Influence of the oxidative thermochemical treatment on the chemical composition of hardwood kraft black liquor

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ABSTRACT: We thermochemically treated hardwood kraft black liquor to evaluate viscosity reduction with and without NaOH addition (1% of black liquor dry solids) at 115°C and 145°C for 45 min using three oxygen dosage levels (0.83, 1.24, and 2.07 mol/kg d.s.). All black liquors were analyzed for viscosity. In addition, selected liquors were characterized by residual effective alkali, molecular mass distribution of lignin, and chemical composition of aliphatic carboxylic acids. In these cases, we determined the total content of lignin, aliphatic carboxylic acids, and polysaccharides. The most significant viscosity reduction (about 60% of the initial viscosity at 70% d.s. content) occurred at 145°C with NaOH addition using an oxygen dosage of 1.24 mol/kg black liquor d.s. No clear changes in the average molecular mass of lignin or the content of polysaccharides were detected during the treatments. However, a decrease in the highest fraction (M > 10,000 Da) of lignin observed was considered to be the main reason for the viscosity decrease.

Application: This alternative for black liquor processing in modern pulp mills can reduce viscosity and have other beneficial on black liquor evaporation and combustion

The main structural constituents of wood are carbohydrates (cellulose and hemicelluloses) and lignin [1]. In addition, small amounts (< 5% of the wood dry solids) of nonstructural constituents, such as extractives, are present. During kraft pulping, lignin and a significant part of carbohydrates (mainly hemicelluloses) are degraded by alkali–catalyzed reactions. The degradation products are dissolved together with extractives into the cooking liquor ("black liquor") [2]. Thus, black liquor is a complex mixture of water, residual inorganic cooking chemicals, and organic material containing certain amounts of chemically bound sodium and sulfur. Organic material consists primarily of lignin fragments (mainly high molecular mass fragments) and low molecular mass aliphatic carboxylic acids originating from wood carbohydrates. Organic material also contains minor amounts of hemicellulose residues (i.e., poly- and oligosaccharides) and extractives-derived low molecular mass compounds. In spite of these general features, the composition of black liquor depends greatly on the wood species and the cooking conditions.

Black liquor is concentrated and burned, after the separation of extractives as raw tall soap, in the mill's recovery furnace to produce energy and to regenerate cooking chemicals [2]. Each liquor component plays an important role in the thermochemical properties of black liquor. In addition, black liquor exhibits a significant increase in viscosity as a function of its dry solids content [3, 4]. For this reason, viscosity is the limiting factor in raising the dry solids content of black liquor. The maximum dry solids content is, for example, of benefit to an increase in the energy efficiency of the recovery process [5, 6] and, on the other hand, to a decrease in sulfur dioxide emissions [7, 8]. The dry solids content of black liquor prior to combustion is typically about 70%, although different methods, such as heat [9-12] and black liquor oxidation [13, 14] treatments have been developed for obtaining even higher contents (i.e., for reducing the liquor viscosity as much as possible during evaporation).

Our previous experiments [15] focused on influences of oxidative thermochemical treatment on the physical and chemical properties of softwood kraft black liquor. This study reports on similar changes in the chemical composition and viscosity of hardwood black liquor under the corresponding conditions.

EXPERIMENTAL

Black liquor samples and heat treatments

The industrial hardwood black liquor from kraft pulping was treated to reduce its viscosity in a reactor described in detail by Porter *et al*. [16]. Different temperatures and oxygen dosages were used in the treatments with and without NaOH addition (**Table I**). In each case treatment time was 45 min. Temperatures presented in Table I are the temperatures at which oxygen was added to the liquor. Reactions of the liquor components caused by oxygen addition increased the liquor temperature [12]. Thus, the maximum temperatures of the liquor samples were somewhat higher than those showed in Table I. The samples in **Table II** were analyzed in more detail.

Analytical determinations

The hydroxy monocarboxylic and dicarboxylic acids of the black liquor were determined as their per(trimethylsilyl)-ated derivatives by GC [17]. Formic and acetic acids were determined as their benzyl esters by GC [18]. We used the following procedure to analyze the content of polysaccharides. We started by purifying samples by dialysis for six days (a cut-off value of 6000-8000 Da), hydrolyzed them with sulfuric acid (TAPPI T249 cm-00), and then per(trimethylsilyl)ated and determined by GC the monosaccharides obtained.

The lignin content of the black liquor was determined by UV/Vis spectrophotometry at 280 nm after dilution (absorbance in the range 0.3-0.8) using an absorptivity value of 22.8 L/gcm [19]. The molecular mass distribution of lignin

NAOH ADDITION % d.s.	TEMP.* °C	TIME min	O_2 DOSAGE mol/kg d.s.	pH	EFFECTIVE ALKALI (Na_2O) % d.s.	TOTAL SULFUR % d.s.
—	—	—	—	13.9	4.9	5.6
—	115	45	0.83	—	—	—
—	115	45	1.66	—	—	—
—	115	45	2.07	11.3	0.0	5.2
—	145	45	0.83	13.6	2.9	5.5
—	145	45	1.04	—	—	—
—	145	45	1.24	—	—	—
1	115	45	0.83	13.8	3.9	5.0
1	115	45	1.66	—	—	—
1	115	45	2.07	12.3	0.4	4.9
1	145	45	0.83	13.9	2.9	5.1
1	145	45	1.04	—	—	—
1	145	45	1.24	13.6	2.4	5.0

*Values refer to temperatures at which oxygen was charged to the liquor.

I. Treatment data and the measured pH, effective alkali, and total sulfur content of black liquors.

was determined by gel permeation chromatography (GPC) [20]. The GPC device was a Waters HPLC system equipped with a Waters 510 pump, a 717 autosampler, and a 996 photodiode array detector. A Sephadex G50F gel (1 cm · 122 cm) was employed. We used aqueous 0.1 M NaOH as eluent and a flow-rate of 0.3 mL/min. The system was calibrated by various lignin standards [20].

The sulfur content was determined by an energy dispersive X-ray fluorescense analyzer (X-MET 920XRT). The residual effective alkali content of the black liquor was determined by potentiometric titration according to the standard KCL 67a:87. The dry solids content of the black liquor was measured according to the standard SCAN 22:77. The viscosity of the black liquor was determined by a dynamic viscometer at 110°C, 50%-70% d.s. content, and shear rate of 288 1/s at Oy Keskuslaboratorio-Centrallabora-torium Ab (KCL) [9].

RESULTS AND DISCUSSION

Viscosity of black liquor

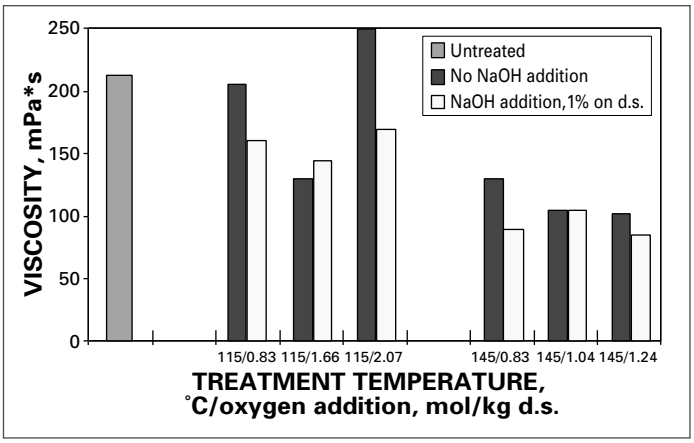
The viscosity of black liquor decreased in all treatments except the treatment at 115°C without NaOH addition and with the greatest charge of oxygen addition (2.07 mol/kg d.s.) (**Fig. 1**). In this case the residual effective alkali content of the treated black liquor was zero. The reason for the low alkalinity was neutralization of various acidic reaction products formed in reactions between oxygen and the black liquor constituents.

The liberation of phenolic groups in lignin along with the pH decrease has been suggested to be the main reason for the association of lignin particles [21]. This phenomenon is due to the formation of both intramolecular hydrogen bonds within surface regions in a single lignin particle and, on the other hand, intermolecular hydrogen bonds between individual lignin particles. Thus, low viscosity of black liquor provides that hydrophilic groups of lignin are fully dissociated, and an excess in free hydroxide ions is required to reach a minimum of viscosity [14, 22]. Furthermore, it has been observed that there is an upper limit for the alkalinity when minimizing liquor viscosity. Liquors with a residual effective alkali of 4% [14] or 3% of dry solids [23] (as Na_2O) have exhibited an increase in viscosity with alkali addition, although the reason for this behavior is so far unclear.

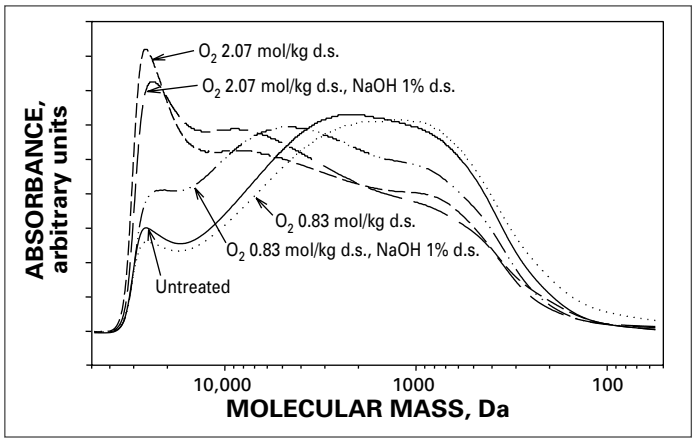
In this study, all NaOH additions intensified the viscosity decrease during the treatments regardless of temperatures or oxygen dosages (Fig. 1). In our experiments, residual effective alkali of the original liquor was higher than that presented above as an upper limit (i.e., 3%-4% of d.s. as Na_2O), especially when NaOH was added (Table II). However, the residual effective alkali was decreased in the treatments levelling to the range where lignin was amenable to the viscosity decrease, except in two samples with the biggest oxygen charge. The viscosity of the sample with NaOH addition of 1% d.s. (115°C, O_2 2.07 mol/kg d.s.) was lower (170 mPa*s) than that of the untreated liquor (215 mPa*s) (Fig. 1). This confirmed the fact that although the partial association of lignin occurred, the remaining alkalinity (0.4% of d.s.) was still enough to avoid a significant increase in viscosity.

NaOH ADDITION % d.s.	TEMP. °C	TIME min	O_2 mol/kg d.s.	LIGNIN CONTENT % d.s.	$\bar{M}w$, Da	POLYDISPERSITY $\bar{M}w/\bar{M}n$	LIGNIN FRACTION >10,000 Da %	LIGNIN FRACTION <1000 Da %
—	—	—	—	39.7	4671	4.3	13	30
—	115	45	0.83		4379	4.5	12	33
—	115	45	1.66		4977	4.6	15	29
—	115	45	2.07	42.1	8161	5.5	31	21
—	145	45	0.83	39.5	6183	4.3	21	22
—	145	45	1.24		4604	4.2	13	29
1	115	45	0.83	37.0	5911	4.4	20	24
1	115	45	2.07	38.8	7971	4.8	31	19
1	145	45	0.83	38.1	4299	3.9	12	29
1	145	45	1.24	38.0	4697	4.1	14	27

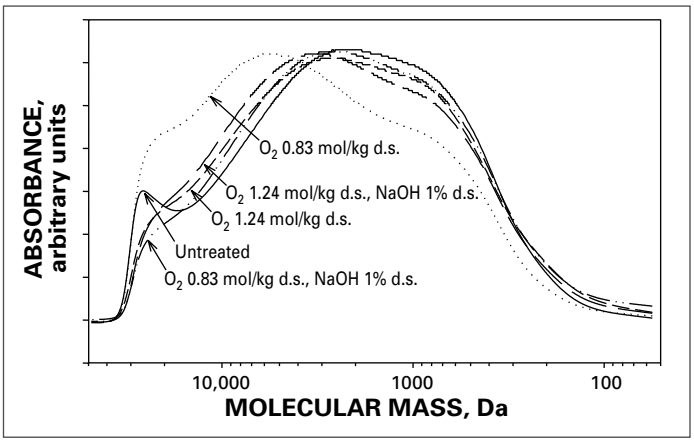
Table II. Lignin content, weight average molecular mass ($\bar{M}w$), polydispersity ($\bar{M}w/\bar{M}n$), and the percentages of high- and low molecular mass fractions of lignin in black liquor samples.



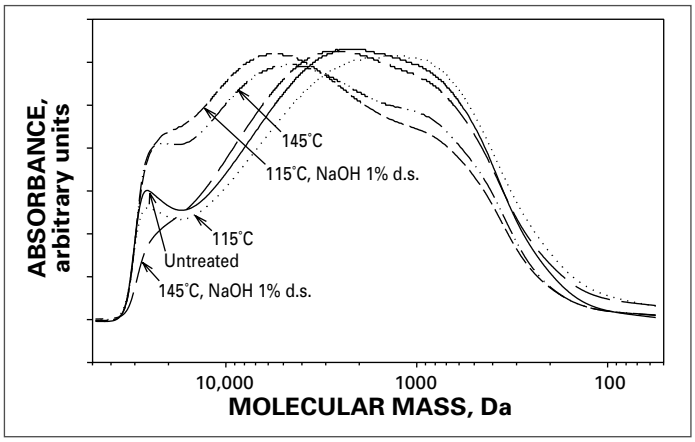
1. Changes in the viscosity of the original black liquor (untreated) and the liquor samples from the treatments (45 min) with and without NaOH addition. Viscosity was measured in each case at 70% d.s. content.



2. Changes in the molecular mass distribution of lignin in the original black liquor (untreated) and the liquor samples from the treatments (45 min) at 115°C with and without NaOH addition. The oxygen dosage was either 0.83 or 2.07 mol/kg d.s.



3. Changes in the molecular mass distribution of lignin in the original black liquor (untreated) and the liquor samples from the treatments (45 min) at 145°C with and without NaOH addition. The oxygen dosage was either 0.83 or 1.24 mol/kg d.s.



4. Changes in the molecular mass distribution of lignin in the original black liquor (untreated) and the liquor samples from the treatments (45 min) at 115°C and 145°C with and without alkali addition. Oxygen dosage was 0.83 mol/kg d.s.

Lignin molecular-mass distribution

Figure 2 shows the influence of different oxygen dosages at 115°C on the molecular mass distribution of lignin. It indicates that the high oxygen dosage resulted in the increase in the high molecular mass fragments. The phenomenon was not seen when less oxygen was charged.

There are no clear trends in different parameters describing the molecular mass of lignin during treatments (Table II). Neither the content of high- and low molecular mass fractions nor the polydispersity and weight average molecular mass changed much during the treatments. However, the shape of the molecular mass distribution curves of the samples with the lowest viscosity were very similar (**Fig. 3**). The difference between the untreated liquor and the four samples shown was seen within the highest molecular mass area (M > 10,000 Da) of the distribution curves. **Figure 4** shows the effects of both temperature and NaOH addition on the molecular mass distribution. The most significant changes occurred within the high molecular mass area. Based on these findings (Figs. 2-4) it seemed that a correlation between the high molecular mass fraction and viscosity existed. Thus, we concluded that viscosity was also influenced by the temperature, oxygen dosage, and alkali addition.

We calculated the lignin content of black liquor using the same absorptivity value for all samples. Thus, the reported differences in lignin contents indicated mainly chemical changes in the lignin fraction rather than changes in the actual content of lignin.

The total sulfur content of black liquor decreased in all treatments indicating the formation of volatile sulfur compounds (Table I). Alkali addition increased sulfur emissions, while temperature or oxygen dosage did not effect sulfur release as much.

Carboxylic acids and polysaccharides in black liquor

The composition and the total amount of carboxylic acids of black liquor were not significantly affected by different treatment conditions (**Table III**). Surprisingly, even variable oxygen dosages did not cause chemical changes in this compound group. In kraft cooking, most of the carboxylic acids are formed from polysaccharides by the end-wise peeling reactions during the heating stage,

NaOH addition, % of d.s.	0			1			
Temperature, °C	0*	115	145	115		145	
Oxygen dosage, mol/kg d.s.	0	2.07	0.83	0.83	2.07	0.83	1.24
Monocarboxylic acids							
Formic	14.1	17.2	16.5	16.2	16.1	15.0	15.0
Acetic	20.8	20.2	21.7	21.3	21.1	20.0	21.0
Glycolic	5.6	6.0	5.9	5.6	6.2	6.3	6.5
Lactic	8.3	7.9	8.4	8.1	7.9	8.8	8.8
3-Hydroxypropanoic	3.1	3.8	1.9	2.4	3.1	2.3	2.4
Glyceric	0.5	0.5	0.5	0.5	0.5	0.5	0.5
2-*C*-Methylglyseric	0.2	0.2	0.2	0.2	0.2	0.2	0.2
2-Hydroxybutanoic	4.7	4.2	4.5	4.4	4.2	4.6	4.5
4-Hydroxybutanoic	0.3	0.4	0.4	0.3	0.4	0.4	0.4
3-Deoxytetronic	1.6	1.5	1.6	1.5	1.6	1.6	1.7
2-Hydroxypentenoic	0.5	0.4	0.4	0.5	0.4	0.5	0.4
3,4-Dideoxypentonic	4.0	3.5	3.7	3.7	3.5	3.8	3.6
3-Deoxy-*erythro*-pentonic	1.0	1.0	1.1	1.0	1.0	1.1	1.2
3-Deoxy-*threo*-pentonic	2.6	2.6	2.5	2.4	2.6	2.4	2.4
Xyloisosaccharinic	3.4	2.8	3.3	3.4	3.0	3.5	3.4
Anhydroglucoisosaccharinic	0.8	1.0	0.8	0.8	0.9	0.8	0.8
3,4-Dideoxyhexonic	1.2	1.1	1.1	1.1	1.1	1.1	1.1
α-Glucoisosaccharinic	3.0	2.4	2.9	3.0	2.6	2.9	2.8
β-Glucoisosaccharinic	9.3	7.8	8.7	9.0	8.0	8.9	8.5
Dicarboxylic acids							
Malonic	1.4	1.5	0.7	1.2	1.4	1.2	1.2
Methyltartronic	0.2	0.3	0.3	0.3	0.3	0.3	0.4
Succinic	0.7	0.8	0.7	0.7	0.8	0.7	0.7
Methylsuccinic	0.2	0.2	0.1	0.2	0.2	0.1	0.2
Malic	0.6	0.5	0.3	0.4	0.4	0.3	0.3
2-Hydroxyglutaric	1.5	1.4	1.8	1.7	1.6	2.1	2.0
Miscellaneous	10.4	10.8	10.0	10.3	10.8	10.6	10.3
Total amount, % of d.s.	23.3	24.4	22.6	21.9	21.4	22.3	21.8

*The untreated black liquor.

III. Main aliphatic carboxylic acids in black liquor samples (% of the total acids).

NaOH addition, % of d.s.	0			1			
Temperature, °C	0*	115	145	115		145	
Oxygen dosage, mol/kg d.s.	0	2.07	0.83	0.83	2.07	0.83	1.24
Arabinose	14	16	13	10	17	9	8
Xylose	62	66	69	65	53	51	52
Galactose	15	12	11	10	8	9	8
Glucose	7	5	6	14	21	30	31
Mannose	2	1	1	1	1	1	1
Polysaccharides, % of d.s.	3.0	1.3	1.3	1.7	2.3	2.7	2.5

*The untreated black liquor.

IV. Relative percentages of the monosaccharide moieties in polysaccharides and the total amount of polysaccharide material in the black liquor samples.

although this formation also steadily continues at the maximum cooking temperature [2]. In addition, polysaccharides (M > 6000-8000 Da) did undergo some degradation reactions, because the amount of them decreased during the treatments without NaOH addition (**Table IV**). This was probably due to the alkaline hydrolysis of the glycosidic bonds of polysaccharides, differing thus mechanistically from the end-wise peeling reactions. Hydrolysis of the glycosidic bonds of polysaccharides result in new reducing end groups, but these groups are not expected to undergo peeling reactions in these oxidative treatments.

An apparently conflicting result is that NaOH addition resulted only in a small decrease in the amount of polysaccharides, although at the same time the composition of polysaccharides changed to some extent. At higher treatment temperatures this phenomenon was more clearly observed. Amount of the glucose moieties in the polysaccharides increased during the treatments with NaOH addition, which probably indicated some condensation reactions between carbohydrates and lignin during treatments. Obviously, the degradation of polysaccharides occurred also in these treatments, but degradation led to formation of high molecular mass lignin-carbohydrate complexes, which remained in a dialysis membrane tube and were detected in polysaccharide analysis. Such condensation reactions between hemicelluloses and lignin under kraft cooking conditions have been detected in earlier studies [24, 25]. Glucomannan, especially, has been noted [25] to form condensates with lignin, which could explain in this case the increase in glucose units in polysaccharides. In contrast, as expected in the treatments without NaOH addition, the composition of the polysaccharides remained almost unchanged.

CONCLUSIONS

The results indicated that the oxidative heat treatment with the presence of excess alkali decreased significantly the viscosity of hardwood kraft black liquor. It can be expected that viscosity of black liquor is greatly dependent on various macromolecules present in black liquor. In this study, the main reason for viscosity decrease was considered to be the degradation of the high molecular mass fraction (M > 10,000 Da) of lignin. In contrast, the other macromolecular component, polysaccharides, was not affected much by the treatment conditions. In addition, the chemical composition of low molecular mass aliphatic acids was not changed during the treatments. Due to the small changes observed, a clear relationship between the viscosity and the chemical composition of black liquor could not be established. These findings indicate that some other factors, such as changes in physical properties of black liquor during the treatments might have an important role in viscosity reduction. **TJ**

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INSIGHTS FROM THE AUTHORS

I have done a lot of studies concerning the chemical composition of different black liquors, so it was interesting to combine this knowledge with the important physical properties of these liquors. With respect to the industrial recovery of cooking chemicals, this kind of understanding is of great importance. The topic has also been the main focus of my postgraduate studies.

This research differs from previous studies by showing an interesting treatment method of black liquor for reducing the liquor's viscosity.

The most difficult aspect of this study was to detect detailed chemical changes taking place within the constituents of black liquor caused by this oxidizing treatment. However, we performed several relevant analyses to answer this question.

Due to the complex nature of black liquor, it was surprisingly difficult to find any straightforward reason for the decrease in viscosity that occurred during this treatment.

This paper shows many useful findings. The research shows that oxidative heat treatment significantly reduces black liquor viscosity. Thus, this treatment provides evaporation capacity and decreases the black liquor heating value. That, in turn, reduces the recovery boiler hearth heat release, which is beneficial when firing high solids black liquor. For this reason, this technique could offer an interesting alternative for reducing viscosity of black liquors.

One of the further steps would be to study, for example, the combustion properties of the oxidized black liquors.

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