

Precipitation of Lignin from Softwood Black Liquor: An Investigation of the Equilibrium and Molecular Properties of Lignin

Weizhen Zhu ^a and Hans Theliander ^{a,b,*}

Extracting lignin from black liquor is an attractive option in modern pulp mills as a unit process for a combined biorefinery. The lignin obtained can be utilized as solid fuel or other high-value added products. The precipitation equilibrium of kraft lignin from softwood black liquor was studied in this work. It was found that with decreasing pH and temperature, or increasing ion strength, the solid yield increases. Moreover, precipitated softwood kraft lignin has a higher molecular weight and contains lower amounts of carbohydrates and phenolic groups than lignin precipitated from mixed hardwood/softwood black liquor. The content of methoxyl groups in softwood kraft lignin was found to decrease with increasing precipitation yield. An empirical model for estimating the precipitation yield of lignin was proposed and evaluated.

Keywords: Softwood black liquor; Carbohydrate analysis; ¹H and ¹³C NMR spectra of kraft lignin; Lignin precipitation; LignoBoost process; Molecular weight of lignin

Contact information: a: Forest Products and Chemical Engineering, Department of Chemical and Biological Engineering, Chalmers University of Technology, SE 41296 Gothenburg, Sweden; b: Wallenberg Wood Science Center, Chalmers University of Technology/Royal Institute of Technology Kemigården 4, SE 412 96 Gothenburg, Sweden; *Corresponding author: hanst@chalmers.se

INTRODUCTION

There is a great potential within the pulp and paper industry to produce high-value products other than pulp and paper. Implementing technology most recently available in pulp and paper mills could make it possible to improve the degree of utilization of renewable resources further, *e.g.*, lignin recovered from black liquor. The precipitation of lignin from black liquor by acidification has been investigated for a long time, and industrial production was started on a very small scale during the 1960s. There are also a number of studies that investigate the yield/equilibrium of lignin precipitation from black liquor. Alén *et al.* (1979) used both CO₂ and sulfuric acid to precipitate lignin from black liquor at 80 °C. They found, among other things, that a lignin precipitation yield of 90% was achieved when the black liquor was acidified to pH 2.0 using sulfuric acid. The yield was also found to increase for black liquor with a higher total dry solids (TDS) content. Uloth and Wearing (1989) compared two lignin separation procedures: acid precipitation, using pure sulfuric acid or chlorine dioxide generator waste acid (GWA), and ultrafiltration. The conclusion was that the former had a better recovery yield.

Recently, a novel method called “LignoBoost” (Theliander 2008) has been introduced and commercialized. Its final product is highly purified lignin (< 1 wt.% ash). The technical/scientific background to the LignoBoost process has been summarized in a number of papers (*e.g.*, Öhman *et al.* 2007; Wallmo *et al.* 2007, 2009a,b).

For energy applications, LignoBoost lignin can be used internally in the pulp mill as a biofuel to replace fuel oil in the lime kiln or coal in pressurized fluid bed combustion (PFBC) boilers (Tomani *et al.* 2011). For chemical and material applications, it has the potential to produce more valuable products, such as carbon fibers (Sudo and Shimizu 1992; Gellerstedt *et al.* 2010) and phenolic-based chemicals (Gellerstedt *et al.* 2012).

The pH of black liquor is rather high (pH 13 to 14), and the phenolic groups on lignin molecules are ionized, making the lignin soluble in a water solution. The precipitation (coagulation) of lignin from black liquor by acidification occurs because of the protonation of ionized phenolic groups on the lignin molecules. Protonation is more favorable for lignin molecules with a higher pK_a value; the apparent pK_a of kraft lignin has been found to be influenced by temperature, ion strength of solution, type of solvent, and the molecular structure of lignin (Rudatin *et al.* 1989; Norgren and Lindström 2000a; Ragnar *et al.* 2000). The protonation of phenolic groups reduces the electrostatic repulsive forces between lignin molecules (Gilardi and Cass 1993; Sundin 2000; Vainio *et al.* 2004), which then become less hydrophilic, leading to precipitation.

There are also some studies (Theliander 2010; Zhu *et al.* 2013) on how the yield/equilibrium in the precipitation step of LignoBoost process is influenced by different process conditions, *i.e.*, the pH, temperature, and ion strength of black liquor. One of the conclusions reached is that a higher precipitation yield of lignin can be achieved at a lower precipitation pH and temperature, or at a higher level of ion strength. The major subunit type in softwood lignins is the guaiacyl unit (G), whereas hardwood lignins contain approximately equal amounts of G and syringyl (S) units. The G-type lignins (mainly in softwood) consist of more carbon-carbon bonds, such as β -5 and 5-5' (Sjöström 1993) than S-type lignins (in hardwood) because of the greater availability of the C₅ position. This fact, together with the different amounts of functional groups present in softwood and hardwood lignins, has implications not only for the reactivity of lignin during kraft cooking but also for the resulting properties of softwood and hardwood kraft lignins.

Our previous work (Zhu *et al.* 2013) includes the investigation of macromolecular properties and the determination of functional groups (such as phenolic and methoxyl groups) of precipitated kraft lignin from mixed hardwood/softwood black liquor. Very little research of this type has been carried out on softwood lignin. Stoklosa *et al.* (2013) fractionated lignin in softwood black liquor by gradient acidification at elevated temperature and pressure (115 °C and 6.2 bar), and the resulting lignin was referred to as “liquid lignin”. They found that the molecular weight was lower, but the phenolic content was higher in the lignin fraction precipitated at lower pH.

In this work, softwood black liquor was used in a lignin precipitation study. The primary objectives were to investigate the influence of process conditions, *i.e.*, pH, ion strength, and temperatures (lower than those Stoklosa *et al.* (2013) used) on the equilibrium of lignin precipitation from softwood black liquor. Furthermore, characterizations of the chemical (Klason lignin, acid-soluble lignin, and carbohydrate content) and molecular properties (average molecular weight and content of functional groups) of the lignin precipitated were undertaken. The results in this study are compared with previous studies on mixed hardwood/softwood black liquor, regarding both the precipitation equilibrium and characterization of lignin. An empirical model for predicting the precipitation yield of lignin at a given condition is proposed and compared with the literature.

EXPERIMENTAL

Raw Material

A softwood (80% spruce and 20% pine) black liquor was used in this study. It was obtained from a Swedish batch kraft pulp mill producing bleachable-grade pulp. The sodium/potassium concentration was adjusted by adding deionized water (adjusted from 3.70 mol kg⁻¹ liq. to 2.87 mol kg⁻¹ liq.) so that it would be possible to compare the results from the authors' earlier study of mixed hardwood/softwood black liquors (Zhu *et al.* 2013).

Precipitation of Lignin from Black Liquor

The lignin precipitation experiments were carried out at laboratory scale using a procedure published previously (Zhu *et al.* 2013). This can be summarized as follows: 100 g of black liquor in a plastic bottle was placed in a water bath for 1 h to reach the target temperature. Sodium sulfate (Fisher Scientific, 99.5%) was added when a higher ion strength was required. Once the target temperature was reached, 6 M sulfuric acid was added to reach the target pH. The pH measurement was performed at room temperature using a JENWAY Model 370 pH/mV Meter with temperature correction. The electrode used was an Epoxy bodied combination pH electrode (924 005) suitable for pH measurement between 10 °C and 105 °C. A three-point calibration at pH 7.00, 10.00, and 12.00 was performed before the measurements were made. The sample was then shaken every 10 min for 1 h to obtain an apparent equilibrium. When precipitation was complete, the black liquor was filtered (dead-end filtration, using Munktell qualitative filter paper, Grade 5) using a Büchner funnel set-up; the filtrate was collected and stored at 4 °C. The filter cake (a dark-colored solid) was then washed with acidified (H₂SO₄) deionized water (pH approx. 3) and dried at 105 °C for 8 h. The experimental conditions were chosen within the optimized process conditions that can be expected in industrial units (Theliander 2008). The details are given in Table 1.

Table 1. Parameters used in the Lignin Precipitation Experiments

Temperature (°C)	Na Content (%)	pH
45, 65	Original	~11, ~10.5, ~10, ~9.5
45, 65	Original + 10 %	~11, ~10.5, ~10, ~9.5
45, 65	Original + 20 %	~11, ~10.5, ~10, ~9.5
75	Original	11

Analytical Methods

Characterization of the black liquor

The total dry solids (TDS) content of the black liquor was determined according to the TAPPI T650 om-09 method in which the sample was dried at 105 °C for 24 h; the experimental deviation was ±0.6%. The concentrations of NaOH and Na₂S were measured according to a titration method proposed by Wilson (1968). The errors in measurement of NaOH and Na₂S content were ±0.6% and ±2.2%, respectively. After wet combustion in a microwave oven, the Na and K concentrations of the black liquor were measured by atomic absorption spectroscopy (AAS) (Thermoscientific iCE 3000), with the errors in measurement being ±1.6% and ±6.0%, respectively. The Na concentration of the washed

lignin filter cake was also measured by AAS after wet combustion. The concentration of lignin was determined by UV light absorption using a Specord 205, Analytik Jena, with a wavelength of 280 nm. The absorption constant for softwood lignin was $24.6 \text{ dm}^3 \text{ g}^{-1} \text{ cm}^{-1}$ (Fengel *et al.* 1981). The experimental error of the UV measurements was estimated to be $\pm 0.9\%$.

Klason lignin and acid-soluble lignin

Klason lignin in the sample is the solid residual material after hydrolysis treatment with 72% sulfuric acid. A detailed description of the procedure can be found in a previous study (Zhu *et al.* 2013), in which Klason lignin, acid-soluble lignin, and monomeric sugars in the samples were analyzed. The concentration of acid-soluble lignin was measured by UV at 205 nm in a Specord 205, Analytik Jena. The absorption constant was $110 \text{ dm}^3 \text{ g}^{-1} \text{ cm}^{-1}$ (Dence 1992). The deviation of the results was estimated to be $\pm 0.9\%$.

Analysis of carbohydrates

The analysis of monomeric sugars in the samples was performed by high-performance anion exchange chromatography with pulsed amperometric detection (HPAEC-PAD) measurement, as described earlier (Zhu *et al.* 2013). The amounts of sugar analyzed were corrected for the acid hydrolysis yield (Janson 1974), which varies for different sugars; the values used were collected from experimental results reported by Wigell *et al.* (2007). The amounts of xylan and (galacto)glucomannan (GGM) were calculated using the algorithm described in Appendix A. The estimated error for determination is about 1% based on the calibration curve of standard samples.

Analysis of molecular weight

A gel permeation chromatograph (GPC) was used to determine the molecular weight of the precipitated lignin. The dried sample was dissolved in a dimethyl sulphoxide (DMSO)/LiBr (0.01 M) mixture to a concentration of 0.25 g L^{-1} . The measurement was performed on a PL-GPC 50 Plus, Integrated GPC System from Polymer Laboratories (A Varian Inc. Company) equipped with a detection system consisting of a refractive index (RI) and Ultraviolet (UV) detector. The UV measurement was performed at a wavelength of 280 nm, which is generally associated with lignin; the RI responses corresponded to both lignin and carbohydrates.

The system was equipped with two PolarGel-M (300×7.5 mm) columns and a PolarGel-M Guard column (50×7.5 mm). The mobile phase was a DMSO/LiBr (0.01 M) mixture; the sample was injected via a PL-AS RT GPC Autosampler at a flow rate of 0.5 mL min^{-1} . The sample was analyzed using the software Cirrus GPC Version 3.2. Pullulan of nine different molecular weights (708, 375, 200, 107, 47.1, 21.1, 5.9, 0.667, and 0.18 kDa) was employed for calibration (Polysaccharide Calibration Kit, PL2090-0100, Varian). The estimated error for determination is about 5% based on the calibration curve of standard samples. All the results obtained were baseline corrected.

Analysis of quantitative functional groups

^1H and ^{13}C nuclear magnetic resonance spectroscopy (NMR) was performed to analyze the content of functional groups in precipitated lignin. Prior to the NMR examination, the samples were acetylated using the method proposed by Lundquist (1992b). The acetylated lignin sample was dissolved in DMSO- d_6 (99.8%, ARMAR Chemicals) with a concentration of approximately 200 g L^{-1} . The ^1H and ^{13}C NMR spectra

were recorded at 25 °C on a Bruker Avance III HD 18.8 T NMR spectrometer equipped with a 5-mm TCI Cryoprobe (cold ^1H and ^{13}C channels) operating at a frequency of 800 MHz for ^1H and 201 MHz for ^{13}C detection. The ^1H spectra were recorded with a 90° pulse angle, 5-s pulse delay, 1024 scans, and 2.56-s acquisition time. The ^{13}C spectra were recorded with an inverse-gated decoupling sequence, 90° pulse angle, 12-s pulse delay, 3200 scans, and 1.36-s acquisition time. The resulting spectra were baseline corrected and processed by MestreNove (Mestrelab Research); the standard deviation estimated by Landucci (1985) and Pu and Ragauskas (2005) is 3.0%.

RESULTS AND DISCUSSION

Characterization of Black Liquor

Results from the chemical analysis of the diluted softwood black liquor used are shown in Table 2. An acid titration was also made: the resulting titration curve (not presented in this paper) was similar to those obtained by Wallmo *et al.* (2007) for typical softwood black liquors. This indicates that the protonation of the different compounds in the two black liquors is very similar.

Table 2. Some Important Characteristics of the Softwood Black Liquor* Sample

Characteristic	Content (g kg ⁻¹ liq.)
Na	61.5
K	7.7
Lignin UV	118.5
Lignin Klason	98.8
Acid-soluble Lignin	24.0
NaOH	11.2
Na ₂ S	14.7
Carbohydrates	5.5
-Arabinose	1.2
-Galactose	2.0
-Glucose	0.6
-Xylose	1.6
-Mannose	0.1

* The dry solids content of black liquor is 32.0%

Equilibrium of Lignin Precipitation

In this work, the precipitation yield of lignin (*Yield*) was calculated as,

$$Yield = \frac{L_{BL} - L_F}{L_{BL}} \times 100\% \quad (1)$$

where L_{BL} is the lignin concentration of the black liquor and L_F is the lignin concentration of the lignin-lean filtrate after precipitation. The concentration values are determined as Klason lignin.

In Fig. 1, it can be clearly seen that the precipitation yield of lignin increased with decreasing pH or temperature, as well as with increasing ion strength of the black liquor. This is in agreement with recent studies (Theliander 2010; Zhu *et al.* 2013). A higher concentration of hydrogen ions promotes the protonation of phenolic groups on the lignin molecules and neutralizes the surface charges. The repulsive forces between molecules are

decreased, such that the lignin molecules coagulate and the precipitation occurs. The pK_a of kraft lignin is higher at lower temperatures, and thus the solubility is decreased (Norgren and Lindström 2000a). A higher ion strength is also favorable for lignin precipitation due to the repulsive forces between lignin molecules being screened (Norgren *et al.* 2001), *i.e.*, increasing the ion strength will reduce the range of repulsive interactions between lignin molecules. The lignin molecules then become close enough for attractive forces to become dominant.

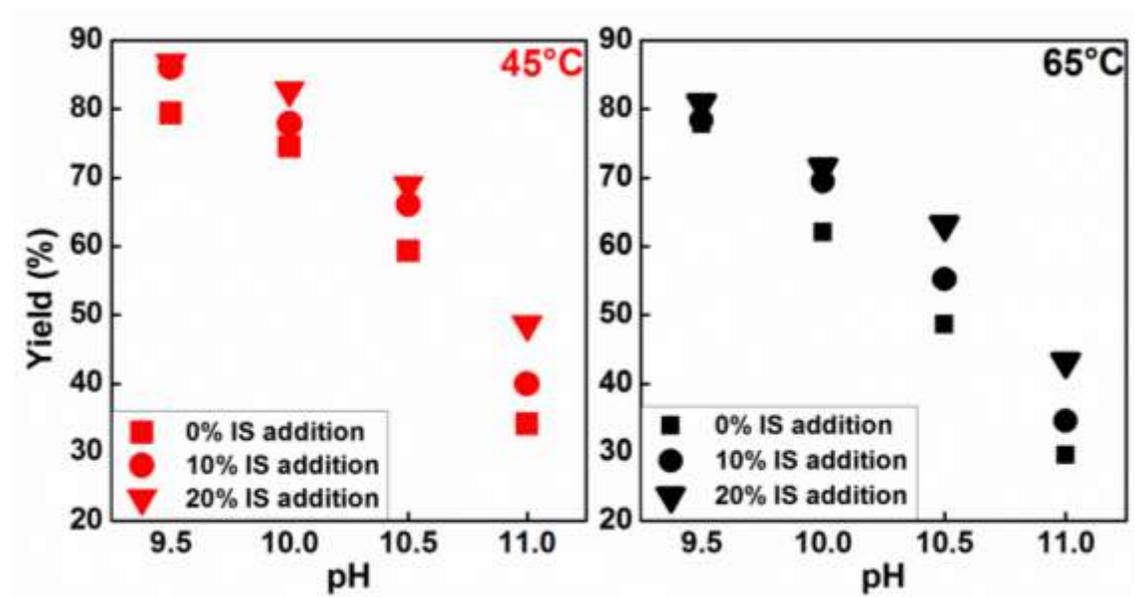


Fig. 1. Precipitation yield of lignin from softwood black liquor at various temperatures, pH, and ion strength (IS) additions

Characteristics of Precipitated Kraft Lignin

Determination of average molecular weight

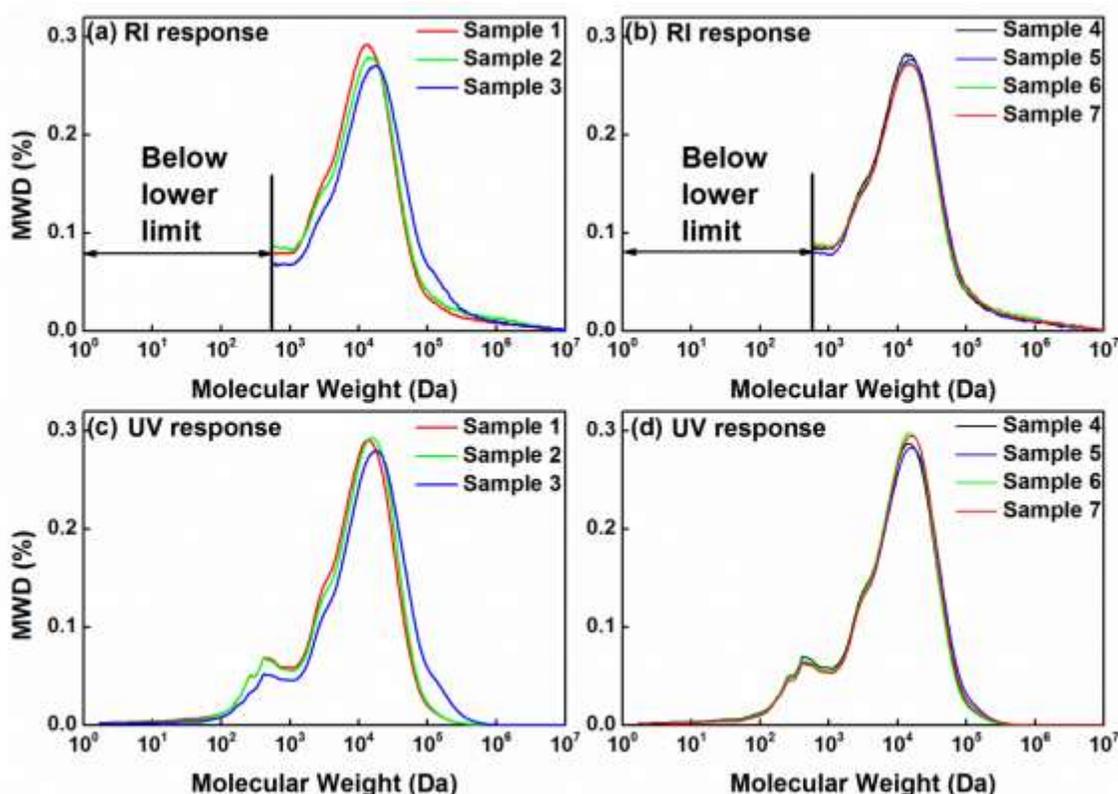
Seven samples of precipitated lignin were selected for GPC and NMR analysis (Table 3). Samples 1 through 3 are those that achieved at the highest, medium, and lowest precipitation yields, respectively. The precipitation conditions of samples 4 through 7 were 65 °C with no extra addition of salt and varying pH levels, *i.e.*, 9.5, 10, 10.5, and 11.

The relationship between the precipitation yield of lignin and the weight-average molecular weights (M_w) of lignin are also given in Table 3. It can be seen that the M_w value measured by RI response was higher than that measured using the UV response, which is mainly due to the RI detector having a lower sensitivity than the UV detector in the region of lower molecular weight, and therefore the molecular weight fraction below the detect limitation of RI has been omitted (Fig. 2). The results show that the M_w of lignin was lower at higher precipitation yield. The number-average molecular weight (M_n) of lignin precipitated by RI and UV detection was also measured: for samples 1 through 3, a clear increasing trend (RI response) with decreasing precipitation yield was found, whereas only a weak tendency between the precipitation yield and the M_n in samples 4 through 7 was observed. These findings are in agreement with our previous study (Zhu *et al.* 2013).

The molecular weight distribution (MWD) profiles of the lignin samples are reported in Fig. 2. In general, the MWD profiles produced from the RI and UV responses are similar. Moreover, the molecular weight profile confirms yet again that the molecular weight of precipitated lignin decreases with increasing precipitation yield.

Table 3. Weight-Average Molecular Weight (M_w) of Softwood Kraft Lignin and its Corresponding Precipitation Yield

Sample No.	Ion Strength Addition (%)	Precipitation pH	Temperature (°C)	Mw (kDa)		Mn (kDa)		Precipitation Yield (%)
				RI	UV	RI	UV	
1	20	9.5	45	16.7	14.5	8.0	2.0	86.7
2	10	10	65	17.7	15.2	8.6	1.7	69.5
3	0	11	75	26.9	24.9	10.3	2.2	26.4
4	0	9.5	65	17.3	15.0	8.6	1.8	77.8
5	0	10	65	18.1	15.2	8.9	2.0	62.0
6	0	10.5	65	18.3	15.4	8.6	1.9	48.6
7	0	11	65	19.7	16.2	9.0	2.0	29.4

**Fig. 2.** Molecular weight distribution (MWD) of the precipitated softwood kraft lignin samples

Analysis of Functional Groups

^{13}C NMR spectroscopy

The ^{13}C NMR spectra of acetylated lignin samples are presented in Fig. 3. The chemical shift (δ) is the difference (parts per million, ppm) of the resonant frequency of a nucleus (^{13}C) relative to a standard (tetramethylsilane, TMS, defined as zero). The chemical shift assignments of lignin moieties and its integrated peak areas are based on the literature (Mörck and Kringstad 1985; Pu and Ragauskas 2005) and summarized in Table 4. The integral of the aromatic region (δ_c 106 to 154 ppm) was calibrated to 6, which represents 6 aromatic carbons (Landucci *et al.* 1998; Ralph and Landucci 2010; Min *et al.* 2013; Wells Jr. *et al.* 2013).

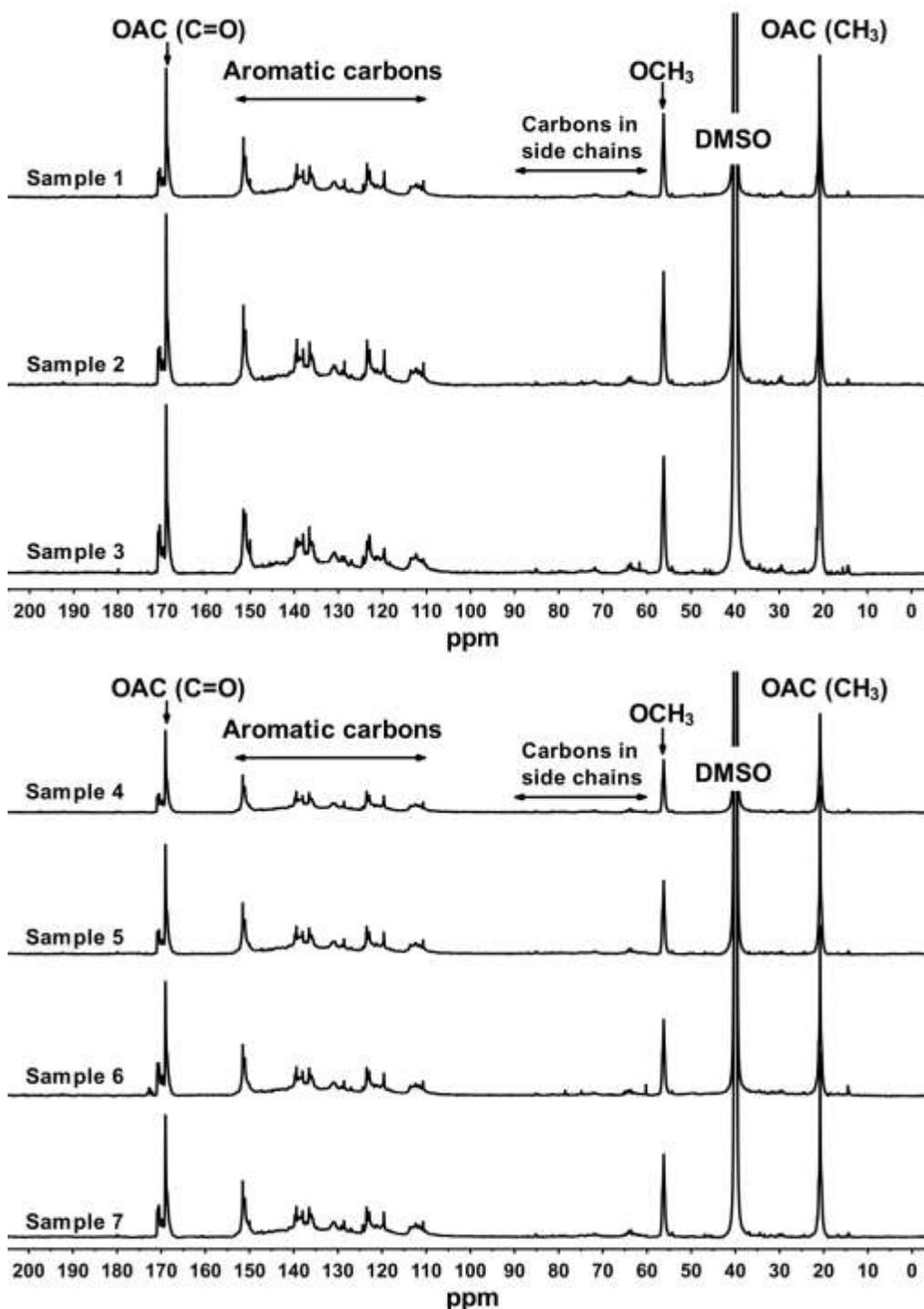


Fig. 3. ^{13}C NMR spectra of the precipitated softwood kraft lignin

The quantitative evaluation of functional groups (OH_{phen} and OMe) was thus integrated relative to this value (Robert 1992; Faix *et al.* 1994; Ralph and Landucci 2010; Choi and Faix 2011). The chemical shift region (δ_{C} 166 to 168.8 ppm) originates from the carbonyl in acetoxy groups ($\text{Ac.OH}_{\text{phen}}$). The signal of methoxyl groups (OMe) appears in chemical shift regions between δ_{C} 54 and 57.5 ppm.

Table 4 shows that the content of phenolic groups decreased from samples 1 through 3 and from samples 4 through 7, *i.e.*, as the precipitation yield decreased. It can also be seen from Table 3 that the molecular weight of lignin increased from samples 1 through 3 and 4 through 7, which indicates that larger lignin molecules had fewer phenolic groups, per unit mass, than smaller ones. The content of methoxyl groups in the precipitated lignin increases from samples 1 through 3 and 4 through 7 with increasing molecular weight of the lignin, which is in agreement with previous studies (Wada *et al.* 1962; Lin and Detroit 1981; Mörck *et al.* 1986). This may occur because lignin has a lower molecular weight and is degraded more extensively during kraft cooking; more methyl-aryl ether linkages on the lignin aromatic ring could also have been cleaved off (Gellerstedt 2009), resulting in smaller lignin molecules having a lower methoxyl content.

Table 4. Quantitative Analysis of the Softwood Kraft Lignin Based on ^{13}C NMR and ^1H NMR Spectra

Sample No.	^{13}C -NMR		^1H -NMR	
	Ac. OH _{phen}	OMe	Ac. OH _{phen}	OMe
	166-168.8 ppm	54-57.5 ppm	2.1-2.4 ppm	3.4-4.0 ppm
1	89	70	224	333
2	86	74	208	347
3	80	79	188	376
4	87	72	211	343
5	85	75	205	351
6	83	77	200	361
7	81	78	195	370

All values calculated on 100 C₉ basis.

^1H NMR spectroscopy

^1H NMR spectroscopy was also used for the characterization of functional groups in the precipitated kraft lignin. The spectra of lignin samples are shown in Fig. 4; the chemical shifts of phenolic acetate ($\delta_{\text{H}} \approx 2.3$) and OMe ($\delta_{\text{H}} \approx 3.8$) can be found in the literature (Lundquist 1991, 1992a,b). The number of protons *per* aromatic ring ($\delta_{\text{H}} \approx 7$) is assumed to be 2.5 for kraft lignin (Li and Lundquist 1994), allowing the quantitative integration of phenolic (acetylated) and OMe groups.

Table 4 also reports the content of phenolic and methoxyl groups in lignin by ^1H NMR; the trends of these groups with the change in molecular weights of the lignin are in accordance with the results obtained from ^{13}C NMR spectra.

Analysis of carbohydrates and lignin

The concentrations of xylan and GGM in the filter cake (precipitated lignin) and filtrates are listed in Table 5. It can be seen that, at 45 °C and a precipitation pH between 9.5 and 11, the concentration of GGM in the filter cake increased with increasing pH (*i.e.*, with lower yield). As discussed earlier in this study, the precipitated lignin had a higher molecular weight at higher pH levels. Thus, the higher concentration of GGM in large lignin molecules could occur because they were actually linked together, as the latter have been degraded/decoupled to a lesser degree during the cooking operation.

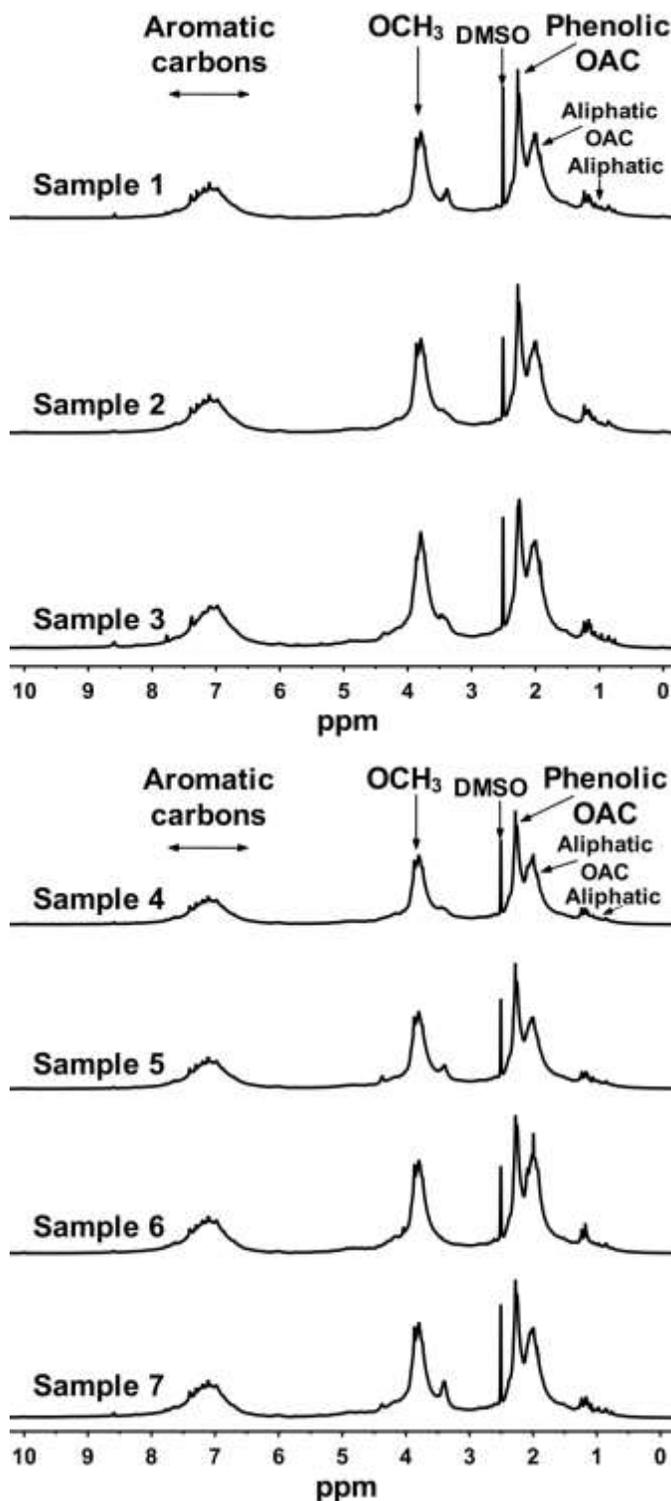


Fig. 4. ^1H NMR spectra of the precipitated softwood kraft lignin

The same trend was also found for xylan in filter cakes at 45 °C, but the increase was not as large as for GGM. A plausible reason for this might be that the yield loss is higher for GGM than xylan (Sjöström 1993) in kraft cooking; compared to xylan, GGM had thus been degraded/decoupled to a larger degree. Also, at 65 °C, the concentration of

GGM in filter cakes increased with increasing precipitation pH, while that of xylan seems to have been independent of pH. Another interesting observation is that the overall GGM content was much higher at 65 °C than that at 45 °C, especially at pH levels of 9.5 and 10. This is in agreement with the discussion above: at low temperatures, lignin molecules of low molecular weight were also precipitated, and thus the precipitated lignin contained less amounts of GGM. Moreover, it has also been suggested by Lawoko *et al.* (2005) that, during pulping, glucomannan-linked lignin undergoes a partial condensation that causes larger molecules to be formed. This is in agreement with the observation made in this paper, *i.e.*, the GGM content of the precipitated lignin was higher with higher M_w .

Values for the sum of Klason lignin, acid-soluble lignin, and total carbohydrates of precipitated lignin are shown in Table 5. The average Na content of the precipitated lignin is 0.4 ± 0.2 wt.%, which indicates that the lignin was well washed after precipitation.

The concentrations of xylan and GGM in the filtrates seem to remain constant compared with those in the filter cakes.

Comparison between the Precipitation of Lignin from Softwood and Mixed Hardwood/Softwood Black Liquor

In a previous study (Zhu *et al.* 2013), the equilibrium of lignin precipitation and the molecular/chemical characterization of precipitated lignin from mixed hardwood (birch)/softwood (pine and spruce) black liquor was investigated. It should be kept in mind that the properties of the black liquor depend on both the type of raw material used and the process conditions of the pulp mill in question. Our comparison is therefore based on the characterizations performed on the filtrate and precipitated lignin. As stated earlier, it was ensured that the sum of the sodium and potassium content of the softwood black liquor used in this study was the same as in a mixed hardwood/softwood black liquor. Although the Klason lignin content in the mixed black liquor was found to be lower, the acid-soluble lignin concentration was higher than the black liquor from this study. However, the mixed black liquor has a higher concentration of carbohydrates, especially xylan, which is the major hemicellulose component of hardwood (Sjöström 1993).

Precipitation yield of lignin

The precipitation yields of lignin from the mixed hardwood/softwood and softwood black liquors are listed in Appendix B. In general, the trends of the yield from the mixed hardwood/softwood black liquor at various conditions (Zhu *et al.* 2013) were the same as for the softwood black liquor (Fig.1). However, it is difficult to compare the overall precipitation yield of lignin obtained from these two black liquors: the differences in yield were small, often close to the experimental error. Nevertheless, at the lowest/highest precipitation yield points, the mixed black liquor lignin showed a slightly lower precipitation yield than softwood black liquor. One reason could be the following: the molecular weight of lignin in mixed black liquor was found to be lower than in softwood black liquor; NMR analysis also showed that the content of phenolic groups in mixed hardwood/softwood lignin was higher than in softwood lignin. This is in agreement with an earlier study by Norgren and Lindström (2000b), who found that kraft lignin with lower molecular weights and a higher content of phenolic groups has a lower pK_a value and therefore a lower precipitation yield (*i.e.*, higher solubility).

Table 5. Concentrations of Xylan, GGM, Total Carbohydrates, Klason Lignin and ASL (g kg^{-1} Total Dry Solid (TDS)) of Filter Cakes (precipitated softwood kraft lignin) and Concentration of Xylan and GGM of Filtrates at Various pH, Temperatures, and Additions of Ion Strength (IS)

Temperature (°C)	pH	Filter cake					Filtrate	
		GGM	Xylan	Total carbohydrates	Klason lignin	ASL	GGM	Xylan
45	9.5	3.1 ± 0.4	5.9 ± 0.6	9.9 ± 1.1	936 ± 1	8 ± 0.2	5.3 ± 0.5	7.6 ± 0.9
	10	4.9 ± 1.0	6.6 ± 0.7	13.9 ± 2.7	924 ± 4	10 ± 0.3	5.3 ± 0.5	7.9 ± 1.0
	10.5	6.5 ± 0.5	6.8 ± 0.9	14.7 ± 1.6	929 ± 11	10 ± 2	5.2 ± 0.5	8.0 ± 1.0
65	11	9.7 ± 0.4	7.8 ± 0.7	19.4 ± 0.7	916 ± 1	9 ± 1	5.1 ± 0.5	8.0 ± 0.8
	9.5	7.3 ± 0.3	6.6 ± 0.2	16.6 ± 0.5	899 ± 17	10 ± 1	5.9 ± 0.5	8.5 ± 0.7
	10	7.5 ± 0.3	6.7 ± 0.3	15.7 ± 0.6	904 ± 3	11 ± 3	5.7 ± 0.4	8.6 ± 0.7
IS Addition to Black Liquor (%)	10.5	8.5 ± 0.2	6.6 ± 0.5	16.6 ± 0.5	893 ± 39	10 ± 1	5.6 ± 0.3	8.7 ± 0.6
	11	10.7 ± 0.5	6.7 ± 0.6	19.2 ± 0.6	899 ± 29	10 ± 1	5.4 ± 0.4	8.5 ± 0.6
	0	7.0 ± 2.5	6.3 ± 0.7	15.3 ± 3.2	908 ± 31	10 ± 2	5.9 ± 0.2	9.0 ± 0.3
IS Addition to Black Liquor (%)	10	7.4 ± 2.4	7.0 ± 0.5	16.0 ± 3.0	911 ± 22	10 ± 1	5.4 ± 0.3	8.2 ± 0.4
	20	7.2 ± 2.5	7.2 ± 0.8	15.9 ± 3.5	919 ± 10	10 ± 1	5.0 ± 0.3	7.4 ± 0.6

One reason for this could be that mixed black liquor consists of a large fraction of hardwood lignin that contains a high amount of β -aryl ether linkages (Larsson and Miksche 1971; Sjöström 1993); these linkages are heavily degraded during the kraft pulping process and, consequently, more free phenolic groups are released. Moreover, fewer C-C bonds between the S-type lignins, along with the lack of reactive C₅ positions in aromatic nuclei for condensation reactions (Mörck *et al.* 1988), also result in hardwood kraft lignin having a lower M_w. Another reason for the precipitation yield of lignin from mixed black liquor being lower might be that after the ion strength of both black liquors has been adjusted to the same value (2.87 mol kg⁻¹ liq.), the mixed hardwood/softwood black liquor has a slightly lower concentration of lignin, which may influence the result to some extent (Öhman *et al.* 2007; Wallmo *et al.* 2009a). In short, the differences in the highest/lowest

precipitation yields obtained from the two black liquors could be due to differences in the molecular structure (M_w and phenolic group) of the lignin as well as slightly different concentrations of lignin in the black liquors.

The mixed lignin was also found to have more methoxyl groups than the softwood lignin, which might be a result of the S-type lignin present in hardwood. Moreover, the OMe content increased as the M_w of softwood kraft lignin increased, as found earlier in this study. However, as shown in a previous study, the OMe content decreased as the M_w of mixed hardwood/softwood lignin increased, which might occur because the fraction of S-type lignin in precipitated lignin at higher M_w is lower for mixed lignins (Zhu *et al.* 2013). The concentrations of xylan and GGM in filter cakes and filtrates at different additions of ion strength for softwood black liquor are given in Table 5. The precipitated softwood lignin contains higher amounts of GGM but lower amounts of xylan than the mixed hardwood/softwood lignin, which is in agreement with earlier studies (Sjöström 1993; Henriksson 2009).

Estimation of the lignin precipitation yield

A simple model for estimating the precipitation yield of lignin from softwood black liquor, based on that proposed by Theliander (2010), has been developed in Eq. 2, in which the average molecular weight of precipitated lignin is also considered:

$$Yield = a \times \exp\left(\frac{b}{T}\right) (H^+)^c (Na^+ + K^+)^d \times M_w^{-e} \quad (2)$$

In Eq. 2 the *Yield* is the precipitation yield of lignin (%), *T* is the temperature in Kelvins, H^+ is the hydrogen ion concentration (mole L⁻¹), and Na^+ and K^+ are the sodium and potassium concentrations (g kg⁻¹ liq.), respectively, of the black liquor. M_w is the weight-average molecular weight of lignin in the black liquor, which is determined by precipitating lignin at pH 2.5, 45 °C and measuring the M_w of the precipitated lignin (using GPC, UV detector). The values of M_w are approx. 9000 and 11,800 Da for mixed hardwood/softwood and softwood lignin, respectively.

The values of parameters *a*, *b*, *c*, *d*, and *e* are obtained by fitting Eq. 2 to the experimental data (Appendix B); the values of the parameters are presented in Table 6. It can be seen that *a*, *b*, *c*, and *d* are relatively similar for both liquors. Parameter *e*, on the other hand, differs significantly. This is probably because the M_w values of the kraft lignin in these black liquors are rather different. The yields estimated by Eq. 2 are illustrated in Fig. 5. The parameters used were derived from Table 6. Compared with the yield estimated in a previous study (Zhu *et al.* 2013), it can be concluded that introducing the new term M_w improved the accuracy of estimation only slightly in this model. It is obvious that a more mechanistic model is required if greater accuracy is to be achieved.

Table 6. Numerical Values of the Parameters in Eq. 2 valid for a Previous Study and This Work

Application	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>	Error (%)
This work	160	503	0.197	0.674	0.077	10.6
Zhu <i>et al.</i> (2013)	181	425	0.264	0.901	0.008	14.6

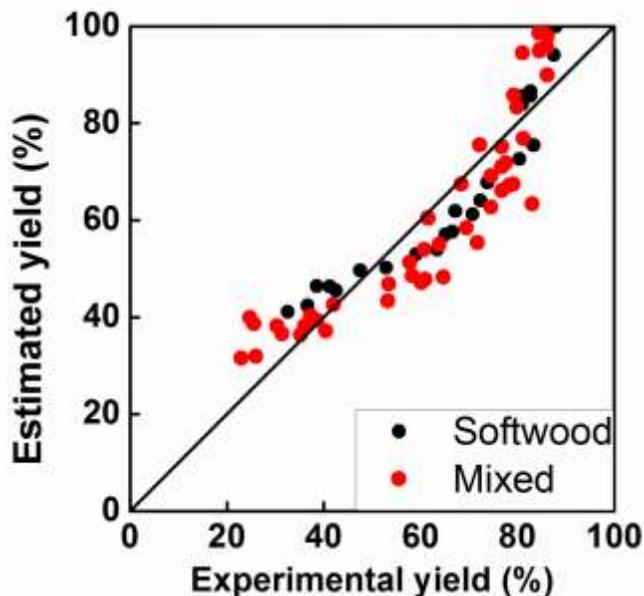


Fig. 5. Experimental versus estimated yields of lignin

CONCLUSIONS

1. The average molecular weight of kraft lignin precipitated from softwood black liquor decreases as the precipitation yield increases, *i.e.*, lower pH and/or temperature, and higher ion strength.
2. The amount of phenolic groups in precipitated softwood lignin increases with an increase in the precipitation yield, whereas the amount of methoxyl groups decreases.
3. The content of carbohydrates in precipitated softwood kraft lignin decreases with either a decrease in pH or an increase in ion strength in the precipitation. Also, softwood kraft lignin with a higher M_w contains higher amounts of GGM.
4. In a comparison of the properties of softwood and mixed hardwood/softwood lignin respectively, it was found that:
 - a. The precipitation yield was about the same.
 - b. The content of phenolic groups increases with increasing yield/decreasing molecular weight for lignin precipitated from both softwood and mixed hardwood/softwood. This is due to the fact that phenolic groups are formed when the lignin is degraded during kraft cooking.
 - c. The content of methoxyl groups, however, decreases with increasing yield/decreasing molecular weight for softwood lignin whilst the opposite is found for the mixed hardwood/softwood lignin. This is most likely due to the differences in structure of the two types of lignin. Moreover, the precipitated softwood lignin also contains lower amounts of phenolic and methoxyl groups but higher amount of GGM than mixed hardwood/softwood lignin.

ACKNOWLEDGMENTS

Thanks are due to Mr. Göran Karlsson and Mr. Maxim Mayzel at The Swedish NMR Centre in Gothenburg for their help in executing the ^1H and ^{13}C NMR spectroscopy. Chalmers Energy Initiative (CEI) is gratefully acknowledged for their financial support.

REFERENCES CITED

- Alén, R., Patja, P., and Sjöström, E. (1979). "Carbon dioxide precipitation of lignin from pine kraft black liquor," *TAPPI* 62(11), 108-110.
- Choi, J. W., and Faix, O. (2011). "NMR study on residual lignins isolated from chemical pulps of beech wood by enzymatic hydrolysis," *Journal of Industrial and Engineering Chemistry* 17(1), 25-28. DOI: 10.1016/j.jiec.2010.10.004
- Dence, C. W. (1992). "The determination of lignin," in: *Methods in Lignin Chemistry*, S. Y. Lin and C. W. Dence (eds.), Springer-Verlag, Heidelberg, Germany, pp. 33-58.
- Faix, O., Argyropoulos, D. S., Robert, D., and Neirinck, V. (1994). "Determination of hydroxyl groups in lignins evaluation of ^1H -, ^{13}C -, ^{31}P -NMR, FTIR and wet chemical methods," *Holzforschung* 48(5), 387-394. DOI: 10.1515/hfsg.1994.48.5.387
- Fengel, D., Wegener, G., and Feckl, J. (1981). "Contribution to characterization of analytical and technical lignins. (2) Physical-chemical and electron microscopical studies," *Holzforschung* 35(3), 111-118. DOI: 10.1515/hfsg.1981.35.3.111
- Gellerstedt, G. (2009). "Chemistry of chemical pulping," in: *The Pulp and Paper Chemistry and Technology, Volume 2 Pulping Chemistry and Technology*, M. Ek, G. Gellerstedt, and G. Henriksson (eds.), De Gruyter, Berlin, pp. 91-120.
- Gellerstedt, G., Sjöholm, E., and Brodin, I. (2010). "The wood-based biorefinery: A source of carbon fiber?," *Open Agriculture Journal* 4(2), 119-124. DOI: 10.2174/1874331501004010119
- Gellerstedt, G., Tomani, P., Axegård, P., and Backlund, B. (2012). "Lignin recovery and lignin-based products," in: *Integrated Forest Biorefineries: Challenges and Opportunities*, C. Lew (ed.), Royal Society of Chemistry, Cambridge, UK, pp. 180. DOI: 10.1039/9781849735063-00180
- Gilardi, G., and Cass, A. E. G. (1993). "Associative and colloidal behavior of lignin and implications for its biodegradation in vitro," *Langmuir* 9(7), 1721-1726. DOI: 10.1021/la00031a019
- Henriksson, G., Brännvall, E., and Lennholm, H. (2009). "The trees," in: *The Pulp and Paper Chemistry and Technology, Volume 1 Wood Chemistry and Wood Biotechnology*, M. Ek, G. Gellerstedt, and G. Henriksson (eds.), De Gruyter, Berlin, pp. 13-44.
- Janson, J. (1974). "Analysis of the polysaccharides in wood and pulp," *Faserforschung und Textiltechnik* 25(9), 375-382.
- Landucci, L. L. (1985). "Quantitative ^{13}C NMR characterization of lignin 1. A methodology for high precision," *Holzforschung* 39(6), 355-360. DOI: 10.1515/hfsg.1985.39.6.355
- Landucci, L. L., Ralph, S. A., and Hammel, K. E. (1998). " ^{13}C NMR characterization of guaiacyl, guaiacyl/syringyl and syringyl dehydrogenation polymers," *Holzforschung* 52(2), 160-170. DOI: 10.1515/hfsg.1998.52.2.160

- Larsson, S., and Miksche, G. E. (1971). "Gaschromatographische Analyse von Ligninoxidationsprodukten. IV. Zur Struktur des Lignins der Birke," *Acta Chemica Scandinavica* 25, 647-662. DOI: 10.3891/acta.chem.scand.25-0647
- Lawoko, M., Henriksson, G., and Gellerstedt, G. (2005). "Structural differences between the lignin-carbohydrate complexes present in wood and in chemical pulps," *Biomacromolecules* 6(6), 3467-3473. DOI: 10.1021/bm058014q
- Li, S., and Lundquist, K. (1994). "A new method for the analysis of phenolic groups in lignins by ^1H NMR spectroscopy," *Nordic Pulp & Paper Research Journal* 9(3), 191-195. DOI: 10.3183/NPPRJ-1994-09-03-p191-195
- Lin, S. Y., and Detroit, W. (1981). "Chemical heterogeneity of technical lignins - Its significance in lignin utilization," *The 1st International Symposium on Wood and Pulp Chemistry*, Stockholm, Sweden, pp. 44-52.
- Lundquist, K. (1991). " ^1H NMR spectral studies of lignins quantitative estimates of some types of structural elements," *Nordic Pulp & Paper Research Journal* 6(3), 140-146. DOI: 10.3183/NPPRJ-1991-06-03-p140-146
- Lundquist, K. (1992a). " ^1H NMR spectral studies of lignins. Results regarding the occurrence of beta-5 structures, beta-beta structures, non-cyclic benzyl aryl ethers, carbonyl groups and phenolic groups," *Nordic Pulp & Paper Research Journal* 6(1), 4-8,16.
- Lundquist, K. (1992b). "Proton (^1H) NMR spectroscopy," in: *Methods in Lignin Chemistry*, S. Y. Lin and C. W. Dence (eds.), Springer-Verlag, Heidelberg, Germany, pp. 242-247. DOI: 10.1007/978-3-642-74065-7_17
- Meier, H. (1958). "Studies on hemicelluloses from pine (*Pinus silvestris* L.)," *Acta Chemica Scandinavia* 12, 1911-1918. DOI: 10.3891/acta.chem.scand.12-1911
- Min, D.-y., Smith, S. W., Chang, H.-m., and Jameel, H. (2013). "Influence of isolation condition on structure of milled wood lignin characterized by quantitative ^{13}C nuclear magnetic resonance spectroscopy," *BioResources* 8(2), 1790-1800. DOI: 10.15376/biores.8.2.1790-1800
- Mörck, R., and Kringstad, K. P. (1985). " ^{13}C -NMR spectra of kraft lignins II. Kraft lignin acetates," *Holzforschung* 39(2), 109-119. DOI: 10.1515/hfsg.1985.39.2.109
- Mörck, R., Yoshida, H., Kringstad, K. P., and Hatakeyama, H. (1986). "Fractionation of kraft lignin by successive extraction with organic solvents. I. Functional groups, ^{13}C NMR-spectra and molecular weight distributions," *Holzforschung* 40(Supplement issue), 51-60.
- Mörck, R., Reimann, A., and Kringstad, K. P. (1988). "Fractionation of kraft lignin by successive extraction with organic solvents. III. Fractionation of kraft lignin from birch," *Holzforschung* 42(2), 111-116. DOI: 10.1515/hfsg.1988.42.2.111
- Norgren, M., and Lindström, B. (2000a). "Dissociation of phenolic groups in kraft lignin at elevated temperatures," *Holzforschung* 54(5), 519-527. DOI: 10.1515/hf.2000.088
- Norgren, M., and Lindström, B. (2000b). "Physico-chemical characterization of a fractionated kraft lignin," *Holzforschung* 54(5), 528-534. DOI: 10.1515/hf.2000.089
- Norgren, M., Edlund, H., Wågberg, L., Lindström, B., and Annergren, G. (2001). "Aggregation of kraft lignin derivatives under conditions relevant to the process, Part I: Phase behaviour," *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 194(1-3), 85-96. DOI: 10.1016/S0927-7757(01)00753-1
- Öhman, F., Wallmo, H., and Theliander, H. (2007). "Precipitation and filtration of lignin from black liquor of different origin," *Nordic Pulp & Paper Research Journal* 22(2), 188-193. DOI: 10.3183/NPPRJ-2007-22-02-p188-193

- Pu, Y., and Ragauskas, A. J. (2005). "Structural analysis of acetylated hardwood lignins and their photoyellowing properties," *Canadian Journal of Chemistry* 83(12), 2132-2139. DOI: 10.1139/v05-231
- Ragnar, M., Lindgren, C. T., and Nilvebrant, N.-O. (2000). "pKa-values of guaiacyl and syringyl phenols related to lignin," *Journal of Wood Chemistry and Technology* 20(3), 277-305. DOI: 10.1080/02773810009349637
- Ralph, J., and Landucci, L. L. (2010). "NMR of lignins," in: *Lignin and Lignans: Advances in Chemistry*, C. Heitner, D. Dimmel, and J. A. Schmidt (eds.), CRC Press, Boca Raton, FL, pp. 137-234. DOI: 10.1201/EBK1574444865-c5
- Robert, D. (1992). "Carbon-13 nuclear magnetic resonance spectrometry," in: *Methods in Lignin Chemistry*, S. Lin and C. Dence (eds.), Springer-Verlag, Heidelberg, Germany, pp. 250-273. DOI: 10.1007/978-3-642-74065-7_18
- Rudatin, S., Sen, Y. L., and Woerner, D. L. (1989). "Association of kraft lignin in aqueous solution," in: *Lignin: Properties and Materials*, W. G. Glasser and S. Sarkanen (eds.), American Chemical Society, Washington, DC, pp. 144-154. DOI: 10.1021/bk-1989-0397.ch011
- Sjöström, E. (1993). *Wood Chemistry: Fundamentals and Applications*, Academic Press, Waltham, MA. DOI: 10.1016/B978-0-08-092589-9.50002-4
- Stoklosa, R. J., Velez, J., Kelkar, S., Saffron, C. M., Thies, M.C., and Hodge, D.B. (2013). "Correlating lignin structural features to phase partitioning behavior in a novel aqueous fractionation of softwood Kraft black liquor," *Green Chem.* 15, 2904–2912. DOI: 10.1039/c3gc41182f
- Sudo, K., and Shimizu, K. (1992). "A new carbon fiber from lignin," *Journal of Applied Polymer Science* 44(1), 127-134. DOI: 10.1002/app.1992.070440113
- Sundin, J. (2000). *Precipitation of Kraft Lignin under Alkaline Conditions*, Ph.D dissertation, Royal Institute of Technology, Stockholm, Sweden.
- Theliander, H. (2008). "Withdrawing lignin from black liquor by precipitation, filtration and washing," *Nordic Wood Biorefinery Conference*, Stockholm, Sweden, pp. 36-42.
- Theliander, H. (2010). "The Lignoboost process: Solubility of lignin," *International Chemical Recovery Conference*, Williamsburg, VA, pp. 33-42.
- Tomani, P., Axegård, P., Berglin, N., Lovell, A., and Nordgren, D. (2011). "Integration of lignin removal into a kraft pulp mill and use of lignin as a biofuel," *Cellulose Chemistry and Technology* 45(7), 533-540.
- Uloth, V. C., and Wearing, J. T. (1989). "Kraft lignin recovery - Acid precipitation versus ultrafiltration. 1. Laboratory test-results," *Pulp & Paper-Canada* 90(9), 67-71.
- Vainio, U., Maximova, N., Hortling, B., Laine, J., Stenius, P., Simola, L. K., Gravitis, J., and Serimaa, R. (2004). "Morphology of dry lignins and size and shape of dissolved kraft lignin particles by X-ray scattering," *Langmuir* 20(22), 9736-9744. DOI: 10.1021/la048407v
- Wada, S., Iwamida, T., Iizima, R., and Yabe, K. (1962). "The bonds between thiolignin and synthetic rubber. VII. Fractional precipitation of thiolignin from kraft pulping waste liquor with the variation of pH and reinforcement of SBR with each fraction," *Kobunshi Kagaku (The Chemistry of High Polymers)* 19(211), 699-703. DOI: 10.1295/koron1944.19.699
- Wallmo, H., Richards, T., and Theliander, H. (2007). "Lignin precipitation from kraft black liquors: Kinetics and carbon dioxide absorption," *Paperi Ja Puu-Paper and Timber* 89(7-8), 436-442.

- Wallmo, H., Richards, T., and Theliander, H. (2009a). "An investigation of process parameters during lignin precipitation from kraft black liquors: A step towards an optimised precipitation operation," *Nordic Pulp & Paper Research Journal* 24(2), 158-164. DOI: 10.3183/NPPRJ-2009-24-02-p158-164
- Wallmo, H., Theliander, H., Jönsson, A.-S., Wallberg, O., and Lindgren, K. (2009b). "The influence of hemicelluloses during the precipitation of lignin in kraft black liquor," *Nordic Pulp & Paper Research Journal* 24(2), 165-171. DOI: 10.3183/NPPRJ-2009-24-02-p165-171
- Wells Jr., T., Kosa, M., and Ragauskas, A. J. (2013). "Polymerization of kraft lignin via ultrasonication for high-molecular-weight applications," *Ultrasonics Sonochemistry* 20(6), 1463-1469. DOI: 10.1016/j.ultsonch.2013.05.001
- Wigell, A., Brelid, H., and Theliander, H. (2007). "Degradation/dissolution of softwood hemicellulose during alkaline cooking at different temperatures and alkali concentrations," *Nordic Pulp & Paper Research Journal* 22(4), 488-494.
- Wilson, K. (1968). "Bestämning av effektivt alkali i svartlut," *Svensk Papperstidning* 71(11), 446-447.
- Zhu, W., Westman, G., and Theliander, H. (2013). "Investigation and characterization of lignin precipitation in the LignoBoost process," *Journal of Wood Chemistry and Technology* 34(2), 77-97. DOI: 10.1080/02773813.2013.838267

Article submitted: October 21, 2014; Peer review completed: January 3, 2015; Revised version received and accepted: January 23, 2015; Published: January 29, 2015.

APPENDIX A

Carbohydrate Analysis

The contents of cellulose, (galacto)glucomannan, and xylan were calculated following carbohydrate analysis, using the following assumptions/corrections.

The amounts of sugars analyzed were corrected for the acid hydrolysis yield. Anhydro sugars were calculated from sugar monomers by the withdrawal of water (multiplied by 0.88 in the case of pentosans and 0.90 in the case of hexosans). Glucomannan was calculated as the sum of galactan, mannan, and part of the glucan. The molar ratio between the mannose and the glucose in (galacto)glucomannan was assumed to be 3.5:1 (Meier 1958). All of the galactan measured was included in the (galacto)glucomannan. Acetyl groups were, however, not included. Xylan was calculated as the sum of xylan and arabinan. All of the arabinan measured was included in the xylan. Cellulose was calculated as the content of glucan after withdrawal for the contribution of glucan to (galacto)glucomannan.

$$\text{Cellulose} = \text{Glucose} - (1/3.5) \times \text{Mannose}$$

$$\text{(Galacto)glucomannan} = \text{Galactose} + [1 + (1/3.5)] \times \text{Mannose}$$

$$\text{Xylan} = \text{Xylose} + \text{Arabinose}$$

The analyses were summed up in a mass balance based on the assumption that the carbohydrates were divided into cellulose, (galacto)glucomannan, and xylan, which were calculated as described above.

APPENDIX B

Table 7. The Yields of Lignin Precipitated at Various pH Values, Temperatures (T), and Ion Strength (IS) Addition of the Black Liquor (BL) Used Here and in a Previous Study (Zhu *et al.* 2013)

IS Addition (%)	pH	T (°C)	Precipitation Yield of Lignin (%)	
			Mixed Hardwood/Softwood BL	Softwood BL
0	11	45	34.3	34.2
0	11	65	23.8	29.6
0	11	75	22.0	26.4
0	10.5	45	61.9	59.3
0	10.5	65	49.9	48.6
0	10	45	76.6	74.5
0	10	65	71.4	62.0
0	9.5	45	82.7	79.4
0	9.5	65	74.9	77.8
10	11	45	42.7	40.0
10	11	65	40.3	34.5
10	10.5	45	69.8	66.1
10	10.5	65	58.9	55.3
10	10	45	75.7	77.9
10	10	65	71.6	69.5
10	9.5	45	84.9	86.1
10	9.5	65	84.7	78.3
20	11	45	52.9	48.6
20	11	65	45.1	43.2
20	10.5	45	69.4	68.9
20	10.5	65	61.4	63.2
20	10	45	81.8	82.7
20	10	65	75.8	71.5
20	9.5	45	83.3	86.7
20	9.5	65	82.0	80.9