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Modification of acid hydrolysis lignin for value-added applications by micronization followed by hydrothermal alkaline treatment

Abstract: Technical hydrolysis lignin (THL) was micronized by grinding in a rotary-jet mill to obtain a fraction of approximately 5 mm. Both initial and milled THLs were liquefied by thermal alkaline treatment at 220°C for 2 h. Upgraded THLs that were nonmilled (L1) and milled (L2) were desalted by treatment with cation-exchanged resin and were dried. Micronization affected the course of hydrothermal alkaline treatment and the structure and composition of the obtained lignin. Thus, L2 contained much less concomitant polysaccharides and extrac- tives than L1 and was more condensed. The molecular weights of L1 and L2 were 1100 and 1000 Da, respectively, as determined by size-exclusion chromatography. Structural characterization carried out by employing tandem electrospray ionization-mass spectrometry and 1D and 2D nuclear magnetic resonance spectroscopy revealed that small amounts of β -O-4 (~6 mol.%), β -5, and β - β structures still remained in L1 and L2. Overall, upgraded lignins are oligomers (trimers-pentamers) with highly degraded propane chains and possess polyconjugated condensed aromatic structures. Upgraded THL seems to be a promising raw material for polymeric formulations.

Keywords: ^{13}C NMR, electrospray ionization-mass spectrometry (ESI-MS), micronization, size-exclusion chromatography (SEC), technical hydrolysis lignin

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Introduction

The biorefinery concept is a synonym for striving for a more efficient utilization of biomass without losses by means of environment-friendly technologies aiming at the production of value-added products in a production cascade. In recent years, the application of this concept was focused mainly on existing pulping technologies and fractionation and more effective utilization of their technical lignins as by-products (Brodin et al. 2009, 2012; Gosselink et al. 2010; Ropponen et al. 2011; Duva et al. 2015; Zhu et al. 2015).

One of the recognized tools for biomass conversion is acidic hydrolysis focused mainly on the production of ethanol, feed yeast, furfural or levulinic acid derivatives, and sugar alcohols (e.g., xylitol and sorbitol). Basically, this process consists of the catalytic conversion of wood polysaccharides (cellulose and hemicellulose) into monosaccharides. One way is the acidic (or enzymatic) treatment of biomass before pulping as prehydrolysis (Gütsch and Sixta 2011; Hörhammer et al. 2011; Testova et al. 2011; Rodríguez-López et al. 2012). Another approach is an exhaustive acidic hydrolysis of biomass with diluted sulfuric acid, which was widely applied in approximately 50 plants in the 20th century in the former Soviet Union (Chudakov 1972; Rabinovich 2014). Synthetic ethanol-based rubber was produced in the beginning of 1930 by means of the method by S.V. Lebedev, whereas ethanol was produced by the hydrolysis of wood (Chudakov 1972; Blažej and Košic 1993). Technical hydrolysis lignin (THL) is a large-scale underutilized by-product of the hydrolysis industry, the end disposal of which may cause serious environmental problems. Only in Russia, dumps accumulated more than 50 millions tons of THL (Rabinovich 2014). Today, the amount of THL produced in the Russia Federation

is 100 000 tons y^{-1} , which is almost 20 times less than was produced annually in 1980s. Most of the programs on biomass hydrolysis in other countries are just in the beginning, and it is possible that this technology will be revitalized within the scope of the biorefinery concept and the problem of THL utilization will become hot enough in the future. The difficulties in THL utilization are related to its complex structure and poor reactivity.

Significant contributions to the structure of THL and its applications were made in the All-Union Research Institute VNIIGidroliz and in other laboratories worldwide (Blažej and Košic 1993). It was found that THL is a residue containing approximately 20%–30% of polysaccharides (mainly cellulose) embedded into hydrolysis lignin (“cellolignin”), which is more condensed than the native lignin (Chudakov 1972; Blažej and Košic 1993). In the literature, various applications of THL are described, such as pyrolysis and gasification (Domburg 1982; Carrott and Carrott 2007; Kulikov et al. 2012), as a biofuel (Nowakowski et al. 2010), aminated organic fertilizer (Chudakov 1972; Forostyan et al. 1987), adsorbents (Podterob et al. 2004; Carrott and Carrott 2007; Liang et al. 2013), nitrolignin and chlorolignin (Chudakov 1972), new polymeric materials (Sazanov 2009; Hatakeyama and Hatakeyama 2010; Zhou et al. 2013), polymer cathode materials (Gnedekov et al. 2013), and additives for oil bituminous compositions (Schiling 2000). However, the aforementioned research trends were not applied in a large scale in industrial practice (Vishtal and Kraslawski 2011; Rabinovich 2014). The production of THL-based enterosorbents Polyphapan™ for medicinal application can be considered as the most successful approach (Blažej and Košic 1993; Podterob et al. 2004). In short, THL can be used

(1) in its original form or (2) after heat pretreatment, (3) as fuel, and (4) after chemical processing.

THL is a promising feedstock for the production of aromatic compounds for further organic syntheses, and

its degradation to low molecular weight (M_w) compounds was proposed, namely, by pyrolysis, biological degradation, radiolysis, acid hydrolysis, and hydrothermal treatment (Zarubin and Krutov 2003; Gribkov et al. 2007;

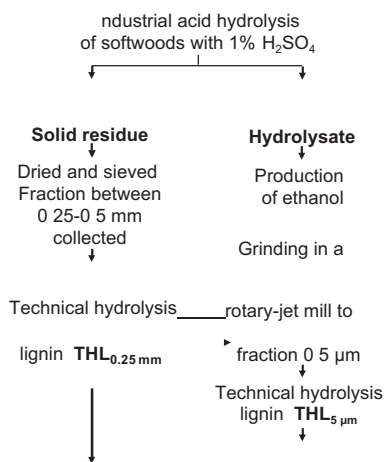
Kumar et al. 2009; Hatakeyama et al. 2010; Sumerskiy et al. 2010; Ponomarev et al. 2011; Evstigneev 2013; Mu et al. 2013). Alkaline degradation is one of the promising techniques for THL depolymerization (Zarubin and Krutov 2003; Sazanov 2010).

The present work deals with the alkali-catalyzed hydrothermal upgrading of THL, aiming its transformation into a series of soluble products that could be suitable for polymeric formulations. The obtained lignin fragments

Materials and methods

The outline of the experiments is presented in Figure 1. Air-dried THL was obtained by industrial percolation with diluted acid hydrolysis of softwoods and it was supplied by a Kirovsk hydrolysis plant. THL was sieved to obtain a fraction of 0.25 mm (retained between the sieves of 0.25 and 0.50 mm, $THL_{0.25\text{ mm}}$). These lignin particles were additionally grounded in a rotary-jet mill OMICRON 60 (New Technol. Disperse Systems, St. Petersburg, Russia) to obtain a fraction of approximately 5 μm [weight-median-diameter as analyzed by Laser Particle Sizer ANALYSETTE 22 MicroTec plus (Fritsch, Idar-Oberstein, Germany), $THL_{5\text{ }\mu\text{m}}$]. The hydrothermal treatments were carried out under alkaline conditions (5% NaOH) in an autoclave at 220°C for 2 h. The yield of THL was approximately 95% for $THL_{0.25\text{ mm}}$ and approximately 99% for $THL_{5\text{ }\mu\text{m}}$. The dissolved alkaline lignin was filtered off on a glass filter, and the filtrate was treated by a 0.3- to 1.2-mm-diameter cation-exchanged resin KU 2-8 (Aqua-Venture, St. Petersburg, Russia) to remove the cations and to decrease the pH to 4. In a typical trial, 5 g degraded lignin dissolved in 200 ml alkaline spent solution was treated with 35 g resin in H^+ form with 4 mmol g^{-1} ion-exchange capacity. The resin was further separated from the solution by filtration on a glass filter and washed with distilled water and ethanol. The filtrate with soluble lignin was further vacuum dried. The yields of lignins $THL_{0.25\text{ mm}}$ and $THL_{5\text{ }\mu\text{m}}$ were 98% and 94%, respectively, based on the weight of Klason lignin in the initial THL.

Lignins L1 obtained from $THL_{0.25\text{ mm}}$ and L2 obtained from $THL_{5\text{ }\mu\text{m}}$ were analyzed by wet chemistry methods, M_w by size-exclusion chromatography (SEC), and electrospray ionization-mass spectrometry (ESI-MS) and structurally characterized by 1D/2D ^{13}C nuclear magnetic resonance (NMR) and tandem ESI-MS (ESI-MSⁿ). The ash content was determined by the calcination of the material at 525°C according to Tappi T 211 om-93. The extractive content in hexane, dichloromethane, and acetone was determined by consecutive Soxhlet extraction



were characterized in terms of their M_w and general structural features.

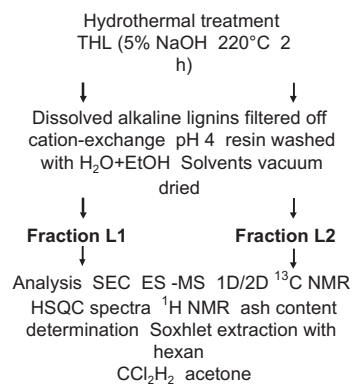


Figure 1 Outline of the experimental design.

according to Tappi T 204 om-88. The Klason lignin content was determined with 72% H₂SO₄ adapted from Tappi T 204 om-88 standard. SEC analysis was carried out according to the study of Evtuguin et al. (2001). ESI-MS and ESI-MS^a analyses were performed on an LXQ linear ion-trap mass spectrometer (Thermo Finnigan, San Jose, CA, USA). The

lignins sample (~1 mg) was first dissolved in 100 ml of 0.1% ammonium hydroxide solution followed by the addition of 900 ml acetonitrile. The final sample was diluted approximately 30–50 times with methanol before the direct injection in the electrospray source. The spectra were acquired on an LCQ Fleet ion-trap mass spectrometer (Thermo Finnigan, San Jose, CA, USA) equipped with an electrospray ionization source (negative mode). The protecting gas was nitrogen. The spray voltage was 5 kV and the capillary temperature was 275 °C. The capillary and tune lens voltages were set at -28 and -115 V, respectively. The CID-MS^a experiments were performed on the mass-selected precursor ions in the range of *m/z* 150–2000. The isolation width of precursor ions was 1.0 mass unit. The scan time was equal to 100 ms and the collision energy was optimized between 20 and 35 (arbitrary units) with He as the collision gas. Data acquisition was achieved by means of Xcalibur[®] data system.

The quantitative ¹³C NMR spectra of lignins (L1 and L2) were recorded on a Bruker AVANCE 300 spectrometer (Wissembourg, France) operating at 75.47 MHz (323 K) with TMS as the internal reference. Lignins were dissolved in DMSO-*d*₆ (~25% concentration)

and placed into 5-mm-diameter tubes. The acquisition parameters

were as follows: 4.1 ms pulse width (90° pulse angle), 12 s relaxation delay, 16 K data points, and 18 000 scans. The same lignin sam-

ples in DMSO-*d*₆ were placed into 5-mm-diameter tube, and 2D NMR spectra were recorded on a Bruker AVANCE 300 spectrometer. The phase-sensitive ¹H-detected heteronuclear single quantum coherence (HSQC) spectrum was acquired over an F1 spectral width of 12 000 Hz and an F2 width of 2000 Hz with a 2048×1024 matrix and 128 transients per increment. The delay between scans was 2 s and the

delay for polarization transfer was optimized for ¹J_{CH}=149 Hz. The ¹H NMR spectrum of acetylated L2 dissolved in chloroform-*d*₁ (concentration ~3%), placed in 5-mm-diameter tube, have been carried out on a Bruker AVANCE 300 spectrometer operating at 300.1 MHz (298 K). The acquisition parameters were 12.2 ms pulse width (90°), 3 s relaxation delay, and 300 scans.

Results and discussion

Chemical composition of THL

Two THL fractions were chemically analyzed (i.e., THL_{0.25 mm} and THL_{5 μm}). The latter was obtained by micronization in a rotary-jet mill to the weight-median-diameter (D₅₀) of 5 mm. The corresponding data in Table 1 include acid-insoluble lignin, ash, extractives, and polysaccharide contents. THL_{0.25 mm} had similar content of acid-insoluble lignin as THL_{5 mm}, but the former contained much more extractives. The major difference between these two fractions was the amount of neutral extractives soluble in

Table 1 General chemical composition of THL fractions.

Data	THL fractions	
	THL _{0.25 mm}	THL _{5 μm}
Klason lignin (%)	65.3	66.6
Ash (%)	6.9	7.5
Extractives		
Hexane (%)	5.91	0.84
Chloroform (%)	5.96	4.31
Acetone (%)	2.43	2.15
Total (%)	14.30	7.30
Polysaccharides (%) ^a	20.4	26.1

^aObtained by difference.

from percolation hydrolysis always contains 20%–30% of polysaccharides (essentially cellulose) embedded into the lignin matrix (Chudakov 1972; Rabinovich 2014).

These THL fractions were further subjected to hydrothermal treatment under alkaline conditions (HT_A) at

220 °C for 2 h giving rise to water-soluble lignins L1 from

THL_{0.25 mm} and L2 from THL_{5 mm}. The basic idea behind

HT_A was the transformation of insoluble THL to soluble

product with low M_w and free of concomitant polysaccharides, ash, and extractives, which were suitable for the products of value-added products, such as a component of polymer formulations.

The conversion rate of THL was approximately 95%–99%. The ash contents (<1%) and acid-insoluble

lignin contents (83% for L1 and 92% for L2) were fairly

hexane in THL_{0.25 mm}. The considerable amount of carbohydrates in both fractions is not surprising, because THL

satisfactory. Therefore, the obtained upgraded THLs were further submitted to M_w determination and spectroscopic characterization.

M_w determination

The two THL fractions (L1 and L2) display similar M_w distributions (MWD) in SEC analysis (not shown), although the M_w of L1 (1100 Da) is slightly higher than the M_w of L2 (1000 Da) with a lower polydispersity (1.25 vs. 1.17). More detailed information on the abundance of lignin oligomers was obtained from ESI-MS spectra (Figure 2).

The ESI-MS spectra revealed wide MWDs of oligomers (200–1500 Da) with a predominant presence of trimers (at ~550 Da) and pentamers (at ~900 Da), taking into account the average M_w of a softwood phenyl propane unit of approximately 180 Da. The structural elucidation of lignin oligomers by ESI-MSⁿ was only partially successful due to the prevalence of alkyl-aryl and alkyl-alkyl linkages between structural units. An intensive signal at m/z 179 was assigned to coniferyl alcohol, which was presented

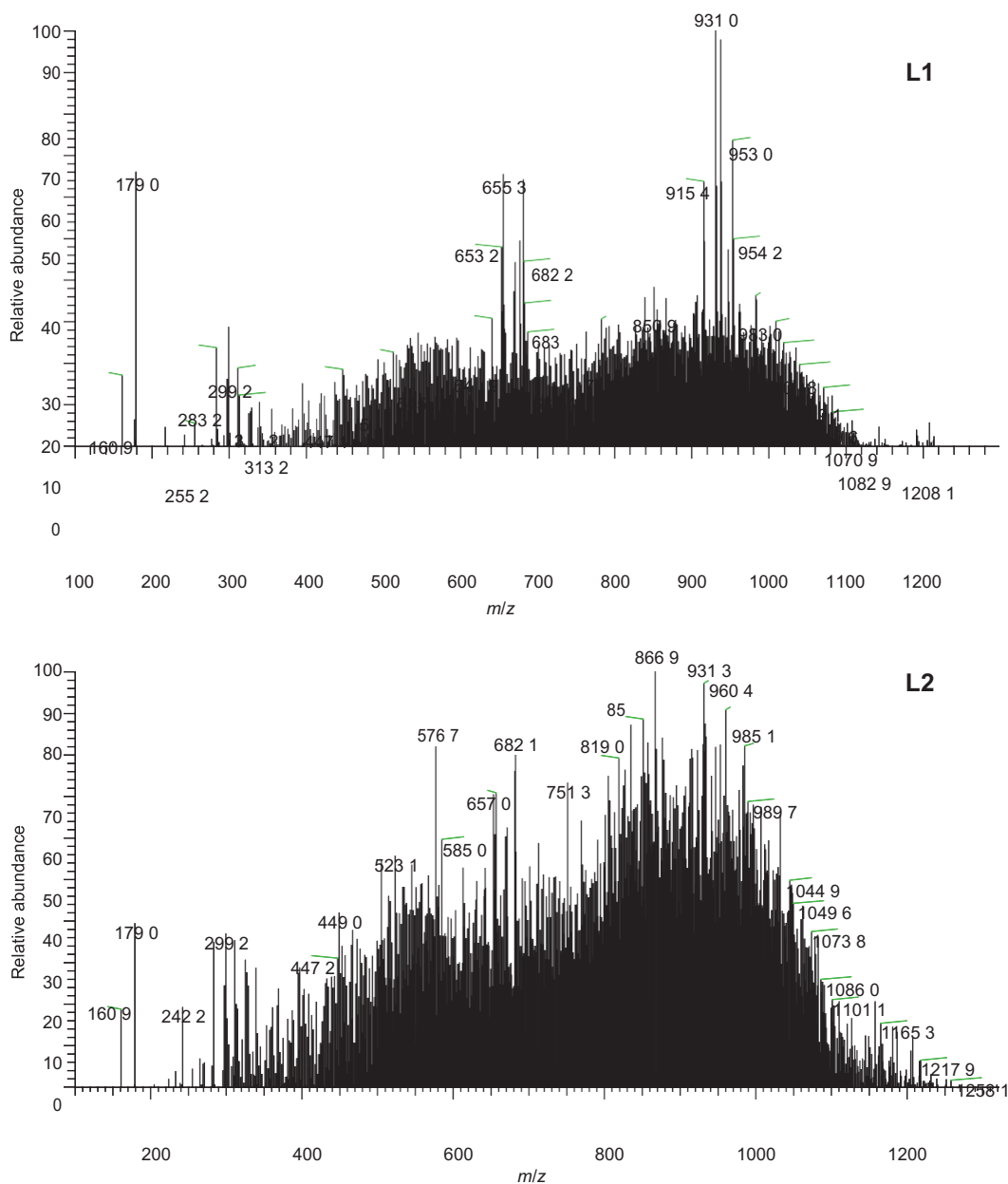


Figure 2 ESI-MS spectra of L1 and L2 acquired in a negative mode.

in both L1 and L2. Two dimers at m/z 299 and 319 were tentatively assigned, according to the analysis of ESI-MSⁿ spectra (not shown), to be partially degraded dimers linked by β -O-4 bonds.

A series of rather abundant oligomers at m/z 653 and 655 in ESI-MS spectra of L1 showed the characteristic loss of MeGlcA (-206 Da) and were assigned, based on ESI-MSⁿ spectra (not shown), to partially degraded acidic xylo-oligosaccharides (XOS) of general composition Xyl₃₋₄MeGlcA. These XOS were not found in the ESI-MS spectrum of L2.

Proton-carbon correlation (HSQC) and quantitative ¹³C NMR spectra were recorded. The signal assignments were made based previously published data on native

Structural studies

lignins (Evtuguin et al. 2001; Prozil et al. 2014) and lignin model compounds (Ralph et al. 2004). The HSQC spectrum of L2 (Figure 3) shows that certain amounts of β -O-4, β - β , and β -5 lignin units are still maintained in upgraded THLs despite drastic conditions of industrial acid hydrolysis and posterior alkaline treatment in the lab. A series of H/C signals at 3.5–3.8/40–50 ppm, unusual for native lignin, belong probably to aliphatic moieties in newly formed alkyl-aryl condensed structures. The strong intensity group of H/C signals at 2.0–2.7/20–40 ppm was assigned to CH and CH₂ moieties in concomitant extractives always present in THLs. The HSQC spectrum of L2 also revealed the presence of carbohydrates associated to lignin due to the characteristic signals detected in the region of oxygenated carbons (Figure 3). This fact corroborates the lower Klason lignin content in L2 (~92%), as expected.

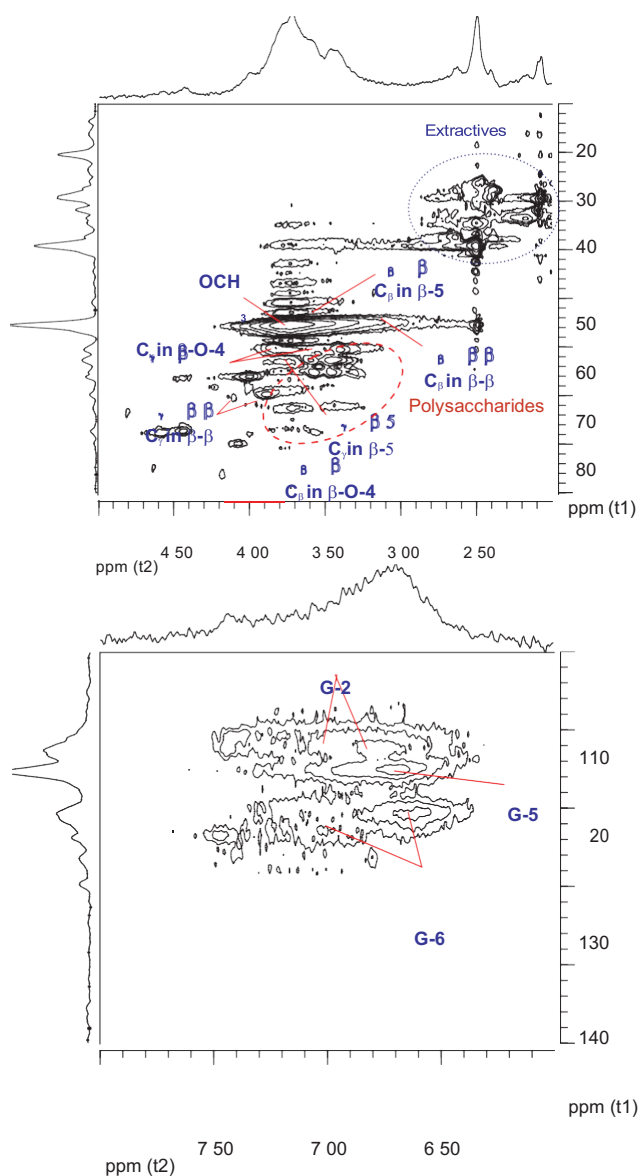


Figure 3 Aliphatic and aromatic regions of the HSQC spectrum of L2 (DMSO- d_6 ; 40°C). The signals from polysaccharides and extractives are depicted by dashed circles.

The comparison of quantitative ^{13}C NMR spectra is meaningful concerning the structure of both upgraded THLs. The L2 fraction contains less polysaccharides than L1 (Figure 4), which is an indirect confirmation of its higher Klason lignin content (92%) compared with that of L1 (83%). Probably, during micronization, carbohydrates suffered strong mechanical degradation and became more accessible to hydrothermal treatment. The strong signals at 173–178 ppm in L1, assigned essentially to carboxylic moieties in extractives, are less abundant in L2. The same is true for the CH and CH_2 signals from extractives at 20–35 ppm. Accordingly, $\text{THL}_{0.25\text{ mm}}$ contains less neutral extractives than $\text{THL}_{5\text{ mm}}$, from which the L1 and L2 fractions were

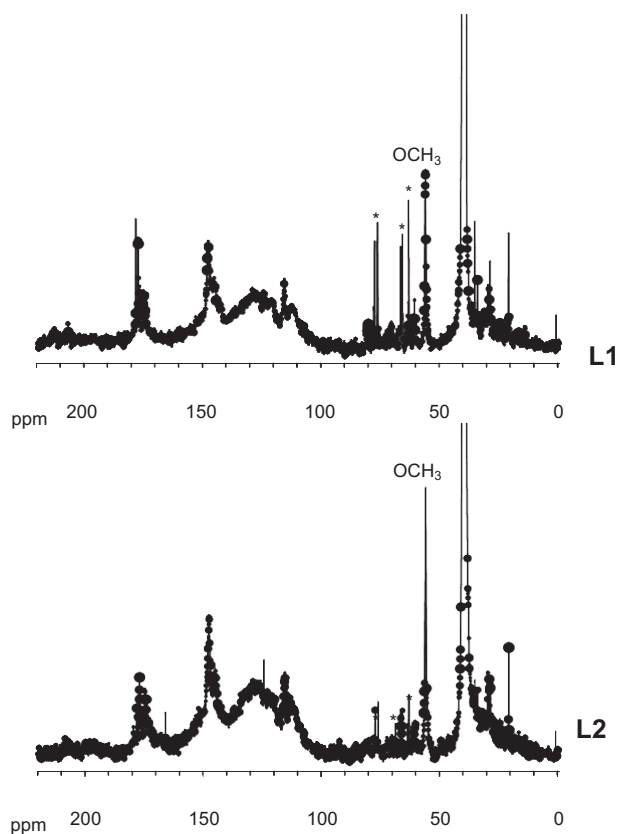


Figure 4 Quantitative ^{13}C NMR spectra of upgraded hydrolysis lignins L1 and L2 (DMSO- d_6 ; 50°C). The signals from polysaccharides are marked by asterisks.

The ^{13}C NMR spectrum of L1 reveals more structures with nonconjugated ketone groups (200–215 ppm) than L2. Both lignins showed the presence of quinone groups as visible on characteristic resonances at 180–190 ppm (Figure 4). L2 contains ferulic acid (FA)- and vanillic acid isolated, respectively (Table 1).

(VA)-type structures in much higher abundance than L1 as seen from signal intensities at approximately 166–168 ppm assigned to COOH in the aforementioned units (Ralph et al. 2004). In summary, it can be safely concluded that L2 from THL_{5μm} is less contaminated with polysaccharides and extractives than L1. The structures of the two fractions are similar, but L1 contains more oxidized functional groups (Table 2).

The calculations presented in Table 2 have been carried out per one aromatic ring as previously suggested (Evtuguin et al. 1994, 2001). The aromatic region equivalent to six carbon atoms was integrated between 103 and 158 ppm. The abundance of lignin structures linked by β-O-4' bonds was calculated based on C_g integrals at 59.5–60.5 ppm. Both upgraded lignins contained little amounts of β-O-4 structures and were significantly demethylated (by almost 50%). The relatively low content of OMe groups may be explained by their partial hydrolysis during industrial hydrolysis at approximately 175°C. Some OMe loss is

Table 2 Quantitative estimation of structural elements in upgraded THLs as revealed by ^{13}C NMR and ^1H NMR spectroscopy.

Structural element	Integrated region (ppm)	Amount, per 100 C ₆	
		L1	L2
$\beta\text{-O-4}$	59.5–60.5 (Cg in $\beta\text{-O-4}$)	6	6
OCH_3	54.5–56.7 (methoxy C)	47	52
Ar–H	103.0–126.0 (tert. C)	207	194
Ar–C	125.0–140.0 (quat. C)	186	196
Ar–O	140.0–158.0 (ox. quat. C)	207	209
FA+VA	166.0–168.0 (COOH)	3	6
BA ^a	9.80–9.90 (CHO)	n.d.	2
OH ^a	1.80–2.10 (CH ₂ CO)	n.d.	38
OH ^{al}	2.10–2.50 (CH ₂ CO) ^{al}	n.d.	72
OH ^{ph}	2.10–2.50 (CH ₂ CO) ^{ph}	n.d.	72

^aData obtained from the ^1H NMR spectrum of acetylated L2. n.d., not

determined.

also expected during HT_A. In addition, both lignins are strongly condensed as follows from the unusually high abundance of quaternary aromatic carbons (Table 2), which are about twice as high as that found in spruce dioxane lignin (Evtuguin et al. 1994). It is worth noting the higher condensation degree of L2 compared with L1. This fact can be explained both by the mechanical degradation of lignin upon THL micronization and by some fractionation that occurred during the micronization procedure. Taking into account the strong signals from quaternary carbons at 125–130 and 132–140 ppm assigned to C5 and C6, respectively, the condensation occurred via the formation of new aryl-aryl linkages (see the biphenyl structures described by Ralph et al. 2004). This explains the established polyconjugated aromatic structures in THL (Chudakov 1972).

Another structural feature of upgraded lignins is the strong degradation of propane chains. The corresponding

signals between 60 and 90 ppm are fairly low apart from the signals belonging to polysaccharides (Figure 4). This explains the relatively low amounts of aliphatic

hydroxyl groups in L2 even in the presence of the polysaccharide impurities (Table 2). The amount of phenolic

groups detected in L2 (38 per 100 C₆) was typical of that usually found in technical lignins. The amount of aliphatic OAc groups (aliph-O-CO-CH₃ at 1.80–2.10 ppm) and

phenolic OAc groups (phen-O-CO-CH₃ at 2.10–2.50 ppm)

was estimated by the ^1H NMR spectroscopy of acetylated L2 (Figure 5). The data were related per one OMe group (integral at 3.5–4.0) and then recalculated per one aromatic ring (C₆) in the knowledge of the OMe content from

the ^{13}C NMR spectrum. Among the structures containing

aldehyde groups, only the benzaldehyde (BA) type was detected based on its characteristic resonance of formyl protons at 9.80–9.90 ppm (Figure 5).

Conclusions

HT_A is promising for the liquefaction of THL into water-soluble lignin. The micronization of THL by milling in a rotary-jet mill allowed the collection of a fraction with 5 mm particle size, which leads via HT_A to lignin L2. This contains less polysaccharides and extractives than lignin L1 obtained from the original THL without micronization. The L2 fraction is more condensed and contains more oxidized groups than L1. The M_w of L1 and L2 were also slightly different (1100 and 1000 Da, respectively). Hence, the micronization affected the course of HT_A and the structures of the upgraded lignins. THLs are strongly condensed with highly degraded propane chain. The water-soluble lignin from THL may find interesting applications, for example, in different polymeric formulations.

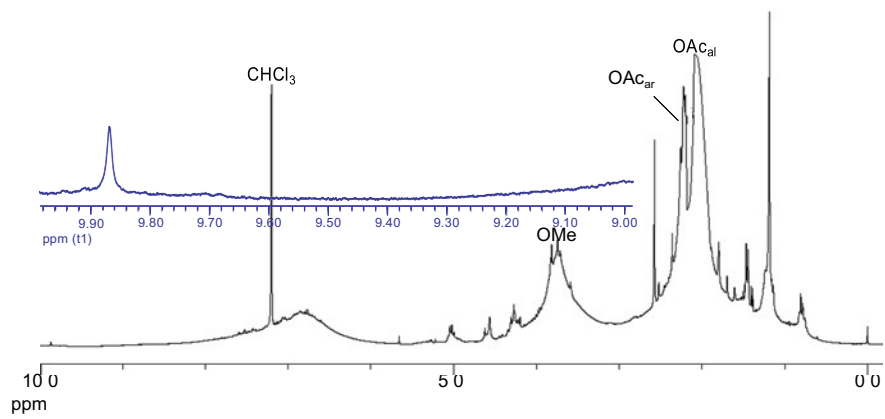


Figure 5 ¹H NMR spectrum of acetylated L2 (chloroform-d₃; 30 C).
The expanded range from 9 to 10 ppm shows the resonances of formyl protons.

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