

# Organic Material Dissolved During Oxygen-Alkali Pulping of Hot-Water-Extracted Spruce Sawdust

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Untreated and hot-water-extracted (HWE) Norway spruce (*Picea abies*) sawdust was cooked using the sulfur-free oxygen-alkali (OA) method under the following conditions: temperature, 170 °C; liquor-to-wood ratio, 5:1 L/kg; and NaOH charge, 19% on the oven-dry sawdust. In comparison with earlier studies conducted with birch sawdust, the spruce cooking yield data, together with the amount of the pulp rejects (78% to 86% for reference pulps from the initial feedstock and 73% to 83% for pulps from the HWE feedstock), revealed that the pretreatment stage prior to spruce OA pulping caused different effects on pulping performance. The analyses of the three main compound groups (*i.e.*, lignin, volatile acids, and hydroxy acids) in black liquor indicated that slightly higher contents (25.5 to 45.9 g/L) of dissolved lignin were detected in black liquors originating from the HWE sawdust than in the black liquors from the reference material (27.2 to 39.6 g/L). In contrast, considerably lower (~20% decrease) volatile acid contents and similar or slightly decreased hydroxy acids contents were detected in the black liquors from the HWE sawdust.

*Keywords:* Autohydrolysis; Biorefining; Black liquor; Hot-water extraction; Hydroxy acids; Lignin; Norway spruce; Oxygen-alkali pulping; Volatile acids

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## INTRODUCTION

In the quest for replacing materials, chemicals, and energy manufactured from fossil resources, forest biomass and integrated forest biorefineries (IFBRs) play a particularly important role (Kamm *et al.* 2006; Carvalheiro *et al.* 2008; Alén 2011; Baijpai 2012; Lehto 2015). IFBRs modified from conventional pulp and paper mills can utilize the already existing logistical and industrial infrastructure of the existing production plants, thus minimizing the investment costs compared to those resulting from building a stand-alone biomass conversion facility from the beginning (van Heiningen 2006; FitzPatrick *et al.* 2010; Huang *et al.* 2010; Moshkelani *et al.* 2013; Machani *et al.* 2014). The integration of the production of high-value byproducts into conventional pulp and paper mill operations allows the evolution of pronounced full-scale utilization of biomass, thus increasing the profitability of the mills and enlarging the product repertory.

In conventional pulp mills, most hemicelluloses and lignin are dissolved into alkaline cooking liquor (Sjöström 1993; Alén 2000b). The waste liquor (*i.e.*, black liquor) is then concentrated and combusted in a recovery boiler for producing energy and for recovering the cooking chemicals (Adams 1997). However, given the low heating value of hemicelluloses and their degradation products (*i.e.*, various small-size organic acids) compared with aromatic lignin, alternative methods for separating and refining this underutilized carbohydrate fraction for the production of bio-based products have been suggested (Huang *et al.* 2010). One promising alternative for recovering hemicelluloses is

a pre-extraction step prior to pulping (Carvalho *et al.* 2008; Mansoornejad *et al.* 2013; Martin-Sampedro *et al.* 2014). There are many potential pre-extraction methods to fractionate hemicelluloses from lignocellulosic biomass, the most common methods being dilute acid pretreatment, hot-water extraction, steam explosion, and alkaline extraction (Carvalho *et al.* 2008; Lehto 2015). Depending on the chosen pretreatment, the chemical composition of the resulting aqueous process liquors varies distinctly. While acidic pretreatments result in hydrolysates with mostly monomeric carbohydrates, hot-water extraction and alkaline pretreatments produce effluents containing polymeric carbohydrate structures.

In addition to the varying chemical composition of the produced aqueous pretreatment liquors, pretreatments have an effect on the chemical and morphological composition of the pretreated wood and also on the subsequent delignification behavior of the pretreated material (Duarte *et al.* 2011; Borrega *et al.* 2013; dos Santos Muguét *et al.* 2013; Huang and Ragauskas 2013a,b). In particular, hot-water extraction and dilute acid pretreatments have been proposed to enhance the delignification rates compared with untreated feedstocks (Yoon and van Heiningen 2008; Lu *et al.* 2012; Chirat *et al.* 2013; Hamaguchi *et al.* 2013). This cooking modification leads to savings in pulping and bleaching costs, reduced cooking times, and lower energy demands. The pulping performance is improved by the following factors: enhanced impregnation of cooking chemicals due to the increased pore volume and permeability of the fiber cell wall together with the hydrolytic cleavage of lignin; removal of hemicelluloses and their degradation products (otherwise consuming the cooking chemicals); and cleavage of the bonds of lignin-carbohydrate complexes. However, there are also negative effects caused by hot-water and dilute acid pretreatments (Yoon and van Heiningen 2008; Duarte *et al.* 2011; Saukkonen *et al.* 2012a,b; Hamaguchi *et al.* 2013). The most profound negative effects include the reduced yield of pulp compared with the reference kraft cooks conducted without pre-extraction, reduced refining response, and decreased strength properties of the produced pre-hydrolysis kraft pulps.

In a previous study (Lehto and Alén 2015), birch sawdust was pretreated with hot-water prior to oxygen-alkali (OA) pulping to facilitate delignification, leading to well-defibrated pulp with a low amount of pulp reject and a low kappa number. Furthermore, the pretreatments had a profound effect on the chemical composition of the black liquors. The main aim of the present study was to clarify the effects of hot-water extraction on the OA pulping of Norway spruce and to compare these results with those previously determined for hardwood. In addition, the detailed composition of black liquor organics was determined, emphasizing the dissolution of lignin and the formation of carbohydrates-derived aliphatic carboxylic acids.

## EXPERIMENTAL

### Feedstock Materials

Untreated (reference) and hot-water-extracted (HWE) Norway spruce (*Picea abies*) sawdust samples were provided by the Finnish Forest Research Institute (Metla; Helsinki, Finland). Pressurized hot-water pretreatments were performed with a pilot-scale flow through extraction system (constructed by Viitos-Metalli Ltd., Heinola, Finland) that consisted of a pump, a water-heating unit, heat exchange systems, a hot-water reservoir, an extraction chamber, and extract collection vessels. The water flow rate was controlled by

five valves, and the pressure was kept automatically at 20 bars. During autohydrolysis, spruce sawdust was extracted for about 32 min at 180 °C, and the corresponding P-factor value (Tunc and van Heiningen 2009) was approximately 680. After the pretreatment, the HWE sawdust was unloaded from the reactor and air-dried. For the chemical analyses (*i.e.*, to determine the content of carbohydrates, lignin, and extractives), the reference and the extracted sawdust samples were stored in a freezer (-18 °C), and their moisture contents were determined. All of the wet-chemistry analysis results were an average of two parallel determinations and expressed as a percentage of dry sample weight.

The extractives content of sawdust was determined according to the TAPPI test method T280 pm-99 (1999) by extracting the sample with acetone for 4 h in a Soxhlet apparatus (6 to 10 percolations per hour). Before weighing, the extract was dried by vacuum evaporation with a rotary evaporator (Heidolph VV2000, Gemini BV Laboratory, Apeldoorn, Netherlands) and nitrogen gas stream.

The lignin content of the extractives-free sawdust sample (approximately 200 mg) was determined as the sum of the “acid-insoluble Klason lignin” and the “acid-soluble lignin” (TAPPI test methods T222 om-98 (1998), T249 cm-00 (2000), and T250 um-00 (2000)). Using these determinations, the sawdust was first treated with 72% H<sub>2</sub>SO<sub>4</sub>, followed by an autoclave treatment (1 bar, 1 h, and 120 °C). After this, the lignin precipitated was filtered off, washed, dried, and weighed. The content of acid-soluble lignin was determined using a Beckman DU 640 UV/Vis-spectrophotometer (Beckman Instruments Inc., Fullerton, CA, USA) at 205 nm after dilution of one portion of the hydrolysate with the corresponding aqueous solution of H<sub>2</sub>SO<sub>4</sub> (0.5%) until the absorbance (*A*) was in the range from 0.3 to 0.8. The concentration of dissolved lignin (*C*, g/L) was calculated according to Eq. 1,

$$C = \frac{A}{a \cdot b}, \quad (1)$$

where *a* is the absorptivity (120 L/(g·cm)) (Swan 1965) and *b* is the light path (cm).

The content of different monosaccharides (*i.e.*, arabinose, galactose, glucose, mannose, and xylose) in the Klason hydrolysates was determined using a Hewlett Packard 5890 Series II Plus GC gas chromatography (GC) system (Hewlett Packard, Palo Alto, CA, USA) equipped with an Agilent DB-1701 column (60 m × 0.32 mm inner diameter), with a film thickness of 0.25 μm (Agilent Technologies, Palo Alto, CA, USA), and a flame ionization detector (FID) operated at 300 °C. The column temperature program was: 2 min at 100 °C, 2 °C/min to 185 °C (27 min), 39 °C/min to 280 °C, and 15 min at 280 °C. For GC-FID, a 10 mL liquor sample was neutralized with anion exchange resin (Amberlite IRA 68) until the hydrolysate reached pH 4. The resin was filtered, and 1 mL of an aqueous mixture (*i.e.*, ultra-high quality water (UHQ) obtained from a Milli-Q Plus water system (Millipore, Bedford, MA, USA)) of internal standard (ISTD; xylitol, 0.25 mg/mL (Fluka Chemical Corp., Seelze, Germany)) was added to the filtrate. Next, the sample was evaporated with a vacuum evaporator. Finally, the residue was per(trimethylsilyl)ated by adding 1.25 mL of pyridine and 0.75 mL of *N,O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA; Regis Technologies, Morton Grove, IL, USA) containing 1% trimethylchlorosilane (TMCS; Regis Technologies), and the mixture was shaken for approximately 60 min at room temperature. Samples were filtered into sample vials and analyzed by GC. The peak identification and the mass-based response factors between the ISTD and each monosaccharide were based on separate analyses with model monosaccharides (Fluka Chemical Corp., Seelze, Germany).

## Oxygen-alkali Pulping

Laboratory-scale OA cooking experiments of the sawdust samples were conducted in 1.25-L rotating stainless steel autoclaves heated in an oil bath (CRS Autoclave System 420, CRS Reactor Engineering AB, Stenkullen, Sweden). During the pulping experiments, the liquor-to-wood ratio was 5:1 L/kg, and the alkali (NaOH) charge was 19% on the oven-dry (o.d.) sawdust. Oxygen was bubbled through the cooking liquor for 5 min prior to charging sawdust into the reactors, which were then closed; finally, oxygen was introduced through the reactor lid (for 2 min) to ensure an oxygen atmosphere. The maximum cooking temperature was 170 °C, and the cooking times were 30, 60, 90, 120, and 150 min. At the end of each experiment, the autoclaves were removed from the oil bath and cooled rapidly in cold tap water. The black liquor was separated from the pulp by pressing and stored in storage bottles. Pulp was thoroughly washed with hot (for 20 min) and cold (for 10 min) tap water and finally dried with a vacuum rotary drier. The amount of pulp reject was determined with a pulp screening device (0.2-mm screen).

## Analysis of Black Liquors

The content of dissolved lignin in the OA black liquors was determined using a Beckman DU 640 UV/Vis-spectrophotometer at 280 nm, according to the previously described method (Alén and Hartus 1988). Samples were diluted with 0.1 M NaOH until the absorbance was within the range from 0.3 to 0.8. The content of dissolved lignin was calculated according to Eq. 1. The absorptivity value used in this determination was 18.7 L/(g·cm).

Acetic and formic acids (referred to as “volatile acids”) were determined by the previously described method (Käkölä *et al.* 2008) using a Dionex (Dionex Corp., Sunnyvale, CA, USA) chromatography system equipped with an AS50 autosampler, a LC25 chromatography oven, an EG40 eluent (KOH/UHQ water) generator, and an IC 25 ion chromatograph. The system was equipped with an anion trap column (IonPac ATC-1), and the separation column was an IonPac AS 11-HC analytical column combined with an AG11-HC guard column (Dionex Corp., Sunnyvale, CA, USA). Samples were injected *via* a 25 µL-loop and eluted (KOH/UHQ water) at a flow rate of 1.0 mL/min. Data were stored and processed using a Dionex Chromeleon (6.50) data system. The identification of the chromatographic peaks was based on the model substances, sodium acetate (J.T. Baker, Deventer, Netherlands) and sodium formate (Riedel-de Haën, Seelze, Germany).

Hydroxy acids (*i.e.*, hydroxy mono- and dicarboxylic acids) were determined using an Agilent 6850 Series gas chromatograph (Agilent Technologies, Palo Alto, CA, USA) equipped with a HP-5 column (30 m × 0.32 mm i.d., film thickness 0.25 µm) and a FID operating at 300 °C with a hydrogen and air flow rate of 40.0 mL/min and 450.0 mL/min, respectively (Käkölä *et al.* 2007). The column temperature program was 5 min at 60 °C, 2 °C/min to 200 °C, 70 °C/min to 290 °C, and finally 15 min at 290 °C. For GC-FID, a 1.0 mL liquor sample (1/10 dilution) and a 1.0 mL ISTD (xylitol, Fluka Chemical Corp., Seelze, Germany) UHQ water solution (concentration 0.1 mg/L) were mixed and passed through a column filled with weakly acidic cation exchange resin (approximately 10 mL, Amberlite IRC-50, 16-50 mesh, NH<sub>4</sub><sup>+</sup>-form, Fluka Chemical Corp., Seelze, Germany) (Alén *et al.* 1984). The column was washed with UHQ water to obtain a sample volume of 30 to 40 mL, and this aqueous sample was then evaporated under a reduced pressure at approximately 35 °C. Finally, the residue was per(trimethylsilyl)ated by adding 1.0 mL of pyridine and 0.5 mL of BSTFA containing 1% TMCS), and the mixture was shaken for approximately 60 min at room temperature. The individual acid derivatives were identified

using the same GC system, which was equipped with a mass selective detector (GC-MSD). The interpretation of the mass spectra was based on data from previous studies and performed using a HP ChemStation (A06.03) chromatography data system. For the quantitative calculations, the mass-based response factors between xylitol (1.00) and the peaks derived from the acids were based on the previous data (Alén *et al.* 1984).

## RESULTS AND DISCUSSION

### Pretreatment and Pulping of the Feedstock Materials

The chemical compositions of the sawdust samples before and after hot-water extraction are presented in Table 1. The main effect of the pretreatment was the removal of hemicelluloses, as their contents clearly decreased due to the hot-water extraction. Approximately 61% of the hemicelluloses-derived monosaccharides (*i.e.*, arabinose, galactose, glucose (in part), mannose, and xylose) were removed from the feedstock material during the pretreatment. However, the relative content of lignin and glucose (mostly incorporated in cellulosic fiber) in the extracted residue increased.

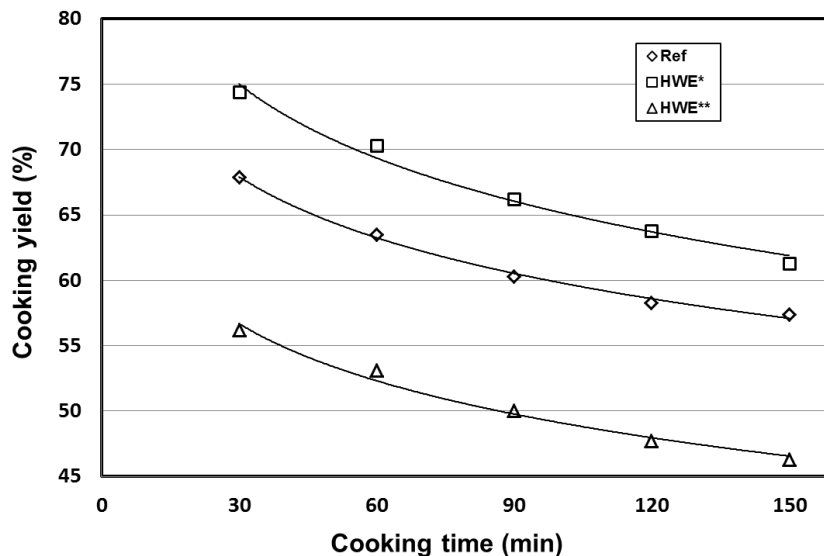
**Table 1.** Chemical Composition of the Feedstock Materials (% of Dry Matter)

Component	Ref	HWE
Monosaccharides*	62.0	65.7
Arabinose	1.1	0.1
Galactose	2.0	0.5
Glucose	42.5	57.2
Mannose	11.4	4.0
Xylose	5.0	3.9
Lignin	27.0	30.1
Klason	26.7	29.8
Acid soluble	0.3	0.3
ASMs** (“extractives”)	1.5	1.0
Others	9.5	3.2

Ref, untreated feedstock; HWE, hot-water-treated feedstock; the yield of pretreatment was 75.5% of the o.d. wood  
 \*Monosaccharide moieties are presented as their anhydro forms  
 \*\*Acetone-soluble materials

The yield data of OA pulping conducted with the reference (*i.e.*, without hot-water extraction) and the HWE spruce sawdust samples are presented in Fig. 1. When the yields were calculated as a percentage of the material loaded into the reactors, clearly higher yields were obtained for the cooks with the HWE feedstock than those with the initial feedstock. However, when the yields were calculated as the total yield (*i.e.*, the material removed during the pretreatments was also taken into consideration), the total yields for cooks with the HWE feedstock were lower than those with the initial feedstock.

The amount of pulp rejects (*i.e.*, material that did not pass through a 0.2-mm screen) after each cooking experiment is shown in Table 2. In a previous study (Lehto and Alén 2015) conducted with HWE birch sawdust, hot-water extraction performed prior to OA pulping notably enhanced the delignification and defibration by lowering the amount of pulp rejects and decreasing the kappa number. However, similar beneficial effects were not observed for spruce feedstock because neither the reference nor the HWE feedstock was properly defibrated.



**Fig. 1.** Cooking yields of the reference (Ref, cooks with untreated feedstock), HWE\* (cooks with hot-water-treated feedstock as a % of the material charged into reactors), and HWE\*\* (cooks with hot-water-treated feedstock as a % of the initial feedstock)

The amount of pulp rejects (*i.e.*, material that did not pass through a 0.2-mm screen) after each cooking experiment is shown in Table 2. In a previous study (Lehto and Alén 2015) conducted with HWE birch sawdust, hot-water extraction performed prior to OA pulping notably enhanced the delignification and defibration by lowering the amount of pulp rejects and decreasing the kappa number. However, similar beneficial effects were not observed for spruce feedstock because neither the reference nor the HWE feedstock was properly defibrated. The amount of pulp rejects was quite high for both materials (78% to 86% for reference pulps and 73% to 83% for pulps from HWE feedstock) compared with the corresponding birch pulps (47% to 70% and 0% to 30%, respectively). For spruce, there was only a very small improvement after the pretreatment of sawdust prior to pulping. Because of the very low screened pulp yield, kappa numbers were not determined.

**Table 2.** Amount of Pulp Rejected\*

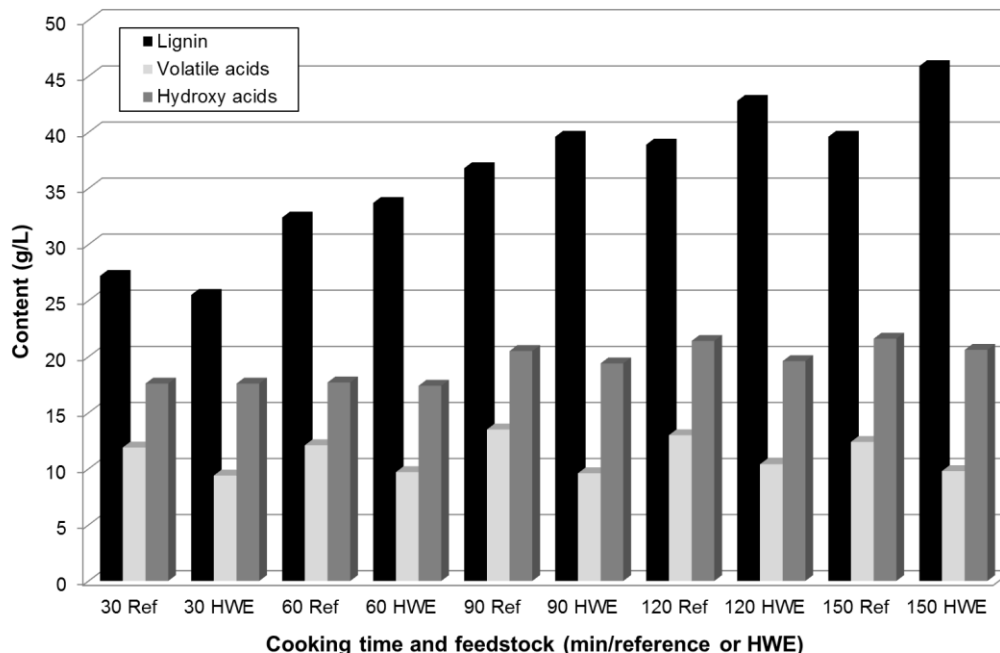
Cooking time (min)	Ref	HWE
30	86.0	82.6
60	85.4	79.9
90	81.5	76.6
120	78.1	75.8
150	80.7	73.4

Values expressed as a % of the cooking yield. Ref, pulps from untreated feedstock; HWE, pulps from hot-water-treated feedstock  
\*Material that did not pass through a 0.2-mm screen

### Black Liquor Composition

The contents of the three main compound groups (*i.e.*, lignin, volatile acids, and hydroxy acids) determined from the black liquors are presented in Fig. 2. In general, slightly higher contents (25.5 to 45.9 g/L) of dissolved lignin in the black liquors originated from the HWE sawdust compared with those cooked with the reference material (27.2 to

39.6 g/L). Furthermore, clearly lower (approximately 20%) content of volatile acids were determined in the HWE black liquors than in the corresponding reference black liquors. In contrast, no significant difference in the content of total hydroxy acids was observed between various black liquors.



**Fig. 2.** Chemical composition of oxygen-alkali black liquors obtained from the cooks with untreated (Ref) and hot-water-extracted (HWE) spruce sawdust

The contents of individual volatile acids in different black liquors, together with the concentration ratios (*i.e.*,  $\text{volatile acids}_{\text{HWE}}/\text{volatile acids}_{\text{Ref}}$ ), are listed in Table 3. A decreased total content of the volatile acids in the HWE black liquors was mainly explained by the decreasing content of acetic acid. The decline in total volatile acid content most likely resulted from a partial removal of acetyl groups in hemicelluloses, which had already occurred during the pretreatment.

**Table 3.** Content of Volatile Acids in Black Liquors (g/L)

Cooking time (min)/Acid	Ref	HWE	Ratio
30/Acetic	6.9	4.2	0.6
60/Acetic	6.8	4.4	0.6
90/Acetic	7.4	4.2	0.6
120/Acetic	7.0	4.6	0.7
150/Acetic	6.8	4.4	0.6
30/Formic	5.0	5.2	1.0
60/Formic	5.3	5.3	1.0
90/Formic	6.1	5.4	0.9
120/Formic	6.0	5.8	1.0
150/Formic	5.6	5.4	1.0

Ref, pulps from untreated feedstock; HWE, pulps from hot-water-treated feedstock; Ratio,  $\text{volatile acids}_{\text{HWE}}/\text{volatile acids}_{\text{Ref}}$

**Table 4.** Hydroxy Acids (*i.e.*, Hydroxy Monocarboxylic and Dicarboxylic Acids) in Black Liquors (g/L)

Cooking time (min)	30			60			90			120			150		
	Ref	HWE	Ratio*	Ref	HWE	Ratio	Ref	HWE	Ratio	Ref	HWE	Ratio	Ref	HWE	Ratio
Monocarboxylic acids	15.5	16.3	1.1	15.5	16.0	1.0	18.0	17.9	1.0	18.9	18.1	1.0	19.1	19.1	1.0
Glycolic	1.7	2.1	1.2	1.7	2.1	1.2	1.9	2.3	1.2	2.1	2.3	1.1	2.2	2.4	1.1
Lactic	2.6	2.4	0.9	2.7	2.5	0.9	3.2	3.0	0.9	3.5	2.9	0.8	3.7	3.4	0.9
3-Hydroxypropanoic	+**	0.3	n.c.**	+	0.3	n.c.	+	0.3	n.c.	+	0.3	n.c.	+	0.3	n.c.
Glyceric	0.2	0.3	1.5	0.2	0.2	1.0	0.2	0.2	1.0	0.2	0.2	1.0	0.2	0.2	1.0
2-Hydroxybutanoic	0.5	0.8	1.6	0.6	0.9	1.5	0.8	1.1	1.4	1.0	1.0	1.0	1.0	1.0	1.0
4-Hydroxybutanoic	0.1	0.2	2.0	0.1	0.2	2.0	0.2	0.2	1.0	0.2	0.2	1.0	0.2	0.2	1.0
2-Deoxy-tetronic	0.3	0.5	1.7	0.1	0.2	2.0	0.1	0.1	1.0	0.1	+	n.c.	0.1	+	n.c.
3-Deoxy-tetronic	0.1	0.2	2.0	0.1	0.2	2.0	0.2	0.2	1.0	0.2	0.2	1.0	0.2	0.2	1.0
3-Deoxy-pentonic***	1.9	1.6	0.8	1.9	1.6	0.8	2.1	1.8	0.9	2.3	1.8	0.8	2.3	1.8	0.8
2,5-Dihydroxypentanoic	1.1	1.2	1.1	1.2	1.1	0.9	1.5	1.3	0.9	1.6	1.4	0.9	1.6	1.5	0.9
4,5-Dihydroxypentanoic	+	0.1	n.c.	0.1	0.1	1.0	+	0.2	n.c.	+	0.2	n.c.	+	0.2	n.c.
Xyloisosaccharinic	0.5	1.1	2.2	0.5	1.1	2.2	0.6	1.2	2.0	0.6	1.3	2.2	0.6	1.3	2.2
3,4-Dideoxy-hexaric***	0.2	0.3	1.5	0.2	0.3	1.5	0.2	0.3	1.5	0.3	0.3	1.0	0.3	0.3	1.0
$\alpha$ -Glucoisosaccharinic	1.5	1.2	0.8	1.4	1.2	0.9	1.6	1.3	0.8	1.5	1.4	0.9	1.6	1.4	0.9
$\beta$ -Glucoisosaccharinic	4.5	3.9	0.9	4.4	3.9	0.9	5.1	4.4	0.9	5.2	4.5	0.9	5.0	4.8	1.0
Dicarboxylic acids	1.8	1.1	0.6	1.8	1.1	0.6	2.1	1.2	0.6	2.2	1.3	0.6	2.2	1.3	0.6
Oxalic	0.2	0.2	1.0	0.2	0.2	1.0	0.2	0.2	1.0	0.3	0.2	0.7	0.3	0.2	0.7
Succinic	0.2	0.1	0.5	0.2	0.1	0.5	0.3	0.1	0.3	0.3	0.1	0.3	0.3	0.1	0.3
Methylsuccinic	0.2	0.2	1.0	0.2	0.2	1.0	0.2	0.2	1.0	0.2	0.2	1.0	0.2	0.2	1.0
Malic	0.3	0.3	1.0	0.3	0.2	0.7	0.3	0.2	0.7	0.3	0.2	0.7	0.3	0.2	0.7
2-Hydroxyglutaric	0.3	0.2	0.7	0.3	0.2	0.7	0.4	0.2	0.5	0.4	0.3	0.8	0.5	0.3	0.6
$\alpha$ -Glucoisosaccharinaric	0.4	0.1	0.3	0.4	0.1	0.3	0.5	0.2	0.4	0.5	0.2	0.4	0.5	0.2	0.4
$\beta$ -Glucoisosaccharinaric	0.2	+	n.c.	0.2	+	n.c.	0.2	+	n.c.	0.2	+	n.c.	0.2	+	n.c.
Total	17.3	17.4	1.0	17.3	17.1	1.0	20.1	19.1	1.0	21.0	19.4	0.9	21.3	20.3	1.0

\*Ratio: hydroxy acids<sub>HWE</sub>/hydroxy acids<sub>Ref</sub>  
\*\*+: concentrations below 0.1 g/L and n.c.: not calculated. Black liquors obtained from the cooks with untreated (Ref) and hot-water-extracted (HWE) spruce sawdust.  
\*\*\*Includes *erythro* and *threo* isomers



Softwood galactoglucomannans are partly acetylated at the C<sub>2</sub>-OH and C<sub>3</sub>-OH positions (the acetyl group content equaling approximately 6%, or on the average, one acetyl group per 3-4 hexose units) (Alén 2000a). However, there was only a minimal change in the formic acid content between the black liquors from different feedstocks. Thus, the HWE spruce black liquors differed from the birch HWE black liquors (Lehto and Alén 2015), where the content of formic acid was considerably higher (15 to 30%) in the HWE black liquors.

The total content of hydroxy acids (*i.e.*, hydroxy monocarboxylic and dicarboxylic acids), as well as the content of individual acids in different spruce black liquors, are presented in Table 4. Again, the cooking behavior and the formation of various hydroxy acids from spruce sawdust during OA cooking were profoundly different from those reported earlier for the corresponding birch cooks (Lehto and Alén 2015).

First, such an increase as in the corresponding birch cooks (Lehto and Alén 2015) was not observed in the total content of hydroxy monocarboxylic acids caused by the pretreatment in the experiments conducted with spruce sawdust. In the birch cooks, the total content of hydroxy monocarboxylic acids was clearly (30 to 40%) higher in the HWE black liquors, but the total content of hydroxy monocarboxylic acids in the spruce black liquors was similar or slightly lower than in the reference cooks. Secondly, a similar increase in the total contents of low-molar-mass (glycolic and lactic acids) and glucoisosaccharinic acids ( $\alpha$ - and  $\beta$ -glucoisosaccharinic acids) that were evident in birch cooks were not observed in this case. In contrast, the hot-water extraction decreased the formation of these acids during OA cooking. Considerable increases in acid content from hot-water extraction occurred only for a few of the acids, such as xyloisosaccharinic acid.

The total content of hydroxy monocarboxylic acid remained relatively constant despite the pretreatment. However, the effect of hot-water extraction on the formation of hydroxy dicarboxylic acids was noteworthy in both wood species because a clear decrease in the total content of hydroxy dicarboxylic acids was observed when the HWE black liquors were compared to the reference black liquors.

## CONCLUSIONS

1. Negligible positive effects of hot-water pretreatment conducted prior to the OA pulping of spruce sawdust were observed. When calculating the yields based on the material loaded into the reactors after the pretreatment stage, distinctly higher yields (61 to 74%) were obtained for the pretreated sawdust than those (57 to 68%) for the initial sawdust. However, when the yield was calculated based on the total material removed during the pretreatments, lower total cooking yields (46 to 56%) were determined for the pretreated material.
2. The amount of pulp rejects was high (78 to 86% for reference and 73 to 83% for HWE spruce pulp), and only a minimal decrease in the amount of the rejected material was achieved by hot-water pretreatment. Compared with the previous experiments with HWE birch sawdust, a similar beneficial effect on the defibration caused by the hot-water extraction was not achieved with spruce.
3. Of the organic material dissolved in the black liquors, dissolved lignin accounted for the major portion (45 to 55%). A somewhat higher content of dissolved lignin was

determined from the HWE black liquors (25.5 to 45.9 g/L) than in the corresponding black liquors (27.2 to 39.6 g/L).

4. The content of volatile acids (formic and acetic acids) was markedly lower in the HWE black liquors than in the corresponding reference black liquors. The decreasing content of these acids in the HWE black liquors was explained by the removal of acetyl groups (present in galactoglucomannan) during the hot-water pretreatment. In contrast, the content of formic acid in the black liquors was not significantly affected by the pretreatment stage.
5. Compared with previous experiments performed with the HWE birch sawdust, a similar increase in the total content of hydroxy monocarboxylic acids from the pretreatment stage was not observed in the present study.

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