EWLP 2014

13TH EUROPEAN WORKSHOP ON LIGNOCELLULOSICS AND PULP

June 24-27, 2014 - Seville, Spain

Proceedings

EWLP 2014

13TH EUROPEAN WORKSHOP ON LIGNOCELLULOSICS AND PULP

PROCEEDINGS

24-27 June 2014
Seville, Spain

Editors: J.C. del Río, A. Gutiérrez, J. Rencoret and Á.T. Martínez
Printed in Spain, 2014
Cover design: E.D. Babot

ISBN: 978-84-616-9842-4

STRUCTURAL CHARACTERISTICS OF INDUSTRIAL LIGNINS IN RESPECT TO THEIR VALORIZATION

Liitiä, T.[1]*, Rovio, S.[1], Talja, R.[1], Tamminen, T.[1], Rencoret, J.[2], Gutiérrez, A.[2], del Río, J.C.[2], Saake, B.[3], Schwarz, K.U.[3] Vila Babarro, C.[4], Gravitis, J.[5], Marco Orlandi[6]

*[1] VTT Technical Research Centre of Finland, P.O. Box 1000, FI-02044 VTT, Finland; [2] IRNAS-CSIC, P.O.Box 1052, 41080-Seville, Spain; [3] University of Hamburg, Department of Wood Science, Germany, Leuschnerstrs. 91, D-21031 Hamburg, Germany; [4] Thünen Institute for Wood Research, Leuschnerstr. 91, D-21031 Hamburg, Germany; [5] Latvian State institute of Wood Chemistry, 27 Dzerbenes Str., LV-1006-Riga, Latvia; [6]University of Milan-Bicocca, Department of Earth and Environmental Science, Piazza della Scienza 1, 20126 Milan, Italy (*Email of corresponding author: Tiina.Liitia@vtt.fi)*

ABSTRACT

The effect of raw material and pretreatment procedure on the structure and properties of industrial lignins was evaluated by detailed chemical and physical characterization. The application potential of studied lignins was considered based on those. Hydrolysis lignin and steam exploded lignins had clearly distinct characteristics compared to the spent liquor lignins; higher molar mass, significantly higher amount of native aryl ether linkages and thereby low phenol content. The hydrolysis lignin also contained significant amount of carbohydrate and protein residues, which may affect the applicability. For resin applications, the kraft lignins seem most reactive in respect of high phenol content. The high molar mass of hydrolysis lignin and steam exploded lignins could be beneficial for dispersants and composites.

I. INTRODUCTION

In future bioeconomy, there is need to generate new biobased fuels, chemicals and materials utilising lignocellulosic feedstocks in order to provide more sustainable renewable alternatives for present oil based products. For transportation, bioethanol is a potential substitute, but its high production costs inhibit rapid commercialisation. Also traditional pulping industry is looking for new added value products. As a phenolic biopolymer, lignin is a potential raw material for the production of biobased aromatic chemicals, as well as building blocks for materials and fuels. The competitiveness of traditional pulp and bioethanol production processes could thus be increased by conversion of the side-stream lignins into new biobased high-value products instead of incineration. Depending on the used feedstock and biomass processing technology, lignin by-products with distinct structural features and variable application potential are produced. Compared to the traditional industrial lignins, the sulphur-free lignin residues produced by lignocellulosic bioethanol plants are not so extensively studied. Especially the utilisation potential of the lignin rich hydrolysis residue recovered after steam explosion pretreatment followed by saccharification and fermentation stages should be better explored.

In this paper, the effect of raw material (softwood, hardwood, wheat straw, bagasse) and pretreatment procedure (kraft, soda, soda-AQ, ethanol organosolv, steam explosion) on the structure and properties of lignin was evaluated by detailed chemical and physical characterization. The application potential of studied lignins was considered based on those. In addition to the purity and composition, the lignin structure (S/G/H ratio, inter-unit linkages) was analyzed using both the degradative (Py-CG/MS) and spectroscopic techniques (2D ^{1}H-^{13}C NMR). Lignin functionalities were analysed by ^{31}P NMR spectroscopy, and molar mass was determined by size exclusion chromatography. Thermal properties were evaluated by DSC. Lignins from industrial or pilot scale processes were mainly used.

II. EXPERIMENTAL

Raw materials. Industrial softwood and hardwood (eucalypt) kraft lignins (**Kraft-SW, Kraft-HW**) were obtained from Stora Enso and Suzano, respectively. Commercially available soda wheat straw lignin (**Soda-WS**) was purchased from Green Value. Wheat straw hydrolysis lignin (**HL-WS**) was obtained from the pilot plant of a bioethanol producer. Steam exploded wheat straw, birch and grey alder lignins (**SE-WS, SE-birch, SE-GA**) were also prepared at lab scale. Steam explosion (SE) was performed at 235°C with 3.2MPa pressure for 1min, after which the lignins were extracted by 0.4% NaOH. Organosolv lignin (**OS-HW**) of *E. globulus* was produced at pilot scale using the lignofibre (LGF) process [1] with ethanol/water (85/15) solvent and 3.5% phosphinic acid [2]. The OS lignin was precipitated by dilution with water (1:4) after some concentration by

evaporation of ethanol. Bagasse (**SAQ-B**) lignin was produced at lab scale by soda-AQ cooking (kappa 9.5) using 16.5% effective alkali in presence of 0.1% anthraquinone (AQ), followed by LignoBoost type lignin separation with two stage pH drop at 35% dry solids with CO_2 and H_2SO_4.

Analytical methods. For composition analyses, the lignin was hydrolysed [3], and the acid insoluble Klason lignin was quantified gravimetrically. Acid soluble lignin was determined spectroscopically at 205 nm (TAPPI UM250 um-83, 1991). The carbohydrate content of hydrolysate was analysed by borate anion-exchange chromatography with post-column derivatisation and detection at 560 nm [4]. The ash content was gravimetrically determined after incineration at 800 °C. The complete oxidation method was used for elemental analysis on a CE Instruments CHNS Flash 1112 Analyzer system. Methoxyl groups were determined according to [5].

The molar mass distributions of lignins were determined by size exclusion chromatography in 0.1M NaOH using MCX 1000 and 100 000 columns with UV detection (280 nm) and polystyrene suphonate (Na-PSS) calibration.

Lignin functionalities were determined by ^{31}P NMR according to Granata and Argyropoulos [6]. Accurately weighted samples (40 mg) were dissolved in 150 µL of *N,N*-dimethylformamide. After dissolution, 100 µL pyridine, 200 µL internal standard solution of 0.05 M *endo*-N-Hydroxy-5-norbornene-2,3-dicarboximide in pyridine/$CDCl_3$ (1.6/1, v/v) and 50 µL $Cr(acac)_3$ solution (11.4 mg/1 mL) in pyridine/$CDCl_3$ (1.6/1, v/v) were added. Then, 100 µL 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphopholane was added drop-wise, followed by 300 µL of $CDCl_3$. The ^{31}P NMR measurements were performed immediately after sample preparation at room temperature with Bruker Avance 500 MHz NMR spectrometer using 90° pulse and 5s pulse delay for 512 scans.

2D HSQC (heteronuclear single quantum coherence) NMR spectra were recorded at 25ºC by a Bruker AVANCE III 500 MHz, equipped with a cryogenically-cooled 5 mm TCI gradient probe with inverse geometry using 'hsqcetgpsisp2.2' pulse sequence (adiabatic-pulsed version). Lignin samples were dissolved (40mg/0.75 mL) in DMSO-d_6. Spectral widths of 5000 Hz (10-0 ppm) and 20,843 Hz (165-0 ppm) for the ^{1}H- and ^{13}C-dimensions were used. The number of transients was 64 for 256 time increments, with $^{1}J_{CH}$ of 145 Hz. The semiquantitative analysis of the correlation peaks was performed using Brukers Topspin 3.1 software. The lignin inter-unit linkages based on C_α–H_α correlations were calculated as described previously [7].

Pyrolysis was performed with a 2020 micro-furnace pyrolyzer (Frontier Laboratories Ltd.) connected to an Agilent 6890 GC/MS system equipped with a DB-1701 fused-silica capillary column and an Agilent 5973 mass selective detector. The pyrolysis was performed at 500 ºC. The GC oven temperature was programmed from 50 ºC (1 min) to 100 ºC at 30 ºC/min and then to 290 ºC (10 min) at 6 ºC/min. Helium was the carrier gas. Peak areas were calculated for the lignin-degradation products, the summed areas were normalized, and the data for two repetitive analyses were averaged and expressed as percentages to determine the proportion of syringyl (S), guaiacyl (G) and p-hydroxy phenyl (H) type lignin units.

The lignin glass transition (Tg) temperatures were determined by Mettler Toledo Differential Scanning Calorimeter model DSC820 system STARe SW 9.20. Temperature profile with following steps was used: 1) heating from 25 ^{o}C to 105 ^{o}C with 20 min isothermic phase for drying, 2) cooling phase to -60 ^{o}C, 3) first actual heating phase from -60 ^{o}C to 200 ^{o}C, 4) cooling phase to -60 ^{o}C, and 5) second heating phase from -60 ^{o}C to 250 ^{o}C. Heating and cooling rate of 10°C/min was used in all cases.

III. RESULTS AND DISCUSSION

Lignins from different raw materials and pretreatment processes were characterized in detail, and their application potential was evaluated based on chemical characteristics. According to the chemical compositions given in Table 1, the actual lignin content varied between 82-96% in most lignins. In hydrolysis residue the lignin content was clearly lower, being only 55%, which is mainly due to the carbohydrate residues of unhydrolysed cellulose. Somewhat higher nitrogen content of hydrolysis lignin also indicates protein residues (Table 2). The impurities may have significant effect on hydrolysis lignin applicability, and based on requirements of the target applications some lignin purification procedure may be needed. Also in Soda-AQ bagasse lignin, the carbohydrate content originating from xylan was slightly higher compared to the others. The high ash contents of HL, SAQ-B and Kraft-HW lignins are probably raw material related, or indications of insufficient washing. The sulphur content of kraft lignins was below 4% (Table 2). Surprisingly, also the wheat straw lignins (Soda-WS, HL-WS) showed some traces of sulphur. The composition in terms of the H:G:S ratios, also widely varied among the lignin samples of different raw materials, the S/G ratio being higher for the hardwood lignins compared to the wheat straw and bagasse lignins (Table 2).

Molar mass is an essential structural feature affecting lignin applicability. Compared to the other lignins, the hydrolysis lignin had significantly higher molar mass, although it was only partly soluble in alkali used as an eluent (Table 2). The high molar mass could be an advantage in lignin based dispersants, providing better

adsorption properties. High molecular weight lignin could also be beneficial in respect of mechanical properties of lignin based composites. For these applications, the hydrolysis lignin solubility and thermoplasticity, respectively, should however be improved by chemical modification. The molar mass of all the other lignins was clearly lower, although the SE lignins and the SW kraft lignin had somewhat higher molar mass compared to the others. The lower molar mass level of the other spent liquor lignins could be beneficial in polyurethane (PU) resin applications to prevent the excess increase of viscosity, or to improve the lignin solubility.

Table 1. Lignin compositions.

Sample	Ash content, %	Klason lignin, %	Acid soluble, %	Total lignin, %	Total carbohydrates, %	Xyl, %	Glc, %	Man, %	Gal, %	Ara, %
Kraft-SW	0.6	90.2	5.1	95.3	2.2	0.8	0.2	0.1	0.8	0.3
Kraft-HW	10.5	82.6	0.0	82.6	1.2	0.5	0.2	0.0	0.3	0.2
Soda-WS	2.7	85.0	7.8	92.8	2.9	1.6	0.5	0.1	0.2	0.5
SAQ-B	6.6	82.8	4.5	87.3	7.1	5.7	0.2	0.1	0.2	0.9
OS-HW	0.6	91.1	2.6	93.7	0.8	0.4	0.1	0.1	0.1	0.1
SE-Birch	0.8	92.4	2.9	95.3	1.2	0.8	0.1	0.1	0.1	0.1
SE-GA	0.7	89.1	2.2	91.3	2.3	1.5	0.3	0.2	0.2	0.1
SE-WS	1.6	91.8	2.0	93.8	1.4	0.6	0.5	0.1	0.1	0.1
HL-WS	12.1	52.9	2.2	55.1	35.3	5.2	29.2	0.4	0.3	0.2

Table 2. Elemental compositions and methoxyl contents together with the average molar masses (Mn, Mw, PD), as well as the proportions of S, G and H type units (by Py-GC/MS) and the glass transitions of first and second heating (Tg_{1st}, Tg_{2nd}).

Sample	Elemental composition*					MeO %*	Type of aromatic units				Molar mass			Glass transition	
	C, %	H, %	O, %	N, %	S, %		S, %	G, %	H, %	S/G	Mn, g/mol	Mw, g/mol	PD	Tg 1st	Tg 2nd
Kraft-SW	65.2	5.9	25.6	0.2	3.1	12.7	-	94	6	-	2400	4700	2.0	140.4	146.7
Kraft-HW	65.0	5.9	26.2	0.2	2.7	16.2	67	32	1	2.1	1800	2800	1.6	177.3	182.0
Soda-WS	65.0	6.0	27.0	0.8	1.1	11.2	40	34	26	1.2	2000	3300	1.7	137.7	140.6
SAQ-B	64.6	6.0	28.9	0.5	0.0	n.d.	33	29	38	1.1	2300	4000	1.7	150.1	151.8
OS-HW	63.8	6.4	29.4	0.4	0.0	23.7	68	31	1	2.2	2000	3100	1.6	121.0	130.6
SE-Birch	63.0	6.1	30.7	0.2	0.0	18.0	75	24	1	3.1	2200	5200	2.4	153.5	162.6
SE-GA	63.1	5.8	30.6	0.5	0.0	n.d.	63	31	6	2.1	2300	5200	2.3	150.3	165.4
SE-WS	n.d.	n.d	n.d.	n.d	n.d	n.d.	27	54	19	0.5	2800	7000	2.5	160.6	186.4
HL-WS	54.8	6.4	37.2	1.3	0.2	nd	nd	nd	nd	nd	.2200	15800#	7.2	-	182.6

* Elemental composition and methoxyl contents have been corrected by ash content. # HL only partly soluble in 0.1M NaOH used as an eluent. n.d. = not determined.

Table 3. Content of most typical lignin inter-unit linkges per 100 C9 unit determined by 2D NMR, and the lignin functionalities determined by ^{31}P NMR (mmol/g lignin, calculated according to the lignin content of the samples, the effect of carbohydrates on aliphatic hydroxyls not taken into account).

Sample	β-O-4	β–β	β-5	β-1	Aliph OH, mmol/g	C + S, mmol/g	G, mmol/g	Catechol, mmol/g	p-OH, mmol/g	Phenolic OH, mmol/g	Total OH, mmol/g	COOH mmol/g
Kraft-SW	2.5	0.8	0.8	-	2,1	1,8	2,2	0,0	0,1	4,1	6,2	0,5
Kraft-HW	2.4	1.5	0.1	-	1,6	3,3	0,9	0,0	0,0	4,2	5,8	0,6
Soda-WS	3.9	0.9	0.4	-	1,4	2,0	0,9	0,0	0,5	3,4	4,8	0,9
SAQ-B	3.0	0.2	0.6	-	1,1	1,6	0,6	0,0	0,9	3,2	4,3	0,5
OS-HW	4.7	3.0	1.6	-	1,7	2,5	0,4	0,2	0,0	3,1	4,9	0,0
SE-Birch	22.3	4.7	1.6	-	2,4	1,9	0,5	0,0	0,0	2,4	4,7	0,3
SE-GA	24.5	2.4	3.9	0.3	3,1	1,7	0,6	0,3	0,2	2,7	5,8	0,2
SE-WS	7.9	3.3	0.8	-	1,4	1,0	0,9	0,0	0,2	2,1	3,5	0,5
HL-WS	20.1	1.9	8.1	-	8,5	0,3	0,3	0,0	0,1	0,7	9,2	0,4

The lignin inter-unit linkages were detected by 2D-NMR measurements, and ^{31}P NMR spectroscopy was used to quantify the different types of lignin functionalities (Table 3). Both methods well describe the depolymerisation occurring during biomass pretreatment. Among the aliphatic hydroxyl and carboxylic acid groups, the phenolic units formed as a result of cleavage of aryl ether linkages are the key functional groups in respect of lignin solubility and reactivity towards crosslinking and further modifications to adjust the lignin properties.

The main inter-unit linkages detected in all the technical lignins were the alkyl-aryl ethers (β–*O*–4´), followed by resinols (β–β´) and phenylcoumarans (β–5´) in different proportions. The abundance of native aryl ether linkages was high in the industrial hydrolysis lignin, which was accompanied with very low phenol content, indicating rather mild biomass pretreatment process. The lignins extracted from steam exploded hardwoods also had high content of alkyl-aryl ether linkages and rather low proportion of phenolic units, whereas the steam explosion clearly had more drastic effect on wheat straw in the same conditions. If the hydrolysis lignin with extremely high content of carbohydrates and thus poor solubility is excluded, the highest total hydroxyl content was detected for kraft lignins and SE-GA, providing highest amount of reactive sites e.g. for crosslinking with isocyanates for polyurethane resins. The proportion of phenolic hydroxyl groups was higher in all spent liquor lignins, but especially in kraft lignins, compared to the HL and SE lignins. The amount of C5 unsubstituted phenols, which is a prerequisite for the reactivity in phenol formaldehyde (PF) resins, was highest in SW kraft lignin. Due to the non-methoxylated *p*-hydroxyphenyl groups detected, also the SAQ bagasse and soda wheat straw lignin could provide sufficient reactivity for PF resin applications. In bagasse the proportion of non-methoxylated *p*-hydroxyphenol groups was higher than in wheat straw.

Thermal properties of lignins were evaluated according to the Tg values (Table 2), which varied between 121 and 177 °C in the first heating. Both the Kraft-HW and the steam exploded lignin of wheat straw had the highest Tg indicating more rigid/condensed structure compared to the other lignins. The lowest Tg was detected for the OS-HW. Some condensation took place during the first heating, which slightly increased the Tg values of all lignins in the 2nd heating. Similarly, some condensation may occur also in process temperatures typically used for processing of thermoplastic composites, unless this could be prevented by chemical modification.

IV. CONCLUSIONS

The hydrolysis lignin and the steam exploded lignins had clearly distinct characteristics (high molar mass, low phenolic content) compared to the spent liquor lignins. For the reactivity required in PU resins, also aliphatic hydroxyl groups are essential. If the hydrolysis lignin with carbohydrate residues and limited solubility is excluded, the highest total hydroxyl content was detected for Kraft lignins and SE-GA. The Kraft-SW had most C5 unsubstituted phenols, which is a prerequisite for the reactivity in phenol formaldehyde (PF) resins. Soda-AQ bagasse and soda wheat straw lignins contain non-methoxylated *p*-hydroxyphenyl groups either as part of the lignin macromolecule or in p-coumaryl esters. These structures may also improve reactivity for PF resin applications. The hydrolysis and SE lignins had the highest molar mass, assumedly providing better adsorption properties for dispersants. Higher molar mass lignin could be beneficial also for the mechanical properties of lignin based composites. However, the effect of carbohydrate and protein impurities may also significantly affect the applicability of hydrolysis lignin. The LGF organosolv lignin had clearly lowest Tg, being in that sense most thermoplastic, although chemical modification is still needed to obtain mouldable thermoplastic lignin for thermal processing. Obviously, only hypothesis on applicability can be made based on chemical characteristics, and these need to be verified with the actual testing in the target applications.

V. ACKNOWLEDGEMENT

WoodWisdom-EraNet and the national funding agencies (Tekes, MIPAFF, INIA-Spain, FNR, Latvian Ministry of Agriculture) are acknowledged for the funding of ProLignin project. Stora Enso, Suzano and Valmet are also acknowledged for providing the industrial and pilot scale lignins.

VI. REFERENCES

[1] Mikkonen, H., Peltonen, S., Kallioinen, A., Suurnäkki, A., Kunnari, V., Malm, T. Process for defibering a fibrous material. **2009**, Patent WO2007/066007.

[2] Liitiä, T.; Barth, D.; Tamminen, T.; Colodette, J.L. Organosolv pulping as a pretreatment for bioethanol production from Eucalyptus and Elephant grass. *17th International symposium on wood, fibre and pulping chemistry.* June 12-14, **2013**, Vancouver, Canada.

[3] Puls, J. Substrate analysis of forest and agricultural wastes. In: *Biotechnology in agriculture; bioconversion of forest and agricultural plant residues*. Ed. Saddler, J.N. CAB International, **1993**, 13-32.

[4] Willför, S.; Pranovich, A.; Tamminen, T.; Puls, J.; Laine, C.; Suurnäkki, A.; Saake, B.; Uotila, K.; Simolin, H.; Henning, J.; Holmbom, B. Carbohydrate analysis of plant materials with uronic acid-containing polysaccharides – A comparison between different hydrolysis and subsequent chromatographic analytical techniques. *Industrial crops and products* **2009**, *29*, 571-580.

[5] Vieböck, F., Schwappach, A. Eine neue Methode zur maßanalytischen Bestimmung der Methoxyl- und Äthoxylgruppe. I. Makro-analyse. *Berichte der deutschen chemischen Gesellschaft (A and B Series)*, **1930**, *63*, 2818–2823.

[6] Granata, A., Argyropoulos, D.S. 2-Chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane, a reagent for the accurate determination of the uncondensed and condensed phenolic moieties in lignins. *J. Agric. Food Chem.***1995**, *43*, 1538-1544.

[7] del Rio, J.C.; Princen, P.; Martinez, A.T.; Ralph, J.; Gutiérrez, A. Structural characterization of wheat straw lignin as revealed by analytical pyrolysis, 2D-NMR, and reductive cleavage methods. *J. Agric. Food. Chem.* **2012**, *60*, 5922-5935.