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Role of lignin and sodium carbonate on the swelling behavior of black liquor droplets during combustion

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Abstract: A partial removal of lignin from black liquor (BL) by carbonation and lignin precipitation was studied. In lignin-lean BL droplets during combustion in a laboratory furnace at 800°C in stagnant air, the maximum swelling was decreased. This observation was interpreted as showing that the lignin content decrement is due mainly to removal of higher molar mass (HMM) lignin and that the Na₂CO₃ content of the BL is increased. Stepwise precipitation experiments with industrial softwood and hardwood kraft BLs by carbonation (resulting in pH decrement from 13 to 9) indicated that a fraction of HMM lignin (MM >10 kDa) with a higher amount of carbohydrates precipitated more prominently and earlier than the fraction with lower molar mass (LMM) lignin (MM <10 kDa) containing less amounts of carbohydrates. Separate experiments with a 50/50 (by wt) mixture of different lignin fractions (1–5, 5–10 and >10 kDa) and BL-originated aliphatic carboxylic acids were performed and found that the mixture of medium MM fraction (MM 5–10 kDa) swelled more than the other lignin fractions. The addition of Na₂CO₃ to BL also reduced the maximum swelling of a BL droplet.

Keywords: black liquor, chemical recovery, droplet swelling, high definition video camera, lignin, kraft lignin, maximum swelling of droplets, molar mass, sodium carbonate

Introduction

Kraft pulping in the white liquor (aqueous solution of NaOH and Na₂S) removes the majority of the non-cellulosic wood materials and the cellulosic fiber (pulp) is retained. The spent cooking liquor [black liquor (BL)] is typically burned to recover the cooking chemicals (Na and S) and the energy deliberately provides heat, steam and electric power (Sjöström 1993; Alén 2011). The major organic component of BL is lignin, and its more sophisticated utilization than a simple energy source is still the matter of intensive investigation (Stewart 2008; de Wild et al. 2009; Kühnel et al. 2015; You et al. 2015; Li et al. 2016; Xiong et al. 2016; Cortés-Trivino et al. 2017; Park et al. 2017; Schmitt et al. 2017). The recovery of lignin from BL as a renewable resource is considered as a potentially profitable business for the pulping industry, which may also increase the pulping capacity by lowering the material load of the recovery boiler (Gellerstedt et al. 2012).

Lignin can be precipitated from the BL by introducing carbon dioxide (carbonation) to lower the pH, which has been commercially applied since the 1940s (Plunguian 1940; Alén et al. 1979). In practice, the CO₂-containing flue gas is mainly from the burning of lime mud in a lime kiln, and the precipitation is applied only to a part of the main BL stream (Tomani 2010). The precipitated lignin is removed by filtration, and the BL left is called lignin-lean BL. Figure 1 shows the LignoBoost lignin precipitation process. The filtrated lignin is washed and dried and has a wide application (Wallmo 2008). Both the filtrate and the lignin-lean BL are returned to the evaporation plant and mixed again into the main BL stream. Of course, this BL has a lower gross heating value and its combustion behavior is different from that of the initial BL (Vähä-Savo et al. 2014; Zhao et al. 2015). No explanation has been given as to why its maximum swelling is lower. On the other hand, swelling is the most important behavior of the in-flight droplets burning in the recovery boiler. High swelling droplets tend to be entrained more easily in the recovery boiler (harmful for the upper heat exchangers), while low swelling droplets tend to end up in the char bed still at their early devolatilization stage. The latter is disadvantageous for

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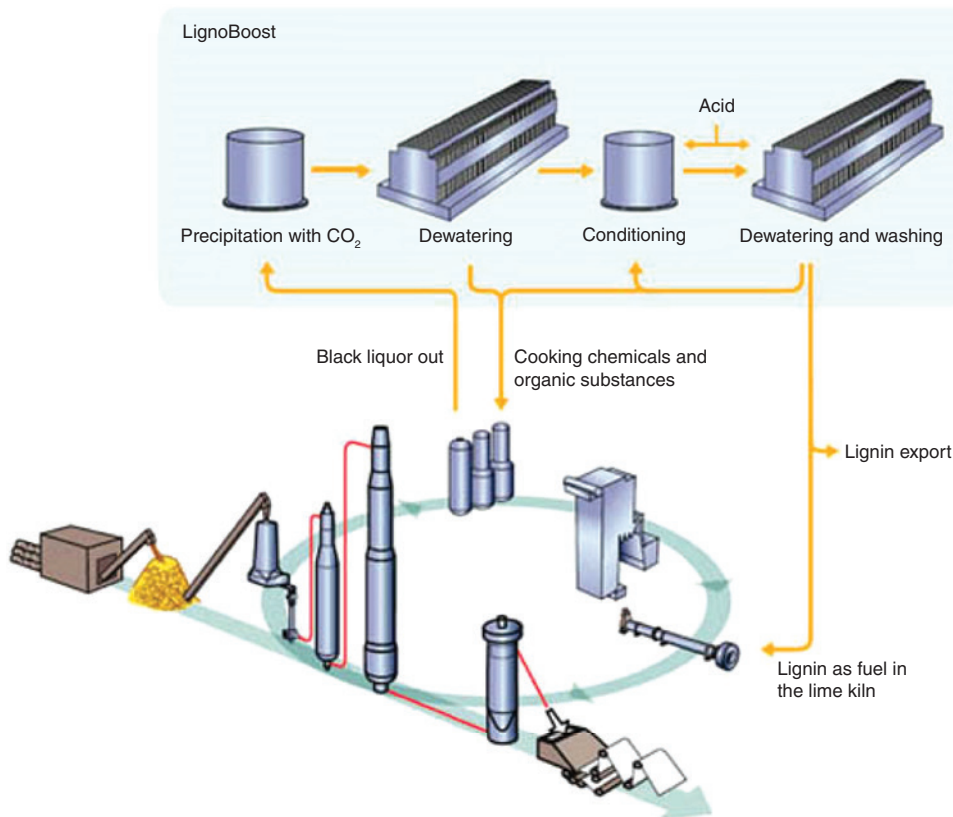


Figure 1: LignoBoost process (courtesy of Valmet).

the condition of the char bed. The BL carbonation process inevitably introduces a substantial amount of sodium carbonate into the BL, which is the major deadload and undesirable chemical in the recovery boiler (Adams 1997). The effect of Na_2CO_3 on the combustion behavior of BL droplets has not been investigated so far.

The present paper discusses the compositional changes of the carbonated lignin-lean BLs and the subsequent effect on the BL droplet swelling behavior in the recovery boiler. Special focus will be on (1) the role of lignin, including its content in BL and its molar mass distribution (MMD) and (2) the influence of Na_2CO_3 on swelling. These parameters are fundamental, if an integrated sub-biorefinery process of lignin precipitation is realized in the praxis.

Materials and methods

Carbonation of BL: Industrial softwood (SW, a mixture of 70% Scots pine, *Pinus sylvestris*, and 30% Norway spruce, *Picea abies*) and hardwood (HW, 100% birch, *Betula pendula*) kraft BLs were taken after pulping and subjected to a stepwise carbonation process to progressively separate lignin from the liquor. The initial pH for SW and HW BLs were about 14 and 13.5, respectively. Pure CO_2 was bubbled

through the BL at room temperature during the carbonation. When the target pH was reached, half of the carbonated BL was withdrawn from the reaction container and subjected to centrifugation (g value 2400, for 30 min) for lignin separation. The remaining BL underwent a second carbonation stage at an even lower pH value, in the course of which five to six target pH levels were considered, i.e. pH 12, 11.5, 11, 10.5, 10 and 9).

Fractionation of lignin: Three lignin fractions were prepared by membrane ultrafiltration of the SW and HW BLs, while the process was conducted by means of a Millipore pump (Millipore Pellicon Laboratory Cassette System; Merck Millipore, Darmstadt, Germany) with three different membranes with the cut-offs of 1 kDa, 5 kDa and 10 kDa. The BL circulated through the 10 kDa membrane, and the larger molecules retained by the membrane were flowing back to the stock as retentate and the smaller molecules which passed through were collected as the dilute permeate. A 0.1 M NaOH (Merck KGaA, Darmstadt, Germany) aqueous solution was added to the retentate and the filtration was repeated 3 times to flush as many of the smaller particles towards the permeate as possible. The permeate then served as the stock for the next filtration via the 5 kDa and 1 kDa membrane cut-offs, respectively. Finally, three fractions of lignin were obtained: (1) low-molar-mass (LMM) lignin (MM is 1–5 kDa) (2) medium-molar-mass (MMM) lignin (MM is 5–10 kDa) and (3) high-molar-mass (HMM) lignin (MM is >10 kDa). The lignin fraction without fractionation (the initial lignin) was prepared by adding 2 M sulfuric acid to the BL (for both SW and HW BLs) until a pH value of 2–3 was reached. The precipitated lignin was separated from the

acids fraction by centrifugation (g value 2400, for 30 min), which was then washed with deionized water thoroughly. After dissolving in a 0.1 M NaOH solution, this initial lignin was subjected to ultrafiltration on the 1 kDa membrane.

Organic acids fraction: The brown upper layer (almost transparent) of the acidified hardwood BL was used for the preparation of a BL organic acid fraction (BL-orgA). NaOH was added to neutralize the acidified liquid, and a large volume of methanol (MeOH) (Merck KGaA, Darmstadt, Germany) was added to it to precipitate sodium sulfate Na_2SO_4 (Fleischmann and Mersmann 1984). The precipitated Na_2SO_4 was removed by filtration. MeOH was recovered by vacuum evaporation of the liquor. The carbohydrate-derived aliphatic carboxylic acids were quantitatively characterized (see below).

Preparation of lignin-organic acids (L-orgA) mixtures: Different L-orgA mixtures were prepared by mixing the initial lignin and the other three lignin fractions and the orgA in a ratio of 50/50 (by wt). Additional initial L-orgA mixtures were synthesized by varying the lignin content, calculated as the mass ratio of L/total organics.

Combustion of BL droplets: All the synthetic BL samples were evaporated under reduced pressure at 40°C to a dry solids content of 55–75%. Then, 15–20 individual droplets around 9 mg in wet mass were burned in a laboratory furnace (Nabertherm L3, Nabertherm GmbH, Lilienthal, Germany) at 800°C in stagnant air (Figure 2) (Hupa et al. 1987). Droplet combustion was recorded by a high definition video camera (Cannon 60D, Japan). The pyrolysis and char burning times ($s\text{ mg}^{-1}$) were obtained from the video recording with the assistance of the VirtualDub software. The maximum swelling S_{max} of each droplet ($\text{cm}^3\text{ g}^{-1}$) was calculated based on an approximation of the swollen particle as an ideal sphere (Frederick et al. 1991; Frederick and Hupa 1997):

$$S_{\text{max}} = \frac{4}{3} A \sqrt{\frac{A}{\pi}} / m,$$

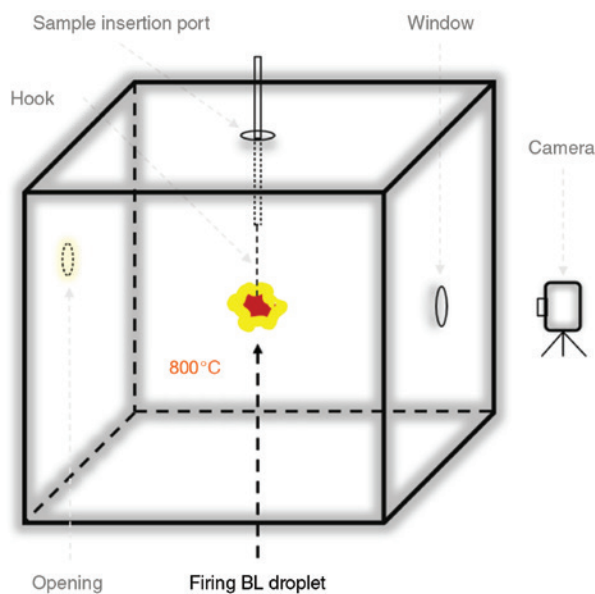


Figure 2: Model of muffle furnace for combustion tests.

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

Analytical methods: The lignin content of the carbonated BLs was determined via ultraviolet (UV) spectrophotometry (Beckman DU 640; Beckman Instruments Inc., Fullerton, CA, USA) at 280 nm (Alén and Hartus 1988). The samples were diluted with 0.1 M aqueous NaOH until the detected absorbance was between 0.3 and 0.8. The concentration (c) of dissolved lignin (g l^{-1}) was calculated according to the Beer-Lambert equation as $c = A / (a \cdot b)$, where A is the absorbance value (0.3–0.8), a is the absorptivity value, and b is the length of the light path (cm). The a values of 22.8 and 20.3 $\text{l g}^{-1}\text{ cm}^{-1}$ were used for mixed SW BL and birch HW BL, respectively.

A gel permeation chromatography (GPC) system [a Waters (Waters Corp., Milford, MA, USA) high performance liquid chromatography (HPLC) equipped with a Superdex 75 gel column (GE Healthcare, Amersham, UK) using 0.1 M aqueous NaOH as the eluent at a flow rate of 0.3 ml min^{-1}] was applied to determine the MMD of dissolved lignin in BL. A Waters 996 photodiode array detector at 280 nm served for detection. Calibration of the GPC system was carried out with a commercial set of protein standards (Sigma-Aldrich, St. Louis, MO, USA) and a number of lignin-like monomer and oligomer model compounds (Pakkanen and Alén 2012).

The volatile formic and acetic acid were determined as their benzyl esters by GC/FID. The sodium salts of the acids were acidified to obtain the free acids, and then converted into tetra-*n*-butyl ammonium (TBA) salts, and then esterified to benzyl esters prior to GC/FID (Agilent 6850 Series GC, Agilent Technologies, Palo Alto, CA, USA) (Alén et al. 1985).

Aliphatic hydroxy acids (hydroxy mono- and dicarboxylic acids) were determined as their per(trimethylsilyl)ated derivatives by GC/FID (Agilent 7820 Series GC, Agilent Technologies, Palo Alto, CA, USA). This method involves the conversion of the sodium salts into their ammonium salts before silylation for GC (Alén et al. 1984).

The content of carbohydrates in the lignin fractions was determined via sulfuric acid hydrolysis (TAPPI T 249 cm-00) combined with a Dionex HPAEC-PAD detection (Dionex, Sunnyvale, CA, USA) (Pakkanen and Alén 2013). A Dionex CarboPac PA-1 column (length 250 mm, 4 mm internal diameter) (Dionex, Sunnyvale, CA, USA) was applied to the separation at a flow rate of 1.0 ml min^{-1} . Post-column alkali (300 mM NaOH) addition was performed at a flow rate of 0.2 ml min^{-1} to enhance the PAD performance. The peak identification and the mass-based calibrations between an internal standard (L-fucose; Fluka Chemical Corporation, Seelze, Germany) and each monosaccharide were based on separate runs with model monosaccharides (all from Fluka Chemical Corporation, Seelze, Germany) (Pakkanen and Alén 2013).

Results and discussion

As pointed out in the Experimental section, different amounts of lignin separated from industrial hardwood (HW) and softwood (SW) kraft BLs were mixed with the organic acids (orgA) prepared from the same HW BL to observe the trend of their swelling behavior during combustion. It was found that increased lignin content had a

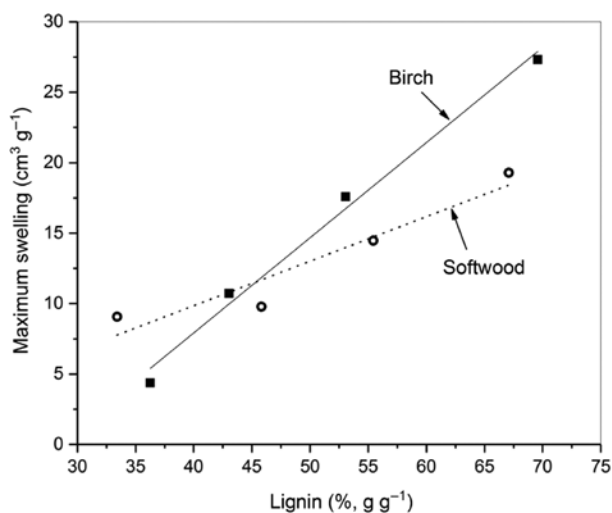


Figure 3: The influence of lignin content on droplet swelling.

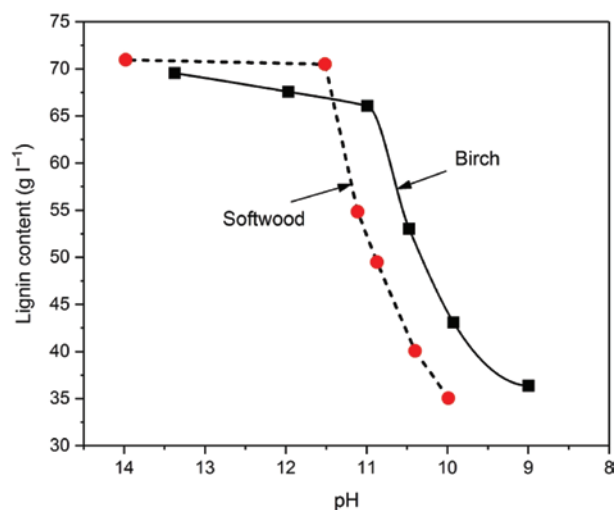


Figure 4: Dissolved lignin in the BL after stepwise carbonation.

positive and linear correlation with the maximum swelling of the L-orgA mixtures (Figure 3), indicating that lignin content has a direct influence on the degree of maximum swelling of BL droplets. Besides, HW L-orgA mixtures tended to swell more than the softwood mixtures as the lignin content increased. A similar trend has been observed previously (Alén 1994). Such a difference might be associated with the fact that HW lignin contains higher amounts of carbohydrates which facilitate the swelling of BL droplets during combustion (Chen et al. 2017).

As visible in Figure 4, the SW and HW lignin started to precipitate rapidly when pH was lower than 11.5 and 11.0, respectively. The removal of lignin was also demonstrated by the relative low lignin content compared to total organics in the BLs (Table 1). During the carbonation

Table 1: Main organic components of hardwood BLs after carbonation.

Component	Relative masses (%) at pH values of					
	13	12	11	10.5	10	9
Volatile acids	19	21	19	24	26	29
Hydroxy acids	20	16	23	22	25	27
Lignin	61	63	58	54	49	44

experiment, a considerable amount of carbohydrate-dominant sediment was obtained from the HW BL already at pH 12 prior to the rapid precipitation of lignin, while this was not observed in the case of SW BL. Accordingly, carbohydrates precipitate at a higher pH than lignin, which has also been observed during the acidification of bamboo

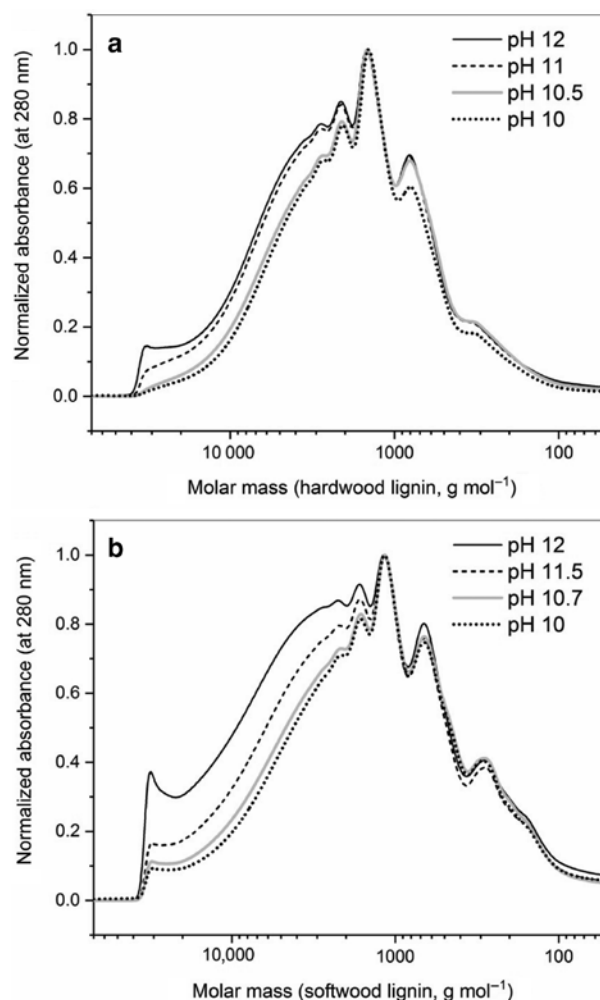


Figure 5: Higher MM lignins precipitated earlier than lower MM lignins. MM distribution of lignin after carbonation of hardwood (a) and softwood (b) BLs.

Table 2: Molar mass distribution of dissolved lignin in hardwood BLs [relative molar mass fraction (%) from the total lignin distribution].

MM (kDa)	Relative masses (%) at pH values of					
	13	12	11	10.5	10	9
>10	8	8	7	4	3	3
5–10	11	12	12	10	9	10
1–5	50	50	51	52	56	56
<1	31	30	30	34	32	31

BLs (Pakkanen et al. 2005). It is obvious that a considerable amount of carbohydrates is removed from the BL besides lignin during the practical carbonation process, which probably has also a negative effect on the droplet

swelling (Alén 1994). Additionally, a high content of carbohydrate-derived impurities in precipitated lignin is not desirable for many industrial applications.

The lignin MMD of the carbonated HW BLs indicates that the HMM lignin tended to precipitate earlier than the LMM lignin with a gradual decreasing pH (Figure 5). A comparison of the MMDs of dissolved lignins in the carbonated BLs shows in Table 2 that the proportion of the HMM lignin (MM >10 kDa) reduced significantly (from 8% down to 3%), while the relative proportion of the LMM fractions (MM <10 kDa) was stable or slightly increased (by up to 12%). Accordingly, the lignin separated during the carbonation process has a relatively high average MM (Figure 5).

The membrane ultrafiltration experiment demonstrated a good separation of lignin into three fractions, which can be seen from their molar mass distribution in Figure 6. The results of the exact carbohydrate

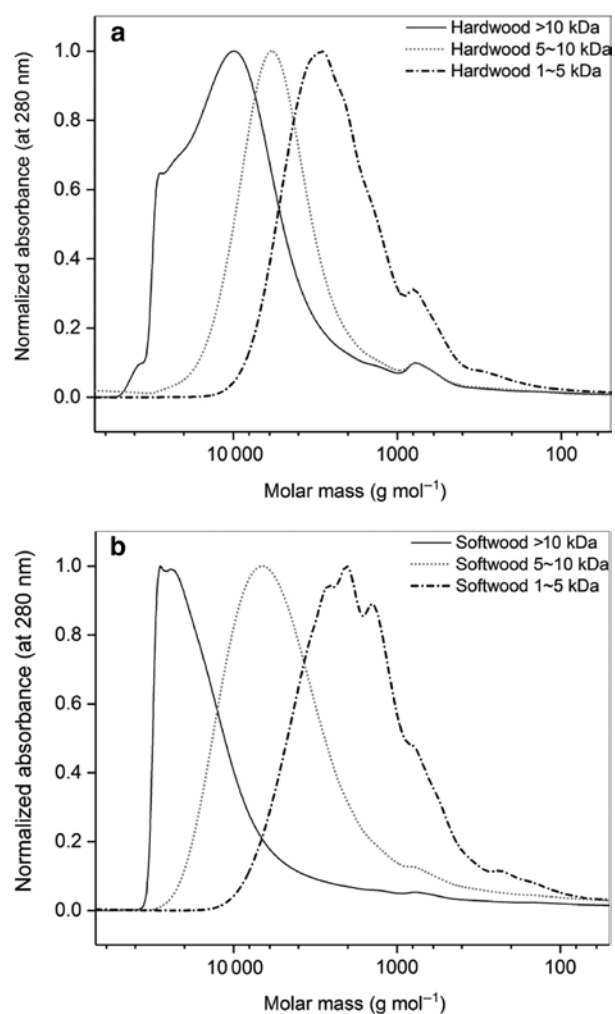


Figure 6: The irregular shape of hardwood lignin >10 kDa might be an effect of carbohydrates. MM distribution of different ultrafiltrated hardwood (a) and softwood (b) lignin fractions.

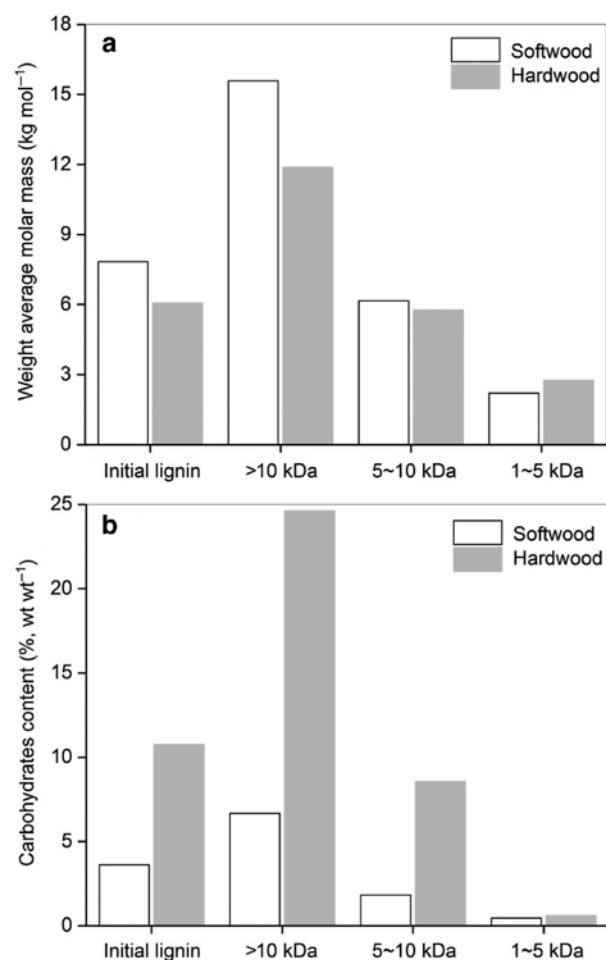


Figure 7: Higher molar mass was associated with higher carbohydrates content. Weight-average MM (a) and carbohydrates content (b) of different lignin fractions.

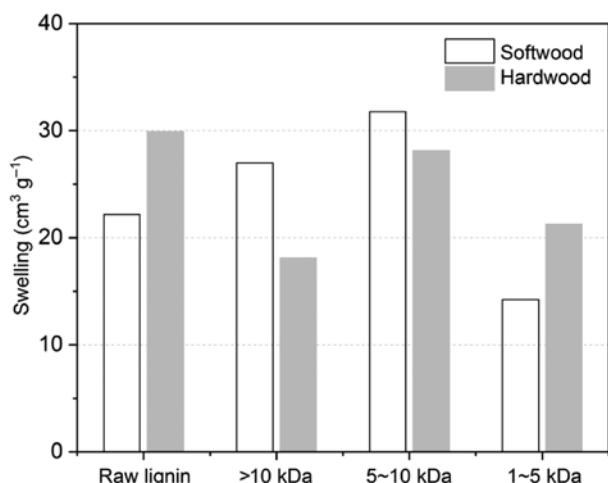


Figure 8: The swelling of different lignin-organic acids mixtures.

determination by membrane ultrafiltration in LMM, MMM and HMM lignins are presented in Figure 7. The MMDs of the fractions are different and HMM lignin contains substantially higher amounts of carbohydrates than the LMM fraction. As expected, the HW lignin contains much more carbohydrates than the SW lignin (Sjöström 1993). The carbohydrates in the former are mostly xylan (over 90% of the polysaccharides), while in the latter xylan accounts for 50–60% of the carbohydrates.

Concerning the swelling behavior, it was found that SW MMM lignin (5–10 kDa) swelled to the highest degree compared to other SW lignin fractions (Figure 8), while the HW MMM lignin swelled in a comparable degree to the initial lignin, but its swelling was more pronounced than that of the other two fractions. Two previous studies

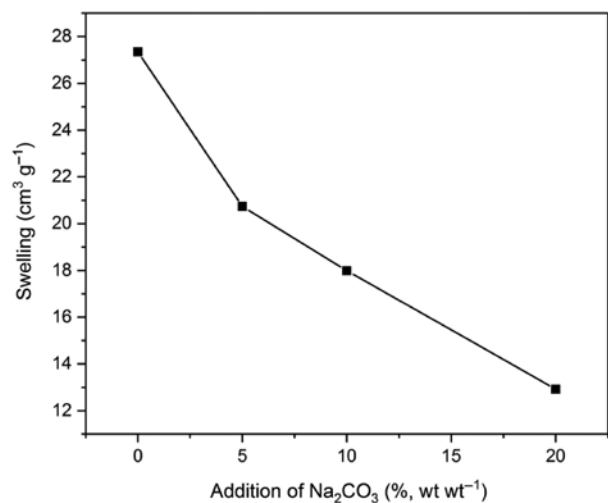


Figure 9: Influence of the addition of Na₂CO₃ on hardwood droplet swelling.

revealed contradictory swelling data: Miller et al. (1989) found a higher swelling for LMM, while Alén (1994) reported that HMM lignin (3.5–5 kDa) is associated with higher swelling.

The dead load chemical Na₂CO₃ plays a negative role in the course of chemical recovery operations: it leads to higher energy consumption, greater chemical losses, reduced equipment capacity and other operating problems. The differences in energy demand between a low and high dead load operation can be as much as 0.7 GJ per metric tons of pulp. Evaporators are likely to be affected most, but the green and white liquor system and recovery boiler are also influenced (Grace and Tran 2009). To collect more data in this context, different amounts of Na₂CO₃ were added to the HW BL and the following samples were obtained concerning their soda contents: 0% (initial BL), 5%, 10% and 20%. A 25% decrease in the maximum swelling was observed, when only 5% Na₂CO₃ was added to the BL (Figure 9). In practice, a slightly lower amount of Na₂CO₃ may be introduced, however, depending on the amount of BL subjected for carbonation. Moreover, a decrease in droplet swelling would influence the control and performance of the recovery boiler.

Conclusions

Carbonation of BL for lignin precipitation results in various changes, generally causing a droplet swelling decrement of the lignin-lean BL. The precipitated lignin is mostly a fraction of HMM lignin (MM >10 kDa) and it contains a significant amount of hemicelluloses as well. There is a linear correlation between maximum swelling and lignin content in BL. The BL swelling is not affected by the MMD of the residual dissolved lignin. Carbonation introduces more Na₂CO₃ to BL resulting in a marked decreasing droplet swelling.

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