kraft cooking.  $[\text{OH}^-] = 0.26 \text{ mol kg}^{-1}$  (b.o. solvent);  $[\text{HS}^-] = 0.26 \text{ mol kg}^{-1}$  (b.o. solvent);  $T = 158^\circ\text{C}$ .

(Figure 5a–d). The results obtained at the shortest cooking time (0–10 min) differs from the other samples in that the Glc and Man yields are comparably high. After 10 min of cooking time, however, only a trace amount of Man is found in the  $L_{\text{prec}}$  fractions (from 20 to 180 min) and there is no clear tendency in terms of the Glc yield. The traces of Man detected indicate that the Gal and Glc are not from GGM (Tamminen et al. 1995).

## Arabinose:xylose ratios

The Ara:Xyl ratios in the BL and  $L_{\text{prec}}$  (Figure 6) show similar tendencies, i.e. both data are increasing at higher  $[\text{Na}^+]$  levels (Figure 6). The Ara:Xyl ratio in the wood meal of Scots pine was found to be approx. 0.22:1 (Table 1), but this ratio in AGX of softwood is about 0.13:1 (Sjöström 1993). Besides AGX, the Ara units may also originate from AG and arabinans (Sjöström 1993). As seen in Figure 6,

Ara:Xyl ratios in BL and  $L_{\text{prec}}$  are almost unchanged in the cooking time between 20 to 180 min. In general, the Ara:Xyl ratio in the BL (0.34:1) is higher than in the wood meal, but lower than that in  $L_{\text{prec}}$  (0.48:1). These data are for the cooking series with  $0.52 \text{ mol kg}^{-1} [\text{Na}^+]$  (Figure 6a, b). One possible interpretation is that there are covalent linkages between lignin and AGX with Ara being the linking unit between lignin and the residue of the xylan chain (Fengel and Przyklenk 1975; Eriksson and Lindgren 1977; Eriksson et al. 1980; Tamminen et al. 1995). Furthermore, the Ara:Xyl ratio in both the  $L_{\text{prec}}$  and BL was very high and increased during the first 20 min of cooking. The reason for this is the easy extractability of Ara-rich polysaccharides (e.g. AG and arabinan), during the first 20 min of cooking. The high Ara:Xyl ratios in the two first  $L_{\text{prec}}$  samples (0–10, 10–20 min) presented in Figure 6b imply that a substantial part of the Ara is originated from AG and arabinan linked to lignin (Tamminen et al. 1995; Balakshin et al. 2007).



**Figure 6:** Ratio of arabinose to xylose during flow-through kraft cooking.  $[\text{OH}^-] = 0.26 \text{ mol kg}^{-1}$  (b.o. solvent);  $[\text{HS}^-] = 0.26 \text{ mol kg}^{-1}$  (b.o. solvent);  $T = 158^\circ\text{C}$ .  $[\text{Na}^+]$  was controlled by the addition of  $\text{Na}_2\text{CO}_3$ .

## Conclusions

There is a large difference between the content of AHSs in BL and those calculated from the AHSs removed from the wood residue during pulping. The loss of Man during pulping is accompanied by chemical degradation of the sugar residues. Some of the Xyl, Ara and Gal remained detectable partly as carbohydrates in the BL. The dissolution of AGX is hampered substantially at higher ionic strength, probably, because of the lower solubility of xylan at high ionic strength. The effects of  $\text{Na}_2\text{CO}_3$  and NaCl on carbohydrate dissolution are similar, although a slight decrease in the Ara and Xyl amounts in the BL was seen in the case of NaCl addition. The carbohydrate contents of  $L_{\text{prec}}$  increased at longer cooking times and decreased at higher  $[\text{Na}^+]$  levels. Xyl, Ara, Gal, Glc and Man were detected in all  $L_{\text{prec}}$ . Xyl, originating from AGX is the dominant sugar detected in  $L_{\text{prec}}$ , while only traces of Man were found. The amounts of Xyl, Ara and Gal in  $L_{\text{prec}}$  increased with increasing cooking time, and decreased at higher  $[\text{Na}^+]$  levels. The Glc yield does not show any trend. It is possible that several types of LCCs exist, as appreciable amounts of Xyl, Ara, Gal and Glc were detected in the  $L_{\text{prec}}$  samples. Based on the literature reports it can be assumed that the Glc detected in these samples may originate from 1,3-linked  $\beta$ -glucan bound to lignin.

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