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Combustion properties of spruce black liquor droplets: Sulfur-free pulping and influence of hot-water pretreatment

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SUMMARY: Hot-water pretreatment of lignocellulosics prior to sulfur-free alkaline pulping is an interesting approach for recovering value-added carbohydrate- and lignin-derived materials. This paper investigated the chemical composition variations and combustion properties of the black liquors (BLs) from three different cooking processes: two sulfur-free soda-anthraquinone (soda-AQ) and oxygen-alkali (O_2-NaOH) cooks and kraft cook, before and after hot-water pretreatment of the spruce sawdust. Relatively less aliphatic acids but more lignin were present in the BLs after hot-water pretreatment as cooking time prolonged. In general, the burning time decreased as follows: soda-AQ BL > O_2-NaOH BL $\cong$ kraft BL. With the same cooking time, the increase in the total burning time for soda-AQ BLs compared with kraft BLs was 11-17% (without pretreatment) and 25-39% (with pretreatment). Compared to kraft BLs with the same cooking time, the swelling for soda-AQ and O_2-NaOH BLs decreased by 8-25% and 4-23%, respectively.

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The pulping process is a typical forest biorefinery process that uses wood as the raw material to produce pulp, energy, and chemical products such as turpentine, tall oil, and lignin (Grace et al. 1989; Alén 2015). However, for a number of commonly recognized reasons, modern pulp mills can serve as a promising platform for even more efficient use of raw wood materials. One motivation for developing more effective concepts is that fiber, which is suitable for versatile utilization in paper or paperboard, is already a well-established main product. One of the most interesting novel techniques is based on hot-water extraction (HWE) of feedstock prior to alkaline pulping to recover carbohydrate-derived fragments that can be converted into value-added chemicals and other bio-products (Wayman, Chua 1979; Mosier et al. 2005; Kamm et al. 2006; van Heiningen 2006; Carvalheiro et al. 2008; Yoon et al. 2008; Alén 2011; Lehto 2015).

Combustion of black liquor (BL) from alkaline pulping plays a key role in supplying energy and recovering inorganic cooking chemicals for the fiber refinery system. BL is combusted as sprayed droplets, undergoing three sequential stages: drying, pyrolysis, and char burning, and exhibits volumetric swelling, which influence the performance of the recovery boiler in terms of deposition in the upper furnace and condition of the char bed (Frederick, Hupa 1997). In our previous study (Chen et al. 2016), the combustion properties of birch black liquors (BLs) based on sulfur-free soda-AQ and O_2-NaOH cooks with and without the feedstock HWE were investigated. It was found that sulfur-free BLs swell less than kraft BLs, and hot-water pretreatment of feedstock result in lower swelling for kraft and soda-AQ liquors but higher swelling for O_2-NaOH liquors. However, the information available in the literature on the combustion properties of sulfur-free softwood BLs is very limited.

This work was undertaken to compare the combustion properties of kraft BL with those of spruce BLs from sulfur-free soda-AQ and O_2-NaOH cooks. In all cases, the cooking experiments were performed with both the untreated and HWE feedstocks. To obtain variations in the pretreatment stage, the treatment phase was made both as a batch (followed by the soda-AQ cook) and a continuous (followed by the O_2-NaOH cook) process. Combustion tests were carried out with single BL droplets at 800°C in stagnant air.

Materials and Methods

Sawdust materials

Raw Norway spruce (*Picea abies*) sawdust (<5 mm) was provided by the Finnish Forest Research Institute (Metla). The HWE of sawdust was conducted in two different methods: a batch process and a continuous process. The yields after the treatment were 80.0% and 75.5%, respectively. Chemical composition of untreated and treated raw materials subjected to pulping are given in *Table 1*.

In the batch process, the pressurized HWE of non-dried sawdust was performed using a pilot-scale batch system (VTT Technical Research Center of Finland Ltd., Espoo, Finland). The extraction liquid (i.e., hot water) was circulated during the extraction which was performed in two stages (liquor-to-wood ratio in both stages was 5 l/kg): the first stage at 160°C for 40 min (P-factor ~181, Tunc and van Heiningen 2009) and the second stage at 170°C for 60 min (P-factor ~597 and the combined P-factor ~780). Between these two stages, the hydrolysate was drained from the reactor as completely as possible. After both extraction steps, the extracted material was washed with water (50°C, liquor-to-wood ratio was 5 l/kg) for 30 min and removed from the reactor.

In the continuous process, the HWE of non-dried sawdust was performed with a pilot-scale flow through extraction reactor (Viitos-Metalli Ltd., Heinola, Finland). During extraction, spruce sawdust was treated for ~32 min at 180°C, and the corresponding P-factor was ~680. After the treatment, the sawdust was immediately removed from the reactor without being washed.

The untreated and treated sawdust samples were stored in a freezer at -18°C. The moisture content of feedstock

was determined according to the TAPPI Test Method 264 cm-97 in an oven at 105°C. In all wet chemistry analyses for compositional determination (i.e., carbohydrates, lignin, and extractives), the results were an average of two parallel determinations and calculated as percentage of dry sample.

Pulping experiments

Soda-AQ, O_2-NaOH, and kraft BLs were prepared by pulping both the untreated and HWE sawdust in 1.25-liter rotating stainless steel autoclaves heated in an oil bath (CRS Autoclave System 420, from CRS Reactor Engineering AB, Stenkullen, Sweden). In the O_2-NaOH pulping, pure oxygen was bubbled through the cooking liquor for 5 min prior to charging sawdust into the reactors. Then, the reactors were closed and purged with oxygen through the lid for two minutes to ensure an oxygen atmosphere. The specific pulping conditions are given in *Table 2*. Pulp yields were calculated on the oven dry basis of the initial feedstock (*Table 3*).

Analyses of sawdust

The extractives content was determined according to the TAPPI Test Method T280 pm-99 by extracting the sample with acetone in a Soxhlet apparatus (extraction time 4 h, 6 to 10 percolations per hour). The obtained extract was concentrated using vacuum evaporation with a rotary evaporator (Heidolph VV2000, from Gemini BV Laboratory, Apeldoorn, the Netherlands), exposed to a nitrogen gas stream until it was dried, and finally weighed. The lignin content of the extractive-free sawdust sample was determined as the sum of "acid-insoluble Klason lignin" and "acid-soluble lignin" (TAPPI Test Methods T222 om-98 and T249 cm-00). In this determination, sawdust was first treated with 72% H_2SO_4 followed by an autoclave treatment after dilution, and the precipitated Klason lignin was filtered off (degraded carbohydrates remained in the hydrolysate), washed, dried, and weighed. The acid-soluble lignin content was determined using a Beckman DU 640 UV/Vis-spectrophotometer (Beckman Instruments Inc., Fullerton, CA, USA) at 205 nm (to avoid the interfering influence of furans at 280 nm) after diluting one portion of hydrolysate with a corresponding aqueous solution of H_2SO_4 (0.5%) until the absorbance (*A*) was in the 0.3 to 0.8 range.

Table 1 - Chemical composition of feedstock materials (% of the dry solids).

Component	Ref	HWE-B	HWE-C
Carbohydrates [a]	60.0	60.4	65.7
Arabinose	1.0	<0.1	0.1
Galactose	1.8	0.4	0.5
Glucose	41.1	51.6	57.2
Mannose	11.1	4.8	4.0
Xylose	5.0	3.7	3.9
Lignin	28.4	35.2	30.1
Klason	28.0	34.9	29.8
Acid-soluble	0.4	0.3	0.3
Acetone-soluble materials	1.4	2.6	1.0
Others	10.1	1.8	3.2

Ref: untreated feedstock.
HWE-B: Hot-water extracted feedstock using a batch process by VTT.
HWE-C: Hot-water extracted feedstock using a continuous process by Metla.
[a] Monosaccharide moieties are presented as their anhydro forms

Table 2 - Cooking data.

Parameter	Soda-AQ	O_2-NaOH	Kraft
Effective alkali, %	20	19	19
Sulfidity, %	–	–	35
Anthraquinone, %	0.1	–	–
Oxygen bubbled, min	–	5	–
Liquor-to-wood ratio, l/kg	5	5	5
Maximum temperature, °C	170	170	160
Cooking time, min	30, 60, 90, 120, and 150	30, 60, 90, 120, and 150	30, 60, 90, 120, and 150

Table 3 - Pulp yields [a] of different cooks. For abbreviations, see *Tables 1* and *2*.

Cooking time, min	Soda-AQ		O_2-NaOH (Lehto 2015)		Kraft	
	Ref	HWE-B	Ref	HWE-C	Ref	HWE-B
30	60.2	48.8	67.9	56.2	63.3	48.2
60	53.7	43.2	65.3	53.1	57.7	44.8
90	49.9	39.6	60.3	50.1	54.3	41.1
120	50.4	38.0	58.3	48.2	52.5	44.1
150	48.4	36.2	57.4	46.3	51.8	38.1

[a] Pulp yields (%) are based on the initial o.d. feedstock.

The concentration of dissolved lignin c (g/l) was calculated according to the Beer-Lambert equation (*Eq 1*).

$$c = A/ab, \qquad [1]$$

where a is absorptivity (120 l/(g•cm), Swan 1965), and b is the light path length (cm).

The carbohydrates presented as different mono-saccharide moieties (i.e., arabinose, galactose, glucose, mannose, and xylose) in the Klason hydrolysates were determined with a Hewlett Packard 5890 Series II Plus GC gas chromatography system equipped with an Agilent DB-1701 column (60 m × 0.32 mm inner diameter, film thickness 0.25 μm) and a 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 (for 27 min), 39°C/min to 280°C, and finally 15 min at 280°C. For GC/FID, a liquor sample of 10 mL was neutralized with anion exchange resin (Amberlite IRA-68, Alfa Aesar, Karlsruhe, Germany) until the hydrolysate pH value was approximately 4. The resin was filtered off, and 1 mL of an aqueous (i.e., ultra-high quality water (UHQ) obtained from a Milli-Q Plus water system; Millipore, Bedford, MA, USA) mixture of an internal standard (ISTD, xylitol, 0.25 mg/mL; Fluka Chemical Corporation, Seeltze, Germany) was added to the filtrate, and the sample was evaporated to complete dryness using a vacuum evaporator. Finally, the residue was per(trimethylsilyl)ated by adding 1.25 mL pyridine (Fluka Chemical Corporation, Seeltze, Germany) and 0.75 mL *N,O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA, Regis Technologies, Morton Grove, IL, USA) containing 1% trimethylchlorosilane (TMCS, Regis Technologies, Morton Grove, IL, USA), and the mixture was shaken for approximately 60 min at room temperature. The samples were filtrated to sample vials and analyzed using GC. Peak identification and mass-based response factors between the ISTD and each monosaccharide were based on separate runs with model monosaccharides (Fluka Chemical Corporation, Seeltze, Germany).

Analyses of BLs

Determination of dry BL solids was conducted based on the TAPPI Test Methods T650 om-09.

Formic and acetic acids (later referred to as "volatile acids"), which were in their sodium salt forms under alkaline conditions, were determined as their benzyl esters using gas chromatography equipped with a flame-ionization detector (GC/FID) (Alén et al. 1985). In this analysis, these acids in liquor samples were first converted to their tetra-*n*-butylammonium salts, and then benzyl esters of these salts were prepared and introduced to the GC/FID system.

Aliphatic hydroxy carboxylic acids were separated as their per(trimethylsilyl)ated derivatives using GC/FID, and the same derivatives were identified using gas chromatography equipped with a mass-selective detector GC/MSD (Alén et al. 1984). This method involved the conversion of these acids first into their ammonium salts that were then per(trimethylsilyl)ated with BSTFA containing 1% TMCS.

The content of dissolved lignin in BLs was determined using UV/Vis-spectrophotometry at 280 nm (Alén, Hartus 1988). In this determination, the samples were diluted with 0.1 M NaOH until the absorbance was in the 0.3 to 0.8 range. The content of dissolved lignin was calculated according to the Beer-Lambert equation (*Eq 1*); the absorptivity values used were 22.8, 17.1, and 20.3 l/(gcm) for soda-AQ, O_2-NaOH, and kraft lignins, respectively.

A size exclusion chromatographic system (a Waters HPLC system equipped with a column filled with Superdex 75 gel using 0.1 M aqueous NaOH as the eluent) was applied to determine the molar mass (MM) distribution of dissolved lignin in BL (Pakkanen, Alén 2012). For these analyses, the BLs were diluted with the NaOH eluent to achieve a dilution ratio of 1/20.

Combustion tests

Combustion tests were carried out using a laboratory furnace at the University of Jyväskylä. The furnace is equipped with a glass window from aside for observing the combustion process using a video camera, a hole from the top for insertion of BL droplet using a glass rod with a platinum hook, and a small opening for air inlet. BLs were concentrated to a dry solids content of 55-65% via evaporation under reduced pressure at 40°C. In each test, 15 to 20 individual BL droplets approximately 9 mg in wet mass were burnt at 800°C in stagnant air, as described in Louhelainen (2003). The progression of droplet combustion was recorded using a high resolution video camera. The pyrolysis and char burning time of the BL dry solids (s/mg) was obtained from the video with the assistance of the VirtualDub software. The maximum specific swelling of each droplet S_{max} (cm^3/g) was calculated by approximating swollen particles as ideal spheres (*Eq 2*).

$$S_{max} = \frac{4}{3} A \sqrt{\frac{A}{\pi}} \; /m, \qquad [2]$$

where A is the cross sectional area of a swollen particle measured using the ImageJ software at the point of maximum swelling as observed in a selected frame of video recording, and m is the dry mass of a droplet.

Results and discussion

Feedstock materials and delignification

The chemical composition of sawdust samples before and after hot-water treatment is presented in *Table 1*. The yields of the batch (sample HWE-B) and continuous (sample HWE-C) extraction were similar: 80.0% and 75.5% of the o.d. raw material, respectively. In both cases, approximately 70% of the hemicellulose-derived materials (i.e., the hemicellulose monosaccharide moieties arabinose, galactose, glucose (only partly in hemicelluloses), mannose, and xylose), besides acetic acid from the partial deacetylation of glucomannans (Alén 2011; Lehto 2015), were removed from the initial feedstock. Therefore, due to this primary effect, the relative proportions of glucose (mostly incorporated in cellulosic fiber) and lignin were slightly increased.

The principal purpose of this investigation was to study the effects of hot-water pretreatment on the combustion properties of BLs. The approach was to prepare and test BLs with varying compositions rather than to clarify in detail, for example, the influence of cooking parameters on delignification. The cooking data and pulp yields are shown in *Tables 2* and *3*. In general, it can be noted that the pretreatment stage significantly facilitated the cooking performance. This trend was clear because the pretreatment rendered the feedstock more accessible to cooking chemicals and also caused the cleavage of major lignin-hemicellulose bonds (Lehto 2015).

BL composition

The concentration of aliphatic carboxylic acids (volatile acids and hydroxy acids) and lignin in BLs obtained from different cooking methods of the untreated and HWE sawdust is presented in *Fig 1* shows the relative composition of these substances. The primary difference between various BLs was the content of aliphatic acids. The difference was attributed to deacetylation of glucomannans during the pretreatment stage resulting in a lower concentration of acetic acid in BLs from the HWE feedstocks than those from the untreated sawdust. In contrast, the changes in concentrations of another volatile acid, formic acid, were not significant because this acid was obtained from carbohydrates via peeling reactions (Alén 2000). Thus, its formation rate was similar to that of hydroxy acids.

The results indicated that in all cases the formation of hydroxy acids was slightly more intense from the HWE sawdust than from the untreated sawdust (*Table S2*). This phenomenon could be primarily explained by the partial removal of acetyl groups during the pretreatment stage; thus, less alkali was needed to neutralize acetic acid in the cooking stage, and more alkali (i.e., higher alkalinity)

was available for various alkaline degradation reactions of polysaccharides leading to a more pronounced degradation of hemicelluloses and cellulose (Alén 2000). HWE causes acid hydrolysis, giving rise to new reducing end groups that are prone to peeling reactions in the alkaline cooking. Another clear reason was a more effective diffusion of the cooking chemicals into the wood matrix due to partial removal of the acetyl groups (Sjöström et al. 1965). Furthermore, the pretreatment stage and prolonged cooking time seemed to promote the formation of hydroxy acids (10-35%) in the soda-AQ and kraft pulping. However, there were no significant differences in the formation of individual acids. One minor exception was, for example, the increased amount of xyloisosaccharinic acid in the BL from the HWE feedstocks.

In general, the concentration of lignin was higher in the BLs from the HWE feedstocks compared with those from the untreated feedstock (*Table S2*). As expected from the pulp yield data in *Table 3*, the lignin concentration in the O_2-NaOH BL was clearly at a lower level than that in the soda-AQ and kraft BLs. It was shown that the cooks performed with the HWE feedstocks resulted in higher MM fractions (*Fig 2*). Furthermore, the weight average MM of dissolved lignin in the BLs from the HWE feedstocks was the highest in the soda-AQ BLs (*Table 4*).

Fig 2 shows the examples of MM distributions of lignin in different BLs. Additionally, these data clearly suggested that the higher-MM fraction (> 5000 g/mol) of lignin was somewhat pronounced in BLs from the HWE feedstocks than that in BLs from the untreated BLs. In addition, especially for the O_2-NaOH and kraft BLs, the prolonged cooking times resulted in more high-MM dissolved lignin.
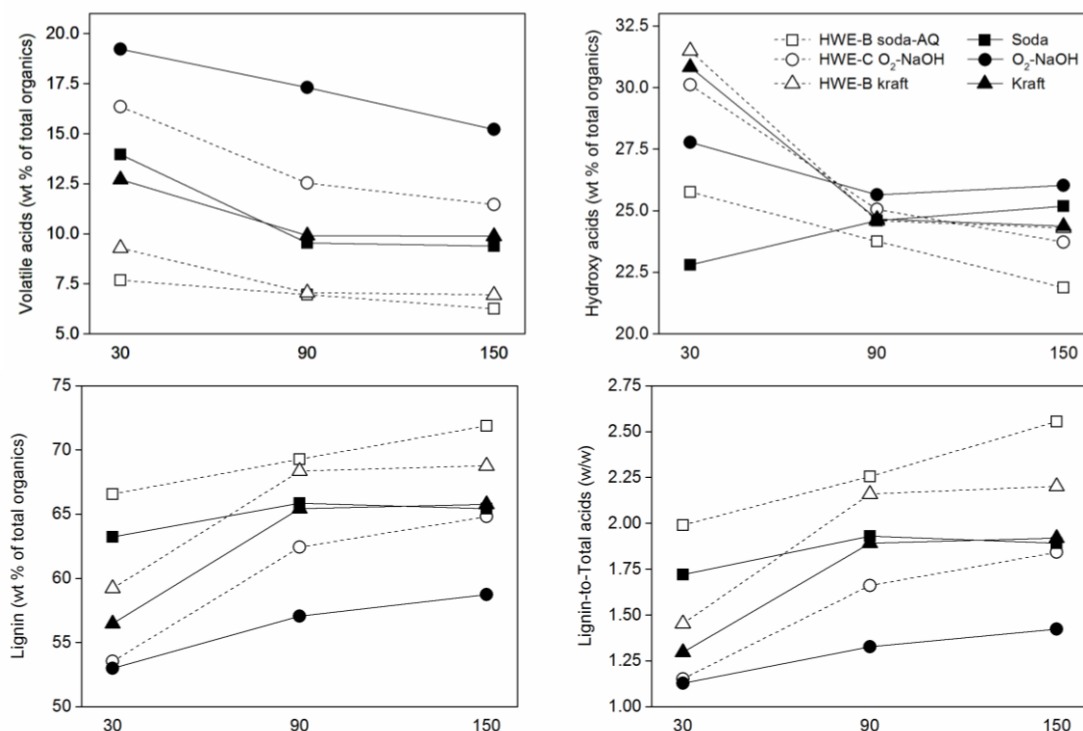

Fig 1- Comparison of the main organic composition of BLs. HWE-B and HWE-C refer to hot-water extractions of feedstock (see *Table 1*). 30, 90, and 150 are cooking times (min)

Table 4 - Weight average MM (g/mol) of lignin in BLs. For abbreviations, see *Tables 1* and *2*.

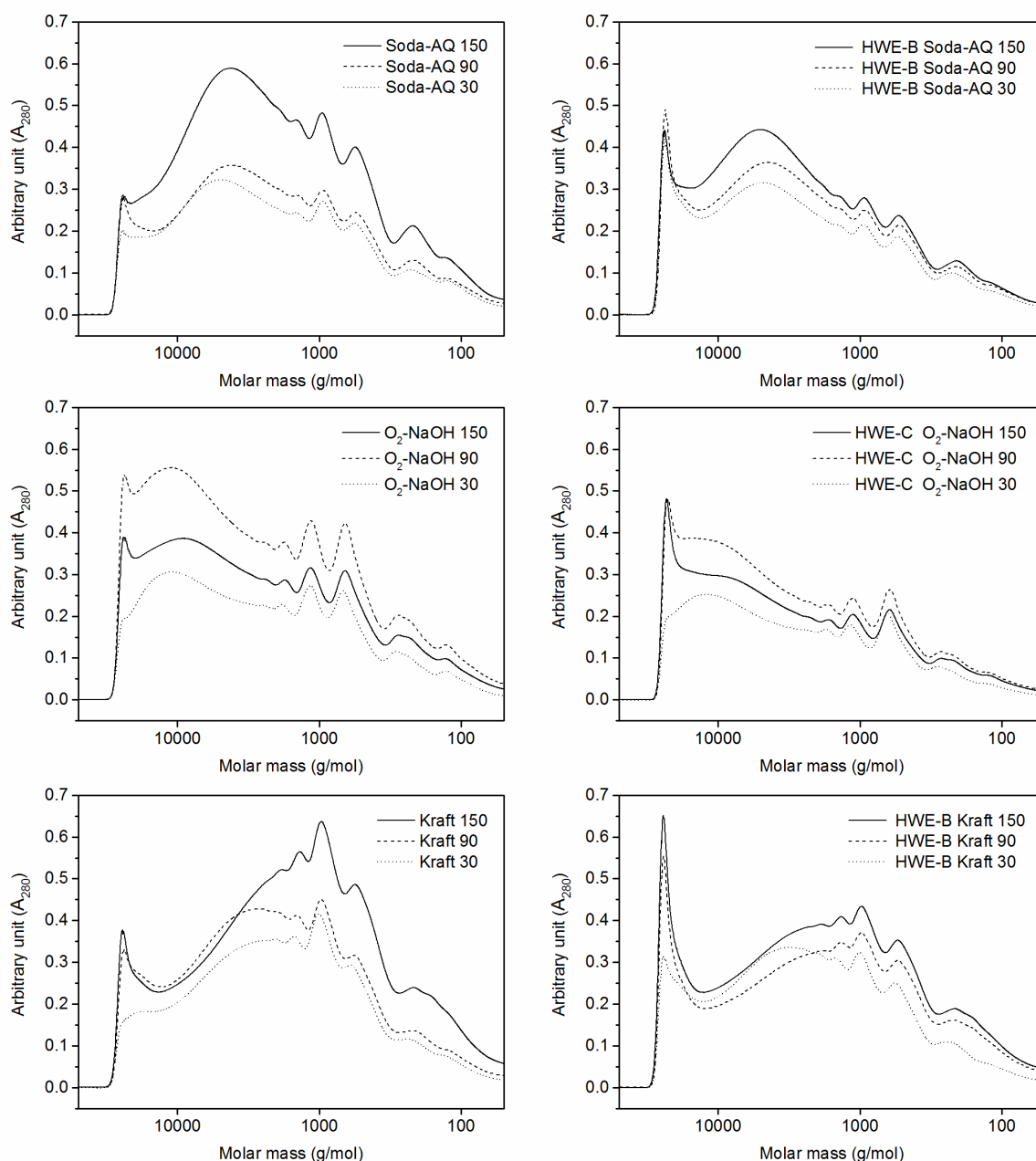| Cooking time (min)	Soda-AQ		O₂-NaOH		Kraft	
	Ref	HWE-B	Ref	HWE-C	Ref	HWE-B
30	6 080	7 340	5 410	6 160	5 310	6 770
60	6 150	7 520	5 940	6 770	4 840	6 340
90	6 070	7 200	6 340	7 130	6 290	6 900
120	5 920	6 830	6 440	7 450	5 360	7 220
150	5 560	7 080	6 290	7 420	5 180	6 960

Fig 2 - Molar mass distribution of lignin. HWE-B and HWE-C refer to hot-water extractions of feedstock (see Table 1). 30, 90, and 150 are cooking times (min).

In all BLs, of the main organic compound groups, dissolved lignin corresponded to the highest relative proportion, and volatile acids represented the lowest one (*Fig 1*). These values may have an interesting role in the combustion properties of BL (Noopila et al. 1991; Alén et al. 1992; Alén 1997, 2000;). For example, higher mass ratios of lignin-to-total acids (1.2-2.6 vs. 1.1-1.9) were observed for the BLs from HWE feedstocks. It should be noted that O₂-NaOH BLs had clearly lower corresponding ratios (1.1-1.8) than those for other BLs (1.3-2.6).
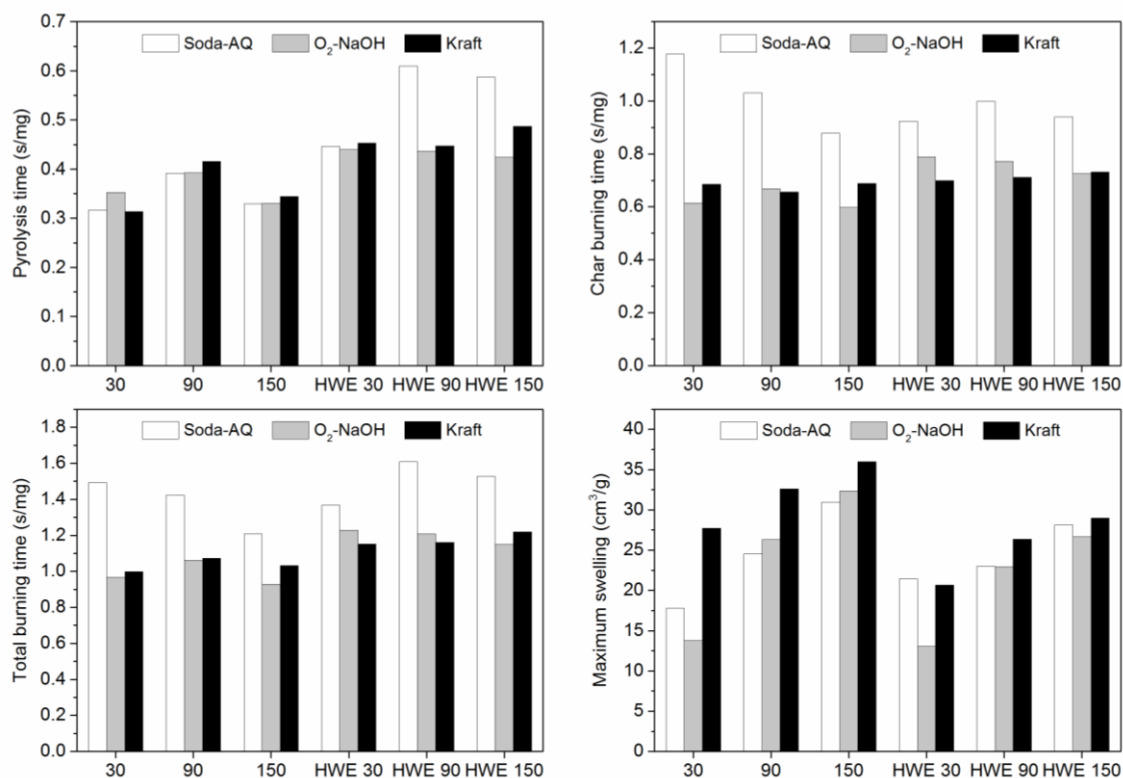
Fig 3 - Combustion properties of BLs. HWE refers to hot-water extractions of feedstock (see Table 1). 30, 90, and 150 are cooking times (min).

Combustion properties of BLs

Fig 3 illustrates the pyrolysis time, char burning time, and total burning time (i.e., pyrolysis time plus char burning time) as well as specific maximum swelling of the studied BLs. Based on the earlier research (Alén, 2000, Alén 2011), variations in the chemical composition of BL were expected to be characteristically reflected on the combustion properties of BL. First, aliphatic organics (i.e., organic acids and hemicellulose residues are relatively unstable upon heating) release significant amounts of volatile compounds that are important, especially in the pyrolysis phase and swelling of BL droplets. Second, aromatic organics (i.e., lignin is relatively stable upon heating) influence the char burning phase and determine the purity of carbon (residual char skeleton) necessary to reduce sodium sulfate to be recovered as sodium sulfide. In addition, it has been suggested that the average MM of dissolved lignin is an important factor for swelling.

In our experiments, the straightforward interpretation of combustion results based only on variations in the relative proportions of main organic compound groups of BLs showed to be somewhat difficult. However, except for BLs from an early cooking time of 30 min, the pyrolysis time and to some extent the char burning time decreased for the BLs from the untreated feedstock with an increase in cooking time (*Fig 3*). Furthermore, it was noted that BLs from the soda-AQ cooks from the pretreated feedstocks clearly had longer pyrolysis times than those from other cooking methods; for example, with the same cooking time, 4-36% higher than those for the kraft BLs. In general, the BLs from pretreated feedstocks have a longer pyrolysis time and char burning time than those from the untreated feedstock; with the same cooking time, the increase in pyrolysis time for the soda-AQ BLs was 7-45%, for the O_2-NaOH BLs 5-28%, and for the kraft BLs 7-45%.

It should be further noted that the lignin-to-total acids mass ratio (*Fig 1* and *Table S1*) typically increased along with delignification, and for each cooking time, this ratio was also higher for BLs from the HWE feedstocks than those from the untreated feedstocks. In addition, the average MM of lignin was higher in the BLs from HWE feedstocks than in the corresponding BLs from the untreated feedstock. This seemed to have resulted in longer burning times. For example, both the pyrolysis time and total burning time were higher for BLs from pretreated feedstocks. The char burning times for soda-AQ BLs from pretreated feedstocks were 33-41% higher than those for the corresponding kraft BLs with the same cooking time.

In summary, the total burning time of BLs for both the untreated and pretreated feedstocks was shown to decrease as follows: soda-AQ BL > O_2-NaOH BL > kraft BL. In addition, with the same cooking time, compared to the corresponding kraft BLs, higher total burning times were noted for BLs from pretreated feedstocks than those from the untreated BLs; for the soda-AQ BLs 1-27%, for the O_2-NaOH BLs 3-24%, and for the kraft BLs 6-19%. This parameter was also similar to that detected for the corresponding birch BLs (Chen et al. 2016). In general, char burning times were clearly higher for the sulfur-free BLs than for the corresponding kraft BLs.

The swelling occurring simultaneously in the pyrolysis stage is a significant parameter in the combustion of BL droplets. Swelling is mainly a result of the interaction

between lignin and aliphatic acids, which is also affected by other liquor compositions (e.g., polysaccharides, extractives, and inorganics) and furnace conditions (e.g., temperature, pressure, and atmosphere) (Hupa et al. 1987; Milanova 1988; Frederick et al. 1991; Noopila et al. 1991; Alén et al. 1992; Frederick, Hupa 1994; Alén 1997, 2000; Whitty et al. 1997, Whitty et al. 2008; Maček 1999). In our experiments, the maximum swelling was observed near the end of pyrolysis stage, and swelling increased with an increase in cooking time (*Fig 3*). It could be concluded that the amount of dissolved lignin and particularly the higher-MM fraction of lignin play an important role in hindering the escape of volatile products from aliphatic constituents within a BL droplet. The BLs from pretreated feedstocks swelled less than those from the untreated feedstock: with the same cooking time, a decrease of 2-11%, 5-18%, and 12-26% for the soda-AQ, O_2-NaOH, and kraft BLs, respectively. Furthermore, the soda-AQ and O_2-NaOH BLs (from the untreated feedstock) swelled less than the corresponding kraft BLs (8-25% and 4-23%, respectively). In general, a similar level of swelling was obtained for the corresponding birch BLs (Chen et al. 2016), while the most significant swelling occurs for the kraft BLs.

Conclusions

The hot-water pretreatment of the feedstock prior to alkaline pulping resulted in a varied chemical composition of the BLs and thus, their combustion properties. New data on the combustion properties of sulfur-free spruce BLs from soda-AQ (with pretreatment) and O_2-NaOH pulping are shown. Soda-AQ BLs were higher in char burning time (and total burning time) than the O_2-NaOH and kraft BLs; O_2-NaOH BLs behaved similarly to the reference kraft BLs in burning times; sulfur-free BLs were generally lower in swelling than the kraft BLs, especially for those without HWE. In addition, the pretreatment generally increased the total burning time and decreased the swelling of BLs.

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Appendix

Table S1 - Content of the main compound groups in BLs (% of total).

Parameter/cooking time (min)		Ref [a]					HW [a]				
		30	60	90	120	150	30	60	90	120	150
Volatile acids	Soda-AQ	14.0	10.9	9.5	9.8	9.4	7.7	7.2	7.0	6.6	6.3
	O_2-NaOH	19.2	17.7	17.3	15.8	15.2	16.4	14.4	12.5	12.8	11.5
	Kraft	12.7	10.7	9.9	10.0	9.9	9.3	8.0	7.1	6.9	6.9
Hydroxy acids	Soda-AQ	22.8	23.7	24.6	24.6	25.2	25.8	25.0	23.8	23.1	21.9
	O_2-NaOH	27.8	25.2	25.6	25.5	26.0	30.1	25.3	25.1	23.8	23.7
	Kraft	30.8	26.2	24.7	24.8	24.4	31.5	27.6	24.6	24.8	24.3
Lignin	Soda-AQ	63.2	65.4	65.9	65.6	65.4	66.6	67.8	69.3	70.3	71.9
	O_2-NaOH	53.0	57.1	57.0	58.7	58.7	53.5	60.3	62.4	63.5	64.8
	Kraft	56.5	63.1	65.4	65.2	65.7	59.2	64.4	68.4	68.3	68.8
Lignin-to-total acids (ratio)	Soda-AQ	1.7	1.9	1.9	1.9	1.9	2.0	2.1	2.3	2.4	2.6
	O_2-NaOH	1.1	1.3	1.3	1.4	1.4	1.2	1.5	1.7	1.7	1.8
	Kraft	1.3	1.7	1.9	1.9	1.9	1.5	1.8	2.2	2.2	2.2

[a] BLs obtained from the cooks with untreated (ref) and HW treated feedstocks.

Table S2 - The main organic composition of BLs (g/l). For abbreviations, see *Table 2*.

Component/cooking time, min		Ref					HW feedstocks				
		30	60	90	120	150	30	60	90	120	150
Total volatile acids	Soda-AQ	9.5	8.5	8.0	8.3	8.3	6.4	6.6	6.6	6.8	6.9
	O₂-NaOH	11.9	12.1	13.5	13.0	12.4	9.4	9.7	9.6	10.4	9.8
	Kraft	8.9	8.7	9.0	9.3	9.4	7.4	7.3	7.2	7.3	7.4
Formic		4.4	4.2	4.2	4.5	4.5	4.4	4.6	4.7	4.8	5.0
		5.0	5.3	6.1	6.0	5.6	5.2	5.3	5.4	5.8	5.4
		4.5	4.5	4.9	5.2	5.3	5.4	5.5	5.4	5.6	5.7
Acetic		5.1	4.3	3.8	3.8	3.8	2.0	2.0	1.9	2.0	1.9
		6.9	6.8	7.4	7.0	6.8	4.2	4.4	4.2	4.6	4.4
		4.4	4.2	4.1	4.1	4.1	2.0	1.8	1.8	1.7	1.7
Total hydroxy acids	Soda-AQ	15.6	18.6	20.5	21.0	22.2	21.4	23.0	22.6	23.3	24.0
	O₂-NaOH	17.2	17.3	20.0	21.0	21.2	17.3	17.1	19.2	19.4	20.3
	Kraft	21.6	21.4	22.4	23.0	23.2	25.1	25.2	25.1	26.2	25.9
Glycolic		1.7	2.2	2.5	2.6	2.8	1.8	2.3	2.3	2.5	2.7
		1.7	1.7	1.9	2.1	2.2	2.1	2.1	2.3	2.3	2.4
		0.8	0.9	1.0	1.0	1.1	1.0	1.1	1.1	1.2	1.2
Lactic		2.0	2.6	3.1	3.2	3.5	2.9	3.5	3.5	3.7	4.0
		2.6	2.7	3.2	3.5	3.7	2.4	2.5	3.0	2.9	3.4
		2.7	2.8	3.2	3.1	3.2	3.4	3.7	3.9	4.0	3.8
2-Hydroxybutanoic		0.4	0.5	0.7	0.8	0.9	1.2	1.4	1.3	1.3	1.4
		0.5	0.6	0.8	1.0	1.0	0.8	0.9	1.1	1.0	1.0
		0.6	0.7	0.8	0.9	0.9	1.5	1.6	1.6	1.7	1.7
Xyloisosaccharinic		0.6	0.6	0.7	0.7	0.8	2.0	2.0	2.0	2.0	2.0
		0.5	0.5	0.6	0.6	0.6	1.1	1.1	1.2	1.3	1.3
		0.7	0.7	0.7	0.7	0.7	2.3	2.2	2.1	2.2	2.2
Glucoisosaccharinic		5.7	7.0	7.6	7.6	7.9	7.4	7.7	7.6	7.8	7.8
		6.0	5.8	6.7	6.7	6.6	5.1	5.1	5.7	5.9	6.2
		10.1	9.9	9.7	10.2	10.1	9.4	9.1	8.9	9.4	9.5
Others [a]		5.2	5.7	5.8	6.0	6.4	6.1	6.2	6.0	6.0	6.2
		5.9	6.0	6.8	7.1	7.1	5.8	5.4	5.9	6.0	6.0
		6.7	6.4	7.0	7.1	7.2	7.5	7.5	7.5	7.7	7.5
Lignin	Soda-AQ	43.2	51.3	54.8	55.8	57.8	55.2	62.3	65.8	71.1	78.9
	O₂-NaOH	32.8	39.2	44.5	48.4	47.8	30.8	40.8	47.8	51.8	55.4
	Kraft	39.6	51.5	59.4	60.5	62.6	47.2	58.8	69.8	72.1	73.3
Total	Soda-AQ	68.3	78.5	83.2	85.1	88.3	83.0	91.8	95.0	101.1	109.8
	O₂-NaOH	61.9	68.6	78.0	82.4	81.4	57.5	67.6	76.6	81.6	85.5
	Kraft	70.1	81.6	90.8	92.8	95.2	79.7	91.3	102.1	105.6	106.6

[a] Mainly 3,4-dideoxy-pentonic and 3-deoxy-pentonic acids.