

EWLP | 2014

13TH EUROPEAN WORKSHOP ON
LIGNOCELLULOSICS AND PULP



PROCEEDINGS

24-27 June 2014
Seville, Spain

© Institute of Natural Resources and Agrobiology of Seville (IRNAS-CSIC), 2014
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

EFFECT OF STEAM EXPLOSION ON FIBRE LIGNIN STRUCTURE FOR SELF-BINDING FIBER BOARDS

Liitiä, T.^{1*}, Rovio, S.¹, Talja, R.¹, Tamminen, T.¹, Rencoret, J.², Gutiérrez, A.², del Río, J.C.², Sutka, A.³, Tupciauskas, R.³, Andzs, M.³, Gravitis, J.³

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 Latvian State Institute of Wood Chemistry, 27 Dzerbenes Str., LV-1006-Riga, Latvia; (*Tiina.Liitia@vtt.fi)

ABSTRACT

The structural changes induced in fiber lignin by steam explosion was studied to better understand the effect of steam explosion conditions on bonding mechanisms of lignin containing fibers in self-binding fiber boards. In all the steam exploded lignin samples, the main lignin inter-unit linkage after 1 min treatment was the β -O-4' alkyl aryl ether that accounts for up to nearly 80% of all inter-unit linkages. With increased steam explosion times a drastic decrease in the content of β -O-4 linkages was detected, which was accompanied with the formation of new phenolic units and decrease in molar mass. However, at the same time, some condensation of lignin occurred as well. After steam explosion, the lignin was more prone to thermally induced condensation reactions. The formation of the new phenolic groups during steam explosion, and the enhanced tendency to condensate during thermal processing, most likely contribute to the higher bonding ability of steam exploded fibers when manufacturing self-binding fiber boards.

I. INTRODUCTION

Steam explosion (SE) is a potential pretreatment method to produce self-binding fiber boards, utilizing the fiber lignin as such or together with added lignin as a binder without any synthetic resins [1-3]. This way the negative effects of synthetic phenol-formaldehyde resins, e.g. emissions of volatile formaldehyde, could be avoided. It has also been shown that the properties of produced boards in many cases are comparable with the conventional commercial boards, especially for dry-use in interior grades [1]. To better understand the effect of steam explosion conditions on bonding mechanisms of lignin containing fibers, it is essential to better understand the structural changes induced in fiber lignin.

In this study, steam explosion was performed in different conditions at laboratory scale for grey alder, birch, and wheat straw, and fiber lignin was isolated by alkaline extraction for chemical characterization. The lignin samples were analyzed in detail by 2D ¹H-¹³C correlation NMR spectroscopy that provided information of the structure of the whole lignin macromolecule and is a powerful tool for lignin structural characterization revealing both the aromatic units and the different inter-unit linkages present in the lignin polymer [4]. The functional groups of lignin, *i.e.* aliphatic and phenolic hydroxyls and carboxylic acids, were detected by ³¹P NMR spectroscopy, and the lignin molar mass distributions were detected by size exclusion chromatography (SEC). Thermal properties were evaluated by differential scanning calorimetry (DSC).

II. EXPERIMENTAL

Steam explosion. Steam explosion (SE) was performed for wheat straw (WS), birch and grey alder (GA) at 235°C with 3.2MPa pressure for 1min. For gray alder also longer SE times of 2 and 3 min were performed. The steam exploded fibers were used for production of fiber boards. For the analytical purposes, lignin was extracted from steam exploded fibers by 0.4% NaOH and precipitated by acid.

Analytical methods. The molar mass distributions of lignins were determined by size exclusion chromatography (SEC) in 0.1M NaOH eluent using MCX 1000 and 100 000 columns with UV detection (280 nm). The molar mass distributions and the average molar mass values (Mn, Mw) were calculated relative to the polystyrene sulphonate (Na-PSS) calibration using Waters Empower 3 software.

Lignin functionalities were determined by ³¹P NMR according to Granata and Argyropoulos [5]. Accurately weighted samples (40 mg) were dissolved in 150 μ L of *N,N*-dimethylformamide. After dissolution, 100 μ L pyridine, 200 μ L internal standard solution of 0.05 M *endo*-*N*-Hydroxy-5-norbornene-2,3-dicarboximide in pyridine/CDCl₃ (1.6/1, v/v) and 50 μ L Cr(acac)₃ solution (11.4 mg/1 mL) in pyridine/CDCl₃ (1.6/1, v/v) were

added. Then, 100 μL 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane 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 ^1H - ^{13}C HSQC (heteronuclear single quantum coherence) NMR spectra were recorded at 25°C 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 $\text{DMSO}-d_6$. Spectral widths of 5000 Hz (10-0 ppm) and 20,843 Hz (165-0 ppm) for the ^1H - and ^{13}C -dimensions were used. The number of transients was 64 for 256 time increments, with $^1J_{\text{CH}}$ of 145 Hz. The semiquantitative analysis of the correlation peaks was performed using Bruker's Topspin 3.1 software. The lignin inter-unit linkages based on C_α - H_α correlations were calculated as described previously [2].

The lignin glass transition (T_g) 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°C to 105°C with 20 min isothermic phase for drying, 2) cooling phase to -60°C , 3) first actual heating phase from -60°C to 200°C , 4) cooling phase to -60°C , and 5) second heating phase from -60°C to 250°C . Heating and cooling rate of $10^\circ\text{C}/\text{min}$ was used in all cases.

III. RESULTS AND DISCUSSION

The structural changes induced in fiber lignin by steam explosion was studied to better understand the effect of steam explosion conditions on bonding mechanisms of lignin containing fibers. Based on 2D ^1H - ^{13}C HSQC NMR results given in Table 1, the main lignin substructure present in all the steam exploded lignin samples was the β -O-4' alkyl aryl ether. It accounts for up to nearly 80% of all inter-unit linkages in 1 min steam exploded wood lignin, while condensed linkages (β - β' resinols, β -5' phenylcoumarans and β -1' spirodienones) were present in lower amounts. Interestingly, the 2D-NMR data also indicated that the steam exploded grey alder lignins showed a drastic decrease in the content of lignin substructures, particularly β -O-4 linkages, with increasing steam explosion time. Compared to the hardwoods, the steam explosion had more drastic effect on wheat straw in the same conditions.

The cleavage of β -O-4 linkages during steam explosion pretreatment was accompanied with the formation of new phenolic units (Table 2) and decrease of molar mass (Mw) (Table 3). However, at the same time, some condensation of lignin occurred as well. As shown in the molar mass distributions (Figure 1), the decrease of molar mass was mainly due to the degradation of high molecular weight lignin or lignin-carbohydrate complexes (LCCs), whereas the molar mass of the main lignin fraction increased at the same time. Also the proportion of condensed phenolic units (C+S) was increased (Table 2). It is thus evident that both lignin degradation and condensation takes place during steam explosion.

Table 1. Content of most typical lignin inter-unit linkages per 100 C9 unit determined by 2D NMR.

Sample	β -O-4	β - β	β -5	β -1
SE-WS	7.9	3.3	0.8	-
SE-Birch	22.3	4.7	1.6	-
SE-GA-1	24.5	2.4	3.9	0.3
SE-GA-2	12.5	2.4	3.4	0.3
SE-GA-3	4.6	1.4	1.9	0.1

Table 2. The lignin functionalities determined by ^{31}P NMR (mmol/g lignin, calculated according to the lignin content of the samples).

Sample	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
SE-WS	1,4	1,0	0,9	0,0	0,2	2,1	3,5	0,5
SE-Birch	2,4	1,9	0,5	0,0	0,0	2,4	4,7	0,3
SE-GA-1	3,1	1,7	0,6	0,3	0,2	2,7	5,8	0,2
SE-GA-2	2,1	1,9	0,6	0,2	0,2	2,9	5,0	0,3
SE-GA-3	1,4	2,3	0,7	0,3	0,2	3,5	4,9	0,3

The glass transition temperatures detected after second heating cycle (Table 3) were higher than after the first heating, which indicates that some condensation reactions most likely takes place during thermal processing of steam exploded lignins. Also here, the prolonged steam explosion slightly increased the tendency for thermally induced condensation. Formation of the new phenolic units during steam explosion, and the enhanced tendency to condensate during thermal processing most likely contribute to the higher bonding ability of steam exploded fibers in self-binding fiber boards.

Table 3. The average molar masses (Mn, Mw, PD) and the glass transitions of first and second heating (T_{g1st} , T_{g2nd}).

Sample	Molar mass			Glass transition	
	Mn, g/mol	Mw, g/mol	PD	Tg 1st	Tg 2nd
SE-WS	2800	7000	2.5	160.6	186.4
SE-Birch	2200	5200	2.4	153.5	162.6
SE-GA-1	2300	5200	2.3	150.3	165.4
SE-GA-2	2400	5000	2.1	154.2	166.4
SE-GA-3	2500	4800	1.9	150.5	168.5

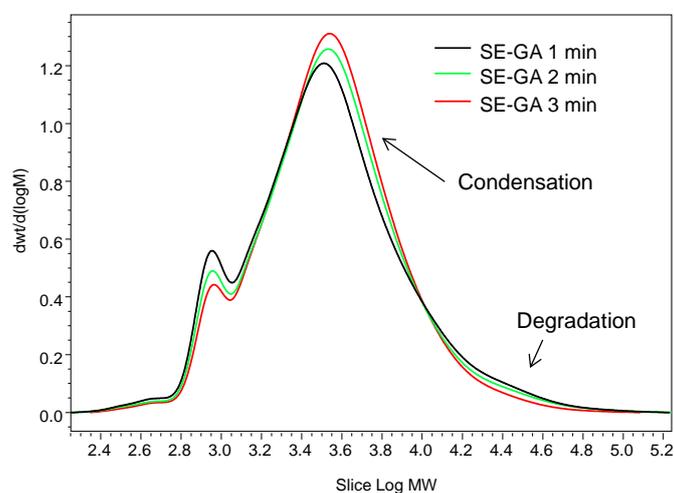


Figure 1. The molar mass distributions of the SE-GA lignins after variable steam explosion times of 1-3 min.

IV. CONCLUSIONS

In all the steam exploded lignin samples, the main lignin substructure present was the β -O-4' alkyl aryl ether that accounts for up to nearly 80% of all inter-unit linkages in 1 min steam exploded wood lignin. Interestingly, the steam exploded grey alder lignins showed a drastic decrease in the content of β -O-4 linkages with increasing steam explosion time, which was accompanied with the formation of new phenolic units and decrease of molar mass. However, at the same time, some condensation of lignin occurred as well. After steam explosion, the lignin was also more prone to thermally induced condensation reactions. Both the formation of the new phenolic groups during steam explosion, and the enhanced tendency to condensate during thermal processing most likely contribute to the higher bonding ability of steam exploded fibers when manufacturing self-binding fiber boards.

V. ACKNOWLEDGEMENT

WoodWisdom-EraNet and the national funding agencies (Tekes, INIA-Spain, Latvian Ministry of Agriculture) are acknowledged for the funding of ProLignin project.

VI. REFERENCES

[1] Gravitis, J., Abolins, J., Tupciauskas, R., Veveris, A., Alksnis, B. Substitution of phenolic components by steam-exploded lignin in plywood and self-binding boards with account of energy necessary for steam explosion

treatment, *Scientific Journal of Riga Technical University – Material Science and Applied Chemistry*, **2010**, *21*, 7-11.

[2] Tupciauskas, R., Gravitis, J., Belkova, L., Tuherm, H., Grey alder fiber board processed by modified steam explosion unit, *16th International Scientific Conference on Research for Rural Development 2010*, Jelgava, Latvia, May 19-21, **2010**, 248-254.

[3] Tupciauskas, R., Gravitis, J., Veveris, A., Tuherm, H., *Forest & Landscape Working Papers*, **2009**, *43*, 141.

[4] del Rio, J.C.; Prinsen, 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.

[5] 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.