

# The influence of hemicelluloses during the precipitation of lignin in kraft black liquor

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**SUMMARY:** Removing lignin from black liquor is one way of recovering valuable organic substances for alternative use as well as reducing the energy surplus in a modern, energy-optimised kraft pulp mill. By using the recently developed “LignoBoost” process it is possible to upgrade black liquor streams of different origin to form valuable chemicals. In this investigation a combination of membrane filtration and the LignoBoost concept was used. The primary objective of the work was to investigate whether or not the filtration properties of the black liquor were affected by its hemicellulose content. The hemicellulose content in the black liquors was lowered prior to precipitation using three different pre-treatment techniques, and the filtration properties were compared to the reference black liquors of evaporated softwood and hardwood black liquor. The pre-treatment methods used were heat-treatment, ultrafiltration and a combination of ultrafiltration and nanofiltration. It was shown that the filtration resistance was lowered considerably when the hemicellulose content in the black liquor was reduced prior to precipitation. The experiments also showed that it was possible to produce a hardwood lignin product of high purity i.e. low sodium (0.2 w-% of TDS) and hemicellulose content (0.7 w-% of TDS)

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The black liquor produced by kraft pulp mills plays a key role in being a potential source of renewable energy and a raw material for the chemical industry. The scale of the pulp and paper industry is such that huge volumes of bio-feedstock and large production units with good scale economy are available. Furthermore, since the organic material in the black liquor already is partly processed, and part of the organic material has already been separated off (i.e. the cellulose), a large part of the separation work has already been done. A kraft pulp mill using the best technology available has a large surplus of bio-material. This surplus is currently being burnt and some electrical power is produced. In the future, a modern mill cannot only be regarded as a supplier of sustainable produced pulp fibres, but also as a supplier of other bio-based materials/chemicals, e.g. lignin and

xylose. Apart from the potential of being used as a solid biofuel, refined lignin also has the potential of being a raw material for several new products such as carbon fibres/materials, phenols, adhesives/binders, dispersant and metal chelating agents. Neither phenols nor carbon fibres are currently being produced from renewable raw material.

There are currently two interesting methods being used to remove lignin from black liquor. One is the recently developed LignoBoost process that allows a solid lignin, with a high degree of purity, to be separated from black liquor (Öhman et al., 2007a). The second method is membrane-based (e.g. ultrafiltration); in this case, a solution with rather a high concentration of lignin can be obtained (Wallberg et al., 2003). Various aspects of the LignoBoost process have been investigated in a series of papers (e.g. Öhman et al., 2007a, 2007b, 2007c) and, among other things, it was found that the filtration properties of the lignin produced may be influenced by the hemicellulose content. The membrane method has also been investigated recently in several papers (e.g. Wallberg et al., 2003, Wallberg et al., 2006). It was found, among other things, that it is possible to decrease the hemicellulose concentration of the lignin-rich stream from the membrane separation unit.

In this investigation several different black liquors of varying hemicellulose content have been used in lignin extraction experiments using the LignoBoost process. The primary objective of the work was to use different pre-treatment techniques to lower the content of hemicellulose in the black liquor prior to precipitation and to investigate the filtration properties of the precipitated lignin. Reference tests were made using evaporated softwood and hardwood black liquor. Three different pre-treatment methods were used: heat-treatment, ultrafiltration and a combination of ultrafiltration and nanofiltration. In addition, displacement washing of the precipitated lignin was performed with the aim of producing a highly purified grade of lignin for possible use as a raw material for chemical products, using hardwood black liquor (birch) as the raw material.

## Materials and Methods

### Precipitation, filtration and washing

#### Precipitation

The precipitation experiments were carried out at atmospheric pressure in a tank reactor with a total volume of 2.5 litres and equipped with four baffles. The reactor was immersed in an oil bath to control the temperature during

the experiments. Carbon dioxide was introduced via a sparger located underneath the impeller. The solution was stirred during carbonation with a Rushton turbine to provide adequate mixing conditions and a high mass transfer rate of carbon dioxide to the liquor. During precipitation, small samples of black liquor were removed from the reactor at different time intervals by means of a syringe, and the pH was measured.

Prior to each experiment approximately 2 litres of black liquor was weighed and loaded into the reactor. Once the target temperature was reached, carbon dioxide was allowed to bubble thorough the liquor at a constant flow of 1.0 L/min to obtain the target pH. The solution was stirred at a constant speed of 300 rpm during precipitation. When the target pH was reached the suspension was left with the stirring equipment in operation for another 60 min at the target temperature to allow for the complete reaction and formation of the precipitate.

### Filtration

After precipitation the suspensions were transferred to test filter equipment (filter area of 20 cm<sup>2</sup>) designed to provide well-defined conditions during filtration: constant pressure and constant solids concentration of the feed suspension. After transfer of the suspension into the storage vessel (a pressure vessel equipped with a mixer), it was pressurized, using compressed air, and a valve was opened to start the filtration process. More details can be found elsewhere (Öhman and Theliander 2007).

The precipitate was filtered through a filter medium (a standard filter cloth from Tamfelt S-2108-L1) at constant pressure of 1.5 bar. The filtration time and filtrate weight was recorded for every experiment so that the filtration properties of the lignin could be analysed. The filter cake was removed for weighing and analysis of its dry content directly after filtration. Part of the filtrate was transferred to a capped bottle where it was allowed to cool to room temperature before further analysis. The experiment was stopped at this point when the filtration properties of the intermediate product, i.e. unwashed lignin, were to be evaluated.

### Washing

The unwashed lignin was re-dispersed in 200 ml of de-ionised water when the average specific filtration resistance of the second filtration step and washing characteristics of the precipitated lignin were to be evaluated. The pH of the slurry was adjusted to 2 by the addition of 6M H<sub>2</sub>SO<sub>4</sub> and the solution was stirred for an additional 30 minutes before being transferred to a laboratory piston filter press with a filter area of approximately 20 cm<sup>2</sup> and a volume of 0.15 dm<sup>3</sup>. The suspension was filtered at a constant pressure of 1.5 bar and the filtrate weight and time were recorded. Further details can be found elsewhere (Öhman 2006). A sample of the filtrate was removed for further analysis. The lignin was washed by applying wash water (de-ionised water pH-adjusted with H<sub>2</sub>SO<sub>4</sub> to the same level as in the re-slurry stage) through the piston at a constant pressure of 0.5 bar. Small samples of the spent wash water leaving the cake were taken continuously during the washing pro-

cedure, whilst time and filtration weight were noted until a filtrate weight of 1 kg was obtained.

## Pre-treatment methods

### Heat treatment

Heat treatment involved the black liquors being held at 170°C in rotating autoclaves immersed in a temperature controlled oil bath for 3 hours. Details of the equipment can be found elsewhere (Bogren et al., 2007).

### Ultrafiltration and nanofiltration

Experiments were performed with the aim of fractionating lignin and hemicelluloses by ultrafiltration prior to the precipitation of hardwood lignin. Two hardwood liquors were used as feed in the membrane experiments: evaporated black liquor (withdrawn from the evaporation unit) and non-evaporated black liquor (withdrawn before the evaporation unit). Only a brief summary of the procedure is presented below. A detailed description of the equipment and experimental procedure used in the separation of lignin and hemicelluloses in black liquor by membrane filtration can be found elsewhere (Jönsson and Wallberg 2008 and Jönsson et al., 2008 and Jönsson and Wallberg 2009).

The lignin and hemicelluloses in the black liquor were separated by ultrafiltration (UF). A ceramic KERASEP membrane from Orelis (now Novasep), France, with a cut-off of 15000 g/mole, was used. The black liquor was concentrated by withdrawing permeate whilst recycling the retentate into the feed tank. The transmembrane pressure was 100 kPa, the cross-flow velocity 5 m/s and the temperature 90°C during the concentration procedure. The volume reduction VR (defined as the ratio between the permeate volume withdrawn and the initial feed volume) was 66% during ultrafiltration of evaporated black liquor and 90% during ultrafiltration of non-evaporated black liquor (i.e. withdrawn before the evaporation unit). The lower volume reduction in the experiment with the evaporated black liquor is due to its higher initial concentration.

The concentration of lignin in the permeate after ultrafiltration in the evaporated black liquor experiment was high enough for precipitation. The concentration of lignin in the permeate obtained from ultrafiltration of the non-evaporated black liquor was, on the other hand, very low. The lignin in this permeate was therefore concentrated by nanofiltration (NF). A polymeric NF membrane with excellent alkali stability, Koch SelRO<sup>®</sup> MPT-36 manufactured by Koch Membrane Systems, was used. The cut-off of this membrane is 1000 g/mole. Volume reduction of the UF permeate (VR=70%) was performed at 60°C; the transmembrane pressure was 2.5 MPa and the cross-flow velocity 4 m/s. *Fig 1* shows a simple schematic flow sheet of the membrane experiments.

### Analyses

The total dry solids (TDS) content of black liquors and filtrated was determined by drying weighed samples at 105°C for 24 hours and determining the weight of the

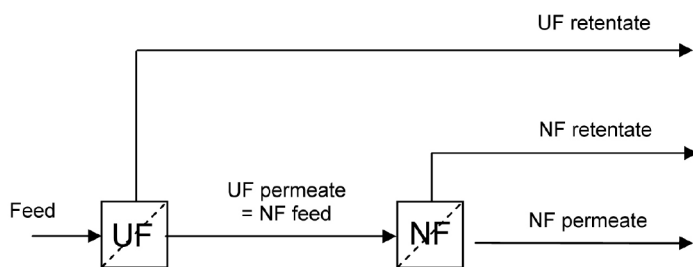


Fig 1. A schematic flow sheet of the membrane trials. UF = Ultrafiltration, NF = Nanofiltration.

residue. The error using this method was estimated to be less than 0.5%. The density was determined by weighing samples in a calibrated 25 ml volumetric flask; error estimated to be  $\pm 0.3\%$ . Sodium concentrations of black liquor, filtrates and solid lignin were measured after wet combustion in a microwave oven (Varian AAS). The viscosity was measured using a rheometer from Bohlin instruments (CS50) equipped with an integrated temperature controlled oil bath. The error from the viscosity measurements was estimated to be  $\pm 1\%$ . From these data the total error for the average specific filtration resistance was calculated to be less than 2%.

UV light absorption at 280 nm was measured using a Shimadzu UV-160 spectrophotometer (Kyoto, Japan). The samples were diluted with 0.1 M NaOH prior to measurement. The absorption constant used for softwood lignin was 24.6 (litre/g·cm) (Fengel et al., 1981) and for hardwood lignin 21.2 (litre/g·cm). The value for hardwood lignin was obtained by linear regression of a plot of UV absorbance data and lignin concentration determined by Klason lignin and acid-soluble lignin in hardwood liquors from pulp mill C. The absorption constant is similar to that determined by Alén and Hartus (1988) for lignin obtained from birch wood pulping, i.e. 20.8 (litre/g·cm).

The concentration of hemicelluloses was measured after acid hydrolysis of the sample. The monosaccharides detected after acid hydrolysis are therefore assumed to originate from polysaccharides. Hydrolysis was performed by adding 72% (w/w)  $H_2SO_4$  to the sample until pH < 1 was reached. The acid hydrolysate was autoclaved at 121°C for 60 minutes before the sample was filtered through a 0.2  $\mu m$  filter prior to analysis. High-performance anion-exchange chromatography, coupled with pulsed amperometric detection (HPAEC-PAD) using an ED40 electrochemical detector (Dionex, Sunnyvale, CA, USA), was used to analyse the monomeric sugars. The chromatograph was equipped with a gradient pump (GP40, Dionex), an autosampler (AS50, Dionex), a Carbo Pac PA1 guard and a PA10 analytical column (Dionex). Millipore water with 2 mM NaOH was used as eluent at a flow rate of 1 ml/min, with an injection volume of 10 ml. D-mannose, D-glucose, D-galactose, D-xylose and L-arabinose (Fluka Chemie AG, Buchs, Switzerland) were used as standards. The amount of sugar was corrected for acid hydrolysis yield.

Acid hydrolysis was performed on lignin samples for Klason lignin, acid-soluble lignin and hemicellulose content, and on black liquors for Klason lignin and acid-

soluble lignin. The samples were hydrolysed in an autoclave at 1.4 bar pressure according to TAPPI T249 cm-00. The lignin samples were extracted with petroleum ether before hydrolysis. The solubilised monosaccharides were quantified using Ion Chromatography with a pulse amperometric detector (IC-PAD). The insoluble residue, i.e. Klason lignin, was measured gravimetrically according to TAPPI T222 cm-00. The acid-soluble lignin was measured with UV at 205 nm with absorptivity factor -113 ( $g^{-1}\cdot cm^{-1}$ ) for hardwood and -128 ( $g^{-1}\cdot cm^{-1}$ ) for softwood.

Two different methods were used to determine the total sulphur content: Schöniger combustion and ICP. The latter method was in fact preferred due to easier sample handling and lower scattering of the results obtained. The experiments to determine the total sulphur content of lignin and black liquors using Schöniger combustion were performed according to SCAN-CM 57:99 and SCAN-N 35:96, respectively. Samples analysed with ICP-AES were prepared by wet digestion according to SCAN-CM 54:97 and SCAN-P 73:97.

The phenolic content was measured spectrophotometrically using Folin Ciocalteu's reagent (de Sousa et al., 2001) with a minor modification: the lignin was dissolved in alkali before dilution with water instead of vice versa.

The molecular mass distributions (MMDs) of lignin were measured with size exclusion chromatography (SEC). Lignin was acetylated in pyridine with acetic acid anhydride. Methanol was added to end the reaction and toluene was added and evaporated three times to remove the solvent. Prior to the measurements being made, the samples were dissolved in tetra hydro furan (THF) and filtrated through a 0.22  $\mu m$  PTFE filter. The chromatographic system consisted of three columns coupled in series: Styragel HR2, Styragel HR1, Ultrastaygel 104Å (Waters Corp.) and a Waters 410 refractive index detector. The system was calibrated with polystyrene standards with peak molecular masses of 106 kDa, 34.5 kDa, 19.9 kDa, 5.03 kDa, 2.36 kDa and 0.58 kDa.

## Filtration theory

The equation used to evaluate the average specific filtration resistance,  $\alpha_m$ , originates from the Darcy equation, which describes a fluid flow through a porous medium. Eq 1 shows a commonly-used form of the filtration equation. The mathematical rearrangement to obtain Eq 1 from Darcy's equation can be found elsewhere (Grén and Theliander 1998).

$$\frac{dV}{dt} = \frac{A\Delta P}{\mu(\alpha_w w_c + R_m)} \quad [1]$$

$V$  is the filtrate volume,  $t$  the filtration time,  $A$  the filtration area,  $\Delta P$  the total pressure drop across the filter cake and filter media (i.e. the driving force behind the separation),  $\mu$  the viscosity of the fluid,  $w_c$  the surface weight of the filter cake and  $R_m$  the resistance of the filter media. Eq 1 can be combined with Eq 2 and integrated over the

filtrate volume and time. By assuming constant filtration pressure and variable flow and after some rearrangements, Eq 3 is obtained.

$$C = \frac{w_c A}{V} \quad [2]$$

$$\frac{t_2 - t_1}{V_2 - V_1} = \frac{\mu}{A^2 \Delta P} \left[ \frac{\alpha_{av} C}{2} (V_2 - V_1) + C \alpha_{av} V_1 + R_m A \right] \quad [3]$$

Eq 3 is very useful in the evaluation of filtration experiments. If  $(t_2 - t_1)/(V_2 - V_1)$  is plotted versus  $(V_2 - V_1)$ , a straight line is obtained, and the average specific filtration resistance ( $\alpha_{av}$ ), can then be calculated from its slope.

## Result and Discussion

### The black liquors used

The pulping liquors used in this investigation were supplied by two Swedish pulp mills. The properties analysed of the black liquors are shown in Table 1. Liquor A1 is a softwood black liquor withdrawn from the 3<sup>rd</sup> evaporation step and liquor C1 is a hardwood black liquor also withdrawn from the 3<sup>rd</sup> evaporation step. Liquor C2 is the same black liquor as C1 with the exception that it was heat treated prior to precipitation. Liquors C3 and C4 are membrane-treated black liquors. In the case when the fractionation of lignin and hemicellulose was performed by ultrafiltration using the evaporated hardwood black liquor (liquor C1), as described above, the concentration of lignin in the permeate was high enough for precipitation (see liquor C3). In the case of the non-evaporated black liquor, however, the amount of lignin in the hemicellulose-depleted permeate was very low. This permeate was therefore subjected to nanofiltration to increase its lignin concentration (liquor C4). The hemicellulose concentration of liquor C4 is rather high due to the concentration step, i.e. nanofiltration, as can be seen in Table 1. However, the molecular mass of the hemicelluloses is significantly lower in this liquor than in the evaporated black liquor, C1, as the high-molecular mass molecules were removed during the preceding ultrafiltration procedure.

Table 1. The analysed properties of the black liquors used in the experiments.

A1	Softwood evaporated liquor withdrawn from the third evaporation stage.							
C1	Hardwood evaporated liquor withdrawn from the third evaporation stage.							
C2	Hardwood evaporated liquor withdrawn from the third evaporation stage; heat-treated.							
C3	Ultrafiltered evaporated black liquor: permeate from ultrafiltration of C1.							
C4	Ultrafiltered and nanofiltrated black liquor: retentate from nanofiltration of ultrafiltered hardwood black liquor withdrawn before the evaporation unit.							

Liquor	UV Lignin <sup>1</sup> (g/l)	TDS <sup>2</sup> (%)	Sodium conc. (g/l)	Hemicelluloses (g/l)	Ara <sup>3</sup> (g/l)	Gal <sup>4</sup> (g/l)	Glu <sup>5</sup> (g/l)	Xyl <sup>6</sup> (g/l)
A1	120	28.2	70.4	4.8	1.1	1.6	0.4	1.5
C1	131	32.7	75.2	15.7	1.7	1.7	1.6	10.7
C2	138	32.3	73.7	7.6	1.3	1.0	0.8	4.5
C3	102	28.5	58.6	4.1	0.7	0.9	0.4	2.1
C4	174	28.6	40.9	9.5	1.3	1.8	0.3	6.1

<sup>1</sup> Constants used: SW = 24.6 litre/g·cm and HW = 21.2 litre/g·cm, <sup>2</sup> TDS = Total Dry Solids,

<sup>3</sup> Ara = Arabinose, <sup>4</sup> Gal = Galactose, <sup>5</sup> Glu = Glucose, <sup>6</sup> Xyl = Xylose

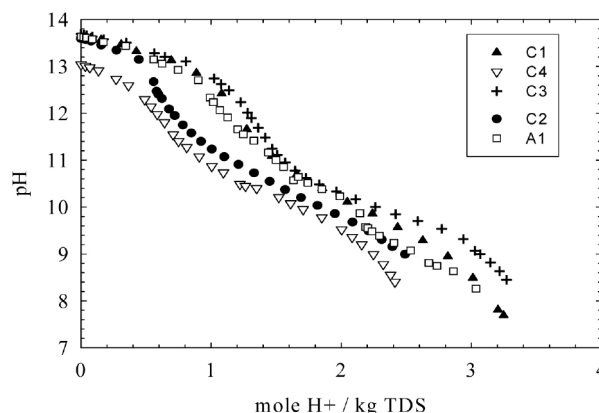


Fig 2. Titration curves for all of the hardwood black liquors investigated.

The results from the titration experiments, using 1M HCl can be seen in Fig 2. The amount of hydrogen ions needed to lower the pH to a certain level (presented in the figure as mole H<sup>+</sup>/kg DS) is an important property when the consumption of carbon dioxide is considered. The first reaction to occur when an acid is added to black liquor to lower its pH is that the hydroxide ions are neutralized by the hydrogen ions. After this has occurred, most of the hydroxide ions are consumed and the hydrogen ions start to neutralize the charged groups on the lignin molecule, i.e. the lignin starts to precipitate. At lower pH levels (~below 11) some hydrogen sulphide and some hydrogen carbonate are formed.

As far as the hardwood black liquors are concerned, liquors C2 and C4 have the lowest consumption of hydroxide ions per kg total dry solids, see Fig 2. The lignin content of liquor C4 is considerably higher due to the concentration process, i.e. nanofiltration. It can also be noticed that there is less residual alkali in these two liquors: the inflection point before the first incline can be observed as early as at around 0.5 mole H<sup>+</sup>/kg TDS, whereas the inflection point for the other liquors is at about 1.0 mole H<sup>+</sup>/kg TDS. Although the solutes are fractionated to a large degree by size during ultrafiltration, there will be no, or negligible, separation of the smallest components (such as the remaining cooking chemicals), so the concentration of these chemicals will be about the same in both the permeate and retentate. This will however affect the amount of hydroxide ions in relation to lignin and other larger molecules. It is also interesting to note that liquor C2, the heat-treated hardwood liquor, contains a lower amount of residual alkali than C1, the untreated hardwood liquor. The most likely explanation here is that some of the alkali has been consumed in various reactions with lignin and/or carbohydrates during heat treatment.

### Precipitation, filtration and washing

All of the black liquors were precipitated to the same pH value of 9.5 except for the heat-treated evaporated liquor, which was precipitated to a value of 9.0. However, different precipitation temperatures were used in order to obtain the best possible conditions for each liquor. A temperature of 75°C was used when liquor A1 was precipitated; during the experiments with the hardwood

evaporated black liquor, C1, and the heat-treated hardwood liquor, C2, the temperature used was 60°C. The temperature during precipitation of the membrane-treated liquors, C3 and C4, was 45°C. When a higher temperature, i.e. 75°C, was used during the precipitation of liquors C2, C3 and C4 large black lumps of lignin were obtained. This may be due to the occurrence of a different coagulation mechanism at higher temperatures that, in turn, results in the formation of denser particles (Norgren and Notley 2007).

### Precipitation and filtration of the evaporated black liquors

Earlier investigations (Öhman and Theliander 2007) have shown that the filtration resistance is affected by the precipitation pH. Fig 3 shows the filtration resistances for lignin precipitated from the softwood black liquor, A1, and the untreated hardwood black liquor, C1, at different pH values.

In general the lignin precipitated from liquor A1 can be considered as being easy to filter and, as can be seen in Fig 3, affected by the precipitation pH: the lower the pH in the range studied, the easier it is to separate. However, the filtration resistance of the hardwood lignin, C1, was very high compared to the softwood samples. The difference in filtration resistance between the softwood and the hardwood liquors may be due to several reasons: one possible reason could be that the hardwood

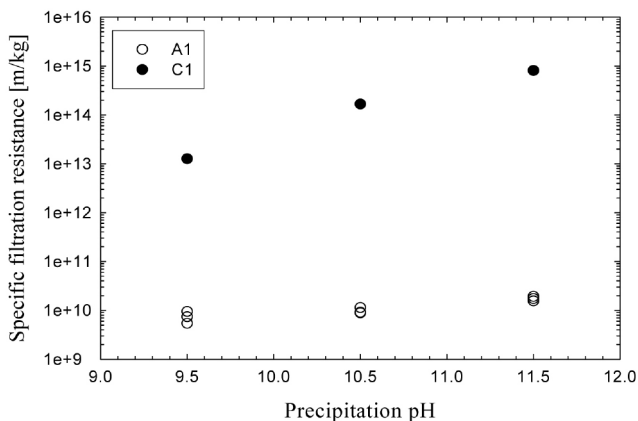


Fig 3. Specific filtration resistance of the evaporated softwood black liquor, A1, and the untreated hardwood black liquor, C1, at different precipitation pH.

liquor contains a higher amount of hemicellulose, see Table 1.

### Precipitation, filtration and washing of the pre-treated black liquors

In an attempt to reduce its hemicellulose content prior to precipitation, and possibly also improve filtration properties, the hardwood liquor was pre-treated using three different techniques: heat-treatment, ultrafiltration and a combination of ultrafiltration and nanofiltration.

The hemicellulose content of the black liquor decreased by about 50% (see Table 1) during the heat treatment. Fig 4 shows the average specific filtration resistance of the heat-treated black liquor. As can be seen the heat treatment has a very positive impact on the filtration properties, lowering the filtration resistance considerably (c.f. Figs 4 and 5).

If the average specific filtration resistance obtained after precipitation, to a pH value of 9.5, is plotted versus the hemicellulose content in the black liquors it can be seen that the average specific filtration resistance increases with increasing hemicellulose concentration (see Fig 5). The most abundant sugar in hardwood birch black liquor is xylose. In Fig 6 the hemicellulose content is substituted with xylose (i.e. xylane) concentration and the result shows the same trend as in Fig 5: the average specific filtration resistance increases when the xylose concentration increases.

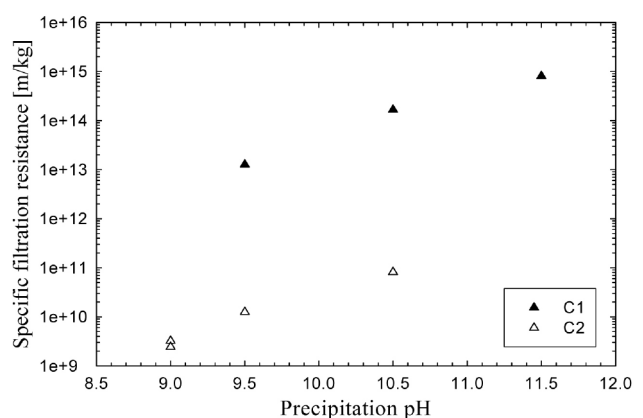
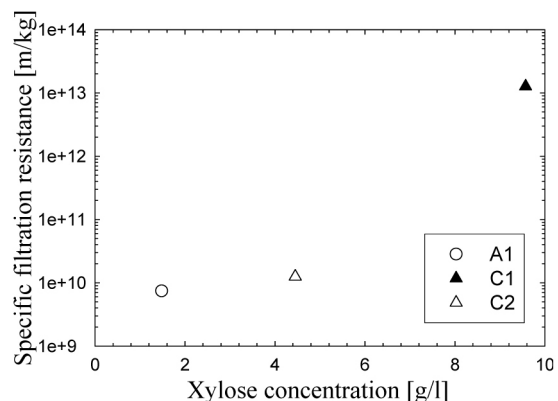
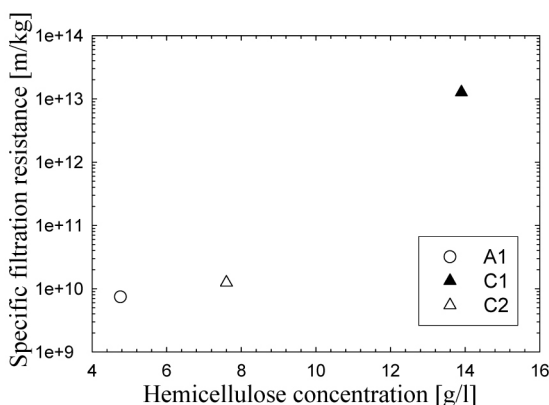


Fig 4. Specific filtration resistance of the evaporated hardwood liquor, C1, and heat-treated hardwood black liquor, C2, at different precipitation pH.



back Figs 5 and 6. Specific filtration resistance of the black liquors with different initial concentrations of hemicelluloses and xylose.

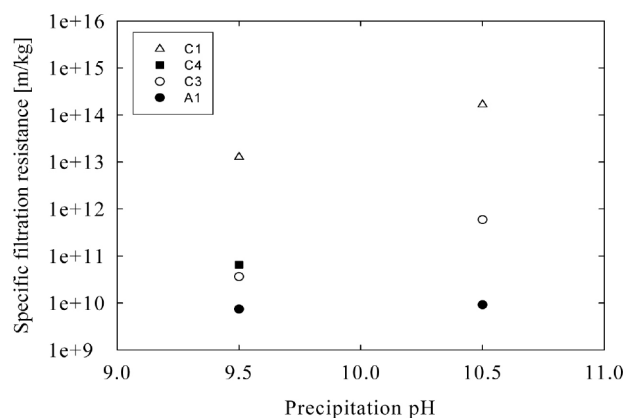


Fig 7. Filtration properties of lignin precipitated from the membrane-treated black liquors, C3 and C4, at different precipitation pH compared to the original hardwood black liquor (C1) and softwood black liquor (A1).

In Fig 7 the filtration properties of the membrane treated black liquors is shown. The UF permeate with low concentration of hemicelluloses, C3, shows the same behaviour as the evaporated liquors i.e. a higher filtration resistance at higher pH. Fig 7 also shows that when the hemicelluloses are removed prior to precipitation, the filtration properties are improved considerably: the filtration resistance was lowered from  $1.3 \cdot 10^{13}$  m/kg before treatment to  $3.6 \cdot 10^{10}$  m/kg after treatment. The filtration resistance of the lignin precipitated from the NF retentate (liquor C4) is at a relatively low level despite the fact of the high concentration of carbohydrate. This indicates that carbohydrates of low-molecular mass will not affect the filtration properties negatively (i.e. increase filtration resistance). The result shows that not only does the concentration of the hemicelluloses have a big impact but also that size may be of importance.

### Final purity of the lignin product

The chemical composition of the washed lignin cakes are shown in Table 2. As can be seen the hemicellulose content of the washed hardwood lignin is high: at a level of 5.07 w-% of TDS. This is, of course, due to the high initial concentration in the hardwood black liquor, see Table 1. After heat treatment, the hemicellulose content decreased considerably in the hardwood liquor (see liquor C2 in Table 1). Analysis of the washed lignin precipitated from the heat-treated hardwood liquor (C2) showed that the hemicelluloses were still present in the lignin cake to a great extent. When removing the hemicelluloses in the liquor by membrane filtration prior to precipitation the content in the washed lignin was considerably lowered (see C3 in Table 2). It should however be pointed out that the lignin from the heat-treated liquor was precipitated at pH 9.0 and the others at pH 9.5. The chemical character-

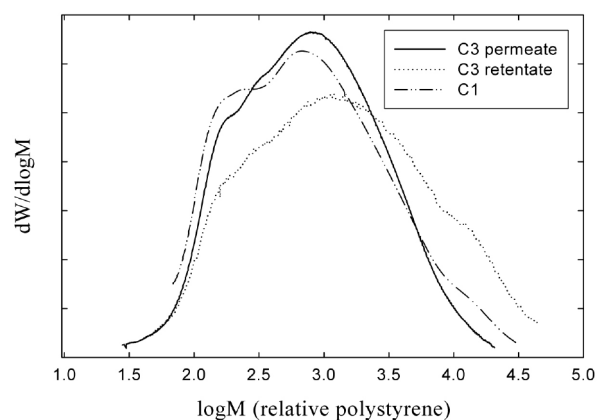


Fig 8. Size exclusion chromatograms for the acetylated lignin samples precipitated from retentate (liquor C3) and permeate after ultrafiltration of evaporated black liquor (C1).

istics of the lignin precipitated from the NF retentate, liquor C4, are similar to the lignin from the UF permeate, C3. Although the carbohydrate content is somewhat higher in the lignin from liquor C4, it is still very low for a hardwood lignin.

It can also be seen that the sodium content of all the washed lignin samples is at very low levels. One possible drawback of using lignin produced from membrane-filtrated liquors is that it has a higher content of sulphur than the washed lignin from the other liquors. Although the reason for the higher sulphur concentration in the permeate is not fully understood, a reasonable explanation may be that more sulphur is attached to the smaller fragments of lignin that have been broken down to a larger degree during the digestion process. The molecular mass is, as expected, lower for lignin precipitated from UF permeate (liquor C3) than for retentate, as shown in Fig 8. Lignin molecules of low-molecular mass pass through the membrane during ultrafiltration, thus increasing the average molecular mass of the lignin remaining in the retentate. The molecular mass is lower for the heat-treated lignin (see Table 2), which indicates a degradation of lignin into smaller molecules during heat treatment along with the degradation of hemicelluloses. The amount of phenolic hydroxyl groups is higher in lignin from the permeate than in lignin from the retentate, which is to be expected as the content of phenolic groups is inversely proportional to the molecular mass of the lignin.

### Conclusions

Lignin was precipitated successfully from softwood black liquor at different pH values; precipitates of good quality, i.e. with low contents of sodium and hemicelluloses, were produced. The filtration resistance was found to be

Table 2. Analyses performed on the washed lignin precipitated from all of the washed lignin samples. Sulphur content measured using 1) Schöninger combustion or 2) ICP. <sup>3</sup> The phenolic hydroxyl content is presented in mmol/g (Klason + acid soluble) lignin.

Liquor	Klason lignin (w-% of TDS)	Acid soluble Lignin (w-% of TDS)	Total sulphur (w-% of TDS)	Hemicelluloses (w-% of TDS)	Sodium (w-% of TDS)	Mw	Mn	PD (Polydispesity)	Phenolic-OH <sup>3</sup>
A1	94.3	5.8	1.5 <sup>1</sup>	0.97	0.02	5100	1160	4.4	3.2
C1	71.4	13.6	2.9 <sup>2</sup>	5.07	0.12	2000	390	5.2	4.0
C2	83.0	15.1	2.5 <sup>1</sup>	3.86	0.11	1700	540	3.2	4.1
C3	81.5	12.0	4.0 <sup>2</sup>	0.38	0.07	1600	370	4.4	4.9
C4	87.9	13.0	3.2 <sup>2</sup>	0.70	0.19	2400	470	5.1	4.2

affected by the precipitation pH, which is in accordance with earlier findings. However, the filtration resistance was significantly higher for lignin precipitated from evaporated hardwood black liquor than for lignin precipitated from evaporated softwood black liquor, one possible reason being the higher concentration of hemicelluloses in hardwood lignin.

The filtration resistance of precipitated lignin from hardwood black liquor was improved considerably when the hemicelluloses were lowered prior to precipitation either by ultrafiltration or heat treatment. The largest decrease was obtained when ultrafiltration was used to pre-treat the liquor.

The filtration resistance remained at low levels when lignin was precipitated from a nanofiltrated (i.e. lignin concentrated) hemicellulose-depleted black liquor.

Analyses of the washed lignin showed that the hemicellulose content in precipitated lignin from UF permeate and NF retentate was significantly lower than when using hardwood black liquor that had not been subjected to pre-treatment. The sodium content in the final product was also very low. The content of sulphur, on the other hand, was shown to be higher in the lignin produced from membrane-filtrated liquors than in the washed lignin from the other liquors.

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