Organic material dissolved during oxygen-alkali pulping of hot water-extracted birch sawdust

JONI LEHTO AND RAIMO ALÉN

ABSTRACT: Untreated and hot water-treated birch (*Betula pendula*) sawdust were cooked by the oxygen-alkali method under the same cooking conditions (temperature = 170°C, liquor-to-wood ratio = 5 L/kg, and 19% sodium hydroxide charge on the ovendry sawdust). The pretreatment of feedstock clearly facilitated delignification. After a cooking time of 90 min, the kappa numbers were 47.6 for the untreated birch and 10.3 for the hot water-treated birch. Additionally, the amounts of hydroxy acids in black liquors based on the pretreated sawdust were higher (19.5-22.5 g/L) than those in the untreated sawdust black liquors (14.8-15.5 g/L). In contrast, in the former case, the amounts of acetic acid were lower in the pretreated sawdust (13.3-14.8 g/L vs. 16.9-19.1 g/L) because the partial hydrolysis of the acetyl groups in xylan already took place during the hot water extraction of feedstock. The sulfur-free fractions in the pretreatment hydrolysates (mainly carbohydrates and acetic acid) and in black liquors (mainly lignin and aliphatic carboxylic acids) were considered as attractive novel byproducts of chemical pulping

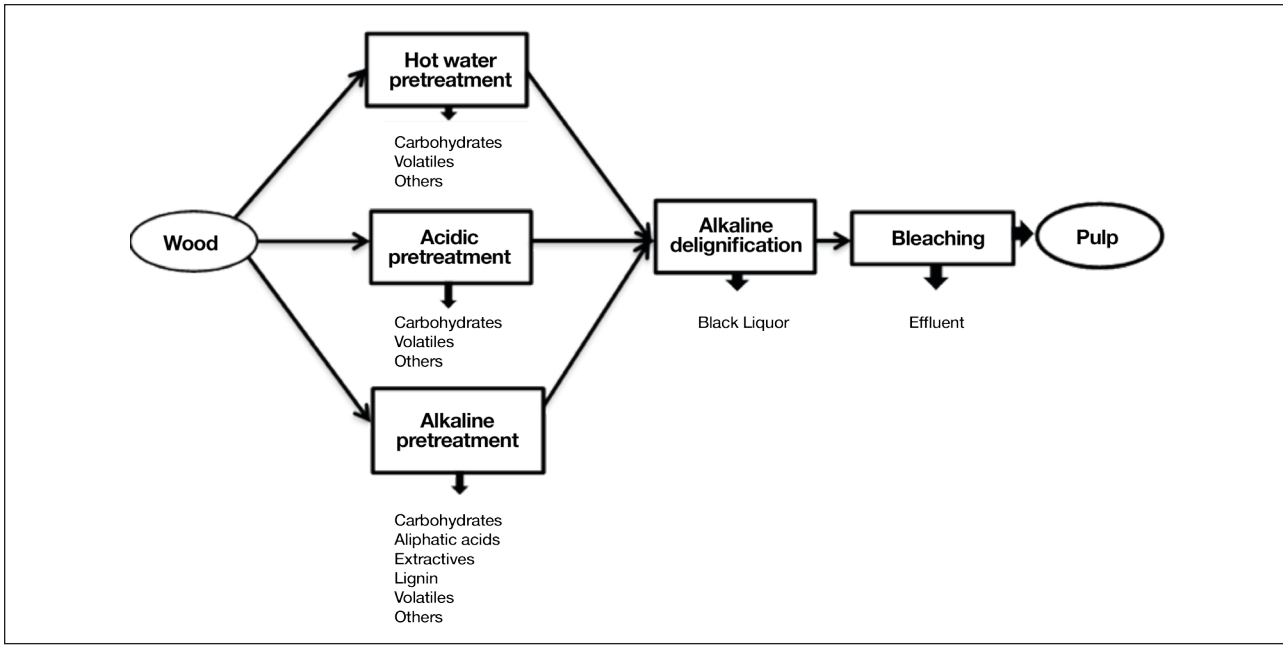
Application: Enhanced use of feedstocks, with the simultaneous increases in profitability and decreases in greenhouse gas emissions, can result from a better understanding of the behavior of wood constituents, especially hemicelluloses in potential integrated forest biorefinery concepts, and particularly autohydrolysis before sulfur-free pulping.

Extraction of wood chips with hot water (autohydrolysis) before alkaline pulping, mainly for producing carbohydrate-rich hydrolysates and dissolving or paper grade pulps, is one of the most investigated integrated forest biorefinery (IFBR) concepts [1-4]. Removed carbohydrates can be further converted into a wide spectrum of value-added chemicals and fuels, such as organic acids and alcohols, or they can be used to make biodegradable films and hydrogels [5-19]. The main reasons for combining such straightforward pretreatment processes conducted under varying conditions with the existing pulp mill operations are for more effective use of feedstock constituents with a simultaneous increase in the total profitability of forest industry operations [20-23].

Pretreatments carried out with hot water are of special interest for several reasons [24-27]. When compared with similar acidic processes with aqueous dilute mineral acids, for example, autohydrolysis is an environmentally friendly, noncorrosive, and inexpensive process. During pretreatment, hydronium ions formed from water autoionization cause hydrolysis of acetyl groups in wood hemicelluloses, resulting in simultaneous liberation of acetic acid [28-33]. Hydrolysate pH decreases through the formation of acetic and other organic acids (such as formic and uronic acids), which gradually leads to partial solubilization of hemicelluloses and their hydrolyzed fragments, as well as lignin and extractives. However, it is also obvious that the pretreatment stage can be put in practice at varying pH values and conducted in various ways. **Figure 1** presents possible IFBR concepts, including the pretreatment, delignification, and bleaching stages.

Oxygen-alkali delignification has traditionally been used to remove residual lignin from kraft brownstock before bleaching [34-36]. Oxygen under alkaline conditions is an efficient oxidizing agent for organic substances because of the formation of various reactive oxygen intermediates, such as hydroperoxyl and hydroxyl radicals, hydrogen peroxide, and hydroperoxide anions [37-40]. Complicated oxidation reactions primarily include several radical chain reactions between the oxygen-derived compounds and organic material compounds originating from lignin, carbohydrates, and extractives.

Oxygen-alkali delignification of the hot water-treated feedstock would be one attractive possibility when the aim is pulp together with the formation of sulfur-free degradation byproducts present in black liquor. In addition to pulp production, this approach could include, for example, the recovery and purification of sulfur-free product fractions derived from lignin and hemicelluloses (i.e., phenolics and aliphatic carboxylic acids). However, it is a nonselective process, and a significant degradation of feedstock polysaccharides takes place during lignin removal [35,40]. The direct peeling reactions of polysaccharides and the random cleavage of polysac-



1. Schematic representation of alternative integrated forest biorefinery concepts, including pretreatment, delignification, and bleaching stages.

charide chains and the subsequent peeling reactions are the main reactions responsible for carbohydrate-based mass losses. These also lead to a decrease in pulp viscosity and pulp strength properties. Alkaline degradation of polysaccharides eventually results in the formation of a wide range of water-soluble products, such as "volatile" acids (i.e., acetic and formic acids), various "nonvolatile" hydroxy monocarboxylic and dicarboxylic acids, hemicellulose residues, and methanol.

The main aim of this study was to obtain a better understanding of the effect of hot water extraction (HWE) on the subsequent oxygen-alkali pulping of hardwood-based feedstock. This approach entailed various cooking experiments conducted with reference (i.e., without autohydrolysis before pulping) and hot water-treated birch sawdust. In these experiments, sawdust was selected as the feedstock material to especially enhance the pretreatment stage through an effective mass transfer. The black liquors were principally analyzed in terms of various aliphatic carboxylic acids and lignin.

EXPERIMENTAL

Analyses of feedstock materials

Untreated (reference) and hot water-extracted sawdust samples of silver birch (*Betula pendula*) were provided by the Finnish Forest Research Institute (Metla). During autohydrolysis, materials were extracted for ~38 min at 170°C, corresponding to a P-factor [3,41] value of ~380. After each pretreatment, the HWE sawdust was unloaded from the reactors and air dried. The yield after hot water extraction was 71.9% of the ovendry (o.d.) raw material. For the chemical analyses (i.e., content of carbohydrates, lignin, and extractives), the reference and extracted sawdust samples were stored as such in a freezer, and their moisture contents were determined. In all wet chemistry analyses, the results were an average of two parallel determinations and calculated as percentage of dry sample.

The extractives content of sawdust was determined by extracting the sample with acetone for 4 h in a Soxhlet apparatus. The extract obtained was dried before weighing by vacuum evaporation with a VV2000 rotary evaporator (Heidolph; Schwabach, Germany) and was finally accomplished by means of a gentle nitrogen gas stream.

The lignin content of the extractives-free sawdust sample (about 200 mg) was determined as the sum of "acid-insoluble Klason lignin" and "acid-soluble lignin" (TAPPI Standard Test Methods T 222 om-98 "Acid-insoluble lignin in wood pulp" and T 249 cm-00 "Carbohydrate composition of extractive-free wood and wood pulp by gas-liquid chromatography"). In this determination, the method used was that sawdust was first treated with sulfuric acid, and 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 Coulter; Brea, CA, USA) at 205 nm after dilution of one portion of the hydrolysate with the corresponding aqueous solution of H_2SO_4 (0.5%) until the absorbance (A) was in the range 0.3 to 0.8. The concentration of dissolved lignin (C, g/L) was calculated according to Eq. (1):

$$c = \frac{A}{a*b} \quad (1)$$

where a is absorptivity (110 L/(gcm) [42]) and b is light path (cm).

The content of different monosaccharides (i.e., arabinose, galactose, glucose, mannose, and xylose) in the Klason

hydrolysates was gathered by using a HP 5890 Series II Plus gas chromatography system (Hewlett-Packard; Wilmington, DE, USA) equipped with an Agilent DB-1701 column (60 m × 0.32 mm inner diameter, film thickness 0.25 μm) (Agilent Technologies; Santa Clara, CA, USA) and a gas chromatography-flame ionization detector (GC-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 liquor sample of 10 mL was neutralized with Amberlite IRA68 anion exchange resin (Alfa Aesar; Ward Hill, MA, USA) until the pH value of the hydrolysate was about 4. The resin was filtered off; 1 mL of an aqueous (i.e., ultra-high quality [UHQ] water) mixture of an internal standard (xylitol from Fluka, 0.25 mg/mL) (Sigma-Aldrich; St. Louis, MO, USA) was added to the filtrate, and the sample was evaporated to complete dryness with a vacuum evaporator. Finally, the residue was per(trimethylsilyl)ated by adding 1.25 mL pyridine and 0.75 mL *N,O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA) containing 1% trimethylchlorosilane (TMCS), and the mixture was shaken for approximately 60 min at room temperature. Samples were filtrated to sample vials and analyzed by GC. The peak identification and the mass-based response factors between the internal standard and each monosaccharide were based on separate runs with model monosaccharides, all from Fluka.

Cooking experiments

Laboratory-scale oxygen-alkali cooking experiments of the sawdust samples were conducted in a 1.25 L rotating stainless steel autoclave heated in an oil bath. During the pulping experiments, the liquor-to-wood ratio was 5 L/kg and alkali (sodium hydroxide) charge 19% on the o.d. sawdust. Oxygen was bubbled through the cooking liquor for 5 min before charging sawdust into the reactors, which were then closed, and finally oxygen was introduced through the reactor lid to ensure an oxygen atmosphere. The maximum cooking temperature was 170°C. Cooking times were 30, 60, 90, 120, and 150 min. At the end of each cooking experiment, the autoclave was removed from the oil bath and cooled rapidly in cold tap water. The black liquor was then separated from the pulp by pressing and stored in storage bottles.

Analysis of pulps

The pulp obtained was thoroughly washed with water, and the amount of removed organic material ("yield") was calculated on the basis of o.d. initial and pretreated feedstock. Pulp samples were screened with a 0.1-mm laboratory screening device, and the amount of reject was determined. Kappa numbers were determined according to the respective standard method (SCAN-CI:59 "Kappa number of pulp"). Structural images of the screened pulp samples were determined with a Zeiss EVO·50 scanning electron microscope (SEM) (Carl Zeiss AG; Oberkochen, Germany).

Analysis of black liquors

The amount of residual lignin in the birch pulps was calculated based on kappa number [43,44] using Eq. (2):

$$\text{Lignin (\%)} = \text{kappa number} \bullet 0.15 \quad (2)$$

The amount of lignin dissolved during the cooks was calculated based on the difference of lignin contents of the original feedstock and the cooked pulp.

Acetic and formic acids were determined by the previously described method [45] using a Dionex chromatography system (Thermo Fisher Scientific; Sunnyvale, CA, USA) equipped with an AS50 autosampler, a LC25 chromatography oven, an EG40 eluent (potassium hydroxide/UHQ water) generator, and an IC 25 ion chromatograph. The system was equipped with an IonPac ATC-1 anion trap column, and the separation column was an IonPac AS 11-HC analytical column combined with an AG11-HC guard column (Dionex). Samples were injected via a 25 μL loop and were eluted (potassium hydroxide/UHQ water) at a flow rate of 1.0 mL/min. Data were stored and processed

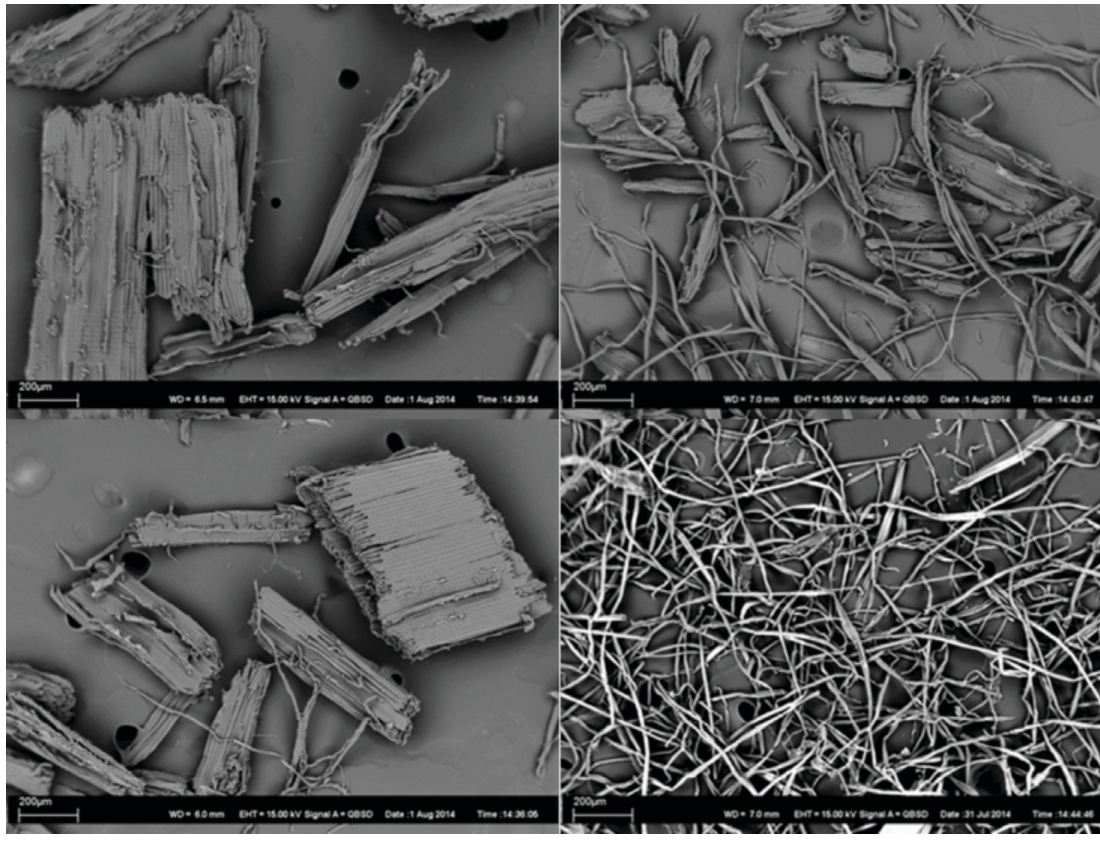
Component	Reference	Hot Water-Extracted
Monosaccharides*	67.5	72.7
Arabinose	0.4	0.1
Galactose	1.0	0.6
Glucose	43.4	60.8
Mannose	1.4	1.0
Xylose	21.3	10.2
Lignin	22.1	20.7
Acid soluble	4.5	2.5
Acid precipitated	17.6	18.2
Extractives	2.9	2.8
Others	7.5	3.8
* Monosaccharide moieties are presented as their anhydro forms.		

I. Chemical composition of feedstock birch materials (% of the dry matter).

Cooking	Pulp Yield*			Reject, %		Kappa Number	
Time, min	Ref	HW	HW**	Ref	HW	Ref	HW
30	59.5	59.7	42.9	70.2	29.9	68.9	24.4
60	56.8	54.7	39.3	68.9	11.5	52.7	13.9
90	55.4	52.4	37.9	64.6	3.8	47.6	10.3
120	54.1	52.3	37.6	57.9	1.7	38.0	8.3
150	51.2	50.0	36.0	47.2	ND***	31.3	7.7

* % of the dry material charged into the reactor
** Total cooking yield (% of the original o.d. feedstock material before pretreatment)
*** ND = not detected

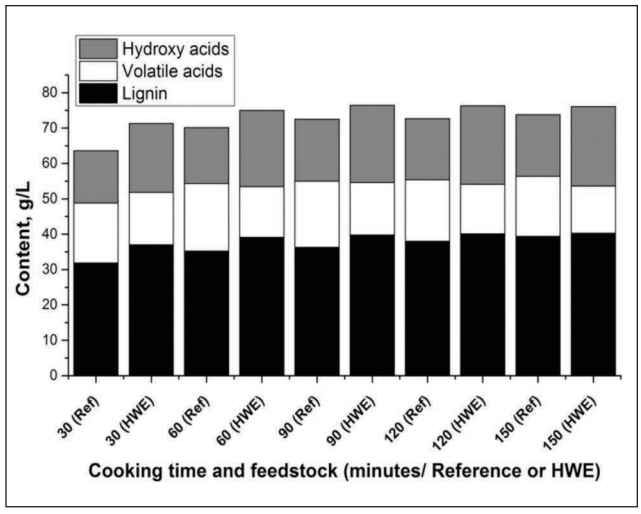
II. Cooking data (Ref = cooks without pretreatment; HW = cooks after hot water treatment).



2. Scanning electron microscope images of pulp samples cooked for 30 min (top) and for 150 min (bottom). Reference samples (i.e., from cooks without pretreatment) are presented on the left, and samples from cooks with pretreated sawdust are on the right.

using a Dionex Chromeleon (6.50) data system. The identification of the chromatographic peaks was based on the model substances, sodium acetate and sodium formiate.

Hydroxy monocarboxylic and dicarboxylic acids were determined using an Agilent 6850 Series gas chromatograph equipped with an HP-5 column (30 m × 0.32 mm inner diameter with 0.25 µm film thickness) and FID operating at 300°C with a hydrogen and air flow of 40.0 mL/min and 450.0 mL/min, respectively [46,47]. The column temperature program was 5 min at 60°C, 2°C/min to 200°C, 70°C/min to 290°C, and 15 min at 290°C. For GC-FID, a liquor sample of 1 mL and an internal standard (xylitol) of 1 mL UHQ water solution (concentration 0.1 mg/L) were mixed and passed through a column filled with weakly acidic cation exchange resin (about 10 mL, Amberlite IRC-50, 16-50 mesh, ammonium-form, from Fluka). The column was washed with UHQ water



3. Content of aliphatic carboxylic acids and lignin in black liquors from different cooks (g/L). Ref = reference cooks without pretreatment and HWE = cooks after hot water extraction.

to obtain a sample volume of 30-40 mL. This aqueous sample was then evaporated to dryness under reduced pressure at about 35°C. Finally, the residue was per(trimethylsilyl)ated by adding 1 mL pyridine and 0.5 mL BSTFA containing 1% TMCS, and the mixture was shaken for approximately 60 min at room temperature. The identification of the individual acid derivatives was made 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 with an 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 studied were based on the data given elsewhere [47].

RESULTS AND DISCUSSION

Feedstocks and cooking experiments

HWE had a distinct effect on the chemical composition of feedstock materials used for cooking (**Table I**). The most important reactions and phenomena responsible for the loss in feedstock mass during HWE included the hydrolysis of acetyl groups in xylan and the dissolution of degraded and nondegraded hemicellulose fragments, as well as a removal (~33% decrease) of lignin and extractives. For this reason, a particularly clear decrease (~38%) in the relative content of xylose (i.e., the main monosaccharide moiety in xylan) could be detected. In contrast, the relative content of glucose (i.e., the monosaccharide moiety of cellulose and glucomannan) clearly increased because cellulose was not significantly affected by HWE.

Data on the oxygen-alkali cooking experiments also typically revealed the effect of HWE on cooking performance (**Table II**). The results indicated that compared to the reference cooks without pretreatment, the delignification with the pretreated sawdust was more effective, although the cook yields were at a somewhat lower level: 51.2% (150 min) to 59.5% (30 min) vs. 50.0% (150 min) to 59.7% (30 min), respectively.

The SEM-images of the screened pulp samples (**Fig. 2**) also revealed the effect of HWE on pulping. The pulp samples from the untreated reference sawdust were not properly fibrillated, whereas the pretreated sawdust was readily fibrillated, even at the shortest cooking time. Pretreatment generally rendered feedstock more accessible to cooking chemicals. Another probable reason for the enhanced delignification of the pretreated material was the cleavage of major lignin-hemicellulose bonds during HWE. Although not studied in this connection, the detailed optimization of the cook with the pretreated sawdust seemed to lead, compared to the reference cook, to significant economical savings when aiming at the same target kappa number.

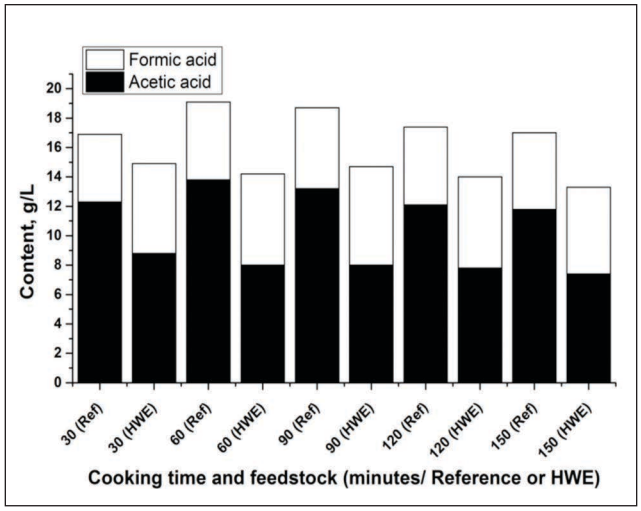
Black liquor composition

Figure 3 shows the content of aliphatic carboxylic acids and lignin in the black liquors from different feedstocks under various delignification conditions. **Table III** shows the mass ratios between some selected individual components and component groups in the black liquors. In general, higher amounts of dissolved lignin could be observed in the pretreated sawdust black liquors (37.0-40.3 g/L) than in the corresponding reference black liquors (31.9-39.4 g/L). For this reason, these results confirmed a more efficient removal of lignin

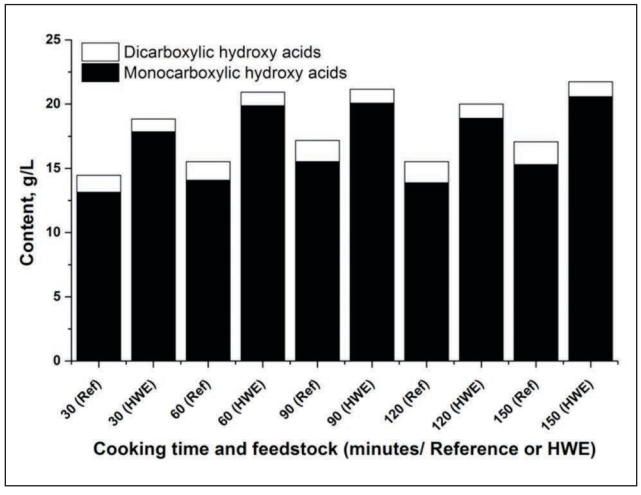
Cooking Time, min	Lignin	Acetic Acid	Formic Acid	Total Volatile Acids	Monocarboxylic Acids	Dicarboxylic Acids
30	1.16	0.72	1.33	0.88	1.36	0.75
60	1.11	0.58	1.17	0.74	1.41	0.73
90	1.10	0.61	1.22	0.79	1.29	0.65
120	1.06	0.64	1.17	0.80	1.36	0.67
150	1.02	0.63	1.13	0.78	1.35	0.64

* Mass ratio = content of compound or compound group in black liquor from cook with pretreated sawdust/content of compound or compound group in black liquor from cook with untreated sawdust.

III. Examples of mass ratios* between some compounds and compound groups in various black liquors.



4. Content of volatile acids in black liquors from different cooks (g/L). Ref = reference cooks without pretreatment and HWE = cooks after hot water extraction.

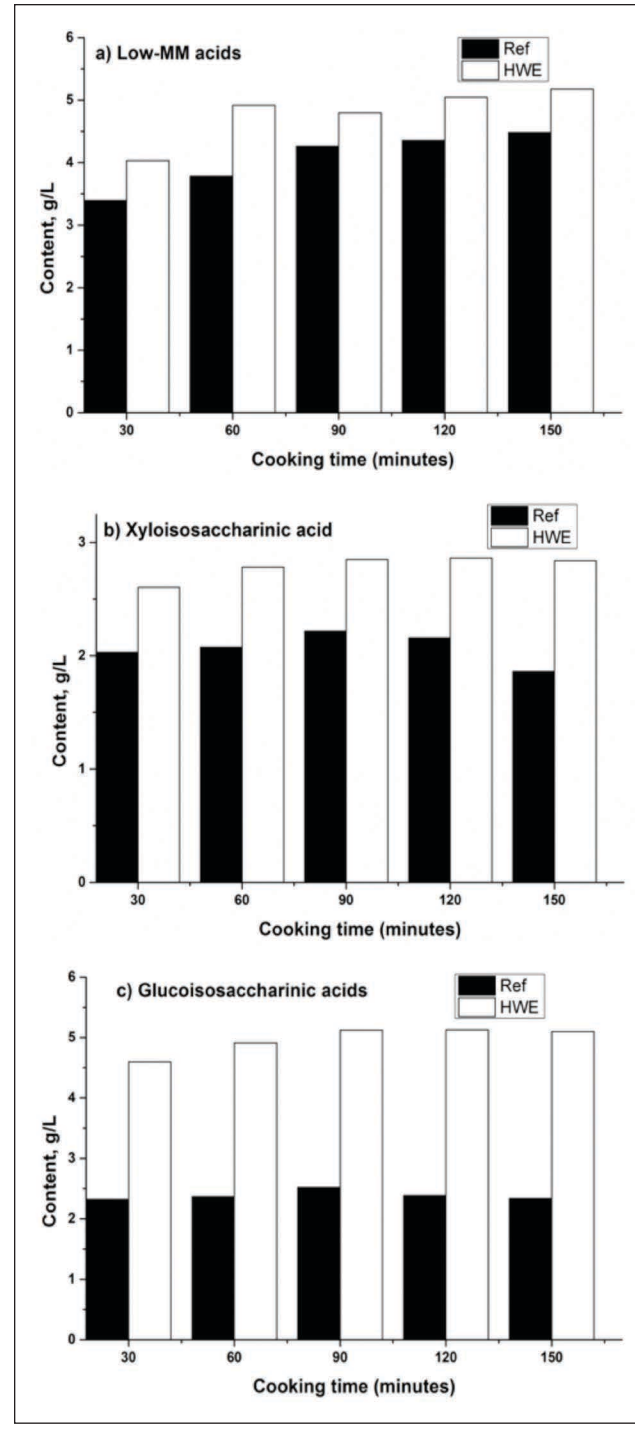


5. Content of monocarboxylic and dicarboxylic acids in black liquors from different cooks (g/L). Ref = reference cooks without pretreatment and HWE = cooks after hot water extraction.

from the pretreated sawdust than from the initial feedstock.

Conversely, with respect to volatile acids (acetic and formic acids), clearly lower amounts of these acids could be determined in the black liquors of the pretreated sawdust (13.3-14.8 g/L) than in the corresponding reference black liquors (16.9-19.1 g/L) (**Fig. 4**). This finding could be explained by the deacetylation of xylan already during the HWE. Another explanation is that formic acid was formed rather evenly, like hydroxy acids, during the alkaline cook [35] (Table III).

In addition to the formation of volatile acids, the HWE of sawdust also had a profound effect on the formation of various hydroxy acids (**Fig. 5**). In this case, the total amounts of hydroxy acids were higher in the black liquors of the pretreated sawdust (19.5-22.5 g/L) than those in corresponding reference black liquors (14.8-17.5 g/L) (Table III). This trend could be ex-



6. Content of (a) low-molecular-mass (low-MM) acids (glycolic and lactic acids), (b) xyloisosaccharinic acids, and (c) glucoisosaccharinic acids in black liquors from different cooks (g/L). Ref = reference cooks without pretreatment and HWE = cooks after hot water extraction.

plained by the lower formation acetic acid in the former cases, thus releasing more alkali for various peeling reactions and leading to the enhanced formation of hydroxy acids and formic acid in the latter case. The increase in the amounts of total hydroxy acids was caused by the increasing content of monocar-

boxylic hydroxy acids. Their contents were 30%-40% higher in the black liquors of the pretreated sawdust compared to those found in the corresponding reference black liquors. In contrast, the contents of dicarboxylic hydroxy acids were 25%-35% lower in the former case than in the latter case.

Finally, the formation of the main individual hydroxy acids was studied during the oxygen-alkali delignification of the untreated and pretreated sawdust. In this case, the acids were divided into low-molecular-mass (low-MM) hydroxy acids (i.e., glycolic and lactic acids), xyloisosaccharinic acid, and glucoisosaccharinic acids (i.e., α- and β-glucoisosaccharinic acids). The formation of isosaccharinic acids was accelerated in the cooks with pretreated sawdust (**Fig. 6**).

CONCLUSIONS

Pretreatment of birch sawdust with hot water (the total amount of removed material about 30%) before the subsequent oxygen-alkali pulping seemed to clearly facilitate delignification, leading to well-fibrillated pulp (produced under "optimal conditions") with a low amount of pulp reject. The formation of acetic acid was significantly lower in the cooks with pretreated sawdust compared to the cooks with untreated sawdust, because the acetyl groups in xylan were already partly hydrolyzed in the hot water pretreatment of feedstock. More hydroxy acids (especially monocarboxylic hydroxy acids) were formed during the cooks with the pretreated sawdust compared to the cooks with the untreated sawdust. Under the same cooking conditions as in the former case, more alkali was available for various peeling reactions (i.e., through less of a need for neutralizing acetic acid). **TJ**

ACKNOWLEDGEMENTS

We gratefully acknowledge Olli Byman and Petri Kilpeläinen from the Finnish Forest Research Institute (Metla) at Tikkurila, Finland, for kindly providing the sawdust materials needed for this study. Hannu Salo is acknowledged for SEM-imaging of the pulp samples. We also gratefully acknowledge financial support within the framework of the Future Biorefinery Joint Research 2 (FuBio JR2) Research Program (Finnish Bioeconomy Cluster [FIBIC]). In addition, financial support from the Fortum Foundation is gratefully acknowledged.

LITERATURE CITED

1. Bajpai, P., *Biotechnology for Pulp and Paper Processing*, Springer, New York, NY, USA, 2012, pp. 375-402.
2. Bajpai, P., *Biorefinery in the Pulp and Paper Industry*, Academic Press, London, UK, 2013, pp.17-28.
3. Sixta, H., Potthast, A., and Krotschek, A.W., in *Handbook of Pulp* (H. Sixta, Ed.), Wiley-VCH Verlag GmbH, Weinheim, Germany, 2006, pp. 325–366.
4. Sixta, H. and Schild, G., *Lenzinger Ber.* 87: 26(2009).
5. Alén, R., in *Biorefining of Forest Resources* (R. Alén, Ed.), Paper Engineers´ Association, Helsinki, Finland, 2011, pp. 55-114.
6. Chirat, C., Lachenal, D., and Sanglard, M., *Process Biochem.* 47(3): 381(2012).
7. Mendes, C.V.T., Carvalho, M.G.V.S., Baptista, C.M.S.G., et al., *Food Bioprod. Process.* 87(3): 197(2009).
8. Lu, H., Hu, R., Ward, A., et al., *Biomass Bioenergy* 39(1): 5(2012).
9. Ragauskas, A.J., Nagy, M., and Kim, D.H., *Ind. Biotechnol.* 2(1): 55(2006).
10. Koutinas, A.A., Du, C., Wang, R.H., et al., in *Introduction to Chemicals from Biomass* (J. Clark and F. Deswarte, Eds.), John Wiley & Sons Ltd., Chichester, UK, 2008, pp. 78–100.
11. Sánchez, Ó.J. and Cardona, C.A., *Bioresour. Technol.* 99(13): 5270(2008).
12. Sun, Y. and Cheng, J., *Bioresour. Technol.* 83(1): 1(2002).
13. Edlund, U. and Albertsson, A.-C., *J. Bioact. Compat. Polym.* 23(2): 171(2008).
14. Egüés, I., Eceiza, A., and Labidi, J., *Ind. Crops Prod.* 47(1): 331(2013).
15. Stevanic, J.S., Joly, C., Mikkonen, K.S., et al., *J. Appl. Polym. Sci.* 122(2): 1030(2011).
16. Gabrielii, I., Gatenholm, P., Glasser, W.G., et al., *Carbohydr. Polym.* 43(4): 367(2000).
17. Peng, X.-W., Ren, J.-L., Zhong, L.-X., et al., *Biomacromol.* 12(9): 3321(2011).
18. Peng, X.-W., Ren, J.-L., Zhong, L.-X., et al., *J. Agric. Food Chem.* 59(15): 8208(2011).
19. Söderqvist-Lindblad, M., Albertsson, A.-C., Ranucci, E., et al., *Biomacromol.* 6(2): 684(2005).
20. Huang, H.-J., Ramaswamy, S., Al-Dajani, W.W., et al., *Bioresour. Technol.* 101(2): 624(2010).
21. Helmerius, J., von Walter, J.V., Rova, U., et al., *Bioresour. Technol.* 101(15): 5996(2010).
22. Kamm, B. and Kamm, M., *Appl. Microbiol. Biotechnol.* 64(2): 137(2004).
23. Liu, S., Lu, H., Hu, R., et al., *Biotechnol. Adv.* 30(4): 785(2012).
24. Amidon, T.E. and Liu, S., *Biotechnol. Adv.* 27(5): 542(2009).
25. Tunc, M.S. and van Heiningen, A.R.P., *Holzforschung* 62(5): 539(2008).
26. Tunc, M.S. and van Heiningen, A.R.P., *Ind. Eng. Chem. Res.* 47(18): 7031(2008).
27. Song, T., Pranovich, A., Sumerskiy, I., et al., *Holzforschung* 62(6): 659(2008).
28. Borrega, M., Nieminen, K., and Sixta, H., *Bioresour. Technol.* 102(22): 10724(2011).
29. Borrega, M., Nieminen, K., and Sixta, H., *BioResources* 6(2): 1890(2011).
30. Borrega, M., Niemelä, K., and Sixta, H., *Holzforschung* 67(8): 871(2013).
31. Garrote, G., Domínguez, H., and Parajó, J.C., *J. Chem. Technol. Biotechnol.* 74(11): 1101(1999).
32. Garrote, G., Domínguez, H., and Parajó, J.C., *Bioresour. Technol.* 79(2): 155(2001).
33. Garrote, G., Domínguez, H., and Parajó, J.C., *Holz Roh- Werkst.* 59(1-2): 53(2001).

34. McDonough, T.J., in *Pulp Bleaching - Principles and Practice* (C.W. Dence and D.W. Reeve, Eds.), TAPPI PRESS, Atlanta, GA, USA, 1996, pp. 213-239.
35. Alén, R., in *Forest Products Chemistry* (P. Stenius, Ed.), Fapet Oy, Helsinki, Finland, 2000, pp. 58-104.
36. Gellerstedt, G., in *Lignin and Lignans - Advances in Chemistry* (C. Heitner, D. Dimmel, and J. Schmidt, Eds.), CRC Press, Boca Raton, FL, USA, 2010, pp. 393-429.
37. Starnes Jr., W.H., in *Chemistry of Delignification with Oxygen, Ozone, and Peroxides* (J.S. Gratzl, J. Nakano, and R.P. Singh, Eds.), UNI Publishers, Tokyo, Japan, 1980, pp. 3-25.
38. Salmela, M., Alén, R., and Vu, M.T.H., *Ind. Crops Prod.* 28(1): 47(2008).
39. Laitinen, E., Tornberg, J., and Alén, R., *Anal. Lett.* 35(15): 2539(2002).
40. Alén, R. and Sjöström, E., *Holzforschung*, 45(1): 83(1991).
41. Tunc, M.S. and van Heiningen, A.R.P., *Nord. Pulp. Pap. Res. J.* 24(1): 46(2009).
42. Swan, B., *Svensk Papperstidn.* 68(22): 791(1965).
43. Tasman, J.E. and Berzins, V., *Pulp Pap. Can.* 60:231 (1959).
44. Biermann, C.J., *Handbook of Pulping and Papermaking*, Academic Press, San Diego, CA, USA, 1996, p. 127.
45. Käkölä, J.M., Alén, R.J., Isoaho, J.P., et al., *J. Chromatogr. A.* 1190(1-2): 150(2008).
46. Käkölä, J., Alén, R., Pakkanen, H., et al., *J. Chromatogr. A*. 1139(2): 263(2007).
47. Alén, R., Niemelä, K., and Sjöström, E., *J.Chromatogr.* 301: 273(1984).

ABOUT THE AUTHORS

Hot water pretreatment is one of the most studied biorefinery options, showing promising potential for the production of value-added chemicals and for integration with existing pulping processes. Understanding the effects of hot water extraction on the subsequent pulping operations is of practical importance to avoid disturbing the pulping process. Oxygen-alkali pulping was chosen as the pulping method because it enables production of sulfur-free lignin and other organics from the feedstock.

In general, a very limited amount of data is available concerning the hot water extractions combined with sulfur-free cooking operations for producing not only pulp, but also sulfur-free byproduct streams, such as lignin and aliphatic carboxylic acids. When aiming toward full-scale integrated forest biorefineries (IFBRs), all possible side processes have to be taken into consideration.

Because of the complex chemical composition of black liquor, its analysis is a very challenging task. However, by using sophisticated analysis techniques, a significant part of the black liquor components formed during oxygen-alkali cooking could be identified.

The effect of hot water pretreatment on the composition of black liquors and pulping efficiency was very clear. It is widely accepted that the formation of organic acids (volatile and nonvolatile) has a significant role in the performance of alkaline cooking. For example, a major part of the charged alkali is consumed in various neutralization reactions of these acids. Hot water treatment conducted before alkaline cooking also has a great effect on the chemical composition and cooking behavior of wood feedstocks, especially through partial removal of hemicelluloses, acetyl groups, and lignin. All these changes caused by the applied pretreatment clearly influence the subsequent pulping operations and the formation of various potential product fractions, such as sulfur-free lignin and hydroxy acids.

The data can be used when clarifying the recovery possibilities of novel byproducts. Chemical pulp mills are typical examples of chemical/thermochemical biorefineries that use different technological innovations to fractionate and convert woody biomass into a wide range of products. A modern IFBR approach could include the opportunity to produce the main product (pulp fiber), plus value-added green chemicals, such as fuel grade ethanol, cellulose, hemicelluloses together with their derivatives, and low-volume-high value lignin/extractives-based fine chemicals, thus resulting in an enhanced use of feedstocks with the simultaneous increase in profitability and decrease in greenhouse gas emissions.

Lehto

Alén

Fractionation and purification of various sulfur-free organic components from black liquors are of special interest for future studies because of the many potential applications in which these components can be used. In addition, the effect of hot water pretreatment on the burning behavior of black liquor in a recovery furnace is an interesting topic to clarify the overall material and energy balances of the modern pulp mill.

Lehto is a post-doctoral researcher and Alén is professor, Department of Chemistry, Laboratory of Applied Chemistry, University of Jyväskylä, Jyväskylä, Finland. Email Lehto at joni.t.lehto@jyu.fi.