*CELLULOSE CHEMISTRY AND TECHNOLOGY*

# CHARACTERIZATION OF LIGNIN DISSOLVED DURING ALKALINE SODIUM BOROHYDRIDE AND HYDROGEN PEROXIDE PRETREATMENTS OF SUGAR MAPLE (*ACER SACCHARUM*)

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Sugar maple (*Acer saccharum*) wood chips were pretreated with aqueous sodium hydroxide, sodium borohydride, and hydrogen peroxide pretreatments, and the characterization (*i.e.*, amount, molar masses, and molar mass distributions) of the lignin dissolved during the pretreatments was performed. Of the applied pretreatments, especially borohydride pretreatments were efficient in dissolving lignin from this feedstock, as 20% to 28% of the dissolved organics were found to consist of dissolved lignin, contributing to 3.4% to 9.0% of the initial wood lignin. Corresponding values for 2.5% and 5.0% alkaline peroxide pretreatments were from 5.9% to 9.2% dissolved lignin of the total dissolved organics and from 1.1% to 3.2% of the initial wood lignin. Additionally, determined molar masses and molar mass distributions indicated that borohydride pretreatments generally led to the formation of smaller-molar-mass lignin fragments when compared to reference pretreatments and to pretreatments conducted with alkaline peroxide process, indicating more efficient lignin degradation caused by borohydride addition. For example, Mn and Mw values of the analyzed reference effluents were 54%-62% and 66%-71% higher when compared to the corresponding borohydride effluents, respectively.

***Keywords***: hydrogen peroxide, lignin, molar mass distribution, pretreatment, sodium borohydride, sugar maple

## INTRODUCTION

Emerging bio-based industries, comprising various novel biorefinery operations integrated into conventional chemical pulping processes, have gained an increasing interest due to their potential for green manufacturing and business opportunities.[1-4] This interest is mainly due to the desire for utilizing the renewable lignocellulosic material more comprehensively, minimizing the formation of waste, and diversification of the product portfolio of the forest companies *via* utilizing whole lignocellulosic biomass in manufacture of biochemicals, composites, biofuels, chemical precursors, and commodities in an economically viable and sustainable way.[5-9] Integrated biorefineries are highly interdisciplinary ecosystems, which are based on numerous research fields, including process engineering, physico-chemical operations, biotechnology, agronomy/forestry, and environmental/techno-economic impact assessment.[10] Additionally, the diversity of available feedstocks, together with a plethora of pretreatment, conversion, and separation process options, by which biomass is transformed into value-added chemicals and biofuels, make this a complex topic. In a modern lignocellulosic biorefinery, currently under-utilized hemicellulose and lignin fractions are also recovered and utilized in manufacture of bio-based products.

Different pretreatment operations conducted prior to pulping operations have been proven to offer a promising pathway for producing hemicelluloses- and lignin-containing hydrolysates, which can be further refined into biochemicals and polymer precursors.[11-14]

Additionally, they can be used for enhancing the subsequent pulping operations in different ways.[15-19] During pretreatment, the structure and chemical composition of lignocellulosic materials are made increasingly accessible for cooking chemicals, rendering them more prone for delignification operations. On the other hand, by selecting pretreatment chemicals correctly, hemicelluloses can be partly preserved, and lignin dissolved more efficiently during the pulping operations.

One such chemical is sodium borohydride ($NaBH_4$), by which the reducing aldehyde end groups of carbohydrate chains can be transformed to primary alcohols and the effect of alkali-catalyzed primary peeling reactions can be decreased, leading to increased stability of hemicelluloses toward alkaline degradation and hence, to increased pulp yield.[20,21] On the other hand, also certain oxidative methods, such as utilization of alkaline hydrogen peroxide ($H_2O_2$) together with related hydroperoxide anion ($HOO^-$) and hydroxyl and superoxide anion radicals as mild oxidizing agents, have been used for enhancing the oxidation of lignin, leading to increased lignin solubility during pretreatments.[22-24]

As lignin is a complex three-dimensional amorphous polymer, which provides strength, rigidity, and resistance against degradation, its behavior during various biorefinery operations (*i.e.*, including pretreatments) lies at the heart of process design and efficient manufacturing practices.[25] From a chemical point of view, lignin is a complex polyphenol-derived polymeric resin, consisting of three main phenylpropane biosynthesis precursors: *trans*-coniferyl alcohol, *trans*-sinapyl alcohol, and *trans-p*-coumaryl alcohol, which all behave differently during chemical treatments.[26,27]

The main aim of this study was to characterize different lignin fractions dissolved after alkaline pretreatment using $NaBH_4$ and $H_2O_2$ at varying pretreatment time/temperatures in terms of lignin content, molar mass (MM), and molar mass distribution (MMD).

## EXPERIMENTAL

### Wood materials and pretreatments

Alkaline $NaBH_4$ and $H_2O_2$ pretreatments were conducted with screened sugar maple (*Acer saccharum*) wood chips (having maximum thickness of 7 mm, maximum width of 23 mm, and minimum width of 7 mm) dried at room temperature. Visible impurities, such as knots, bark pieces, and non-wood materials were removed manually prior to analytical procedures and pretreatments. Pretreatment experiments were conducted in an oil bath equipped with stainless steel reactors. In each experiment, 25 grams of screened oven-dried wood (odw) chips were loaded into the reactors, together with the chosen pretreatment chemicals. All chemical solutions were prepared with ultra-high quality (UHQ) water. Applied pretreatment conditions are presented in Table 1.

Stainless steel reactors loaded with chips and needed chemicals were immersed in an oil bath and heated until the total treatment time was achieved. In each case, a heating-up period of 15 min was added to the total treatment times. The liquid-to-wood ratio used in the experiments was adjusted to 5 L/kg. After each pretreatment, the reactors were cooled under cold tap water. Pretreatment effluents were separated from the treated chips by using nylon filtration bags. Effluents were collected in plastic storage bottles and stored in a freezer for further analyses. Determination of the dissolved materials was based on the yield analysis after each pretreatment. Oven-dried (dried at 105 °C) mass of the pretreated sample was subtracted from the original mass of the sample before pretreatment and the difference was expressed as "material dissolved during the pretreatment". Treated chips were forwarded to a subsequent pulping stage.

Table 1
Applied pretreatment conditions

| Pretreatment | Alkali charge (%/odw) | Additive (% of odw) | Temperature (°C) | Time (min) |
|---|---|---|---|---|
| $NaBH_4$ + NaOH | 4, 6, and 8 | 0.5% $NaBH_4$ | 50 and 80 | 60 and 120 |
| $H_2O_2$ (1) + NaOH | 4, 6, and 8 | 2.5% $H_2O_2$ | 50 and 80 | 60 and 120 |
| $H_2O_2$ (2) + NaOH | 4, 6, and 8 | 5.0% $H_2O_2$ | 50 and 80 | 60 and 120 |
| NaOH (reference)* | 4, 6, and 8 | - | 50 and 80 | 60 and 120 |

*Selected pretreatment conditions

### Analytical determinations – wood chips

For chemical analyses, air-dried wood chips were ground using a Wiley mill equipped with a bottom sieve with circular holes having perforation size <0.5 mm. The results reported are an average of duplicate determinations and calculated as percentage of dry sample. The extractives content of the wood samples was determined by Soxhlet extraction performed with 150 mL of acetone for an extraction time of 4 hours (6-10 percolations per hour). The mass of extractives was determined by evaporating the acetone in a fume hood. The lignin content of the wood chips used in the experiments was determined from extractives-free wood according to TAPPI Test Methods T222 om-98 and T249 cm-00 (for Klason and soluble lignin, respectively). The content of acid soluble lignin was determined using a Thermo Fisher Scientific's Nicolet Evolution 100 UV/Vis-spectrophotometer at 205 nm. The concentration (*c*) of dissolved lignin was calculated according to Equation 1:

$$c = \frac{A}{a * b} \tag{1}$$

where A is absorbance, *a* is absorptivity (110 L/(gcm))[28], and *b* is light path (cm).

The uronic acid anhydride content was determined using the chromophoric group analysis method described elsewhere.[29] The content of different monosaccharides (*i.e.*, arabinose, xylose, galactose, glucose, and mannose) in the Klason hydrolysates was determined using a Dionex high performance anion exchange chromatography system, equipped with a pulsed amperometric detector (HPAEC-PAD) and a CarboPac PA-1 column (250 mm x 4 mm inner diameter (i.d.)). Fucose was used as an internal standard to correct for the variation in the detector's response and an external standard called Paprican (unbleached eastern softwood kraft pulp, from FPInnovations, Quebec, Canada) was used along with five-level monosaccharide calibration standards to validate the accuracy of the analysis. The chemical composition of the carbohydrate fraction in each sample was calculated based on the anhydrosugars, as one water molecule is added to each monosaccharide moiety during the hydrolysis, along with the earlier data on the detailed chemical composition of cellulose, xylan, and glucomannans. Additionally, the assumed yield decrease (about 10%)[30] of these polysaccharides caused by different side reactions (*e.g.*, formation of furans) during acid hydrolysis is taken into account.

### Analytical determinations – pretreatment effluents

The content of dissolved lignin in the pretreatment effluents was determined with a Varian Cary 100 Conc UV/Vis -spectrophotometer at 280 nm. Samples were diluted until the absorbance of the samples was in the range 0.3 to 0.8 (*i.e.*, linear measurement range of the used spectrophotometer). The absorptivity value used for calculating the content of dissolved lignin was 21.7 L/(gcm).[31] The concentration (*c*) of dissolved lignin was calculated according to Equation 1.

The relative MMDs of the dissolved lignin were determined from alkaline effluents by size exclusion/gel permeation chromatography (SEC/GPC) using a Waters high-performance liquid chromatography (HPLC) system, equipped with an autosampler and a column (460 mm x 10 mm i.d.) filled with Superdex 75 gel (Pharmacia).[32] Prior to the analyses, samples were diluted with the used eluent (0.1 M NaOH filtered with a 0.45 µm membrane) and filtered with a 0.45 µm nylon syringe filter. The flow rate of the eluent was adjusted to 0.3 mL/min at room temperature. Detection was performed by using a Waters 996 photodiode array (PDA) detector within a wavelength range of 240–400 nm, and the wavelength of 280 nm was used for the determination of MMs. The calibration of the GPC system was performed with a commercial set of protein standards (MM range from 6,500 g/mol to 2,000,000 g/mol, from Sigma Aldrich) and a number of lignin-like monomer/oligomer model compounds (*i.e.*, vanillin, dehydrodiacetovanillone, rutin, and tannic acid, molar mass range from 152 g/mol to 1,701 g/mol).[33]

## RESULTS AND DISCUSSION

### Wood materials and pretreatments

The chemical composition of the feedstock material is presented in Table 2.

The amounts of material removed by the pretreatments are presented in Table 3. In general, all additives (*i.e.*, $NaBH_4$ and $H_2O_2$) increased the dissolution of the wood materials when compared to reference NaOH pretreatments. Higher alkali additions, longer pretreatment time, and higher pretreatment temperature led to higher removal rates of the wood material. Additionally, when the effects of the different pretreatment additives on the dissolution rates were compared, the addition of $H_2O_2$ to the pretreatment solution led to higher dissolution when compared to $NaBH_4$ pretreatments, especially when the pretreatment time was long, and temperature was high.

### Dissolved lignin from NaOH/$NaBH_4$ and NaOH pretreatments

Lignin parameters measured from NaOH/$NaBH_4$ pretreatment effluents are presented in Table 4. In general, more lignin was dissolved when the pretreatment time was prolonged, or the temperature was increased. Dissolved lignin contributed to 0.9%-2.4% of the total wood mass, and 3.4%-9.0% of the total wood lignin. Of the dissolved materials, lignin comprised 20.0%-27.7% of the total dissolved organics. Additionally, increasing the alkali charge also increased the amount of dissolved lignin.

The effects of applied alkali charge and pretreatment temperature/time on the $M_w$ of the dissolved lignin are presented in Figure 1. The effects of the pretreatment time and temperature on $M_n$ and $M_w$ values were clear, as the increase in these parameters caused $M_n$, $M_w$, and polydispersity values to increase. On the other hand, increasing alkali charge decreased all these values, indicating degradation of the dissolved lignin and formation of lower-MM lignin components.

Table 2
Chemical composition of sugar maple (*Acer saccharum*) wood chips (% of dry matter)

| Component | Content |
|---|---|
| Carbohydrates | 65.6 |
| Arabinan | 1.0 |
| Galactan | 0.5 |
| Glucan | 41.6 |
| Mannan | 2.0 |
| Xylan | 20.5 |
| Lignin | 26.3 |
| Acid-soluble | 2.6 |
| Klason | 23.7 |
| Acetone-soluble extractives | 1.4 |
| Others | 6.7 |
| 4-*O*-Methyl uronic anhydride | 3.5 |
| Acetyl groups | 2.9 |
| Ash | 0.3 |
| Total | 100.00 |

Table 3
Materials dissolved during $NaBH_4$+NaOH and NaOH pretreatments (% of odw)

| NaOH/$NaBH_4$ pretreatments | | | |
|---|---|---|---|
| Alkali charge (%/odw) | 4 | 6 | 8 |
| $NaBH_4$/50°C/60 min | 4.5 | 5.0 | 5.8 |
| $NaBH_4$/50°C/120 min | 5.3 | 6.3 | 6.3 |
| $NaBH_4$/80°C/60 min | 5.7 | 6.8 | 6.9 |
| $NaBH_4$/80°C/120 min | 6.1 | 8.1 | 8.5 |
| NaOH/$H_2O_2$ pretreatments with 2.5% $H_2O_2$ charge | | | |
| Alkali charge (%/odw) | 4 | 6 | 8 |
| 50°C/60 min | 3.9 | 5.2 | 6.0 |
| 50°C/120 min | 4.3 | 5.8 | 6.9 |
| 80°C/60 min | 5.4 | 7.0 | 8.3 |
| 80°C/120 min | 5.8 | 10.1 | 12.4 |
| NaOH/$H_2O_2$ pretreatments with 5.0% $H_2O_2$ charge | | | |
| Alkali charge (%/odw) | 4 | 6 | 8 |
| 50°C/60 min | 4.0 | 5.8 | 6.6 |
| 50°C/120 min | 5.0 | 6.6 | 8.1 |
| 80°C/60 min | 5.2 | 7.3 | 9.7 |
| 80°C/120 min | 6.0 | 10.2 | 12.9 |
| NaOH reference pretreatments | | | |
| Alkali charge (%/odw) | 4 | 6 | 8 |
| 50°C/60 min | 2.8 | 3.4 | nd* |
| 50°C/120 min | nd | 4.4 | nd |
| 80°C/60 min | nd | 5.4 | nd |
| 80°C/120 min | nd | 7.0 | 7.8 |

*not determined

The addition of alkali, while keeping temperature and time constant decreased the MM of the dissolved lignin (Fig. 1A). This could be connected to various alkaline degradation reactions, which led to fragmentation of the dissolved lignin into smaller MM fragments. On the other hand, increasing the pretreatment severity in terms of temperature and treatment time, while keeping the applied alkali charge constant tended to increase the MM of the dissolved lignin, *i.e.*, the higher the temperature or the longer the time was, the higher MM lignin could be observed in the hydrolysates. However, especially at low alkali charge pre-treatments, the increase of lignin MM in the hydrolysates could also be connected to condensation reactions caused by lower pH values. With low alkali additions, relatively more alkali was consumed in neutralization of the formed organic acids, especially acetic acid formed due to deacetylation of the acetyl groups present in xylan. Hence, the pH of the pretreatments conducted with low alkali additions decreases and might contribute to the MM of the dissolved lignin.

With respect to polydispersity, alkali additions led to decreased values, indicating that due to the added alkali, various degradation reactions started to take place and that the MM of the dissolved lignin was starting to reach more uniform values. On the other hand, keeping the alkali additions constant, but increasing the pretreatment severity otherwise resulted in higher variability with respect to lignin polydispersity, indicating a larger distribution in the structures of dissolved lignin when the overall pretreatment conditions become harsher.

The relative MMDs of the dissolved lignin from the NaOH/$NaBH_4$ pretreatments are presented in Figure 2. As already noticed in comparing, *e.g.*, the $M_w$ values, the effects of treatment time, temperature, and alkali addition on the MMs and MMDs could be clearly seen. In all cases, the relative MMDs were shifted to higher MM regions when alkali additions were low. Additionally, keeping the alkali additions constant, but simultaneously increasing the pretreatment severity otherwise (*i.e.*, increasing the treatment temperature and time) caused the MMDs to shift toward higher average MM.

Table 4
Lignin content, $M_n$, $M_w$ and $M_w/M_n$ of NaOH/$NaBH_4$ pretreatment effluents

| Pretreatment (temperature/time/ alkali charge) | Lignin (g/L) | Lignin (% of odw) | Lignin (% of dissolved materials) | Lignin (% of original lignin) | $M_n$ (g/mol) | $M_w$ (g/mol) | $M_w/M_n$ |
|---|---|---|---|---|---|---|---|
| 50°C/60min/4%[a] | 1.8 | 0.9 | 20.0 | 3.4 | 386 | 2,680 | 6.9 |
| 50°C/60min/6% | 2.1 | 1.1 | 21.0 | 4.0 | 392 | 2,620 | 6.7 |
| 50°C/60min/8% | 2.6 | 1.3 | 22.4 | 5.0 | 393 | 2,080 | 5.3 |
| 50°C/120min/4% | 2.5 | 1.3 | 23.6 | 4.8 | 408 | 3,120 | 7.6 |
| 50°C/120min/6% | 3.2 | 1.6 | 25.4 | 6.1 | 426 | 2,730 | 6.4 |
| 50°C/120min/8% | 3.2 | 1.6 | 25.4 | 6.1 | 396 | 2,110 | 5.3 |
| 80°C/60min/4% | 3.1 | 1.6 | 27.2 | 5.9 | 490 | 3,810 | 7.8 |
| 80°C/60min/6% | 3.6 | 1.8 | 26.5 | 6.9 | 424 | 2,840 | 6.7 |
| 80°C/60min/8% | 3.5 | 1.8 | 25.4 | 6.7 | 398 | 2,510 | 6.3 |
| 80°C/120min/4% | 3.2 | 1.6 | 26.2 | 6.1 | 608 | 5,540 | 9.1 |
| 80°C/120min/6% | 4.3 | 2.2 | 26.5 | 8.2 | 431 | 3,250 | 7.5 |
| 80°C/120min/8% | 4.7 | 2.4 | 27.7 | 9.0 | 421 | 3,080 | 7.3 |

[a] $NaBH_4$ charge 0.5% in all cases

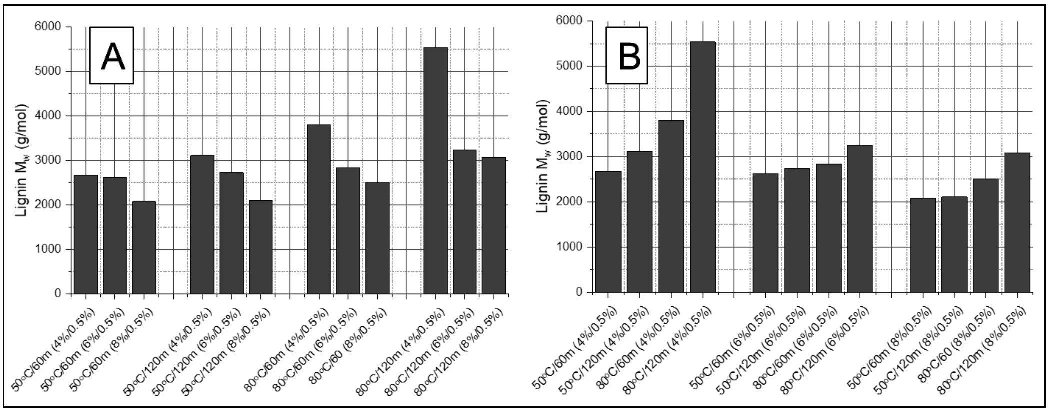

Figure 1: $M_w$ of dissolved lignin in NaOH/NaBH$_4$ effluents; effect of alkali charge (A) and effect of temperature/time (B) of the pretreatment

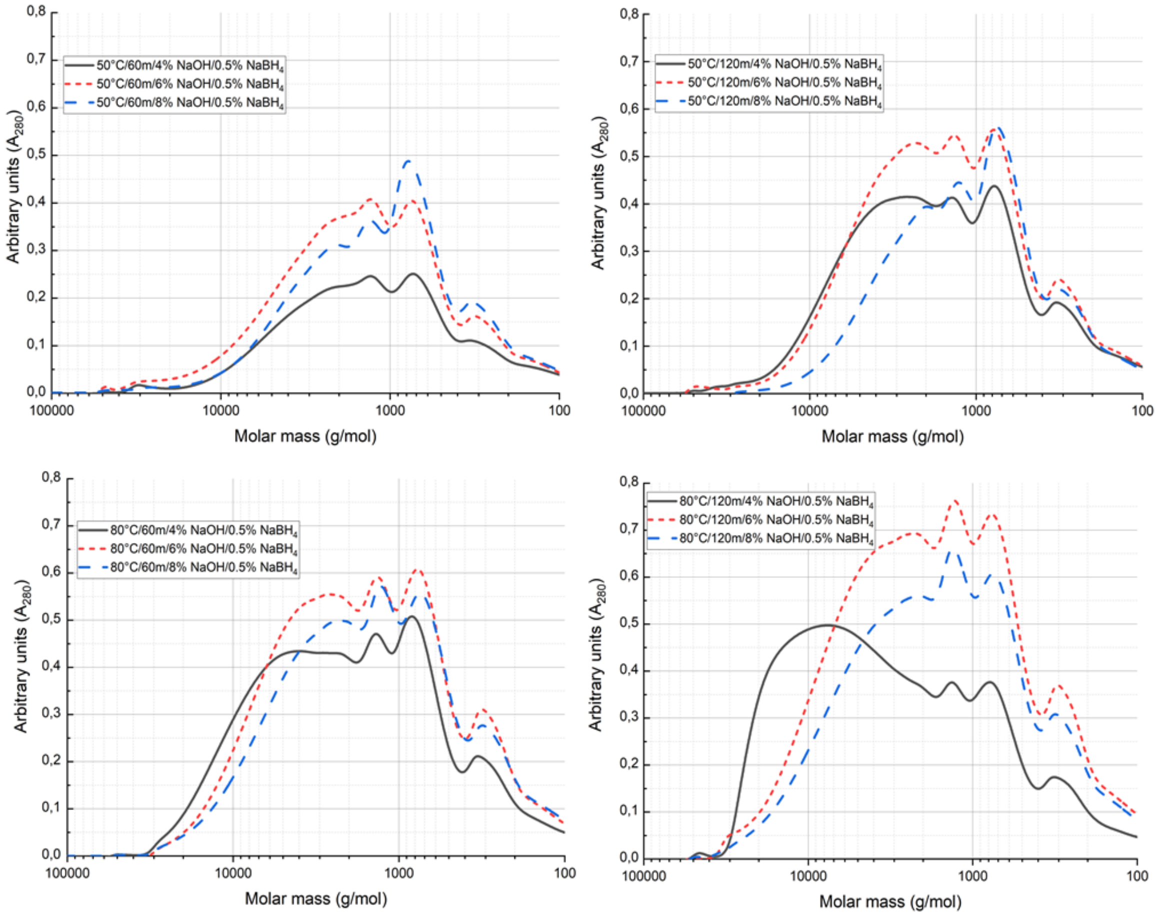

Figure 2: MMDs of dissolved lignin in NaOH/NaBH$_4$ effluents

Lignin parameters measured from the reference alkali pretreatment (*i.e.*, NaOH treatments without NaBH$_4$ addition) effluents are presented in Table 5. Clearly, less lignin was dissolved during the reference pretreatments conducted without NaBH$_4$ additions, when compared to NaOH/NaBH$_4$ pretreatments, the dissolved lignin contributing only 1.0% to 3.4% of the original wood lignin (3.4% to 9.0% in NaOH/NaBH$_4$ pretreatments). Of the dissolved materials, the reference pretreatment lignin contributed from 9.0% to 11.6% of the total dissolved organics, whereas in the NaOH/NaBH$_4$ pretreatments, the corresponding values were from 20.0% to 27.7% of the total dissolved organic material. This indicated clearly more efficient dissolution of lignin during NaBH$_4$ pretreatments.

The $M_w$ and relative MMDs of the dissolved lignin from the reference NaOH pretreatments are presented in Figures 3 and 4, respectively. In terms of MM and polydispersity, smaller variation was observed in reference NaOH pretreatment effluents, when compared to the NaOH/NaBH$_4$ effluents. $M_w/M_n$ of the reference effluents varied between 5.5 and 6.3, which indicated clearly more uniform size dissolved lignin between the analyzed samples when compared to corresponding NaOH/NaBH$_4$ pretreatments having $M_w/M_n$ between 5.3 and 9.1. In general, the measured $M_w/M_n$ in NaOH/NaBH$_4$ effluents was 12%-26% higher when compared to the reference pretreatments, indicating more heterogeneous lignin in these effluents. On the other hand, $M_n$ and $M_w$ values were clearly higher in reference effluents. In the measured samples, $M_n$ and $M_w$ values of the analyzed reference effluents were 54%-62% and 66%-71% higher when compared with the corresponding NaOH/NaBH$_4$ effluents, respectively. However, it should be noted that the reference cooking set did not comprise completely the same set of treatment conditions as $NaOH/NaBH_4$ pretreatments, which could cause some uncertainty in result comparison.

Table 5

Lignin content (actual and relative contents), $M_n$, $M_w$, and $M_w/M_n$ of reference (NaOH pretreatment without $NaBH_4$ additions) effluents

| Pretreatment (temperature/time/ alkali charge) | Lignin (g/L) | Lignin (% of odw) | Lignin (% of dissolved materials) | Lignin (% of original lignin) | $M_n$ (g/mol) | $M_w$ (g/mol) | $M_w/M_n$ |
|---|---|---|---|---|---|---|---|
| 50°C/60min/4% | 0.5 | 0.3 | 9.0 | 1.0 | 720 | 4,080 | 5.7 |
| 50°C/60min/6% | 0.7 | 0.4 | 10.4 | 1.3 | 694 | 3,800 | 5.5 |
| 50°C/120min/6% | 0.8 | 0.4 | 9.1 | 1.5 | 682 | 3,880 | 5.7 |
| 80°C/60min/6% | 1.2 | 0.6 | 11.0 | 2.3 | 752 | 4,260 | 5.7 |
| 80°C/120min/6% | 1.6 | 0.8 | 11.4 | 3.1 | 752 | 4,770 | 6.3 |
| 80°C/120min/8% | 1.8 | 0.9 | 11.6 | 3.4 | 746 | 4,350 | 5.8 |

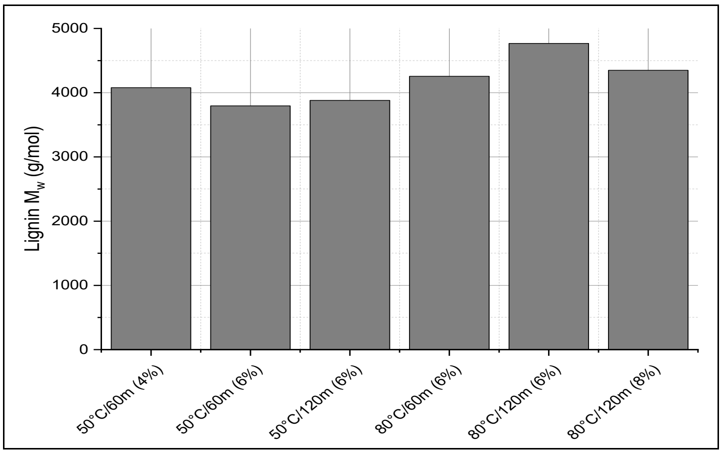

Figure 3: $M_w$ of dissolved lignin in NaOH reference effluents

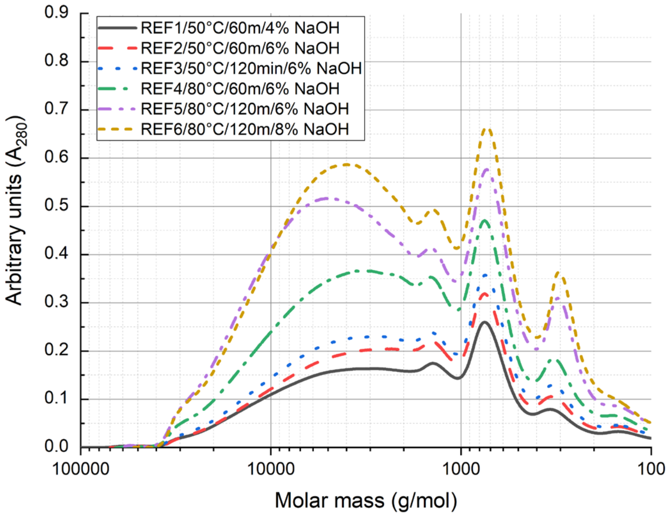

Figure 4: MMDs of dissolved lignin in NaOH reference effluents

### Dissolved lignin from $NaOH/H_2O_2$ pretreatments

Lignin parameters measured from $NaOH/H_2O_2$ (2.5% $H_2O_2$ addition) effluents are presented in Table 6. In terms of dissolution efficiency, adding 2.5% $H_2O_2$ to the pretreatment liquor did not cause any large beneficial effect on the lignin solubility, the values for lignin solubility being very close to those analyzed from the NaOH reference effluents. When compared to the reference pretreatments conducted only with NaOH, $H_2O_2$ addition resulted in a formation of smaller MM size lignin fragments in the effluents. $M_n$ and $M_w$ values were 0.15% to 15.8% and 5.1% to 18.1% higher in NaOH reference effluents compared to peroxide effluents, respectively. Additionally, $M_w/M_n$ of the dissolved lignin in reference effluents was found to be 1.8% to 10.3% higher, indicating more uniform size for the dissolved lignin in $H_2O_2$ effluents. For the above-mentioned reasons, it seemed that adding 2.5% $H_2O_2$ resulted in slightly higher lignin fragmentation.

The $M_w$ and relative MMDs of the dissolved lignin from the NaOH/2.5% $H_2O_2$ pretreatments are presented in Figures 5 and 6, respectively. When the samples from NaOH/$NaBH_4$ and NaOH/$H_2O_2$ pretreatments were compared, the differences between the two pretreatments were even more pronounced. Lignin analyzed from NaOH/$H_2O_2$ effluents was clearly of larger size, compared to that analyzed from NaOH/$NaBH_4$ pretreatment effluents. $M_n$ and $M_w$ values were 49.3% to 71.3% and 20.3% to 34.7% higher in NaOH/$H_2O_2$ effluents, respectively. In general, the overall phenomena (in terms of lignin MMs) taking place in NaOH/$NaBH_4$ and NaOH/$H_2O_2$ treatments followed the same path. When the pretreatment time and temperature were kept constant and alkali charge was increased, smaller MM lignin fragments were analyzed in the liquors for both cases. On the other hand, when the alkali charge was kept constant and temperature/time of the pretreatments were increased, the formation of higher MM lignin was observed. However, these differences were clearly more pronounced in the NaOH/$NaBH_4$ effluents when compared to NaOH/$H_2O_2$ pretreatment effluents after 2.5% $H_2O_2$ additions.

Table 6
Lignin content, $M_n$, $M_w$, and $M_w/M_n$ in NaOH/2.5% $H_2O_2$ pretreatment effluents

| Pretreatment (temperature/time/ alkali charge) | Lignin (g/L) | Lignin (% of odw) | Lignin (% of dissolved materials) | Lignin (% of original lignin) | $M_n$ (g/mol) | $M_w$ (g/mol) | $M_w/M_n$ |
|---|---|---|---|---|---|---|---|
| 50°C/60min/4%[a] | 0.6 | 0.3 | 7.6 | 1.1 | 612 | 3,410 | 5.6 |
| 50°C/60min/6% | 0.8 | 0.4 | 7.7 | 1.5 | 654 | 3,460 | 5.3 |
| 50°C/60min/8% | 0.9 | 0.5 | 7.5 | 1.7 | 658 | 3,130 | 4.8 |
| 50°C/120min/4% | 0.8 | 0.4 | 9.2 | 1.5 | 562 | 3,420 | 6.1 |
| 50°C/120min/6% | 0.9 | 0.5 | 7.8 | 1.7 | 681 | 3,680 | 5.4 |
| 50°C/120min/8% | 1.1 | 0.6 | 9.1 | 2.1 | 667 | 3,340 | 5.0 |
| 80°C/60min/4% | 0.9 | 0.5 | 8.3 | 1.7 | 588 | 3,730 | 6.3 |
| 80°C/60min/6% | 1.2 | 0.6 | 8.6 | 2.3 | 633 | 3,570 | 5.5 |
| 80°C/60min/8% | 1.4 | 0.7 | 8.4 | 2.7 | 700 | 3,620 | 5.2 |
| 80°C/120min/4% | 0.9 | 0.5 | 7.8 | 1.7 | 676 | 4,230 | 6.3 |
| 80°C/120min/6% | 1.4 | 0.7 | 6.9 | 2.7 | 679 | 3,900 | 5.7 |
| 80°C/120min/8% | 1.7 | 0.9 | 6.9 | 3.2 | 721 | 3,780 | 5.2 |

[a] $H_2O_2$ charge 2.5% in all cases

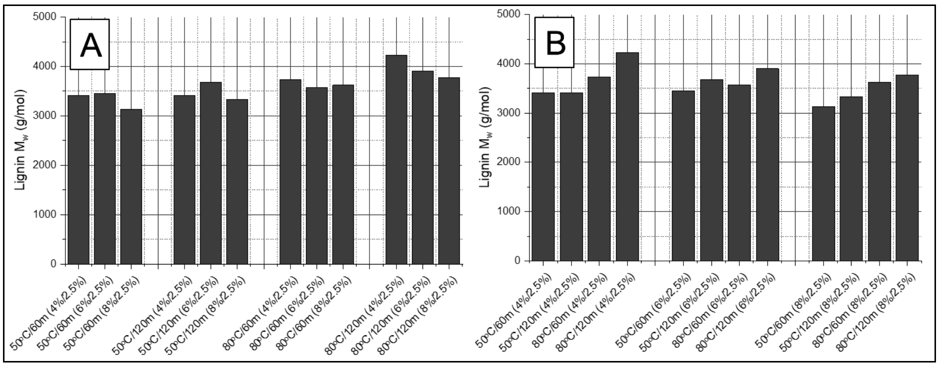

Figure 5: $M_w$ of dissolved lignin in NaOH/$H_2O_2$ (2.5% $H_2O_2$) effluents; effect of alkali charge (A) and effect of temperature/time (B) of the pretreatment

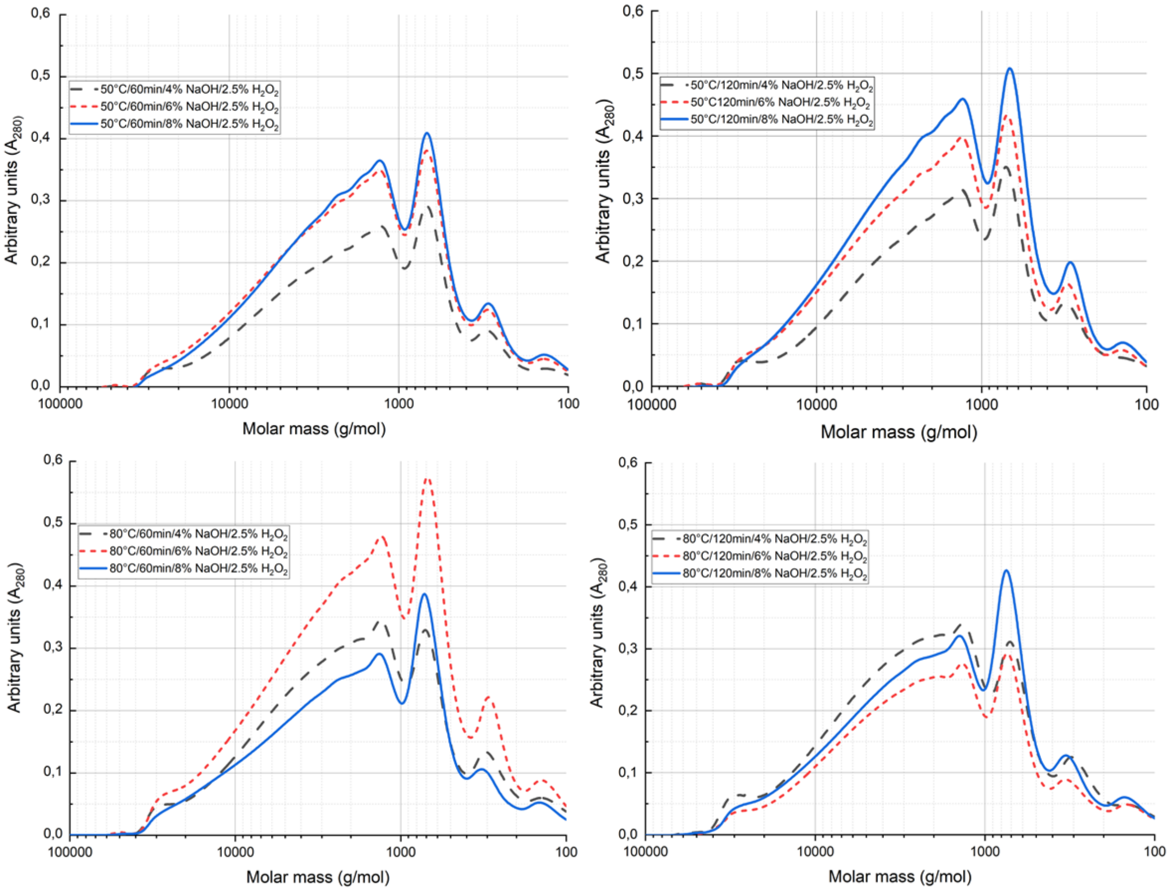

Figure 6: MMDs of dissolved lignin in NaOH/$H_2O_2$ (2.5% $H_2O_2$) effluents

Table 7
Lignin content, $M_n$, $M_w$, and $M_w/M_n$ in NaOH/5.0% $H_2O_2$ pretreatment effluents

| Pretreatment (temperature/time/ alkali charge) | Lignin content g/L | Lignin (% of odw) | Lignin (% of dissolved materials) | Lignin (% of original lignin) | $M_n$ (g/mol) | $M_w$ (g/mol) | $M_w/M_n$ |
|---|---|---|---|---|---|---|---|
| 50°C/60min/4%[a] | 0.5 | 0.3 | 6.2 | 1.0 | 649 | 3,510 | 5.5 |
| 50°C/60min/6% | 0.8 | 0.4 | 6.9 | 1.5 | 673 | 3,500 | 5.2 |
| 50°C/60min/8% | 1.0 | 0.5 | 7.6 | 1.9 | 670 | 3,440 | 5.1 |
| 50°C/120min/4% | 0.6 | 0.3 | 5.9 | 1.1 | 555 | 3,490 | 6.3 |
| 50°C/120min/6% | 0.9 | 0.5 | 6.8 | 1.7 | 672 | 3,760 | 5.6 |
| 50°C/120min/8% | 1.1 | 0.6 | 6.8 | 2.1 | 849 | 3,860 | 4.5 |
| 80°C/60min/4% | 0.9 | 0.5 | 8.7 | 1.7 | 716 | 4,170 | 5.8 |
| 80°C/60min/6% | 1.2 | 0.6 | 8.2 | 2.3 | 667 | 3,700 | 5.5 |
| 80°C/60min/8% | 1.5 | 0.8 | 7.7 | 2.9 | 712 | 3,640 | 5.1 |
| 80°C/120min/4% | 0.9 | 0.5 | 7.4 | 1.7 | 680 | 3,780 | 5.6 |
| 80°C/120min/6% | 1.4 | 0.7 | 6.8 | 2.7 | 789 | 4,460 | 5.7 |
| 80°C/120min/8% | 1.7 | 0.9 | 6.6 | 3.2 | 663 | 3,590 | 5.4 |

[a] $H_2O_2$ charge 5% in all cases

Lignin parameters measured from NaOH/$H_2O_2$ (5% $H_2O_2$ addition) effluents are presented in Table 7. In general, no clear difference in the amount of dissolved lignin could be observed between the pretreatments conducted with 2.5% and 5.0% $H_2O_2$ additions as the differences between the lignin dissolved at 2.5% and 5.0% $H_2O_2$ pretreatments were relatively small. The $M_w$ and relative MMDs of the dissolved lignin from the NaOH/5% $H_2O_2$ pretreatments are presented in Figures 7 and 8, respectively. $M_w$ values of the dissolved lignin were slightly higher in the effluents from 5% $H_2O_2$ additions when compared to 2.5% $H_2O_2$ pretreatments. However, as with

2.5% $H_2O_2$ pretreatments, the lignin dissolved in 5% $H_2O_2$ treatments was also clearly of larger size when compared to the $NaOH/NaBH_4$ pretreatments, indicating smaller degradation of the dissolved lignin during $NaOH/H_2O_2$ treatments.

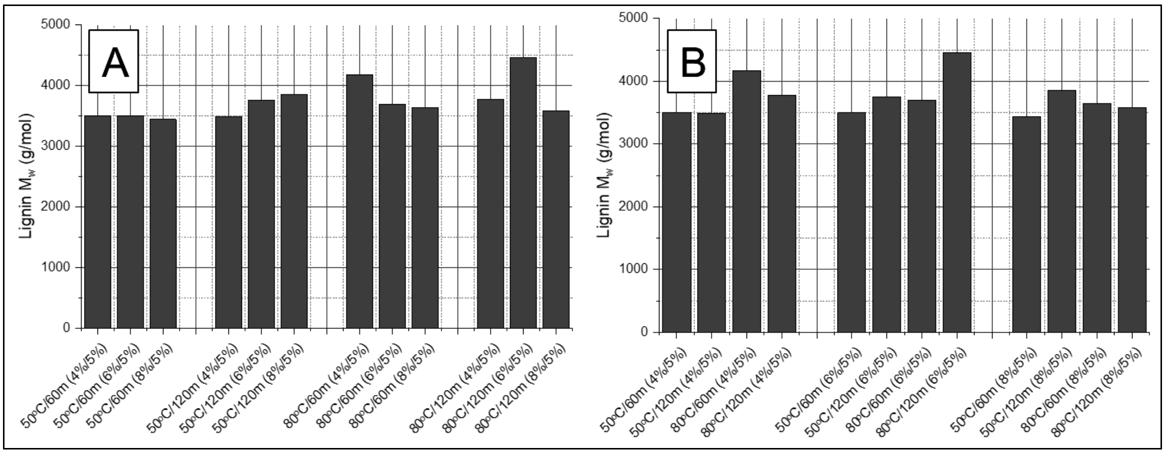

Figure 7: $M_w$ of dissolved lignin in $NaOH/H_2O_2$ (5% $H_2O_2$) hydrolysates; effect of alkali charge (A) and temperature/time (B) of the pretreatment

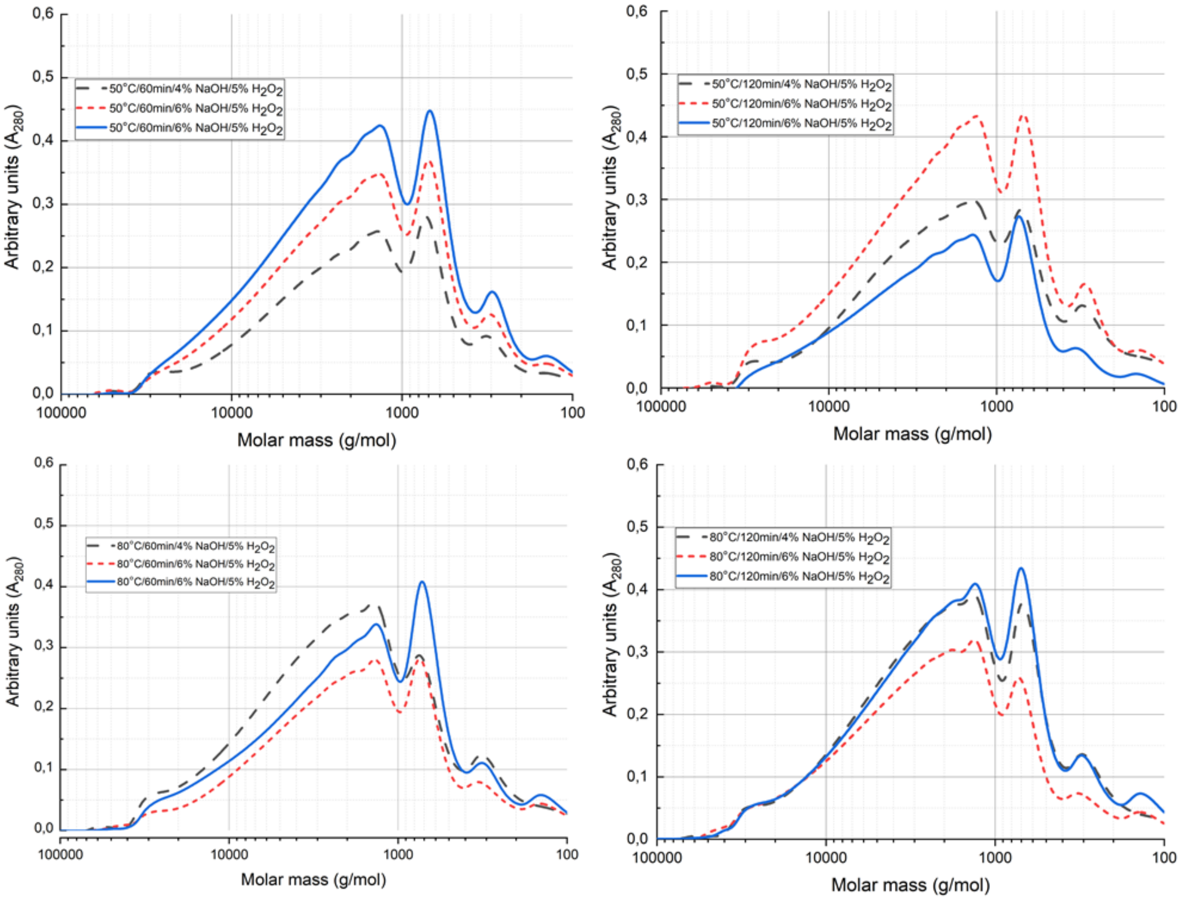

Figure 8: MMDs of dissolved lignin in $NaOH/H_2O_2$ (5.0% $H_2O_2$) effluents

When compared to the NaOH reference pretreatments, it could be concluded that, as with 2.5% $H_2O_2$ addition, 5% $H_2O_2$ addition led to the formation of smaller MM size lignin fragments in the effluents. $M_n$ and $M_w$ values were 3.1% to 12.7% and 3.3% to 21.2% higher in reference effluents compared to 5% $H_2O_2$ effluents, respectively. Additionally, the $M_w/M_n$ of the dissolved lignin in reference NaOH effluents was found to be 1.8% to 10.5% higher, again indicating more uniform size for the dissolved lignin present in $H_2O_2$ effluents.

## CONCLUSION

Aqueous $NaOH/NaBH_4$ and $NaOH/H_2O_2$ pretreatments, together with straightforward NaOH pretreatment as a reference method, were used for pretreating sugar maple wood chips prior to chemical pulping. The main aim of the pretreatments was to investigate if especially the dissolution of lignin could be enhanced by the applied pretreatments with additives. The pretreatments conducted with $NaOH/H_2O_2$ processes were found to be the most efficient in dissolving total wood material. However, of the used processes, the pretreatments conducted with $NaOH/NaBH_4$ were the best in dissolving lignin from the wood material, as the share of the dissolved lignin in these effluents reached up to 20.0%-27.7% of the total dissolved organics. The corresponding shares for dissolved lignin in 2.5% or 5.0% $NaOH/H_2O_2$ and NaOH pretreatments were clearly lower with 6.9%-9.2% (2.5% $H_2O_2$ addition), 6.2%-8.7% (5% $H_2O_2$ addition), and 9.0%-11.6% (NaOH pretreatment) shares, respectively. In terms of lignin MM and MMDs, the smallest lignin fragments were formed during $NaOH/NaBH_4$ pretreatments, indicating enhanced degradation of the dissolved lignin during these pretreatments. Clearly, the highest MMs were determined from the reference NaOH pretreatment effluents prepared without $NaBH_4$ or $H_2O_2$ additives.

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