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Non-thermal Gas-phase Pulsed Corona Discharge for Lignin

Modification

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Abstract

Lignin has the potential to become a significant resource of renewable aromatics for the chemical industry. The current work studies pulsed corona discharge (PCD) as an alternative method for lignin modification. The effect of initial lignin concentration and gas phase composition on aldehydes formation was studied experimentally. Kraft lignin was used as a test compound. It was concluded in the work, that treatment in low oxygen content atmosphere and high initial lignin concentration leads to higher lignin conversion to aldehydes. Despite the proven aldehydes formation, the precise nature of the changes in the lignin structure during oxidation with PCD remained unclear. To address this question, a number of advanced analytical techniques were implemented: NMR, GPC, HSQC, HPSEC, and GCMS. The effect of PCD treatment on lignin structure was studied for two types of lignin: kraft lignin, purchased from Sigma Aldrich, and birch lignin acquired from a pressurized hot water extraction and soda pulped biorefinery process (BLN lignin). Changes in solubility, molecular weight and proportion of phenolic and aliphatic OH groups, as well as lignin repolymerization were detected. The findings are of value to efforts to make lignin modification tunable to the production of desired products.

Keywords. Lignin; Modification; Aldehydes; Cold Plasma; AOPs.

1. Introduction

Lignin is a potential raw material for the production of various products including phenolic substances and aromatic aldehydes. The pulp and paper industry is currently the main source of lignin. For annual production of 130 million tons of chemical pulps, approximately 60 million tons of kraft lignin and 4 million tons of liginosulfonates are produced. It has been estimated that only 1-2 % of the lignin is isolated from pulping liquors and used for chemical and material applications; the major part of industrial lignin is used as fuel for the production of process steam and energy [1].

Lignin decomposes very slowly and generates very high amounts of solid residue compared to other lignocellulose components. Thus, most biorefinery processes focus on utilization of more easily convertible fractions, and lignin has attracted much less attention [2]. However, lignin is a complex chemical compound and potentially a good source of valuable chemicals. One of the main challenges to its utilization is the irregular structure of lignin arising from the uncertain order of the phenylpropane unit linkages. Moreover, the structure of isolated lignin differs from that of native lignin, and composition, structure, types of monolignols and their combinations depend on the origin of the lignin, the pulping method, and the lignin isolation method [3–5]. The proportions of the structural elements derived from the three phenylpropanoid units (trans-coniferyl, trans-sinapyl, and trans-p-coumaryl alcohols) can vary significantly [6,7].

In spite of the difficulties, the subject of lignin chemical modification and its conversion to more value-added products has attracted researchers' attention since the beginning of the twentieth century. Currently, products obtained from lignin are mostly phenolic products. The reported yields for production of vanillin and syring aldehydes range from

8 to 15 % depending on the lignin type [8]. However, drawbacks of existing methods include severe toxicological problems with nitrocompounds. Furthermore, current methods are only effectively applicable to lignosulfonates and are not well-suited to kraft and hydrolysis lignins. Since only lignosulphonates are used as a raw material, the production of phenolic products, especially vanillin, exists as a supplementary operation in pulp mills with sulphite cooking. Other lignin types give much smaller yield [9–11].

The pulp and paper industry generates a significant amount of wastewater containing high concentrations of lignin, which cause increased COD and brown-colored effluents. The problem of high lignin concentration in wastewaters is more acute with thermomechanical and mechanical pulping processes than chemical pulping [12]. Lignin is difficult to degrade by microorganisms, and the lifetime of lignin in aqueous media in nature is counted in months. Consequently, conventional biological wastewater treatment is insufficient from the lignin removal point of view [13].

Pulsed corona discharge (PCD) can be applied as a treatment process not only for lignin removal from water but also for lignin modification to transform the lignin into a high value feedstock. The method has hydroxyl-radicals and ozone as the main oxidation species and is effective in oxidation of many organic molecules. The application of this electric discharge technique has previously been investigated by [14–17]. These studies showed a concentration of gas-phase discharges in close vicinity of the gas-liquid border.

The commercial application of electric discharge systems for such treatments is still in its infancy, and they are the subject of much study. The various systems and phenomena studied include: pulsed streamer discharges in liquid and gas-bubbled reactors with pulses at micro-second diapason [18,19], gas-phase dielectric barrier discharge (DBD) of various configurations [16,20,21], spark discharge (SD) in gas bubbles [22], pulsed

corona discharge (PCD) over the water surface [23,24], plasmotrons utilizing gliding arc discharge (GAD) for bombardment of treated surfaces with ionized gas [25–27], and PCD in water aerosol [28].

PCD generates plasma in the gas-phase atmosphere. While some research has been presented investigating how plasma affects lignin, very little work has specifically considered effect of plasma on lignin structure modification. Zhou et al. [29] studied the effect of oxygen plasma treatment on the glass transition temperature of enzymatic hydrolysis lignin. However, the lignin structure after treatment was not reported. Chirila et al. [30] and Nistor et al. [31] investigated modification of organosolv lignin powder with different carboxylic acids such as oleic, lactic and butyric acids and butyrolactone under cold plasma discharge. Although these papers studied the influence of carboxylic acids and butyrolactone, the plasma effect was not considered. In general, most work on lignin and plasma discharge effects presents information about changes in solubility, decrease in particle size, reduction in conductivity of the aqueous solutions and decrease in homogeneity, whereas consideration of changes in phenolic and aliphatic OH groups of lignin and changes in molecular weight have attracted less attention.

Panorel et al. [32] investigated implementation of PCD for lignin removal from water and for conversion of lignin into aldehydes. The PCD method was found to be an energy-efficient form of wastewater treatment, including for lignin removal from water. It was shown that the lignin oxidation efficiency of PCD is significantly higher than that of ozonation. Aldehydes formation was also detected during PCD treatment, but the yield was insignificant. Panorel used tannin-lignin method for determination of lignin concentration [33], however the test measures all hydroxylated aromatic compounds, including tannin, lignin, phenol and aldehydes. Therefore, it is not possible to accurately measure the concentration of lignin. Due to this reason, the results of calculations reported

by Panorel can be unreliable. Nevertheless, the main findings of the Panorel's research are unquestionable – if recovery of aldehydes is the main purpose, reduced oxygen content and high initial lignin concentration would offer potential for higher yields.

In spite of recent research, PCD methods can be considered as being under-investigated, especially as regards their use in modification of various materials into valuable products. This study has two main goals: to improve the lignin conversion to aldehydes during PCD treatment, and to investigate the influence of PCD treatment on phenolic and aliphatic OH groups and changes in molecular weight.

2. Materials and methods

Kraft lignin was selected as a test compound for investigation of the lignin conversion to aldehydes. The kraft lignin was a commercially available lignin purchased from Sigma Aldrich. Two types of lignin were selected for investigate the influence of PCD treatment on phenolic and aliphatic OH groups and changes in molecular weight; Sigma Aldrich kraft lignin and BLN lignin. BLN lignin was a birch lignin acquired from a pressurized hot water extraction and soda pulped biorefinery process [34,35].

The experimental system contains a pulsed corona discharge reactor and a high voltage pulse generator in the setup illustrated in Figure 1.

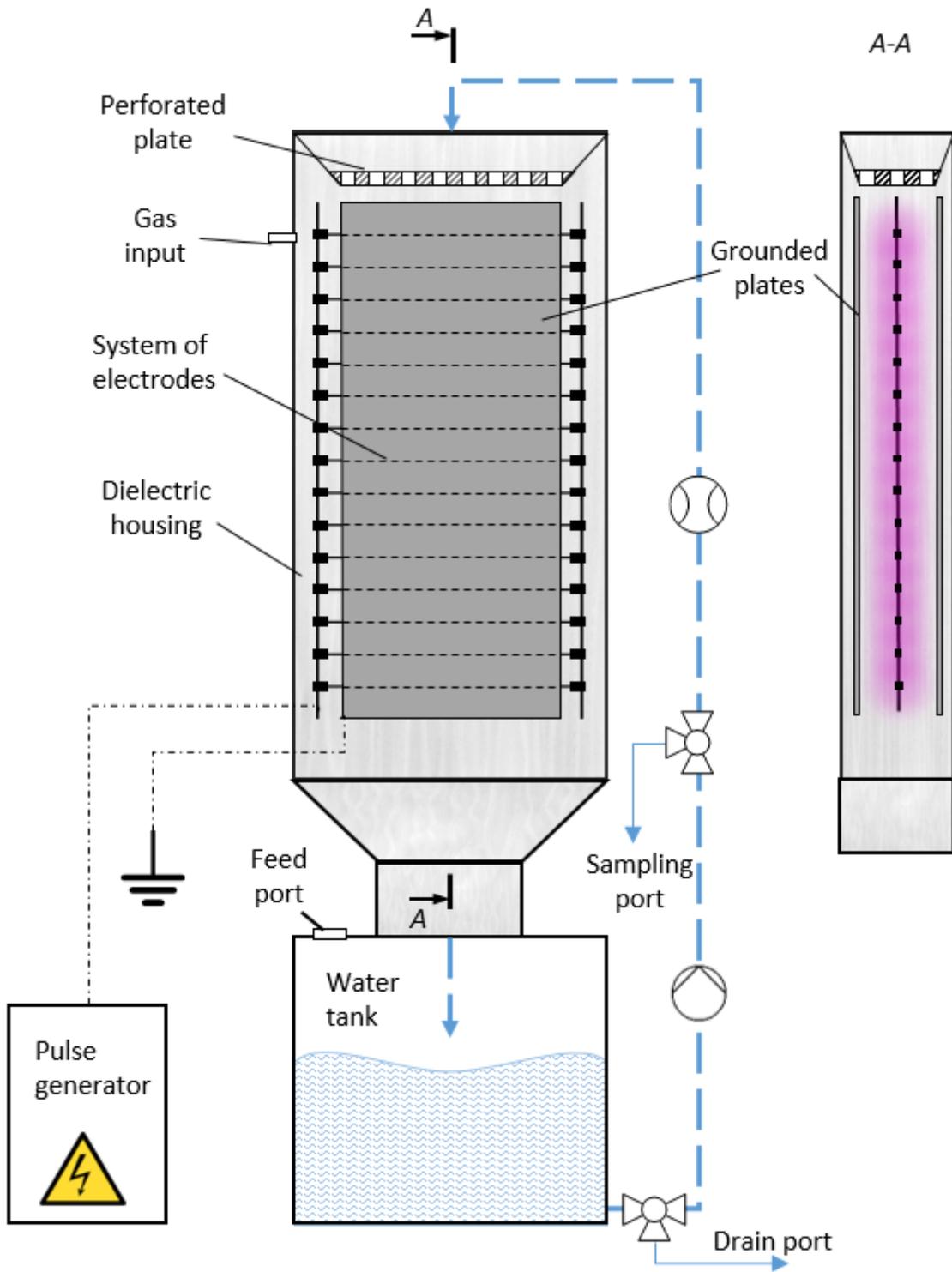


Figure 1. Experimental setup

The reactor has a wire-plate corona geometry typical for electrostatic precipitators where the electrode wires are located between grounded plate electrodes. The high voltage

electrodes are made from stainless steel, have a diameter of 0.5 mm, and are located 17 mm from the vertical grounded plate electrodes. The distance between the HV-electrodes is 30 mm. The discharge pulse parameters are voltage amplitude of 20 kV, current of 400 A, and pulse duration of 100 ns, giving single pulse energy of 0.33 J at a pulse repetition frequency of 840 pulses per second (pps). The treated solution is circulated from the 100-L tank through the reactor by a pump. The solution is dispersed between the electrodes, where it is treated with the oxidants.

The main parameters of estimation of the efficiency of PCD treatment are energy efficiency (ϵ , g/kWh) and lignin conversion rate to aldehydes (hereinafter - conversion rate, φ , %). The energy efficiency shows how much energy PCD consumes for lignin conversion to aldehydes and is calculated with following equation:

$$\epsilon = \Delta C/E \quad (1)$$

where ΔC is the difference between the initial and the final concentration of aldehydes, g/m³; E is the delivered energy dose, kWh/m³, calculated with the equation:

$$E = P \times t/V \quad (2)$$

where P is the pulse integral power delivered to the reactor, 0.25 kW; t is the treatment time, h; and V is the volume of the treated sample, m³.

The conversion rate is the ratio of aldehydes formed per oxidized lignin. It is calculated according to the equation:

$$\varphi = \frac{\Delta C_{Aldehydes}}{\Delta C_{Lignin}} \times 100\% \quad (3)$$

where $\Delta C_{Aldehydes}$ is the increase in aldehydes concentration; and ΔC_{Lignin} is the oxidized lignin concentration.

The oxidized lignin concentration is the difference between initial lignin concentration and lignin concentration after PCD treatment. It should be noted here, that tannin-lignin method (see description below) is used for determination of lignin concentration. This method measures all hydroxylated aromatic compounds. Due to this reason, the results of lignin concentration measurements are not absolute but indicative.

To prepare working solutions, the lignin was dissolved in 1 L of millipore water in the presence of NaOH. This solution was later diluted with tap water at ambient temperature in the reactor tank. The desired volume was 50 L. The flow rate of the re-circulating water was 15 L/min, which ensured sufficient trickling and mixing. The samples were taken after 5, 10, 20, 30 and 40 minutes of PCD treatment. After each interval, but before sample collection, the treated solution circulated continuously for 7 min without power supply for PCD in order to unify the concentration in the tank. The experiments were carried out with different initial concentrations of 370 to 1400 mg/l of lignin. The pH was in the range 11-12 during all experiments. The temperature was around room temperature (20°C). The composition of the gas phase was air and nitrogen-enriched air with volumetric oxygen concentration of 5 to 7 % and 2 to 3 %, respectively. Every experiment was repeated several times to ensure accuracy and increase reliability.

The concentration of lignin was measured photometrically using the tyrosine method (tannin-lignin method). In this colorimetric method, the chromogenic reaction of the sodium carbonate solution and Tanniver® solution (tannin-lignin reagent, HACH), also known as a folin tannin-lignin reagent, which contains tungstophosphoric and molybdophosphoric acids, forms a blue colour with phenolic groups [33]. The result is reported as mg/l of tannic acid recalculated to lignin mass concentration units based on a calibration plot for the particular lignin. A HACH DR/2000 spectrophotometer was used as the analytical tool.

Aldehydes concentration was determined by the colorimetric method presented in [36]. A mixture of 5 mL of lignin-containing sample, sulphuric acid, sodium arsenite solution and 3-methylbenzothiazol-2-one hydrazone hydrochloride was immersed in boiling water for 6 minutes with subsequent cooling to room temperature. Iron (III) chloride-sulphamic acid reagent was then added to the cooled mixture, which was then allowed to stand for 20 min before measurement. An HACH DR/2000 spectrophotometer was used for aldehydes quantitative analysis. The analysis was carried out at a wavelength of 630 nm and absorbance was shown in relative units. The aldehydes concentration was recalculated based on a calibration curve where the absorbance was related to the concentration of glyoxylic acid.

NMR, GPC and HPSEC analyses were carried out to determine the effect of PCD treatment on phenolic and aliphatic OH groups and changes in molecular weight of the lignin.

³¹P NMR sample preparation: 20 to 25 mg of the lignin sample was dissolved in 400 μ L of a 1.6/1 (v/v) mixture of dry pyridine and deuterated chloroform. 100 μ L of a standard solution comprising 1 mmol of cholesterol and 50 mg of a spin relaxing agent Cr(III) acetyl acetonate in 10 mL of the aforementioned solvent mixture was added. For characterization of aromatic OH groups, 100 μ L of 2-chloro-4,4,5,5 tetramethyl-1,3,2 dioxaphospholane was added, and the reaction mixture was stirred at room temperature for two hours. For characterization of aliphatic OH groups, 2-chloro-1,2,3 dioxaphospholane was used instead of 2-chloro-4,4,5,5 tetramethyl-1,3,2 dioxaphospholane. The mixture was directly transferred into an NMR tube, and the sample was measured immediately.

GPC analysis of the Kraft lignin after acetobromination: A 5 mg sample was stirred for 2 h at room temperature in a 9/1 (v/v) mixture of glacial acetic acid and neat acetyl bromide before the reagents were removed in a vacuum. The residue was dissolved in 1 mL of HPLC grade tetrahydrofuran (THF) and the volatiles were removed, again in a vacuum. This procedure was repeated once. Final residues were dissolved in 1 mL of HPLC grade THF and filtered through a 5 µm syringe filter before being injected into a 20 µL sample loop. GPC-analyses were performed using a set-up consisting of a pumping unit (LC 20AT), a degasser unit (DGU-20A3), a column oven (CTO-20AC), a diode array detector (SPD-M20A), a refractive index detector (RID-10A) and, if required, a controller unit (CBM-20A). For the analyses, two analytical GPC columns (each 7.5 x 30 mm) were connected in series: an Agilent PLgel 5 µm 500 Å column followed by an Agilent PLgel 5 µm 1000 Å column. The columns were heated to 30 °C. HPLC-grade THF was used as a solvent for sample preparation and GPC analyses. An isocratic flow rate of 0.5 mL/min was applied for a run-time of 60 min. Calibration was performed using polystyrene beads with molecular weights in the range between 100000 and 200 Da. Final analyses of each sample were performed using the intensities of the UV signal at $\lambda = 280$ nm.

HPSEC analysis of the crude lignin: 10 mg of lignin sample was dissolved in 5-10 mL of DMSO, ultrasonicated for 20 min and stirred overnight. The solutions were filtered with a Teflon syringe filter, 0.2 µm, and then subjected to HPSEC analysis. The molar-mass characteristics of underivatized lignins were determined by HPSEC using an Agilent 1100 Series liquid chromatograph (Hewlett-Packard Comp., USA) equipped with either a Jordi Gel GBR Mixed Bed (Glucose) 250 mm x 10 mm i.d. column + a Jordi Gel (Glucose) DVB 500°A 50 mm x 7.8 mm i.d. guard column or a Waters Linear column, with DMSO and 0.05 M LiBr as the mobile phase with the flow rate 0.5 ml min⁻¹. The temperature of the column oven was 60°C. An Agilent 1100 Series G1315B diode-array

detector and a Shimadzu RID-10A refractive index detector were connected in series. The injection volume was 30 μl .

3. Results and Discussion

Previous research [32] has reported that the highest lignin conversion to aldehydes was obtained by increasing initial lignin concentration to 600 mg/L for a reaction in a 5-7 % volumetric oxygen gas phase. With the aim of improved conversion rate, lignin concentration was raised to 1400 mg/l and the volumetric oxygen content was reduced to 2-3 %. The results of these experiments are given in Figure 2.

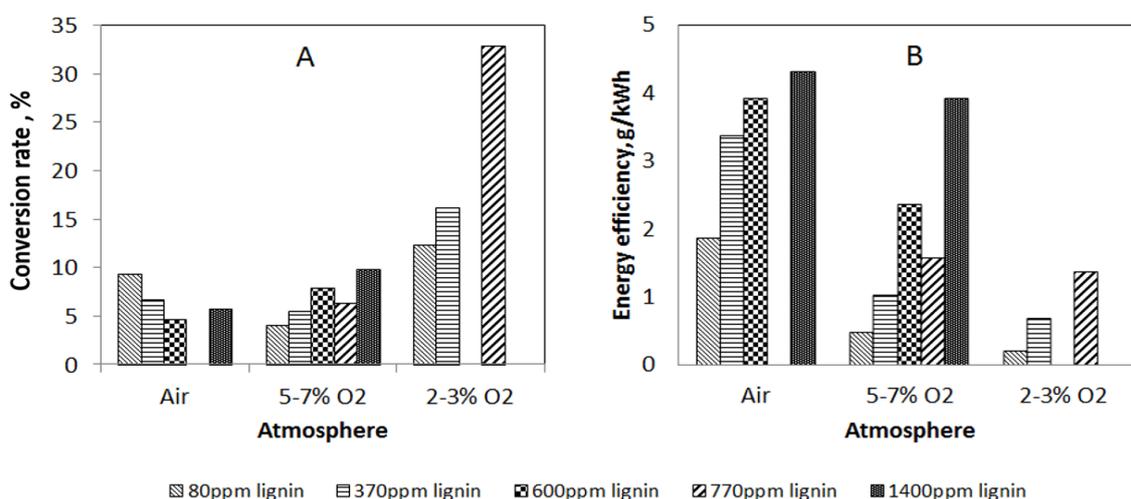


Figure 2. Conversion rate (A) and energy efficiency (B) of aldehydes formation in different atmospheres with different initial lignin concentration

The trend of improved conversion rate with increasing initial lignin concentration in a low oxygen content atmosphere can be clearly seen. The opposite trend is observed in the air atmosphere. The highest recorded conversion rate was around 33 % at 2-3 % oxygen content with 770 mg/l initial lignin concentration.

However, determination of aldehydes and lignin concentration after PCD treatment in an oxygen-thin atmosphere is rather complex. At 2-3% volumetric oxygen, the oxidation

rate is rather low and changes in concentrations insignificant. Analytical tools with higher accuracy are thus required, and it would be rash to assert the high accuracy of the obtained results without additional investigation using more advanced analytical tools. Nevertheless, an oxygen-thin atmosphere provides less harsh reaction conditions due to limited availability of oxidants[37,38]. Based on results of our experiments, it is possible to say, that such atmosphere is favorable for aldehydes formation.

From the energy efficiency point of view, PCD treatment in oxygen-thin conditions is less efficient than treatment in an air atmosphere (see Figure 2). At the same time, higher initial lignin concentration contributes to better energy efficiency. However, it is significant that the relationship between energy efficiency and initial lignin concentration is not linear, especially in air conditions. In air conditions, increase in initial lignin concentration by 17.5 times, from 80 mg/l to 1400 mg/l, results in energy efficiency enhancement of 2.3 times only. Furthermore, the rate of increase in energy efficiency slows with increasing initial lignin concentration. As can be observed in Figure 2, energy efficiency increases rapidly at first, as the lignin concentration rises from 80 mg/l to 370 mg/l, and is then followed by a reduction in the energy efficiency growth rate. It is arguable that further increase in initial lignin concentration will not lead to any significant improvements in energy efficiency. Similar calculations for the oxygen-thin atmospheres show that energy efficiency increases 8.3 times (at 5-7 % O₂) and 6.7 times (at 2-3 % O₂) with increased initial lignin concentration of 17.5 times and 9.6 times, respectively. It is possible to conclude that the energy efficiency growth rate will continue to increase with increasing initial lignin concentration and will not decline in the same way as with the experiment in an air atmosphere. Consequently, by increasing the lignin concentration and using oxygen-thin conditions, it may be possible to exceed the energy efficiency rate of the experiment in an air atmosphere.

To study the effect of the PCD treatment on lignin, two types of lignin were tested: kraft lignin and BLN lignin. Initially the kraft lignin was subjected to the PCD treatment for 40 min in air atmosphere and 2.2 % O₂ in N₂ atmosphere. Each of the solutions was then acidified to pH 5.5, freeze-dried and analyzed by HP-SEC (see figure 3).

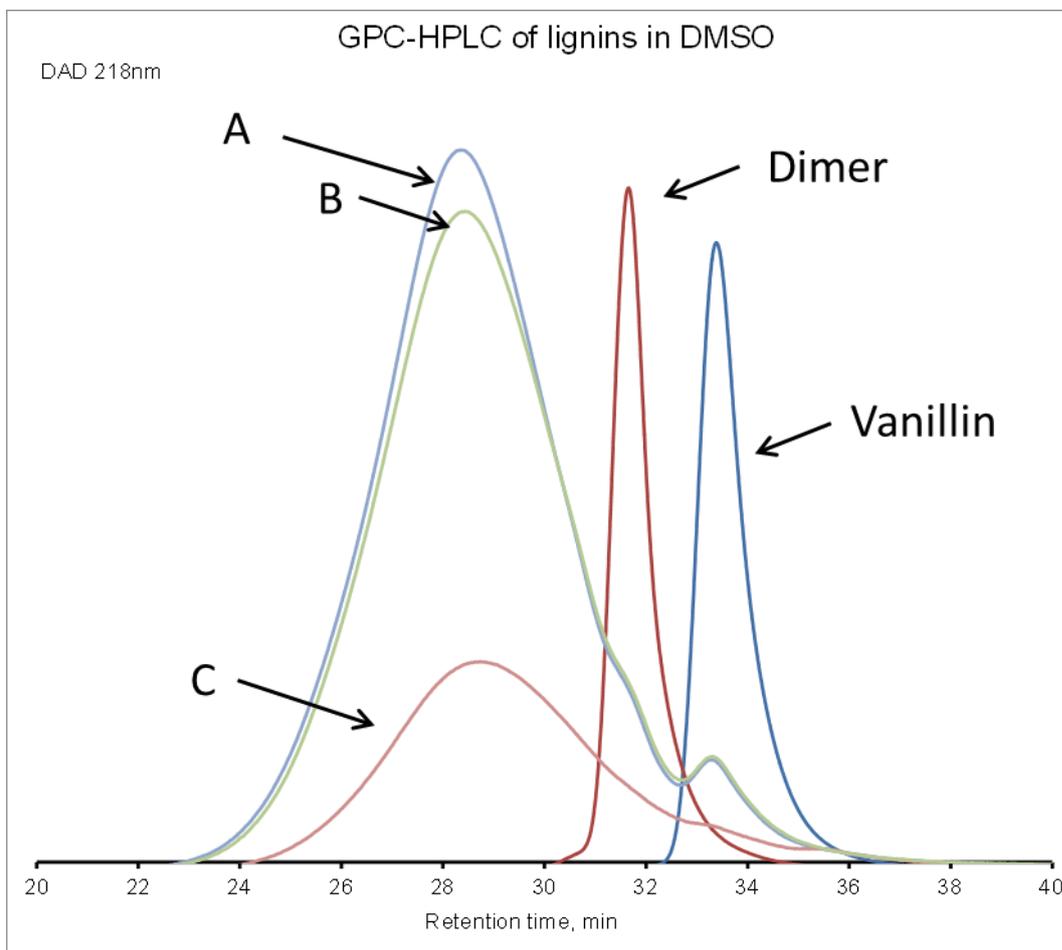


Figure 3. HPSEC using DMSO as eluent and a UV-detector. A) Sigma Aldrich kraft lignin, B) 40 min in air atmosphere and C) 40 min in 2.2 % O₂ in N₂ atmosphere

The kraft lignin PCD treated in air atmosphere was not completely soluble in DMSO which indicates a change in solubility during the treatment but both of the lignin analyzed was still polymeric. The kraft lignin was then subjected to further PCD treatment for 20 and 40 min in an air atmosphere, in 5-7 % O₂ in N₂ atmosphere and in 2-3 % O₂ in N₂

atmosphere (see Table 1). All experiments were performed with three different concentrations of lignin (400, 800 and 1600 ppm).

Table 1. PCD treatment of kraft lignin

	Air	5-7 % O ₂ ; rest N ₂	2-3 % O ₂ ; rest N ₂
0 min, untreated sample	GPC: M _n = 5951 M _w =16711. NMR: primary aliphatic OH groups = 4.34 mmol/g, secondary aliphatic OH groups = 1.89 mmol/g, coniferyl alcohol = 1.05 mmol/g, sinapyl-type phenolic end groups = 1.83 mmol/g, p-coumaryl-type phenols = 0.32 mmol/g		
initial lignin concentration 400 ppm			
20 min	no precipitate	no precipitate	small precipitate, no enough for full NMR. Only aromatic OH characterization was done. No significant changes comparing with untreated sample. GPC: M _n = 3484 M _w =10029 - significant decreasing comparing with untreated sample
40 min	no precipitate	small precipitate, not enough for NMR. GPC: M _n = 3287 M _w =10995, significant decreasing comparing with untreated sample	NMR: Significantly increasing of primary (from 4.34 mmol/g to 7.51 mmol/g) and secondary (from 1.89 mmol/g to 4.46 mmol/g) aliphatic OH groups comparing with untreated sample. Coniferyl alcohol and sinapyl phenolic units stay in the same level; the p-coumaryl-type phenols seem to be slightly decreased. GPC: M _n = 6579 M _w =19020 increased and exceeded of untreated sample values
initial lignin concentration 800 ppm			
20 min	no precipitate	no precipitate	no precipitate
40 min	no precipitate	small precipitate. NMR: slight increasing of coniferyl end groups, and slight decreasing amounts of p-coumaryl and sinapyl-type phenolic end-groups. M _n = 5715 M _w =15109 GPC: insignificant decreasing of M _n and M _w comparing with untreated sample	small precipitate, small precipitates, no enough for full NMR. Only aromatic OH characterization was done. No significant changes. GPC: M _n = 5271 M _w =15230 insignificant decreasing of M _n and M _w comparing with untreated sample
initial lignin concentration 1600 ppm			
20 min	no precipitate	no precipitate	no precipitate
40 min	no precipitate	no precipitate	small precipitates, no enough for full NMR. Only aromatic OH characterization was done. No significant changes comparing with untreated sample. GPC: M _n = 5842 M _w =19877

It was then attempted to precipitate the lignin from the alkaline solution by neutralization with aqueous HCl followed by isolation by centrifugation. With most of the samples, no

precipitate could be isolated; and where precipitate could be isolated, only small amounts were found. In an attempt to isolate any lignin degradation fragments from the samples, the water phase was extracted with EtOAc. However, no EtOAc soluble compounds could be isolated. Based on these results it was concluded that the solubility of the treated lignin had changed to a more water soluble lignin. The small amount of precipitate that had been isolated was analyzed by GPC and ^{31}P NMR and the differences between the experiments were summarized in Table 1. It should be noted that the samples are not representative of the whole lignin but the precipitated fraction could give us information of the PCD induced changes to the lignin. The experiments in an air atmosphere yielded no precipitates; the experiments done in 5-7 % O_2 in N_2 atmosphere yielded small amounts of precipitate from experiments of 40 min duration with concentrations of 400 and 800 ppm; and all of the experiments performed in 2-3 % O_2 in N_2 atmosphere yielded small amounts of precipitate except for experiments of 20 min duration with concentrations of 800 and 1600 ppm lignin, which yielded no precipitate. Based on the change in solubility, the PCD treatment clearly induces changes in the kraft lignin, and as most of the precipitation occurs after the longer 40 min PCD treatment, it would appear that the lignin continues to react, possibly in the form of condensation of the lignin. The PCD treatment with the lowest O_2 concentration yielded the most filtrate, which indicates that it is less oxidized and as such is possible to re-polymerize.

To study the PCD induced structural changes further, a lignin isolated from a pressurized hot water extraction and soda pulp biorefinery process (BLN lignin) was subjected to PCD treatment. All the PCD treatments were done for 40 min at a concentration of 400 ppm lignin in either air atmosphere, 5-7 % O_2 in N_2 atmosphere or 96 % O_2 atmosphere. The experimental procedure after the PCD treatment was similar to that of the kraft lignin; the pH of the alkaline solution was reduced to pH 2.5 with 1 M HCl. The aqueous solution

was then extracted with MTBE to remove any small organic compounds that could have been cleaved during the process. Both the MTBE and aqueous phases were then concentrated separately by evaporation. Only small amounts of MTBE soluble compounds were isolated, and based on GCMS analysis, the compounds consisted of fatty acids, impurities and small amounts of lignin fragments (see Figure 4 and 5).

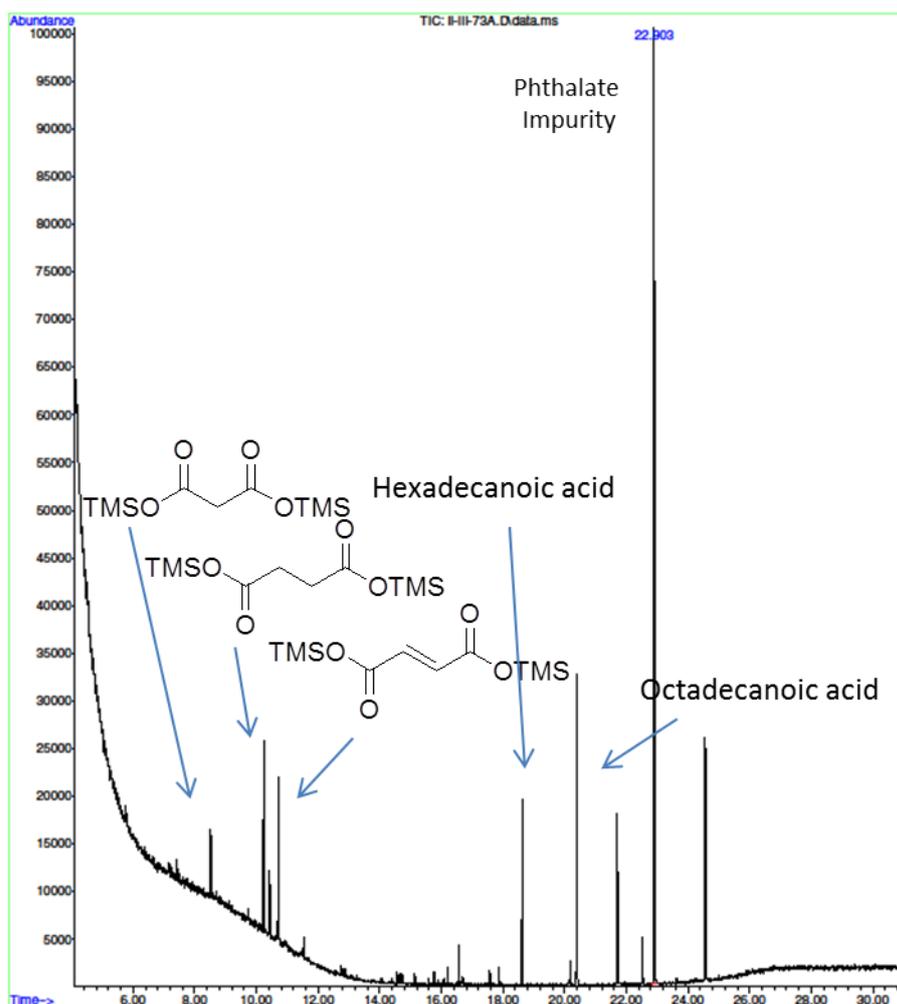


Figure 4. GC-MS of salivated MTBE soluble compounds after 40 min of PCD treatment of BLN lignin in air atmosphere

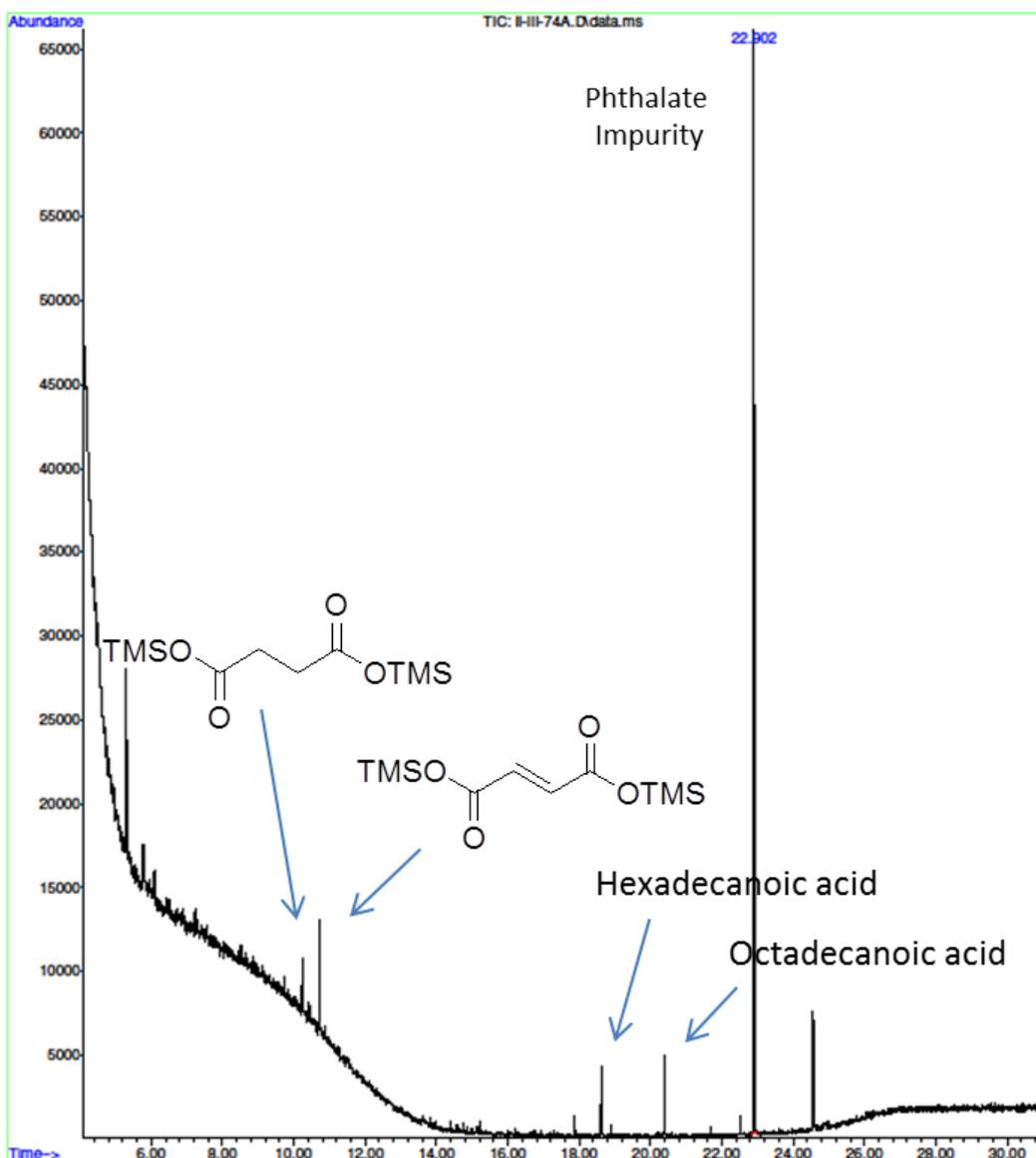


Figure 5. GC-MS of salivated MTBE soluble compounds after 40 min of PCD treatment of BLN lignin in 5-6 % O₂ in N₂ atmosphere

Due to the high amount of inorganics in the remaining solid, attempts were made to selectively dissolve the organics from the dried aqueous phase with organic solvents (THF and acetone). However, all attempts were unsuccessful or only partially dissolved the lignin. All the samples were dried and analyzed as such with HPSEC, ¹³C NMR and HSQC. While the size of the PCD treated lignin was slightly reduced in all samples (see

Figure 6) the lignin was still polymeric or oligomeric and no smaller structures could be observed in the HPSEC-chromatogram.

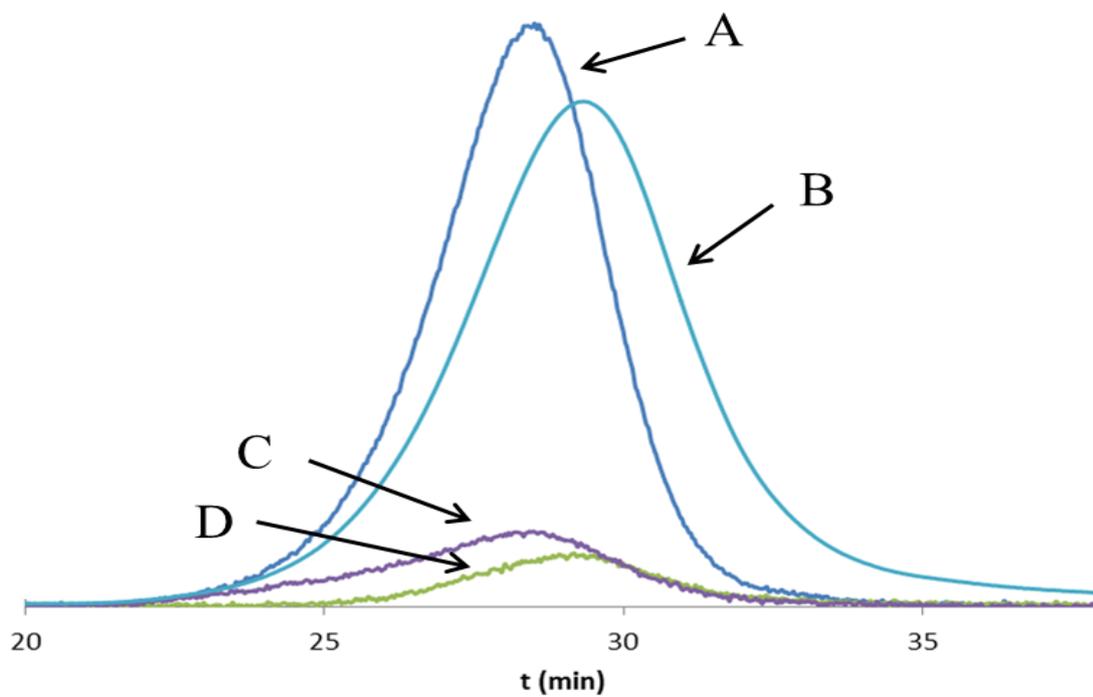


Figure 6. HPSEC using DMSO as eluent and a UV-detector. A) BLN Lignin; B) 40 min in 96 % O₂ atmosphere; C) 40 min in air atmosphere; and D) 40 min in N₂ atmosphere with 5-7 % O₂

From the NMR experiments, it was concluded that the aromatic rings were partially cleaved compared to the starting material and it was noted that a large amount of carboxyl/carbonyl groups were formed (see Figure 7).

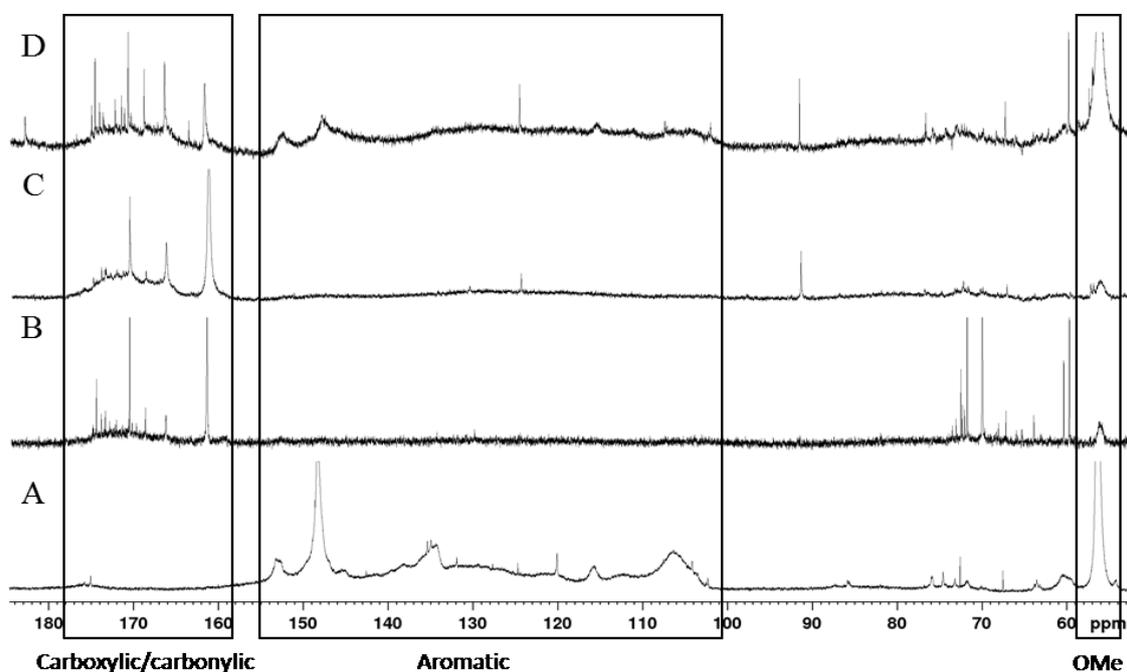


Figure 7. C-13 NMR spectra. A) BLN lignin; B) 40 min in 96 % O₂ atmosphere; C) 40 min in air atmosphere; D) 40 min in 5-6 % O₂ in N₂ atmosphere

The amount of oxygen used in the treatment seems to correlate to the amount of degradation of the starting material. Aromatic signals could still be seen in the ¹³C NMR spectrum of the sample subjected to PCD treatment in 5-6 % O₂ atmosphere, but the samples PCD treated at higher O₂ concentrations had considerably less aromatic signals. From the HSQC spectra (see Figure 8) a clear degradation of the aromatic C-H correlation peaks approximately at δ_C/δ_H (120-105/6.0-7.5) ppm is observed, which indicates degradation of the aromatic rings or reactions at the aromatic C-H positions.

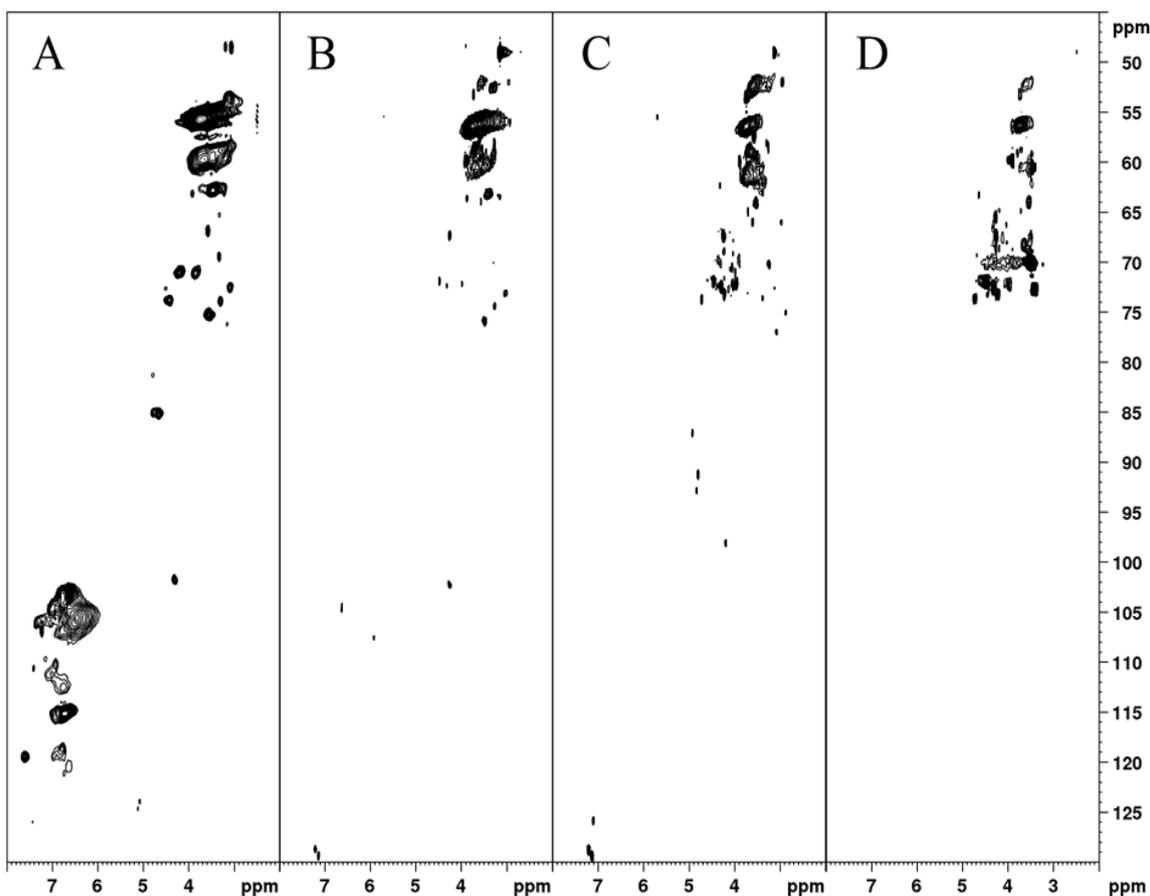


Figure 8. HSQC spectra. A) BLN lignin; B) 40 min 5-6 % O₂ in N₂ atmosphere; C) 40 min in air atmosphere; and D) 40 min in 96 % O₂ atmosphere

The formation of carboxylic functional groups may explain the drastic change in solubility of the lignin. The sharp peaks from the NMR experiments indicate the presence of small molecules, presumably water soluble, such as carboxylic acids, which would explain why the MTBE extraction was unsuccessful. Low or no UV-absorbance could explain the absence of these molecules in the HPSEC-chromatogram.

4. Conclusion

PCD treatment is able to oxidize lignin to aldehydes, but also may further oxidize aldehydes to carboxylic acids and induces oxidative cleavage of aromatic rings. To avoid this undesirable effect, softer oxidation conditions are required.

Increasing the lignin concentration in oxygen-deficient conditions consequently increased the aldehydes formation relative to the oxidized lignin.

Diminished oxygen conditions are more favorable for aldehydes formation, as seen by the higher conversion rate, and potentially have better energy efficiency

Two different lignins, a kraft lignin and BLN lignin, were subjected to PCD treatment. The treatment considerably altered the structure of the lignins. The results indicate that the formed structure is polymeric or oligomeric and contains a high degree of carboxyl or carbonyl groups. The amount of degradation seems to be a direct function of the oxygen concentration in which the PCD treatment is performed.

Under less harsh conditions with lower oxygen content, initial depolymerization of lignin occurs at the beginning of the PCD treatment with subsequent polymerization of lignin fragments.

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