

SORPTION AND DESORPTION OF BLACK LIQUOR XYLAN ONTO CELLULOSE FIBERS – A NEW SEPARATION TECHNIQUE

SVERKER DANIELSSON

Innventia AB, Stockholm, Sweden

✉ *Corresponding author: sverker.danielsson@innventia.com*

The potential of xylan as a polymer in different new materials is large and not yet utilized. The availability in kraft pulp mills is large as the polymeric xylan dissolved in process liquors corresponds to up to 160 kg/adt and is today burnt to recover energy. A pre-requisite for using black liquor xylan in high-value products is to purify it from inorganic material and lignin in a technically effective and economical feasible way. This study combines two known properties of xylan: its affinity to cellulose and its solubility in alkali. The aim is to design an efficient separation process to produce black liquor xylan of high purity. A very pure xylan was reached with as low lignin contents as 1%. The hydroxide ion concentration was varied in the sorption step and it was found that an increase in hydroxide ion concentration resulted in a decreased amount of isolated xylan, decreased degree of substitution of uronic acids, but no effect on the lignin content and ash content was seen.

Keywords: hardwood xylan, kraft pulping, separation, purification, precipitation, 4-O-methylglucuronic acid, hexenuronic acid, black liquor

INTRODUCTION

In the kraft pulping process, large amounts of xylan are dissolved in the cooking liquor and end up as heat in the recovery boiler. The liquor is an attractive source for xylan production as the availability is high and the heat value for xylan relatively low. Dissolved xylan is a polymer and holds a great potential as a raw material for many different products such as oxygen barriers in packaging, paper strength additive or consistency contributor. The great challenge in designing a xylan production process is the development of technically effective and economically viable separation stages in order to produce xylan with high purity. The highest concentration of xylan in black liquor is found early in the birch kraft cooks. Peak concentration of xylan from 8-10 g/L¹ up to around 20 g/L^{2,3} have been reported for laboratory kraft cooks of birch. The lignin content in early withdrawn cooking liquors is relatively low. This makes the early cooking liquor more promising than liquors withdrawn later or even after the cook. When xylan is precipitated in alcohol from black liquor, lignin and inorganic salts are also precipitated. These are usually difficult to separate from the pure xylan, which is a prerequisite when xylan is to be used in high value products. There is a need of a more selective separation process than direct precipita-

tion from black liquor. The separation technique used in this study combines two well-known phenomena of dissolved xylan in alkali: the tendency of attaching to cellulose fibres⁴⁻⁷ and the possibility of dissolving xylan in alkali.⁸⁻¹⁰ Lignin seems on the other hand not to be molecularly adsorbed on cellulose, but rather to be washed away from the pulp.¹¹ These known properties motivated an evaluation of a sorption-desorption separation method.

A study of sorption-desorption of xylan on pulp fibers was carried out to investigate the potential of such a technique as a separation process. The idea is to use pulp fibers as providers of cellulose surfaces at which sorption can take place. The fibers will not be used in any product. The goal is to find a process to produce xylan with high purity from black liquor that can be implemented industrially. The invented process is depicted in Figure 1.

EXPERIMENTAL

Kraft cooking and ultrafiltration

To produce black liquor, a kraft cook was performed as follows. Dried Scandinavian hardwood chips (80% birch and 20% aspen) with the total dry weight of 40 kg were charged to a cooking vessel, which was evacuated prior to the charge of cooking

chemicals. A conventional kraft cook was carried out with the liquor to wood ratio of 6:1, effective alkali of 18% and sulfidity of 35%. The initial cooking temperature was 25 °C and the temperature was raised 1°C/min. When 130 °C was reached, the cook was

interrupted and the cooking liquor was collected after cooling. 110 liters of black liquor was ultrafiltered at 120 °C through a ceramic membrane with the cut off 15 kDa. The final volume of retentate was 15 liters.

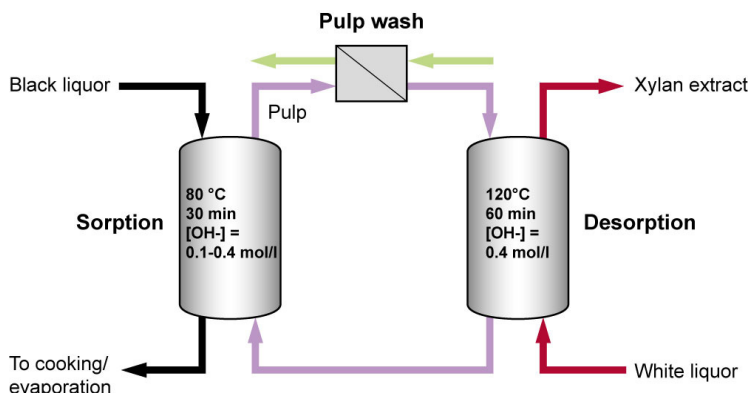


Figure 1: A potential xylan separation process based on the sorption-desorption technique

Table 1
Mass balance for ultrafiltration

| | Black liquor | Diafiltration H ₂ O | Permeate | Retentate |
|-----------------------|--------------|--------------------------------|----------|-----------|
| Xylose (g) | 606 | | 38 | 442 |
| Lignin (g) | 1588 | | 1032 | 101 |
| Sulphur (g) | 840 | | 803 | 25.5 |
| Sodium (g) | 3768 | | 3543 | 144 |
| Calcium (g) | 3.9 | | 2.6 | 0.56 |
| Ash (kg) | 9.9 | | 9.9 | 0.4 |
| Total dry matter (kg) | 12.5 | 0 | 11.6 | 1.1 |
| Total wet mass (kg) | 126 | 30 | 140 | 14 |

Numbers are calculated based on total weight and results from the analysis of samples from the respective liquid

Sorption-desorption of black liquor xylan

An ECF bleached softwood pulp was treated either with the retentate from an ultrafiltration of the black liquor or the black liquor itself at specific hydroxide ion concentration (0.1-0.4 mole/L) and sodium ion concentration (0.5 & 1.0 mole/L), adjusted by addition of sodium hydroxide and sodium carbonate. The fiber/liquor suspension was thoroughly mixed and put in a water bath at 80°C for 70 minutes. The pulp was dewatered and washed twice with 25 mL/g fiber deionized water at 60°C. The xylan-sorbed pulps were subjected to alkaline extraction in order to desorb the xylan molecules in the following way. The pulps were treated in alkali solutions of 0.4 mole/L sodium hydroxide at a pulp concentration of 10% at 120°C for 70 minutes. The free liquor was collected as the pulp was filtered off. Xylan was precipitated by adding 500 mL ethanol to 500 mL filtrate at pH 12. The solids were separated by centrifugation and washed once with 100 mL 50% ethanol solution. The light phase was decanted off and the samples were dried at room temperature in a fume hood overnight.

Analysis

The wood raw material was dried and ground. Wood and xylan samples were subjected to acid hydrolysis (SCAN-CM 71:09) and characterized with respect to their chemical composition (carbohydrates quantified with ion-chromatography and IC-PAD, SCAN CM 71), acid-insoluble lignin (gravimetric TAPPI T222 om-00) and acid-soluble lignin (UV-spectrophotometry at 205 nm, absorptivity coefficient 128 L/g, cm). The ash content was determined through combustion of the sample at 550°C (SS-EN14775:2009) & (ISO1762) and the metal content was determined through ICP-AES. For some samples, the total carbohydrate composition was determined through enzymatic hydrolysis.¹² The kappa number (ISO 302:2004) was also used to estimate the lignin content of some samples. Cooking liquors were analyzed regarding their hydroxide ion concentration (SCAN-N 33:94) and hydrogen sulfide ion concentration (SCAN-N 31:94).

RESULTS

Xylan separation by membrane filtration

As black liquor as such is rather low in xylan content and rich in both ash and lignin, a pre-treatment was included in the study where the black liquor was membrane filtered. This opened opportunities to study the process in a wider range of hydroxide ion concentration. Table 1 shows a mass balance over the ultrafiltration. Polymeric xylan is concentrated as low-molecular weight substances passing through the membrane.

The xylose concentration is increased 6 times and the lignin content is halved from virgin black liquor. The total amount of outgoing xylose differs from the total amount of ingoing xylose. The reason is likely an effect of degradation reactions of xylose similar to those in the kraft cook.^{13,14} The total inorganic material is effectively separated from xylose, with the exception of the divalent ions such as calcium. This is in accordance with earlier findings (e.g.).^{15,16}

Amount of sorbed and desorbed material

Both retentate from ultrafiltered black liquor and black liquor as such sorbed on fully bleached pulp fibers and desorbed by alkaline extraction. In order for xylan to attach onto cellulose fibers, the attractive non-electrostatic forces must overcome the electrostatic repulsion between the negatively charged polymer and the negatively charged cellulose surface. At high sodium ion concentration, the electrostatics is screened more efficiently and the tendency of xylan to adsorb is thus increased, as seen in Figure 2. The amount of sorbed and desorbed material decreases with an increased hydroxide ion concentration in the sorption step as seen in Figure 2. This was expected as xylan is more soluble at high alkalinities.¹⁷ The amount produced from black liquor as such is a third of what was seen for the same treatment of retentate, whereas the xylan concentration differs by a factor of 6. It is also seen that at the sodium ion concentration of 1 mole/L, the amounts of xylose recovered at the hydroxide ion concentration of 0.1 and 0.2 mole/L are the same.

The amount of dry matter in the precipitate is very dependent on the dryness of the pulp after desorption. In the case shown, the dryness was around 20%, which means 80% of the wet pulp mass is actually extract liquid containing the same concentration of xylan as the collected extract. In an industrial process the liquids and pulps will be

recirculated and hence it can be assumed that also the xylan in the trapped liquid will finally be found in the precipitate. If it is assumed that all extract liquid is taken care of, the total yield from the black liquor to precipitate is between 40% and 60% at the hydroxide ion concentration of 0.3 mole/L. For the retentate, the yield was only 20% at the same hydroxide ion concentration and around 30% at its maximum ($[\text{OH}^-] = 0.1-0.2$). The reason is that the pulp fibers are likely saturated with xylan and there was a surplus of xylan in the sorption step when retentate was used, while and when black liquor as such was used, the match between available cellulose surface and xylan present was better.

Chemical composition of sorbed and desorbed material

The isolated xylan samples were analyzed by enzymatic hydrolysis and the xylan content and total carbohydrate contents are shown in Figure 3.

The hydroxide ion concentration also affects the xylan content as seen. A low hydroxide ion concentration in the sorption stage seems to yield high amounts of a relatively pure xylan product. High ionic strength during sorption also seems to be positive for the purity of the xylan. Sorbed and desorbed xylan from unfiltered black liquor contains more of other carbohydrates than xylose, mainly glucose and arabinose, compared to the xylans originating from the ultrafiltration retentate. The reason is likely that the alkaline extraction also dissolves these carbohydrates and when a small amount of xylan is sorbed onto the pulp, the dissolution of other carbohydrates is relatively greater.

The hexenuronic acids contribute to the charge of xylan, influencing its solubility in water. Also the methylglucuronic acids are charged and, in Figure 4, the degree of substitution of both types of uronic acids is shown for the xylan samples. At high alkalinities, highly charged xylan stays in solution. The xylan that originates from black liquor as such contains smaller amounts of uronic acids and very small amounts of hexenuronic acids. This is explained by peeling reactions of unsubstituted segments of xylan that does not only take place in cooking but also in ultrafiltration. The results show that conditions in the sorption stage can be chosen to produce a high or low uronic acid content, depending on the wanted product properties.

As hexenuronic acid is a part of xylan it should not be seen as impurity of the product. To

estimate the lignin content the “non-HexA” kappa number is used, meaning the hexenuronic acid kappa number subtracted from the measured kappa number according to Li and Gellerstedt.¹⁸

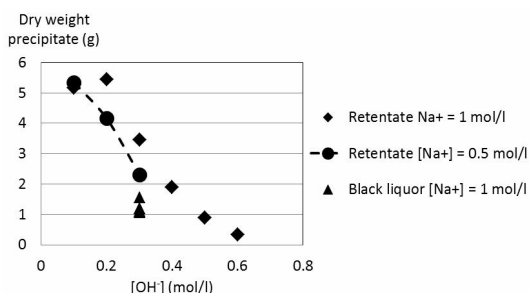


Figure 2: Weight of dry precipitate collected from 1 kg of extract, plotted against the hydroxide ion concentration during sorption of xylan onto pulp fibers. The sodium ion concentrations denote the condition in the sorption stage. During desorption, constant conditions were used

As seen in Figure 5, the lignin content is not very different between the samples, but they all have a “lignin” kappa number between 5 and 9. If the correction factor of 6.161 kappa units per % lignin¹⁹ for birch pulp is used, the lignin content can be estimated to range between 0.9 and 1.4%. This value should only be seen as an indication of the lignin content and not mixed up with more accurate methods. These lignin contents are all very low and could be parts of the so-called lignin-carbohydrate complexes,²⁰ which in that case are very difficult to separate from xylan. To purify the xylan further from lignin, it might be necessary to bleach the xylan, by e.g. oxygen delignification or peroxide bleaching. The largest impurity in this xylan is however inorganic material, as can be seen in Figure 6. The ash

Of course, other carbohydrate structures could also be present and contribute to the kappa number, but those should be small and are thus neglected in this study.

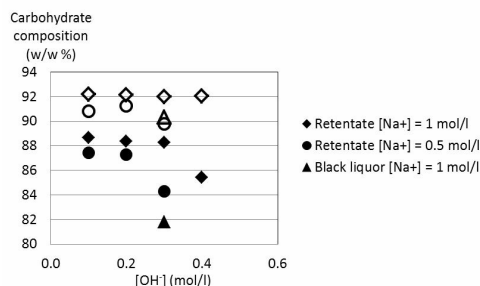


Figure 3: Xylan content is denoted by filled symbols and the total carbohydrate content by unfilled symbols for same samples as in Figure 1. The values were calculated by assuming no significant mass contributor other than lignin, carbohydrates and ash. The total analytical yield for all samples is in the range 95-101%

content is between 6 and 8% for these xylan samples and quite surprisingly it seems like higher ionic strength in the sorption stage yields xylan with lower amounts of ash compared to when the sorption was carried out at lower ionic strength. The electrostatics are effectively screened at high ionic strength and more xylan can attach as seen in Figure 2. The high ionic strength may also affect the interaction of xylan and calcium, as they are attached by ionic bonds.

Overall, it seems like high ionic strength is an advantage both in terms of xylan recovery and purity of the product. The hydroxide ion concentration affects the xylan recovery and the charge of the xylan product, but does not seem to influence the purity in terms of lignin content and ash content.

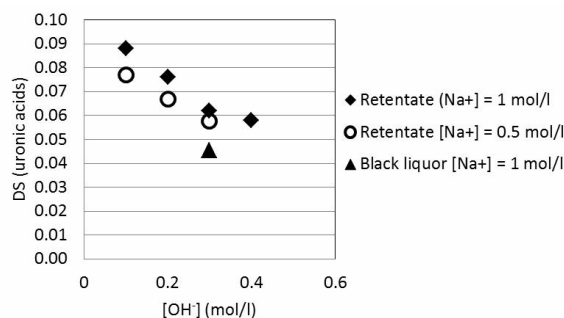


Figure 4: The degree of substitution of isolated xylans as a function of hydroxide ion concentration

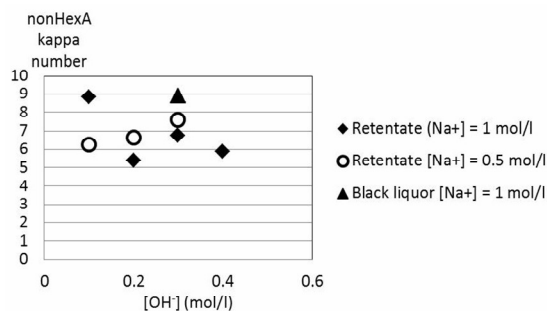


Figure 5: Kappa number contribution from non HexA structures, mostly lignin

Industrial application

The separation technique suggested in this paper consists in well-known unit operations at mill scale. The conditions in the sorption stage are similar to those in oxygen delignification and it would be possible to perform at industrial scale. The pulp is then washed according to a standard procedure. The excess black liquor can be transferred directly back to the digester or to the evaporation unit to recover cooking chemicals, whereas the pulp with sorbed xylan enters a desorption/extraction stage. This type of alkaline extraction of bleached kraft pulp to recover xylan has been tried at pilot scale and seems possible to implement it in the industrial process.²¹ Desorbed pulp is finally used again when new black liquor is added to the sorption stage, as shown in Figure 1.

CONCLUSION

- The sorption-desorption technique was found to be successful.
- High ionic strength during sorption yields xylan with high purity (6% ash and 1% lignin) and high recovery.
- The amount of sorbed material was decreased by an increase in hydroxide ion concentration, as expected.
- The degree of substitution for isolated xylans was decreased by an increase of the hydroxide ion concentration during sorption.
- It seems possible to exclude the membrane filtration in this process.

ACKNOWLEDGEMENTS: RISE Holding is acknowledged for funding this project in 2010 and Mikaela Kubat is recognized for her skilful laboratory work. Fredrik Lundqvist and Peter Axegård are acknowledged for having initiated

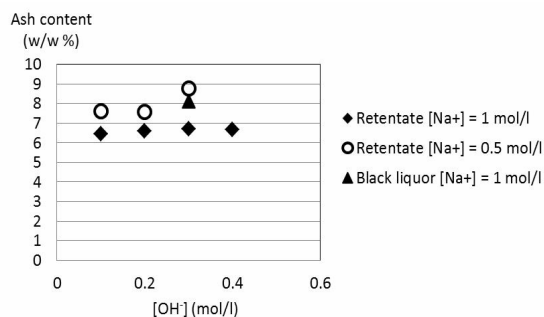


Figure 6: Ash content of the produced xylan samples

the idea and Fredrik Öhman for valuable discussions.

REFERENCES

- ¹ R. Simonson, *Sven. Papperstidn.*, **68**, 275 (1965).
- ² S. Axelsson, I. Croon, and B. Enstrom, *Sven. Papperstidn.*, **65**, 693 (1962).
- ³ S. Danielsson and M.E. Lindström, *Nordic Pulp Pap. Res. J.*, **20**, 436 (2005).
- ⁴ S. Yllner and B. Enström, *Sven. Papperstidn.*, **59**, 229 (1956).
- ⁵ S. Yllner and B. Enström, *Sven. Papperstidn.*, **60**, 549 (1957).
- ⁶ D.W. Clayton and J.E. Stone, *Pulp Pap. Mag. Can.*, **64**, 11 T459 (1963).
- ⁷ J.A. Hansson and N. Hartler, *Sven. Papperstidn.*, **72**, 521 (1969).
- ⁸ J. Saarnio and C. Gustafsson, *Pap. Timb.*, **115**, 65 (1953).
- ⁹ W. Corbett and J. Ewart, *Sven. Papperstidn.*, **62**, 277 (1959).
- ¹⁰ R. Scott, *J. Wood Chem. Technol.*, **4**, 199 (1984).
- ¹¹ N. Maximova, P. Stenius, and J. Salmi, *Nordic Pulp Pap. Res. J.*, **19**, 135 (2004).
- ¹² O. Dahlman, A. Jacobs, A. Liljenberg and A. I. Olsson, *J. Chromatogr. A*, **891**, 157 (2000).
- ¹³ I. Forsskåhl, T. Popoff and O. Theander, *Carbohydr. Res.*, **48**, 13 (1976).
- ¹⁴ M.J. Antal Jr., T. Leesomboon, W. S. Mok and G. N. Richards, *Carbohydr. Res.*, **217**, 71 (1991).
- ¹⁵ F. Lundqvist, in "Report number 2009-476, STFI-Packforsk", 2009.
- ¹⁶ O. Wallberg, M. Linde, and A.-S. Joensson, *Desalination*, **199**, 413 (2006).
- ¹⁷ R. Aurell, *Sven. Papperstidn.*, **66**, 437 (1963).
- ¹⁸ J. Li and G. Gellerstedt, *Carbohydr. Res.*, **302**, 213 (1997).
- ¹⁹ B. Kyrklund and G. Strandell, *Pap. Puu*, **51**, 299 (1969).
- ²⁰ M. Lawoko and A.R.P. van Heiningen, *J. Wood Chem. Technol.*, **31**, 183 (2011).
- ²¹ E. Saukkonen, K. Lyytikäinen, and K. Backfolk, *Tappi J.*, **11**, 37 (2012).

