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Lignin Valorization Hot Paper

Peroxodicarbonate as a Green Oxidizer for the Selective Degradation of Kraft Lignin into Vanillin

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Abstract: Lignin, the world's largest resource of renewable aromatics, with annually roughly 50 million tons of accruing technical lignin, mainly Kraft lignin, is highly underdeveloped regarding the production of monoaromatics. We demonstrate the oxidative depolymerization of Kraft lignin at 180°C to produce vanillin **1** in yields up to 6.2 wt% and 92% referred to the maximum yield gained from the quantification reaction utilizing nitrobenzene. Using peroxodicarbonate ($C_2O_6^{2-}$) as "green" oxidizer for the degradation, toxic and/or harmful reagents are prevented. Also, the formed waste can serve as makeup chemical in the pulping process. $Na_2C_2O_6$ is synthesized in an ex-cell electrolysis of aqueous Na_2CO_3 at BDD anodes, achieving a yield of $Na_2C_2O_6$ with 41%. At least, the oxidation and degradation of Kraft lignin is analysis via UV/Vis and NMR spectroscopy.

Introduction

As a result of increasing greenhouse gas emission and finite petroleum resources, it is essential to substitute fossil raw material by renewable feedstock to produce fuel and chemicals.[1] Part of a future solution is the efficient utilization of lignocelluloses biomass, where lignin accounts for up to 35%.[2–4] Lignin is formed from up to three different phenylpropanoid compounds (coumaryl, coniferyl, and sinapyl alcohol) resulting in a complex, three-dimensional and cross-linked biopolymer.[5] Due to the polyphenolic structure of lignin it is the largest renewable source of aromatics.[3,5,6] Additionally, lignin is a massive side stream during pulp production, which annually generates roughly 50 million tons of technical lignin.[6] The predominate

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technology to fabricate cellulose is the Kraft process, where caustic soda and sodium sulfide are initialized as pulping agents.[2] During this process significant modifications in the structure of the biopolymer emerge. Common aryl ether bonds, mainly β-O-4 linkages, are cleaved and new C,C bonds are formed via condensation, resulting in tremendous structural changings compared to native lignin.[2,7] Hence, the obtained technical Kraft lignin is characterized through a higher stability towards depolymerization. Therefore, protocols targeting the β-O-4 linkages in lignin model compounds, often failed for the degradation of Kraft lignin, due to strongly reduced amount of this structural features.[2] Through the condensed and highly recalcitrant structure of Kraft lignin, combined with a distinct sulfur contamination, the conversion of this lignin to low molecular weight aromatics is still a challenge. Since today, Kraft lignin is mainly combusted to produce energy.[2] Nevertheless, different methods have been reported for the conversion of lignin,[6,8,9] including thermal,[10] biochemical,[11,12] oxidative,[13,14] and reductive treatment.[15,16] But, mostly the degradation protocols have serious drawbacks as low selectivity, using toxic and harmful chemicals, harsh reaction conditions, and/or accruing reagent waste. Utilizing nitrobenzene as oxidizer to convert softwood Kraft lignin under alkaline conditions, vanillin **1** is produced in yields up to 13 wt% (Scheme 1).[17–19] Delivering high yields of the aroma chemical **1**, the nitrobenzene oxidation (NBO) of Kraft lignin is often used to quantify the depolymerization referring to the maximum amount of generated vanillin **1**.[18,19] But, this method suffers from tremendous drawbacks,

Scheme 1. Selected strategies for the oxidative degradation of Kraft lignin to produce vanillin **1**.

particular from the toxic and cancerogenic nature of nitro-benzene and arising by-products (azobenzene, aniline, etc.).

Socha et al. published the oxidative depolymerization of Kraft lignin to produce vanillin **1** in a yield by GC of 5.3 wt % , applying optimized reaction conditions (197 °C for 2.4 h) and an initial O_2 pressure of 2.2 atm.[20] However, using molecular oxygen needs a specialized pressure reactor and causes safety issues. Renneckar et al. reported the generation of vanillin **1** through the degradation of Kraft lignin utilizing a magnetically recyclable TEMPO nano-catalyst and sodium hypochlorite as primary oxidizer.[21] They obtained 20 % of phenolic monomers with a high selectivity (about 60 %) towards vanillin **1**. According to their data, this should be equal to around 15 wt % yield of vanillin **1** (Scheme 1).[21] But the values given are not completely unambiguous for the exact yield of **1**. Even though this method achieves high yields of vanillin **1**, it has the disadvantage of the elaborated synthesis of the nano-catalyst in four steps. Today, there is one industrial process to produce vanillin **1** from the renewable feedstock lignin. Here, lignosulfonate is depolymerized in a copper-based aerobic process by the Borregaard company. Applying an oxygen pressure of up to 15 bar under alkaline conditions, vanillin **1** is formed in yields up to 7 wt %.[22] However, this technique suffers from the utilization of copper, which causes cost-intensive purification steps. Consequently, for the industrial process the yield of vanillin **1** drops to around 0.3 wt %.[23] Further the raw material lignosulfonate, obtained from sulfite pulping, is currently an underrepresented process compared to Kraft pulping.[2]

In contrary, the direct use of electricity as oxidizer or reducing agents is inherent safe, inexpensive and avoids waste generation. Furthermore, conventional reducing or oxidizing reaction, which are often harmful, toxic and/or cost-intensive, can be substituted.[24] Therefore, electro-organic synthesis has experienced a renaissance in the field of preparative organic synthesis.[25,26] Combining all these benefits with power supply from renewable energies it represents a "green" method.[26,27] Utilizing electrosynthesis for the anodic degradation of lignin has been published[13] for different native-like lignins and lignin model compounds,[12,28] lignosulfonate,[22,29] organosolv lignin[15,30,31] and Kraft lignin.[32,33] We reported the high-temperature electrolysis for the selective anodic degradation of Kraft lignin into vanillin **1** at nickel electrodes in yields up to 4.2 wt %.[33] Additionally, the protocol of the high-temperature electrolysis was adapted and optimized for the depolymerization of various organosolv lignins to produce phenolics like vanillin **1**, acetovanillone **2**, syringaldehyde **3**, etc.[31] A simple and efficient work-up protocol was developed to separate valuable products from the mixture without neutralization.[34]

In the last decades, the utilization of boron-doped diamond (BDD) anodes to synthesize sodium peroxodicarbonate ($Na_2C_2O_6$) from aqueous Na_2CO_3 has been published.[35–37] Due to a high over-potential for the oxygen evolution reaction, using BDD anodes, the electrolysis could be conducted at ≥ 0 °C. For previously reported methods, utilizing Pt anodes, an electrolysis temperature below

−15 °C was crucial.[38,39] Compared to percarbonate, an adduct of carbonate and H_2O_2, peroxodicarbonate ($C_2O_6^{2-}$) can be understood as the dimer of CO_3^{2-} connected via an O–O bond and is only electrochemically accessible.[39] However, the reported batch-electrolysis provided only low concentrations of peroxodicarbonate (< 0.06 M). [35,36] Chardon et al. achieved peroxodicarbonate concentrations up to 0.28 M (21 % yield) operating in a cycled flow-electrolysis and applying current densities above 0.7 A cm^{-2}.[37] But, working at this high current density a more distinct cooling is necessary due to arising heat generation. Also, the reported current efficiency of 76 % was only achieved when an insufficient amount of charge was supplied (about 0.1 F). To generate $Na_2C_2O_6$ at the indicated concentration of 0.28 M, applying a larger amount of charge ($> 1 F$) was required, resulting in a significantly lower current efficiency. Nevertheless, peroxodicarbonate seems to be a promising oxidizer, which is environmentally safe, biodegradable and easily electro-synthesized from aqueous carbonate at BDD anodes.[36]

Results and Discussion

Since the Kraft process is the predominant technique to produce pulp,[2] the corresponding Kraft lignin was chosen as starting material for this research. Initial experiments, utilizing commercially available oxidizer as peroxodisulfate, Oxone®, percarbamide, and percarbonate, delivered insufficient amounts of vanillin **1** for the degradation of Kraft lignin under tested condition. On the contrary, using a freshly electrolyzed peroxodicarbonate solution, a higher yield of **1** was achieved applying similar condition. Nevertheless, the received amount of vanillin **1** was quite low, wherefore an optimization was mandatory. Previously, temperatures above 100 °C were identified as essential for an efficient depolymerization of Kraft lignin into vanillin **1**.[29] Whereas for the electrosynthesis of peroxodicarbonate temperatures about 0 °C are crucial.[35–37] Due to this large temperature discrepancy, the process steps have been separated (Scheme 2).

Besides converting the starting material directly, intermediates or oxidizer can be formed in an ex-cell approach, for example the electrochemical synthesis of periodate, which opened the field for pharmaceutical applications of this oxidizer.[40] Thus, peroxodicarbonate was synthesized via ex-cell electrolysis at ≤ 5 °C (Scheme 3). We utilized a
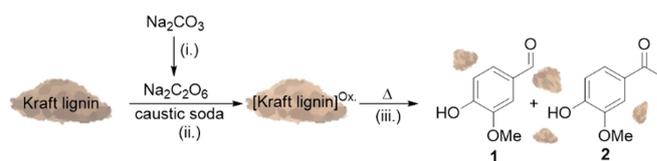
Scheme 2. Overview of the depolymerization of Kraft lignin into vanillin **1** and acetovanillone **2**. (i.) ex-cell electrosynthesis of peroxodicarbonate; (ii.) addition of aqueous peroxodicarbonate to Kraft lignin in caustic soda; (iii.) thermal treatment.

$$2\ Na_2CO_3 + 2\ H_2O \xrightarrow[\text{flow-electrolyzer}]{\text{BDD anode, <5 °C}} Na_2C_2O_6 + 2\ NaOH + H_2$$
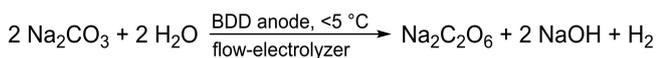
Scheme 3. Electrochemical synthesis of peroxodicarbonate and hydrogen from an aqueous sodium carbonate solution at boron-doped diamond (BDD) anodes.

previously developed flow-electrolyzer[41] with an implemented BDD anode and a stainless-steel cooling jacket, which also serves as cathode (Figure S4 left). All electrolysis were performed in cycled-flow (Scheme S4 right) and constant current mode using the undivided flow-electrolyzer. Aqueous sodium carbonate was implemented as cost-efficient and non-toxic starting material. Firstly, the electrochemical synthesis of peroxodicarbonate was investigated regarding flow rate, applied charge and current density to obtain high product concentrations (Figure 1). The concentration of the oxidizer was determined by iodometry after the electrolysis (details are given in the Supporting Information).

Increasing the current density and flow rate up to a certain level was preferred to achieve a high oxidizer concentration. Operating above $240\ mA\,cm^{-2}$ a slightly declined in the concentration was observed. This can be attributed to a growing heat generation observed during electrolysis, which promotes the decomposition of $C_2O_6^{2-}$. Raising the applied charge, a rising peroxodicarbonate concentration can be reached until a kind of saturation occurs at about 2 F. This can be explained by the decay of the oxidant, which is more pronounced at lager electrolysis times. Applying optimized electrolysis parameters (Table S7) a concentration of peroxodicarbonate above 180 mM, equals to 36% yield, was achieved. Furthermore, hydrogen was formed as valuable co-product.

To determine the possible yield of vanillin **1** obtained from the depolymerization of Kraft lignin, nitrobenzene was used as oxidizer (NBO) according to the literature.[18,19] Different Kraft lignins were quantified regarding the max-

imum yield of **1** (Table S3). A low-quality lignin, containing impurities like ash and fiber, was chosen as starting material to develop a robust degradation method, tolerating those impurities. Caustic soda was implemented as aqueous, non-toxic, and cost-efficient solvent and serves as deprotonation agent, which is needed for the degradation mechanism of the lignin later. Additionally, caustic soda is the solvent used during Kraft pulping. The oxidative depolymerization of Kraft lignin ($>100\,°C$) was carried out in a pressured vessel (Figure S3). As oxidizer, a freshly electrolyzed peroxodicarbonate solution was added to the lignin solution at the beginning of the reaction. Different experiments, varying the amount of oxidizer, temperature of the oxidation and thermolysis time, were carried out to improve the yield of vanillin **1** (Table S11–13). In general, the yield of vanillin **1** increased with rising reaction time up to a certain point (Table S13, entry 1–3). Thereafter, a decrease of the yield of **1** was found, suggesting the degradation of **1** (Table S13 entry 4 and 5). An oxidation temperature of $50\,°C$ enabled the highest yield of vanillin **1** (Table S12 entry 2). This indicates that an efficient oxidation of lignin with peroxodicarbonate occurred at $50\,°C$, without being significantly affected by the decay of peroxodicarbonate due to its temperature sensitivity. Furthermore, a control experiment revealed the partial oxidation of vanillin **1** at $50\,°C$ using $Na_2C_2O_6$ in alkaline media. If the oxidizer is added at higher temperatures, where vanillin **1** is already formed through the partly thermal degradation of lignin, it will be oxidized, resulting in a reduced yield of **1** after the completed thermal treatment. Using those optimized conditions, the desired product **1** was received in a high yield of 4.6 wt%, equals to 84% compared to the quantification reaction utilizing nitrobenzene (NBO). All yields of vanillin **1** are uncorrected and correspond to the amount of **1** obtained after the respective reaction.

Even though the generated yield of vanillin **1** was already high, a screening experiment using a statistical approach (full factorial design) was performed. Firstly, to get a better understanding of the parameters' influence and secondly to maximize the yield of **1**. Here, the temperature and heating time of the thermolysis and the amount of oxidizer were chosen as factors, with three levels each (Table S15). Furthermore, a commercially available Kraft lignin from SIGMA ALDRICH was initialized as feedstock. The experiments were examined regarding the obtained yield of vanillin **1**. The analysis of the received main effects chart revealed, that the temperature and heating time of the thermolysis strongly influence the yield of **1** up to a certain limit (Figure S7). Whereby, the effect of the oxidizer's amount is mediocre but necessary for an efficient depolymerization into vanillin **1**. At least, a correlation between heating time and amount of the oxidizer is observed. Where lowering the quantity of peroxodicarbonate, an increase in the heating time is required to obtain similar yields of **1**. Applying the optimized reaction parameters, using 12.6 mmol (or 6.3 mmol) peroxodicarbonate for the oxidation of lignin and afterwards perform the depolymerization at $180\,°C$ for 6 h (or 12 h), the desired product **1** was formed in 5.7 wt% yield, equals to 91% compared to the yield from

Figure 1. Analysis of the oxidative degradation of Kraft lignin using $Na_2C_2O_6$ via UV/Vis spectroscopy. a) UV/Vis spectra of different samples from the oxidative degradation of Kraft lignin using $Na_2C_2O_6$. b) UV/Vis spectrum of dissolved Kraft lignin at $50\,°C$. c) UV/Vis spectrum of dissolved Kraft lignin at $50\,°C$ after addition of $Na_2C_2O_6$. d) UV/Vis spectrum of Kraft lignin after 12 h of heating at $180\,°C$, which was previously treated with $Na_2C_2O_6$ at $50\,°C$.

the nitrobenzene oxidation. Additionally, acetovanillone **2**, was produced as valuable by-product in a yield of 2.2 wt% (Scheme 4). In comparison, using a sodium carbonate solution instead of a sodium peroxodicarbonate solution for this reaction, the desired product **1** is only obtained in a yield of 2.3 wt%. Furthermore, replacing the oxidizer sodium peroxodicarbonate with hydrogen peroxide, vanillin **1** was received in an insufficient yield of 3.0 wt%, applying similar reaction conditions. These reactions demonstrate the advantages of using sodium peroxodicarbonate to convert Kraft lignin into vanillin **1**.

After successful depolymerization of the technical lignin into vanillin **1**, the electrosynthesis of $Na_2C_2O_6$ was scaled-up. Using a larger flow electrolyzer (Figure S5), the (geometric) anode surface was increased from 12 cm^2 to 76 cm^2, simultaneously shorten the electrolysis time to one sixth. Analogous to before, different electrolysis parameters (electrolysis temperature, applied charge and current density) were investigated (Table S8). Here, we successfully increased the electrolysis temperature from 0°C to 5°C, without lowering the oxidizer's concentration, which reduces the energy consumption of the system. Temperature above 5°C resulting in a decreased concentration of $Na_2C_2O_6$ (Table S8), that can be attributed to the temperature-dependent decomposition of peroxodicarbonate, which is intensifies with growing temperature.[35–37] In contrary to the previously reported study,[37] applying current densities above 240 mA cm^{-2} led to a decrease in the oxidizer's concentration and a rising electrolysis temperature was observed. Applying 1 F respective to the amount of starting material (Na_2CO_3), sodium peroxodicarbonate was synthesized in 33% yield, with a current efficiency of 33% (Table S9). Increasing the applied charge to 2 F the yield was further improved to 41% (Table S9). But, due to the longer electrolysis time and the excess applied charge, the current efficiency was lowered to 21%. Nevertheless, in contrast to the previously reported benchmark reaction from Chardon et al.[37] yielding 21% of $Na_2C_2O_6$, we were able to double the yield to 41%. The scaled-up electrolysis provides an improved yield, current and time efficiency compared to the previously used set-up for the electrosynthesis of $Na_2C_2O_6$. Peroxodicarbonate, produced under those optimized conditions (Table S9, entry S1), was utilized for final degradation reactions of Kraft lignin to vanillin **1** (Table 1).

The investigation revealed similar insight as the statical optimization before. A longer reaction time led to an
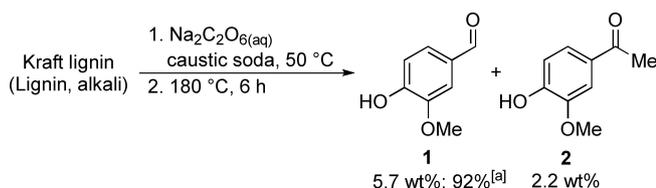
Table 1: Oxidative degradation of Kraft lignin towards vanillin **1** and acetovanillone **2** using ex-cell produced $Na_2C_2O_6$.

#	$Na_2C_2O_6$ [mmol][a]	t [h][b]	yield **1**[c]	yield **1** vs. NBO[d]	yield **2**[c]
1	2.8	6	4.0 wt%	65%	1.2 wt%
2	2.8	12	5.6 wt%	89%	2.2 wt%
3	5.8	6	3.5 wt%	56%	1.4 wt%
4	5.8	8	5.8 wt%	92%	2.0 wt%
5	5.8	12	5.0 wt%	79%	2.3 wt%
6	11.6	2	3.8 wt%	60%	1.1 wt%
7	11.6	6	4.7 wt%	75%	1.6 wt%
8	11.6	12	5.1 wt%	81%	1.9 wt%

[a] Different amounts of a peroxodicarbonate solution with a concentration of 166 mM were used. [b] Temperature of the thermolysis: 180°C. [c] The yield was determined by GC using *n*-dodecylbenzene as internal standard and refers to the amount of lignin employed. [d] Related to the yield of **1** from the NBO (Table S3).

improve in the yield of **1** up to a certain level. Using less oxidizer, the reaction time for the thermally induced degradation must be prolonged to receive similar yields of **1**. The investigation revealed similar insight as the statical optimization before. A longer reaction time led to an improve in the yield of **1** up to a certain level. Using less oxidizer, the reaction time for the thermally induced degradation must be prolonged to receive similar yields of **1**. Hence, utilizing 2.8 mmol of peroxodicarbonate a heating time of 12 h is necessary to obtain vanillin **1** within a yield of 5.6 wt%, which corresponds to 89% compared to the quantification reaction (NBO). Whereas, using 5.8 mmol of the oxidizer, the heating period is shortened to 8 h, receiving vanillin **1** in a slightly higher yield of 5.8 wt%, corresponds to 92% compared to the NBO. Additionally, acetovanillone **2** was obtained with 2.0 wt% yield as valuable by-product. After successful degradation of the tested lignin towards vanillin **1**, the developed method was adapted to further Kraft lignins (Table 2).

Here, the method utilizing $Na_2C_2O_6$ as green oxidizer confirmed its effectivity and robustness to convert Kraft lignin into vanillin **1**. A yield of vanillin **1** with up to 6.2 wt% was achieved (Table 2, entry 2). Furthermore, we

Kraft lignin (Lignin, alkali) → 1. $Na_2C_2O_{6(aq)}$ caustic soda, 50°C, 2. 180°C, 6 h →

1 5.7 wt%; 92%[a] + **2** 2.2 wt%

Scheme 4. The oxidative depolymerization of Kraft lignin into vanillin **1** and acetovanillone **2** using ex-cell electrosynthesized $Na_2C_2O_6$, [a] yield compared to the NBO.

Table 2: Oxidative degradation of several Kraft lignins to vanillin **1** at 180°C using electrosynthesized peroxodicarbonate as oxidizer.

#	Kraft lignin	yield **1**[a]	yield **1** vs. NBO[b]	yield **2**[a]
1	Lignin, alkaline (SIGMA ALDRICH)	5.8 wt%	92%	2.0 wt%
2	Indulin AT (WESTROCK)	6.2 wt%	89%	2.1 wt%
3	Indulin AT[c] (WESTROCK)	5.0 wt%	72%	1.6 wt%

[a] The yield was determined by GC using *n*-dodecylbenzene as internal standard and refers to the amount of lignin employed. [b] The yield of vanillin **1** is referred to the quantification reaction using nitrobenzene (NBO, Table S3). [c] The concentration of lignin was increased by factor 5.

were able to strongly enhance the concentration of starting material by factor 5, without significantly decreasing the yield of vanillin **1** (Table 2, entry 3). This observation reinforces the economy of the process. Using peroxodicarbonate as sustainable oxidizer, toxic reagents, like nitrobenzene, are replaced. Furthermore, the formed waste can serve as makeup chemical in the pulping process.

After developing a successful way to depolymerize Kraft lignin to vanillin **1** utilizing $Na_2C_2O_6$ as oxidizer, different analytical tools were employed to get deeper insights into this reaction. Using UV/Vis spectroscopy and a reactor equipped with a sample valve (Figure S3, right), time-dependent spectra of the degradation were recorded (Figure 1).

A broad signal around 290 nm is obtained (Figure 1b) for the dissolved lignin, which intensity decreased after the addition of $Na_2C_2O_6$ (Figure 1c), whereas a peak at around 270 nm appears. After starting the thermal treatment at 180 °C, an arising signal at around 344 nm can be observed, whereby its intensity strongly increases with rising heating time up to a certain limit (12 h, Figure 1c). To compare these signals, UV/Vis spectra of different lignin monomers were recorded (Figure S8). Here, vanillin **1** (346 nm) and acetovanillone **2** (342 nm) showed an absorption in the same area as the arising signal at 344 nm (Figure 1d). Thus, this arising peak may be assigned to the desired products **1** and **2**. Furthermore, the experimental data from the depolymerization of lignin supports this assumption, since the yield of **1** and **2** increases with rising heating time up to a certain level (Table S16). Additionally, different UV/Vis spectra were recorded for the oxidation of Kraft lignin with $Na_2C_2O_6$, varying the oxidation temperature and time and the used amount of peroxodicarbonate (Figure S9–11). The analysis is according to the experimental data, where applying 50 °C, 5.8 mmol of peroxodicarbonate showed an efficient decrease of the lignin's signal at 290 nm, without the appearing of new signals. A time-depend decrease of the signal at 290 nm was only found applying 2.8 mmol of peroxodicarbonate, which fits the data, hence using less oxidizer the reaction time needs to be prolonged. Overall, UV/Vis spectroscopy was employed as simple and time-efficient technique to monitor the conversion of Kraft lignin into vanillin **1** and further substantiate the experimental data.

To investigated detailed structural changes of the Kraft lignin, 2D HSQC NMR spectroscopy was employed according to previously reported protocols.[7,8] Two regions of interest were regarded: the aliphatic oxygenated side chain region (δ_C/δ_H 50–90/2.7–5.7) and the aromatic/unsaturated region (δ_C/δ_H 90–140/5.5–8.6). The corresponding cross-peak assignment is found in Table S19. For the aliphatic oxygenated side chain region of the Kraft lignin (Figure 2, top left) the distinctive methoxy groups (yellow peaks) are observed. Additionally, β-aryl ether (A: β-O-4), phenylcoumaran (B: β-5) and resinol (C: β-β) linkages are identified. All the determined linkages/units agree with previously reported structural analysis of the analyzed Kraft lignin Indulin AT from WESTROCK.[8,19] After oxidation (Figure 2, top right), besides the appearing of a cross-peak, which can be attributed to a Hibert's ketone (Hk) structure,
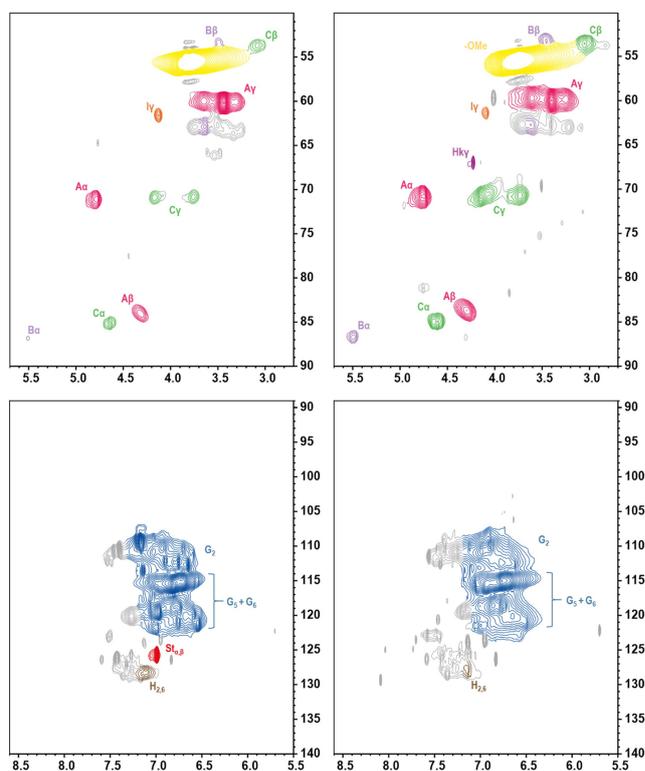
Figure 2. 2D HSQC NMR spectra of Kraft lignin (aliphatic oxygenated region, top left); Kraft lignin after oxidation (aliphatic oxygenated region, top right); Kraft lignin (aromatic region, bottom left); Kraft lignin after oxidation (aromatic region, bottom right). The main lignin structures identified (A) β-O-4, (B) β-5, (C) β-β, (Hk) Hibert's ketone, yellow peaks correspond to -OMe groups, (I) cinnamyl alcohol, (G) guaiacyl, (H) *p*-hydroxyphenyl, and (St) stilbene.

no significant structural changings are found. Thus, these linkages are not directly affected from the oxidation with $Na_2C_2O_6$. For the aromatic regions of the investigated Kraft lignin, as expected, mainly guaiacyl cross-peaks are found (Figure 2 bottom). Due to the origin of this lignin (softwood) no syringyl units are present. The cross-peak obtained at 125.8/7.0 ppm corresponds to stilbene units (St) and is well known for Kraft lignin.[7,8,19] Comparing the spectra of the lignin before and after oxidation, the signal assigned to stilbene (St) units disappeared. Additionally, the signals corresponding to guaiacyl moieties decline. This becomes clearer comparing the quantification of the different linkages (Table S20). Referencing the bonds to Aα = 5.6 the amount of guaiacylic units decrease by 24 % after oxidation. Whereas the amount of the typical lignin linkages, as β-O-4, β-5, and β-β seems to be unaffected after the oxidation. This suggests the oxidation of the guaiacylic backbone of the lignin using peroxodicarbonate. Hence, phenoxy radicals could be formed, which are known to be responsible for the oxidative bleaching in lignin[42] and could explain the decrease in the lignin's absorption during the investigation via UV/Vis spectroscopy. Furthermore, the analysis using 2D HSQC NMR showed the efficiency of the oxidation with peroxodicarbonate.

Conclusion

In conclusion, sodium peroxodicarbonate was synthesized through the electrolysis of aqueous sodium carbonate in yields up to 41 %. Utilizing $Na_2C_2O_6$ as "green" oxidizer, we were able to oxidative depolymerize Kraft lignin into vanillin **1**. Here, the aroma chemical vanillin **1** was produced in yields up to 6.2 wt % and up to 92 % referring to the maximum yield obtained from the quantification reaction using nitrobenzene. Furthermore, acetovanillone **2** was generated as valuable by-product in 2.3 wt % yield. Toxic, and harmful reagents were avoided. Using $Na_2C_2O_6$ as oxidizer, the formed waste can serve as makeup chemical in the pulping process. In combination with the experimental data, UV/Vis spectroscopy was employed as simple technique to monitor the oxidation and degradation of the lignin. Analysis of the Kraft lignin via 2D HSQC NMR spectroscopy suggest the oxidation of the guaiacylic backbone of the polymer, whereas typical lignin linkages seem to be unaffected by the treatment with $Na_2C_2O_6$.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: Electrochemistry · Green Chemistry · Lignin · Peroxodicarbonate · Vanillin

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