Electronic Supporting Information for:

A Comparative Study of Secondary Depolymerization Methods on Oxidized Lignins

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Materials and Methods

Commercially available reagents were used as received. 2-ethoxyethanol, NH_4Cl, 1,2-dimethoxyethane, formic acid (85%), $Cu(OAc)_2$, tert-butyl nitrite (^tBuONO) (90%), and *N*,*O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA) were purchased from Alfa Aesar. H_2O_2 and 1,10-phenanthroline were purchased from VWR. Methanol, tetrahydrofuran, and ethyl acetate were purchased from BDH VWR Chemicals. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) was obtained from Acros Organics. Sodium hydroxide was purchased from Ricca Chemical Company. N,N-dimethylformamide (DMF) was obtained from Honeywell Research Chemicals. Zinc dust was purchased from Ward's Science. Sodium formate was purchased from Sigma-Aldrich.

Heteronuclear Single-Quantum Coherence (HSQC) NMR

Spectra were acquired as described previously[17] at the DOE Great Lakes Bioenergy Research Center (University of Wisconsin, Madison, WI, USA) on a Bruker Biospin (Billerica, MA) Avance 700 MHz spectrometer equipped with a 5-mm quadruple-resonance $^1H/^{31}P/^{13}C/^{15}N$ QCI gradient cryoprobe with inverse geometry (proton coils closest to the sample). Lignin samples were placed directly in NMR tubes (22 mg for each sample) and dissolved using DMSO-d_6/pyridine-d_5 '100%' (4:1 v/v, 0.5 mL). The central DMSO solvent peak was used as an internal reference (δ_C 39.5 ppm, δ_H 2.5 ppm). The $^1H–^{13}C$ correlation experiment was an adiabatic HSQC experiment (Bruker standard pulse sequence 'hsqcetgpsisp2.2'; phase-sensitive gradient-edited 2D HSQC using adiabatic pulses for inversion and refocusing).[19] Experiments were carried out using the following parameters: acquired from 11.5 to -0.5 ppm in F2 (^1H) with 3366 data points (acquisition time 200 ms), 215 to -5 ppm in F1 (^{13}C) with 620 increments (F1 acquisition time 8 ms) of 128 scans with a 1 s interscan delay; the d24 delay was set to 0.86 ms (1/8J, J = 145 Hz). The total acquisition time for a sample was 6 h. In all cases, processing used typical matched Gaussian apodization (GB = 0.001, LB = -0.1) in F2 and squared cosine-bell and one level of linear prediction (32 coefficients) in F2. Volume integration of contours in HSQC plots used Bruker's TopSpin 4.0.5 (Mac version) software.

Gas chromatography-mass spectrometry (GC-MS)

Analyses were performed using an Agilent 7890 GC with a tandem Agilent 5975C MS detector. The column used in the GC was a DB-1701 (60 m or 15 m × 0.25 mm × 0.25 μm). Helium was used as carrier gas with the flow rate set to 1 mL/min for the 60 m column and 0.5 mL/min for the 15 m column. The inlet temperature was maintained at 280 °C with a temperature ramp of 60 °C to 80 °C at 2 °C/min, then to 110 °C at 3 °C/min, followed by a 20 °C/min ramp to 190 °C, and finally at 2 °C/min reaching 230 °C. All analyses were quantified using authentic standards and a GC-MS internal standard method by obtaining internal response factors of all starting materials and products using *n*-dodecane as the internal standard.

Gel permeation chromatography (GPC)

Analyses was carried out on an Agilent 1260 Infinity Quaternary LC system equipped with a G1311A Quaternary pump, G1329B Autosampler, G1364C Fraction Collector, G1316A Column Compartment, G1315C Diode-Array Detector (DAD). Samples were analyzed using SUPREMA analytical linear S 10μm (50 x 8 mm) and SUPREMA analytical linear S 10μm (300 x 8 mm) GPC columns (Polymer Standards Services) connected in series, and eluted using inhibitor free THF/DMSO (v/v=1:1, 0.4 mL/min) with a column oven temperature of 25 °C.

Author Contributions

J.K.M. designed the study and analyzed the 2D HSQC NMR data. Y.S. performed all lignin oxidation/secondary depolymerization experiments, GC-MS analysis, and GPC analysis. A.H.M. performed lignin isolation using the GVL method. S.D.K collected 2D HSQC NMR data. J.A.D, J.R. and M.C. provided funding for corresponding experiments and analysis performed. Y.S., J.K.M., and M.C. wrote the paper, and all co-authors provided comments.

Gel permeation chromatograms of lignins pre- and post-DDQ oxidation

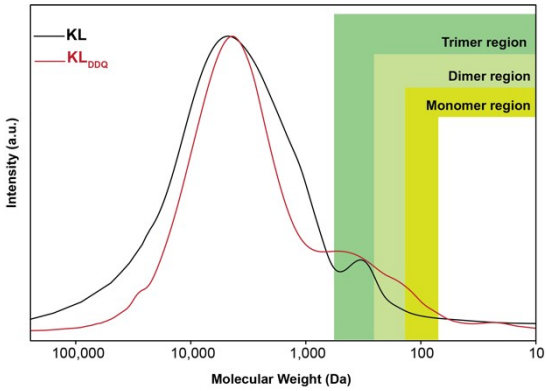

Figure S1. Molecular weight (M*w)* distribution of KL pre-and post-DDQ oxidation

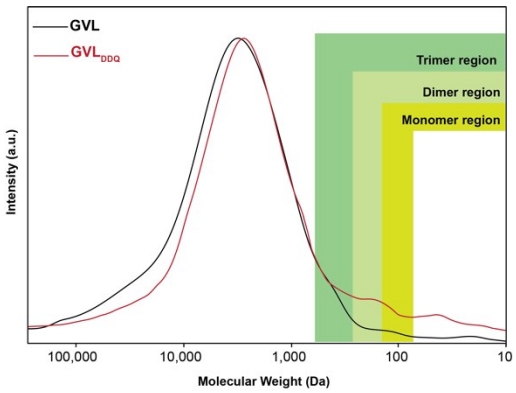

Figure S2. M*w* distribution of GVL pre- and post-DDQ oxidation

Gel permeation chromatograms of EtOAc-soluble content after secondary lignin depolymerization

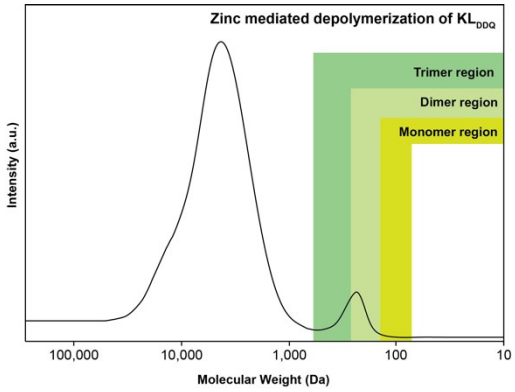

Figure S3. M*w* distribution of KL$_{DDQ}$ post zinc depolymerization

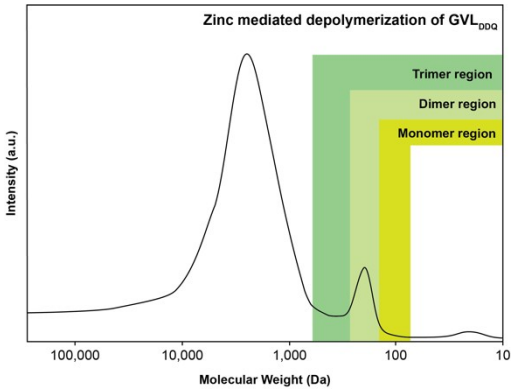

Figure S4. M*w* distribution of GVL$_{DDQ}$ post zinc depolymerization

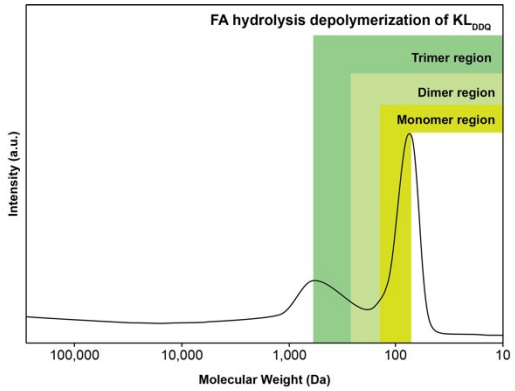

Figure S5. M*w* distribution of KL_{DDQ} post FA hydrolysis depolymerization

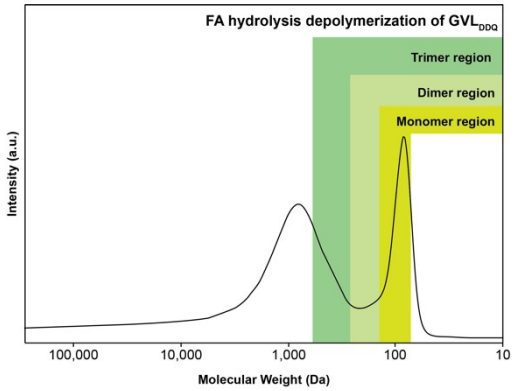

Figure S6. M*w* distribution of GVL_{DDQ} post FA hydrolysis depolymerization

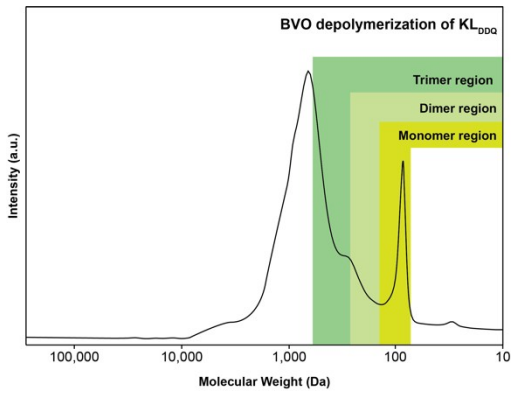

Figure S7. M*w* distribution of KL_{DDQ} post BVO depolymerization

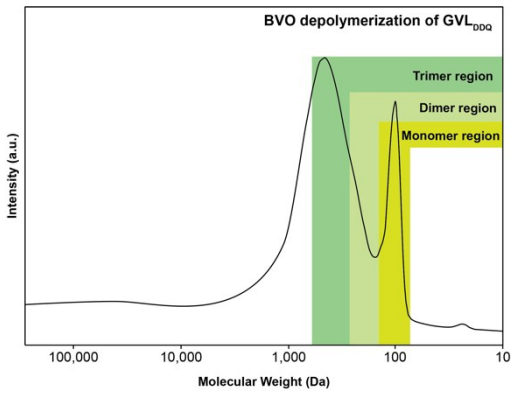

Figure S8. M*w* distribution of GVL_{DDQ} post BVO depolymerization

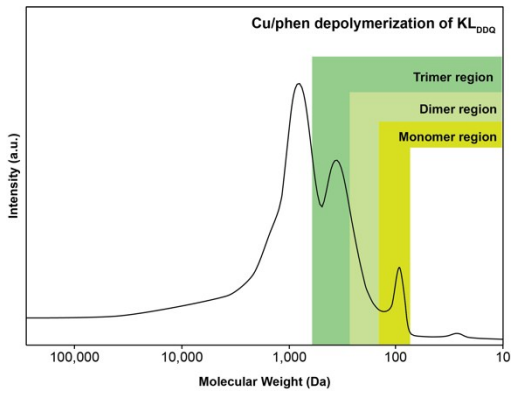

Figure S9. M*w* distribution of KL_{DDQ} post Cu/phen depolymerization

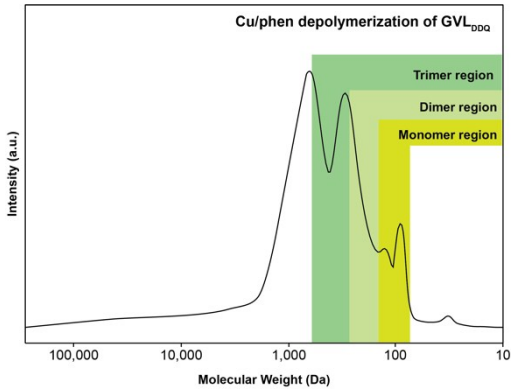

Figure S10. M*w* distribution of GVL_{DDQ} post Cu/phen depolymerization

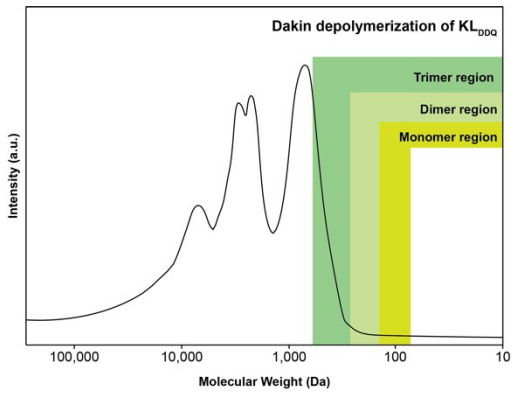

Figure S11. M*w* distribution of KL_{DDQ} post Dakin depolymerization

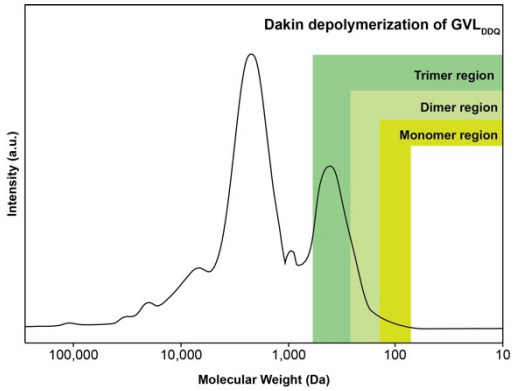

Figure S12. M*w* distribution of GVL_{DDQ} post Dakin depolymerization

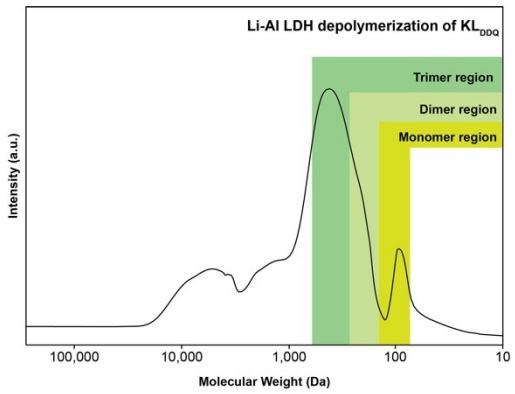

Figure S13. M*w* distribution of KL_{DDQ} post Li-Al LDH depolymerization

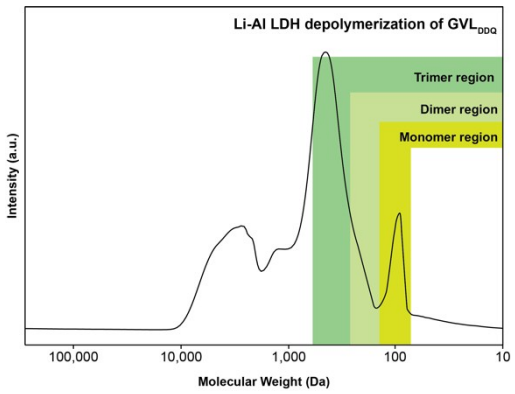

Figure S14. M*w* distribution of GVL_{DDQ} post Li-Al LDH depolymerization

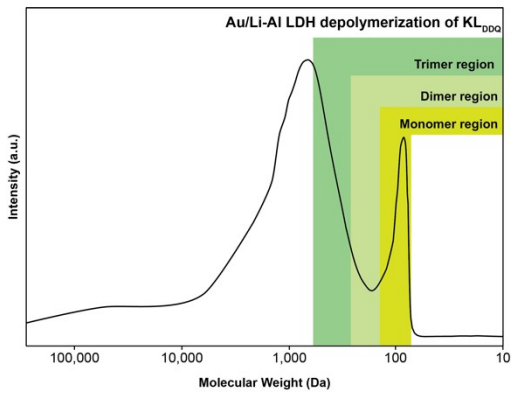

Figure S15. M*w* distribution of KL_{DDQ} post Au/Li-Al LDH depolymerization

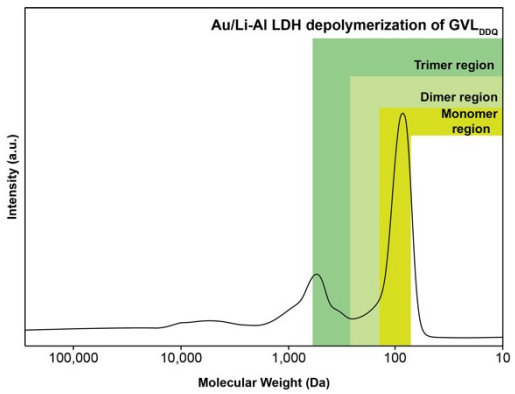

Figure S16. M*w* distribution of GVL_{DDQ} post Au/Li-Al LDH depolymerization

Environmental impact assessment

Table S1. KL_{DDQ}, reagents, catalysts, and solvents required for 1 g monomer yield using each secondary depolymerization method.

	Au/Li-Al LDH*	FA hydrolysis	Au/Li-Al LDH	Li-Al LDH	BVO	Cu/phen
KL_{DDQ} (g)	11.1	11.10	12.50	20.00	25.00	33.30
Reagent (g)	0.22	8.00	0.25	0.40	0.07	3.00
Catalyst (g)	4.40	0.00	5.00	8.00	0.00	3.60
Reaction Solvent (L)	0.44	1.90	0.50	0.80	0.05	1.00
Work-up solvent (L)	3.87	4.44	4.35	4.80	7.50	5.00
Total	20.03	25.44	22.6	34	32.62	45.9

Table S2. GVL_{DDQ}, reagents, catalysts, and solvents required for 1 g monomer yield using each secondary depolymerization method.

	Au/Li-Al LDH*	FA hydrolysis	Au/Li-Al LDH	Li-Al LDH	BVO	Cu/phen
GVL_{DDQ} (g)	2.5	9.10	2.90	11.10	14.30	20.00
Reagent (g)	0.05	6.50	0.05	0.20	0.05	2.20
Catalyst (g)	1.00	0.00	1.20	4.40	0.00	2.20
Reaction Solvent (L)	0.1	1.50	0.29	0.44	0.03	0.60
Work-up solvent (L)	0.6	3.60	0.52	0.66	4.30	3.00
Total	4.3	20.7	5.0	16.8	18.7	28.0

Table S3. KL, reagents, and solvents required for DDQ/^{t}BuONO oxidation to produce sufficient amount of KL_{DDQ} for 1 g monomer yield from each secondary depolymerization method.

	FA Hydrolysis	Au/Li-Al LDH	Li-Al LDH	BVO	Cu/phen
KL (g)	11.20	12.60	20.20	25.20	33.60
2-ethoxyethanol/1,2-dimethoxyethane (2:3) (L)	0.16	0.18	0.28	0.35	0.47
10 wt.% DDQ (g)	1.12	1.26	2.02	2.52	3.40
10 wt.% ^{t}BuONO (g)	1.12	1.26	2.02	2.52	3.40
Diethyl ether (L)	1.10	1.30	2.00	2.50	3.40
Saturated NaHCO3 (L)	1.10	1.30	2.00	2.50	3.40
Total	15.80	17.90	28.52	35.59	47.67

Table S4. GVL, reagents, and solvents required for DDQ/^{t}BuONO oxidation to produce sufficient amount of GVL_{DDQ} for 1 g monomer yield from each secondary depolymerization method.

	FA Hydrolysis	Au/Li-Al LDH	Li-Al LDH	BVO	Cu/phen
GVL(g)	9.18	2.52	11.21	14.40	20.18
2-ethoxyethanol/1,2-dimethoxyethane (2:3) (L)	0.13	0.04	0.16	0.20	0.28
10 wt.% DDQ (g)	0.92	0.25	1.12	1.44	2.04
10 wt.% tBuONO (g)	0.92	0.25	1.12	1.44	2.04
Diethyl ether (L)	0.90	0.26	1.11	1.43	2.04
Saturated NaHCO3 (L)	0.90	0.26	1.11	1.43	2.04
Total	12.95	3.58	15.83	20.35	28.63