A Comparative Study of Secondary Depolymerization Methods on Oxidized Lignins

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Complete List of Authors:	Song, Yang; University of Kentucky, Center for Applied Energy Research; University of Kentucky, Department of Chemistry Motagamwala, Ali Hussain; University of Wisconsin-Madison, Chemical and Biological Engineering Karlen, Steven; University of Wisconsin Madison, Biochemistry Dumesic, James; University of Wisconsin Madison, Chemical and Biological Engineering Ralph, John; U. Wisconsin, Biochemistry Mobley, Justin; University of Kentucky, Chemistry; University of Kentucky Crocker, Mark; University of Kentucky, Center for Applied Energy Research

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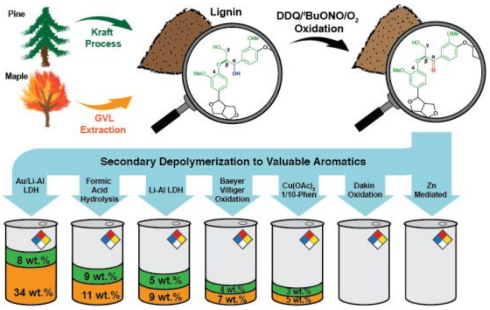
DDQ oxidized lignins were used as substrates to assess the effectiveness of secondary depolymerization methods for the production of aromatics.



A Comparative Study of Secondary Depolymerization Methods on Oxidized Lignins

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Yang Song,[a,b] Ali Hussain Motagamwala,[c,d] Steven D. Karlen,[c,e] James A. Dumesic,[c,d] John Ralph,[c,d,e] Justin K. Mobley*[a] and Mark Crocker*[a,b]

Selective oxidation of lignin's β-aryl ether units combined with secondary chemical treatment for depolymerization can generate valuable oxygen-rich aromatics. Although there have been many reports of the successful oxidative depolymerization of lignin, an accurate assessment of the merits of each method is hampered by the wide array of lignins used. Here, we test a selection of literature methods for secondary lignin depolymerization using a common set of lignin substrates. In an initial step, the lignins were oxidized using 2,3-dichloro-5,6-dicyanobenzoquinone(DDQ)/*tert*-butyl nitrite (^{t}BuONO)/O_2. The oxidized lignins were then subjected to a variety of depolymerization methods, the yield of aromatic monomers being quantified and compared to lignin depolymerized using an Au/Li-Al LDH catalyst followed by hydrolysis without prior C_α-OH oxidation. The Au/Li-Al LDH system gave the highest monomer yield for the untreated lignins, moreover, for DDQ-oxidized lignins, the Au/Li-Al LDH method produced similar monomer yields with high selectivity towards aromatic acids and aldehydes.

Introduction

The finite supply of fossil fuels, coupled with growing environmental concerns surrounding the CO_2 emissions associated with their use, has resulted in extensive research devoted to the development of renewable feedstocks for the production of fuels and chemicals. Lignin, a biopolymer that represents a major component of inedible biomass (~30% by weight and 40% by energy),[1,2] has received particular attention due to its abundance of aromatic substructures and the fact that the valorization of lignin is directly correlated to the cost of cellulosic ethanol production.[3–5] As a result of radical-induced polymerization of monolignols, lignin exhibits an amorphous and complex chemical structure, which hinders efforts to develop effective methods for its conversion to valuable products. However, the presence of specific prominent units within the lignin chemical structure provides a target for chemical deconstruction of this otherwise recalcitrant resource.[6,7] Of all the repeating units within the lignin structure (**Figure 1**), the alkyl aryl ether unit (i.e., the so-called β-aryl ether unit, with its characteristic β–O–4 ether linkage), which comprises as much as 60% of all units in lignin, has received the most attention.[2,8].

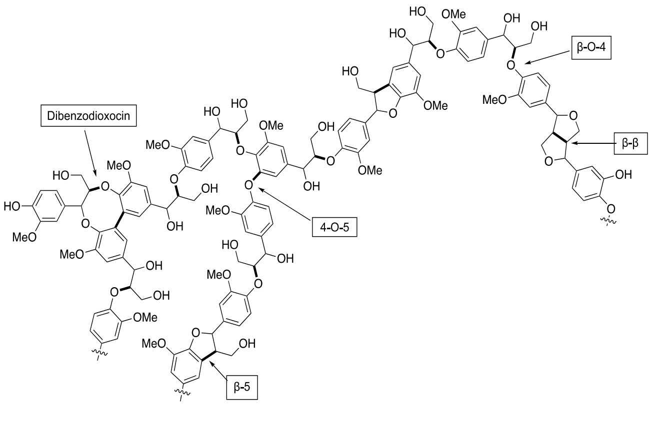

Figure 1. Representation of a fragment of the lignin macromolecule showing selected linkages

Most lignin depolymerization efforts have focused on either hydrogenolytic or oxidative approaches, with the latter being arguably more desirable as the products exhibit higher complexity and functionalization.[6,7,9] Of the oxidative depolymerization methods, the most common approach is to oxidize the C_α-OH located within the β-ether units to the corresponding carbonyl (**Figure 2**). This has the effect of decreasing the C_α–C_β bond energy by 86.8 kJ mol^{-1},[10] such that a variety of methods can be used to cleave this bond.[11,12] In recent years, several research groups have reported approaches for lignin depolymerization using extracted lignins or model oxidized β-ether dimers as the starting material. These

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[a] *Department of Chemistry, University of Kentucky. 505 Rose Street, Lexington, KY 40506, USA.*
**E-mail: justin.mobley@uky.edu; mark.crocker@uky.edu*
[b] *Centre for Applied Energy Research, University of Kentucky. 2540 Research Park Drive, Lexington, KY 40511, USA.*
[c] *Great Lakes Bioenergy Research Center, The Wisconsin Energy Institute, University of Wisconsin-Madison. 1552 University Avenue, Madison, WI 53726, USA.*
[d] *Department of Chemical and Biological Engineering, University of Wisconsin-Madison. 1415 Engineering Drive, Madison, WI 53726, USA.*
[e] *Department of Biochemistry, University of Wisconsin-Madison. 433 Babcock Drive, Madison, WI 53706 USA.*
*Co-corresponding authors
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methods include zinc-mediated depolymerization,[13] formic acid (FA) hydrolysis,[14] H_2O_2/NaOH-mediated selective C–C bond cleavage (Dakin oxidation),[15] Baeyer-Villiger oxidative depolymerization (BVO),[16] and selective C–C bond cleavage catalyzed by $Cu(OAc)_2$/1,10-phenanthroline (Cu/phen).[12]

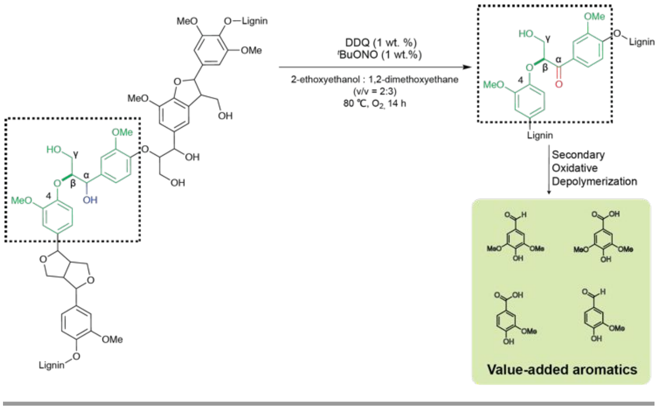

Figure 2. Two-step depolymerization of lignin

We also recently introduced an effective heterogeneous catalyst system consisting of Au nanoparticles supported on Li-Al layered double hydroxide (Au/Li-Al LDH), coupled with hydrolysis, for oxidative lignin depolymerization[17] using O_2 as the terminal oxidant. This system resulted in an unprecedented 40 wt% monomer yield when lignin from maple extracted by γ-valerolactone (hereafter denoted as GL) was used as the starting material.

Although all of the methods mentioned above show potential to oxidatively depolymerize lignin, it is difficult to accurately compare the effectiveness of each due to the wide array of starting materials that have been employed; in some cases, only model dimers were used in these studies, whereas in others different types of extracted lignin were investigated. In the present work, we set out to compare the effectiveness of these oxidative lignin depolymerization methods by applying them to Indulin AT kraft lignin (KL) and GL. Both of these lignins were first oxidized using a catalytic 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ)/*tert*-butyl nitrite (^{t}BuONO) procedure that Westwood and coworkers have shown is effective for oxidation of β-ether units.[13] The results of this experimental review provide a comparison of these secondary depolymerization procedures. The Li-Al LDH support, which is itself a basic heterogeneous catalyst,[18] was also tested in order to examine its ability to depolymerize lignin without the presence of Au nanoparticles.

Experimental Section

Lignin Oxidation

Previously characterized[17] Indulin AT kraft lignin (KL, Ingevity formerly MeadWestvaco) from pine and γ-valerolactone-extracted lignin (GL) from maple were first oxidized using the method described by Lancefield *et al.*[13] To a solution of either KL (10 g) or GL (4 g) in 2-ethoxyethanol/1,2-dimethoxyethane (v/v=2:3, 14 mL/g) was added 10 wt% DDQ followed by 10 wt% ^{t}BuONO. The reaction mixture was stirred at 80 °C for 14 h under an O_2 atmosphere (balloon). Diethyl ether (500 mL for KL, 250 mL for GL) was added to the reaction mixture to precipitate the oxidized lignin, which was isolated by filtration using a PTFE filter membrane, and then washed with additional diethyl ether (1 L for KL, 0.5 L for GL) to remove residual organics. The filtered lignin was then mixed with a saturated $NaHCO_3$ solution (1 L for KL, 0.5 L for GL), filtered, washed with deionized water (2 L for KL, 1 L for GL), and dried *in vacuo* at 40 °C overnight. Oxidized KL and GL are abbreviated as KL_{DDQ} and GL_{DDQ}. Yield: 9.95 g (99%) KL_{DDQ}, 3.72 g (93%) GL_{DDQ}. The oxidized lignins were characterized by 2D heteronuclear single-quantum coherence (HSQC) NMR spectroscopy (see electronic supporting information for details).

Secondary Lignin Depolymerization methods

Zinc-mediated depolymerization

The method used was adapted from a literature procedure.[13] To a solution of KL_{DDQ} or GL_{DDQ} (600 mg) in 2-ethoxyethanol (8.4 mL) was added deionized water (2.1 mL), NH_4Cl (740 mg), and zinc dust (900 mg). The reaction mixture was stirred at 80 °C for 1 h, after which the mixture was cooled and excess zinc was removed via filtration. To precipitate the lignin, the filtered mixture was added to deionized water (30 mL) and acidified using 1 M HCl until pH of 1 was reached, after which the mixture was filtered. The filtered lignin was extracted with EtOAc (3 × 50 mL), and the combined organic extracts were washed with saturated $NaHCO_3$ solution, followed by brine, and then dried over $MgSO_4$, and concentrated *in vacuo*. Yield: 17 mg (3%) for KL_{DDQ}, 30 mg (5%) for GL_{DDQ}.

Formic acid-induced depolymerization

The method used was adapted from a literature procedure.[14] A 25 mL heavy-walled pressure flask equipped with a thermowell was loaded with KL_{DDQ} or GL_{DDQ} (150 mg), aqueous formic acid (85 wt%, 25 mL), and sodium formate (107 mg). A PTFE screw cap was used to seal the reaction vessel and the mixture was stirred at 110 °C for 24 h. Formic acid was then removed under vacuum, and the insoluble fraction was washed thoroughly with diethyl ether, followed by water to remove sodium formate. The resulting mixture was extracted with EtOAc (3 × 20 mL), and the organic soluble fractions were combined, dried over $MgSO_4$, and concentrated under vacuum, resulting in 19 mg (13%) of material being recovered for KL_{DDQ} and 35 mg (23%) for GL_{DDQ}.

Baeyer-Villiger oxidation

This method was adapted from a literature procedure.[16] A 20 mL glass vial was charged with KL_{DDQ} or GL_{DDQ} (150 mg), formic acid (85%, 0.32 mL), H_2O_2 (30%, 0.5 mL), and H_2O (0.4 mL). The vial was sealed using a Teflon-lined cap and stirred for 70 h at 50 °C. Upon completion, water was added until the reaction mixture reached a pH of 4, whereupon the mixture was gravity filtered. The filtrate was extracted with EtOAc (3 × 15 mL), and the combined organic-soluble fractions were dried under vacuum, 31 mg (21%) of material being recovered for KL_{DDQ} and 32 mg (21%) for GL_{DDQ}.

Oxidation using the $Cu(OAc)_2$/1,10-phenanthroline

This method was adapted from a literature procedure,[12] all reagents being scaled accordingly to the assumption that 1 g of lignin contains 3 mmol benzylic alcohol groups. A 50 mL Parr autoclave reactor equipped with an internal Teflon seal was loaded with KL_{DDQ} or GL_{DDQ} (533 mg), $Cu(OAc)_2$ (58 mg), 1,10-phenanthroline (58 mg), and MeOH (16 mL). The reactor was charged with 8% O_2 balanced with N_2 (50 bar total pressure) and heated to 100 °C with a mixing speed of 600 rpm. After 2 h, the reaction mixture was filtered and washed with additional MeOH (80 mL). The combined filtrate was concentrated in vacuo yielding 103 mg (9%) of material for KL_{DDQ} and 128 mg (14%) for GL_{DDQ}.

Dakin oxidation

This method used was adapted from a literature procedure.[15] Either KL_{DDQ} or GL_{DDQ} (67 mg), 2 M NaOH (0.5 mL), and MeOH/THF (v/v = 1:1, 1.2 mL) were loaded into a 5 mL round-bottom flask equipped with a stir-bar. Subsequently, H_2O_2 (30%, 0.1 mL) was slowly added and the mixture was left stirring for 10 h at 50 °C. The reaction mixture was acidified with HCl (0.5 M) to pH ~3. The resulting mixture was extracted using EtOAc (4 × 20 mL), and the organic layers were combined, dried over $MgSO_4$, filtered and concentrated *in vacuo*. Yield: 10 mg (15%) for KL_{DDQ} and 12 mg (18%) for GL_{DDQ}.

Depolymerization over Li-Al LDH and Au/Li-Al LDH

This method was adapted from a literature procedure.[17] Oxidation of KL_{DDQ} and GL_{DDQ} was conducted in a 100 mL 3-neck round-bottom flask using a Radleys StarFish reactor, employing lignin sample (250 mg), Li-Al LDH or Au/Li-Al LDH (100 mg), and dimethylformamide (10 mL) under flowing O_2 (10 mL•min^{-1}) at 120 °C and 500 rpm stirring for 24 h. The resulting mixture was filtered and washed with additional dimethylformamide (15 mL) and concentrated *in vacuo*. The product was further dried in a vacuum oven at 50 °C for 24 h, affording a dark-brown solid. The solid obtained from each lignin (50 mg) was hydrolyzed using 1 M NaOH (5 mL) and stirred for 1 h. Upon reaction completion the mixture was acidified to pH 2 via addition of 1 M HCl and extracted using brine and EtOAc (3 × 15 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Yield for Li-Al LDH: 27 mg (11%) for KL_{DDQ} and 77 mg (31%) for GL_{DDQ}. Yield for Au/Li-Al LDH: 63 mg (25%) for KL_{DDQ} and 124 mg (50%) for GL_{DDQ}.

Control experiments were performed by hydrolyzing KL_{DDQ} (50 mg) and GL_{DDQ} (50 mg) using 1 M NaOH (5 mL) under stirring for 1 h. Upon reaction completion the mixture was acidified to pH 2 via addition of 1 M HCl and extracted using brine and EtOAc (3 × 15 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Yield: 0.5 mg (1%) for KL_{DDQ} and 2.5 mg (5%) for GL_{DDQ}.

Results and Discussion

In order to standardize the preliminary benzylic oxidation, we elected to use 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in combination with $^{t}BuONO/O_2$ as an effective and scalable catalyst for selective β-ether unit oxidation. The use of DDQ for benzylic oxidation in lignin and lignin model compounds has been reported by Lancefield *et al.*,[13] this

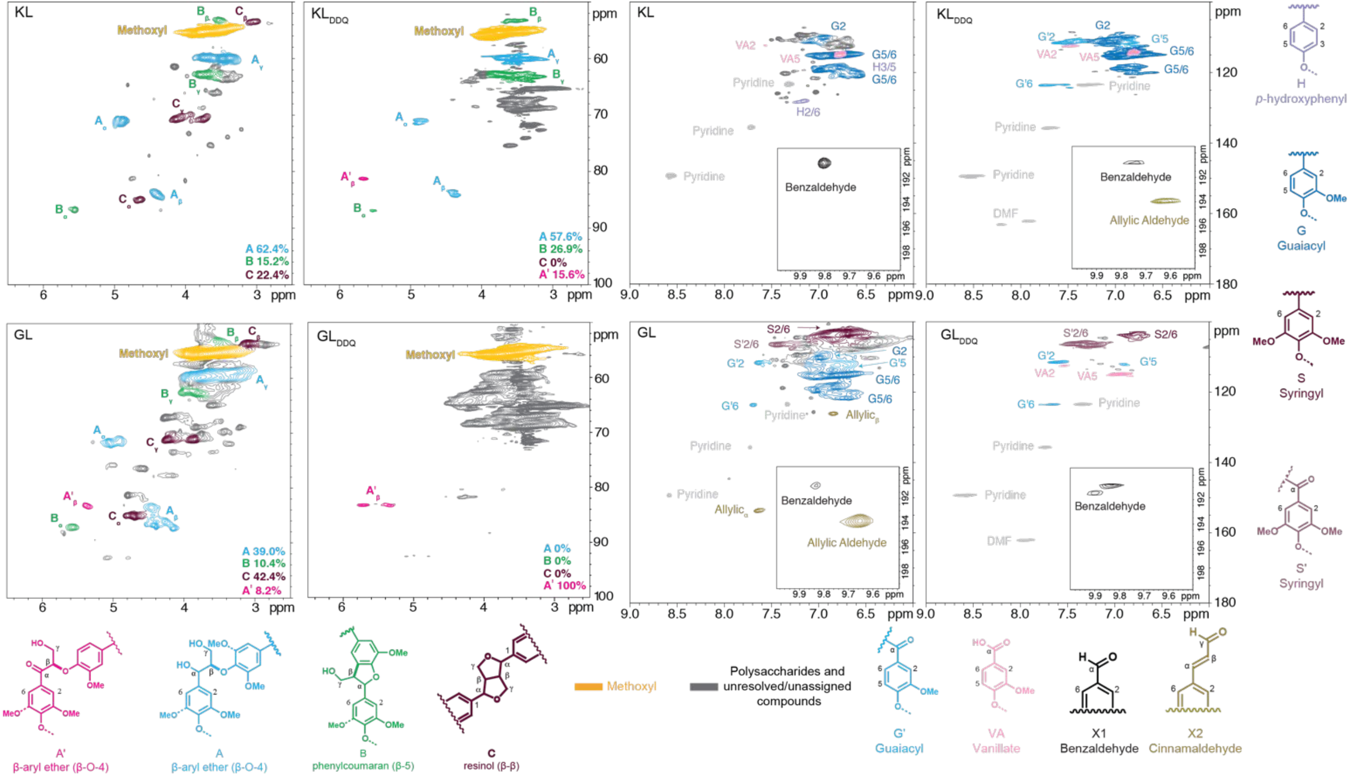

Figure 3. 2D HSQC NMR spectra of KL, KL_{DDQ}, GL, and GL_{DDQ}. All samples were dissolved in 4:1 DMSO-d_6/pyridine-d_5; contours are color-coded to the structures responsible; percentages are determined from volume integrals based on $\alpha_{C–H}$ with the exception of A′ which uses the $\beta_{C–H}$ signal. The assignment of peaks is based on known lignin spectra and available model compound data. Note: volume integrals are considered qualitative due to differences in T_2 relaxations and $J_{C–H}$ coupling constants.

method being suitable for application on the gram scale without specialized equipment. Gel permeation chromatography (GPC) analysis of KL and GL pre- and post-DDQ oxidation (see **Figure S1 and S2** in the electronic supporting information) revealed that DDQ/^{t}BuONO/O_2 oxidation did not affect the molecular weight distribution of either lignin. **Figure 3** shows the 2D HSQC NMR spectra of KL and GL before and after oxidation with the DDQ/^{t}BuONO/O_2 system.

Analysis of the aromatic region of GL_{DDQ} revealed that all of the benzylic alcohol groups in the guaiacyl (**G**) units and most of the benzylic alcohol groups in the syringyl (**S**) units underwent oxidation, giving the corresponding benzylic ketones (**G′** and **S′**). In contrast, the aromatic region of KL showed a significant amount of residual unoxidized benzylic alcohol groups. Examination of the aliphatic region supports this observation, only oxidized β-aryl ether units (**A′**) being observed for GL, whereas only a minor fraction of the β-O-4 linkages was oxidized for KL. The ineffectiveness of the oxidation system on KL can be explained by the recalcitrant nature of the lignin after the kraft process, which also renders KL poorly soluble in the solvent system.[19–22]

The oxidized lignins were subjected to seven secondary depolymerization methods and the results were compared to our previously published Au/Li-Al LDH and O_2 system, which did not require prior C_α-OH oxidation.[17] A control experiment was also performed in which the hydrolysis method used in conjunction with Au/Li-Al LDH and Li-Al LDH was also performed on KL_{DDQ} and GL_{DDQ} in order to establish the effect of the heterogenous catalysts. Results are summarized in **Figure 4**; additionally, GPC analysis (see **Figure S3**-**S16** in the electronic supporting information) of the organic mixtures from each secondary depolymerization method showed molecular weight distributions that represent similar results to those presented in **Figure 4.** In general, much higher yields of organic-soluble products were obtained for GL_{DDQ} compared to KL_{DDQ}. This is not surprising given the limited degree of oxidation observed for KL_{DDQ} by HSQC NMR spectroscopy and the likely substantial degradation of the lignin during the kraft pulping process; GL is less condensed than KL, so more of the β–O–4 ether linkages are preserved, allowing for easier depolymerization.[23]

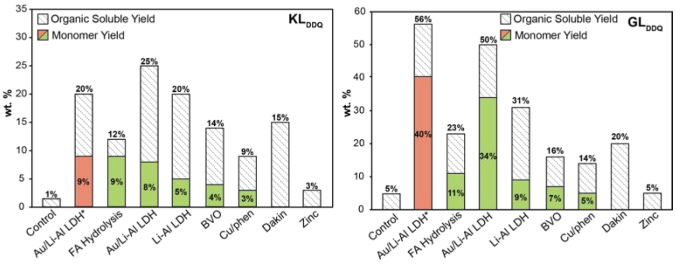

Figure 4. Organic-soluble yield obtained from secondary depolymerization of KL_{DDQ} and GL_{DDQ}. Au/Li-Al LDH* represents results obtained from ref. 17, without prior C_α-OH oxidation.

The resulting ethyl-acetate-soluble product mixtures were analyzed by gas chromatography-mass spectrometry (GC-MS) in order to identify and quantify – using authentic standards and calibration curves – the monomeric products (**Figures 5** and **6**). The results showed that the aromatic acids and aldehydes derived from syringyl (**S**) and guaiacyl (**G**) units were the major oxidative depolymerization products. For the case of KL_{DDQ} (**Figure 5**), FA hydrolysis as reported by Stahl and coworkers[14] was revealed to be the most effective depolymerization method, yielding 4.7 wt% vanillic acid and 3.1 wt% vanillin. An estimated 0.8 wt% yield of the **G**-derived diketone was also observed in the product mixture (based on the total ion chromatogram, i.e., the area of product divided by the summed area of all products). The second most efficient method in this case was the Au/Li-Al LDH catalyst coupled with hydrolysis, yielding a total of 8 wt% monomers with 5.2 wt% vanillic acid and 2.2 wt% vanillin as the major products, representing a higher vanillic acid to vanillin ratio compared to the FA hydrolysis method (2.4 versus 1.5). Three other methods, namely, the Li-Al LDH support, BVO, and Cu/phen also produced monomers from KL_{DDQ}; however, the yields were lower compared to the previous two methods. The Li-Al LDH support alone achieved a 5 wt% monomer yield, vanillic acid being the major product (3.2 wt%). The BVO method produced a similar monomer yield compared to the Li-Al LDH support; however, the method was more selective to vanillin, providing a 2.8% yield. In the literature, the Cu/phen method[12] was tested solely on lignin model dimers containing C_α-OH groups. When the method was applied to KL_{DDQ}, small amounts of acetovanillone (1.9 wt%) and vanillin (0.9 wt%) were obtained, as well as trace amounts of methyl vanillate (resulting from esterification of vanillic acid by the methanol solvent). Methyl vanillate formation was also observed when this method was applied to a β-ether model dimer.[12]

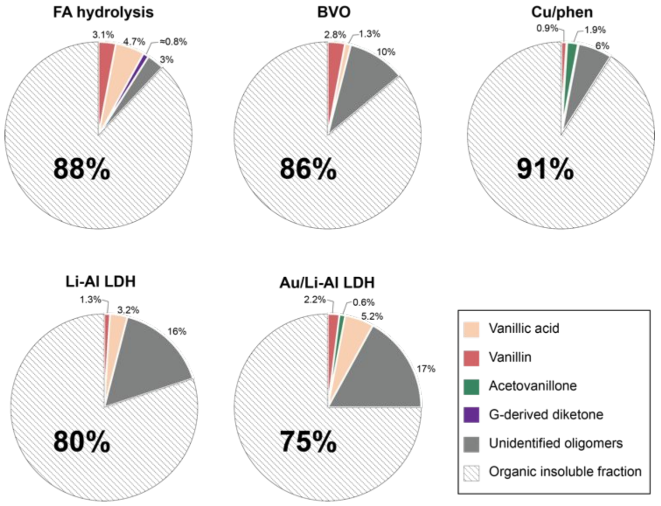

Figure 5. Organic-soluble yield from KL_{DDQ} after secondary oxidative depolymerization

In the case of GL_{DDQ} (**Figure 6**), the application of Au/Li-Al LDH-catalyzed oxidation coupled with hydrolysis gave the highest yield of monomers (34 wt%), the majority of the product consisting of acids derived from lignin's **S** and **G** units (22 wt%

total). Very low organic soluble yields were obtained when hydrolysis was the only step performed on KL_{DDQ} and GL_{DDQ} (1 wt% and 5 wt%, respectively), which demonstrates the necessity of the Au/Li-Al LDH catalyst for monomer production. This monomer yield is significantly higher than those obtained from the remaining six methods. Although FA hydrolysis gave the highest monomer yield for KL_{DDQ}, only 11 wt% of monomers were produced when applied to GL_{DDQ}, making it the second most efficient method. The products observed from GL_{DDQ} depolymerization using the FA hydrolysis method were similar to those reported by Stahl and coworkers;[23] they applied FA hydrolysis to GL which had been first oxidized using 4-acetamido-TEMPO (AcNH-TEMPO), obtaining only 5.2 wt% monomers. This discrepancy in the monomer yields can be attributed to the fact that AcNH-TEMPO did not fully oxidize the GL lignin[24] whereas complete oxidation was achieved using DDQ/^{t}BuONO, as observed by 2D HSQC NMR spectroscopy (**Figure 3**). Similar trends to those noted for KL_{DDQ} were observed for the remaining methods. The Li-Al LDH support alone gave a total monomer yield of 9 wt%, syringaldehyde being the most abundant product (3.1 wt% yield). However, the Li-Al LDH support was not as effective as the Au/Li-Al LDH/O_2 catalyst system, proving that the presence of Au nanoparticles is crucial for the depolymerization process; indeed, the nanoparticles are essential for the activation of molecular oxygen.[25–27] BVO gave a slightly higher yield of monomers when applied to GL_{DDQ} compared to KL_{DDQ}, an increased yield of vanillic acid being obtained (1.6 wt% vs. 1.3 wt%) in addition to syringaldehyde (2.3 wt%). The Cu/phen method also achieved higher yields with GL_{DDQ} compared to KL_{DDQ}, the main products being the phenolic acids derived from **S** and **G** units (total of 3.1 wt%).

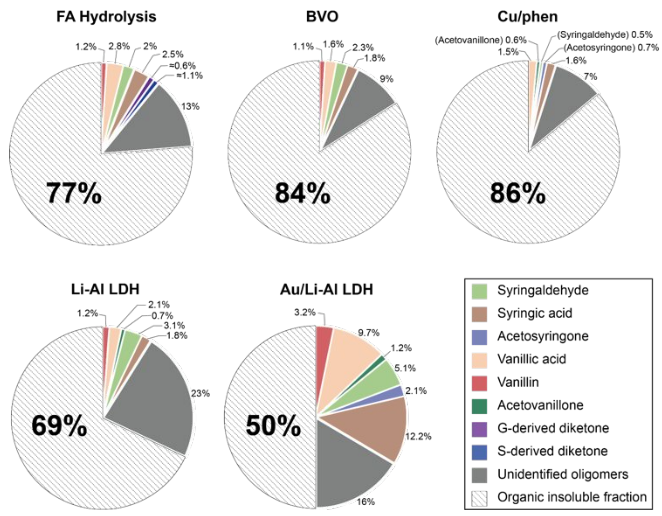

Figure 6. Organic-soluble yield from GL_{DDQ} after secondary oxidative depolymerization

Neither Dakin oxidation nor the zinc-mediated depolymerization method produced any monomers when applied to either KL_{DDQ} or GL_{DDQ}, although Dakin oxidation did achieve a higher yield of soluble material (lignin oligomers). In contrast, Lancefield *et al.*[13] observed a total monomer yield of 6 wt% using zinc-mediated depolymerization method on birch wood lignin extracted by mild-acidolysis (HCl/1,4-dioxane). The fact that monomers were produced for their case may be due to increased solubility of the mild-acidolysis-extracted birch wood lignin in 2-methoxyethanol, which was the solvent used. When we applied the zinc-mediated method to KL_{DDQ} and GL_{DDQ}, very little of the lignin was soluble in the reaction medium, likely limiting the reactivity. Stahl and coworkers[15] used Dakin oxidation on a lignin model β-ether dimer, and they observed 100% conversion of the dimer to the corresponding phenolic acid and alcohol; however, their reaction utilizes MeOH/THF as solvent. When we applied these reaction conditions to KL_{DDQ} or GL_{DDQ}, very little solubility was achieved. Compared to the zinc-mediated method, more organic-soluble content was obtained, which can be attributed to the use of 2 M NaOH in the reaction. Importantly, 2 M NaOH has the ability to depolymerize lignin by cleaving β–O–4 ether linkages.[28,29] Although no monomers were detected using this method, NaOH could have depolymerized KL_{DDQ} and GL_{DDQ} into smaller lignin fragments that are organic soluble.

Comparing these results to our published study in which KL and GL were subjected to oxidation by Au/Li-Al LDH/O_2 without prior C_α-OH oxidation, followed by hydrolysis (**Figure 7**),[17] it is apparent that FA hydrolysis produced an equivalent wt% monomer yield in the case of KL_{DDQ}. However, FA hydrolysis gave slightly higher yields of vanillin and vanillic acid compared to Au/Li-Al LDH/O_2 and hydrolysis (total of 7.8 wt% vs. 6.8 wt%, **Figure 7A**). On the other hand, for GL_{DDQ} (**Figure 7B)** FA hydrolysis gave much a lower total monomer yield compared to Au/Li-Al LDH/O_2 coupled with hydrolysis. Comparing the same Au/Li-Al LDH oxidative depolymerization method pre- and post-C_α-OH oxidation with DDQ, the total monomer yield for KL decreased to 8 wt% from 9 wt%, whereas for GL it decreased from 40 wt% to 34 wt%. This is likely, in part, a consequence of the decrease in lignin solubility after C_α-OH oxidation. Indeed, the lignins were observed to be less soluble in DMF post-DDQ oxidation, this being attributed to the decrease in C_α-OH groups which lowers the hydrogen bonding ability of the lignin macromolecule.[30] Another difference is that ferulic acid and coniferyl alcohol are obtained from the KL and GL depolymerization method using Au/Li-Al LDH/O_2, whereas these monomers are not observed when the same catalyst is applied to KL_{DDQ} or GL_{DDQ}. Although this result requires further investigation, KL and GL most likely underwent different structural changes when oxidized by DDQ compared to the application of Au/Li-Al LDH/O_2, which results in hindered

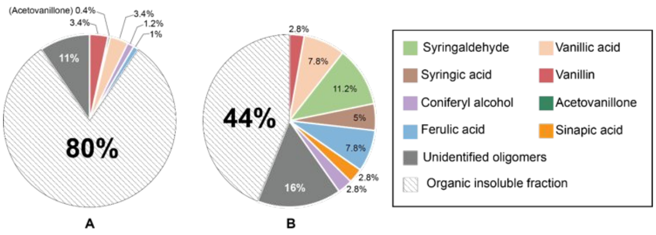

Figure 7. Organic-soluble yield from KL (A) and GL (B) after oxidative depolymerization using Au/Li-Al catalyst and hydrolysis. Adapted from ref. 17.

release of the ferulic acid and coniferyl alcohol. On the other hand, whereas the total monomer yield decreased for KL_{DDQ} and GL_{DDQ}, the selectivity to aromatic acids and aldehydes increased. Prior to C_α-OH oxidation, out of the 40.2 wt% total monomer yield for GL, 26.8 wt% consisted of benzyl acids and aldehydes derived from **S** and **G** units, whereas for lignin first oxidized using DDQ/^{t}BuONO, the yield of benzyl acids and aldehydes reached a total of 30.2 wt%, an increase of 3.4 wt%. A similar trend was observed for KL, although the difference was less significant. This observation is important given that product selectivity is a crucial issue for the integration of lignin into the bioeconomy.[31,32]

The environmental impact of each monomer-producing method was assessed by calculating the mass or volume of reagents and solvents necessary to yield 1 g of monomer from KL_{DDQ} and GL_{DDQ} (Figure 8; for detailed values see Tables S1 and S2 in the electronic supporting information). It should be noted that these calculations do not consider recycling of solvents, acids, and bases for the ease of comparison. While FA hydrolysis produced the highest wt% monomer (9 wt%) from KL_{DDQ} as shown in Figure 4, Au/Li-Al LDH requires the least amount of total reagent/solvent to produce 1 g monomer. For the case of GL_{DDQ}, the Au/Li-Al LDH method was the most efficient secondary depolymerization method (34 wt% total monomer yield), and consequently this method required significantly less reagent/solvent in order to produce 1 g monomer (Figure 8). Another consideration for these secondary depolymerization methods is the quantity of the reagents and solvents used during the DDQ/^{t}BuONO lignin oxidation process in order to obtain sufficient KL_{DDQ} and GL_{DDQ} for subsequent production of 1 g monomers (Figure 9; for the breakdown of each component refer for Tables S3 and S4 in the electronic supporting information). For oxidation of KL (blue and yellow bar graph), FA hydrolysis requires the least amount of KL_{DDQ} for 1 g monomer production, and therefore needs the least amount of KL and solvents/reagents for the first oxidation step. While Au/Li-Al_LDH uses the least amount of solvents/reagents to depolymerize KL_{DDQ} to obtain 1 g monomer, slightly more KL_{DDQ} was necessary as substrate compared to FA hydrolysis, and hence more chemicals are necessary during the initial oxidation process. On the other hand, as shown in Figure 8, Au/Li-Al LDH required significantly less GL_{DDQ} for 1 g monomer production compared to the other methods, and thus the mass and volume of reagents/solvents required for initial GL oxidation are also the lowest (green and grey bar graph in Figure 9). Au/Li-Al LDH is in this case the most environmentally friendly secondary depolymerization method as it required the least amount of chemicals for both the oxidation and secondary depolymerization steps combined. However, all chemicals used during the DDQ/^{t}BuONO can be eliminated for the single-step Au/Li-Al LDH + hydrolysis method, as the method is able to produce 1 g of monomer from KL and GL without prior oxidation (Au/Li-Al LDH* in Figure 8). Hence smaller quantities of reagents/solvents are required overall for this process. Based on these calculations, the single-step Au/Li-Al LDH + hydrolysis method is a much more efficient and environmentally-friendly system for lignin depolymerization for monomer production compared to the other methods tested.

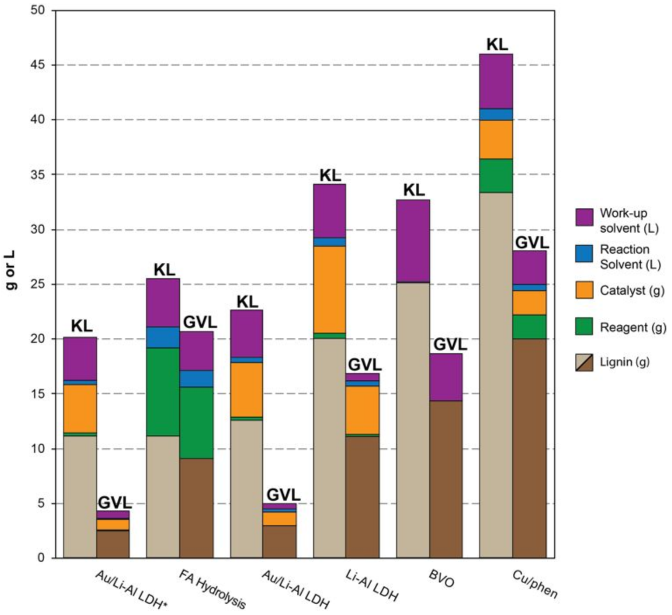

Figure 8. Reagents (g) and solvents (L) required for secondary depolymerization of KL_{DDQ} and GL_{DDQ} for 1 g total monomer yield. Au/Li-Al LDH* represents values for 1 g monomer production without prior lignin oxidation, from ref. 17.

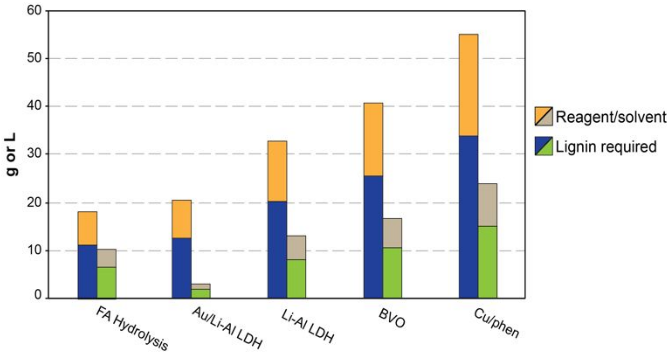

Figure 9. Lignin, reagents, and solvent required for DDQ/^{t}BuONO oxidation of KL (blue and yellow) and GL (green and grey) for 1 g monomer production.

Conclusion

We employed two different DDQ-oxidized lignins in order to facilitate the comparison of seven different secondary depolymerization methods: zinc mediated depolymerization, formic acid hydrolysis, selective C–C bond cleavage using H_2O_2/NaOH (Dakin Oxidation), Baeyer-Villiger oxidative depolymerization, selective C–C bond cleavage using $Cu(OAc)_2$/1,10-phenanthroline, base catalysis using Li-Al LDH followed by hydrolysis, and oxidation using Au/Li-Al LDH followed by hydrolysis. Each method was applied to the same Indulin AT kraft lignin (KL) and a lignin extracted by γ-valerolactone (GL), each of which had been first oxidized using DDQ/^{t}BuONO. Formic acid hydrolysis afforded the highest yield of monomers for kraft lignin whereas Au/Li-Al LDH + hydrolysis gave the highest monomer yield for GL. However, without prior C_α-OH oxidation, Au/Li-Al LDH + hydrolysis gave the same monomer yield for KL as formic acid hydrolysis, and a higher yield of monomers from GL. From a practical standpoint, not only does Au/Li-Al LDH possess the advantage being a heterogenous catalyst, which allows for ease of catalyst recovery, but compared to the two-step oxidation depolymerization experiments presented in this study, it is more effective at lignin depolymerization without a prior benzylic alcohol oxidation step. Based on these results, the use of Au/Li-Al LDH coupled with hydrolysis represents the most promising oxidative system reported to date for lignin depolymerization to valuable low-molecular-weight aromatics.

Conflicts of interest

There are no conflicts to declare.

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