

Supplementary information:

Perspective on Oligomeric Products from Lignin Depolymerization: Its Generation, Identification, and further Valorization

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To make each reference in Fig.1,3, and 4 easily being tracked, detail information about each reference (condition, catalyst, paper title and year) in Fig.1,3 and 4 is listed in table S1, S3, and S4, respectively.

Table S1 References used to build Fig.1

Table S1 (All references used to build Fig.1)										
RCD	ref# in nev	Ref for RCD	Monomer:	Oligomers	Best Condition	Cat/Feed	Paper title			
2014	39	8 Alkali lignin from wheat straw	23	63	CuMgAlOx 300C	4h	Ethanol 10 bar H2 0.5/1	Catalytic Depolymerization of Lignin in Supercritical		
2015	40	17 bamboo Lignin	27.9	72.1	Raney Ni+ 270C	0.5h	Methanol/1bar N2 1+1/1	Depolymerization of Cellulolytic Enzyme Lignin for the Production of		
2015	41	19 organosolv lignin	10.9	90.1	Ni7Au3 160C	2h	NaOH/H2(10 bar H2 0.4/1	Base promoted hydrogenolysis of lignin model compounds and organosolv lignin over metal catalysts in water		
2016	42	21 Hartwig, (miscanthus giganteus lignin)	15.1	67	10% Pd/C 200C	24h	dioxane 1bar H2	Fragmentation of Lignin Samples with Commercial Pd/C under		
2015	19	24 Van den Bosch, (Birch)	51.5 (C yie	48.5	5% Ru/C 250C	6h	Methanol 30bar H2 0.15/1	Reductive Lignocellulose Fractionation into		
2013	24	30 EtOH/Benzene treated Birch	54	46	10% Ni/C 200C	6h	Methanol 1 bar Ar 0.05/1	Lignin Depolymerization (LDP) in alcohol over nickel		
2015	43	31 Poplar lignin	54	46	5% PdZn1C 225C	12h	Methanol 34.5 bar H.0.1/1	A Synergistic biorefinery based on catalytic conversion of lignin		
2015	21	32 Birch lignin	32	68	10%Ni/C 200C	6h	Methanol 2bar N2 0.1/1	Lignin Depolymerization over Ni/C catalyst in methanol,		
2016	44	34 miscanthus lignin	68	32	10%Ni/C 225C	12h	Methanol 60 bar H2 0.15/1	Total Utilization of Miscanthus Biomass, Lignin and Carbohydrates		
2016	45	39 beech lignin	51.4	48.6	10%Ni/C 200C	5h	Methanol/60bar H2 0.1/1	High Yield Productionof NaturalPhenolicAlcoholsfromWoody BiomassUsingaNickel-BasedCatalyst		
2016	46	40 Poplar lignin	43.5	56.5	Pd/C 200C	3h	Methanol/20 bar H2 0.1/1	Synergetic Effects of Alcohol/Water Mixing on the Catalytic Reductive Fractionation of Poplar Wood		
2015	30	41 Birch lignin	43.8	56.2	Pd/C 200C	3h	H2O 30 bar H2 0.1/1	Influence of bio-based solvents on the catalytic reductive fractionation of birch wood†		
2016	31	42 Corn stover lignin	24.5	75.5	10%Ni/C 200C	3h	Methanol/30 bar H2 0.1/1	Reductive Catalytic Fractionation of Corn Stover Lignin		
2017	47	43 Birch lignin	55	45	Pd/C+Al(O 180C	2h	Methanol/30 bar H2 0.1/1	Reductive fractionation of woody biomass into lignin monomers and cellulose by tandem metal triflate and Pd/C catalysi		
2017	48	44 Birch lignin	39.5	60.5	NiFe/C 200C	6h	Methanol 20 bar H2 0.5/1	Depolymerization of lignin via a non-precious Ni–Fe alloy catalyst supported on act		
2017	49	45 Birch lignin	36	64	Ni/Al2O3 250C	3h	Methanol 30 bar H2 0.1/1	Integrating lignin valorization and bio-ethanol production: on the role of Ni–Al2O3 catalyst pellets during lignin-first fractionation		
2017	50	46 Birch lignin	37	63	Pd/C+H3P1 180C	3h	Methanol/30 bar H2 Flow	Lignin depolymerization to monophenolic compounds in a flow-through system		
2017	51	47 Birch lignin	35.5	64.5	Ru/Nb2O5 250C	20h	H2O 7 bar H2 2/1ratio	Selective Production of Arenes via Direct Lignin Upgrading over a Niobium		
2017	52	48 Birch lignin	33	30	MoOx/CN 260C	4h	Methanol 30 bar H2 0.1/1	Catalytic Hydrogenolysis of Lignins into Phenolic Compounds over		
2018	53	49 Poplar (26% lignin)	19.7	80.3	Ni/C 200C	1h	Methanol 30 bar H2 0.2/1	Kinetic Studies of Lignin Solvolysis and Reduction by Reductive Catalytic Fractionation Decoupled in Flow-Through Reactors		
2019	54	50 Birch	46.1	53.9	Pt(1%)/gar 230C	3h	Methanol/30 bar N2 0.25/1	Catalytic Conversion of Lignin in Woody Biomass into Phenolic Monomers in Methanol/Water Mixtures without External Hydrogen		
2020	55	51 Eucalyptus lignin	44.1	38.9	Pd/C 180C	4h	Metahnol 30 bar H2	UnlockingStructure–ReactivityRelationshipsfor Catalytic		
2021	8	52 lignin acid extracted from corn stover	35.53	54.03	NiFeMo2C 260C	4h	water/Me130 bar H2 1/1ratio	Selective production of phenolic monomers via high efficient lignin		
2021	56	53 Corncob lignin	27.12	59.23	Ru/CNT-N 250C	24h	Methanol 10 bar H2 0.2/1	Hydrogenolysis of lignin to phenolic monomers over Ru based catalysts		
2022	57	54 Poplar	40	60	Pd/TiO2 180C	6h	H2O Ar 0.1/1	Self-hydrogen transfer hydrogenolysis of native lignin over Pd-PdO/TiO2		
2022	58	55 Cornstalk lignin	31.2	49.5	Ru/N dope 260C	4h	Ethanol 10 bar H2 0.4/1	Hydrogenolysis of cornstalk lignin in supercritical ethanol over N-doped		
OCD		Ref for RCD								
2017	17	56 Japanese cedar	22.5	77	Bu4NOH.3 air, 120C	43h	Bu4NOH.3 air, 1 bar 7mg/1	Tetrabutylammonium Hydroxide 30-Hydrate as Novel Reaction		
2009	59	57 Cornstalk lignin	18.1	22.9	LaCoO3 120C		H2O, NaO15 bar O2	Activity and Stability of Perovskite-Type Oxide LaCoO3 Catalyst in		
2010	60	58 Beech lignin	32.5	33.8	Mn(NO3)2 100C	24h	EMIM[CF3 17 bar O2 Air	Oxidative Depolymerization of Lignin in Ionic Liquids		
2013	61	59 mixed hardwood lignin	29.5	70.5	CuSO4 175C	1.5h	ionic liquid25 Bar O2 1/100	Process of lignin oxidation in an ionic liquid coupled		
2018	62	60 corn stover lignin	49	51	CuO 175C		NaOH/H2(5 bar O2	Revisiting alkaline aerobic lignin oxidation		
2021	32	61 Poplar	15	56	Co-PANI-C 190C	12h	ACETONE 2.5 bar O2	Oxidative Catalytic Fractionation of Lignocellulosic Biomass under		
2020	63	62 Red oak	10.5	89.5	No 250C	10min	perfluorod20 bar O2	Non-catalytic oxidative depolymerization of lignin		
2013	64	63 Pyrolytic lignin	66	34	H5PMo10 190C	1h	water/Me12 bar O2	Depolymerization of lignin by catalytic oxidation		
2021	65	64 Poplar lignin	28.1	45.9	PMo12 100C	2h	Methanol 9 bar O2	Oxidative Catalytic Fractionation and Depolymerization of Lignin in		
2011	66	65 organosolv lignin	18	45	160C		1:3Lignin/30%H2O2	Selective Production of Organic Acids and Depolymerization of Lignin by Hydrothermal		
2019	67	66 Poplar lignin	8.06	85.02	Phosphotu 250C	6h	Ethanol/W1:4Lignin/30%H2O2	A Comparison of Phenolic Monomers Produced from Different Types of Lignin by Phosphotungstic Acid		
2022	68	67 alkaline lignin	40.97	59.03	100C	2h	IL 11.5 bar O2	Enhanced oxidative depolymerization of lignin in		
2020	34	68 kraft lignin	10.47	71.83	FeCl3 100C	4h	Methanol 10 bar O2	Low temperature lignin depolymerization to aromatic compounds		
2020	69	69 kraft lignin	17	83	CuMn 180C		1:3Lignin/30%H2O2	Alkaline wet oxidation of lignin over Cu-Mn mixed oxide catalysts		
2016	70	70 alkaline lignin	17.92	68.62	NaOH 150C	1h	Methanol 1:6.6Lignin/30%H2O2	Effect of solvent on hydrothermal oxidation depolymerization of lignin		
2021	71	71 alkaline lignin	30.5	69.5	CuSO4 160C	45MIN	NaOH/H2(5 bar O2	From Lignin to Valuable Aromatic Chemicals: Lignin Depolymerization and Monomer		

Table S3 References used to build Fig.3

Table S3 (All references used to build Fig.3)		Maldi	GPC	FT-ICR-MS		Ref in now Title	
		Main inter Range	Average (M Range	Mw	DBE		
OCD	[Ref 110] 100°C, NaOH, 10bar O2	100C, 2h, NaOH, kraft ligin, 10bar O2,			282	7.53	110 Base-catalyzed oxidative depolymerization of softwood kraft lignin
	[Ref 7] 110°C, HCO2H/HCO2Na	110C, TEM 243-434 200-700					7 Valorization of Lignin: Effective Conversion of Depolymerized Lignin to Oil by Simple Chemical Modifications
	[Ref 33] 135°C, Cu(NO3)2, pyridine	135C, V(acac)3, Cu(NO3)2.3H2O, 300					33 Copper- and Vanadium-Catalyzed Oxidative Cleavage of Lignin using Dioxygen
RCD	[Ref 116] 150°C, CuSO4, H2O2	150C, 1.5h, CuSO4, H2O2, Kraft lig	400				116 CuSO4/H2O2-Catalyzed Lignin Depolymerization under the Irradiation of Microwaves
	[Ref 117] 150°C, Ru/C, PL, 35 bar H2	150C, 3h, Ru/C, pyrolytic lignin, f	726		631		117 Functionality and molecular weight distribution of red oak lignin before and after pyrolysis and hydrogenation
	[Ref 55] 180°C, Pd/C, 30 bar H2	180C, 4h, Pd/C, MeOH, 3MPa H2	515				55 Unlocking Structure-Reactivity Relationships for Catalytic Hydrogenolysis of Lignin into Phenolic Monomers
	[Ref 114] 180°C, isopropanol	180C, 0.5h 300-500 300-500					114 Lignin depolymerization to aromatic monomers and oligomers in
	[Ref 113] 190°C, Pd/C, isopropanol	190C, 5h, f 279-399 200-500	700	100-5000Da			113 Highly efficient catalytic transfer hydrogenolysis for the conversion of Kraft lignin into bio-oil over heteropoly acids
	[Ref 118] 220°C, Ni/MSN, 20 bar H2	220C, 5h, Ni/MSN-AI, MeOH, 2M	1000				118 Immobilized Ni Clusters in Mesoporous Aluminum Silica Nanospheres for Catalytic Hydrogenolysis of Lignin
	[Ref 119] 225°C, ethanol	225C, 1h, e 302-480					119 Hybrid microwave-ultrasound assisted catalyst-free depolymerization of Kraft lignin to bio-oil
	[Ref 120] 270°C, Pd/C, DES-EL	270C, 1h, DES-EL, Pd/C, DES-ligni	570				120 Characterization and Catalytic Transfer Hydrogenolysis of Deep Eutectic Solvent Extracted Sorghum Lignin to Phenolic Compounds
	[Ref 109] 300°C, Cu/Cu/ZnAlOx,	300C, 8h, Cu/CuZnAlOx, lignin oil			340	6.5	Production of oxygen-containing fuels via supercritical methanol hydrodeoxygenation of lignin bio-oil over Cu/CuZnAlOx catalyst
	[Ref 9] 300°C, Ni/HZSM-5	300C, 4h, f 320-379 300-700					9 Catalytic depolymerization of organosolv lignin to phenolic monomers and low molecular weight oligomers
	[Ref 121] 360°C, SA-Cu/CuMgAlOx,	360C, 8h, f 272-452 200-900	433	10-2000Da			121 Production of Jet Fuel Precursors from Waste Kraft Lignin with a Complex Copper Acid Catalyst
Pyrolysis	[Ref 111] 500°C, 10 min, 0.1g/min	500C, residence time 10min, 0.1g/min lignin			311	7.54	An insight into the OPAHs and SPAHs formation mechanisms during alkaline lignin pyrolysis at different temperatures
	[Ref 122] 500°C, 5 ton/h, precipitation	500C, 5ton/h, pine wood, water e	690				122 In-depth structural characterization of the lignin fraction of a pine-derived pyrolysis oil
	[Ref 123] 500°C, straw, precipitation	500C, rice straw, water precipita	998				Characterization of pyrolytic lignin and insight into its formation mechanisms using novel techniques and DFT method
	[Ref 124] 550°C, red oak, 6kg/h	550C, red oak, 6kg/h	831		668		The effect of pyrolysis temperature on recovery of bio-oil as distinctive stage fractions
[Ref 98] 600°C, 10min, zeolites	600C, 10min, zeolites, kraft lignin	320				One step thermal conversion of lignin to the gasoline range liquid	

Table S4 References used to build Fig.4

Table S4 (All references used to build Fig.4)		Title
Ref 133(OCF)	133	Depolymerization of Lignin to Aromatics by Selectively Oxidizing Cleavage of C-C and C-O Bonds Using CuCl2/Polybenzoxazine Catalysts at Room Temperature
Ref 65 (OCF)	65	Oxidative Catalytic Fractionation and Depolymerization of Lignin in a One-Pot Single-Catalyst System
Ref 33(OCF)	33	Copper- and Vanadium-Catalyzed Oxidative Cleavage of Lignin using Dioxygen
Ref 97(RCF)	97	Catalytic Biorefining of Plant Biomass to Non-Pyrolytic Lignin Bio-Oil and Carbohydrates through Hydrogen Transfer Reactions
Ref 118 (RCF)	118	Immobilized Ni Clusters in Mesoporous Aluminum Silica Nanospheres for Catalytic Hydrogenolysis of Lignin
Ref 134 (RCF)	134	Tungsten-based catalysts for lignin depolymerization: the role of tungsten species in
Ref 117 (Pyrolysis)	117	Functionality and molecular weight distribution of red oak lignin before and after pyrolysis and hydrogenation