Characterization of Hardwood Soda-AQ Lignins Precipitated from Black Liquor through Selective Acidification

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In the development of integrated biorefinery process alternatives to produce value-added by-products, various black liquors from sulfur-free pulping processes offer potential feedstocks for recovering their main chemical constituents, lignin and aliphatic carboxylic acids. In this study, lignin fractions were obtained from silver birch (*Betula pendula*) soda-anthraquinone black liquor by carbonation (pH to about 8.5) or by acidification (pH to about 2) with H_2SO_4 after carbonation or directly. These fractions were characterized by Fourier transform infrared (FTIR), ultraviolet (UV), energy dispersive X-ray fluorescence (ED XRF), and ^{13}C nuclear magnetic resonance (^{13}C NMR) spectroscopy. In addition, the molecular weight distributions of these lignin fractions were determined. All the experimental data clearly suggested that only small differences between the precipitated lignins existed, and thus, their equal chemical utilization seems possible.

Keywords: Aliphatic acids; Betula pendula; Black liquor; Characterization; Lignin; Precipitation; Soda-AQ pulping

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INTRODUCTION

Lignin is one of the most abundant natural polymers, and it is widely distributed throughout the plant kingdom (Sakakibara and Sano 2001). The main function of lignin is to give strength and mechanical support to the plant. In wood materials its content is normally 20% to 30% of the dry solids. The biosynthetic precursors of this amorphous, polyphenolic heteropolymer are comprised of three phenylpropanoid units (coniferyl, sinapyl, and *p*-coumaryl alcohols) that by various oxidative coupling reactions form a randomly cross-linked macromolecule with different inter-unitary linkages (Brunow *et al.* 1999). The structural building blocks are joined together by ether linkages and carbon-carbon bonds, and consistent with the close association between lignin and hemicelluloses in the wood cell wall, there are also chemical bonds between these constituents (Alén 2000a).

The effective removal of lignin from wood chips, called delignification, is performed to liberate wood fibers, which comprises the basis of chemical pulping (Sjöström 1993; Alén 2000b). Currently, about 90% of chemical pulp (about 130 million tons, annually) is produced by the dominant kraft (sulfate) process (Alén 2011). However, during kraft pulping, roughly half of the wood substance degrades (about 90% of lignin, 60% of hemicelluloses, and 10% of cellulose) and dissolves into the cooking liquor (black liquor (BL)). Due to this low selectivity of kraft pulping, BL contains, besides degraded lignin, a large amount of carbohydrate-derived material (mainly aliphatic carboxylic acids).

BL is generally burned after evaporation in the recovery boiler to recover energy and cooking chemicals. Kraft lignin also can be partly separated from BL and used as a potential feedstock in the production of various chemicals and solid or liquid fuels.

In general, the recovery and versatile utilization of lignosulfonates from sulfite pulping is widely carried out (Fengel and Wegener 1989; Sjöström 1993; Mansouri and Salvadó 2006). However, despite the widespread availability, the chemical utilization of lignin fractions from kraft pulping is practiced only on a limited scale (Gilarranz *et al.* 1998; Lora and Glasser 2002; Calvo-Flores and Dobado 2010; Li and Ge 2011). This is mainly due to their heterogeneous nature, and the lack of capable economic methods in their isolation with high purity (Chakar and Ragauskas 2004; García *et al*. 2009). During kraft pulping, the lignin is degraded and its phenolic hydroxyl groups are dissociated to sodium phenolates (alkali lignin). The alkali lignin can be recovered through the precipitation of BL by decreasing the BL pH with an acidifying agent such as CO_2 or H_2SO_4 (Alén *et al.* 1979; Uloth and Wearing 1989; Nagy *et al.* 2010; Tomani 2010). However, by acidification with H_2SO_4, an effective way of handling the Na_2SO_4 byproduct is required (Alén 2011; Kumar and Alén 2014). The industrial applications of alkali lignins from different origins primarily depends on the economic factor and a better understanding of their specific properties, structures, and recovery methods.

In a previous study, an electrochemical process concept to recover NaOH from Na_2SO_4 formed during the acidification of BL with H_2SO_4 was outlined (Kumar and Alén 2014). In combination with the recovery of the aliphatic carboxylic acids from BL, the main aim of this study was to characterize the precipitated sulfur-free lignin fractions obtained from the hardwood soda-anthraquinone (soda-AQ) BL by carbonation or by acidification with H_2SO_4 after carbonation or directly.The utilization possibilities of the separated lignin feedstocks will be clarified in forthcoming investigations.

EXPERIMENTAL

Black Liquor and Lignin Samples

The BL sample was obtained from a conventional laboratory-scale soda-AQ cook of industrial silver birch (*Betula pendula*) chips. The cook was conducted with an 18 L rotating stainless steel digester. The chips employed for pulping were screened according to standard SCAN-CM 40:01 (2001), and the chip thickness fraction between 7 mm and 13 mm was accepted. Chips with knots and bark residues were also eliminated. The cooking conditions selected were based on the previous study (Kumar and Alén 2014). The BL was separated from the pulp/liquor mixture by pressing it into a nylon-woven fabric bag and stored at about 4 °C prior to further experiments.

The “carbonated lignin” (Fig. 1a) was prepared by treating the initial BL (pH of about 13.5) (0.6 L) with CO_2 to a pH of approximately 8.5 in a pressurized stainless steel reactor (0.8 L) at 80 °C and approximately 1.5 bar for 40 min (Alén *et al.* 1979). The precipitated lignin was separated from the liquid phase (“carbonated BL”) by centrifugation (3000 rpm for 30 min) and freeze-dried (-50 °C at about 0.001 mbar) for 24 h (Kumar and Alén 2014). Finally, the carbonated lignin was crushed and stored at -18 °C prior to further experiments. The carbonated BL was then acidified with 2 M H_2SO_4 to a pH of about 2 at room temperature (Fig. 1a). The precipitated lignin (“acidified lignin”) was centrifuged, vacuum dried, and stored as the carbonated lignin. Additionally, the initial BL was also directly acidified with 2 M H_2SO_4 to a pH of about 2 (Fig. 1b). The precipitated lignin ("directly acidified lignin") was handled and stored as the other lignin samples. All the chemicals and solvents used were of analytical grade.

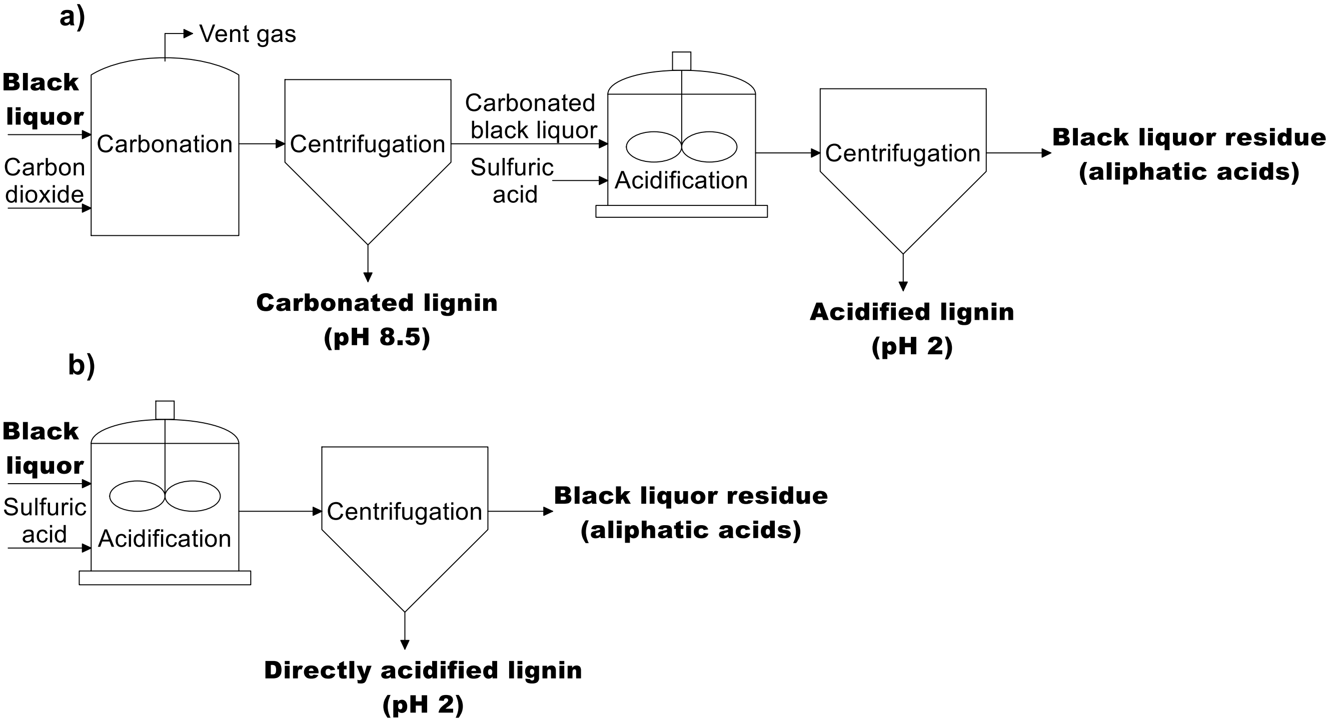

Fig. 1. Schematic representations of the separation methods for producing crude fractions of lignin and aliphatic carboxylic acids from black liquor by carbonation followed by acidification with H_2SO_4 (a) or directly by acidification with H_2SO_4 (b)

Analysis of Lignin

Fourier transform infrared (FTIR) spectra were recorded with a Tensor27 FT-IR spectrometer (Bruker GmbH, Karlsruhe, Germany). The spectra were taken as an average of 32 scans between 400 cm^{-1} and 4000 cm^{-1}, with a resolution of 4 cm^{-1}. The results were stored and analyzed with the Bruker OPUS version 6.5 software.

Ultraviolet (UV) spectra were measured with a Beckman DU 640 spectrometer (Beckman Instruments, Inc., Fullerton, CA, USA) between 205 nm and 300 nm. Prior to the analyses, the samples were dissolved into 0.1 M NaOH solution at a concentration of 30 µg/mL.

The content of sulfur in lignin samples was determined using an energy dispersive X-ray fluorescence (ED XRF) spectrometer (Bruker, GmbH, Germany). The method was first calibrated with thermomechanical pulps with a wide range of sulfur concentration (40 to 5900 mg sulfur/kg pulp).

The molecular weight distributions (MWDs) were determined by gel permeation chromatography (GPC) using a Waters HPLC system (Waters Corporation, Milford, MA, USA). Before the measurements, the lignin samples (about 3 mg/mL) were dissolved into the eluent (0.1 M NaOH) and filtered with a nylon syringe filter (0.45 µm). A column (460 mm × 10 mm i.d.) filled with a Superdex 75 gel (GE Healthcare Bio-Sciences AB, Uppsala, Sweden) was used for the separation of lignin fragments. The flow-rate of the eluent was 0.3 mL/min at room temperature. Detection was carried out using a Waters 996 photodiode array (PDA) detector within a wavelength range of 240 nm to 400 nm, and 280 nm was used for the determination of molecular weights. Calibration of the GPC system was carried out with a commercial set of protein standards (Sigma-Aldrich, St. Louis, MO, USA) (molar mass (MM) range was between 6,500 g/mol and 2,000,000 g/mol) and a number of lignin-like monomer/oligomer model compounds (vanillin, dehydrodiacetovanillone, rutin, and tannic acid; MM range was between 152 g/mol and 1,701 g/mol (Lehto *et al.* 2015).

Qualitative ^{13}C nuclear magnetic resonance (NMR) was performed with Bruker 300 and 400 spectrometers with DMSO-d_6 as the solvent at a sample concentration of 167 mg/mL using a 30° pulse angle with a recycle delay time of 2 s. An acquisition time of 1.82 s and an observed pulse of 6.5 µs were used for a 75 MHz spectrometer (acidified lignin) and 1.48 s and 6.0 µs for a 101 MHz spectrometer (carbonated lignin). The spectra were analyzed with Topspin software (Bruker Corporation, Billerica, MA, USA), and the peaks were assigned the chemical shift with respect to 39.51 (for $(CD_3)_2SO$). The analyses included a decoupling mode to reduce the Nuclear Overhauser Enhancement (NOE) (Gottlieb *et al.* 1997).

Determination of Aliphatic Carboxylic Acids

Volatile acids (formic and acetic acids) were determined as their benzyl esters with a gas chromatograph equipped with a flame-ionization detector (GC/FID) using an Agilent 7820A Series instrument (Agilent Technologies, Santa Clara, CA, USA) (Alén *et al.* 1985) A capillary column Agilent HP-5 (30 m x 0.32 mm I.D., and a film thickness 0.25 µm) was used. The column oven temperature program was 3 min at 60 °C, 3 °C/min to 150 °C, 15 °C/min to 230 °C, and 5 min at 230 °C. The injection port had a temperature of 280 °C, and the FID temperature was 280 °C. Before the GC analysis, the acids were first liberated from their sodium salts with a strongly acidic cation exchange resin (Amberlyst 15), converted into their tetra-*n*-butylammonium (TBA) salts with tetra-*n*-butylammonium hydroxide (TBAH), and then converted into their benzyl esters with a reagent containing benzyl bromide in acetone. An aqueous solution of crotonic acid was used as an internal standard (IS).

Hydroxy carboxylic acids were determined by GC/FID (Alén *et al.* 1984). A capillary column Agilent HP-5 (30 m x 0.32 mm I.D., and a film thickness 0.25 µm) were used. The column oven temperature program was 5 min at 60 °C, 2 °C/min to 200 °C, 30 °C/min to 290 °C, and 15 min at 290 °C. The injection port had a temperature of 290 °C, and the FID temperature was 300 °C. In this quantitative determination, the sodium salts of the acids were first converted into their respective ammonium salts with a cation exchange resin (Amberlite IRC-50) and then per(trimethylsilyl)ated with a mixture of 99% *N*,*O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA) and 1% trimethylchlorosilane (TMCS) in pyridine before the GC analysis. An aqueous solution of xylitol was used as an internal standard. The identification of the chromatographic peaks was conducted by a gas chromatograph equipped with a mass selective detector (GC/MSD) with a capillary column Agilent HP-5 (30 m x 0.25 mm I.D., and a film thickness 0.25 µm) under the same conditions used in GC/FID. The results were analyzed with the Enhanced ChemStation G1701CA software (version C.00.00, Agilent Technologies), and the mass spectra were compared to those in the Wiley 7th Ed. library software (McLafferty 2005).

RESULTS AND DISCUSSION

No important differences were detected in the relative proportions of aliphatic carboxylic acids in the BL residues obtained after carbonation and/or acidification with H_2SO_4 (Table 1). This finding suggested that no specific adsorption of individual aliphatic acids on the lignin precipitates took place. The differences in the total concentrations of aliphatic carboxylic acids in the BL residues were mainly due to an increase in the liquor volume (1:1.3) when added to the aqueous H_2SO_4 solution.

The initial concentration of sodium in BL was around 26.5 g/L. Almost half of the initial lignin was precipitated during carbonation (to a pH of about 8.5) with the simultaneous formation of $NaHCO_3/Na_2CO_3$. Neutralization of the phenolic hydroxyl groups occurs in the pH range of 9 to 11, and a further lowering of the pH to about 2 liberates the carboxylic groups (pK_a 3 to 5) with an enhanced precipitation of lignin (Alén 2011). For this reason, about 90% of the initial lignin was expected to be precipitated by acidification (pH of about 2) of the carbonated BL or by direct acidification of the initial BL with dilute sulfuric acid (Alén *et al.* 1979). These acidifications resulted in the formation of Na_2SO_4.

Table 1. Relative Composition of Aliphatic Carboxylic Acids in Birch Soda-AQ Black Liquors after Carbonation, Carbonation and Acidification, and Direct Acidification (% of the Total Acids)*

Component	Carbonated (%)	Acidified (%)	Directly Acidified (%)
Volatile acids			
Formic	14.2	12.3	13.2
Acetic	36.8	41.5	44.0
Hydroxy acids			
Glycolic	4.5	4.1	4.8
Lactic	5.2	4.7	5.5
2-Hydroxybutanoic	7.3	7.6	7.7
3,4-Dideoxy-pentonic	1.9	1.9	1.8
3-Deoxy-pentonic	3.5	3.2	2.9
Xyloisosaccharinic	8.0	8.5	7.3
Glucoisosaccharinic**	7.5	7.6	6.2
Miscellaneous	11.1	8.6	6.6

*Total amounts of acids in the carbonated, carbonated and acidified, and directly acidified black liquors were 42.4 g/L, 31.6 g/L, and 27.3 g/L, respectively.
**α- and β-isomers (i.e., *erythro*- and *threo*-isomers, respectively).

The FTIR spectra of the precipitated lignins under different conditions are shown in Fig. 2. The spectra almost followed the similar band patterns, except at 430 cm^{-1} to 600 cm^{-1}, which was assumed to be C-S stretching and only observed in the spectrum of sulfuric acid precipitated lignins (Ibrahim *et al.* 2004). Table 2 lists the characteristic band assignments for the FTIR spectra of the three different lignin samples.

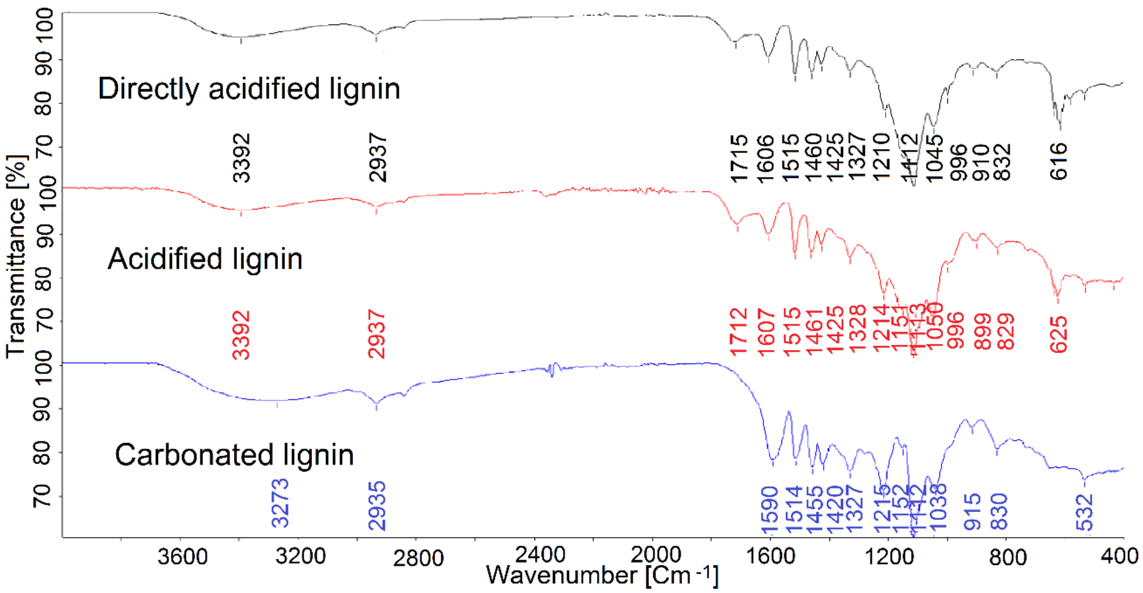

Fig. 2. IR spectra of lignins precipitated from birch soda-AQ black liquor

Table 2. Characteristic Band Assignments for the Precipitated Birch Soda-AQ Lignins by Acidification

Wavenumber (cm^{-1})	Band origin
3273 to 3393	O-H stretch (phenols and aliphatic alcohols)
2928 and 2937	C-H stretch (methyl and methylene groups)
1712 to 1715	unconjugated C=O stretch
1590 to 1607	conjugated C=O stretch
1420 to 1515	aromatic skeletal vibrations and C-H vibrations
1328	O-H bonding vibration
1210 to 1215	C-O, C-C, and C=O stretch
1112	C-O stretch (phenolic hydroxyl groups)
1038 to 1060	C-O stretch (aliphatic alcohols and aliphatic ethers)
830 to 890	C-H out-of-plane bonding
430 to 600*	C-S stretch

* Only for lignin samples precipitated with H_2SO_4.
Note: Band interpretations were based on Faix (1992), Sun and Tomkinson (2001), Ibrahim *et al.* (2004), Tejado *et al.* (2007), and Lisperguer *et al.* (2009).

The UV absorption spectra for the three lignin samples are shown in Fig. 3. Because of its aromatic nature, lignin has a strong absorption potential for UV light and exhibits characteristic maxima in the UV light region (Alén and Hartus 1988; Lin 1992). All spectra showed a maximum absorbance at 220 nm, and it increased in the following order: carbonated lignin > directly acidified lignin > acidified lignin. Differences in the absorbance values (*i.e.*, in the absorptivity values) were probably due to inorganic salt impurities (Ibrahim *et al.* 2004).

The elemental analysis of lignin in ED XRF (Fig. 4) showed that the sulfur content in acidified lignin and directly acidified lignin was about 15 mg/g and 16 mg/g, respectively. On the other hand, only negligible amount (< 1 ppm) of sulfur was present in the carbonated lignin.

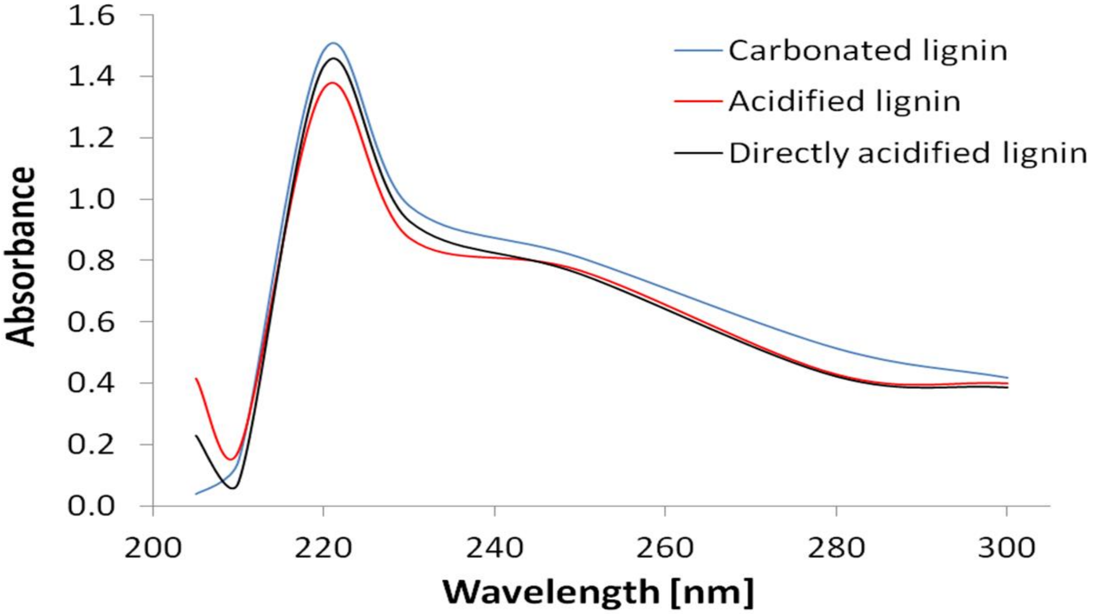

Fig. 3. UV spectra of lignins precipitated from birch soda-AQ black liquor

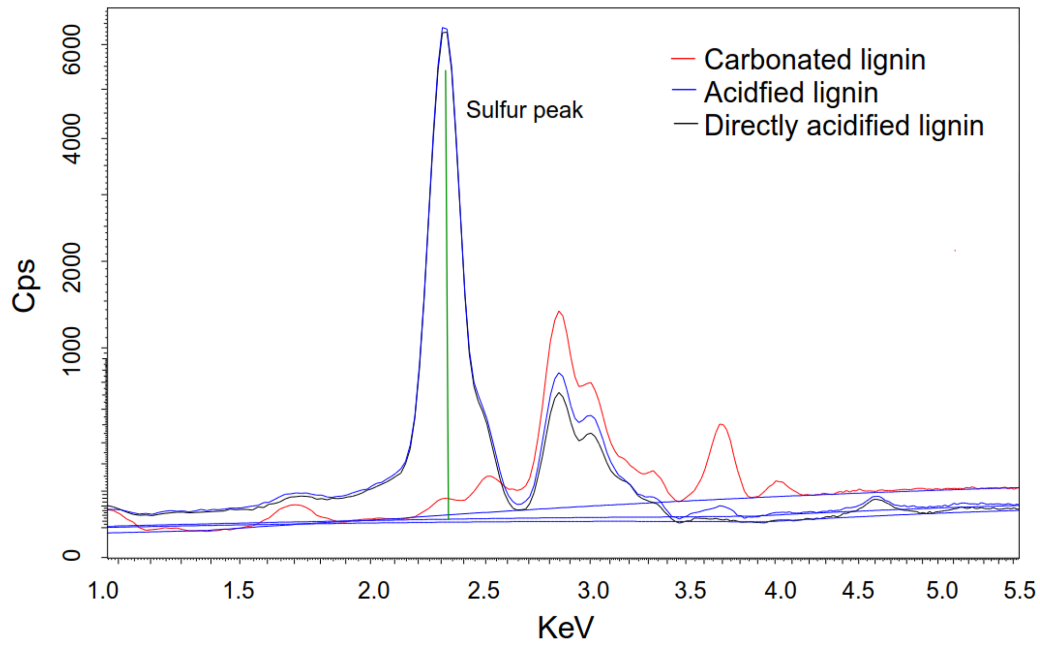

Fig. 4. ED XRF spectra of lignins precipitated from birch soda-AQ black liquor

The normalized MWDs of the precipitated lignins are shown in Fig. 5. Table 3 gives the weight average (M_w) and number average (M_n) molecular weights and polydispersity (M_w/M_n) of these lignin fractions. The results indicated that the M_w and M_w/M_n of the carbonated lignin was somewhat higher than those of the acidified lignins. This trend was expected since the low-molecular-weight lignin fractions precipitated at lower pH values are generally more water soluble than those with higher molecular masses (Pakkanen and Alén 2012).

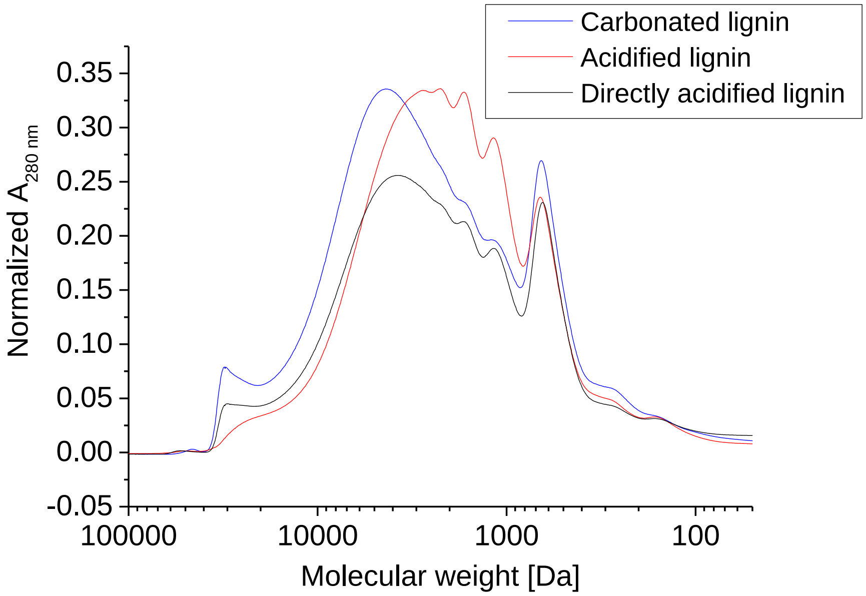

Fig. 5. Normalized MWDs of lignins precipitated from birch soda-AQ black liquor

Table 3. Weight Average (M_w) and Number Average (M_n), and Polydispersity (M_w/M_n) of Lignins Precipitated from Birch Soda-AQ Black Liquor

Lignin Sample	M_w	M_n	M_w/M_n
Carbonated	4728	781	6.0
Acidified	3373	862	3.9
Directly acidified	4253	801	5.3

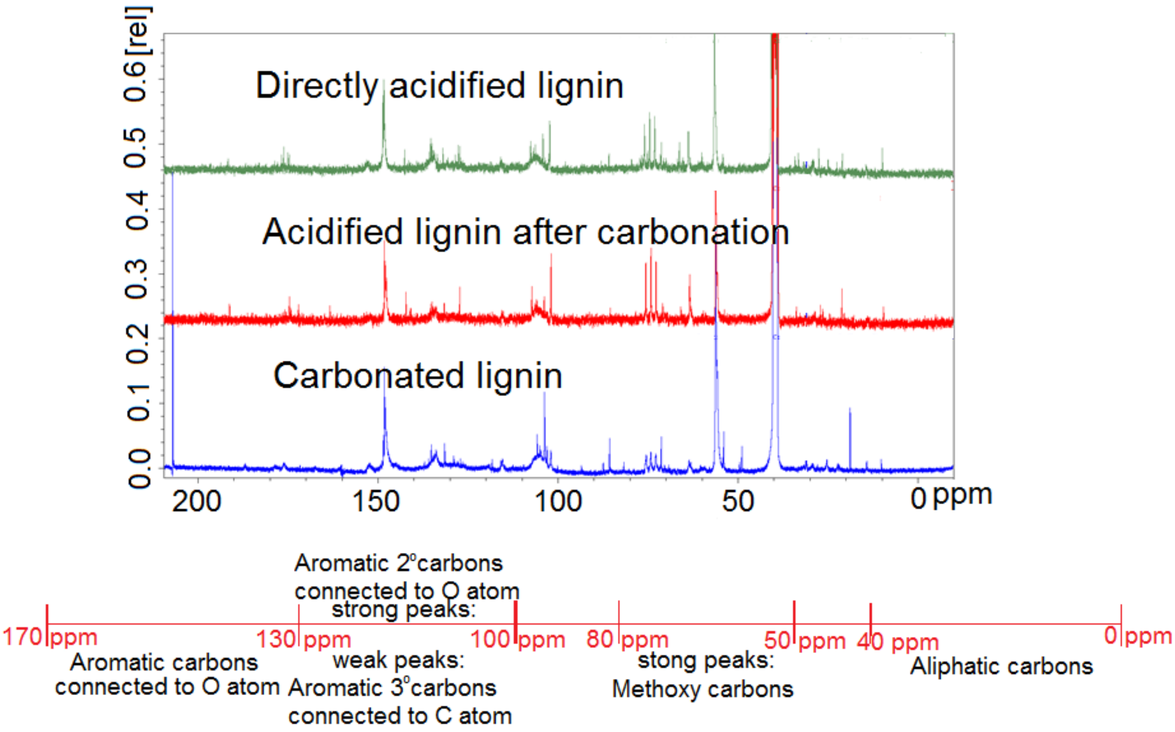

Fig. 6. ^{13}C NMR spectra of lignins precipitated from birch soda-AQ black liquor

Due to the close structural similarities of the precipitated lignins, their ^{13}C NMR spectra were also almost identical (Fig. 6). In these spectra, the weak peaks in the chemical shift ranged from 130 ppm to 170 ppm, corresponding to the aromatic carbons attached to oxygen atoms (=C-O-), strong peaks from 100 ppm to 130 ppm to the secondary aromatic carbons (=CH-C), weak peaks from 100 ppm to 130 ppm to the tertiary aromatic carbons (=C-C), strong peaks in the range 50 ppm to 80 ppm to the (OCH_3) carbons, and other aliphatic carbons attached to oxygen atoms, and the peaks in the range 0 ppm to 40 ppm to the aliphatic carbons (Stoklosa *et al.* 2013).

CONCLUSIONS

1. Today, there is an increased interest to gradually replace fossil carbon sources by alternative raw materials. With this respect, practically sulfur-free lignin from pulping seems to be one of the attractive feedstock possibilities. In this study, to promote the utilization of hardwood alkali lignins, three fractions of lignin from birch soda-AQ pulping were characterized. The fractions originated from carbonation (pH to about 8.5) or acidification (pH to about 2) with H_2SO_4 after carbonation or directly.
2. All of the experimental data (FTIR, UV, and ^{13}C NMR spectra, as well as molecular weight distributions) indicate only small differences between the precipitated lignins and thus, their equal chemical utilization seems possible.
3. However, the carbonated lignin fraction contained slightly more chemically bound sodium than the acidified lignin fractions, since the pK_a values of the phenolic hydroxyl and carboxylic acid groups are 9 to 11 and 3 to 5, respectively.
4. In addition, the results indicated that no selective absorption of aliphatic carboxylic acids, the second main constituents of black liquor, takes place on lignin precipitates.

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