

# **EFFECTS OF HARDWOOD XYLAN DISSOLUTION/SORPTION ON FIBRE CHARGE AND PULP YIELD**

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## **SUMMARY**

The intention of this presentation is to provide a short summary of some of the research that has been carried out over the past decade on the structure of hardwood xylans and various aspects related to the structure of xylan in connection with kraft cooking. In particular, special attention will be paid to analytical characterizations of hexenuronoxylans, the distribution of xylan in the fiber wall of kraft pulps and to the sorption of xylans to pulp fiber and its effects on the surface of the fibers. The identification of new structural elements in hardwood xylans will be discussed briefly. Findings obtained by varying the alkali charge and cooking time under kraft cooking in order to reduce the content of hexenuronic acid residues in birch pulps will be presented. Under the investigated conditions the removal of HexA residues was primarily due to elimination of HexA residues from the xylan polysaccharide and not to dissolution of xylans from the pulps. However, the conditions employed to remove HexA residues affected the pulp yield and viscosity negatively, but the brightness of the pulps was improved. Analytical characterizations performed on pulp mill samples demonstrate that unbleached hardwood kraft fibers exhibit surface layers rich in hexenuronoxylans carrying relatively few uronic acid side-groups. Laboratory experiments demonstrated that the sorption of hexenuronoxylans from cooking liquors to pulps under kraft cooking conditions predominately effects the surface composition of the fibers. Sorption of hardwood black liquor xylan to softwood fibers increases the fiber charge and especially the contents of xylan and hexenuronic acid residues in the surface layer.

## **INTRODUCTION**

During the last decade there has been an increasing interest in the chemistry of wood hemicelluloses and their reactions under conditions employed in modern modified kraft cooking and bleaching processes. Special attention has been paid to the structure of the xylans and the reactions of the uronic acids residues present as side-groups in xylans. The chemical structure of the hemicelluloses in wood was described in detail several decades ago [1], however, new structural elements in these polysaccharides are still being found today. For example, the discovery of hexenuronic acid residues linked to xylans present in alkaline pulps by Teleman et al., [2] some years ago inspired further studies on new analysis methods for hexenuronic acid (HexA) residues [3-5] and many other topics related to hexenuronoxylans and pulping. For example, investigations have been performed dealing with the importance of HexA to the pulp kappa number in cooking [6] and on the reactions of HexA residues with bleaching chemicals in ECF and TCF sequences [7,8]. Later on the reactions of hexenuronic acid groups in pulping and bleaching were summarized in a review article [9].

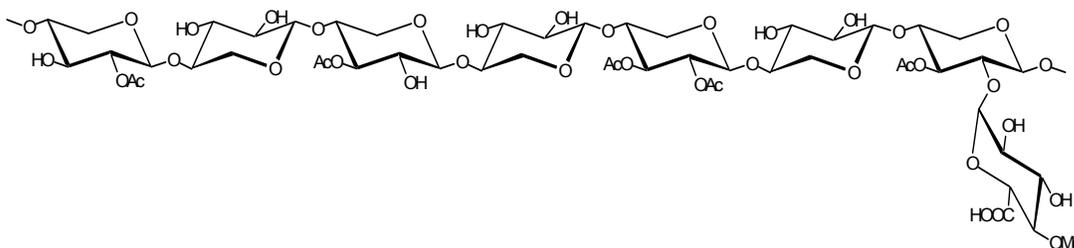
The present paper summarizes some findings from studies performed at our laboratory that were focused on the chemical structure of xylans and the behavior of hexenuronoxylans under kraft cooking conditions, as well as on the distribution of xylans between the fiber wall layers and sorption of xylans to kraft pulps. The findings from these studies are discussed in the light of some earlier studies on hardwood (birch) xylans and kraft cooking.

## HARDWOOD XYLAN

### Chemical structure

The major hemicellulose present in hardwood is an acetylated glucuronoxylan, more correctly referred to as *O*-acetyl-(4-*O*-methylglucurono)xylan [10]. The backbone of this polysaccharide consists of approximately 150  $\beta$ -(1 $\rightarrow$ 4)-linked xylopyranosyl residues and most of the xylans isolated from hardwoods contain, on the average, one 4-*O*-methylglucuronic acid (MeGlcA) side-group per ten xylopyranosyl residues,  $\alpha$ -(1 $\rightarrow$ 2)-linked to the xylan chain [11]. Many of the xylose residues in the xylan backbone contain an *O*-acetyl substituent at position C-2 and/or C-3.

By employing advanced NMR spectroscopic methods and other analysis techniques a new structural element ( $\rightarrow$ 4)[MeGlc $\alpha$ A-(1 $\rightarrow$ 2)][*O*-Ac-(1 $\rightarrow$ 3)]-Xyl-(1 $\rightarrow$ ) was shown to be present in xylans isolated from different Scandinavian hardwoods (aspen, beech and birch) [12,13]. Advanced mass spectroscopic investigations demonstrated that the uronic acid residues are distributed irregularly within the polysaccharide chain of hardwood xylans [14]. Evidently, large domains of the hardwood xylan backbone are virtually free from uronic acid substituents. The structural formulae depicted in Figure 1 summarize our current knowledge about the chemical structure of the xylan present in Scandinavian hardwoods, aspen, beech and birch, commonly utilized for pulping.

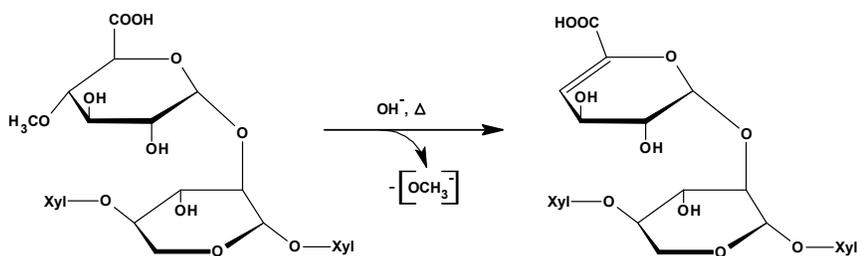


**Figure 1.** Structural formulae of *O*-acetyl-(4-*O*-methylglucurono)xylan in hardwood (aspen, beech and birch).

Earlier structural studies [15,16] on 4-*O*-methylglucuronoxylan from *Eucalyptus globulus* demonstrated several similarities between this xylan and the xylan isolated from birch (*Betula verrucosa*). However, in two recent publications by Pascoal Neto, et al. [17,18], *Eucalyptus globulus* wood was shown to contain an unusual acetylated xylan having galactosyl and glucosyl residues linked to the O-2 of some of the 4-*O*-methylglucopyranosyl side-groups in the polysaccharide chain. Evidently, new knowledge about the chemical structure and composition of hardwood xylans are still being generated. This may at least in part be due to the fact that the techniques for analyzing such polysaccharides have been developed substantially over the past years, thus yielding more detailed structural information today.

### Structure modification

Under the alkaline conditions employed in kraft cooking the acetyl groups originally present in the hardwood xylan are rapidly cleaved off, thus yielding acetic acid together with a deacetylated xylan polysaccharide much less soluble in the cooking liquor. Furthermore, the major part of the 4-*O*-methylglucuronic acid side-groups linked to the xylan polysaccharide chain is removed under the alkaline conditions in hardwood kraft cooking [19]. It was early suggested [20] that under alkaline conditions 4-*O*-methylglucuronic acid residues might undergo an  $\beta$ -elimination reaction splitting off methanol and forming hexenuronic acid residues (i.e., 4-deoxy-L-threo-hex-4-eno-pyranosyluronic acid) according to the scheme depicted in Figure 2. In addition, under sufficiently strong alkaline conditions the HexA residues thus formed could then be further degraded and finally split-off yielding a linear xylan polysaccharide essentially free from side-groups. Such unsubstituted linear xylan chains may form strong aggregates and adsorb onto cellulosic surfaces. Hence, xylans dissolved in the cooking liquor may reabsorb onto the fibers when the uronic acid side-groups are split-off from the xylan chains in the later phase in kraft cooking. The  $\beta$ -elimination reaction yielding HexA residues was later verified [21,22] and, more recently, hexenuronic acid residues were also identified in kraft pulps [2].



**Figure 2.** Alkaline  $\beta$ -elimination of methanol from a 4-*O*-methylglucuronic acid residue and the subsequent formation of a hexenuronic acid residue (HexA) linked to the xylan backbone.

## BIRCH KRAFT COOKING

Some earlier investigations on kraft cooking of birch, performed by Aurell [19,23], demonstrated that it was possible to remove many of the 4-*O*-methylglucuronic acid (MeGlcA) residues from unbleached pulps just by increasing the alkali concentration in the cooking liquor. However, in these previous investigations the content of hexenuronic acid residues in the unbleached pulps was not considered, most probably due to the lack of efficient analysis methods for HexA residues in pulps at that time. Some years ago, after having developed an efficient analysis method for hexenuronic acids and other uronic acids in pulps, we decided to reinvestigate the behavior of uronic acid residues and xylans during kraft cooking of birch wood [24]. To this end, several series of kraft pulps were prepared from the same batch of birch wood chips by employing different conditions in the bulk and final phases during the cooking (i.e., by varying the temperature, time and alkali charge). The birch pulps obtained were then analyzed for the contents of HexA and MeGlcA residues by employing our analysis method that is based on enzymatic hydrolysis and capillary electrophoresis [5]. In addition, several traditional pulp characteristics, such as the kappa number, pulp viscosity and brightness, were also determined on these pulps by employing the usual standard techniques (SCAN methods).

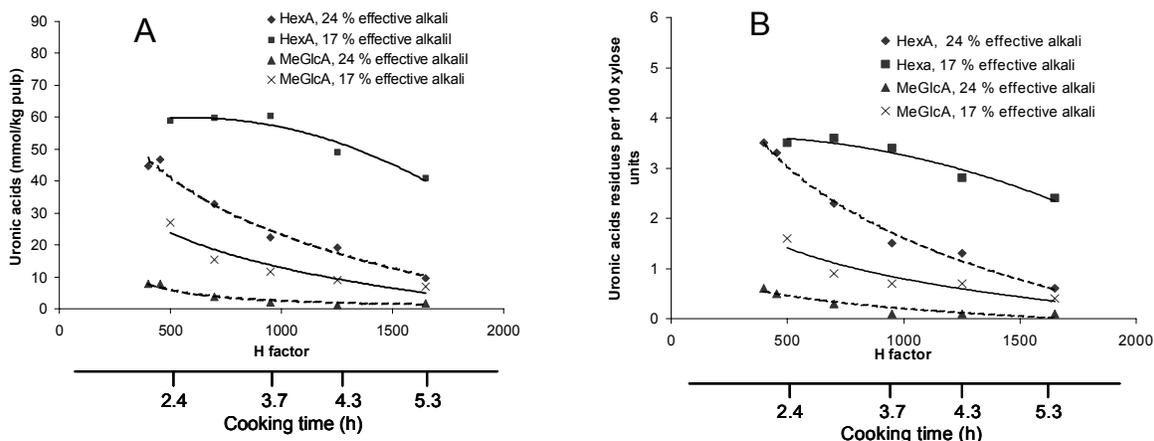
### *Elimination of uronic acid residues*

In agreement with the earlier findings by Aurell on MeGlcA residues and kraft cooking, the alkali charge and cooking time (H factor) were the cooking parameters that exhibited the strongest influence on the content of both HexA and MeGlcA residues in the birch pulps obtained in our investigation [24]. Figure 3 A depicts the contents of HexA and MeGlcA residues in the birch pulps cooked for different length of time (i.e., different H factor) and employing an alkali charge of 17 % and 24 % on wood, respectively, in the cook. In a similar manner, Figure 3 B depicts the number of HexA and MeGlcA residues in the xylan present in these birch pulps.

In the case for the pulps in the series cooked with an alkali charge of 24 % (filled diamonds and broken line in the figure 3 A), the content of HexA residues in the pulps dropped rapidly from around 50 mmol/kg after a cooking time of 2.4 h down to a very low level below 10 mmol/kg in the pulp obtained after 5.3 h (H factor 1650). The corresponding contents of MeGlcA residue in these pulps varied from 8 mmol/kg down to 1 mmol/kg pulp at the longer cooking time. In contrast to this, the contents of HexA residues in the corresponding pulps from the series cooked using a lower alkali charge (17 %, filled squares and solid line in the figure 3A) were much higher and decreased slowly from around 60 mmol/kg down to around 40 mmol/kg in the pulp obtained after the cooking time 5.3 h. The contents of MeGlcA residues in all the pulps obtained with low alkali charge were higher than that in the corresponding pulps cooked using the high alkali charge. pulps.

The diagram in Figure 3 B demonstrates the relationship between the number of HexA and MeGlcA residues in the xylan present in the birch pulps and the cooking time (H factor) for the two series of pulps obtained by using an alkali charge of 17 % and 24 %, respectively. As can be seen, the relationships observed in the diagram in the figure 3 B are very similar to those in 3A, which indicates that the removal of HexA residues from the birch pulps cannot primarily be due to dissolution of xylans from the pulps. Instead, these

diagrams clearly demonstrate that the decrease of HexA residues, in the pulps cooked using a high alkali charge and for extended cooking times, must be due to the elimination of HexA residues from the xylan polysaccharide chains. Thus, cleavage of the glycosidic bond between the hexenuronic acid side-groups and the xylan backbone under the alkaline conditions employed in the cooking explains the removal of hexenuronic acid residues and the subsequent formation of xylans with a low frequency of uronic acid residues.



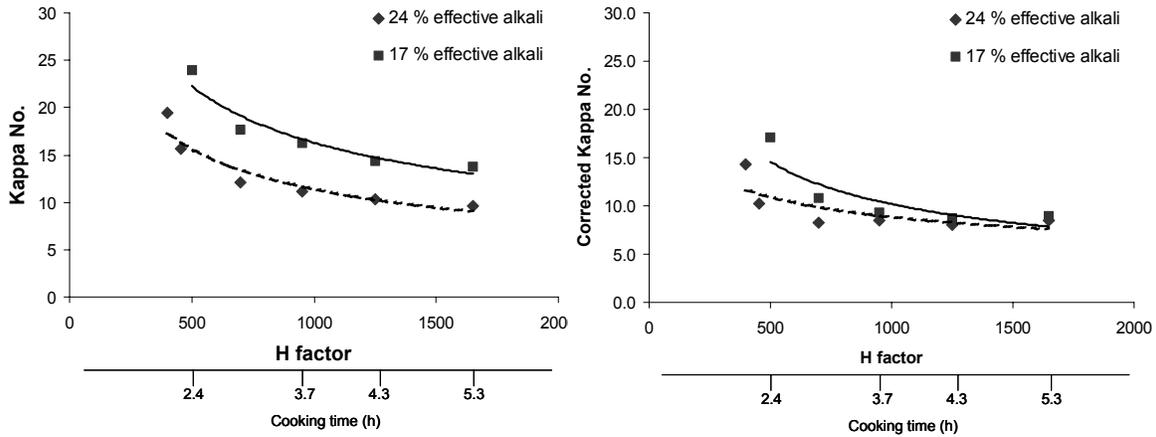
**Figure 3.** (A) The relationship between the H factor and contents of HexA and MeGlcA residues in the birch pulps cooked for different length of time (i.e., different H factor) and using alkali charge of 17 % and 24 % on wood, respectively. (B) The corresponding relationship between the number of uronic acids, expressed as the number of HexA and MeGlcA per 100 xylose residues in the xylan polysaccharide present in the pulps, and cooking time for the two series of birch pulps.

### Kappa number, pulp yield and viscosity

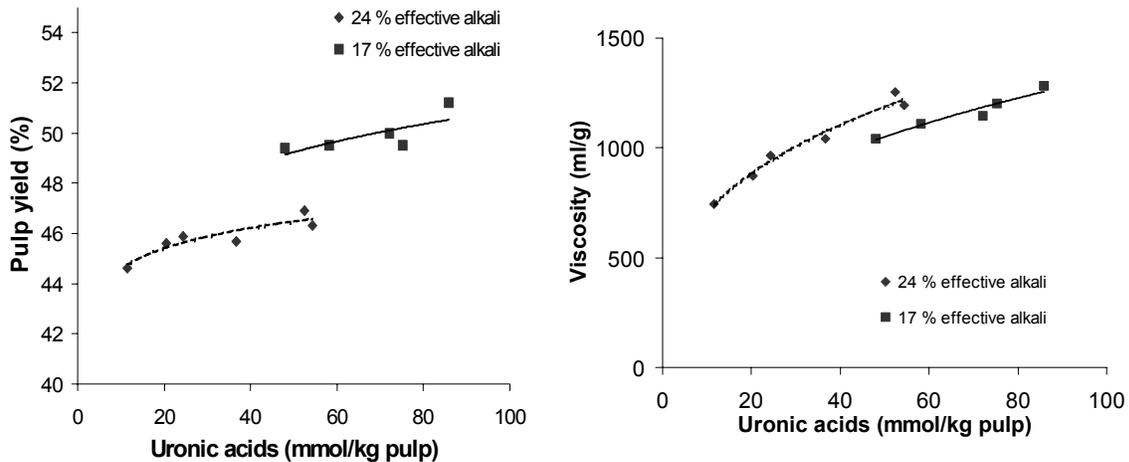
The left diagram depicted in the Figure 4 demonstrate the relationship between the Kappa number and the cooking time, whereas the right diagram reports the relationship between the corrected Kappa number (Kappa No minus the HexA contribution calculated as describe in [6]) and the cooking time. As expected, the Kappa numbers were much lower for the pulps in the pulp series obtained by using the 24 % alkali charge than those for the corresponding pulps in the 17 % alkali charge series. In contrast, when the corrected Kappa number is plotted against the cooking time, the difference between the two pulps series becomes very small (right diagram, Figure 4), especially for the pulps obtained after extended cooking times. For the pulps obtained after a cooking time of 3.7 h or longer, the corrected Kappa numbers are almost the same (around 8 to 9) for the pulps cooked by using alkali charge of 17 % and 24 %, respectively. This shows that the comparatively lower Kappa numbers of the birch pulps in the high alkali charge series were mainly due to the lower contents of HexA residues in these pulps and not to more extensive delignification (i.e., lower content of lignin).

Figure 5 reports the pulp yield and viscosity values for the birch pulps with varying contents of uronic acid groups. As expected, the pulp yields obtained in the birch kraft cooks were lower for all the pulps in the pulp series obtained by using the 24 % alkali charge than that for those in the 17 % alkali charge pulp series. A major reason for this lower pulp yield was the lower content of xylan (about 2 % on wood) in the pulps obtained in the high alkali cooking. Earlier studies [19,23] at our laboratory have shown that there is a rapid dissolution of xylans in the initial phase in birch kraft cooking. The dissolution of xylan to the cooking liquor levels out in the following bulk and residual phase. This rapid initial dissolution of xylan may explain the difference in the contents of xylan between the two pulp series discussed here. Within each pulp series the pulp yield decreased along with the content of uronic acid residues although there are relatively small differences between the pulps in the same series, see figure 5, left diagram.

The pulps from the high alkali charge series demonstrated higher brightness values (~48 %) than those in the low alkali series (~40 %). However, there was no obvious correlation between the pulp brightness and the uronic acid content of the pulps within each pulp series. Furthermore, in each series a clear relationship was found between the viscosity and the content of uronic acid residues in the pulps. The relationships obtained indicates that some depolymerization of the cellulose polysaccharides occurs concurrent with the removal of the HexA residues at extended cooking times, especially in the case of the higher alkali charge pulp series.



**Figure 4.** The relationship between the Kappa No and the H factor for the birch pulps cooked employing different length of time and using 17 % and 24 % effective alkali, respectively, (left diagram). The corresponding relationship between the corrected Kappa No. (Kappa No. - HexA contribution) and the H factor for the pulps of obtained in the two pulp series after different length of cooking time (right diagram).



**Figure 5.** The relationship between the pulp yield and the total content of uronic acid (HexA and MeGlcA) residues in the birch pulps cooked using different length of time and alkali charge of 17 % and 24 %, respectively, (left diagram). The corresponding relationship between pulp viscosity and content of uronic acid residues present in the pulps of obtained in the two pulp series after different length of cooking time (right diagram).

Altogether, these findings showed that kraft cooking of birch employing a high alkali charge and an extended cooking time results in a reduction of the content of HexA residues, down to levels ~10 mmol/kg in the unbleached pulp. Under such cooking conditions the decrease in HexA residues is primarily due to a removal of these residues from the xylan polysaccharide chains and not to dissolution of xylans from the pulps. The pulp yield and viscosity were, however, negatively affected by the pulping conditions employed to obtain the low HexA content, but the pulp brightness was improved by the higher alkali charge. Results somewhat similar to ours obtained on birch pulps in the present investigation were also reported by other investigators [25] for some Eucalyptus kraft pulps.

## **FIBER SURFACE AND XYLAN SORPTION**

As pointed out in the previous section, a rapid dissolution of xylan occurs in the initial heating phase during birch kraft cooking. The concentration of xylan in the cooking liquor reaches a maximum and then slowly drops in the bulk and residual phases of the cook. It has been shown that parts of the dissolved xylans can be regained by sorption to the birch pulp under certain conditions [26]. Sorption of hardwood xylans to fibers has also been studied in detail under laboratory conditions using pure cellulosic fibers [27]. However, the effect of xylan sorption on the pulp yield obtained in kraft cooking employing recirculation of cooking liquors seems to be limited to a only few percent [26,28].

Recently, we have conducted several studies aiming to elucidate the composition of the surface layer of fibers from hardwood and softwood kraft pulps and the effects of sorption of xylan onto the surface of the fibers [29-33]. In these studies comprehensive chemical characterizations have been performed on fiber layer materials isolated from pulps obtained from a kraft pulp mill, as well as from pulps prepared at our laboratory under certain cooking conditions employing black liquors containing hexenuronoxylans. Special analytical procedures were also developed in order to obtain information about the carbohydrate composition and contents of HexA and MeGlcA residues in the fiber surface and inner layers of the pulp fibers investigated [34,35].

### ***Composition of the fiber surface***

The analytical data reported in Table 1 illustrates some of the results obtained for a set of hardwood (mainly birch wood) kraft pulps obtained from pulp mills in Sweden. This set of pulps included several different unbleached pulps cooked to kappa numbers around 13-14 by employing different types of batch and continuous kraft cooking processes. Besides the fiber charge and kappa numbers of the pulps investigated, the polysaccharide contents and contents of uronic acid residues in surface and inner layers, are reported in the table. The carbohydrates in the fiber layers were analyzed by employing a method based on enzymatic treatments followed by capillary electrophoretic determination of the saccharides removed from the layers [35].

As expected, the major polysaccharide components of the surface and inner fiber layers of the hardwood kraft pulps analyzed were cellulose and hexenuronoxylan, with only small amounts of glucomannan being detected. Moreover, in all cases the surface layers of these hardwood kraft fibers exhibited substantially higher contents of xylan (i.e., hexenuronoxylan) than did the corresponding inner layers. The ratios between the contents of xylan in the surface and inner layers varied within the range from 1.5 up to as much as 1.9 for these unbleached pulps. For all pulps analyzed the content of uronic acid residues was somewhat higher in the surface layer than that in the inner layer, but the ratio of uronic acids in surface and inner layers was lower than the corresponding ratio for the xylan contents. This indicates that the xylans located in the surface layer of birch kraft fibers exhibits a slightly lower degree of substitution with uronic acid side-groups than do the xylans present in inner layers. Furthermore, the data presented in Table 1 indicate that the major part (~75 %) of the fiber charge of the analyzed hardwood fibers originates from the uronic acid (HexA and MeGlcA) residues present in these fibers.

In conclusion, these chemical characterizations performed on mill pulps thus demonstrate that unbleached hardwood kraft pulp fibers exhibit surface layers rich in hexenuronoxylans with relatively low frequency of uronic acid side-groups. However, it is not possible from the data in Table 1 to say how much of the surface xylan that actually originated from xylan aggregation and sorption processes occurring during cooking.

**Table 1.** Analytical data including polysaccharide compositions and contents of uronic acid residues in the surface and inner layers of hardwood (birch) kraft pulps obtained from different pulp mills in Sweden (the contents of glucomannan were in all cases around 2-3 %).

Pulp	Kappa No.	Fiber layer	Carbohydrate composition (%)		Uronic acids (mmol/kg)	Xylan ratio (surface/inner layer)	Fiber charge (meqv/kg)
			Xylan	Cellulose			
<b>Batch kraft cooking</b>							
1	14.5	Inner layer	31.8	65.5	83	1.5	114
		Surface layer	48.7	47.7	109		
2	14.9	Inner layer	33.3	62.5	104	1.6	142
		Surface layer	54.5	41.1	142		
3	–	Inner layer	18.2	78.2	8	1.7	-
		Surface layer	30.7	64.8	14		
<b>Continuous kraft cooking</b>							
4	12.4	Inner layer	30.7	67.1	81	1.6	-
		Surface layer	48.7	46.6	-		
5	13.6	Inner layer	27.9	67.1	93	1.7	126
		Surface layer	47.2	48.1	103		
6	14.2	Inner layer	28.7	68.1	-	1.9	-
		Surface layer	55.0	42.9	-		

### Sorption of xylans

Several investigations have recently been carried at our laboratory in order to elucidate the effects of sorption of hardwood hexenuronylans in cooking on the properties of the kraft pulp fibers obtained [31-33]. These investigations included both mill studies and laboratory cooking experiments. The analytical data reported in Table 2 demonstrate some of the results obtained in a study on sorption of hardwood xylan onto softwood kraft fibers and its effect on the fiber surface composition and pulp properties [29]. In order to be able to distinguish between xylan sorption and other effect during softwood kraft cooking hardwood black liquor xylan was added to the cooking liquors. Since arabinose residues are present only in softwood and not in hardwood xylans, we could utilize the arabinose content to distinguish between adsorbed and original xylan in the pulps investigated. Accordingly, when hardwood xylan was adsorbed onto the fibers in the softwood pulps, the ratio of arabinose to xylose residues in the total xylan present was lower than in the pure softwood xylan originally present.

The pulps investigated were prepared from spruce chips by cooking in a laboratory flow-through digester employing four cooking phases, including black liquor additions in some of the cases (see Table 2), and alkali and temperature profile simulating a RDH cooking process. In three of the cooking experiments, pulps denoted B-D, black liquors containing xylans were added. The pulp denoted A was prepared in a similar manner but without any black liquor xylan addition. By adding black liquors containing xylans during the cooking phases the pulp yields increase by some 1.3 – 2.4 % compared to that for the pulp A cooked in absence of black liquor addition [32].

Although the effect of the black liquor xylan additions on the pulp yields was rather limited, the effect on the fiber surface composition was quite substantial. As can be seen in Table 2, the content of xylan in the surface layer of the fibers increase up to about 20 % when the cooking was performed employing black liquor hardwood xylan addition. The carbohydrate analyses showed that the increase in surface xylan content could be attributed to the sorption of hardwood xylans onto the fibers. The data also indicated that the sorption of hardwood xylan was somewhat more effective than that of softwood xylan under comparable cooking conditions. Furthermore, the sorption of black liquor xylans resulted in a substantial increase of the content of hexenuronic acid residues in the fibers, especially, in the surface layer of the fibers (pulp B-D in Table 2).

The total fiber charge of the pulps cooked in presence on black liquor xylan was also somewhat higher compared to the fiber charge of the pulp A cooked in absence of any xylan addition.

**Table 2.** Analytical data including polysaccharide compositions and contents of uronic acid residues in the surface and inner layers of softwood kraft pulps obtained by kraft cooking in the presence and absence of black liquors containing xylan.

Softwood pulp	Addition of black liquor with xylan	Fiber layer	Carbohydrate composition (%)			HexA (mmol/kg)	Xylan ratio (surface/inner layer)	Fiber charge (meqv/kg)
			Xylan	Mannan	Cellulose			
A	non	Inner layer	8.3	9.3	82.4	11	1.6	48
		Surface layer	13.4	10.1	77.5	11		
B	Hardwood xylan (low xylan charge)	Inner layer	8.7	9.4	82.0	19	1.7	49
		Surface layer	15.1	6.9	78.0	28		
C	Hardwood xylan (high xylan charge)	Inner layer	11.0	9.4	79.6	30	1.9	63
		Surface layer	20.5	6.0	74.5	65		
D	Softwood xylan	Inner layer	8.8	10.8	80.4	20	1.6	54
		Surface layer	14.4	10.3	75.3	25		

Based on the results obtained in these investigations it can be conclude that sorption of hexenuronoxylans from the cooking liquors to pulp fibers under kraft cooking conditions predominately effects the fiber surface composition. Sorption of hexenuronoxylan onto the fibers increased the fiber charge of the softwood pulps and especially content of hexenuronic acids in the surface layer of the fibers.

## CONCLUDING REMARKS

The intention of this short summary was to demonstrate some of the important new insights on hardwood xylans and the behavior of xylans in kraft pulping that have been gained over the past decade. In particular, the investigations discussed above pointed out the following conclusions:

- By employing advanced spectroscopic methods new structural elements have been identified in hardwood xylans.
- High alkali charge and extended cooking times in birch kraft cooking were shown to reduce the content of HexA residues in pulps down to levels below 10 mmol/kg pulp.
- The removal of HexA residues under high alkali cooking conditions was primarily due to the elimination of these residues from the xylan polysaccharide and not to dissolution of xylans from the pulp.
- The pulp yield and viscosity were affected somewhat negatively by the conditions employed to remove HexA, but the pulp brightness was improved.
- Analytical characterizations have demonstrated that unbleached hardwood kraft pulp fibers exhibit surface layers rich in hexenuronoxylans with relatively low frequency of uronic acid side-groups.
- In has been demonstrated that sorption of xylans from the cooking liquors to pulp fibers under kraft cooking conditions predominately effects the surface composition of the fibers and that the contents of xylan and hexenuronic acid residues in the surface layer can be increase significantly.

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