Communications

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Chemie

Highly Selective Oxidation and Depolymerization of α,γ-Diol Protected Lignin

Wu Lan, Jean Behaghel de Bueren, and Jeremy S. Luterbacher*

Abstract: Lignin oxidation offers a potential sustainable pathway to oxygenated aromatic molecules. However, current methods that use real lignin tend to have low selectivity and a yield that is limited by lignin degradation during its extraction. We developed stoichiometric and catalytic oxidation methods using 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) as oxidant/catalyst to selectively deprotect the acetal and oxidize the α-OH into a ketone. The oxidized lignin was then depolymerized using a formic acid/sodium formate system to produce aromatic monomers with a 36 mol % (in the case of stoichiometric oxidation) and 31 mol % (in the case of catalytic oxidation) yield (based on the original Klason lignin). The selectivity to a single product reached 80 % (syringyl propane dione, and 10–13 % to guaiacyl propane dione). These high yields of monomers and unprecedented selectivity are attributed to the preservation of the lignin structure by the acetal.

Lignin is a heterogeneous aromatic biopolymer that is present in most plant tissue. It is predominately formed through radical coupling between coniferyl, sinapyl, and *p*-hydroxyphenyl alcohol, which results in different interunit linkages formed by C−C and C−O bonds.[1] The β-aryl ether unit (also known as the β-O-4 linkage) that features a benzylic secondary hydroxyl at Cα position and a primary hydroxyl at Cγ position is the most abundant interunit linkage, and a relatively delicate portion of the lignin polymer.[2] Most delignification and lignin depolymerization processes in the pulp and paper industry and biorefineries are based on the cleavage of these β-O-4 bonds.[3]

Recently, several groups have explored a two-step lignin depolymerization strategy pioneered by Stahl and co-workers[4] based on the selective oxidation of the α-OH into a ketone, which reduces the bond dissociation enthalpy of the associated β-aryl ether bond.[5] This lower energy facilitates the cleavage of the β-O-4 bonds in downstream processes. Several studies have reported successful methods that selectively oxidize the α-OH on β-O-4 dimeric model compounds and real lignin using different oxidation systems, including O_2/4-amino-2,2,6,6-tetramethylpiperidinyloxy (4-AcNH-

TEMPO)/HCl/HNO_3,[4] O_2/2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ)/tBuONO,[6] O_2/DDQ/N-hydroxyphthalimide (NHIP)/$NaNO_2$,[7] and [4-AcNH-TEMPO]BF_4.[8] Various reactions were investigated to cleave the Cα−Cβ bond and Cβ−O4′ ether bond of the oxidized lignin or lignin models to produce aromatic monomers, including those using NaOH/H_2O_2,[4] Zn/NH_4Cl,[6] NiMo sulfide/H_2,[7] HCOOH/NaOOCH,[9] and [Ir(ppy)$_2$(dtbbpy)]PF_6/visible light.[8] However, all of these methods led to either low yields of monomers (i.e. < 6.0 wt %)[6] or poor product selectivity (limited to 26 % for a single product)[10] when they were applied to extracted lignin. One of the most important factors limiting the yield was that the lignin extraction conditions either extracted a small amount of the original lignin, or caused irreversible condensation of the β-O-4 interunits to form interunit C−C linkages, which then cannot be broken selectively and limit attainable yields.[11] As we demonstrate here, selectivity was likely also limited by modification of the lignin structure during extraction.

Recently, we reported a lignin extraction method using formaldehyde as a α,γ-diol-protecting reagent to preserve the β-O-4 interunit linkage and produce aromatic monomers at near-theoretical yield (based on ether cleavage) in the subsequent hydrogenolysis.[12] In further work, we demonstrated that careful choice of the protecting group and hydrogenolysis catalyst could lead to high product selectivity.[13] Considering the high lignin extraction yield and our ability to preserve the lignin structure, this acetal-protected lignin represented an ideal lignin source for the two-step oxidation and depolymerization required to produce oxygenated aromatic monomers. The challenge in using this substrate was to develop an oxidation method that was adapted to the modified chemical structure of protected lignin compared to unprotected lignin. In this work, we developed a method to both selectively deprotect the acetal and oxidize the α-OH of the acetal-protected lignin in a single step (Figure 1). The resulting oxidized lignin could then be depolymerized using HCOOH/NaOOCH to produce phenyl propane diones with high yield and selectivity.

To develop the initial deprotection and oxidation step, we explored previously reported methods, including stoichiometric oxidation using DDQ in dichloromethane (DCM); and catalytic oxidation systems, such as O_2/TEMPO/HCl/HNO_3, O_2/DDQ/tBuONO, and O_2/DDQ/NHIP/$NaNO_2$ using propylidene acetal-protected veratrylglycerol-β-guaiacyl ether (VG) as a model compound (Table 1). None of these methods led to high yield (ranging from 18–33 mol %) of oxidized VG (VG^{ox}, **2a**, Table 1). Presumably, the oxidation of acetal-protected VG occurs in two distinct stages: first, the acetal is deprotected, and second, the α-OH is oxidized. Interestingly,

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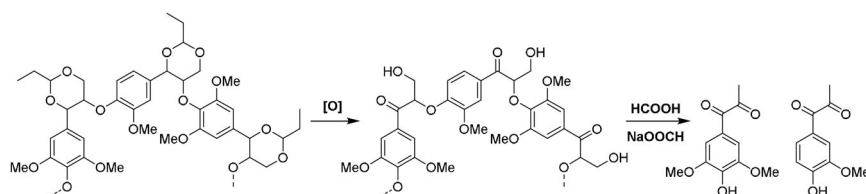https://doi.org/10.1002/anie.201811630.

Figure 1. Oxidation of protected lignin followed by depolymerization to produce syringyl and guaiacyl propane diones as the two major products.

DDQ has been reported as an effective catalyst for acetal removal in wet organic solvents. With water, DDQ has been reported to act similarly to a Lewis acid, increasing the proton concentration and thus promoting acetal removal.[14] Based on these reports, we performed a stoichiometric oxidation using DDQ in wet organic solvents (with 5% H_2O). Reactions in acetic acid (AcOH), DCM, and acetonitrile (MeCN) gave promising yields of VG^{ox} ranging from 82 to 92 mol%, as shown in Table 1 and Table S1 in the Supporting Information. In most cases, the presence of H_2O was critical to the high yield of VG^{ox}, even in the case of DCM, where water was not miscible with the system (Table S1).

Given the high yields obtained with a stoichiometric oxidation, we further investigated the catalytic oxidation using DDQ combined with different co-catalysts in the same solvent systems under O_2 (Table S2), the most successful of which was HNO$_3$. The yields of VG^{ox} were generally higher when reactions were performed in DCM/H_2O than those in AcOH/H_2O or MeCN/H_2O (Table S2). Specifically, the O_2/ DDQ/HNO$_3$ catalytic oxidation system in DCM/H_2O generated 82 to 94 mol% VG^{ox} depending on the loading of DDQ (Table 1). tBuONO had been reported as a good co-

catalyst to selectively oxidize the benzylic alcohol in lignin model compounds with DDQ,[6] but, in our case, the yield was not as good as that obtained using HNO$_3$ (Table S2). The major function of HNO$_3$ was its participation in the NO/ NO$_2$ redox cycle, in which the dihydroquinone (reduction product of DDQ) could be oxidized back to DDQ to complete the catalytic cycle.[15] Another possible function was, as a Brønsted acid, to enhance the acetal cleavage and thereby promote the whole deprotection and oxidation process. Once again, when using DCM, the presence of H_2O was necessary to reach a high yield of VG^{ox} (Table S3), which is consistent with previous observation for acetal removal.[14] The presence of O_2, DDQ, and HNO$_3$ was necessary for efficient catalytic oxidation, and their respective concentrations influenced the result (see Table S3 and our proposed reaction mechanism for the whole process in Scheme S2, further discussion on the effect of each reaction component is also provided in Section S5 of the Supporting Information). We also tested this catalytic oxidation system using other dimeric β-O-4 model compounds with different substitutions of methoxyl group on the aromatic ring and/or different acetal protecting groups. Good to excellent yields (81–95%) of the corresponding oxidized products were achieved in all cases, thus demonstrating the full applicability of this method to α,γ-diol-protected lignin (Table 2).
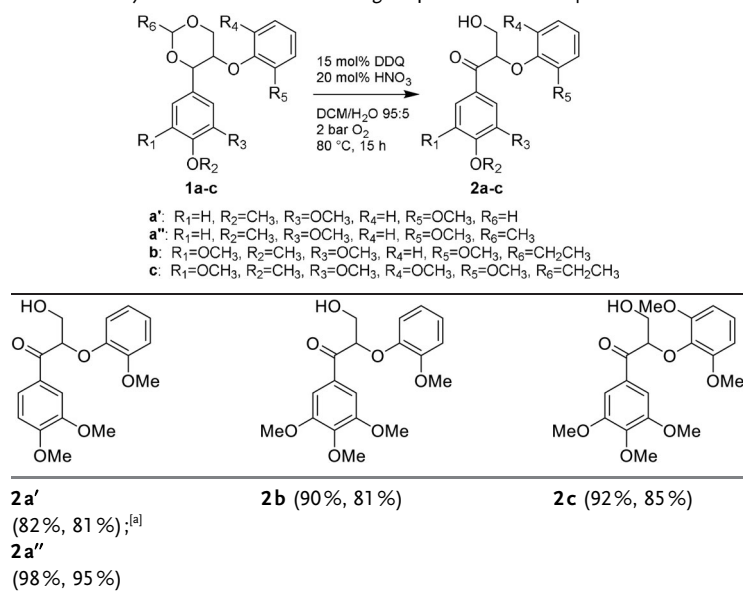
Following the study on model compounds, we successfully used both the stoichiometric and catalytic oxidation conditions on the real propylidene acetal protected lignin (PA-lignin; see Figure 2, Figure S3, and Section S4 in Supporting

Table 1: Selective oxidation of propylidene acetal-protected veratrylglycerol-β-guaiacyl.
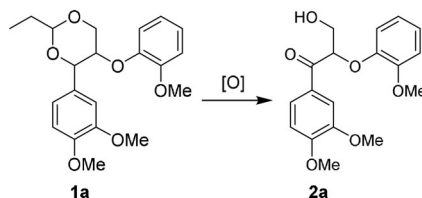
		Methods reported for VG			
Solvent	Catalyst/[Oxidant]	Co-catalyst	Condition	Conv.	Yield
DCM	150 mol% DDQ	–	25°C, 24 h	89%	25%
2-Methoxyethanol[a]	20 mol% DDQ	20 mol% tBuONO	80°C, 15 h	48%	33%
MeCN/H_2O 10:1[a]	10 mol% TEMPO	10 mol% HNO$_3$, 10 mol% HCl	80°C, 20 h	29%	18%
MeCN[a]	23 mol% DDQ	33 mol% NHPI, 60 mol% NaNO$_2$	80°C, 3 h	54%	29%
		Methods developed in this work			
Solvent	Catalyst/[Oxidant]	Co-catalyst	Condition	Conv.	Yield
Stoichiometric oxidation					
AcOH/H_2O 95:5	150 mol% DDQ	–	60°C, 24 h	88%	82%[b]
AcOH/H_2O 95:5	200 mol% DDQ	–	60°C, 24 h	93%	92%[c]
DCM/H_2O 95:5	150 mol% DDQ	–	80°C, 15 h	92%	88%
Catalytic oxidation[a]					
DCM/H_2O 95:5	10 mol% DDQ	20 mol% HNO$_3$	80°C, 15 h	84%	82%
DCM/H_2O 95:5	15 mol% DDQ	20 mol% HNO$_3$	80°C, 15 h	93%	91%
DCM/H_2O 95:5	20 mol% DDQ	20 mol% HNO$_3$	80°C, 15 h	95%	94%

[a] Reactions performed under 2 bar of O_2. [b] The yield included **2a** and acetylated (at the γ position) **2a** with a ratio of 78:22. [c] The yield included **2a** and acetylated (at γ position) **2a** with a ratio of 76:24. A detailed product breakdown is available in Table S1 of the Supporting Information.

Table 2: Catalytic oxidation of different lignin β-O-4 model compounds.

a': R$_1$=H, R$_2$=CH$_3$, R$_3$=OCH$_3$, R$_4$=H, R$_5$=OCH$_3$, R$_6$=H
a": R$_1$=H, R$_2$=CH$_3$, R$_3$=OCH$_3$, R$_4$=H, R$_5$=OCH$_3$, R$_6$=CH$_3$
b: R$_1$=OCH$_3$, R$_2$=CH$_3$, R$_3$=OCH$_3$, R$_4$=H, R$_5$=OCH$_3$, R$_6$=CH$_2$CH$_3$
c: R$_1$=OCH$_3$, R$_2$=CH$_3$, R$_3$=OCH$_3$, R$_4$=OCH$_3$, R$_5$=OCH$_3$, R$_6$=CH$_2$CH$_3$

2a'
(82%, 81%);[a]
2a"
(98%, 95%)

2b (90%, 81%)

2c (92%, 85%)

[a] Numbers represent conversion and yield, respectively.

Information for a detailed discussion). Next, both the stoichiometrically and catalytically oxidized lignin were depolymerized using the HCOOH/NaOOCH system as previously reported,[9] which allowed us to determine the effect of the oxidation on the final monomer yields. The lignin^{ox} samples that were oxidized with 0.5, 1.0, and 1.5 weight equivalents of DDQ, respectively, were depolymerized and the yields were compared (Figure 3), which revealed that aromatic monomer yields increased along with the amount of DDQ, reaching 36% from birch lignin and 52% from F5H poplar lignin (a genetically modified poplar with high syringyl content).[12] The increase in yield follows the increase in oxidation measured by HSQC NMR, which can be explained by protected and unoxidized β-O-4 units undergoing condensation, respectively. Lignin condensation easily occurs in acidic conditions by dehydration of the α-OH followed by condensation of the resulting unsaturation with a neighboring aromatic group.[16] When the α-OH is oxidized, it can no longer dehydrate, which limits lignin condensation. Our best yield was close to the yield obtained from hydrogenolysis of the PA-protected lignin (42%), which is near the maximum attainable yield based on complete ether cleavage (45–50%).[17] This suggests that most of the β-O-4 units were oxidized and depolymerized. The difference in yield could likely be explained by the few groups of unoxidized units that remained (Figure 2B). These groups could have undergone condensation or have not depolymerized for the reasons discussed above. In the case of catalytic oxidation, 0.2 and 0.06 weight equivalents of DDQ and HNO$_3$ were used in oxidation process and the monomer yield was 31% after depolymerization (Figure 3). This lower yield compared to the stoichiometrically oxidized lignin can once again be explained by incomplete oxidation and, in this case, incomplete deprotection of the β-O-4 structure as shown in the HSQC spectrum (Figure 2).

In all cases, the product distributions were similar, with 8–16% G-diketone; 76–82% S-diketone; and less than 10% of syringic acid, vanillic acid, 4-hydroxybenzoic acid, and syringaldehyde (Table S4). The selectivity of the diketones reached 90–93% under the optimal oxidation conditions (Table S4). The significantly higher selectivity to the two diketone products (> 90%) and syringyl diketone (> 80%) compared to previous studies using wild wood (≈ 40% and 25%, respectively)[9, 10] is likely due to the complete preservation of the β-O-4 structure by the protection method before oxidation. In comparison, other methods likely suffer from a certain degree of structure modification during extraction. Additionally, the in situ generated deprotected β-O-4 units were rapidly converted to α-ketones, which limited condensation and other structural modifications resulting in higher yield and product selectivity.

The mass balance of the original birch Klason lignin during the extraction, oxidation, and depolymerization processes was showed in Figure 4. First, 237 mg of PA-lignin were extracted from 1.0 g of biomass (containing 20 wt% of Klason lignin, the difference being the presence of the protecting group and some impurities; Figure 4A). After oxidation, 189 mg of lignin^{ox} were obtained by stoichiometric oxidation. The reduced weight of lignin was largely due to removal of the protecting group. The resulting lignin^{ox} was depolymerized to produce 72 mg of aromatic monomers, representing 38% of the oxidized lignin^{ox}, and 36% of the original Klason lignin. Using the catalytic oxidation, 193 mg lignin^{ox} were obtained and depolymerized and generated 63 mg of aromatic monomers, representing 32% of the oxidized lignin^{ox} and 31% of the original Klason lignin.

Previous work reported that 51 wt% of monomers was achieved when using enzymatically extracted lignin as a feeding source for oxidation and depolymerization. This is so far the highest monomeric aromatics yield for lignin oxidative depolymerization.[9] However, this lignin was produced by extensive ball milling and several enzymatic treatments, and, as such, is not considered industrially scalable. When the same method was applied on chemically isolated lignin, such as that obtained after a mild acid-catalyzed extraction of lignin, the monomer yield decreased to 41 wt%.[10] However, this treatment led to a very low lignin extraction yield (35%; this has not been reported, but the procedure was reproduced here). Furthermore, the most easily extracted lignin fractions tend to give higher monomer yields.[12] Considering this low extraction yield, the overall yield based on the original Klason lignin was about 14%. We also used our oxidation and depolymerization procedure on this lignin and achieved 38% based on the extracted lignin (13% overall) with similar product selectivity (Table S4, entry 4). A longer extraction time increased the extracted lignin yield to over 50% but lowered the overall monomer yield and resulted in worse product selectivity (Table S4, entry 5), likely due to increased degradation.
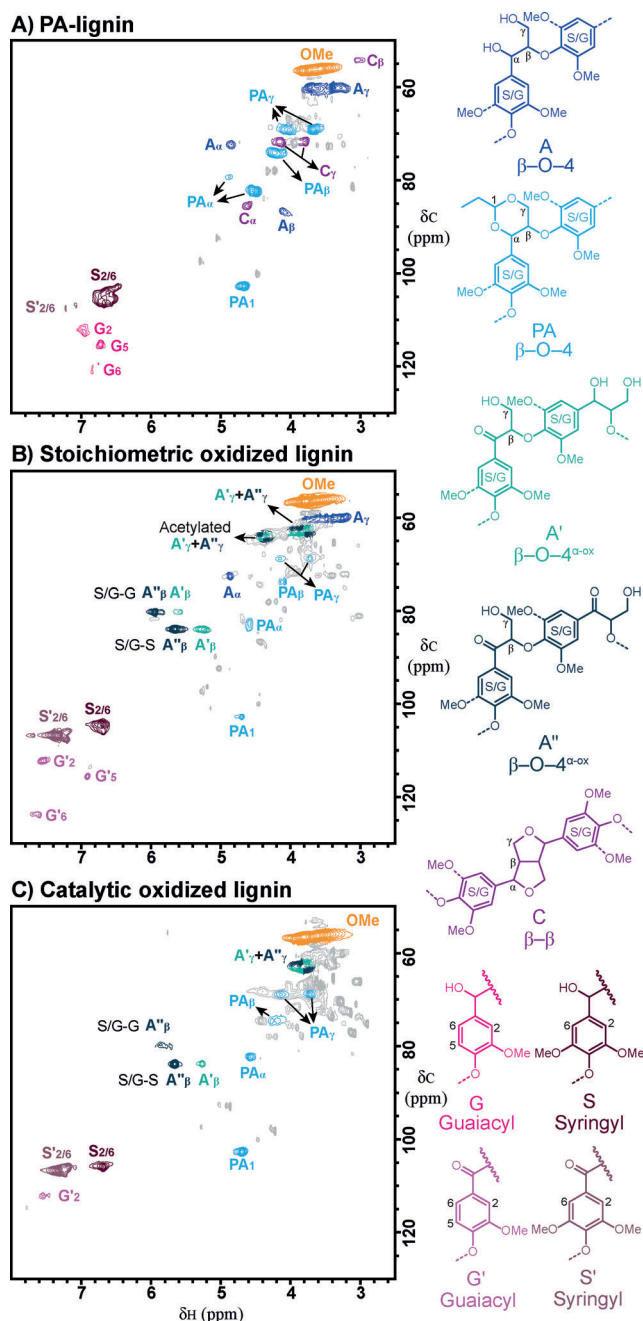
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A) PA-lignin

B) Stoichiometric oxidized lignin

C) Catalytic oxidized lignin

Figure 2. HSQC spectra of propylidene acetal protected lignin isolated from birch and its oxidation products. A) Original propylidene acetal protected lignin. B) Oxidation products of protected lignin resulting from stoichiometric and C) catalytic oxidation. Reaction conditions for (B): 150 wt% DDQ in acetic acid at 60°C for 24 h. Reaction conditions for (C): 20 wt% DDQ/6 wt% HNO$_3$ in DCM with 0.5% H$_2$O, 2 bar O$_2$, at 80°C for 24 h.

Recent studies have shown that efficiently isolating native-like lignin is key to achieving a high overall monomer yield in the following process.[11,18] In an alkaline aerobic oxidation study, a substrate treated with anhydrous ammonia followed by alkaline extraction (70 wt% of the total lignin was recovered in solids with a 30 wt% lignin content) generated yields corresponding to 22 wt% of the original Klason lignin with selectivity lower than 33% to a single

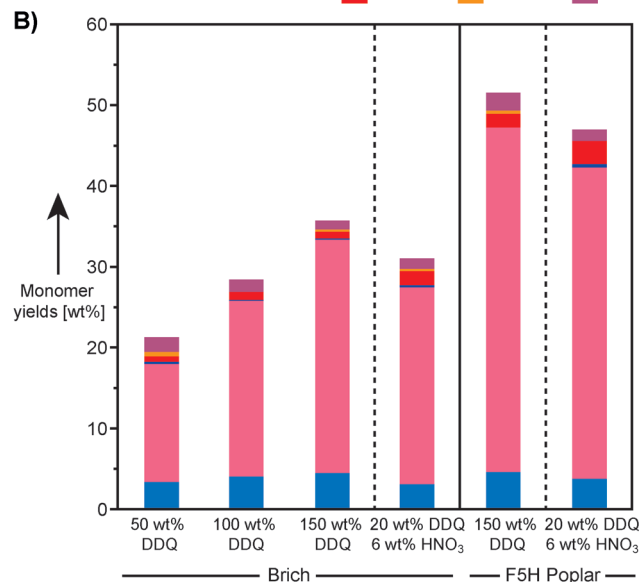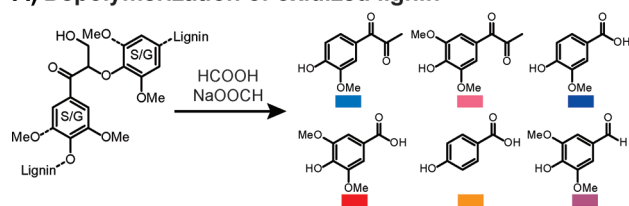## A) Depolymerization of oxidized lignin

B)

Figure 3. Depolymerization of oxidized lignin in HCOOH/NaOOCH. A) Reaction Scheme. B) Monomer yields and product distributions. Reaction condition for the depolymerization were: 100 wt% NaOOCH, HCOOH/H$_2$O 10:1 v/v, 110°C for 48 h. Yield was reported on a Klason lignin basis. The yield calculation is explained in more detail in Section S3 of the Supporting Information. Detailed data is given in Table S4.

product.[18] In another study, GVL lignin from corn stover was oxidatively depolymerized over Au@Li-Al layered double hydroxide and generated 40 wt% of aromatic monomers based on the extracted oxidized lignin. The most abundant product was syringaldehyde with only a 28% selectivity. Furthermore, the extracted lignin yield was not reported, so the overall monomers yield was unknown.[19] Overall, by using both stoichiometric and catalytic oxidation followed by depolymerization, we were able to obtain overall lignin monomer yields by oxidative polymerization that were significantly higher than those attained by these other methods, with typically 2–3-fold increases in the selectivity to a single product. These dramatic selectivity improvements are likely due to our preservation of the native lignin structure by using acetals followed by immediate oxidation after deprotection, which minimized structural changes. Yield was maximized by achieving almost complete extraction of this stabilized lignin thanks to the use of a protecting group on the 1,3-diol moiety.

In summary, we developed a method to selectively deprotect propylidene acetal-stabilized lignin while simultaneously oxidizing the α-OH. The oxidized lignin was then depolymerized by HCOOH/NaOOCH to produce aromatic monomers. We attribute the high overall aromatic monomer
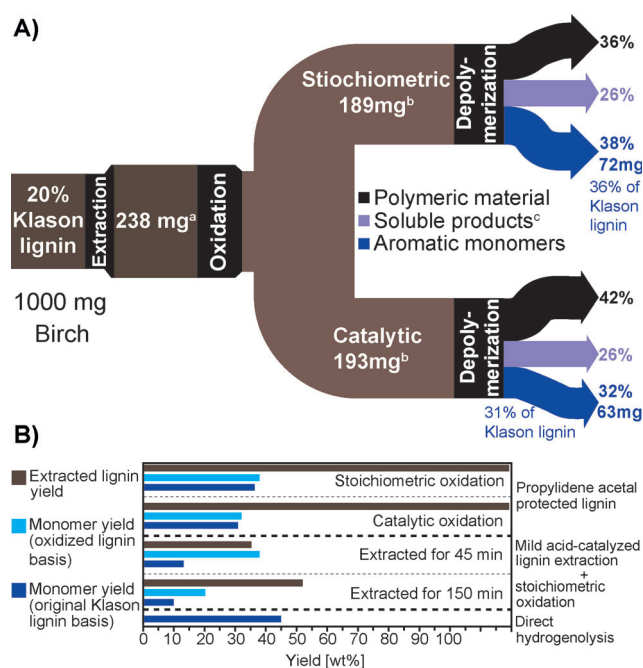
Figure 4. A) Mass balance of the original birch Klason lignin following the extraction, oxidation, and depolymerization processes. Arrow widths are proportional to the amount of material produced. B) comparison of the overall monomer yields to that of using lignin extracted using a mild acid catalyzed process. Reaction conditions are indicated in the caption of Figure 2. [a] The extracted lignin contained the additional protecting group. [b] The weight loss was mainly due to the protecting group removal. [c] Products that are soluble in EtOAc but not detectable in GC, which have been referred to as dimeric and trimeric compounds.[9–10] The monomers were quantified by GC (see Section S3 in the Supporting Information); the soluble products were calculated as the mass of total products extracted by EtOAc minus the mass of monomers; the polymeric material was considered to be the remainder.

yields based on the original Klason lignin (36 mol% for the stoichiometric oxidation strategy and 31 mol% for the catalytic oxidation strategy), and the remarkable selectivity (>90% to syringyl and guaiacyl propane dione) to the preservation of the lignin structure during extraction, which occurs even when the extraction conditions are harsh enough for near-complete lignin recovery. The high yield of products from the original lignin maximizes carbon recovery from the plant. Carbon recovery has important implications for biomass conversion due to the important energetic cost of fixing atmospheric CO_2 by photosynthesis. At the same time, high selectivity to 1–2 dione products could jumpstart the development of valorization processes for oxygenated lignin-derived aromatic molecules, which has so far focused on reduced-lignin monomers.[11]

Acknowledgements

Conflict of interest

The corresponding author (JSL) is an inventor on a European patent application (EP16165180.7) that was submitted by EPFL and covers methods for producing lignin monomers from biomass during biomass depolymerisation.

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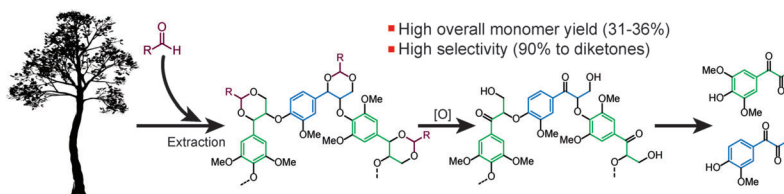↖↖ These are not the final page numbers!

Communications

W. Lan, J. B. de Bueren,
J. S. Luterbacher* ——————— ▌▌▌–▌▌▌

Highly Selective Oxidation and
Depolymerization of α,γ-Diol Protected
Lignin

- High overall monomer yield (31-36%)
- High selectivity (90% to diketones)

Knock on wood: 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone is able to selectively remove the acetal and oxidize the α-OH of acetal-protected lignin. The resultant oxidized lignin generated syringyl and guaiacyl propane diketons in high monomer yield (31–36% on the base of original Klason lignin) and with high selectivity (90%) in formic acid/ sodium formate, thanks to nearly complete extraction of lignin and preservation of the β-O-4 linkages.