

Fractionation of Technical Lignin: Molecular Mass and pH Effects

Mikaela Helander,^a Hans Theliander,^{a,b} Martin Lawoko,^a Gunnar Henriksson,^{a,c} Liming Zhang,^{a,c} and Mikael E. Lindström^{a,c,*}

Today, lignin from kraft pulping is used mainly as fuel, with only very small amounts being used as raw material for chemicals and materials. This work focuses on using a convenient method for separating large amounts of low molecular weight lignin from the kraft process. Low molecular weight lignin contains larger amounts of phenolic structural units, which are possible modification sites and can be used as antioxidants. Moreover, a product that has reduced polydispersity, low molecular weight, and purified lignin could be a potential material for new applications. The studied process for separating lignin from weak black liquor used a membrane with a cut-off of 1000 Da. During precipitation of the 1000 Da permeate, it is necessary to prevent formation of fairly large, rigid particles/agglomerates of lignin by keeping the temperature low. To improve the dead-end filtration, higher ionic strength is needed for the weak black liquor. Additionally, reducing the end pH will cause more material to precipitate. More sulfur was found in the low molecular weight lignin and at lower precipitation pH, indicating that most sulfur left in the lignin samples might be bound to low molecular weight lignin.

Keywords: Lignin; Weak black liquor; Low molecular weight; Cross-flow filtration; Ultrafiltration; Molar mass; Precipitation; Dead-end filtration

Contact information: a: Wallenberg Wood Science Center, KTH Royal Institute of Technology, Chalmers University of Technology, SE-100 44 Stockholm, Sweden; b: Department of Forest Products and Chemical Engineering, Chalmers University of Technology, SE-412 96 Göteborg, Sweden; c: Department of Fiber and Polymer Technology, KTH Royal Institute of Technology, SE-100 44 Stockholm, Sweden;

*Corresponding author: mili@fpt.kth.se

INTRODUCTION

The chemical pulping industry in Sweden produced approximately 5,414,000 metric tons of air-dried sulfate pulp in 2010 (FAO 2011). In a kraft mill producing 500,000 air-dried metric tons (ADMT) of pulp, approximately 239,000 tons of the output is modified lignin, based on a content of 27% lignin in wood. Today, this kraft lignin is used mainly as fuel. However, it would be of economic interest to use the lignin for high value-added products, and it would be of environmental interest to use it for new materials, since it is a renewable resource.

In recent decades, a successful process called LignoBoost (Öhman *et al.* 2008) has been developed, and a demonstration plant has been built that can extract large amounts of polydisperse lignin from black liquor. To process lignin into various end products, it would be advantageous to use material with a more homogenous structure, chemistry, and purity (Stewart 2008). Furthermore, black liquor contains low molecular weight lignin materials, such as various phenolic compounds (Alén and Vikkula 1989). These phenolic structures have interesting properties that could be used in various

applications. They are possible sites for modification and can be used as an antioxidant or a softening agent (Norberg 2012). The present work seeks to produce a lignin of low polydispersity, low molecular weight, and high purity by using a convenient method for separating low molecular weight lignin from softwood weak black liquor.

Lignin is ionized by deprotonation in a highly alkaline solution (Gierer 1985), in which it becomes partly dissolved (Passinen 1968). The dissolved lignin interacts with sodium ions in the liquor and hence behaves as a polyelectrolyte. To extract lignin from black liquor, lignin is separated by solubility, *i.e.*, precipitation followed by filtration/washing. Lowering the pH of the black liquor using either carbon dioxide or mineral acids protonates the phenolic hydroxyl groups in lignin (Alén *et al.* 1979; Passinen 1968). To protonate other acidic groups at a low pH, a strong mineral acid is needed (Sjöström 1993). The protonation depends on the pKa value of the lignin structures, and lignin will coagulate depending on the conditions (Sundin 2000). An average pKa value of kraft lignin is misleading, since lignin consists of many structures having different pKa values. For example, softwood kraft lignin has structures such as phenolic hydroxyl groups (pKa ~ 10) and carboxylic groups (pKa ~ 4.4). However, the pKa value also depends on the temperature, ionic strength, and the solution in which the lignin is dissolved (Ragnar *et al.* 2000). Since the pH of kraft liquors is approximately 13 to 14, the abovementioned groups are almost completely deprotonated. Thus, by lowering the pH to different pKa values, different structures become approximately 50% protonated. The dry content of black liquor also influences the efficiency of precipitation (Alén *et al.* 1979 and 1985; Lin 1992), and thus ionic strength and lignin concentration.

In 1872, Tessié du Motay patented a method in which carbon dioxide is injected into hot liquors obtained by boiling woody fiber, *i.e.*, black liquor. The aim was to precipitate “impurities” to obtain a pure liquor that could be recaustified and reused (Tessié du Motay 1872). Others have also studied the use of carbon dioxide in systems for precipitating material in black liquors (Rinman 1911; Scott 1940; Reboulet 1941; Tomlinson and Tomlinson Jr. 1946, 1948; Pollak *et al.* 1949).

In 1910, Hough patented a method in which lignin and resin are precipitated by acidification of spent liquors from the alkaline pulping process using an acid, such as sulfuric acid. To improve the dead-end filtration, the precipitated solution was filtered at high temperature (Hough 1910). A problem recently solved by the LignoBoost process is the displacement washing of lignin without plugging the filter cake and without large material losses. After precipitation, the material is filtered, and the filtrate cake is redispersed at a low pH (2 to 4). The formed suspension can then be easily filtered and washed using displacement washing (Öhman and Theliander 2006; Öhman *et al.* 2007).

By means of fractionation, technical lignin with varied structures and properties can be enhanced (Brodin *et al.* 2009). It has been demonstrated that when lignin is precipitated from kraft black liquor, the methoxyl content decreases, while the carboxyl and phenolic hydroxyl contents increase at a lower pH (Wada *et al.* 1962; Lin 1992). By means of fractionation with ultrafiltration, it has been demonstrated that the methoxyl and aliphatic hydroxyl contents decrease with lower molecular weight, while the phenolic hydroxyl content increases in the permeate (Griggs *et al.* 1985). The carboxyl content increases with lower molecular weight (Mörck *et al.* 1986; Lin 1992; Rojas *et al.* 2006).

Technical lignin can be fractionated based on differences in either solubility or molecular weight. During the 1960s, kraft liquor was fractionated by acidification of lignin (Wada *et al.* 1962) and by the use of Soxhlet extraction fractionation of kraft lignin

was preformed (Lindberg *et al.* 1964). Two decades later, industrial kraft black liquor was fractionated in small quantities by means of gel permeation chromatography (Mörck *et al.* 1982), and in subsequent work industrial softwood kraft black liquor was fractionated in larger quantities using organic solvents (Mörck *et al.* 1986). In the 1970s, the industrial use of ultrafiltration and reverse osmosis started. One of the major potential application areas for these methods was the pulp and paper industry (Glimentius 1980). By using ultrafiltration it is possible to separate liquids by molecular weight. Early filtration work was done using various sulfite white waters (Wiley *et al.* 1970).

In 1981, kraft liquor was fractionated using ultrafiltration (Lin and Detroit 1981). Crossflow ultrafiltration of kraft black liquor was studied in the mid 1980s. Various parameters were adjusted in trying to optimize the filtration to concentrate and purify high molecular weight lignin (Woerner and McCarthy 1984). Several studies have examined the fractionation of black liquor using ultrafiltration (Forss and Fuhrmann 1976; Woerner and McCarthy 1984; Griggs *et al.* 1985; Alén *et al.* 1986, Kirkman *et al.* 1986; Uloth and Wearing 1989; Rajan *et al.* 1996; Tanistra and Bodzek 1998; Wallberg *et al.* 2003; Liu *et al.* 2004; Brodin *et al.* 2009; Toledano *et al.* 2010). A few studies have examined the possibility of separating lignin from the 1000 Da fraction of kraft black liquor (Keyoumu *et al.* 2004; Rojas *et al.* 2006; Elegir *et al.* 2007; Antonsson *et al.* 2008; Niemi *et al.* 2011). However, to our knowledge, no study has focused on using a convenient method for extracting low molecular weight lignin from black liquor. In the present work, experimental work done to separate low molecular weight lignin from softwood weak black liquor is presented.

EXPERIMENTAL

Materials

Industrial weak black liquor from kraft pulping of softwood was generously supplied by the Billerud Gruvön pulp and paper mill in Sweden. The weak black liquor was taken from the digester extraction going to the evaporator (step C6). The pH and dry matter content were >13 and ~17.6%, respectively. Weak black liquor is black liquor in a low concentration, *versus* strong black liquor, which is evaporated to a higher concentration. The chemicals used were of analytical grade.

Methods

The experimental plan entailed seeking possible conditions/parameters of a method for extracting large amounts of low molecular weight lignin. This resulted in the experimental scheme presented in Fig. 1. The scheme is also showing the four samples that were used for all analyses.

Crossflow filtration

Crossflow filtration was performed using pilot-scale membrane equipment. The system consisted of a 30 L tank equipped with a stirrer, heating element, gear pump, and Kerasept membrane unit (Novasep, Pompay, France). The membranes used were TiO₂ and ZrO₂ ceramic membranes, capable of handling pH 0 to 14, high pressure, and high temperature. A starting volume of 27.8 L of softwood weak black liquor was processed in the filtration unit. The heating element in the pilot plant tank was set to 65 °C, and the

feed flow velocity was 18.3 L/min. The process liquor was filtered through a ceramic membrane of 1000 Da at a transmembrane pressure of 4.6 bar. When the dead volume of the tank was reached, the filtration was ended. Two samples were collected from the crossflow filtration system: 23.4 L of 1000 Da permeate and 4.15 L of concentrated 1000 Da retentate. The samples were kept in a cold room at 4 °C.

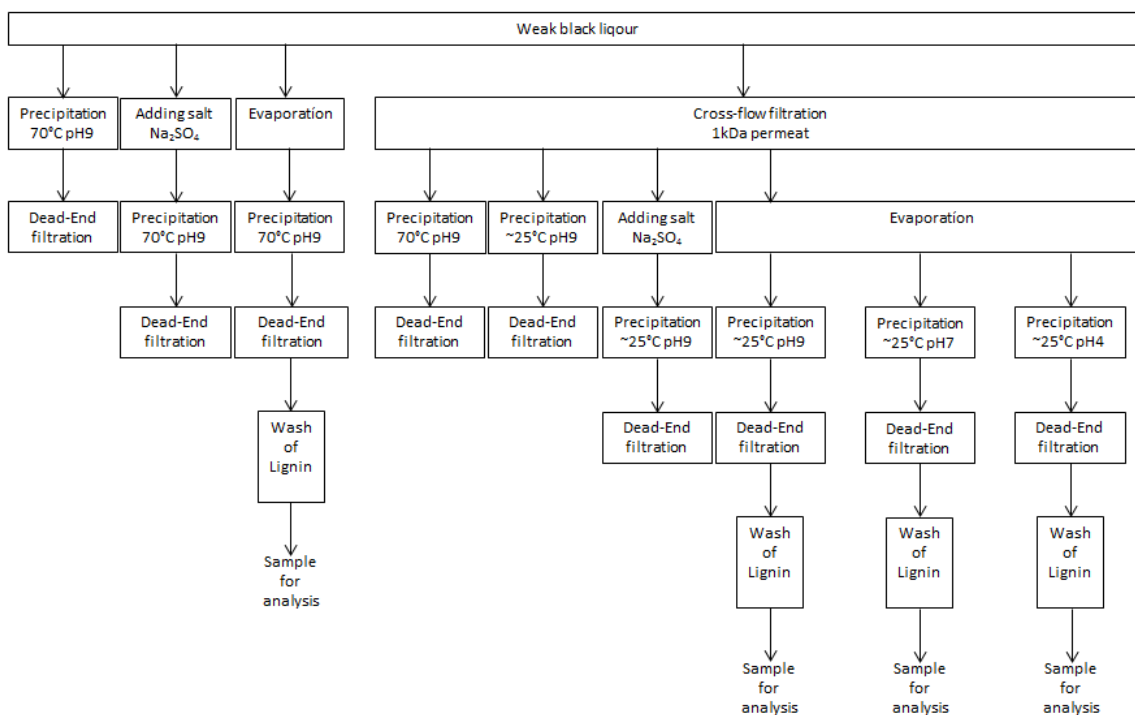


Fig. 1. Scheme of the experimental work

Precipitation, dead-end filtration, and washing of lignin

The black liquor samples were collected in glass beakers containing magnets for stirring and put in water baths. When the desired temperature was reached, 6 M sulfuric acid was added until the slurries reached the desired pH. Before the procedure just described, some samples were adjusted in ionic strength by adding salt or removing 60% of the water by evaporation at 50 °C. The ionic strength measured as the sodium ion concentration was 1.7 mol/L in the weak black liquor and was increased to 3.8 mol/L by the addition of Na₂SO₄ and 4.2 mol/L by evaporation. The original sample was precipitated to pH 9 (9.03), and the 1000 Da permeate was precipitated to different pH levels, *i.e.*, <9 (8.94), <7 (6.51), and >4 (4.08). A Buchner funnel equipped with a fine filter web was used for the dead-end filtration of the precipitated lignin; a 15 µm web could withstand pH 9, and a 20 µm web could withstand pH 7 and 4.

The filter cakes from the pH 9 original sample and the three 1000 Da permeate samples were mixed individually with acidic water (pH <2) filtered, and washed a second time with a volume of acidic water (pH ~2.5) twice as large as that of the filter cake. The filter cake was dried at room temperature and freeze-dried before analysis.

Chemical analysis

The dry content of the extracted material was determined using infrared radiation and a desiccator with Sicapent desiccant (EMD Millipore, Billerica, MA, USA). Acid

hydrolysis for the determination of Klason lignin and carbohydrates was performed according to standards TAPPI 222 om-02 and SCAN-CM 71:09. Ion-exchange chromatography (IC) was performed using a Dionex ICS-3000 IC system (Dionex, Stockholm, Sweden). The carbohydrate standards used for calibration were arabinose, galactose, glucose, xylose, and mannose. Rhamnose was not calibrated due to the small amount in the samples.

Acid-soluble lignin was determined according to *Methods in Lignin Chemistry* (Dence 1992), except for an extra filtration of the filtrate before the acid-soluble lignin measurement. After Klason lignin separation, the filtrate was stored in a fridge overnight, which caused some material to precipitate in the filtrate. The amount of precipitated material was determined gravimetrically. The acid-soluble lignin was analyzed using a Shimadzu dual-beam UV-2550 UV/VIS spectrophotometer (Shimadzu, Kyoto, Japan) and quartz cuvettes, and an extinction coefficient (absorptivity) of 128 L/g-cm.

The ash content was determined according to ISO 1762. Elemental analysis (*i.e.*, C, H, N, and S) of a ~2 mg, vacuum oven-dried sample (40 °C for 48 h) was performed in a Flash EA 1112 elemental analyzer (Thermo Finnigan, Cambridge, MA, USA) by the Elemental Analysis Unit of Santiago de Compostela University (USC, Santiago de Compostela, Spain). Sodium content was determined according to SCAN-N 38 by MoRe Research Örnsköldsvik AB (Örnsköldsvik, Sweden).

Size-exclusion chromatography (SEC) was conducted using two systems: water (alkali) SEC and tetrahydrofuran (THF) SEC. Each system consisted of a Rheodyne 7725i manual injector (Rheodyne, Rohnert Park, CA, USA) and a Waters 515 HPLC pump (Waters, Milford, MA, USA). Samples were filtered through a 0.45 µm PTFE syringe filter; a volume of 20 µL was injected and the absorbance at 280 nm was recorded. The peaks were integrated and quantified using Millennium 3.2 software (Waters, Milford, MA, USA). The aqueous (alkali) SEC system consisted of three TSK-gel columns (Tosoh Bioscience, Tokyo, Japan) coupled in series (G3000PW, 7.5 × 300 mm, 10 µm particle size; G4000PW, 7.5 × 300 mm, 17 µm particle size; G3000PW), a Waters 2487 dual wavelength absorbance detector, and a Waters 2414 refractive index (RI) detector. The mobile phase was 100 mM NaOH. Pullulan standards with specific molecular weights of 320-400,000 were used for calibration to estimate the molecular weights of the samples. The THF SEC system consisted of three Ultrastaygel columns (Waters) coupled in series (*i.e.*, 100, 500, and 1000 Å) and a Waters 2487 dual wavelength absorbance detector. The mobile phase was THF. Linear polystyrene standards with specific molecular weights of 484 to 17,900 were used for calibration to estimate the molecular weights of the samples.

Acetylation was done according to *Methods in Lignin Chemistry* (Gellerstedt 1992), but using ethanol. First, 10 mg of lignin was stirred with 1:1 v/v pyridine (non-stabilized) and acetic anhydride overnight, after which 10 mL of ethanol was added, and the mixture was evaporated to decompose the acetic anhydride. Then, 10 mL of toluene was added and the mixture was evaporated to remove any residual chemicals. This procedure was repeated three times. During sample preparation for the THF SEC, the acetylation behaved differently for the four samples. The original precipitated lignin sample and the 1000 Da permeate lignin sample (precipitated at pH 9) were dissolved, while the 1000 Da permeate precipitated at pH 7 and 4 contained light, undissolved particles. For this reason, another set of all four samples was also prepared, in which the four samples were dissolved directly in THF, *i.e.*, without acetylation.

RESULTS AND DISCUSSION

Precipitation and Filtration

During precipitation of the 1000 Da permeate, fairly large, rigid particles/agglomerates of lignin material were formed at high temperatures. This might be due to the higher reactivity of phenolic hydroxyl structures; however, a physical reaction due to a lower glass transition temperature (T_g) is more likely, since the effect was not seen in the original sample. At temperatures above T_g , an amorphous polymer material becomes softer due to segment movements in the polymer chain. A cut-off of 1000 Da would represent 5 to 6 lignin units. Yoshida *et al.* reported T_g temperatures of 32 °C and 62 °C for weight-average molecular weights (M_w) of 620 and 1300, respectively (Yoshida *et al.* 1987). Similar phenomena have also been reported by other research groups, but not for low molecular weight lignin. In those studies, higher temperatures were reported to cause melting and caking of the precipitate or formation of large tacky clumps (Rinman 1911; Uloth and Wearing 1989). It was suggested that precipitation should be performed just below the coagulation temperature (Merewether 1962). Fractions of 15 to 0 and 15 to 1 kDa black liquor have also been reported to form clumps at higher temperatures, due to higher density coagulation (Wallmo and Theliander 2009).

To enable dead-end filtration of all slurries, a higher ionic strength was needed, where the high salt concentration would increase the coagulation of lignin. The electrical charge created by the ionized hydrophilic groups creates a colloidal lignin, the stability of which is effected by the ionic strength (Passinen 1968). Dead-end filtration was the fastest for the low molecular weight lignin precipitated at pH 4. The reason is probably a larger amount of salts is being created when lowering the pH with sulfuric acid. Furthermore, Rinman (1911) reported that the precipitation is improved by increasing the salt concentration. The pH 9 and 7 filtrates were brown, while the pH 4 filtrate was orange and more transparent. Future work focusing on the behavior of low molecular weight lignin during dead-end filtration would be of interest.

During precipitation, gas bubbles formed at a lower pH. This was also reported by Uloth and Wearing (1989), who noted that lowering the pH below 7 resulted in large amounts of gases (*i.e.*, H₂S and CO₂) evolving. Carbonates in the black liquor formed carbon dioxide, which created bubbles in the suspension.

Mass Balance

The mass balance overview (Table 1) indicates a low content of carbohydrates in both the original sample and the 1 kDa permeate samples. The Klason lignin values were quite high for all samples, at 91.7 to 98.2%. The acid-soluble lignin seemed to increase with decreasing molecular weight and decreasing pH. This indicates that a large amount of acid-soluble lignin is of low molecular weight. In the filtrate, after Klason lignin analysis and before acid-soluble lignin analysis, some material had precipitated, the composition of which was unknown. This material represents 3.3 to 4.3% of the material in the mass balance. As can be seen, the ash content was low for all samples, at 0.1 to 0.9%, which indicates good washing of the samples. The same absorptivity constant was used for all fractions, possibly causing some error in the mass balance. After dead-end filtration of the material precipitated at pH 9 (*i.e.*, not after acid hydrolysis), all filtrates of

each sample were collected. The filtrates were all lowered to pH 2 and the precipitates were collected. This precipitated material from the filtrate was sticky in consistency.

Table 1. Mass Balance of Original and Fractionated Lignin Samples

Sample	Carbohydrate	Klason lignin	Acid-soluble lignin	Precipitated material	Ash	Mass balance
	%	%	%	%	%	%
Original pH 9	2.7 ± 0.2	93.7 ± 0.2	2.0 ± 0.1	3.3 ± 0.2	0.1 ± 0.0	102
1 kDa perm., pH 9	0.2 ± 0.0	98.2 ± 2.2	3.7 ± 0.0	3.5 ± 1.0	0.9 ± 0.0	106
1 kDa perm., pH 7	0.1 ± 0.0	96.1 ± 1.0	3.7 ± 0.0	4.3 ± 0.4	0.5 ± 0.1	105
1 kDa perm., pH 4	0.1 ± 0.0	91.7 ± 0.6	6.2 ± 0.3	4.3 ± 0.4	0.4 ± 0.0	103

Elemental Analysis

From the elemental analysis (Table 2), it can be seen that the precipitated lignin in the original sample contained only approximately 1.7% sulfur, while in the 1 kDa permeate, the sulfur content was approximately 8%. Interestingly, the results indicate increasing sulfur content with 1 kDa permeate samples and also with lower pH, even though the samples were thoroughly washed. Low molecular weight lignin seems to be the main material contributing to the sulfur content of the lignin sample. A plausible explanation for this is the reaction mechanism responsible for the dissolution of lignin in kraft cooking. In the equilibrium with hydrosulfide ions, benzyl thioalcohol is formed, which results in a nucleophilic attack and breakage of the β -O-4 linkages between the phenylpropane units. The product is a thiirane (episulfide) structure containing sulfur (Gierer 1980). It has been suggested that the thiirane structure reacts further, forming a conjugated double bond in residual lignin and producing elementary sulfur, but the mechanism of this reaction is not understood in detail. Other types of reactions may also be generating organically bound sulphur. However, small lignin fragments in the samples would contain a higher ratio of organically bound sulfur.

Table 2. Elemental Analyses of Original and Fractionated Lignin Samples

Sample	S	N	C	H	Total
	%	%	%	%	%
Original, pH 9	1.69	0.10	64.88	6.30	72.97
1 kDa perm., pH 9	8.60	0.10	61.26	5.89	75.84
1 kDa perm., pH 7	33.20	0.13	45.39	4.40	83.11
1 kDa perm., pH 4	31.24	0.11	45.97	4.55	81.87

Fractionation with organic solvents of lignin precipitated at pH 9.5 from industrial softwood kraft black liquor produced an increase in the sulfur content of low molecular weight lignin, though only to a content of 2.7% sulfur (Mörck *et al.* 1986). Ultrafiltration of 15 to 0 and 15 to 1 kDa black liquor fractions indicated contents of 4% and 3.2% sulfur, respectively, while the original sample contained 2.9% sulfur (Wallmo and Theliander 2009). If all of the 1.68% sulfur in the original pH 9 sample is to be found in the 1 kDa permeate (pH 9) as sulfur bound to the lignin, 8.6% sulfur is the limit. Hence, it

is not reasonable that the 30% sulfur in the 1 kDa permeates should be due only to chemically bonded sulfur from the cooking. The reason for the high content of sulfur is not known at this moment and needs to be investigated further.

Lignin Yield

Table 3 shows the amount of lignin precipitated to the desired pH in each weak black liquor sample, the material in the filtrate precipitated to pH 2, and the sum of both. Included in the lignin values are: Klason lignin, acid-soluble lignin, and the material precipitated from the acid-soluble filtrate. The original weak black liquor sample precipitated to pH 9 contained 21.3 g/L lignin and 5.8 g/L material in the filtrate when the filtrate was precipitated to pH 2. This gives 27.2 g/L total precipitated material in the original weak black liquor. In the original black liquor, the amount of Klason lignin was 37 g/L. The precipitated sample did not retain the original amount of lignin due to losses during washing.

The total amount of lignin should have been the same in all 1 kDa permeate samples, but the obtained values were 12.7 g/L, 9.3 g/L, and 14.5 g/L. The value 9.3 might be too low. There were difficulties collecting the precipitated material from the filtrate, since the samples were very sticky.

The amount of lignin available in the pH 9 samples, both original and 1 kDa permeate, was 21.3 g/L and 6.8 g/L, respectively. Subtracting the amount of sulfur (Table 2) present in the samples revealed that the 1 kDa permeate represented ~30% of the original sample. It is well known that the amount of low molecular weight lignin depends on the cooking conditions and that prolonged cooking at the end of the final phase of degradation would increase the amount of low molecular weight lignin fractions (Dong and Fricke 1995).

Reducing the pH of the 1 kDa permeate increased the amount of precipitated material, indicating that a higher yield could be gained by varying the pH. However, the elemental analysis (Table 2) indicated that large amounts of sulfur were being precipitated at a lower pH, which explains the larger amount of material at a lower pH. The sulfur might, to some extent, be linked to the small lignin fragments.

Table 3. Lignin Yield in Original and Fractionated Liquid Samples

Sample	Lignin (excl. filtrate)	Precip. (filtrate)	Total Lignin (incl. filtrate)
	g/L	g/L	g/L
Original, pH 9	21.3	5.8	27.2
1 kDa perm., pH 9	6.8	6.0	12.7
1 kDa perm., pH 6.5	8.8	0.5	9.3
1 kDa perm., pH 4	14.1	0.3	14.5

Comparing the amount of dry matter in the starting material and in the 1000 Da retentate and permeate revealed similar values of 5439 g and 5336 g (Table 4). However, the dry content of the original sample was 196 g/L. Table 3 shows that the amount of lignin in the original sample was 27.2 g/L. Direct analysis of the black liquor determined a Klason lignin value of 37 g/L, which would mean that some of the lignin was lost during the washing step.

In the literature, 59 g/L lignin at a dry solid content of 17% in hardwood black liquor has been reported (Jönsson *et al.* 2008). The difference in these figures was probably due to different pulping conditions.

Table 4. Dry Content in Black Liquor Fractions

Sample	Volume	Dry content	Dry content
	L	g/L	g
Start volume, original	27.8	196	5439
End volume, retentate	4.15	331	1374
End volume, permeate	23.4	169	3962
Sum ret. + perm.	27.6	-	5336

SEC Analysis

THF-SEC analysis (Fig. 2) reveals the effect of membrane separation at different retention times for the samples. The original lignin sample had larger lignin components that eluted earlier from the column. The three samples of 1 kDa permeate lignin eluted later and had a narrower molecular weight distribution. Some material eluted after the maximum volume of the column, especially the low molecular weight compounds. This could be because the material was adsorbed to the column and eluted later than the maximum volume.

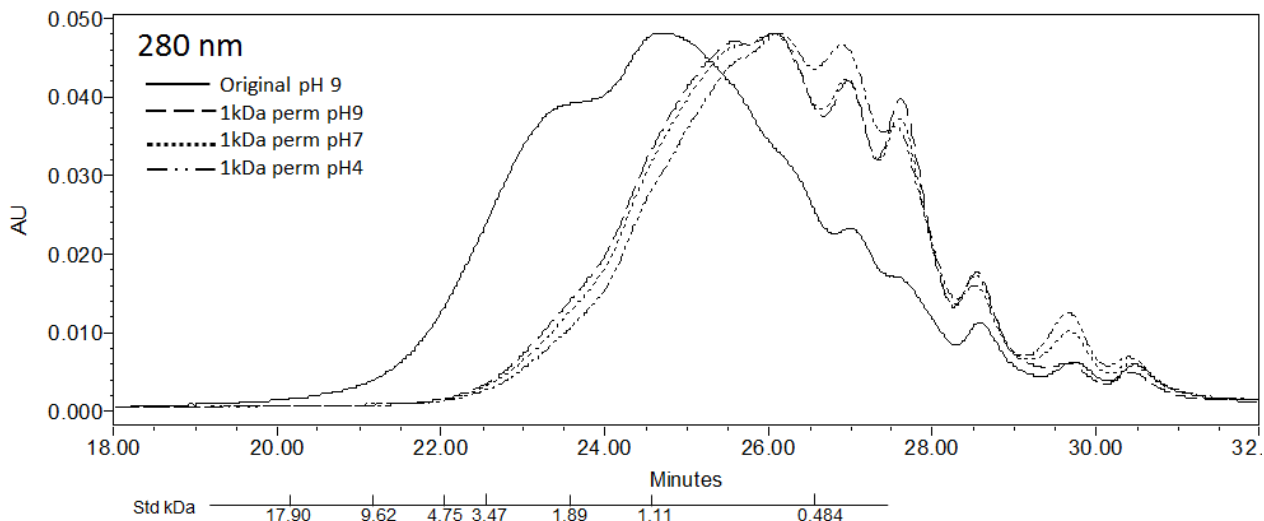


Fig. 2. THF-SEC curves of non-acetylated samples

Comparing the SEC-data (Table 5) for the acetylated and non-acetylated samples reveals that the acetylated samples exhibited shifts toward shorter elution times. This can be expected, since acetylation increases the molecular weight of the sample. This phenomenon was also observed by Mörck *et al.* (1986).

The molecular weights obtained from SEC data should be considered relative values. It should also be mentioned that molar masses measured directly from black liquor might differ from those for precipitated lignin (Sågfors and Hortling 1998).

Furthermore, the ionic strength of the eluent can affect the SEC results (Pellinen and Salkinoja-Salonen 1985).

Table 5. SEC Data for Original and Fractionated Lignin Samples

Sample	Acetylated THF-SEC				Non-acetyl. THF-SEC				Alkali SEC			
	Mz	Mn	Mw	PD	Mz	Mn	Mw	PD	Mz	Mn	Mw	PD
Original pH 9	13109	847	3525	4.2	6417	720	2071	2.9	3503	267	2005	7.5
1 kDa perm., pH 9	2590	508	1096	2.2	1597	484	899	1.9	1843	187	1316	7.1
1 kDa perm., pH 6.5	2355	503	1074	2.1	1522	454	864	1.9	1755	163	1234	7.6
1 kDa perm., pH 4	1954	467	973	2.1	1420	427	806	1.9	1692	196	1227	6.3

CONCLUSIONS

1. When extracting low molecular weight lignin from weak black liquor, the lignin behaved differently when precipitated at different temperatures. Precipitation could not be done at higher temperatures due to the formation of rigid, fairly large lignin particles/agglomerates. Lowering the pH at room temperature results in the formation of fine particles of precipitated lignin.
2. For dead-end filtration of the lignin precipitated from weak black liquor, higher ionic strength was needed.
3. The ionic strength can be improved by either adding salt to the sample or increasing the concentration of ions present in the liquor by evaporation.
4. Precipitation to a lower pH increased the yield of the low molecular weight lignin, but also increased the amount of sulfur.
5. Ultrafiltration results in less polydisperse lignin.
6. Low molecular weight lignin appeared to contain covalently bound (organic) sulfur.
7. By separating low molecular weight lignin, an interesting raw material for new products is received. This approach has the potential to simultaneously increase the production rate at a pulp mill by reducing the recovery boiler as a bottleneck.

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