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Effects of Catalysts and pH on Lignin in Partial Wet Oxidation of Wood and Straw Black Liquors

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ABSTRACT

Partial wet oxidation (PWO) of kraft black liquor (KBL) and wheat straw black liquor (WSBL) was carried out at temperatures 170–230 °C. PWO was conducted under oxygen gas only, or in the presence of iron catalysts or hydrogen peroxide as an additional oxidant. Unlike the catalysts, increasing temperature enhanced the PWO process in general. Lignin concentration decreased 57–64% and weight average molar mass of lignin from 2.7–3.3 kDa of original black liquors to 1.5–1.8 kDa after PWO at 210–230 °C. Unlike in KBL, presence of hemicellulose in WSBL was responsible for increasing total acid concentration from 16 g/L to 30 g/L in PWO at 230 °C. A two-stage process comprising lignin precipitation before subsequent PWO decreased chemical oxygen demand of the liquid fraction by 38–41%. Lignin was fractionated into a solid fraction and a water-soluble fraction which showed 21–26% lower polydispersity compared to lignin in the original black liquors.

1. INTRODUCTION

Lignin is the second most abundant biopolymer after cellulose and the first one based on aromatic groups. There is growing interest in converting lignin isolated from plant biomass to value-added chemicals or materials.¹ The largest industrial source of lignin is from cellulose pulp production, where lignin is thermochemically dissolved from wood. Kraft process is the dominant industrial pulping process where sodium sulfide and sodium hydroxide are the main chemical catalysts. The latter is the catalyst used in soda delignification of mainly annual plants.¹ Alkaline pretreatment of wheat straw is an efficient technique before subsequent enzymatic hydrolysis in a biorefinery of the biochemical type.²

The chemical recovery process of the modern pulp mill produces surplus energy from combustion of lignin.³ However, isolation of lignin may help to increase the production capacity of the pulp mill by debottlenecking the recovery boiler. Recovery of chemicals by combustion of soda black liquor may not be affordable due to the smaller capacity of these pulp mills. In contrast, isolation of lignin by precipitation could generate revenues and reduce chemical oxygen demand of the effluent.¹ Wet oxidation is an alternative method applied in treating industrial effluents and wastewater.⁴

In contrast to wet oxidation that aims at extensive conversion of organic material to carbon dioxide,⁵ partial wet oxidation (PWO) generates mainly water-soluble low molecular weight oxidation products. Some of these compounds are found at low concentrations in black liquor from which for instance hydroxy acids have been isolated by chromatographic and eletrodialysis techniques after separation of lignin.^{6,7} While alkaline wet oxidation has been assessed as lignocellulose pretreatment ahead of enzymatic hydrolysis of cellulose,^{8,9} PWO would be an advantageous option for processing of black liquors since they already comprise the alkaline catalyst.

A previous work on alkaline wet oxidation reported up to 13.5% yield of organic acids and 0.5% of low molecular weight phenolic compounds from wheat straw on weight basis.¹⁰ Muddassar and co-workers found recently that PWO of wheat straw black liquor yielded more organic acids than obtained from PWO of kraft black liquor.¹¹ A range of organic acids including formic acid, acetic acid, lactic acid, malic acid, succinic acid, oxalic acid and heavier hydroxy acids were detected. However, data is lacking concerning the effect of pH and process conditions on yield of organic acids and properties of lignin from PWO of black liquor. This information would be important for instance because oxidation of lignin may help to avoid its co-precipitation with silicates, an inherent problem involved in desilication of soda black liquors.¹² In the current work, effect of temperature and iron and hydrogen peroxide catalysts on PWO of wood and straw black liquors was investigated. In the second part of the work, concentrated black liquors were subjected to a two-stage process comprising carbonation before PWO of the liquid phase. Efficacy of the processes is discussed relative to the treatment conditions, yield of organic acids, and changes in concentration and molar mass properties of lignin.

2. EXPERIMENTAL DETAILS

2.1 Materials

The raw materials used in the experiments were kraft black liquor (KBL) and wheat straw black liquor (WSBL). KBL was obtained from a commercial kraft pulping plant in Finland and WSBL from a bench-scale process comprising 5 h cooking of pre-extracted wheat straw at 140 °C in 4 w-% NaOH solution.¹³ Pure oxygen (99.99 w-%) and carbon dioxide (99.99 w-%) were purchased from AGA (Finland). Iron supported by activated carbon (Fe/AC), Fe/AC with hydrogen peroxide (H₂O₂) from 35 w-% aqueous solution (Sigma-Aldrich), and ferric sulfate, Fe₂(SO₄)₃ (MP Biomedicals) were the catalysts used in the current work. This selection was made based on reported potential of these catalysts. Activated carbon (AC) has a high surface area and potential to generate oxygenated free radicals that initiate the oxidation reaction.¹⁴ Supplementation of AC with iron increased its

activity by added acidity, while leaching and deactivation caused by coke deposition was also reduced.^{15,16} A small amount of hydrogen peroxide with AC may enhance the reaction rates.¹⁷ Ferric sulfate was an efficient catalyst in wet oxidation of pulp and paper mill effluents.¹⁸ The Fe/AC catalyst was prepared using a wet impregnation method. In this case, 3.876 g of AC (Merck, CAS#7440-44-0, 0.105–0.149 mm) was mixed with 8.0 mL of water containing 0.747 g of ferric nitrate nonahydrate, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Sigma-Aldrich). Drying at 70 °C overnight and then at 190 °C for 6 h gave iron content of 2.23 w-% in the Fe/AC catalyst. In order to minimize internal mass transfer resistance, the solid catalysts used were ground and sieved through a mesh size 0.149 mm stainless steel sieve (Oy Santasalo-Sohlberg Ab).

2.2 Black liquor treatments in the pressure reactor

Carbonation, PWO, and catalytic PWO experiments were carried out in a 100 mL AISI 316 SS high-pressure micro reactor (Parr model 4590) with maximum allowable operating pressure of 6 MPa.¹¹ The reactor was equipped with a mechanically driven four blade impeller operated at 800 rpm. The upper section of the reactor was equipped with a pressure gauge, a pressure relief valve, a gas inlet and outlet and a cooling water feed line. The reactor vessel was mounted to a temperature-controlled external electric heating jacket. The gases were fed from bottles via pressure regulator that maintained constant pressure in the reactor. The objective in the first experimental series was to determine how the catalysts affect PWO of KBL and WSBL. The experiments were performed in single batches containing 75 g of black liquor, either alone or in the presence of the solid catalyst or hydrogen peroxide as oxidant. The reactor was closed and preheated to 105 °C, and the remaining air was purged out of the reactor to avoid accumulation of nitrogen in the gas phase. The oxygen line was opened for a short period 30 °C below the desired reaction temperature of 170 °C or 230 °C. When the reaction temperature was reached the oxygen partial pressure was raised to 0.5 MPa. The pressure and temperature were constant during the treatment. After 30 min the oxygen feed was stopped and the reactor was cooled to room temperature in 5 minutes, and depressurized. The oxidation products from single

treatments were recovered for various analyses. Table 1 shows the operating conditions of the experiments.

Table 1: Operating conditions and catalysts used in the 30 min PWO treatments of WSBL and KBL at 0.5 MPa oxygen pressure.

Catalyst system	Catalyst in reaction mixture (w-%)	Fe content of catalyst (w-%)	H ₂ O ₂ in reaction mixture (w-%)	Temperature (°C)
-	-	-	-	170
Fe/AC	0.30	2.59	-	170
Fe/AC, H ₂ O ₂	0.29	2.59	1.0	170
Fe ₂ (SO ₄) ₃	0.30	27.9	-	170
-	-	-	-	230
Fe/AC	0.30	2.59	-	230
Fe/AC, H ₂ O ₂	0.29	2.59	1.0	230
Fe ₂ (SO ₄) ₃	0.30	27.9	-	230

The weight percentage concentrations of catalyst and 100% hydrogen peroxide are given relative to the total weight of the reaction mixture.

In the second experimental series, a two-stage process investigated effect of lignin concentration on PWO of black liquor (Fig. 1). This selection was made because it was anticipated that high lignin concentration might obstruct generation of oxidation products. To produce starting materials with varying lignin concentration, WSBL and KBL were concentrated two-fold by evaporation, and the concentrated liquors (80 g) were carbonated in the batch reactor for 5, 20, 30, or 45 min at 80 °C under 0.5 MPa CO₂ in order to decrease the pH and precipitate lignin. The liquid phase was separated by centrifugation, sampled for analysis, and subjected to 30 min PWO at 210 °C under 0.5 MPa O₂ partial pressure. The liquid fractions from single carbonation and PWO treatments were recovered for various analyses.

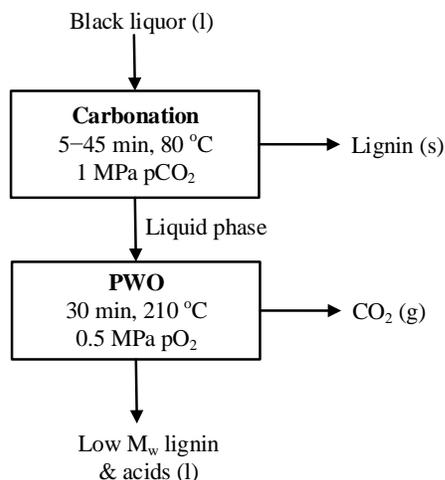


Figure 1: Flow diagram of the two-stage process approach.

2.3 Analysis of the black liquors

Original KBL and WSBL were quantitatively titrated until neutral pH using 12 M sulfuric acid, and the resulting suspensions were lyophilized. Lignin content of the lyophilized material was determined according to the two-stage sulfuric acid hydrolysis procedure.¹⁹ In the adapted method, 300 mg of material was mixed with 3 mL of 72 w-% sulfuric acid at 30 °C. After 1 h, the reaction mixture was diluted to 4 w-% sulfuric acid concentration by addition of water, and the suspension was heated in an autoclave at 121 °C for 1 h. The solid and liquid phases of the hydrolysis mixture were separated by filtration using glass crucible and a type GF/F (Whatman) glass fibre filter. Acid-insoluble lignin content was obtained from gravimetric analysis of the solid residue remaining on the filter after drying at 105 °C, and correction for its ash content. Absorbance at 205 nm of the filtrate was measured and used to calculate the acid-soluble lignin content from Beer-Lambert law ($\epsilon=110 \text{ mL}/(\text{mg}\cdot\text{cm})$). Carbohydrates were converted to monosaccharides by hydrolysis in 4% sulfuric acid (121 °C, 1 h) and analyzed with high-performance liquid chromatography (HPLC) system equipped with a type SPO810 (Shodex) chromatography column maintained at 60 °C. The column was eluted with deionized water at 0.7 mL/min, and the column effluent was monitored using a RID-10A refractive index (RI) detector (Shimadzu).²⁰ Glucose, xylose, galactose, arabinose, and mannose in the injected sample

(10 μL) were identified and quantified relative to the authentic standards used for external calibration in the linear concentration range 0.25–4.0 g/L. The composition results were corrected with the amount of sulfate originating from the neutralization step. The organic acids were determined using a type 2690 HPLC module (Waters) equipped with a Hi-Plex 300 mm \times 7.7 mm chromatography column (Agilent Technologies), and a type 2414 RI detector (Waters). In the HPLC analysis, 0.7 M sulfuric acid was added into the samples in order to reduce the pH suitable for the HPLC column. The injection volume was 10 μL , and the column at 65 $^{\circ}\text{C}$ was eluted with 0.005 mol/L sulfuric acid at flow rate 0.6 mL/min. The pH of the black liquors was measured at room temperature using a VWR pH100 meter. Concentration of dissolved solids was determined by the weight difference of 10 g sample that was evaporated to constant weight at 120 $^{\circ}\text{C}$. Weight average molar mass (\bar{M}_w), number average molar mass (\bar{M}_n), and polydispersity ($PD = \frac{\bar{M}_w}{\bar{M}_n}$) of lignin in the liquid fractions were determined with high-performance size-exclusion chromatography (HPSEC) using the previously described aqueous system.²¹ Lignin concentration was determined based on integration of the chromatograms obtained from VWD detector at 280 nm, and using original WSBL and KBL for calibration. Chromatographic analyses were carried out as single determinations unless otherwise mentioned.

3. RESULTS AND DISCUSSION

Alkaline black liquors are heterogeneous mixtures of lignin, carbohydrates, inorganic salts, organic acids, and various lignocellulose degradation products. KBL and WSBL contained approximately equal amounts of dissolved solids and lignin (Table 2). The organic acids present in KBL and WSBL may originate from hydrolytic cleavage of acetyl groups or base-catalyzed sugar degradation.²² It is suspected that the concentrations of lactic acid shown in Table 2 incorporate glycolic acid because these hydroxy acids were not resolved in the HPLC analysis. However, the focus in this investigation was on the effect of PWO on lignin rather than complete identification of the organic acids. One interesting feature of the black liquors was their relative high proportion of acid-soluble lignin (ASL) in addition

to acid-insoluble lignin (AIL). In WSBL, ASL comprised 23% of total lignin, compared to much lower proportion of 5–6% in isolated wheat straw lignins.²⁰

Table 2: Composition of the original and concentrated black liquors KBL and WSBL used as feedstock in the PWO treatments.

Feedstock	pH	Density (g/cm ³)	Dissolved solids (w-%)	AIL (g/L)	ASL (g/L)	Sugar (g/L)	Formic Acid (g/L)	Acetic Acid (g/L)	Lactic Acid (g/L)
KBL	12.8	na	10.8	62.6	14.5	3.5	9.4	3.1	5.1
c-KBL	13.0	1.13	19.3	111.9	25.9	6.2	16.8	5.6	9.0
WSBL	13.4	1.08	10.3	53.9	16.2	25.8	10.8	2.2	6.2
c-WSBL	13.3	na	21.5	112.5	33.8	53.9	22.7	4.6	13.0

c-, concentrated by evaporation; na, not analyzed; AIL, acid-insoluble lignin; ASL, acid-soluble lignin, Sugar, monosaccharides released from black liquors' carbohydrates in 4% sulfuric acid hydrolysis were calculated as anhydrous sugars. The data for pH and organic acids were obtained from single determinations. Other data are mean values of duplicate determinations, with average deviation relative to the mean < 5%.

3.1 Effect of catalysts and temperature on partial wet oxidation

The PWO treatments caused marked changes in KBL and WSBL. One of the key effects was the reduced alkalinity of KBL and WSBL from their initially highly alkaline pH of about 13. Apart hydrogen peroxide, the catalysts did not affect pH compared to the non-catalyzed PWO (Fig. 2). In contrast, when treatment temperature increased from 170 °C to 230 °C, pH decreased further with both black liquors. The final pH of the KBL treated at 230 °C was almost neutral, whereas WSBL remained slightly alkaline, given its higher initial pH. The resulting pH levels suggested acid formation as confirmed with HPLC analysis of the liquors (Fig. 3). Interestingly, the tested catalysts did not increase generation of organic acids compared to the sole PWO, but higher acid levels were obtained at 230 °C than at 170 °C with WSBL compared to smaller increases with KBL. Carbohydrates might play a role here since WSBL contained initially 25.8 g/L hemicellulose compared to 3.0 g/L in KBL (Table 2). A majority (96%) of the sugar residues of WSBL consisted of xylose and arabinose, the two pentose sugars being the main components of grass hemicellulose.²³ In KBL, 60% of sugars were glucose and galactose and the rest consisted of arabinose and

xylose. The higher initial concentration of more reactive pentose sugars in WSBL was the probable source of organic acids in PWO since lignin is suspected to be more resistant towards oxidation compared to hemicellulose. Moreover, reduction of TOC and COD after the PWO treatments indicated possible formation of carbon dioxide from further oxidation of the organic compounds (Fig. S1).

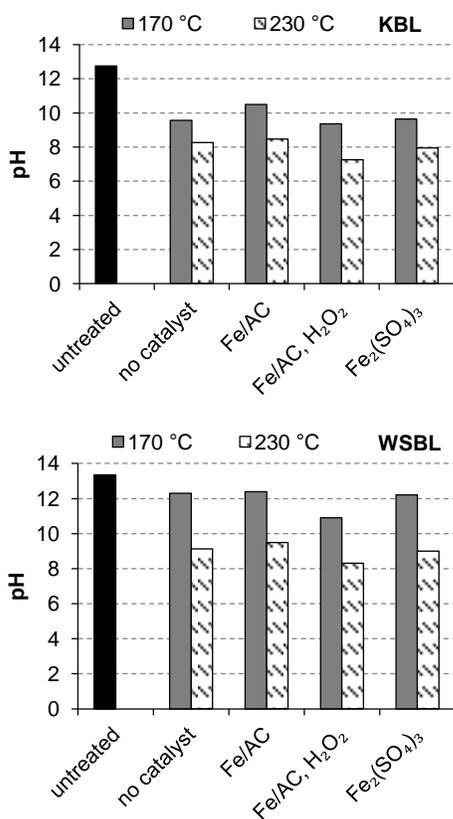


Figure 2: The effect of heterogeneous catalysts on pH of kraft black liquor (KBL) and wheat straw black liquor (WSBL) after PWO at 170 °C or 230 °C.

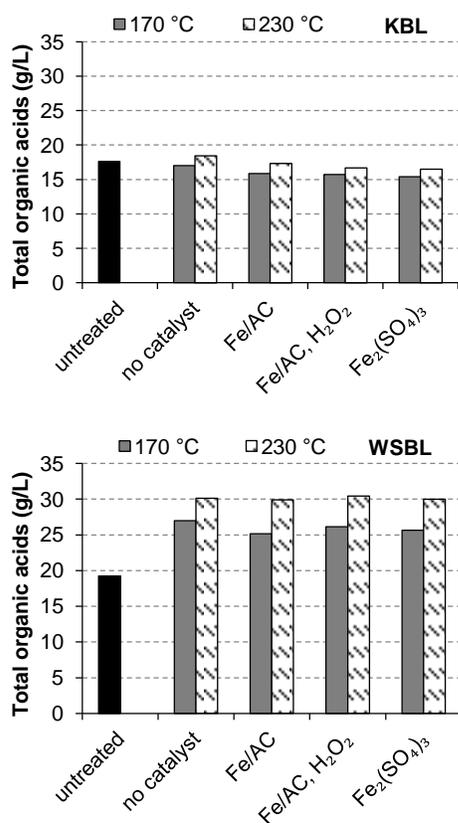


Figure 3: The effect of heterogeneous catalysts on total concentration of detected organic acids in kraft black liquor (KBL) and wheat straw black liquor (WSBL) after PWO at 170 °C or 230 °C.

The efficacy of the PWO treatments was followed by analysis of the concentration and molar mass distribution of lignin. Changes in lignin concentration were similar with KBL and WSBL (Fig. 4). Lignin concentration decreased most in the presence of H₂O₂. This strong degradative effect of hydrogen peroxide on lignin is in agreement with its well-known oxidative bleaching action.²⁴ Although the Fe/AC supplemented with H₂O₂ led to the lowest lignin concentration after PWO at 230 °C, other catalysts showed similar results as the non-catalytic PWO. Therefore, a portion of the lignin units which had resisted chemical cleavage in the pulping conditions degraded in the more severe PWO conditions.

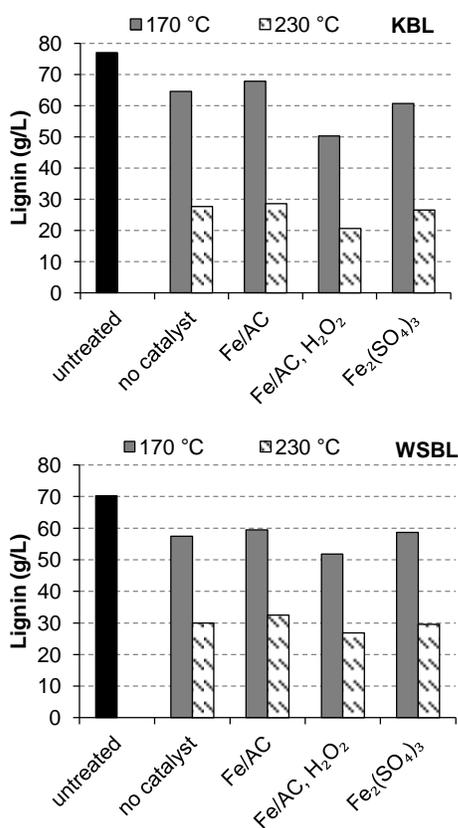


Figure 4: The effect of heterogeneous catalysts on concentration of lignin in kraft black liquor (KBL) and wheat straw black liquor (WSBL) after PWO at 170 °C or 230 °C.

Molar mass distribution is one of the key parameters of lignin with respect to its material properties.²⁵ Without PWO, the weight average molar mass (\bar{M}_w) of lignin was 3300 g/mol in KBL and 2730 g/mol in WSBL. These values are in agreement with the literature values.^{21,26} The treatments at 230 °C decreased weight average molar mass (\bar{M}_w) of lignin in KBL and WSBL more than PWO at 170 °C (Fig. 5). PWO at 230 °C decreased \bar{M}_w of KBL to 1800 g/mol and \bar{M}_w of WSBL to 1700 g/mol. However, while the use of hydrogen peroxide led to the lowest lignin concentration, this effect could not be observed in the \bar{M}_w of lignin. Thus, hydrogen peroxide did not selectively degrade lignin of any particular molecular weight. Instead, depolymerization of lignin occurred rather homogeneously and the main driver was the reaction temperature. Since the heterogeneous catalysts had only minor effect on the PWO process, further investigation was undertaken without heterogeneous catalyst in the two-stage process.

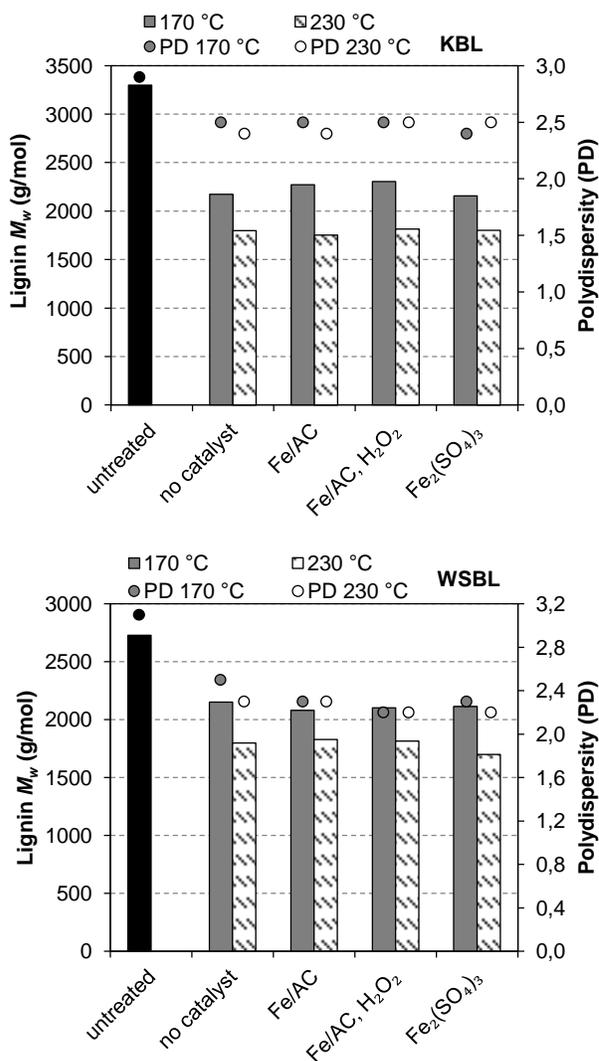


Figure 5: The effect of heterogeneous catalysts on weight average molar mass (\bar{M}_w) of lignin in kraft black liquor (KBL) and wheat straw black liquor (WSBL) after PWO at 170 °C or 230 °C.

3.2 Effect of carbonation of black liquor on partial wet oxidation

A two-stage process comprising carbonation of black liquor prior to PWO was investigated as a possible way to enhance oxidation of dissolved organic material. One of the key parameters of PWO in addition to temperature is the pH which was expected to decrease as a result of carbonation. Accordingly, pH of KBL and WSBL dropped from their initial values of 13.0 and 13.3 to 7.6 and 7.8 as a function of carbonation time (Fig. 6). PWO

decreased pH of the untreated black liquors and the liquid phases obtained from carbonation. However, no additional drop in pH occurred in PWO when the initial pH was below 8. Instead, PWO increased pH of the liquid obtained from WSBL with carbonation times exceeding 20 min. This observation could be explained by dissolution of alkaline carbonate salts and removal of carbon dioxide after PWO. Oxidation of lignin organic material might be obstructed at these near-neutral pH conditions. It was nonetheless apparent that precipitation occurred during carbonation of the black liquors. The chemical oxygen demand (COD), total organic carbon (TOC) and total suspended solids in the two black liquors were thus determined.

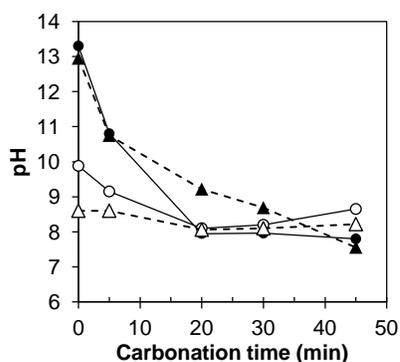


Figure 6: Effect of carbonation time on pH of kraft black liquor (triangles) and wheat straw black liquor (circles) before PWO (black markers) and after PWO of the liquid phase (white markers) at 210 °C.

As a result of carbonation, percentage of total suspended solids decreased in WSBL from 21.5% to 14.9%, but less in KBL (from 19.3% to 17.6%) (Fig. S2). It can be speculated that this difference resulted from the higher amount of hemicellulose precipitated from WSBL, given its nearly nine times higher initial carbohydrate content compared to KBL (Table 2). The above hypothesis is consistent with the COD which decreased more as a result of carbonation of WSBL than KBL (Fig. 7). Correlation of COD with pH suggested that precipitation was the main reason for the COD reduction after carbonation (data not shown). PWO decreased the solid concentrations further, as also observed from decreasing TOC levels. The final COD of KBL (115 g/L) was slightly lower than that of WSBL (123 g/L). The minimum TOC and COD concentrations obtained from concentrated KBL were

equal to the values of direct PWO of original KBL at 230 °C (Fig. S1). However, the percentage reduction of COD after carbonation and PWO was three times higher when KBL was concentrated to two-fold higher dissolved solids content relative to the original KBL. This difference suggests that lower pH resulting from carbonation could promote reduction of COD in PWO. The mechanism of alkaline oxidation of organic material is known to be combination of various free radical reactions involving reactive hydroxyl radicals.⁴ Formation of lignin in plants occurs via free radicals during lignification. It is thus expected that reactions between lignin-derived active radicals may compete with formation of low molecular weight products.

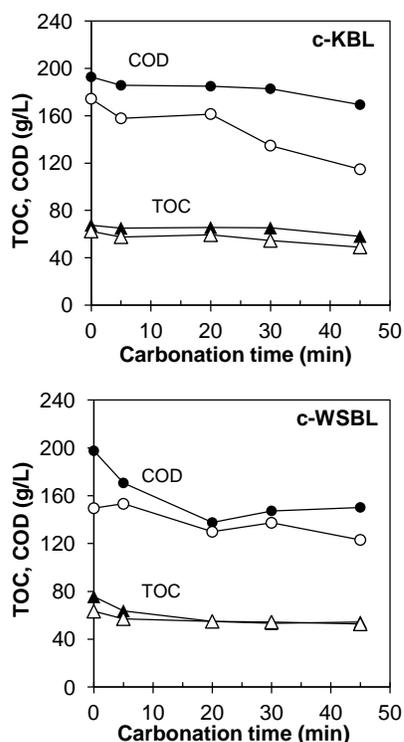


Figure 7: Effect of carbonation of kraft black liquor (KBL) and wheat straw black liquor (WSBL) on chemical oxygen demand (COD, circles) and total organic carbon (TOC, triangles) before PWO (black markers) and after PWO treatments of the liquid phase (white markers) at 210 °C.

The main target of carbonation in the two-stage process was to precipitate and intensify depolymerisation of lignin in order to obtain higher yield of organic acids. As was expected, lignin concentration of KBL and WSBL decreased rapidly, driven by pH

dependent precipitation (Fig. 8). With KBL, carbonation decreased concentration of lignin 57% from the initial level of 138 g/L to 58.6 g/L, while with WSBL the reduction was 67% from the initial level of 146 g/L to 48.3 g/L. The lowest lignin concentrations of 18–24 g/L were obtained from PWO of the liquid phase isolated after 20 min carbonation, and corresponding to pH values in the range of 8–9. Compared to the direct PWO of black liquors (Fig. 4), the two-stage process with 20 min carbonation involved much lower pH in PWO. Percentage reductions in lignin concentrations were either unaffected (KBL) or increased slightly (from 57.3% to 64.5% with WSBL) despite the differences in initial alkalinity. Previous studies have identified several alkaline oxidation products from lignin. Acetovanillone, vanillin, vanillic acid, and the corresponding syringyl compounds were detected from alkaline oxidation of wheat straw lignin in the presence of cupric oxide.²¹ These keto-, aldehyde, and carboxylic phenolic derivatives have also been observed after alkaline oxidation of hardwood kraft lignin,²⁷ whereas vanillin can be more selectively produced from softwood kraft lignin.²⁸ However, it is obvious that the products from alkaline oxidation of lignin are mixtures of low molecular weight phenolic derivatives and residual lignin. The first arise from units linked with alkali-labile aryl ether linkages, whereas the residual lignin skeletons are enriched in alkali-stable units linked via carbon-carbon bonds. Therefore, complete structural identification of the oxidation products may not be feasible. Molar mass properties of lignin were thus chosen for more detailed investigation.

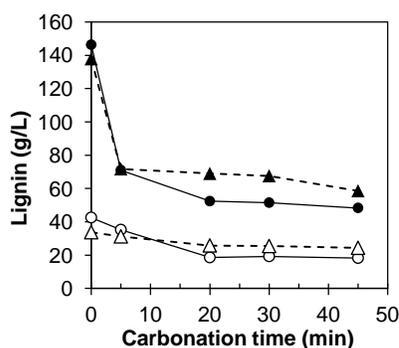


Figure 8: Effect of carbonation time on lignin concentration in concentrated kraft black liquor (c-KBL, triangles) and wheat straw black liquor (c-WSBL, circles) before PWO (black markers) and after PWO of the liquid phase (white markers) at 210 °C.

Unlike with the direct PWO treatments without carbonation, \bar{M}_w and PD of lignin were followed now in relation to the initial lignin concentration. Interestingly, 5 min carbonation increased lignin \bar{M}_w which thereafter dropped to a level only slightly lower compared to 3300 g/mol of non-concentrated KBL (Fig. 9). Similar trend was observed with WSBL with the exception that 20–45 min carbonation gave slightly higher \bar{M}_w of 3100–3200 g/mol compared to non-concentrated WSBL (2730 g/mol). After the liquid phases from carbonation were subjected to PWO at 210 °C, lignin \bar{M}_w from KBL decreased to 1500–1900 g/mol compared to almost similar values (1600–2000 g/mol) from WSBL. Changes in polydispersities followed those of \bar{M}_w . The lowest PD of 2.3 was obtained when lignin concentration before PWO was 50–60 g/l. These results suggest that concentration of lignin or prevailing pH had only minor effect on the depolymerization process. Instead, oxidative degradation of lignin appears to be possible at almost neutral pH.

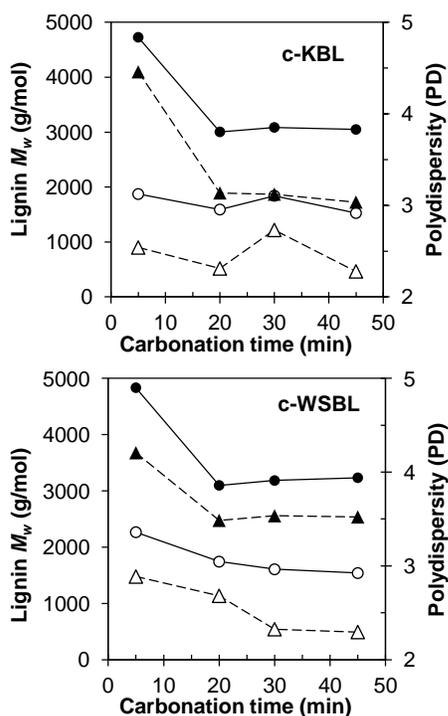


Figure 9: Effect of carbonation time on weight average molar mass (\bar{M}_w) (circles) and polydispersity (triangles) of lignin in concentrated kraft black liquor (c-KBL) and wheat straw black liquor (c-WSBL) before PWO (black markers) and after PWO treatments of the liquid phase (white markers) at 210 °C.

The main organic acids detected in the black liquors were formic acid, acetic acid and unresolved lactic acid and glycolic acid (Fig. S3). The obtained levels of organic acids revealed differences between the two black liquors. With KBL, concentrations of organic acids remained at 30–35 g/L regardless of carbonation or PWO (Fig. 10). With WSBL, the acid concentration increased in PWO compared to the values after carbonation. However, the highest level of organic acids (54.7 g/L) was obtained without carbonation from the direct PWO of concentrated WSBL. Comparison to the data in Fig. 3 shows that percentage increase in concentration of organic acids was lower in the two-stage process (35.7%) compared to the one obtained from direct PWO of WSBL (56.5%). Hence, the yield of organic acids could not be improved by removal of lignin from WSBL. It can be speculated that the acid-induced precipitation removed hemicellulose that is physically associated with and covalently linked to lignin in wheat straw.²⁹ Moreover, a majority of lignin was probably incompletely oxidized, or released different type of organic acids than arising from carbohydrates.

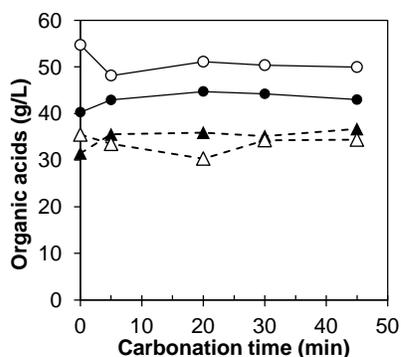


Figure 10: Effect of carbonation time on concentration of detected organic acids in concentrated kraft black liquor (c-KBL, triangles) and wheat straw black liquor (c-WSBL, circles) before PWO (black markers) and after PWO of the liquid phase (white markers) at 210 °C.

4. CONCLUSIONS

Partial wet oxidation of kraft and soda black liquors without catalyst gave results comparable to the catalyzed treatments. The two-stage process comprising carbonation

before subsequent PWO of the liquid phase was superior compared to the direct PWO, because it enabled a high level of lignin precipitation from either of the black liquors, while having only a minor impact on the yield of organic acids. To our surprise, degradation of lignin was not impeded by lower initial pH. This information could be exploited in the treatment of effluents of small-scale soda pulping plants or lignocellulosic biorefineries. Further work should elucidate the physicochemical properties of lignin resulting from the PWO process. More efficient depolymerization and separation of the low molecular weight lignin fractions could be investigated in view of finding suitable precursors for chemicals or new bio-sourced materials.

ACKNOWLEDGMENTS

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ASSOCIATED CONTENT

Fig. S1: COD and TOC of KBL and WSBL after PWO or catalytic PWO at 170 °C or 230 °C. Fig. S2: Total suspended solids of KBL and WSBL and the liquid phases from carbonation and after PWO at 210 °C. Fig. S3: organic acids detected in KBL and WSBL after carbonation and PWO of the liquid phase at 210 °C. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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