PRODUCTION OF A PURE LIGNIN PRODUCT PART 2: SEPARATION OF LIGNIN FROM MEMBRANE FILTRATION PERMEATES OF BLACK LIQUOR

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Future high value lignin-based products, such as carbon fibers, require a lignin raw material with a high purity level. Lignin with low inorganic content can be separated from kraft black liquor by the LignoBoost process. This laboratory scale study focuses on the effect of micro- and ultrafiltration of black liquor on the content of impurities in the LignoBoost lignin. Two black liquors, obtained from pulping of eucalyptus and softwood, were used in this study. The black liquors were micro- and ultrafiltered and thereafter lignin was separated from these permeates according to the LignoBoost process. It was found that micro- and ultrafiltration significantly reduced the amounts of carbohydrate residuals in the separated lignin. Eucalyptus lignin separated from permeates contained similar amounts of Al, Mn, Mg, Fe and Si, but significantly less Ca than the reference sample separated from unfiltered black liquor, resulting in 50% lower ash content. Softwood lignin separated from permeates contained lower amounts of Al, Mn, Mg, Fe, Ca and Si than the reference. In both cases, the Na and K content were unaffected by the introduction of micro- and ultrafiltration.

Keywords: lignin, separation, precipitation, LignoBoost, microfiltration, ultrafiltration, inorganic impurities, black liquor

INTRODUCTION

A process for lignin separation from alkaline black liquors, LignoBoost, has been developed in earlier work[1,2,3] and has now been installed as a full-scale process.[4] The process is well described in a number of publications.[5,6,7]

Lignin separated with the LignoBoost process is of such purity (ash content ~1 wt%) that it can be used in a number of applications, for example as solid fuel in combustion applications.[8,9] However in some potential high value applications, e.g. carbon fiber, it would be advantageous to produce lignin with even lower ash content.[10,11] Lignin with low ash content can today be achieved by using ion exchange technology[12] or by additional washing.[13,14] Ziesig *et al*.[14] showed that the lower ash content by additional washing is primarily an effect of reduced Na and K content. The content of Ca, Mn, Mg, Fe, Al and Si was, however, difficult to reduce by extended washing, and these were found to be present as inorganic particles, such as Ca-oxalate, in the lignin product. Micro- (MF) and Ultrafiltration (UF) are processes in which components in a liquid are separated by a membrane with respect to the size of particles (MF) or both particles and molecules (UF). This type of process has been performed on both hardwood and softwood black liquors and is described in a number of papers.[15-18] Wallberg *et al*.[15] observed that the elements Fe, Ca, Mg, Mn and Al were retained during ultrafiltration of black liquor. Wallmo *et al*.[19] showed that lignin precipitated from UF permeates is easier to filter and has a lower content of hemicelluloses than untreated black liquors.

A schematic drawing of the LignoBoost process is found in Figure 1. The process uses black liquor (30-45% DS) from the black liquor evaporation plant as raw material. The pH of the black liquor is lowered to a pH ofabout 10 by addition of CO_2 (g). This causes the lignin molecules to aggregate and precipitate as agglomerates. Thereafter the solid material is filtered off. The lignin filter cake is then re-suspended at a lower pH (about 2-4), using sulfuric acid or/and spent acid from ClO_2

generation. After re-suspension, the solids are filtered off again and washed with diluted sulfuric acid at pH 2-3. After washing, the lignin cake is dewatered by pressing and by blowing compressed air through the filter cake.

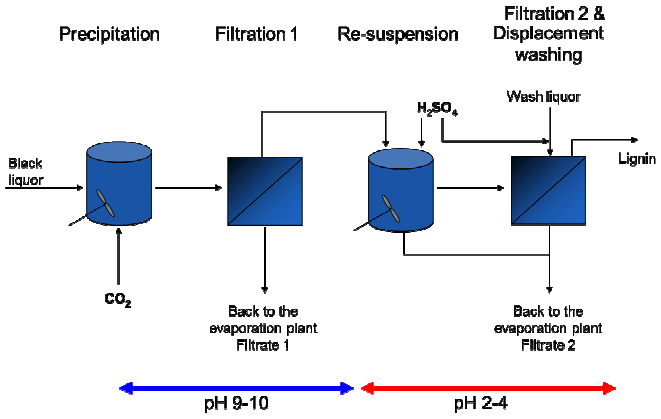

Figure 1: General principles of the LignoBoost process

Table 1
Chemical analysis, methods and measurement uncertainty

	Method	Measurement uncertainty*
Inorganics	ICP-AES	Na, Al, S: ±5-6% Ca, Mn, Si, Mg: ±7-9% Fe: ±22%** Total inorganics: ±6%
Carbohydrate and lignin	Acid hydrolysis (SCAN-CM 71:09) followed by quantification of monosaccharides (IC-PAD), gravimetrical determination of acid-insoluble residue (TAPPI T222 of -00), and measurement of acid-soluble residue using UV spectrophotometry at 205nm	±10%
Oxalate/oxalic acid	As described by Reimann *et al.*[20]	±6%

*The measurement uncertainty is given with approximately 95% confidence interval
**High uncertainty due to low concentrations

The aim of this study was to investigate the behavior of the elements Al, Si, Ca, Mn, Mg and Fe in lignin separation from membrane filtration permeates, using the LignoBoost process. Na and K as well as the carbohydrate impurities were also considered. For simplicity, the above mentioned elements will be referred to as *inorganics*.

EXPERIMENTAL

Black liquor

Two black liquors are used in this study, one from a kraft pulp mill using *Eucalyptus globulus* as raw material and one from a kraft pulp mill using a softwood mixture of *Pinus sylvestris* and *Picea abies* as raw material. The DS content of the black liquors was approximately 40%DS for both liquors. Both liquors were initially filtered using a 90 µm mesh to remove any larger fiber fragments in the liquor.

Experimental setup

The black liquors were filtered at 120 °C in a membrane filtration unit with ceramic membrane having a pore size of 0.2 µm (MF). The membranes had 19 channels, with a channel diameter of 3.5 mm. Cross flow velocity was around 4 m/s. Volume Reduction Factor (VRF) was 0.7 in the experiment using eucalyptus black liquor and 0.4 in experiments using softwood black liquor. The trans-membrane pressure (TMP) was 2 bars and 4 bars when filtering eucalyptus and softwood black liquors, respectively. Part of the eucalyptus MF permeate was subsequently filtered at 70-85 °C in UF equipment operating at VRF 0.15-0.35. Ceramic membranes with both 300 kDa and 15 kDa cut-off were used. These membrane were of monochannel type and had an inner diameter of 6 mm. The cross flow velocity was 5-8 m/s and the TMP was around 2 bars. Lignin in these four permeates (two MF

and two UF) and the two black liquors (reference samples) were then precipitated, filtered and washed in accordance with the methods used by Ziesig *et al.*[14] The precipitation temperature for the permeates was adjusted to a lower range, 40-53°C, in order to obtain reasonable yields, in line with the findings of Wallmo *et al.*[19]

Chemical analysis

Analytical methods are briefly described in Table 1.

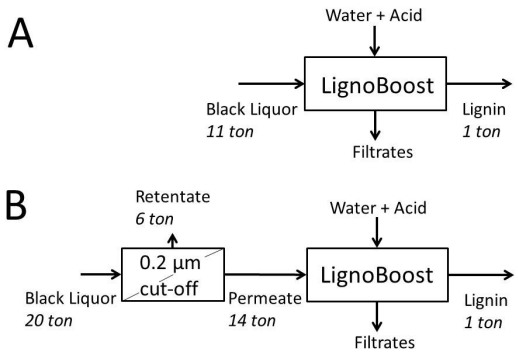

Figure 2: An example of a simplified mass balance for production of 1 ton of *Eucalyptus globulus* lignin using A) LignoBoost, yield 220 kg lignin/ton BLS, and B) Microfiltration (0.2 µm cut-off, VRF 0.7) followed by LignoBoost, yield 185 kg lignin/kg PS, permeate dry solids (PS) 37%

Table 2
Dry solids (DS) (%), total carbohydrate and total lignin content in black liquors and permeates (g/kg DS)

		DS	Total carbohydrate content	Total lignin content
Eucalyptus	Black liquor	40.6	38	389
	0.2 µm perm.	37.9	23	399
	300 kDa perm.	31.3	10	330
	15 kDa perm.	27.6	9	318
Softwood	Black liquor	40.8	20	337
	0.2 µm perm.	36.3	12	242

RESULTS AND DISCUSSION

As expected, it was found that the yield (kg lignin/ton liquor solids) was lower when lignin was separated from permeates as compared to when separated from black liquor. This is due to the fact that some high molecular lignin was separated in the membrane filtration step. This affected, for example, the amount of black liquor required to produce a certain amount of lignin, see Figure 2.

Organic content

As can be seen in Table 2, the eucalyptus 0.2 µm, 300 kDa and 15 kDa permeates contained significantly less carbohydrates than the unfiltered black liquor. Furthermore, microfiltration of the softwood black liquor resulted in lower carbohydrate content, but also, in contrast to the eucalyptus results, lower lignin content compared to the black liquor. The reason for this is unknown. This must be considered when the results related to microfiltration of softwood are discussed below.

As can be seen in Figure 3, one lignin sample separated from 15 kDa permeate contained 0.3 wt% carbohydrates, which is similar to earlier reported results.[20] However, the relatively low amount of carbohydrates in the lignin separated from 0.2 µm permeates have, to the authors' knowledge, not been reported earlier. The carbohydrate residuals retained in the 0.2 µm membrane were most likely wood fiber fragments or gels rather than dissolved molecules. The presence of wood fiber fragments or fibril hemicelluloses aggregates, previously described by Westbye *et al.*,[21] in the softwood reference sample was confirmed by SEM microscopy, see Figure 4.

Inorganics

Black liquor

The two black liquors used had a similar composition of inorganics, see Table 3. However some differences should be noted such as the higher Ca content and lower Mg and Mn content in eucalyptus black liquor, compared to the studied softwood black liquor.

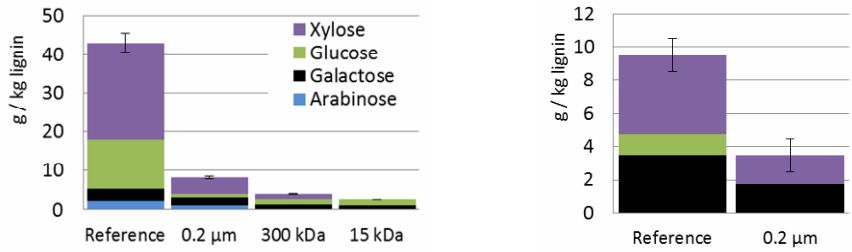

Figure 3: Carbohydrate content given as anhydrosugars in eucalyptus (left) and softwood lignin (right) separated from black liquors (Reference) and permeates. All samples were precipitated at a pH level between 9.6 and 9.8, and washed at pH 2.3

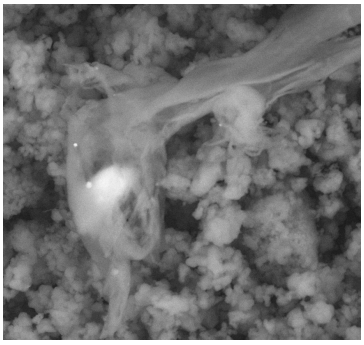

Figure 4: SEM image showing a wood fibre fragment or fibril hemicellulose aggregate and lignin agglomerates. The fibre fragment/hemicellulose aggregate is approx. 5 µm wide

Table 3
Content of inorganics in black liquors (mg/kg DS)

	Na	K	Al	Ba	Ca	Cu	Fe	Mg	Mn	Si
Eucalyptus	217,000	12,300	32	3.1	660	1.4	12	210	36	230
Softwood	227,000	14,900	18	4.4	160	1.1	12	280	62	220

Inorganics in permeates

Na, K and Si were permeable in the MF and the UF process, see results for Si in Figure 5. This finding is in agreement with earlier studies on UF.[15,22]

Furthermore, in Figure 5 it can also be observed that Ca, Mn and Mg were retained in the MF/UF process. Fe and Al were also retained, but those results are not displayed here. This resulted in a reduced content of these elements in permeates compared to the content in the black liquor, which is in agreement with earlier studies.[15] It is thus likely that Ca, Mn, Mg, Fe and Al were present either as inorganic particles and/or had a high affinity for the removed organic material. This is in agreement with the findings obtained by Kirbawy and Hill[22] for Ca, Mn, Mg and Fe.

Inorganics in first stage filter cake and washed lignin

The composition of the inorganics in the first stage filter cake was related to the composition in the black liquor/permeates: compare Figure 6 to Figure 5. The lower concentration in the black liquor/permeate rendered a lower content in the

first stage filter cake. The content of Si in first stage filter cakes from the MF and UF permeates was higher compared to the reference. This may be due to the fact that the relative amount of Si compared to lignin was larger in the MF and UF permeates than the black liquor; as the Si content was unaffected by the filtration (Figure 5), whereas the lignin concentration was decreased (Table 2).

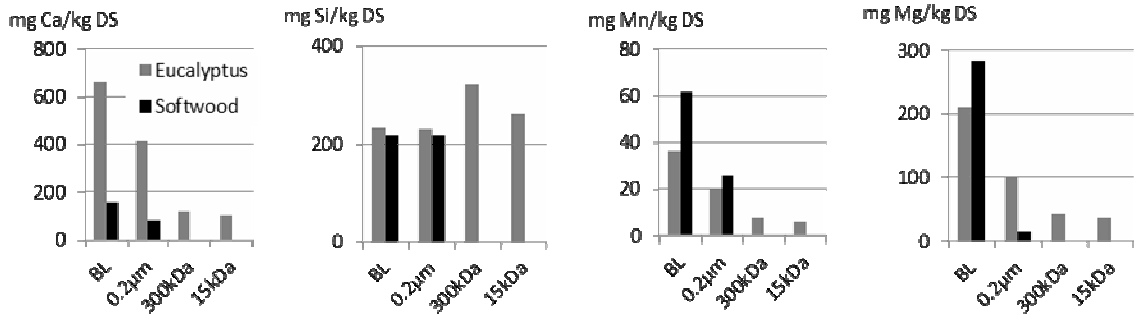

Figure 5: Ca, Si, Mn and Mg concentration in eucalyptus (grey) and softwood (black) black liquor and permeates. The DS in the permeates is lower than in black liquor

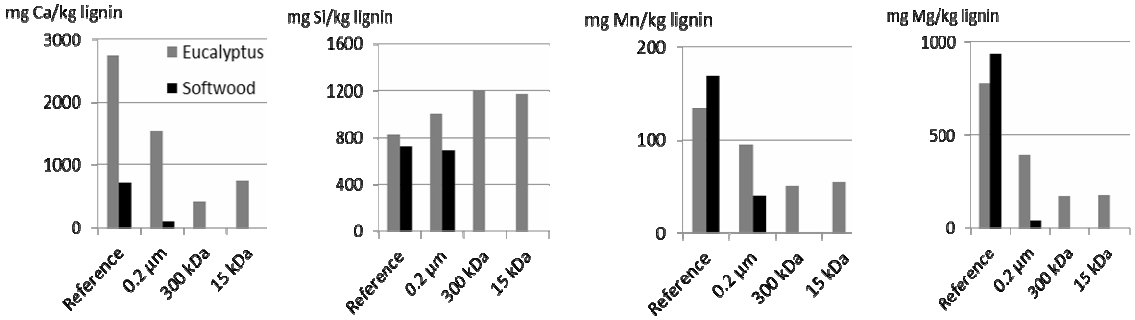

Figure 6: Ca, Si, Mn and Mg content in first stage filter cakes produced from the eucalyptus (grey) and softwood (black) black liquors (Reference) and permeates. All samples were precipitated at a pH between 9.6 and 9.8

The calcium content was significantly lower in washed lignin separated from eucalyptus permeate, compared to the reference, see Figure 7. This was most likely due to the fact that the oxalate content in permeates (34 mmol/kg DS in MF eucalyptus permeate) was lower than in black liquor (61 mmol/kg DS).[14] Furthermore, this resulted in lower oxalate content in washed lignin samples: 37 and 2 mmol/kg lignin for the reference and the permeate lignin, respectively; thus, the Ca-oxalate precipitation, previously observed by Ziesig *et al.*,[14] was partially avoided. The Ca content in the softwood samples was very low (< 50 mg/kg lignin) compared to the eucalyptus samples, see Figure 7.

In Figure 8, the Al, Fe, Mg Mn and Si contents in washed lignins from black liquors (Reference) and permeates are shown. The trend for a lower content of Al, Fe, Mg and Mn observed in the permeates (Figure 5) and the first stage filter cakes (Figure 6) was also observed for lignin from MF permeate and 300 kDa permeate. However, the trend was less pronounced than it was in the earlier stages of the LignoBoost process. Furthermore, the lignin sample that had been separated from the 15 kDa permeate showed a significantly higher Fe and Si content than the reference. The reasons for this is not known, but it might have been due to differences in the chemical composition of this permeate, when compared to the other liquors. The above presented results indicate that lignin separated from MF-permeates have a higher purity than lignin separated from unfiltered black liquor. However, compared to MF-permeates, no further effect on the inorganic content in lignin seems to be achieved by separating lignin from UF-permeates.

Figure 8 also shows that the softwood permeate-lignin had a significantly lower content

of Si, but also of Mg and Mn, when compared to the reference. Aluminium and silicon are known to precipitate together with Na and Mg[23] in the evaporators. Furthermore, multivalent ions of Al, Ca, Mg and Fe are known to lower the solubility of silicate in water solutions.[24] It is thus possible that the lower content of Al, Ca, Mg and Fe in the softwood permeate, compared to black liquors and eucalyptus permeates, increased the solubility of the aluminium and silicon precipitates previously observed in lignin.[14] As mentioned earlier, care must be taken when interpreting the microfiltration softwood results. However the results of the inorganics content in the separated lignin are valid for lignin separated from a liquor with the same composition as this permeate. Furthermore, it emphasizes that a reduced content of inorganics in the raw material could reduce the content in the final washed lignin.

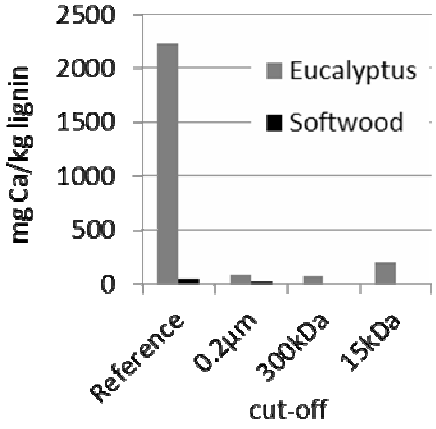

Figure 7: Ca concentration in the washed lignins separated from the untreated black liquors (Reference) and permeates. The samples were precipitated at a pH between 9.6 and 9.8 and washed at pH 2.3

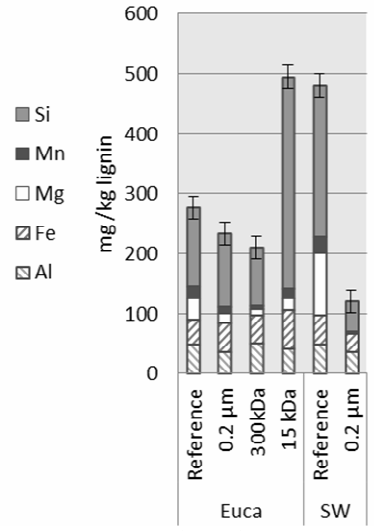

Figure 8: Concentration of Al, Fe, Mn, Mg and Si in the eucalyptus and softwood lignins separated from the black liquors (Reference) and permeates. Error bars represent the standard deviation for double samples precipitated at pH 10.2 and washed at pH 2.3

CONCLUSION

The introduction of micro- and ultrafiltration as black liquor pretreatment prior to the LignoBoost process has been shown to affect the lignin separation in terms of lower yield and lower optimum precipitation temperature. Furthermore, the lignin separated from MF/UF permeates had a higher purity than lignin separated from unfiltered black liquor, with respect to:

- Less carbohydrate residuals;
- Lower content of Ca compared to reference (eucalyptus);
- Lower content of Ca, Al, Si, Mn, Mg and Fe compared to reference (softwood).

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