

# Characterisation of dissolved spruce xylan in kraft cooking

Zheng Li Jansson and Elisabet Brännvall

---

**KEYWORDS:** Kraft cooking, spruce, dissolved xylan, molecular weight, uronic acid content

---

**SUMMARY:** Xylan dissolved during kraft cooking and later redeposited on fibre surfaces has been shown to affect the paper strength properties. Earlier studies have shown that the xylan characteristics, rather than simply the amount of xylan, influence the strength enhancing effect of xylan. In order to obtain an optimal use of the xylan, it is of interest to understand what the beneficial xylan characteristics are and how cooking conditions affect the characteristics.

In this study, kraft cooking of spruce chips was performed at varied cooking conditions and the xylan in the black liquor was characterized. It was found that dissolved spruce xylan had a much higher amount of bound lignin compared to previous studies on xylan dissolved from hardwoods. The ionic strength of the cooking liquor affected the amount of xylan dissolved as well as the uronic acid content of the xylan.

---

**ADDRESSES OF THE AUTHORS:** Zheng Li (zhengl@kth.se), Elisabet Brännvall (bettan@kth.se) KTH, Fiber and Polymer Technology, SE-100 44 Stockholm, Sweden

**Corresponding author:** Elisabet Brännvall

---

The main chemical constituents of wood, as well as of other plants, are cellulose, lignin and hemicelluloses. Depending on species, the relative amounts of the components differ. Generally, hardwoods have lower lignin content than softwoods and consequently higher cellulose and hemicelluloses content. Hemicelluloses are heteropolysaccharides and the monosugars included in the polymers vary between wood species. The main hemicellulose of softwood is glucomannan whereas xyans are the most important hardwood hemicelluloses (Fengel, Wegener 1989; Sjöström 1993). Apart from the difference in amount, softwood xylan usually is substituted with arabinose units, which is not the case with hardwood xylan (Sjöström 1993).

Chemical pulping aims at liberating the fibres from the wood matrix by degradation and dissolution of lignin, which can be seen as the glue holding the fibres together. However, as the active cooking chemicals are not completely selective towards lignin, also carbohydrates will be degraded and dissolved. In alkaline cooking processes, carbohydrates are degraded by peeling reactions, i.e., by splitting off the reducing end groups in the carbohydrate chains (Haas et al. 1967; Green et al. 1977). Hence, the cooking liquor will contain carbohydrate residues, such as isosaccharinic acids, produced by

the peeling reaction (Sjöström 1993). However, the cooking liquor will also contain xylan, as this compound is dissolved into the alkaline liquor as whole molecules (Axelsson et al. 1962).

The dissolution of xylan is fast in the beginning (Danielsson, Lindström 2005). The amount of dissolved xylan in the black liquor is thus high in the beginning of the cook and decreases as the cook proceeds (Yllner, Enström 1957; Danielsson, Lindström 2005). Alkaline hydrolysis and peeling can reduce the molecular weight of dissolved birch xylan (Danielsson, Lindström 2005). However, a study on dissolved eucalyptus xylan showed that it is quite stable in the highly alkaline black liquor (Lisboa et al. 2005). The molecular weight was hardly affected by prolonged pulping time, which was attributed to substituents on the xylan backbone that might stabilize against peeling. The methylglucuronic acid groups will be either transformed to hexenuronic acid groups or split off the xylan chain (Lisboa et al. 2005; Danielsson et al. 2006).

The dissolved xylan molecules may re-deposit on fibre surfaces (Yllner, Enström 1956; 1957; Clayton, Stone 1963) and thus contribute to the strength between fibres in the paper network (Sjöberg et al. 2004; Danielsson et al. 2005; Danielsson, Lindström 2009). It has been shown that addition of xylan with higher molecular weight is more efficient at enhancing softwood pulp strength than addition of xylan with lower molecular weight (Danielsson, Lindström 2005). In a study on kraft cooking of eucalyptus with addition of black liquor, it was concluded that the amount of re-deposited xylan is not the determining factor for pulp strength enhancement (Danielsson, Lindström 2009). In this study, it was also seen that a higher molecular weight of the xylan in black liquor doesn't necessarily lead to higher pulp strength. It seems that the characteristics of the re-deposited xylan, such as degree of substitution and amount of lignin bound to the xylan, also affect the pulp strength. It is of great interest to determine what the most beneficial xylan characteristics are in terms of pulp strength improvements. Since the main raw material for the pulp and paper industry in the northern hemisphere consists of softwood and as the xylan content is so much lower compared to hardwood, it is even more important to ensure that the xylan available is used in an optimal way. By distinguishing how different cooking conditions affect the characteristics of the xylan dissolved in the black liquor, future studies can be designed in

order to evaluate the importance of different xylan properties on pulp strength, i.e. addition of black liquors with certain xylan characteristics to kraft cooks.

The aim of this study was to investigate the characteristics of spruce xylan dissolved in kraft cooking liquors and examine the effect of temperature, alkali charge and ionic strength in cooking liquor.

## Materials and Methods

### Materials

The spruce chips used in the study were industrial chips obtained from the Södra mill Värö. The birch chips were obtained from birch logs chipped in a laboratory chipper at Innventia, Stockholm, Sweden. The chips were dried to a dry solids content of approximately 92% and screened, keeping the fraction with a thickness of 2-8 mm. Knots and bark were removed prior to the cooking.

The stock solution of NaOH for the pulping was prepared from pastilles of puriss grade and the stock solution of Na<sub>2</sub>S from technical grade flakes of sodium sulphide. Sodium chloride used to increase the ionic strength of the pulping liquors was of puriss grade. The ethanol, used in the method for precipitation of xylan, is 96 vol-%. Analytical reagent grade 1,4-dioxane was used in the extraction of precipitate

### Cooking equipment

Steel autoclaves with a capacity of 3 dm<sup>3</sup> were used. The autoclaves were heated in an steam heated oil bath with PEG as heating medium. The autoclaves were mounted in the glycol bath with a slight tilt, which enabled circulation of the liquor within the autoclave as they were rotated in the glycol bath.

### Cooking procedure

Batches of 300 g o.d chips, were placed in the autoclaves and the lid was mounted. The air was removed by vacuum suction for 30 min before white liquor was sucked into the autoclaves by the vacuum created within. The white liquor was prepared from stock solutions of NaOH and Na<sub>2</sub>S, and diluted with deionised water so as to reach a liquor-to-wood ratio of 4 l/kg o.d. wood. The alkali concentration at the start of the cook was 1.2 M, except in the case of low [OH<sup>-</sup>] when it was 1.0 M. The [HS<sup>-</sup>] was 0.26 M and the [Na<sup>+</sup>] was 1.46 M except in the case of high [Na<sup>+</sup>] when it was increased to 2.5 M by addition of NaCl.

The autoclaves were mounted into the glycol bath holding the desired temperature (either 157°C 167°C) and the rotation of the autoclaves was started. The recording of the cooking time (50-250

min) started after a heating up time of 10 min. The cooking was terminated by placing the autoclaves in a water bath for cooling. The black liquor was then separated from the chips.

The delignified chips were washed with de-ionised water for 12-14 hours before defibration in a NAF water jet defibrator at a water pressure of 2 bars (g).

### Precipitation of xylan in black liquor

The xylan in the black liquor was precipitated according to Axelsson et al. (1962), with the exception that acetone (not ethyl ether) was used in the final washing step. Samples of black liquor, 300-450 ml in the case of softwood black liquor and 250-300 ml birch black liquor were collected for the precipitation procedure. Acetic acid was slowly added to the black liquor during mixing until the volume of added acetic acid equaled to the volume of black liquor. This will change the pH of the solution to pH 5.

The black liquor-acetic acid mixture was poured into a volume of ethanol 3 times the volume of black liquor-acetic acid. The solution was placed in a refrigerator at a temperature of 4°C and left for 16-24 hours while the xylan formed a precipitate. The supernatant was decanted off and the precipitate was washed twice with an ethanol:water mixture (1:2), three times with pure ethanol and finally three times with acetone. The precipitate was centrifuged between each washing step, using a centrifuge Potofix 32A, with a rotor speed of 4 000 rpm for 20 min. After washing, the precipitate was dried in a desiccator under vacuum to remove acetone. The dry solid content was determined on an IR balance, Mettler PM 460.

### Dioxine extraction of precipitate

A sample of the precipitate was wrapped in a filter paper and placed in a thimble. After weighing, it was placed in a Soxhlet extractor, connected to a flask containing a 9:1 1,4-dioxane:water solution and connected to a condenser. The extraction was performed for 18 hours under heating adjusted to reach four solvent cycles per hour. The lignin not linked to xylan is supposed to dissolve into the warm solvent. The amount of free lignin was determined as the weight loss after extraction.

### Analysis

*Klason lignin* in black liquor was determined gravimetrically after sulfuric acid hydrolysis at 125°C and in pulp in duplicates by acid hydrolysis at 125°C with sample size 250 mg.

*The carbohydrate analysis* was carried out using acid hydrolysis and gas chromatography (Hewlett-Packard HP-6890) according to Theander and Westerlund (1986).

Calculation of xylan in black liquor: The Klason lignin content in % of the precipitate was determined. The concentration of lignin in the precipitate was calculated as % lignin times the amount of precipitate per liter black liquor,  $L_{BL}$  (g/l). The remaining precipitate was assumed to be carbohydrates,  $C_{BL}$  (g/l). From the carbohydrate analysis of the precipitate the relative percentages of the different monosugars were obtained. The xylan content in the precipitate was calculated as

$$\text{xylan (g/l)} = (\% \text{xylos} + \% \text{arabinose}) \cdot C_{BL}$$

The 4-O-Methyl Glucuronic acid content was quantified using methanolysis and gas chromatography as described by Li et al (2007). The molecular weight of xylan was analyzed by size exclusion chromatography (SEC). The pretreatment of xylan sample was: the xylan was dissolved in 1.9 ml of 8% LiCl /N,N-dimethyl-acetamide(DMAC) solution under 80°C for two hours and then left at 4°C for 5 days with mild magnetic stirring. Finally the samples were diluted to 0.5% LiCl by the addition of 28.4ml DMAC and filtered through a 0.45 μm poly(tetrafluorethylene) filter before SEC characterization. Pulp dry content SCAN C 3-78, Kappa number ISO 302:2004, ISO-brightness ISO 2470:1999.

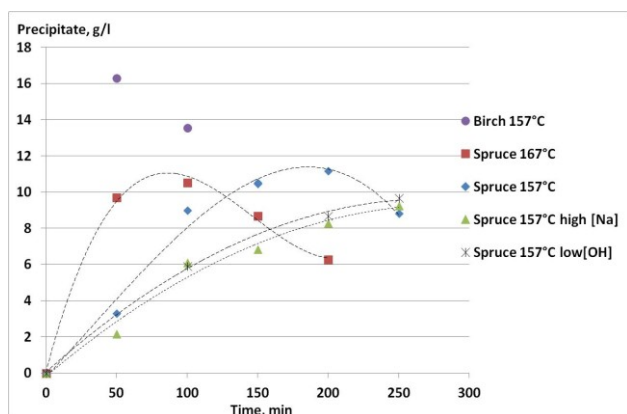


Fig 1. The amount of xylan precipitate from black liquor obtained at different kraft cooking conditions.

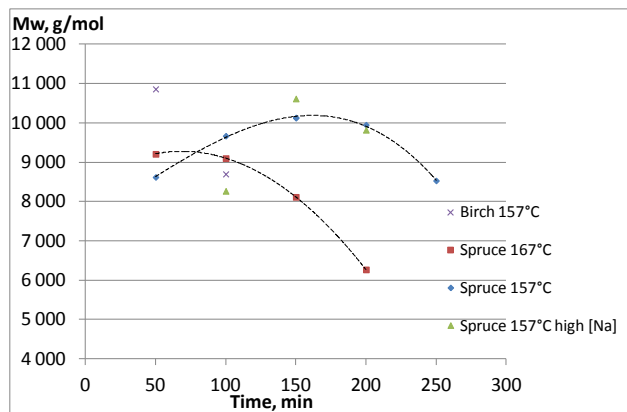


Fig 3. The molecular weight of the dissolved xylan in black liquor obtained at different kraft cooking conditions.

## Results

Kraft cooks of spruce chips were performed and the amount of xylan dissolved into the black liquors was determined by precipitation. In Fig 1, the amount of xylan precipitate is shown for various kraft cooking conditions after different cooking times. As can be seen, the dissolution rate of xylan increased with higher cooking temperature. Higher ionic strength in the cooking liquor or lower alkali charge slowed down the dissolution. As expected, the amount of xylan precipitate from kraft cooking of birch was higher.

However, not all of the precipitate consisted of xylan. In Fig 2, the percentage of the precipitate consisting of Klason lignin is shown. In the case of birch, only around 10% of the precipitate consisted of lignin whereas in the case of spruce, the lignin portion of the precipitate amounted from 30 up to 72%.

The molecular weight of the xylan in the precipitate from black liquor is shown in Fig 3. The molecular weight of the dissolved spruce xylan seemed to reach a maximum after a certain cooking time, whereafter the molecular weight decreased. The decrease in uronic acid content of the dissolved xylan with time is shown in Fig 4.

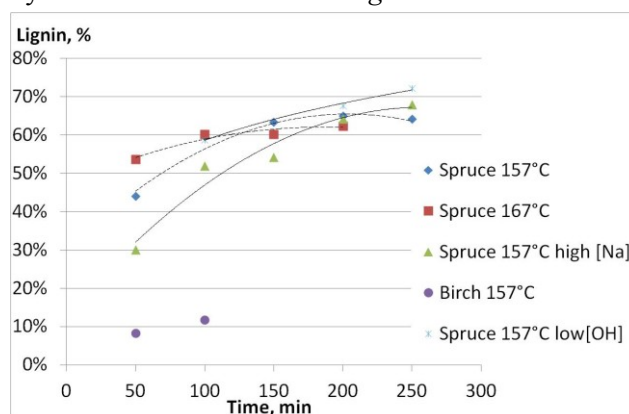


Fig 2. The amount of lignin present in the xylan precipitate from black liquor obtained at different kraft cooking conditions.

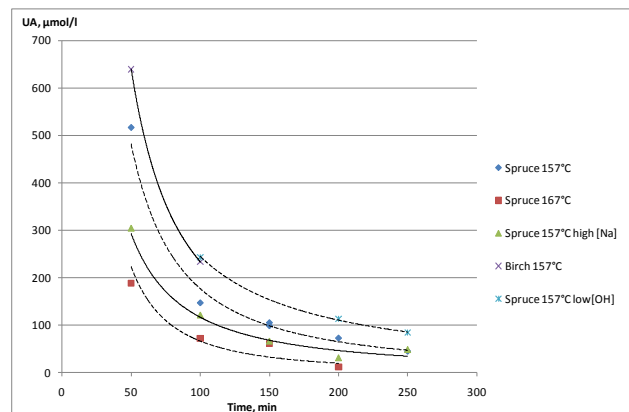


Fig 4. Uronic acid group content of the dissolved xylan in black liquor obtained at different kraft cooking conditions.

## Discussion

The precipitate from black liquor from kraft cooks of spruce contained a large fraction of lignin, 30-72%, as seen in Fig 2. This is much more than has been shown previously for hardwood xylan precipitates. The lignin content in black liquors of kraft cooks of birch is 4-18% (Axelsson et al. 1962; Danielsson 2007) and 12-22% in kraft cooks of eucalyptus (Danielsson et al. 2009). Previously, the lignin content of a hemicelluloses precipitate from black liquor of pine kraft cooks is reported to be only 5-10% (Engström et al. 1995). The precipitation procedure used in their study differs however from the one used in the present study. The main solvent of the previous study was dioxane, whereas ethanol was used in this investigation. The present procedure has been widely used ever since it was introduced by Axelsson et al. (1962) and the lignin content in the precipitate from kraft cooking of birch in this study was consistent with the earlier findings on birch black liquor, around 10% of the birch xylan precipitate consisted of lignin.

The large amount of lignin in the precipitate gives rise to the question whether the lignin in the precipitate is covalently bound to xylan or not. Westbye et al (2007) suggested that agglomerates of lignin molecules might form inclusions complexes with dissolved xylan, i.e. some lignin might be co-precipitated lignin not covalently bound to the xylan. In order to test this, the xylan precipitate was extracted with a water and dioxane mixture. Free lignin assumed to dissolve in the organic solvent whereas lignin bound to xylan can be filtered off. As seen in Fig 5, some lignin could be removed from the precipitate in this way. The xylan portion of the precipitate was 55% after 50 minutes cooking time and it decreased with increasing cooking time. The amount of bound lignin in the precipitate increases

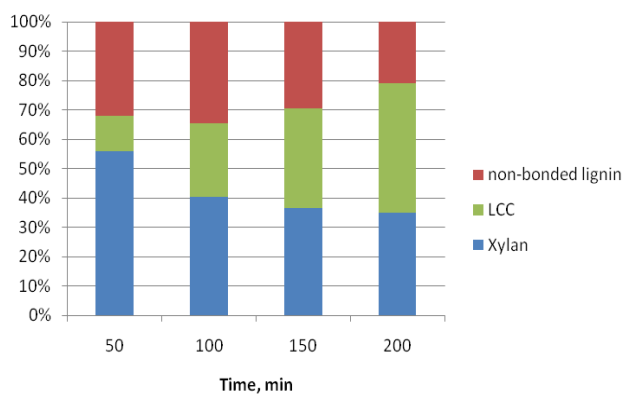


Fig 5. The fraction of free lignin, xylan, and lignin covalently bound to xylan (LCC) in the precipitate from black liquor obtained from cooking at 157°C, [OH<sup>-</sup>]-charge 1.2 mol/l, [HS<sup>-</sup>]-charge 0.26 mol/l, [Na<sup>+</sup>]-concentration 1.5 mol/l.

with time. Tamminen et al. (1995) show that lignin-carbohydrate complexes exists in black liquor. They propose that the arabinose substituent of xylan forms a cross-link to the lignin molecule. Since arabinose substituents are much more common in softwood xylan, the higher amount of lignin in softwood xylan precipitate might be explained by this fact. Eriksson et al. (1980) have shown that lignin is linked to xylan by ether bonds to the arabinose unit.

Lower alkali charge, higher ionic strength and lower temperature retarded the dissolution rate of xylan, Fig 1. The maximum concentration of dissolved xylan in the black liquor was also affected by the conditions in the cook. Lower alkali charge and higher ionic strength resulted in a lower amount of dissolved xylan. Earlier studies on the carbohydrate content in pulp show that lower alkali (Gustavsson, Al-Dajani 2000) and higher ionic strength decreases the dissolution of xylan (Gustavsson, Al-Dajani 2000; Johansson, Germgård 2008).

By plotting the amount of dissolved xylan in black liquor as a function of the degree of delignification, it can be seen, in Fig 6, that the amounts of xylan dissolved when cooking at 157°C and 167°C were quite similar. The amount of xylan is based on the carbohydrate analysis of the precipitate from black liquor, the xylan content calculated as xylose + arabinose. However, lower alkali charge or higher ionic strength resulted in a lower amount of xylan dissolved at a given degree of delignification

The degree of polymerization has been shown to decrease upon prolonged cooking time for of the dissolved birch xylan (Axelsson et al. 1962; Danielsson, Lindström 2005) and eucalyptus xylan (Danielsson, Lindström 2009). Alkaline hydrolysis as well as the peeling reaction leads to a reduction in the molecular weight of the carbohydrate chains.

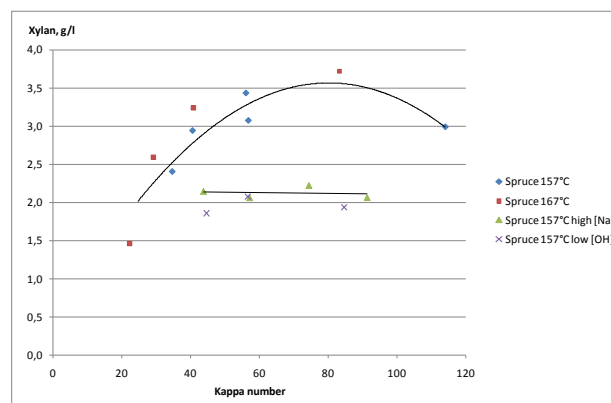


Fig 6. Amount of xylan in black liquor obtained at different cooking conditions. The amount of xylan is based on the carbohydrate analysis of the precipitate from black liquor.

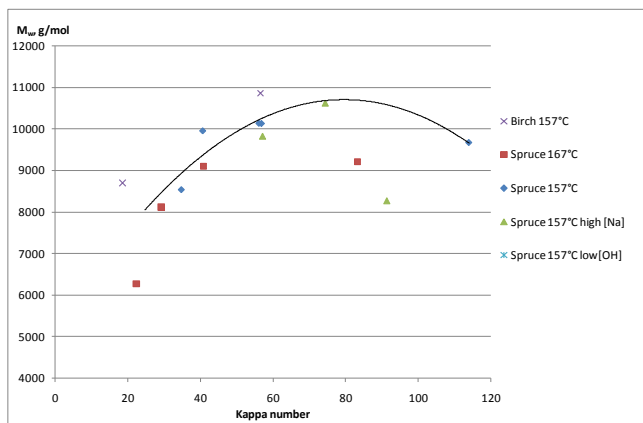


Fig 7. Molecular weight of dissolved xylan in black liquor vs the kappa number of the corresponding pulp.

According to *Fig 3*, higher temperature during the cook led to faster reduction of the molecular weight of the dissolved xylan. However, from *Fig 7* it can be seen that the molecular weight seemed to depend on the degree of delignification. It appears that when the wood was not highly delignified, i.e. at higher kappa numbers, the molecular weight was lower. There seemed to be a maximum in molecular weight around kappa number 70, where after the molecular weight of the dissolved xylan constantly decreased as the delignification proceeded. It has been shown that the pore size of the fibre wall increases as the degree of delignification increases (Andreasson et al. 2003). It might be assumed that as delignification leads to larger the pores in the fibre wall, larger xylan molecules, earlier entrapped in the fibre wall, to be dissolved. However, as the cooking continues the dissolved xylan molecules in the black liquor will be degraded by the alkaline hydrolysis and the peeling reactions, causing the decrease of the molecular weight.

In *Fig 4*, the decrease in the amount of uronic acid content in dissolved xylan molecules is shown. The original methylglucuronic acid substituents on the xylan backbone undergo a number of reactions during the kraft cook. Through elimination of methanol, they can be converted to hexenuronic acids (Clayton 1963; Johansson, Samuelsson 1977; Telemann et al. 1995). As has been shown earlier for birch xylan dissolved in black liquor, the uronic acid content decreases with prolonged cooking time (Axelsson et al. 1962).

It seems from *Fig 4*, that cooking a higher temperature eliminated the amount of uronic acid groups faster. This finding is in accordance with what has been found for cooking of birch (Danielsson et al. 2006). A higher ionic strength also seemed to increase the elimination rate. When the amount of uronic acid groups in dissolved xylan is plotted as a function of kappa number, *Fig 8*, the amount at a given kappa number seems to be independent of However, when the cook had been

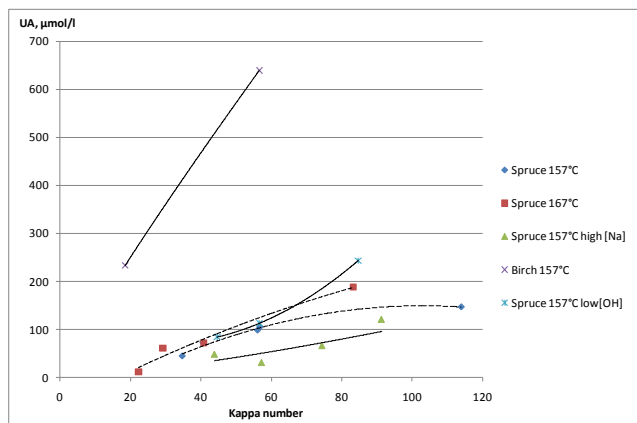


Fig 8. Uronic acid group content in dissolved xylan in black liquor vs the kappa number of the corresponding pulp.

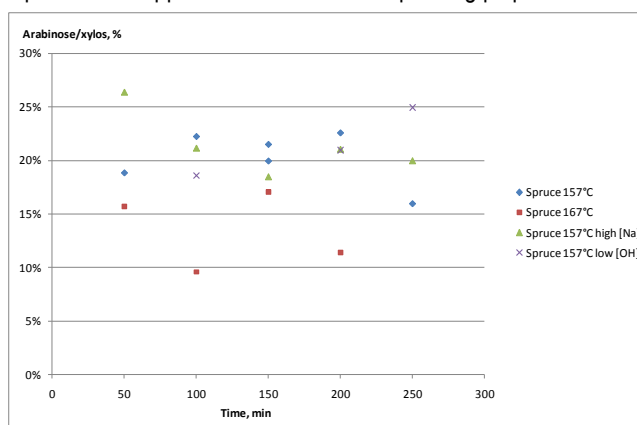


Fig 9. Arabinose content in dissolved xylan.

performed at a higher ionic strength, the amount of uronic acid groups was lower at a given kappa number.

Softwood xylan is substituted with arabinose units. As seen in *Fig 9*, the arabinose content of the xylan precipitate correlated well with the xylose content, suggesting that the degree of arabinose substituents remained the same in the dissolved xylan. There was a slight tendency however, that cooking at a higher temperature resulted in lower degree of arabinose substituents.

## Conclusions

Dissolved softwood xylan contained a much higher amount of bound lignin than what has earlier been reported for birch and eucalyptus xylan

- The molecular weight of the dissolved xylan depended on the degree of delignification of the wood matrix. Delignification of the wood matrix down to kappa number approximately 70 enabled larger xylan molecules to dissolve into the black liquor. Further delignification led to a degradation of the dissolved xylan molecules.
- The ionic strength of the cooking liquor affected the amount of xylan dissolved as well as the uronic acid content of the xylan. Higher ionic strength

gave less xylan dissolved and lower uronic acid content.

- Increased temperature increased the dissolution rate of xylan from the wood matrix. However, at the same degree of delignification of the wood matrix, temperature had no effect on the amount dissolved or the molecular weight of the dissolved xylan.

---

## Acknowledgements

This work was carried out within CRUW (Cooperative Research on the Ultrastructure of Wood Fibres) with financial support from the VINNOVA's Branch Research Program and 6 supporting pulp and paper and chemical industries (Eka Chemicals, Holmen, SCA, SmurfitKappa, Stora Enso, Södra Cell). Docent Jiebing Li is acknowledged for valuable discussions.

---

## Literature

- Andreasson, B., Forsström, J., and Wågberg, L.** (2003): The porous structure of pulp fibres with different yields and its influence on paper strength, *Cellulose* 10(2):111-123.
- Axelsson, S., Croon, I. and Enström, B.** (1962): Dissolution of hemicelluloses during sulphate pulping Part 1. Isolation of hemicelluloses from the cooking liquor at different stages of a birch cook, *Svensk papperstidn.*, 65(18):693-697.
- Clayton, D. W.** (1963): The alkaline degradation of some hardwood 4-O-methyl-D-glucuronoxylans, *Svensk Papperstidn.*, 66(4):115.
- Clayton, D. W. and Stone, J. E.** (1963): The redeposition of hemicelluloses during pulping. i. The use of tritium labelled xylan, *Pulp and Paper Magazine of Canada*, 64(11):T469.
- Danielsson, S. and Lindström, M.E.** (2005): Influence of birch xylan adsorption during kraft cooking on softwood pulp strength, *Nordic Pulp Paper Res J.* 20(4):436
- Danielsson, S., Kisara, K., and Lindström, M.E.** (2006): Kinetic study of hexenuronic and methylglucuronic acid reactions in pulp and in dissolved xylan during kraft pulping of hardwood, *Ind Eng Chem Res* 45(7):2174-2178
- Danielsson, S.** (2007): Xylan reactions in kraft cooking, Doctoral thesis in Pulp and Paper technology, Paper V, KTH, Stockholm, Sweden.
- Danielsson, S., and Lindström, M.E.** (2009): The effect of black liquor exchange in the kraft cook on the tensile properties of Eucalyptus Urograndis pulp, *Papel*, 70(4):35-50.
- Engström, N., Vikkula, A., Teleman, A., and Vuorinen, T.** (1995): Structure of hemicelluloses in pine kraft pulping liquors, 8<sup>th</sup> ISWPC, Helsinki, Finland, 195-200.
- Eriksson, Ö., Goring, D., and Lindgren, B.** (1980): Structural studies on the chemical bonds between lignins and carbohydrates in spruce wood, *Wood Sci. Technol.* 14(4):267-279.
- Fengel, D. and Wegener, G.** (1989): *Wood chemistry, ultrastructure, reactions*, Walter de Gruyter, Berlin, New York. p. 108
- Green, J., Pearl, I., Hardacker, K., Andrews, B., and Haigh, F.** (1977): The peeling reaction in alkaline pulping, *Tappi* 60(10):120-125.
- Gustavsson, C. and Al-Dajani, W.** (2000): The influence of cooking conditions on the degradation of hexenuronic acid, xylan, glucomannan and cellulose during kraft pulping of softwood, *Nordic Pulp Paper Res. J.* 15(2):160-167.
- Haas, D., Hrutfiord, B. and Sarkanen, K.** (1967): Kinetic study of the alkaline degradation of cotton hydrocellulose, *J. Appl. Polymer Sci.*, 11, 587-600.
- Johansson, D. and Germgård, U.** (2008): Carbohydrate degradation during softwood kraft cooking –influence on cellulose viscosity, carbohydrate composition and hexenuronic acid content, *Nordic Pulp Paper Res J* 23(3):292-298.
- Johansson, M. and Samuelson, O.** (1977): Reducing end groups in birch xylan and their alkaline degradation, *Wood Sci. Technol.* 11:251-263.
- Li, J., Kisara, K., Danielsson, S., and Lindström, M.** (2007): An improved methodology for the quantification of uronic acid units in xylans and other polysaccharides, *Carbohydrate Res.* 342(11):1442-1449
- Lisboa, S., Evtugin, D., Neto, P., and Goodfellow, B.** (2005): Isolation and structural characterization of polysaccharides dissolved in Eucalyptus globules kraft black liquor, *Carbohydrate Polymers*, 60, 77.
- Sjöberg, J., Kleen, M., Dahlman, O., Agnemo, R., and Sundvall, H.** (2004): Fiber surface composition and its relations to papermaking properties of soda-anthraquinone and kraft pulps, *Nordic Pulp Paper Res. J.* 19(3):392
- Sjöström E.** (1993): *Wood Chemistry Fundamentals and applications*, San Diego: Academic Press, Chapter 3.
- Tamminen, T., Vuorinen, T., Tenkanen, M., Hausalo, T., and Hortling, B.** (1995): Analysis of lignin and lignin-carbohydrate complexes isolated from black liquor, 8<sup>th</sup> ISWPC, Helsinki, vol II, 297-302.
- Teleman, A., Harjunpää, V., Tenkanen, M., Buchert, J., Hausalo, T., Drakenberg, T., and Vuorinen, T.** (1995): Characterization of 4-deoxy-β-L-threohex-4-endopyranosyluronic acid attached to xylan in pine kraft pulp and pulping liquor by carbon-13 and proton NMR spectrometry, *Carbohydrate Res.* 272(1):55.
- Theander, O. and Westerlund, E.** (1986): Studies on dietary fiber. 3. Improved procedures for analysis of dietary fiber, *J. Agricultural Food Chem.*, 34:330-336
- Yllner, S. and Enström, B.** (1956): "Studies of the absorption of xylan on cellulose fibers during the sulphate cook. Part 1", *Svensk Papperstidning* 59(6):229
- Yllner, S. and Enström, B.** (1957): "Studies of the absorption of xylan on cellulose fibers during the sulphate cook. Part 2", *Svensk Papperstidning* 60(15):549
- Westbye, P., Köhnke, T., Glasser, W. and Gatenholm, P.** (2007): The influence of lignin on the self-assembly behaviour of xylan rich fractions from birch, *Cellulose* 14:603

Manuscript received January 28, 2011

Accepted May 5, 2011