Combustion behavior of kraft black liquor droplets from hot water pretreated hardwood and softwood chips

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ABSTRACT: This paper describes the combustion behavior of birch and spruce kraft black liquors obtained from an integrated forest biorefinery concept in which a hot water extraction of chips was performed before pulping. This pretreatment, aiming mainly at the recovery of various hemicellulose-derived materials, increased the concentrations of lignin and hydroxy acids in black liquors, compared with those in the reference black liquors without any process modification. On the other hand, the pretreatment decreased the concentrations of volatile acids and other organics (extractives and hemicellulose residues). Because of these characteristic changes, the total burning times (pyrolysis time plus char burning time) of the reference black liquors were somewhat longer than those of black liquors from the modified cooking process. The novel biorefinery-based black liquors also swell more than the conventional ones. This phenomenon was primarily associated with the combined effect of high-molar-mass lignin fragments and hydroxy acids. All of the detected changes in combustion behavior were more intense for birch black liquors than for spruce black liquors.

Application: This study clarifies various effects caused by the typical hot water pretreatment of hardwood and softwood chips before kraft pulping on the combustion behavior of black liquor.

Kraft pulping is the dominant delignification process in the production of fiber for papermaking [1,2]. In this process, an aqueous hot alkali solution reacts with the feedstock, resulting in a cooking yield of about 50% of the initial dry solids. The spent cooking liquor or black liquor, with a dry solids content of 10%–15% after delignification, is the most important byproduct of this process. Black liquor contains, in addition to water and residual cooking chemicals, significant amounts of lignin-derived fragments and carbohydrates-derived aliphatic carboxylic acids together with some hemicellulose residues and extractives [3,4]. In practice, for environmental and economic reasons, after evaporation (dry solids content is increased to 65%–85%) black liquor is burned in a Tomlinson-type recovery furnace as sprayed droplets to recover cooking chemicals and to generate energy [5]. Laboratory studies under controlled conditions on the combustion behavior of black liquor have traditionally divided the burning process of a single droplet into sequential stages: drying, pyrolysis (i.e., devolatilization, including specific swelling), char burning, and inorganic coalescence [6,7]. All of these stages are important in the design and operation of a recovery boiler. The results obtained from laboratory-scale tests have also explained much about the combustion behavior of different black liquors.

The combustion behavior of black liquor is greatly affected by operating conditions in the recovery furnace and by liquor composition, wood species, pulping method, and possibly by heating treatment of black liquor [8-18]. Because of the influence of these variables on the chemical composition of black liquor dry solids [4,19], they also play an important role in the combustion behavior of black liquor. According to the integrated forest biorefinery concept [4,20], the existing pulp mill has been considered to be capable of producing novel value-added byproducts. Recently, the most common alternatives studied have been to introduce either an acidic or alkaline pretreatment stage before alkaline pulping, mainly for recovering various carbohydrate-derived materials from the chips [4,21-31]. These types of pretreatment processes have an influence on the main delignification process and thereby the chemical composition of the final black liquor. For this reason, we could expect that pretreatments also cause some variations in the combustion behavior of black liquor. However, there are only limited fundamental data available on these changes.

The aim of this investigation was to study the combustion behavior of kraft black liquors prepared from hot water pretreated birch and spruce chips. Combustion experiments were carried out with single black liquor droplets in stagnant air at 800°C in a laboratory furnace.

EXPERIMENTAL

Pretreatment and pulping

Laboratory-scale hot water pretreatments (HWPs) of screened silver birch (*Betula pendula*) and Norway spruce (*Picea abies*) chips were conducted in 1.25-L rotating stainless steel autoclaves heated in an oil bath [31]. Chips were treated at 150°C for 60 min. The liquor-to-wood ratio was 4.5 L/kg. The HWP yields for birch and spruce chips were 83.0% and 90.7%, respectively.

Kraft black liquors were prepared by cooking untreated and pretreated birch and spruce wood chips in the same laboratory-scale digester as above (**Table I**). At the end of each cook, 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 the pulp was thoroughly washed with tap water. Pulp yield was calculated on the basis of ovendry feedstock and pulp and kappa number of pulps was determined according to standard test method SCAN-C 1:00. The black liquors were stored in a freezer before analyses and combustion tests.

Black liquor analyses

Analyses of lignin and aliphatic carboxylic acids ("volatile" acetic and formic acids and "non-volatile" hydroxy acids) in the black liquors were conducted as follows.

After dilution with 0.1 M aqueous sodium hydroxide, the lignin content was estimated by ultraviolet-visible light spectrometry at 280 nm using an absorptivity value of 22.8 L/(g·cm) and 24.3 L/(g·cm) for birch and spruce liquors, respectively [32]. A gel permeation chromatographic system (Waters [Milford, MA, USA] high-performance liquid chromatography [HPLC] system equipped with a Superdex 75 gel column using 0.1 M aqueous sodium hydroxide as the eluent) was applied to determine the molar masses (MMs) [33].

Volatile and hydroxy acids were determined by gas chromatography (flame ionization detector and mass spectrometer detector) as their benzyl esters [34] and per(trimethylsilyl)ated derivatives [35], respectively.

The overall content of extractives and other organics (e.g., hemicellulose residues) was evaluated by subtracting the amounts of lignin and aliphatic carboxylic acids from the total dissolved organic material.

The residual alkali was determined according to KCL procedure (number 67a:87) by titrating the diluted and carbonate-buffered black liquor sample to pH 11.5 with 1 M hydrochloric acid.

Droplet combustion tests

Black liquor samples were evaporated under reduced pressure at 40°C to a dry solids content of 55%–75%. We burned 15–20 individual droplets around 9 mg in mass in a laboratory furnace at 800°C in the stagnant air [17]. The process of droplet combustion was recorded by a high definition video camera. We used video editing software to obtain pyrolysis and char burning times (s/mg) from the video recording. The maximum swelling of each droplet (S_{max} as cm³/g) was calculated based on an approximation of the swollen particle as an ideal sphere:

$$S_{max} = \frac{4}{3} A \sqrt{\frac{A}{\pi}} / g$$

where A is the sectional area of the swollen particle measured from a selected frame of the video recording (at the point of maximum swelling) and g is the dry mass of the droplet.

RESULTS AND DISCUSSION

Chemical composition of black liquors

Table II presents the organic composition of all studied

Parameter	B52	B65	HW + B52	HW + B 65	S65	S85	HW + S65	HW + S85
Effective alkali as sodium hydroxide, % on o.d. wood	18				19			
Sulfidity, %	35							
Liquor-to-wood ratio, L/kg	4.5							
Maximum cooking temperature, °C	162				170			
Cooking time, min	52	65	52	65	65	85	65	85
H factor	500	600	500	600	1200	1500	1200	1500
Pulping yield, %	55.8	55.6	51.3	49.8	52.8	51.2	49.2	48.0
Residual alkali, g/L	6.8	6.0	4.7	3.9	9.3	9.3	9.5	9.5
Kappa number	31.7	25.9	16.6	16.3	42.7	38.3	36.1	32.9

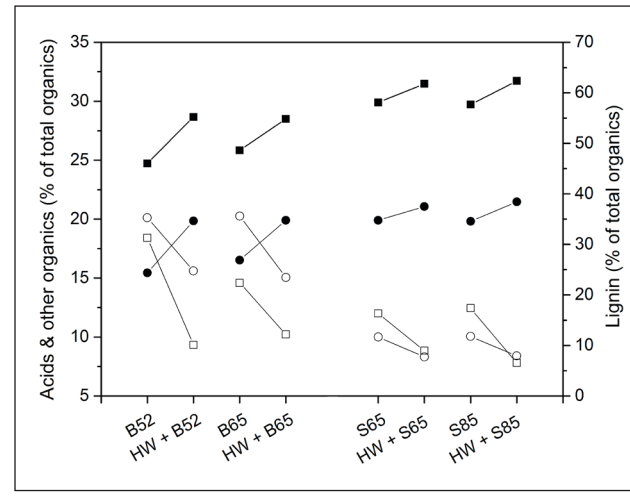
I. Kraft pulping of the untreated and hot water pretreated (HW) birch (B) and spruce (S) chips.

Component	B52	B65	HW + B52	HW + B65	S65	S85	HW + S65	HW + S85
Volatile acids	19.8	20.0	16.9	16.8	10.5	10.9	9.4	9.7
Formic	4.4	4.5	6.5	6.4	5.2	5.5	5.8	5.9
Acetic	15.4	15.5	10.4	10.4	5.3	5.4	3.6	3.8
Hydroxy acids	15.2	16.3	21.5	22.2	20.9	21.5	23.8	24.8
Glycolic	0.8	0.8	1.2	1.3	1.4	1.4	1.4	1.5
Lactic	1.7	1.8	2.2	2.4	3.3	3.5	3.4	3.5
2-Hydroxybutanoic	4.1	4.2	4.9	5.2	0.9	1.0	1.5	1.7
Xyloisosaccharinic	2.5	2.6	4.8	4.9	0.5	0.5	1.5	1.6
Glucoisosaccharinic	2.1	2.2	2.6	2.8	8.1	8.0	8.8	9.1
Others*	4.0	4.7	5.8	5.6	6.7	7.1	7.2	7.4
Lignin	45.3	48.0	59.8	61.2	61.0	62.6	69.8	72.0
Other organics	18.1	14.4	10.1	11.4	12.6	13.5	10.0	9.0
Volatile acids-to-total organics	0.20	0.20	0.16	0.15	0.10	0.10	0.08	0.08
Hydroxy acids-to-total organics	0.15	0.17	0.20	0.20	0.20	0.20	0.21	0.21
Lignin-to-total organics	0.46	0.49	0.55	0.55	0.58	0.58	0.62	0.62

* Mainly 3,4-dideoxy- and 3-deoxy-pentonic.

II. Chemical composition of organic dry solids in untreated and hot water pretreated (HW) birch (B) and spruce (S) kraft black liquors (g/L).

black liquors. During alkaline pulping, in addition to a significant degradation and dissolution of lignin, a substantial amount of polysaccharides (mainly hemicelluloses) is converted to soluble aliphatic carboxylic acids by various alkali-catalyzed degradation reactions [3,36]. The results clearly indicated the effect of wood species on the acid formation (birch samples B52 and B65 vs. spruce samples S65 and S85), because 2-hydroxybutanoic and xyloisosaccharinic acids mainly originated from xylan-rich birch while glucoisosaccharinic acid mainly originated from glucomannan-rich spruce. Acetic acid was mostly formed by deacetylation of the acetyl groups of hemicelluloses, and its higher amount in birch black liquor, compared with that in spruce black liquor, was because of the higher content of acetyl groups in birch xylan than in spruce glucomannan. Of the main other acids, formic, glycolic, and lactic acids were unspecifically formed from all the polysaccharide constituents present in feedstocks. Also, it was noted that the cooking time did not much affect the liquor compositions (B52 vs. B65 and S65 vs. S85), and only a slight increase in the concentration of lignin as well as acids was detected in the course of prolonged delignification. In addition, the decrease in residual alkali (Table I) distinctly suggested the enhanced formation of hydroxy acids in the kraft pulping of the pretreated birch chips, while this phenomenon was not seen for spruce.



1. Contents of lignin, hydroxy acids, volatile acids, and other organics in black liquors based on the total dissolved organics for untreated and hot water pretreated (HW) birch (B) and spruce (S). (Note: ■ – lignin, ● – hydroxy acids, ○ – volatile acids, and □ – other organics.)

Figure 1 compares the variations in black liquor compositions, including lignin, hydroxy acids, volatile acids, and other organics. HWP of chips typically increased the content of lignin and hydroxy acids in all black liquors. An

Molar mass, g/mol	B52	B65	HW + B52	HW + B65	S65	S85	HW + S65	HW + S85
>10000	38.8	60.2	53.0	63.6	40.3	57.0	50.8	59.2
5000–10000	20.8	17.3	19.1	17.0	17.5	19.1	21.2	18.7
3500–5000	11.0	6.6	8.2	6.2	9.9	7.3	8.9	6.9
<3500	29.4	15.9	19.7	13.2	32.3	16.6	19.1	15.2

III. Molar mass distribution of dissolved kraft lignins (% of total lignin) in untreated and hot water pretreated (HW) birch (B) and spruce (S).

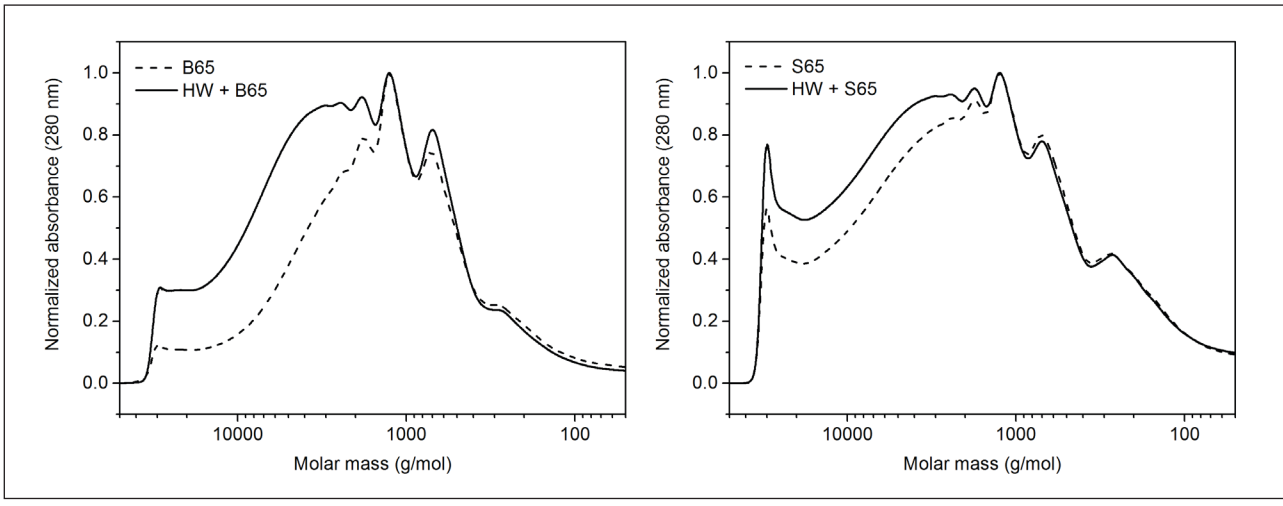
increase (an absolute increase of 30%–40% for birch and about 15% for spruce) in hydroxy acids (B52 vs. HW + B52, B65 vs. HW + B65, S65 vs. HW + S65, and S85 vs. HW + S85) could be primarily explained by the partial removal of acetyl groups from hemicelluloses during the HWP stage [29]. For this reason, less alkali was needed for the hydrolysis of acetyl groups (i.e., neutralization of acetic acid) in the cooking stage than for traditional cooking without the HWP stage, thus offering more alkali (i.e., higher alkalinity) for other degradation reactions of polysaccharide chains.

The HWP stage also caused morphological changes to the chip matrix, making it more accessible to various alkali-catalyzed reactions during pulping [31,37]. As a result of this increase in accessibility, higher amounts of dissolved lignin in black liquors from the pretreated chips (about 30% for birch and 15% for spruce) were obtained, compared with their untreated counterparts (Fig. 1). In addition, after the HWP, the increment of lignin (4%–9%) based on the total dissolved organics (Table II) was higher than that of hydroxy acids (1%–5%), suggesting a more pronounced increase in the mass portion of lignin in black liquors. Unlike lignin and hydroxy acids, the contents of volatile acids and other organics showed a declining trend, although, despite deacetylation in the HWP stage, the concentration of acetic acid was still rather high, especially in birch black liquors.

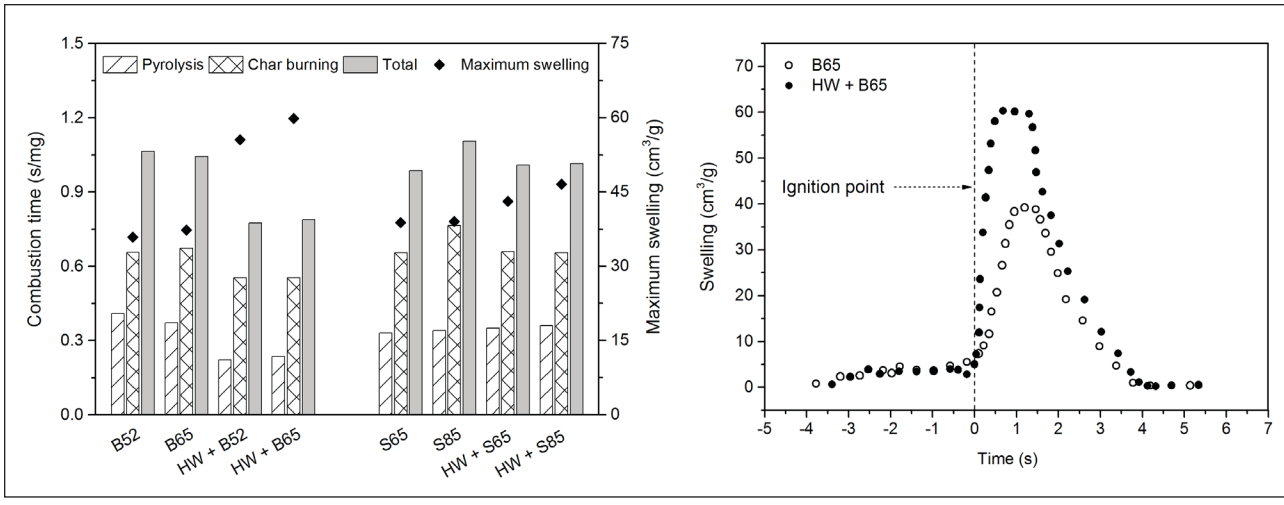
Molar mass distributions of lignin characteristically indicated the influence of cooking time as observed earlier by Pakkanen and Alén [33] (**Table III**). We also noticed that during the HWP, lower-MM lignin fragments were primarily removed, and the removal of high-MM lignin fragments took place more readily during the subsequent cooking phaser (**Fig. 2**). Therefore, a slightly more significant proportion of higher-MM lignin fragments was typically found in black liquors from pretreated chips more so than in those from untreated chips.

Combustion behavior of black liquor droplets

Figure 3 summarizes the combustion behavior of all the black liquors studied, indicating their pyrolysis, char burning, and total burning (i.e., pyrolysis time plus char burning time) times together with specific maximum swelling. In particular for birch, the black liquors from the pretreated chips had a higher swelling capacity than those from untreated chips. This phenomenon seemed mainly associated with higher lignin contents (Table II), although higher contents of high-MM lignin fragments (>10000 g/mol) were also important for the formation of char [4,38]. In addition, the black liquors from pretreated chips contained higher amounts of hydroxy acids



2. Molar mass distributions of dissolved lignin in black liquors from the kraft pulping of untreated and hot water pretreated (HW) birch (B) and spruce (S) chips.



3. Combustion behavior of kraft black liquors for untreated and hot water pretreated (HW) birch (B) and spruce (S) and the swelling profiles of two representative birch liquors.

(Table II), which degrade faster than lignin when heated, thus readily releasing rapidly volatile degradation products [39]. Earlier research shows that hardwood kraft lignin swells considerably more than softwood kraft lignin when mixed with hydroxy acids [12]. One further aspect is that hardwood black liquors typically contain more xylan residues, which have an increasing effect on swelling [4].

Figure 3 also illustrates the "swelling profile" of the liquor droplets B65 and HW + B65, clearly indicating that for HW + B65, a shorter pyrolysis time was needed to reach maximum swelling. The mechanism behind this higher swelling rate for HW + B65 was probably due to the combined effect of high-MM lignin fragments and hydroxy acids [4].

Shorter char burning times together with enhanced swelling (Fig. 3) were observed for black liquors (HW + B52 and HW + B65) from pretreated chips than those from untreated chips (B52 and B65). This might demonstrate that a larger surface is more favorable for the faster char burning [16]. Additionally, lignin is the main component of black liquor organics with the highest tendency to form char [39,40], thus explaining the longer duration of char burning than that of pyrolysis. Char burning rate is significant for phenomena occurring in the char bed, where gasification of carbon and reduction of sodium sulfate are of importance [5]. In contrast, the HWP of spruce chips seemed not to greatly affect the pyrolysis or char burning times of the corresponding black liquors (S65 vs. HW + S65 and S85 vs. HW + S85). In general, the conventional black liquors had the longest total burning times and birch black liquors burned faster than spruce black liquors.

CONCLUSIONS

This study shows new data on the combustion behavior of birch and spruce kraft black liquors obtained from an integrated forest biorefinery concept applying hot water extraction to chips before kraft pulping. Compared with conventional black liquors from untreated chips, the chemical composition of black liquors from pretreated chips varied characteristically. With pretreated chips, higher concentrations of lignin and hydroxy acids were detected, whereas the concentrations of volatile acids and other organics (extractives and polysaccharides) were lower. In particular, the total burning times (pyrolysis time plus char burning time) of the conventional black liquors obtained without any process modification were somewhat longer than those of black liquors from the integrated biorefinery concept. The modified black liquors also swelled more than the conventional ones, probably because of the combined effect of high-MM lignin fragments and hydroxy acids. The effect of the molar mass distribution of lignin on the combustion behavior of black liquor will be studied in forthcoming studies. All of the changes in combustion behavior were more intense for birch black liquors than for spruce black liquors, thus having a minor influence on the operation of the recovery furnace in the latter case. **TJ**

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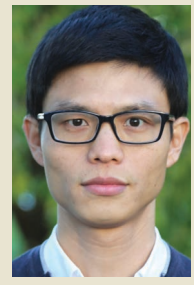
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Integration of a hot water pretreatment of feedstock before chemical pulping has been widely discussed as a potential biorefinery, but the combustion behavior of black liquors from such processes has not been studied in detail.

Earlier, our research group studied the effect of heating treatment on black liquor composition and combustion behavior. This paper is the first to report the combustion behavior of black liquor droplets derived from the modified kraft process (i.e., including the pretreatment and cooking phase).

The most difficult aspect of this research was to find the reason for the changes in the combustion behavior of the biorefinery-based black liquors. Our previous knowledge of the influence of the main organic composition on black liquor's combustion behavior helped a lot.

We discovered that the swelling degree of black liquor droplets is greatly affected by lignin, including its content and molar mass distribution. The most interesting finding was that the black liquor droplets derived from hot water pretreated feedstock swell much more than those from non-treated feedstock. This is useful information for the design and operation of recovery boilers for the combustion of biorefinery-based black liquors.

Out next step is to clarify the mechanism for the swelling of black liquor droplets, which would help to predict the degree of swelling based on liquor composition.

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