Electronic Supplementary Information

Chemicals from lignin: an interplay of lignocellulose fractionation, depolymerisation, and upgrading

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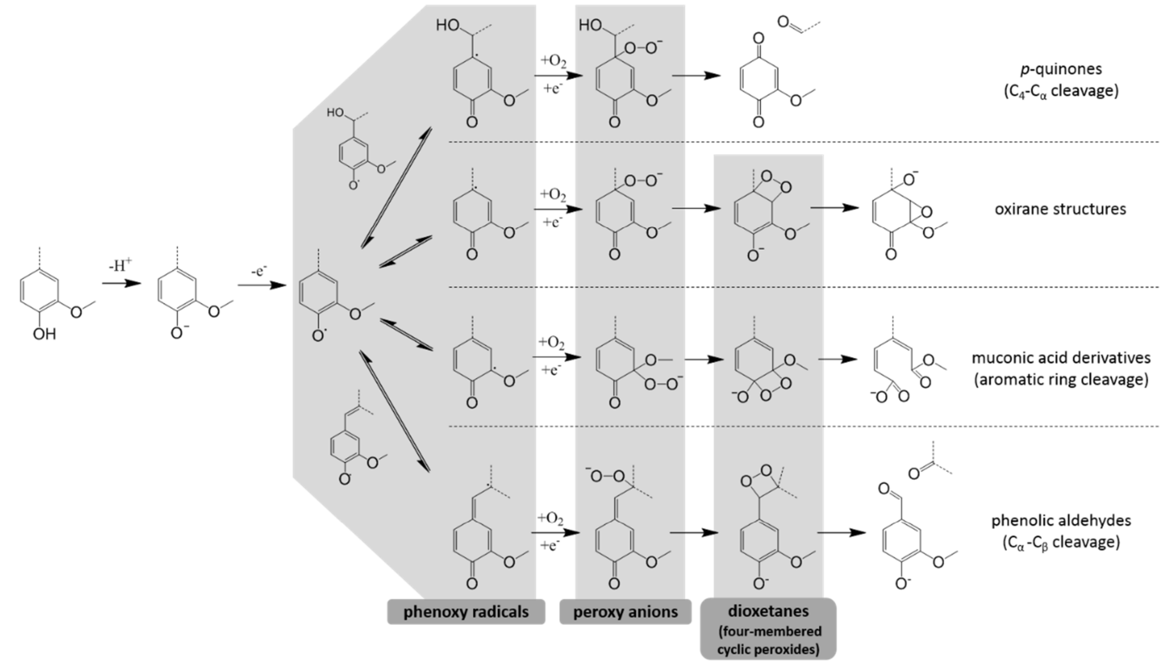
Part A. Figures

A. mechanism according to Gierer *et al.*



B. mechanism according to Tarabanko *et al.*

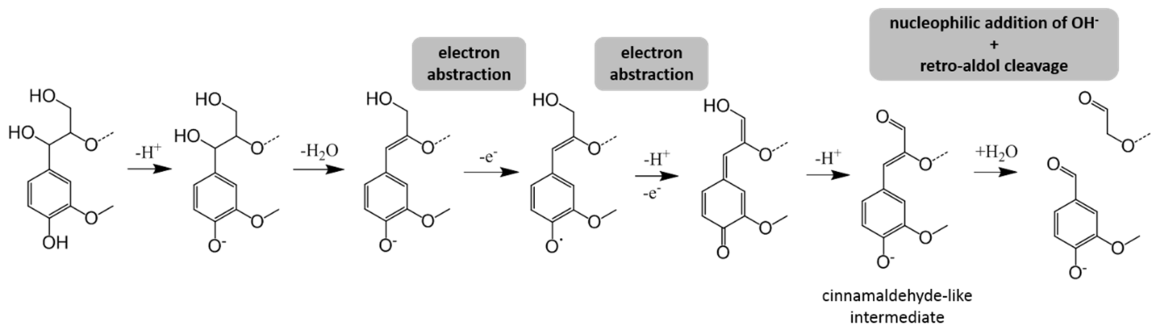


Figure S1. Mechanism of alkaline aerobic lignin oxidation according to Gierer *et al.*[1] (A) and Tarabanko *et al.*[2-5] (B), in support of Figure 7.

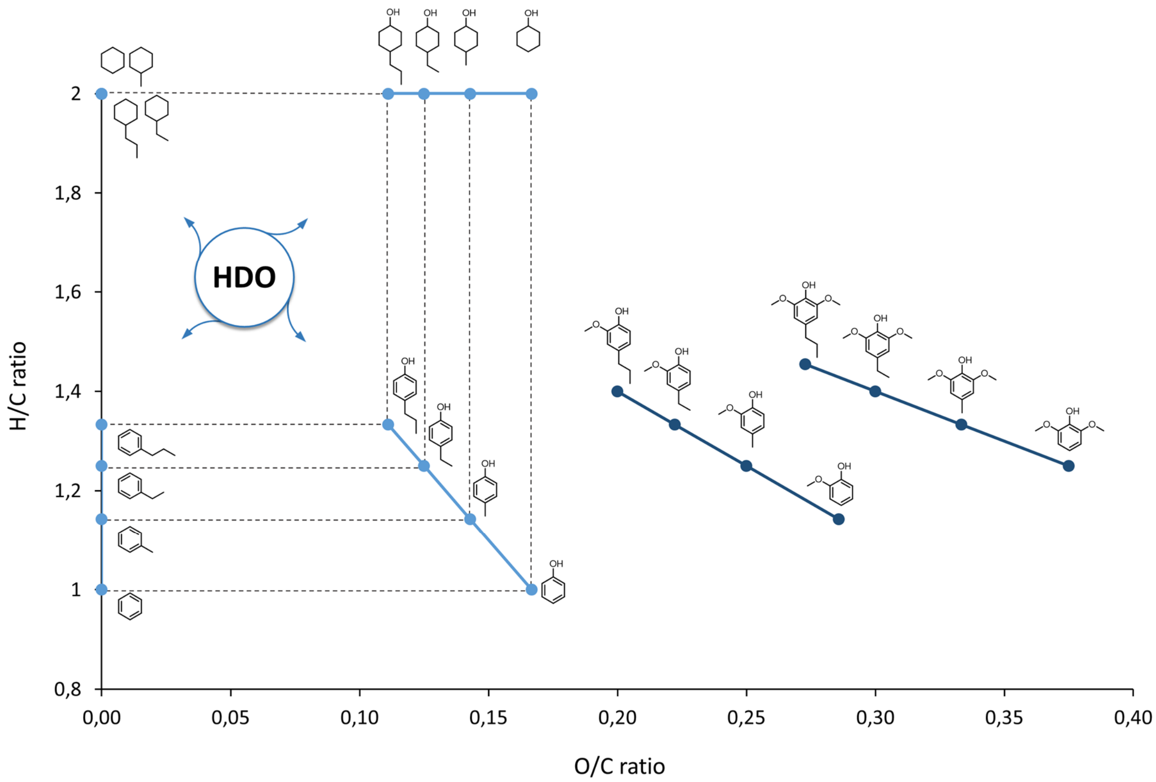


Figure S2. In support of Figure 24 in the main article. HDO can be divided in four sub-domains based on the targeted products: alkanes, aromatic hydrocarbons, phenols, and cyclohexanols. These four classes each display a characteristic O/C and H/C ratio. Demethoxylation (*e.g.*, alkylsyringol to alkylphenol) reduces both the H/C and O/C ratio. Hydrogenation (*e.g.*, alkylphenol to alkylcyclohexanol) corresponds to an increase of the H/C ratio (vertical increase). Removal of hydroxyl groups (*e.g.*, form alkylcyclohexanol to alkylcyclohexane), either through hydrogenolysis or dehydratation-hydrogenation, corresponds to a decrease of the O/C ratio (horizontal decrease).

Part B. Tables with lignin depolymerisation data

Tables S1-S13 indicate the reaction conditions, monomer yields, and monomer structures for selected depolymerisation experiments reported in the various lignin depolymerisation studies. The reference numbers correspond to the reference numbers in the main article. The rows in bold indicate the depolymerisation reactions that achieved the highest (maximum) monomer yields per study and per substrate (if multilple substrates were used). These maxium monomer yields were used to construct the histograms in Figures 14, 15, 17, 18 and 20 and the box plots in Figure 22. The abbreviations used in the tables are indicated below.

Abbreviations

MYC	monomer yield class: **1** = [0-10 wt%]; **2** =]10-20 wt%]; **3** =]20-30 wt%]; **4** =]30-40 wt%]; **5** =]40-50 wt%]; **6** =]50-60 wt%]; **7** =]60-70 wt%]; **8** =]70-80 wt%]; **9** = > 80 wt%
RT	room temperature
OT	operation temperature / reaction temperature
n.i.	*not indicated*
Catalysts	
C	carbon
PMO	porous metal oxides
NPs	nanoparticles
HPA	heteropoly acid
HTC	hydrotalcite
HOTf	triflic acid
(M)OTf	(metal)triflate
Lignocellulose type	
HW	hardwood
SW	softwood
HC	herbaceous crop
Lignin	
MWL	milled wood lignin
EMAL	enzymatic mild acidolysis lignin
AH	acid hydrolysis (the applied acid is usually indicated between brackets)
CAH	concentrated acid hydrolysis (the applied acid is usually indicated between brackets)
EH	enzymatic hydrolysis
AE	alkaline extracted (extracted with aqueous NaOH-solution)
ARP	ammonia recycled percolation
AFEX	ammonia fiber explosion/expansion
SEP	steam explosion pretreatment
DAP	dilute acid pretreatment (the applied acid is usually indicated between brackets)
HWP	hot water pretreatment
ILP	ionic liquid pretreatment
DMR	deacetylation and mechanical refining pretreatment
Protobind 1000	grass/wheat straw soda lignin, Granit lignin
Alcell lignin	mixed hardwood ethanosolv lignin
KL	Klason lignin
Compounds	
<u>*Collective indication of compounds:*</u>	
phenols	collective term for phenols (*i.e.* combination of phenol and substituted phenols)
guaiacols	collective term for guaiacols
syringols	collective term for syringols
catechols	collective term for catechols
APh	collective term for alkylphenols
AG	collective term for 4-alkylguaiacols
Ar	collective term for aromatics

Cat	collective term for catechols
CA	collective term for cyclic alkanes
monoCA	collective term for monocyclic alkanes
biCA	collective term for bicyclic alkanes
nCA	collective term for noncyclic alkanes
CAene	collective term for cyclic alkenes
Alc	collective term for alcohols
Ket	collective term for ketones
BA	collective term for benzyl alcohols
Ox	collective term for oxygenated compounds

Specific indication of compounds:

benz	benzene
tol	toluene
xyl	xylene
Ebenz	ethylbenzene
TMbenz	trimethylbenzene
naphth	naphthalene and alkylated naphthalenes
ind	indene

Most monomer structures are indicated as: *range of substituents - range of phenolic cores*

Specific indication of compounds - phenolic core:

Ph	phenol
G	guaiacol
S	syringol
Cat	catechol
Resorc	resorcinol
Goh	2-methoxycatechol / 2-hydroxyguaiacol
CH	cyclohexane
CHol	cyclohexanol
MCHol	methoxycyclohexanol

Specific indication of compounds - substituents:

H	no substituent (hydrogen)
oh	hydroxy
M	methyl
DM	dimethyl
Mal	formyl (usually in benzaldehyde, vanillin and syringaldehyde)
Mooh	formic acid (usually in *p*-hydroxybenzoic acid, vanillic acid and syringic acid)
MooR	alkyl formate (R = methyl (Me), ethyl (Et), *etc.*)
E	ethyl
V	vinyl
Eoh	ethanol
Eoxo	ethanone (usually in *p*-hydroxyacetophenone, acetovanillone and acetosyringone)
Eal	acetaldehyde
Eooh	acetic acid
EooR	alkyl acetate (R = methyl (Me), ethyl (Et), *etc.*)
E(acetal)	2-methyl-1,3-dioxolane, formed by reaction between acetaldehyde substituent and ethylene glycol
P	propyl
Pene	propenyl
Poh	propanol
P(oh)2	propanediol
PoMe	methoxypropyl
Pal	propanal
Poxo	propanone (usually 2-propanone / acetone)
P(oxo)2	propanedione
Pooh	propionic acid

PooR	alkyl propionate (R = methyl (Me), ethyl (Et), *etc.*)
Pene(oh)	propenol (in p-coumaryl, coniferyl and sinapyl alcohol)
Pene(al)	propenal / acrolein (in *p*-coumaraldehdye, coniferaldehyde and sinapaldehyde)
Pene(ooh)	acrylic acid (in *p*-coumaric and ferulic acid)
Pene(ooR)	alkyl acrylate (R = methyl (Me), ethyl (Et), *etc.*)
Poh(acetal)	2-methanol-2-methyl-1,3-dioxolane, formed by reaction between 3-hydroxy-2-propanone substituent and ethylene glycol
Pene(ketal)	2,3-dihydro-5,6-dimethyl-1,4-dioxin
Alk	collective term for alkyl substituents
Ox	collective term for oxygenated substituents

Table S1. Reductive catalytic fractionation (RCF) *In support of Figure 14 in the main article*

Catalyst	Lignocellulose source	Solvent	T (°C)	p H_2 (bar) at RT	Reaction time (h)	Monomer yield	Monomer structure	Lignocellulose type	MYC	Ref
Raney Ni	**aspen**	**dioxane/water (1:1 v/v)**	**195**	**35**	**5**	**52 wt%**	**Poh - S/G > P, E - S**	**HW**	**6**	359
Pd/C	**spruce**	**dioxane/water (1:1 v/v)**	**195**	**35**	**10**	**17 wt%**	**Poh - G**	**SW**	**2**	354
Pd/C	spruce	dioxane/water (1:1 v/v)	195	35	5	14.7 wt%	Poh - G >> P - G			
Pd/C + HCl	spruce	dioxane/water (1:1 v/v)	195	35	5	10.5 wt%	Poh, P - G			
Pd/C + NaOH	spruce	dioxane/water (1:1 v/v)	195	35	5	7.2 wt%	E - G			
Raney Ni	spruce	dioxane/water (1:1 v/v)	195	35	5	9.5 wt%	Poh - G			
Raney Ni + HCl	spruce	dioxane/water (1:1 v/v)	195	35	5	14.7 wt%	Poh, P - G			
Raney Ni + NaOH	spruce	dioxane/water (1:1 v/v)	195	35	5	9.4 wt%	E - G			
Raney Ni (1 g)	spruce	dioxane/water (1:1 v/v)	195	35	5	16 wt%	Poh - G >> P - G			357
Rh/C	**spruce**	**dioxane/water (1:1 v/v)**	**195**	**35**	**5**	**34 wt%**	**Poh - G > P - G**	**SW**	**4**	
Rh/Alumina	spruce	dioxane/water (1:1 v/v)	195	35	5	13 wt%	Poh - G > P - G			
Pd/C	spruce	dioxane/water (1:1 v/v)	195	35	5	24 wt%	Poh - G			
Raney Ni (10 g)	**spruce**	**dioxane/water (1:1 v/v)**	**195**	**35**	**5**	**17 wt%**	**Poh - CHol >> Poh - MCHol > Poh - G**	**SW**	**2**	360
Ru/C	spruce	dioxane/water (1:1 v/v)	195	35	5	12 wt%	Poh - G > Poh - CHol > Poh - MCHol			
Ru/Alumina	spruce	dioxane/water (1:1 v/v)	195	35	5	15 wt%	Poh - CHol > Poh - G > Poh - MCHol			
Rh/C	**aspen**	**dioxane/water (1:1 v/v)**	**195**	**35**	**5**	**50 wt%**	**Poh - S > P - S > P - G > Poh - G**	**HW**	**5**	361
Rh/C	**spruce**	**dioxane/water (1:1 v/v)**	**195**	**35**	**5**	**21 wt%**	**Poh - G > P - G >> E - G**	**SW**	**3**	355
Rh/C + HCl	spruce	dioxane/water (1:1 v/v)	195	35	5	18 wt%	P - G > Poh - G			
Rh/C + NaOH	spruce	dioxane/water (1:1 v/v)	195	35	5	7 wt%	E - G > Poh - G			
Rh/C (agitated)	aspen poplar	dioxane/water (1:1 v/v)	195	35	5	45 wt%	Poh - S > P - S			362
Rh/C (not agitated)	**aspen poplar**	**dioxane/water (1:1 v/v)**	**195**	**35**	**5**	**46 wt%**	**P - S >> Poh - S**	**HW**	**5**	
D101[a]	**rice husks**	**dioxane**	**250**	**50**	**2**	**33 wt%**	**P - S > Poh - G > E - G > E - Ph > P - G**	**HC**	**4**	363
Ru/C	birch	water	200	40	4	4.6 wt%	Poh, P - S/G			244
Pd/C	birch	water	200	40	4	25.5 wt%	Poh - S/G > P - S/G			
Rh/C	birch	water	200	40	4	19.7 wt%	P - S/G > Poh - S/G			
Pt/C	birch	water	200	40	4	33.6 wt%	P - S/G > Poh - S/G			
Pt/C + H_3PO_4	birch	water	200	40	4	37.9 wt%	P - S/G > Poh - S/G			

Table S1 continued

Catalyst	Lignocellulose source	Solvent	T (°C)	p H_2 (bar) at RT	Reaction time (h)	Monomer yield	Monomer structure	Lignocellulose type	MYC	Ref
Pt/C	birch	dioxane/water (1:1 v/v)	200	40	4	41.7 wt%	P - S/G > Poh - S/G			244
Pt/C + H_3PO_4	**birch**	**dioxane/water (1:1 v/v)**	**200**	**40**	**4**	**46.4 wt%**	**P - S/G > Poh - S/G**	**HW**	**5**	
Rh/C + H_3PO_4	birch	dioxane/water (1:1 v/v)	200	40	4	45.5 wt%	P - S/G > Poh - S/G			
4%Ni-30%W_2C/C	**birch**	**water**	**235**	**60**	**4**	**36.9 wt%**	**Poh, P - S/G**	**HW**	**4**	353
4%Ni-30%W_2C/C	**corn stalk**	**water**	**235**	**60**	**4**	**20.6 wt%**	**Poh, P - S/G**	**HC**	**3**	
4%Ni-30%W_2C/C	birch	methanol	235	60	4	42.2 wt%	Poh, P - S/G			
4%Ni-30%W_2C/C	**birch**	**ethylene glycol**	**235**	**60**	**4**	**46.5 wt%**	**Poh, P - S/G**	**HW**	**5**	
4%Ni-30%W_2C/C	**poplar**	**water**	**235**	**60**	**4**	**32.4 wt%**	**Poh, P - S/G**	**HW**	**4**	
4%Ni-30%W_2C/C	**basswood**	**water**	**235**	**60**	**4**	**37.3 wt%**	**Poh, P - S/G**	**HW**	**4**	
4%Ni-30%W_2C/C	**ashtree**	**water**	**235**	**60**	**4**	**40.5 wt%**	**Poh, P - S/G**	**HW**	**5**	
4%Ni-30%W_2C/C	**beech**	**water**	**235**	**60**	**4**	**26.1 wt%**	**Poh, P - S/G**	**HW**	**3**	
4%Ni-30%W_2C/C	**xylosma, willow**	**water**	**235**	**60**	**4**	**29.3 wt%**	**Poh, P - S/G**	**HW**	**3**	
4%Ni-30%W_2C/C	**bagasse**	**water**	**235**	**60**	**4**	**23.4 wt%**	**Poh, P - S/G**	**HC**	**3**	
4%Ni-30%W_2C/C	**pine**	**water**	**235**	**60**	**4**	**10.1 wt%**	**Poh, P - G**	**SW**	**1**	
Pd-W_2C/C	birch	water	235	60	4	28.4 wt%	Poh - S/G >> P - S/G			
Pt-W_2C/C	birch	water	235	60	4	26.7 wt%	Poh, P - S/G			
Ir-W_2C/C	birch	water	235	60	4	31.5 wt%	Poh, P - S/G			
Ru-W_2C/C	birch	water	235	60	4	trace	/			
Pd/C	**birch**	**water**	**235**	**60**	**4**	**55.1 wt%**	**Poh - S/G >> P - S/G**	**HW**	**6**	
Pt/C	birch	water	235	60	4	44.1 wt%	Poh, P - S/G			
Ir/C	birch	water	235	60	4	41.1 wt%	Poh, P - S/G			
Ru/C	birch	water	235	60	4	11.6 wt%	/			
Pd/C	**pine**	**dioxane/water (1:1 v/v)**	**195**	**35**	**24**	**22 wt%**	**Poh - G >> P - G**	**SW**	**3**	195
Pd/C	SEP pine	dioxane/water (1:1 v/v)	195	35	24	7 wt%	Poh - G >> P - G			
Pd/C	SEP pine (SO_2)	dioxane/water (1:1 v/v)	195	35	24	2 wt%	Poh - G >> P - G			
Ni/C	birch	methanol	200	1 (Ar)	6	49 wt%	P - S/G			235
Ni/C	birch	methanol	200	50	6	41 wt%	P - S/G			
Ni/C	**birch**	**methanol**	**240**	**1 (Ar)**	**6**	**59 wt%**	**P - S/G > Pene - S/G**	**HW**	**6**	

Table S1 continued

Catalyst	Lignocellulose source	Solvent	T (°C)	p H_2 (bar) at RT	Reaction time (h)	Monomer yield	Monomer structure	Lignocellulose type	MYC	Ref
Ni/C	birch	ethanol	200	1 (Ar)	6	47 wt%	P - S/G			235
Ni/C	birch	ethylene glycol	200	1 (Ar)	6	49 wt%	P - S/G			
Ni/C	birch	isopropanol	200	1 (Ar)	6	20 wt%	P, Pene - S/G			
Ni/C	birch	dioxane	200	1 (Ar)	6	15 wt%	iAS, iAG			
Ni/C	birch	1% methanol in water	200	1 (Ar)	6	8 wt%	P - S/G			
Ni/C	birch	25% methanol in water	200	1 (Ar)	6	20 wt%	P - S/G			
Ni/C	birch	cyclohexane	200	1 (Ar)	6	/				
Ni/SBA-15	birch	methanol	200	1 (Ar)	6	27 wt%	Pene - S/G > P - S/G			
Ni/Al_2O_3	birch	methanol	200	1 (Ar)	6	19 wt%	Pene - S/G > P - S/G			
Cu/C	birch	methanol	200	1 (Ar)	6	9 wt%	Pene - S/G			
Cu-Cr oxide	birch	methanol	200	1 (Ar)	6	2 wt%	Pene - S/G			
Pd/C	**pine**	**ethanol/water (1:1 v/v)**	**195**	**4 (Ar)**	**1**	**23 mol%**	**Pene - G**	**SW**	**3**	232
Pd/C	**birch**	**ethanol/water (1:1 v/v)**	**195**	**4 (Ar)**	**1**	**52 mol%**	**Pene - S/G**	**HW**	**6**	
Pd/C	**F-birch**	**ethanol/water (1:1 v/v)**	**210**	**1 (Ar)**	**15**	**35 mol%**	**P - S/G > Pene - S/G**	**HW**	**4**	352
Pd/C	**S-birch**	**ethanol/water (1:1 v/v)**	**210**	**1 (Ar)**	**15**	**36 mol%**	**P - S/G > Pene - S/G**	**HW**	**4**	
Pd/C	**poplar**	**ethanol/water (1:1 v/v)**	**210**	**1 (Ar)**	**15**	**22 mol%**	**P - S/G > Pene - S/G**	**HW**	**3**	
Pd/C	**spruce**	**ethanol/water (1:1 v/v)**	**210**	**1 (Ar)**	**15**	**12 mol%**	**P - G > Pene - G**	**SW**	**2**	
Pd/C	**pine**	**ethanol/water (1:1 v/v)**	**210**	**1 (Ar)**	**15**	**7 mol%**	**P - G > Pene - G**	**SW**	**1**	
ZnPd/C (Pd/C + $ZnCl_2$)	**poplar (WT-717)**	**methanol**	**225**	**35**	**12**	**40 wt%**	**P - S/G**	**HW**	**4**	233
ZnPd/C	**poplar (717-F5H)**	**methanol**	**225**	**35**	**12**	**36 wt%**	**P - S/G**	**HW**	**4**	
ZnPd/C	**poplar (WT-NM-6)**	**methanol**	**225**	**35**	**12**	**44 wt%**	**P - S/G**	**HW**	**5**	
ZnPd/C	**poplar (WT-LORRE)**	**methanol**	**225**	**35**	**12**	**54 wt%**	**P - S/G**	**HW**	**6**	
ZnPd/C	**birch (white)**	**methanol**	**225**	**35**	**12**	**52 wt%**	**P - S/G**	**HW**	**6**	
ZnPd/C	**eucalyptus**	**methanol**	**225**	**35**	**12**	**49 wt%**	**P - S/G**	**HW**	**5**	
ZnPd/C	**lodgepole pine**	**methanol**	**225**	**35**	**12**	**19 wt%**	**P - G**	**SW**	**2**	
Pd/C	**poplar (WT-717)**	**methanol**	**225**	**35**	**12**	**59 wt%**	**Poh - S/G >> P - S/G**	**HW**	**6**	356
ZnPd/C (Pd/C + $Zn(Oac)_2$ of $ZnCl_2$)	poplar (WT-717)	methanol	225	35	12	44 wt%	P - S/G			
Pd/C	**poplar (717-F5H)**	**methanol**	**225**	**35**	**12**	**38 wt%**	**Poh - S/G >> P - S/G**	**HW**	**4**	

Table S1 continued

Catalyst	Lignocellulose source	Solvent	T (°C)	p H_2 (bar) at RT	Reaction time (h)	Monomer yield	Monomer structure	Lignocellulose type	MYC	Ref
ZnPd/C (Pd/C + Zn(Oac)$_2$)	poplar (717-F5H)	methanol	225	35	12	36 wt%	P - S/G			356
Ni/C	**birch**	**methanol**	**200**	**2 (N_2)**	**6**	**32 wt%**	**P - S/G**	**HW**	**4**	358
Ni/C	**poplar**	**methanol**	**200**	**2 (N_2)**	**6**	**26 wt%**	**Pene - G**	**HW**	**3**	
Ni/C	**eucalyptus**	**methanol**	**200**	**2 (N_2)**	**6**	**28 wt%**	**P, Pene - S/G**	**HW**	**3**	
Ni/C (in cage)	**miscanthus**	**methanol**	**225**	**35**	**12**	**68 wt%**	**P - S/G; PooMe - G/Ph**	**HC**	**7**	351
Ru/C	**birch**	**methanol**	**250**	**30**	**6**	**52 wt%**	**P - S/G >> Poh - S/G**	**HW**	**6**	231
Ru/C	birch	water	250	30	6	25 wt%	P - S/G			
Ru/C	birch	methanol	250	30	3	50 wt%	P - S/G			
Ru/C	**poplar**	**methanol**	**250**	**30**	**3**	**44 wt%**	**P - S/G**	**HW**	**5**	
Ru/C	**softwood mixture (spruce and pine)**	**methanol**	**250**	**30**	**3**	**21 wt%**	**P - G**	**SW**	**3**	
Ru/C	**miscanthus**	**methanol**	**250**	**30**	**3**	**27 wt%**	**P - S/G; PooMe - G/Ph > Poh - S/G**	**HC**	**3**	
Ru/C	birch	methanol	250	30	3	48 wt%	P - S/G > Poh - S/G			243
Pd/C	**birch**	**methanol**	**250**	**30**	**3**	**49 wt%**	**Poh - S/G**	**HW**	**5**	
Pd/C	birch	water	200	30	3	44 wt%	Poh - S/G			236
Pd/C	birch	methanol	200	30	3	38 wt%	Poh - S/G			
Pd/C	birch	ethylene glycol	200	30	3	27 wt%	Poh - S/G			
Pd/C	birch	ethanol	200	30	3	17 wt%	Poh - S/G			
Pd/C	birch	isopropanol	200	30	3	12 wt%	Poh - S/G			
Pd/C	birch	1-butanol	200	30	3	11 wt%	Poh - S/G			
Pd/C	birch	tetrahydrofuran (THF)	200	30	3	6 wt%	Poh - S/G			
Pd/C	birch	dioxane	200	30	3	5 wt%	Poh - S/G			
Pd/C	birch	hexane	200	30	3	2 wt%	Poh - S/G			
Pd/C	birch	methanol	250	30	3	49 wt%	Poh - S/G			
Pd/C	**birch**	**ethylene glycol**	**250**	**30**	**3**	**50 wt%**	**Poh - S/G**	**HW**	**5**	
Pd/C	poplar	methanol	250	20	3	44 wt%	Poh - S/G > P - S/G			238
Pd/C	poplar	methanol	200	20	3	26 wt%	Poh - S/G > P - S/G			
Pd/C + H_3PO_4	**poplar**	**methanol**	**200**	**20**	**3**	**42 wt%**	**Poh - S/G > P - S/G**	**HW**	**5**	
Pd/C + NaOH	poplar	methanol	200	20	3	23 wt%	Poh, E - S/G > P - S/G			

Table S1 continued

Catalyst	Lignocellulose source	Solvent	T (°C)	p H_2 (bar) at RT	Reaction time (h)	Monomer yield	Monomer structure	Lignocellulose type	MYC	Ref
Pd/C	poplar	water	200	20	3	34.2 wt%	Poh - S/G > P - S/G			237
Pd/C	poplar	methanol	200	20	3	28.2 wt%	Poh - S/G > P - S/G			
Pd/C	**poplar**	**methanol/water (7:3 v/v)**	**200**	**20**	**3**	**43.5 wt%**	**Poh - S/G > P - S/G**	**HW**	**5**	
Pd/C	poplar	ethanol	200	20	3	19.4 wt%	Poh - S/G > P - S/G			
Pd/C	poplar	ethanol/water (5:5 v/v)	200	20	3	43.3 wt%	Poh - S/G > P - S/G			
Ru/C	**beech**	**methanol**	**250**	**40**	**15**	**48 wt%**	**P - S/G > Poh - S/G**	**HW**	**5**	226
Ru/C	beech	THF	250	40	15	36 wt%	E - S/G >> P - S/G			
Ru/C	**F5H-poplar**	**methanol**	**250**	**40**	**15**	**77 wt%**	**P - S/G > Poh - S/G**	**HW**	**8**	
Ru/C	F5H-poplar	methanol	150	40	20	0.2 wt%	E - S > P - S			
Ru/C + HCl	F5H-poplar	THF	150	40	20	47 wt%	P - S			
Ru/C	**spruce**	**methanol**	**250**	**40**	**15**	**21 wt%**	**P - G > Poh - G**	**SW**	**3**	
Pd/C	birch	methanol	180	30	2	14 wt%	Poh - S/G >> P - S/G			240
Pd/C + $Al(OTf)_3$	birch	methanol	180	30	2	45 wt%	*n.i.*			
Pd/C + $Yb(OTf)_3$	birch	methanol	180	30	2	43 wt%	Poh, P - S/G > E, PoMe - S/G			
Pd/C	birch	methanol	200	30	1	24 wt%	Poh - S/G >> P - S/G			
Pd/C + $Yb(OTf)_3$	birch	methanol	200	30	1	43 wt%	Poh, P - S/G > E, PoMe - S/G			
Pd/C + $Yb(OTf)_3$	**birch**	**methanol**	**200**	**30**	**2**	**46 wt%**	**Poh, P - S/G > E, PoMe - S/G**	**HW**	**5**	
Pd/C	oak	methanol	200	30	1	33 wt%	*n.i.*			
Pd/C + $Yb(OTf)_3$	**oak**	**methanol**	**200**	**30**	**1**	**47 wt%**	***n.i.***	**HW**	**5**	
Pd/C	poplar	methanol	200	30	1	17 wt%	*n.i.*			
Pd/C + $Yb(OTf)_3$	poplar	methanol	200	30	1	29 wt%	*n.i.*			
Pd/C + $Yb(OTf)_3$	**poplar**	**methanol**	**200**	**30**	**2**	**36 wt%**	***n.i.***	**HW**	**4**	
Pd/C	scotch pine	methanol	200	30	1	10 wt%	*n.i.*			
Pd/C + $Yb(OTf)_3$	**scotch pine**	**methanol**	**200**	**30**	**1**	**24 wt%**	***n.i.***	**SW**	**3**	
Pd/C	wheat chaff	methanol	200	30	1	6 wt%	*n.i.*			
Pd/C + $Yb(OTf)_3$	**wheat chaff**	**methanol**	**200**	**30**	**1**	**6 wt%**	***n.i.***	**HC**	**1**	

Table S1 continued

Catalyst	Lignocellulose source	Solvent	T (°C)	p H_2 (bar) at RT	Reaction time (h)	Monomer yield	Monomer structure	Lignocellulose type	MYC	Ref
Pd/C + $Al(OTf)_3$ (Pd/Al 0.3 molar ratio, 20 mg Pd/C & 15 mg $Al(OTf)_3$	**birch**	**methanol**	**180**	**30**	**2**	**55 wt%**	**PoMe - S/G > P - S/G > Poh - S/G**	**HW**	**6**	241
Pd/C + $Al(OTf)_3$	**oak (100 g, 300-1000 µm)**	**methanol**	**180**	**30**	**4**	**46 wt%**	***n.i.***	**HW**	**5**	
Pd/C + $Al(OTf)_3$	oak (100 g, 0-300 µm)	methanol	180	30	4	40 wt%	*n.i.*			
Pd/C + $Al(OTf)_3$	**douglas fir (100 g, 300-1000 µm)**	**methanol**	**180**	**30**	**4**	**17 wt%**	***n.i.***	**SW**	**2**	
Ni/C	corn stover	methanol	250	30	3	29 wt%	PooMe - G/Ph > P - S/G; E - G/Ph			239
Ni/C	corn stover	methanol	200	30	24	29 wt%	PooMe - G/Ph > P - S/G; E - G/Ph			
Ru/C	corn stover	methanol	250	30	3	32 wt%	PooMe - G/Ph > P - S/G; E - G/Ph			
Ru/C	corn stover	methanol	200	30	24	28 wt%	PooMe - G/Ph > P - S/G; E - G/Ph			
Ni/C(H^+)	corn stover	methanol	200	30	6	32 wt%	P(ooMe), Pene(ooMe), E - G/Ph; P, Pene - S/G			
Ni/C + H_3PO_4	**corn stover**	**methanol**	**200**	**30**	**6**	**38 wt%**	**Pene(ooMe) - S/G > P, Pene - S/G; PooMe, E - G/Ph**	**HC**	**4**	
Ni/C	**beech**	**methanol/water (6:4 v:v)**	**200**	**20**	**5**	**51.4 wt%**	**PohS, PohG > PS, PG**	**HW**	**6**	364
Ni/C	beech	methanol	200	20	5	39.3 wt%	Poh - S/G > P - S/G			
Ni/C	beech	dioxane	200	20	5	14.3 wt%	Poh - S/G > P - S/G			

[a] Catalyst consists of a mixture of polyvalent metals modified by additions of alkaline-earth metals.

Table S2 Reductive depolymerisation - Mild hydroprocessing							*In support of Figure 15 in the main article*		
Catalyst	**Lignin[a]**	**Solvent**	**T (°C)**	**p H_2 (bar) at RT**	**Reaction time**	**Monomer yield**	**Monomer structure**	**MYC**	**Ref**
Pd/C	**beech MWL**	**ethanol/water (9:1 v/v)**	**390**	**100 (280 at OT)**	**15 min**	**15.47 wt%**	**P, Poh, E, M, H - S/G/Ph**	**2**	381
Pd/C	**spruce MWL**	**ethanol/water (9:1 v/v)**	**390**	**100 (280 at OT)**	**15 min**	**11.15 wt%**	**P, Poh, E, M, H - G**	**2**	
Pd/C	**bamboo MWL**	**ethanol/water (9:1 v/v)**	**390**	**100 (280 at OT)**	**15 min**	**16.36 wt%**	**P, Poh, E, M, H - S/G/Ph**	**2**	
Pd/C	**teak MWL**	**ethanol/water (9:1 v/v)**	**390**	**100 (280 at OT)**	**15 min**	**12.63 wt%**	**P, Poh, E, M, H - S/G/Ph**	**2**	
$Cu_2Cr_2O_5$	**birch MWL**	**dioxane**	**240-260**	**100**	**48 h**	**21.2 wt%**	**Poh, P, E, M - S/G**	**3**	390
$Cu_2Cr_2O_5$	**oak MWL**	**dioxane**	**240-260**	**100**	**48 h**	**16.7 wt%**	**Poh, P, E, M - /G**	**2**	
$Cu_2Cr_2O_5$	**spruce MWL**	**dioxane**	**225**	**135**	**47 h**	**19.9 wt%**	**P, Poh, E, M - G**	**2**	391
$Cu_2Cr_2O_5$	**pine MWL**	**dioxane**	**225**	**135**	**47 h**	**17.7 wt%**	**P, Poh, E, M - G**	**2**	
$CoMoO_x$ + NaOH	**sweetgum wood AH lignin (HCl)**	**dioxane/3 wt% NaOH-solution (1:1 v/v)**	**250**	**69**	**1 h**	**9.3 wt%**	**E, M, H - S/G/Cat**	**1**	392
Pd/C	**pine EMAL**	**dioxane/water (1:1 v/v)**	**195**	**35**	**24 h**	**21 wt%**	**Poh, P - G**	**3**	195
Rh/C + H_3PO_4	**birch dioxasolv lignin**	**dioxane/water (1:1 v/v)**	**270**	**40**	**10 h**	**15 wt%**	**P - G/Ph**	**2**	393
Ru/C	**birch ethanosolv lignin**	**methanol**	**250**	**30**	**3 h**	**3 wt%**	**P - S/G > Poh, E, M, H - S/G**	**1**	231
Raney Ni	**spruce EH lignin (SEKAB, Sweden)**	**water**	**400**	**10**	**1 h**	**2 wt%**	**H- G/Cat/Ph**	**1**	394
Ru/C	**corn stalk EH-ethanosolv lignin[b]**	**ethanol/water (65:35 v/v)**	**275**	**20**	**1.5 h**	**4.5 wt%**	**E - G/Ph**	**1**	384
Ru/C	corn stalk EH-ethanosolv lignin[b]	ethanol/water (65:35 v/v)	250	20	1.5 h	3.5 wt%	E - G/Ph		
Pt/C, Pd/C	corn stalk EH-ethanosolv lignin[b]	ethanol/water (65:35 v/v)	250	20	1.5 h	1.5-1.6 wt%	E - G/Ph		
Ru/C	**bamboo lignin**	**ethanol/water (65:35 v/v)**	**250**	**20**	**1.5 h**	**1.3 wt%**	**E - G/Ph**	**1**	
Cu-PMO	candlenut methanosolv lignin	methanol	180	40	14 h	54.8 wt%	P, Poh, PoMe - Cat		389
Cu-PMO	**candlenut methanosolv lignin**	**methanol**	**140**	**40**	**20 h**	**63.7 wt%**	**P, Poh, PoMe - Cat**	**7**	
Pt/Al_2O_3	**poplar ethanosolv lignin**	**methanol/water (1:1 v/v)**	**300**	**20**	**2 h**	**7 wt%**	**P, Pene, Poh, PoMe, E, M, H - S/G**	**1**	143
Pt/Al_2O_3	**poplar ARP lignin**	**methanol/water (1:1 v/v)**	**300**	**20**	**2 h**	**14 wt%**	**P, Pene, Poh, PoMe, E, M, H - S/G**	**2**	
Pt/Al_2O_3	**wheat straw AFEX-ethanosolv lignin**	**methanol/water (1:1 v/v)**	**300**	**20**	**2 h**	**10 wt%**	**P, Pene, Poh, PoMe, E, M, H - S/G**	**1**	
Pt/Al_2O_3	**wheat straw soda lignin (Protobind 1000)**	**methanol/water (1:1 v/v)**	**300**	**20**	**2 h**	**6 wt%**	**P, E, M, H - S/G**	**1**	

Table S2 continued

Catalyst	Lignin[a]	Solvent	T (°C)	p H_2 (bar) at RT	Reaction time	Monomer yield	Monomer structure	MYC	Ref
Pt/Al_2O_3	poplar ARP lignin	water	300	20	2 h	11 wt%	P, Pene, Poh, PoMe, E, M, H - S/G (H > Pene, Poh, PoMe > P, E, M)		382
Pt/Al_2O_3	poplar ARP lignin	methanol/water (1:1 v/v)	300	20	2 h	17 wt%	P, Pene, Poh, PoMe, E, M, H - S/G (P, Poh, PoMe, Pene, H > E, M)		
Pt/Al_2O_3	**poplar ARP lignin**	**methanol**	**300**	**20 (160 at OT)**	**2 h**	**44 wt%**	**P, Pene, Poh, PoMe, E, M, H - S/G (Poh, PoMe > P > E, H > Pene, M)**	**5**	
Pt/Al_2O_3	**oak dioxasolv lignin**	**methanol/water (1:1 v/v)**	**300**	**20**	**2 h**	**55 wt%**	**P, Pene, Poh, PoMe, E, M, H - S/G**	**6**	135
Pt/Al_2O_3	**miscanthus ionosolv lignin**	**methanol/water (1:1 v/v)**	**300**	**20**	**2 h**	**32 wt%**	**P, Pene, Poh, PoMe, E, M, H - S/G**	**4**	
WP/C	**softwood kraft lignin (Sigma-Aldrich)**	**ethanol/water (1:1 v/v)**	**280**	**20**	**2 h**	**7 wt%**	**P, E - G > H- G > M, Eoxo - G**	**1**	395
$Ni_{85}Ru_{15}$ NPs	**birch dioxasolv lignin**	**water**	**130**	**10**	**12 h**	**7 wt%**	**Poh - S/G > other monomers**	**1**	396
Ni_7Au_3 NPs	**birch dioxasolv lignin**	**water**	**170**	**10**	**1 h**	**14 wt%**	**Poh - S/G > other monomers**	**2**	397
Ni_7Au_3 NPs	birch organosolv lignin	water	160	10	4 h	8 wt%	Poh, P - S/G (Poh > PS)		388
Ni_7Au_3 NPs + NaOH	**birch organosolv lignin**	**water**	**160**	**10**	**4 h**	**11 wt%**	**Poh, P - S/G (Poh > PS)**	**2**	
Pt/C	**Protobind 1000**	***t*-butanol**	**350**	**30 (150 at OT)**	**40 min**	**4.2 wt%**	**E - G/Ph; P, M, H - S**	**1**	398
Pt/C	**poplar organosolv lignin**	***t*-butanol**	**350**	**30 (150 at OT)**	**40 min**	**4.9 wt%**	**E - G; P, M, H - S**	**1**	
Pt/C	**wheat straw hydrothermal lignin**	***t*-butanol**	**350**	**30 (150 at OT)**	**40 min**	**1.11 wt%**	**E- G/Ph; P, H - S**	**1**	
Pd/C, Pt/C, Ru/C, Ni/C	**Protobind 1000**	**methanol, ethanol, isopropanol**	**350**	**30**	**40 min**	**9-11 wt%**	**P, Pene, E, Eoxo, M, H - S/G/Ph**	**2**	383
Pd/C	softwood kraft lignin (Sigma-Aldrich)	methanol	260	40	5 h	7 wt%	phenols & guaiacols		386
Pd/C + MCl_x (M: Li, Na, K, Ba, Cu, Fe, Ni, Zn, *etc.*)	softwood kraft lignin (Sigma-Aldrich)	methanol	260	40	5 h	7-29 wt%	phenols & guaiacols		
Pd/C + $CrCl_3$	softwood kraft lignin (Sigma-Aldrich)	methanol	260	40	5 h	29 wt%	phenols & guaiacols		
Pd/C + $CrCl_3$	**softwood kraft lignin (Sigma-Aldrich)**	**methanol**	**280**	**40**	**5 h**	**35 wt%**	**phenols & guaiacols**	**4**	
Ru/C	pine ethanosolv lignin	methanol	260	40	4 h	6.1 wt%	phenols & guaiacols		387
Ru/C, Pd/C + NaOH, KOH, Na_2CO_3	pine ethanosolv lignin	methanol	260	40	4 h	8.4-12.7 wt%	phenols & guaiacols		
Ru/C + NaOH	**pine ethanosolv lignin**	**methanol**	**260**	**40**	**4 h**	**12.7 wt%**	**phenols & guaiacols**	**2**	
Pd/C + $CrCl_3$	**softwood kraft lignin (TCI)**	**methanol**	**280**	**40**	**5 h**	**16 wt%**	**phenols & guaiacols**	**2**	400
Pd/C + $CrCl_3$	**lignosulfonate (Na)**	**methanol**	**280**	**40**	**5 h**	**8 wt%**	**phenols & guaiacols**	**1**	
Pd/C + $CrCl_3$	***pennisetum* ethanosolv lignin**	**methanol**	**280**	**40**	**5 h**	**19 wt%**	**phenols & guaiacols**	**2**	
TiN-Ni	**softwood kraft lignin**	**methanol**	**150**	**25**	**< 0.1**	**3 wt%**	**Poh, Mooh, Mal, P(oh)2, Eoh - G**	**1**	399

Table S2 continued

Catalyst	Lignin[a]	Solvent	T (°C)	p H_2 (bar) at RT	Reaction time	Monomer yield[c]	Monomer structure	MYC	Ref
Ni on ZrO_2, ZnO, TiO_2,	corncob EH lignin	*n*-dodecane	250	40	160 min	5-11 wt%	Alk & Ox - S/G/Ph		310
Ni on SiO_2-Al_2O_3	corncob EH lignin	dioxane, benzene, toluene	250	40	160 min	9-12 wt%	Alk & Ox - S/G/Ph		
Ni on SiO_2-Al_2O_3	**corncob EH lignin**	**benzene**	**250**	**40**	**160 min**	**12 wt%**	**Alk & Ox - S/G/Ph**	**2**	
Ni on SiO_2-Al_2O_3	corncob EH lignin	naphtalene, ethanol, THF	250	40	160 min	5-6 wt%	Alk & Ox - S/G/Ph		
Pt/Al_2O_3, Pd/C, Ru/C, Ni/SiO_2	pine kraft lignin (Indulin AT)	ethanol/water (1:1 wt/wt)	200	30	4 h	3.7-6.2 wt%	P, E, M, Mal, H - G		401
Pt/Al_2O_3	**pine kraft lignin (Indulin AT)**	**ethanol/water (1:1 wt/wt)**	**200**	**30**	**4 h**	**6.2 wt%**	**P, E, M, Mal, H - G**	**1**	
Ru/C + HOTf	**wallnut dioxasolv lignin**	**dioxane**	**120**	**24**	**20 h**	**7 wt%**	**E, Eal, Eoh, P - S/G/Ph**	**1**	97
D101[d]	**rice husk hydrolysis lignin**	**dioxane**	**250**	**50**	**2 h**	**8 wt%**	**P, Poh, E, Eoh, M, H - S/G/Ph**	**1**	363
Ru/C	**beech dioxasolv lignin (80 °C, 5h; 77 wt% of lignin)[e]**	**THF**	**200**	**40**	**6 h**	**9 wt% (7 wt%)**	**P, Poh, E - S/G**	**1**	226
Ru/C	formic acid (FA)-assisted beech dioxasolv lignin (80 °C, 5h; 79 wt% of lignin)[e]	THF	200	40	6 h	57 wt% (45 wt%)	P, Poh, E - S/MS/G/MG		
Ru/C	**FA-assisted beech dioxasolv lignin (100 °C, 2h; 72 wt% of lignin)[e]**	**dioxane**	**250**	**40**	**15 h**	**66 wt% (47 wt%)**	**P, Poh, E - S/MS/G/MG**	**7**	
Ru/C	FA-assisted beech dioxasolv lignin (100 °C, 2h; 72 wt% of lignin)[e]	THF	250	40	15 h	64 wt% (46 wt%)	P, Poh, E - S/MS/G/MG		
Ru/C	F5H-poplar dioxasolv lignin (80 °C, 5h; 53% of lignin)[e]	THF	250	40	15 h	46 wt% (24 wt%)	P, Poh, E- S/G		
Ru/C	**FA-assisted poplar dioxasolv lignin (80 °C, 5h; 75 wt% of lignin)[e]**	**THF**	**250**	**40**	**15 h**	**100 wt% (78 wt%)**	**P, Poh, E - S/MS/G/MG**	**9**	
Ru/C + HCl	FA-assisted poplar dioxasolv lignin (80 °C, 5h; 75 wt% of lignin)[e]	THF	150	40	20 h	80 wt% (60 wt%)	P, Poh - S/MS/G/MG		
Ru/C	**FA-assisted spruce dioxasolv lignin (100 °C, 2h)[e]**	**THF**	**250**	**40**	**15 h**	**30 wt% (20 wt%)**	**P, E - G/MG**	**3**	

[a] For commercial lignin substrates, the commercial name (Indulin AT, Alcell lignin, etc.) or provider (Sigma-Aldrich, TCI, SEKAB, etc.) is usually indicated. [b] Lignin obtained by ethanosolv pulping of the enzymatic hydrolysis residue. [c] The monomer yield on native lignin basis is indicated in brackets. [d] Catalyst consists of a mixture of polyvalent metals modified by additions of alkaline-earth metals. [e] The conditions of the lignin extraction prodecure and the isolated lignin yield are indicated in brackets.

Table S3 Reductive depolymerisation - Harsh hydroprocessing *In support of Figure 15 in the main article*

Catalyst & system specifications	Lignin[a]	Solvent	T (°C)	p H_2 (bar) at RT	Reaction time	Monomer yield	Monomer structure	MYC	Ref
$NiMoO_x/SiO_2$-Al_2O_3	**spruce organocell lignin**	**/ (no solvent)**	**420**	**100 (210 at OT)**	**1 h**	**16.3 wt%**	**E, M, H -Ph**	**2**	407
$NiMoO_x/SiO_2$-Al_2O_3 + Cr_2O_3/Al_2O_3	**spruce organocell lignin**	**/**	**400**	**140 (at OT)**	**6 h**	**12.3 wt%**	**P, E, M, DM, H - Ph**	**2**	408
$NiMoO_x/SiO_2$-Al_2O_3 + Cr_2O_3/Al_2O_3 (sulfided)	**pine kraft lignin (Kaukas Oy, Finland), sample 1**	**/**	**395**	**100**	**35 min**	**10.4 wt%**	**P, E, M, DM, H - Ph**	**1**	409
$NiMoO_x/SiO_2$-Al_2O_3 + Cr_2O_3/Al_2O_3 (sulfided)	**pine kraft lignin (Kaukas Oy, Finland), sample 2**	**/**	**430**	**90**	**1 h**	**10.8 wt%**	**P, E, M, DM, H - Ph**	**2**	
$NiMoO_x/SiO_2$-Al_2O_3 + Cr_2O_3/Al_2O_3	**pine kraft lignin (Holmen Paper Ab, Sweden)**	**/**	**395**	**90**	**40 min**	**8.3 wt%**	**P, E, M, DM, H - Ph**	**1**	
$NiMoO_x/SiO_2$-Al_2O_3 + Cr_2O_3/Al_2O_3 (sulfided)	**birch kraft lignin (Kaukas Oy, Finland)**	**/**	**400**	**100**	**30 min**	**5.9 wt%**	**P, E, M, DM, H - Ph**	**1**	
$NiMoO_x/SiO_2$-Al_2O_3 + Cr_2O_3/Al_2O_3 (sulfided)	**spruce organocell lignin**	**/**	**395**	**100**	**30 min**	**10.5 wt%**	**P, E, M, DM, H - Ph**	**2**	
$CoMoO_x/Al_2O_3$ (sulfided), batch mode	aspen methanosolv lignin	1-methylnaphtalene	404	69	1 h	2.2 wt%	M, H - Ph		410
$CoMoO_x/Al_2O_3$ (sulfided), semicontinuous mode	**aspen methanosolv lignin**	**1-methylnaphtalene**	**428**	**69**	**1 h**	**10 wt%**	**M, H - Ph**	**1**	
Ru/C, Ru/TiO_2, Pd/C, Pd/Al_2O_3	Alcell lignin	/	400	100	4 h	19.1-22.8 wt%	APh > Ar, Cat, CA, nCA, Alc, Ket		403
Pd/C	**Alcell lignin**	**/**	**400**	**100**	**4 h**	**22.8 wt%**	**APh > Ar, Cat, CA, nCA, Alc, Ket**	**3**	
Cu/ZrO_2	Alcell lignin	/	400	100	4 h	11.8 wt%	APh > Ar, Cat, CA, nCA, Alc, Ket		
Ru/C	**Alcell lignin**	**/**	**400**	**100**	**4 h**	**21.4 wt%**	**APh > CA, Ar, Cat**	**3**	406
NiMo and CoMo on Al_2O_3, C, MgO-La_2O_3 and ZSM-5 (sulfided)	pine kraft lignin (Indulin AT)	/	350	100	4 h	11-26 wt%	APh > Ar, CA, nCA		404
NiMo/MgO-La_2O_3 (sulfided)	**pine kraft lignin (Indulin AT)**	**/**	**350**	**100**	**4 h**	**26 wt%**	**APh > Ar, CA, nCA**	**3**	
NiMo, CoMo, $NiWO_x$, Wox and NiW on C, ZSM-5, MgO-La_2O_3, MgO-CeO_2, MgO-ZrO_2 (sulfided; DMDS)	pine kraft lignin (Indulin AT)	methanol	320	35	8 h	6.5-28.5 wt%	APh > AG		405
NiW/C (sulfided)	pine kraft lignin (Indulin AT)	methanol	320	35	8 h	28.5 wt%	APh > AG		
NiW/C (sulfided)	**pine kraft lignin (Indulin AT)**	**methanol**	**320**	**35**	**24 h**	**35 wt%**	**APh**	**4**	

[a] For commercial lignin substrates, the commercial name (Indulin AT, Alcell lignin, etc.) or provider (Sigma-Aldrich, TCI, SEKAB, etc.) is usually indicated.

Table S4 Reductive depolymerisation - Bifunctional hydroprocessing *In support of Figure 15 in the main article*

Catalyst	Lignin[a,b]	Solvent	T (°C)	p H_2 (bar) at RT	Reaction time	Monomer yield[c]	Monomer structure	MYC	Ref
Ru/Al_2O_3	corn stover AE lignin	water	250	40	4 h	10 wt%	CA > nCA, Ar; mainly C_{6-11}		413
H-Y	corn stover AE lignin	water	250	40	4 h	14 wt%	Ar > CA, nCA; C_{6-18}		
Ru/Al_2O_3 + H-Y	**corn stover AE lignin**	**water**	**250**	**40**	**4 h**	**22 wt%**	**CA > nCA, Ar; mainly C_{12-18}**	**3**	
Ru/Al_2O_3 + H-Y	**pine FT-DAP lignin (70-79 wt% of lignin; 90 % purity)**	**water**	**250**	**60**	**4 h**	**22 wt%**	**CA > nCA > Ox; mainly C_{9-18}**	**3**	178
Ru/H-Y, Ru-M/H-Y (M: Fe, Ni, Cu, Zn)	pine FT-DAP lignin	water	250	40	4 h	26-32 wt%	CA > nCA > Ox; mainly C_{9-18}		414
Ru-Ni/H-Y	**pine FT-DAP lignin**	**water**	**250**	**40**	**4 h**	**32 wt%**	**CA > nCA > Ox; mainly C_{9-18}**	**4**	
Ru/Al_2O_3 + H-Y	pine FT-DAP lignin	water	250	40	4 h	22 wt%	CA > nCA > Ox; mainly C_{9-18}		
Ni/SiO_2	beech organosolv lignin	*n*-hexadecane	250	20	6 h	23 wt% (27 wt%)	monoCA > monoCHols		411
Ni/H-ZSM-5	beech organosolv lignin	*n*-hexadecane	250	20	6 h	28 wt% (34 wt%)	monoCA > biCA		
Ni/H-Beta	beech organosolv lignin	*n*-hexadecane	250	20	6 h	35 wt% (42 wt%)	monoCA > biCA		
Ni/H-Beta	**beech organosolv lignin**	***n*-hexadecane**	**320**	**20**	**6 h**	**(70 wt%)**	**hydrocarbons (gas (CH_4, C_2H_6) and liquid (monoCA, biCA))**	**7**	
Ni on SiO_2-Al_2O_3	corncob EH lignin	*n*-dodecane	250	40	160 min	18%	monoCA > biCA, Phenols, Alc, Ket		310
Ni on SiO_2-Al_2O_3	**corncob EH lignin**	***n*-dodecane**	**300**	**60**	**160 min**	**46%**	**monoCA > biCA, Phenols, Alc, Ket**	**5**	
Ni/Al-SBA-15	**poplar ethanosolv lignin**	**methycyclohexane**	**300**	**70**	**8 h**	**45 wt%**	**monoCA, biCA**	**5**	415
Ru/C, Pd/C, Pt/C, Rh/C + H_3PO_4	corn stover γ-valerolactone (GVL)-lignin	(i) THF/water/H_3PO_4; (ii) *n*-heptane/water/H_3PO_4	(i) 150; (ii) 250	35	(i) 4 h; (ii) 4 h	17-38 C%	monoCA; Pooh, PooMe - CH		281
Ru/C + H_3PO_4	corn stover GVL-lignin	(i) THF/water/H_3PO_4; (ii) *n*-heptane/water/H_3PO_4	(i) 150; (ii) 250	35	4 h;	38 C%	monoCA; Pooh, PooMe - CH		
Ru/C + H_3PO_4	**corn stover GVL-lignin**	**(i) THF/water/H_3PO_4; (ii) *n*-heptane/water/H_3PO_4/methanol**	(i) 150; (ii) 250	**35**	**4 h;**	**48 C%**	**monoCA; Pooh, PooMe - CH**	**5**	
Ru/C + H_3PO_4	**corn stover AAP-lignin**	**(i) THF/water/H_3PO_4; (ii) *n*-heptane/water/H_3PO_4**	(i) 150; (ii) 250	**35**	**4 h;**	**10 C%**	**monoCA; Pooh, PooMe - CH**	**1**	
Ru/C + H_3PO_4	**corn stover Klason lignin**	**(i) THF/water/H_3PO_4; (ii) *n*-heptane/water/H_3PO_4**	**(i) 150; (ii) 250**	**35**	**4 h;**	**17 C%**	**monoCA; Pooh, PooMe - CH**	**2**	

[a] For commercial lignin substrates, the commercial name (Indulin AT, Alcell lignin, etc.) or provider (Sigma-Aldrich, TCI, SEKAB, etc.) is usually indicated. [b] The isolated lignin yield and lignin purity are indicated in brackets.
[c] The total hydrocarbons yield, comprising gaseous (mainly CH_4 and C_2H_6) and liquid hydrocarbons, is indicated in brackets.

Table S5 Reductive depolymerisation - Liquid-phase reforming									*In support of Figure 15 in the main article*
Catalyst & system specifications	**Lignin[a]**	**Solvent**	**T (°C)**	**p (bar) at RT**	**Reaction time**	**Monomer yield**	**Monomer structure**	**MYC**	**Ref**
Pd/C + Nafion SAC-13	**spruce DAP-EH lignin (H_2SO_4-pretreatment) (SEKAB, Sweden)**	**water/formic acid (24:1 v/v)**	**300**	**95 (at OT)**	**2 h**	**4 wt%**	**H - G, Cat, Resorc**	**1**	424
Pd/C + Nafion SAC-13	**spruce DAP-EH lignin (SO_2 pretreatment) (SEKAB, Sweden)**	**water/formic acid (24:1 v/v)**	**300**	**95 (at OT)**	**2 h**	**5 wt%**	**H - G, Cat, Resorc**	**1**	
Pd/C + Nafion SAC-13	**spruce AH lignin (Statoil, Norway)**	**water/formic acid (24:1 v/v)**	**300**	**95 (at OT)**	**2 h**	**5 wt%**	**H - G, Cat, Resorc**	**1**	
Pd/C + Nafion SAC-13	**spruce AH lignin (Weyland, Norway)**	**water/formic acid (24:1 v/v)**	**300**	**95 (at OT)**	**2 h**	**6 wt%**	**H - G, Cat, Resorc**	**1**	
Pd/C + Nafion SAC-13	**spruce CAH lignin**	**water/formic acid (24:1 v/v)**	**300**	**95 (at OT)**	**2 h**	**6 wt%**	**H - G, Cat, Resorc**	**1**	
Pd/C + Nafion SAC-13	**spruce desulfonated kraft lignin (Sigma-Aldrich)**	**water/formic acid (24:1 v/v)**	**300**	**95 (at OT)**	**2 h**	**11 wt%**	**H - G, Cat, Resorc**	**2**	
Pt/C	**switchgrass ethanosolv lignin**	**ethanol/formic acid**	**350**	***n.i.***	**4 h**	**21 wt%**	**P, E, Eoh, M, H - G**	**3**	425
Pt/Al_2O_3 + H_2SO_4	**pine kraft lignin (Indulin AT)**	**ethanol/water (1:1 wt/wt)**	**225**	**58 He**	**1.5 h**	**18 wt%**	**P, E, Eoxo, Mal, H - G/Cat/Ph**	**2**	401, 423
Pt/Al_2O_3 + HPA	pine kraft lignin (Indulin AT)	ethanol/water (1:1 wt/wt)	225	58 He	1.5 h	13 wt%	P, E, Eoxo, Mal, H - G/Cat/Ph		
Pt/Al_2O_3 + NaOH	pine kraft lignin (Indulin AT)	ethanol/water (1:1 wt/wt)	225	58 He	1.5 h	13 wt%	P, E, Eoxo, Mal, H - G/Cat/Ph		
Pt/Al_2O_3 + H_2SO_4	**Alcell lignin**	**ethanol/water (1:1 wt/wt)**	**225**	**58 He**	**1.5 h**	**9 wt%**	**Pene, E, Eoh, H - S/G/Cat/Ph**	**1**	
Pt/Al_2O_3 + H_2SO_4	**sugarcane bagasse lignin**	**ethanol/water (1:1 wt/wt)**	**225**	**58 He**	**1.5 h**	**16 wt%**	**Pene, Pene(ooEth), E, H - S/G/Cat/Ph**	**2**	
$CuMgAlO_x$	Protobind 1000	ethanol	300	10 N_2	4 h	17 wt%	E, M, H - G; APh, Ar, CA, CAene		416
$CuMgAlO_x$	Protobind 1000	methanol	300	10 N_2	4 h	6 wt%	MG, APh, CA, CAene		
$CuMgAlO_x$	**Protobind 1000**	**ethanol**	**300**	**10 N_2**	**8 h**	**23 wt%**	**Ar, APh, CA, CAene; E, M, H - G**	**3**	
$CuMgAlO_x$	Protobind 1000	methanol/ethanol (1:1 v/v)	300	10 N_2	4 h	9 wt%			417
$CuMgAlO_x$	**Protobind 1000**	**ethanol**	**380**	**10 N_2**	**8 h**	**60 wt%**	**Ar, CA, CAene, APh**	**6**	
$CuMgAlO_x$	**Alcell lignin**	**ethanol**	**380**	**10 N_2**	**8 h**	**62 wt%**	**Ar, CA, CAene, APh**	**7**	
$CuMgAlO_x$	**softwood kraft lignin (Sigma-Aldrich)**	**ethanol**	**380**	**10 N_2**	**8 h**	**86 wt%**	**Ar, CA, CAene, APh**	**9**	
$CuMgAlO_x$	**Protobind 1000**	**ethanol**	**340**	**10 N_2**	**1 h**	**36 wt%**	**APh, Ar, CA, CAene**	**4**	426
NbN	Protobind 1000	ethanol	340	10 N_2		17 wt%	APh, CAene, Ar		427
TiN	**Protobind 1000**	**ethanol**	**340**	**10 N_2**		**19 wt%**	**APh, CAene, Ar**	**2**	
TiN	**wheat straw ethanosolv lignin**	**ethanol**	**340**	**10 N_2**		**16 wt%**	**APh, CAene, Ar**	**2**	
TiN	**poplar ethanosolv lignin**	**ethanol**	**340**	**10 N_2**		**15 wt%**	**APh, CAene, Ar**	**2**	
TiN	**spruce ethanosolv**	**ethanol**	**340**	**10 N_2**		**21 wt%**	**APh, CAene, Ar**	**3**	
Ni/Al-SBA-15, microwave assisted	**olive tree pruning ethanosolv lignin**	**tetralin, isopropanol, glycerol, formic acid**	**150**	***n.i.***	**30 min**	**< 1 wt%**	**Eoxo, Mal, H - S/G**	**1**	428-430

Table S5 continued

Catalyst & system specifications	Lignin[a]	Solvent	T (°C)	p (bar) at RT	Reaction time	Monomer yield	Monomer structure	MYC	Ref
MoC/C	**softwood kraft lignin (Sigma-Aldrich)**	**ethanol**	**280**	**1 N_2**	**6 h**	**28 wt%**	**Ar > BA, AG**	**3**	418, 419
MoC/C	softwood kraft lignin (Sigma-Aldrich)	methanol	280	1 N_2	6 h	2 wt%	AG > Ar, BA		
MoC/C	softwood kraft lignin (Sigma-Aldrich)	water	280	1 N_2	6 h	5 wt%	AG > Ar, BA		
MoC/C	softwood kraft lignin (Sigma-Aldrich)	isopropanol	280	1 N_2	6 h	3 wt%	AG > Ar, BA		
Mo/Al_2O_3	**softwood kraft lignin (Sigma-Aldrich)**	**ethanol**	**280**	**1 N_2**	**6 h**	**33 wt%**	**BA > Ar > AG**	**4**	419, 420
Mo_2N/Al_2O_3	**softwood kraft lignin (Sigma-Aldrich)**	**ethanol**	**280**	**1 N_2**	**6 h**	**28 wt%**	**BA > Ar > AG**	**3**	419
Pd/C	**wheat alkali lignin**	**methanol/formic acid (20:1 v/v)**	**280**	**1 N_2**	**2 h**	**11 wt%**	**Alk & Ox - S/G/Ph**	**2**	431
Pd/C	**sigma lignin**	**methanol/formic acid (20:1 v/v)**	**280**	**1 N_2**	**2 h**	**7 wt%**	**Alk & Ox - S/G/Ph**	**1**	
Pd/C + formic acid	**softwood kraft lignin (Sigma-Aldrich)**	**water**	**264**	**1 N_2**	**6 h**	**26 wt%**	**H - Cat > P, E, M, H - G; H- Ph**	**3**	432
Ru/C + formic acid	Alcell lignin	isopropanol/formic acid (1:1 wt/wt)	400	1 H_2	4 h	32 wt%	Ar, APh, Cat, CA, nCA		422
Ru/C + formic acid	**Alcell lignin**	**methanol/formic acid (1:1 wt/wt)**	**400**	**1 H_2**	**4 h**	**48 wt%**	**Ar, APh, Cat, CA, nCA**	**5**	
Raney Ni + H-USY, H-ZSM-5, H-Beta, Mordenite	bamboo EH-AE lignin	methanol/water (5:2 v/v)	270	1 N_2	30 min	25-28 wt%	P, Pene, Pene(ooh), E, Eooh, EooEth - S/G/Ph		421
Raney Ni + H-USY	**bamboo EH-AE lignin**	**methanol/water (5:2 v/v)**	**270**	**1 N_2**	**30 min**	**28 wt%**	**P, Pene, Pene(ooh), E, Eooh, EooEth - S/G/Ph**	**3**	
Raney Ni	bamboo EH-AE lignin	methanol/water (5:2 v/v)	270	1 N_2	30 min	13 wt%	P, Pene, Pene(ooh), E, Eooh, EooEth - S/G/Ph		
Cu/Mo-ZSM-5 + NaOH	**hardwood kraft lignin**	**methanol/water (1:3 v/v)**	**220**	**1 Ar**	**7 h**	**21 wt%**	**Phenols, Ar, CA, nCA, Ox**	**3**	433
Cu/Mo-ZSM-5 + NaOH	hardwood kraft lignin	methanol	220	1 Ar	7 h	6 wt%	Phenols, Ar, CA, nCA, Ox		
Cu/Mo-ZSM-5 + NaOH	hardwood kraft lignin	water	220	1 Ar	7 h	8 wt%	Phenols		
Ru/C	**switchgrass ILP-EH lignin (58 wt% KL)**	**isopropanol**	**300**	**20 N_2**	**3 h**	**15 wt%**	**Pene, P, Poxo, E, M, H - S/G/Ph**	**2**	309

[a] For commercial lignin substrates, the commercial name (Indulin AT, Alcell lignin, etc.) or provider (Sigma-Aldrich, TCI, SEKAB, etc.) is usually indicated.

Table S6 Oxidative depolymerisation - Alkaline lignin oxidation to phenolic compounds										*In support of Figure 17 in the main article*
Catalyst & system specifications	Lignin[a]	Solvent	T (°C)	p (bar) at RT[b]	Reaction time	Monomer yield	Monomer structure	MYC	Ref	
/	pine kraft black liquor	water + NaOH (2 N)	136	4.5 O_2 (at OT)	50 min	1 wt%	Mal - G (only quantified compound)	1	465	
/ (no catalyst)	pine kraft lignin (60 g/L; Westvaco)	water + NaOH (2 N)	140	3-4 O_2 / N_2 / 9-10 tot (at OT)	60-80 min	10 wt%	Mal - G (only quantified compound)	1	445	
/	pine kraft lignin (60 g/L; Westvaco)	water + NaOH (2 N)	120	3-4 O_2 / N_2 / 9-10 tot (at OT)	60-90 min	8.3 wt%	Mal - G (only quantified compound)			
/	pine kraft lignin (30 g/L; Westvaco)	water + NaOH (2 N)	120	3-4 O_2 / N_2 / 9-10 tot (at OT)	40-80 min	10 wt%	Mal - G (only quantified compound)			
/	pine kraft lignin (120 g/L; Westvaco)	water + NaOH (2 N)	120	3-4 O_2 / N_2 / 9-10 tot (at OT)	45 min	3 wt%	Mal - G (only quantified compound)			
/	pine kraft lignin (60 g/L; Westvaco)	water + NaOH (1 N)	120	3-4 O_2 / N_2 / 9-10 tot (at OT)	*n.i.*	3.8 wt%	Mal - G (only quantified compound)			
/	pine kraft lignin (60 g/L; Westvaco)	water + NaOH (4 N)	120	3-4 O_2 / N_2 / 9-10 tot (at OT)	*n.i.*	10 wt%	Mal - G (only quantified compound)			
$CuSO_4$	pine kraft lignin (60 g/L; Westvaco)	water + NaOH (2 N)	120	3-4 O_2 / N_2 / 9-10 tot (at OT)	45-100 min	8.3 wt%	Mal - G (only quantified compound)			
/	pine kraft lignin (82.5 g/L; Portucel)	water + NaOH (2 N)	127	3-4 O_2 / N_2 / 9-10 tot (at OT)	*n.i.*	6.8 wt%	Mal - G (only quantified compound)	1		
/	pine kraft black liquor (50 g/L; Portucel)	water + NaOH (4 N)	127	3-4 O_2 / N_2 / 9-10 tot (at OT)	*n.i.*	8 wt%	Mal - G (only quantified compound)	1		
/	pine kraft lignin (Westvaco)	water + NaOH (2 N)	133	3 O_2 / N_2 / 10 (at OT)	35 min	10.8 wt%	Mal - G (only quantified compound)	2	446	
/	pine kraft lignin (Indulin AT)	water + NaOH (2 N)	123	5 O_2 / N_2 / 9 tot (at OT)	75 min	3.7 wt%	Mal - G (only quantified compound)	1	[c]	
/, continuous mode	pine kraft lignin (Indulin AT)	water + NaOH (2 N)	160	10 O_2	0.167 L/min	3 wt%	Mal - G (only quantified compound)	1	466	
/	pine kraft lignin (Indulin AT)	water + NaOH (2 N)	123	4-6.5 O_2 / 9-10 tot (at OT)	50-100 min	3.3 wt%	Mal - G (only quantified compound)	1	448	
/	pine kraft lignin (Westvaco)	water + NaOH (2 N)	120	3 O_2 / N_2 / 9 tot (at OT)	30 min	7 wt%	Mal - G > Mooh - G > Eoxo - G > Mal - Ph	1	467	
/	pine kraft lignin (Westvaco)	water + NaOH (2 N)	120	3 O_2 / N_2 / 10 (at OT)	25 min	7 wt%	Mal - G > Mooh - G > Eoxo - G > Mal - Ph	1	468	
/	softwood kraft lignin (LignoBoost, Innventia)	water + NaOH (2 N)	120	3 O_2 / N_2 / 10 (at OT)	40 min	5 wt%	Mal - G > Mooh - G > Eoxo - G > Mal - Ph	1		
/	organosolv beech lignin (Fraunhofer, Germany)	water + NaOH (2 N)	120	3 O_2 / N_2 / 10 (at OT)	20 min	5 wt%	Mal - S/G > Mooh - S/G > Eoxo - S/G > Mal - Ph	1		
/	eucalyptus thin kraft liquor	water + NaOH (2 N)	120	3 O_2 / N_2 / 10 (at OT)	10-20 min	5 wt%	Mal - S/G > Mooh - S/G > Eoxo - S/G > Mal - Ph		338	
/	eucalyptus evaporation kraft liquor	water + NaOH (2 N)	120	3 O_2 / N_2 / 10 (at OT)	10-20 min	4 wt%	Mal - S/G > Mooh - S/G > Eoxo - S/G > Mal - Ph			
/	eucalyptus heat treatment kraft liquor	water + NaOH (2 N)	120	3 O_2 / N_2 / 10 (at OT)	10-20 min	5 wt%	Mal - S/G > Mooh - S/G > Eoxo - S/G > Mal - Ph	1		
/	eucalyptus sulfite liquor (Mg)	water + NaOH (2 N)	120	3 O_2 / N_2 / 10 (at OT)	10-20 min	6 wt%	Mal - S/G > Mooh - S/G > Eoxo - S/G > Mal - Ph	1		

Table S6 continued

Catalyst & system specifications	Lignin[a]	Solvent	T (°C)	p (bar) at RT[b]	Reaction time	Monomer yield	Monomer structure	MYC	Ref
/	**eucalyptus thin kraft liquor lignin**	**water + NaOH (2 N)**	**120**	**3 O_2 / N_2 / 10 (at OT)**	**10-20 min**	**7 wt%**	**Mal - S/G > Mooh - S/G > Eoxo - S/G > Mal - Ph**	**1**	338
/	eucalyptus evaporation kraft lignin	water + NaOH (2 N)	120	3 O_2 / N_2 / 10 (at OT)	10-20 min	6 wt%	Mal - S/G > Mooh - S/G > Eoxo - S/G > Mal - Ph		
/	eucalyptus heat treatment kraft lignin	water + NaOH (2 N)	120	3 O_2 / N_2 / 10 (at OT)	10-20 min	6 wt%	Mal - S/G > Mooh - S/G > Eoxo - S/G > Mal - Ph		
/	**hardwood kraft lignin (LignoBoost, Innventia)**	**water + NaOH (2 N)**	**120**	**3 O_2 / N_2 / 10 (at OT)**	**10-20 min**	**6 wt%**	**Mal - S/G > Mooh - S/G > Eoxo - S/G > Mal - Ph**	**1**	
/	eucalyptus lignosulfonate (Mg)	water + NaOH (0.9 N)	150	6 O_2	20 min	14 wt%	Mal - S/G (only quantified products)		452
$CuSO_4$	**eucalyptus lignosulfonate (Mg)**	**water + NaOH (0.9 N)**	**150**	**6 O_2**	**20 min**	**21 wt%**	**Mal - S/G (only quantified products)**	**3**	
$CuSO_4$ + nitrobenzene	softwood lignosulfonates (Borregard)	water + NaOH	190	15 tot	10 min	6 wt%	Mal - G (only quantified compound)		469
$CuSO_4$	softwood lignosulfonates (Borregard)	water + NaOH	190	15 tot	15 min	5 wt%	Mal - G (only quantified compound)		
$CuSO_4$ + trinitrobenzene	softwood lignosulfonates (Borregard)	water + NaOH	190	15 tot	10 min	4 wt%	Mal - G (only quantified compound)		
Co^{2+}, Cu^{2+}, Ce^{4+}, Ce^{4+}/Cu^{2+}	softwood lignosulfonates (Borregard)	water + NaOH	190	12 tot	70-90 min	4-6 wt%	Mal - G (only quantified compound)		
$CuSO_4$	**softwood lignosulfonates (Borregard)**	**water + NaOH**	**190**		**75 min**	**8 wt%**	**Mal - G (only quantified compound)**	**1**	
$CuSO_4$ + $FeCl_3$	aspen SEP-AE lignin	water + NaOH (3 N)	160	14 O_2	10 min	13 wt%	Mal - S/G > Eoxo - S/G; Mal - Ph		454
CuO + Fe_2O_3	aspen SEP-AE lignin	water + NaOH (3 N)	160	14 O_2	10 min	12 wt%	Mal - S/G > Eoxo - S/G; Mal - Ph		
/	aspen SEP-AE lignin	water + NaOH (3 N)	170	14 O_2	10 min	9 wt%	Mal - S/G > Eoxo - S/G; Mal - Ph		
$CuSO_4$	aspen SEP-AE lignin	water + NaOH (3.65 N)	170	14 O_2	10 min	14 wt%	Mal - S/G > Eoxo - S/G; Mal - Ph		
$FeCl_3$	aspen SEP-AE lignin	water + NaOH (4 N)	170	14 O_2	10 min	12 wt%	Mal - S/G > Eoxo - S/G; Mal - Ph		
$CuSO_4$ + $FeCl_3$	**aspen SEP-AE lignin**	**water + NaOH (3.37 N)**	**170**	**14 O_2**	**10 min**	**16 wt%**	**Mal - S/G > Eoxo - S/G; Mal - Ph**	**2**	
$Cu(OH)_2$	**softwood lignosulfonates**	**water + NaOH**	**160**	**9 O_2**		**14 wt%**	**Mal - G (only quantified compound)**	**2**	453
$CuSO_4$ (16.3 g $Cu(OH)_2$/L)	**fir lignosulfonate**	**water + NaOH (3 N)**	**160**	**2 O_2 (at OT)**	**40 min**	**8 wt%**	**Mal - G (only quantified compound)**	**1**	449
/	fir lignosulfonate	water + NaOH (3 N)	160	2 O_2 (at OT)	> 60 min	4 wt%	Mal - G (only quantified compound)		
$CuSO_4$ (9.75 g $Cu(OH)_2$/L)	fir lignosulfonate	water + NaOH (3 N)	160	2 O_2 (at OT)	40 min	8 wt%	Mal - G (only quantified compound)		
$CuSO_4$ (9.75 g $Cu(OH)_2$/L)	fir lignosulfonate	water + NaOH (2 N)	160	2 O_2 (at OT)	20 min	6 wt%	Mal - G (only quantified compound)		
$CuSO_4$ (9.75 g $Cu(OH)_2$/L)	fir lignosulfonate	water + K_2CO_3 (2.2 N)	160	2 O_2 (at OT)	20 min	0.8 wt%	Mal - G (only quantified compound)		
/	fir lignosulfonate	water + NaOH (3 N)	110	2 O_2 (at OT)	70 min	3 wt%	Mal - G (only quantified compound)		
$CuSO_4$ (9.8 g $Cu(OH)_2$/L)	fir lignosulfonate	water + NaOH (3 N)	110	2 O_2 (at OT)	70 min	4 wt%	Mal - G (only quantified compound)		

Table S6 continued

Catalyst & system specifications	Lignin[a]	Solvent	T (°C)	p (bar) at RT[b]	Reaction time	Monomer yield	Monomer structure	MYC	Ref
/	**softwood soda black liquor**	**water + KOH (2 N)**	**160**	**5 air**	**4 h**	**7 wt%**	**Mal - G (only quantified compound)**	**1**	450
/	**eucalyptus kraft lignin (precipitated with alcoholic solution of $CaCl_3$)**	**water + NaOH (2 N)**	**190**	**O_2 / 15 tot (at OT)**	**90 min**	**7 wt%**	**Mal - S/G > Mooh, Eoxo - S/G**	**1**	451
/	eucalyptus kraft lignin	water + NaOH (1 N)	180	O_2 / 15 tot (at OT)	125 min	7 wt%	Mal - S/G > Mooh, Eoxo - S/G		
$CuSO_4$, $CoCl_2$, Pt/Al_2O_3, $CuSO_4$ + EG, CoSALEN	eucalyptus kraft lignin	water + NaOH (1 N)	180	O_2 / 15 tot (at OT)	125 min	4-7 wt%	Mal - S/G > Mooh, Eoxo - S/G		
/	poplar FT-DAP lignin (70% of lignin, precipitates when cooling down)	water + NaOH (2 N)	170	0.65 g O_2	10 min	10 wt%	Mal -S/G > Eoxo - S/G (only quantified compounds)		180
$CuSO_4$	poplar FT-DAP lignin	water + NaOH (2 N)	170	0.65 g O_2	10 min	14 wt%	Mal -S/G > Eoxo - S/G (only quantified compounds)		
$FeCl_3$	poplar FT-DAP lignin	water + NaOH (2 N)	170	0.65 g O_2	10 min	12 wt%	Mal -S/G > Eoxo - S/G (only quantified compounds)		
$CuSO_4$ + $FeCl_3$	poplar FT-DAP lignin	water + NaOH (2 N)	170	0.65 g O_2	10 min	17 wt% (14 wt%)	Mal - S/G > Eoxo, Mooh - S/G (Mal, Eoxo - S/G in brackets)		
$CuSO_4$ + $FeCl_3$	poplar FT-DAP lignin	water + NaOH (2 N)	160	0.65 g O_2	30 min	23 wt%	Mal - S/G > Mooh - S/G > Eoxo - S/G		
$CuSO_4$ + $FeCl_3$	poplar FT-DAP lignin	water + NaOH (2 N)	170	0.65 g O_2	20 min	23 wt%	Mal - S/G > Mooh - S/G > Eoxo - S/G		
$CuSO_4$ + $FeCl_3$	**poplar FT-DAP lignin**	**water + NaOH (2 N)**	**180**	**0.65 g O_2**	**10 min**	**23 wt%**	**Mal - S/G > Mooh - S/G > Eoxo - S/G**	**3**	
Pd/Al_2O_3 (semibatch setup)	**sugarcane bagasse AH lignin**	**water + NaOH (2 N)**	**140**	**5 O_2 / N_2 / 20 tot (at OT)**	**30 min**	**16 wt%**	**Mal - S/G/Ph**	**2**	456
Pd/Al_2O_3 (continuous setup)	sugarcane bagasse AH lignin	water + NaOH (2 N)	120	4 air	5 L/h	12 wt%	Mal - S/G/Ph		
Pd/Al_2O_3 (semibatch setup)	**sugarcane bagasse AH lignin**	**water + NaOH (2 N)**	**120**	**5 O_2 / N_2 / 20 tot (at OT)**	**60 min**	**9 wt%**	**Mal - S/G/Ph**	**1**	457
/	sugarcane bagasse AH lignin	water + NaOH (2 N)	120	5 O_2 / N_2 / 20 tot (at OT)	60 min	0.6 wt%	Mal - S/G/Ph		
Pd/Al_2O_3 (semibatch setup)	**sugarcane bagasse AH lignin**	**water + NaOH (2 N)**	**120**	**10 O_2 / N_2 / 20 tot (at OT)**	**15 min**	**13 wt% (9 wt%)**	**Mal - S/G/Ph (Mal - S/G in brackets)**	**2**	458
Pd/Al_2O_3 (continuous setup)	sugarcane bagasse AH lignin	water + NaOH (2 N)	120	4 air	5 L/h	7 wt%	Mal - S/G (only quantified products)		
$LaMnO_3$	**cornstalk SEP-EH-AE lignin**	**water + NaOH (2 N)**	**120**	**5 O_2 / N_2 / 20 tot (at OT)**	**30 min**	**15 wt%**	**Mal - S > Mal - G > Mal - Ph**	**2**	462
$MnSO_4$	cornstalk SEP-EH-AE lignin	water + NaOH (2 N)	120	5 O_2 / N_2 / 20 tot (at OT)	30 min	10 wt%	Mal - S > Mal - G > Mal - Ph		
$LaCl_3$	cornstalk SEP-EH-AE lignin	water + NaOH (2 N)	120	5 O_2 / N_2 / 20 tot (at OT)	30 min	8 wt%	Mal - S > Mal - G > Mal - Ph		
/	cornstalk SEP-EH-AE lignin	water + NaOH (2 N)	120	5 O_2 / N_2 / 20 tot (at OT)	30 min	9 wt%	Mal - S > Mal - G > Mal - Ph		
$LaCoO_3$	**cornstalk SEP-EH-AE lignin**	**water + NaOH (2 N)**	**120**	**5 O_2 / N_2 / 20 tot (at OT)**	**50 min**	**16 wt%**	**Mal - S > Mal - G > Mal - Ph**	**2**	460
$CoSO_4$	cornstalk SEP-EH-AE lignin	water + NaOH (2 N)	120	5 O_2 / N_2 / 20 tot (at OT)	30-60 min	11 wt%	Mal - S > Mal - G > Mal - Ph		
$LaFeO_3$	cornstalk SEP-EH-AE lignin	water + NaOH (2 N)	120	5 O_2 / N_2 / 20 tot (at OT)	30 min	14 wt%	Mal - S > Mal - G > Mal - Ph		459
$LaFe_{0.9}Cu_{0.1}O_3$	cornstalk SEP-EH-AE lignin	water + NaOH (2 N)	120	5 O_2 / N_2 / 20 tot (at OT)	30 min	16 wt%	Mal - S > Mal - G > Mal - Ph		

Table S6 continued

Catalyst & system specifications	Lignin[a]	Solvent	T (°C)	p (bar) at RT[b]	Reaction time	Monomer yield	Monomer structure	MYC	Ref
$LaFe_{0.8}Cu_{0.2}O_3$	**cornstalk SEP-EH-AE lignin**	**water + NaOH (2 N)**	**120**	**5 O_2 / N_2 / 20 tot (at OT)**	**30 min**	**18 wt%**	**Mal - S > Mal - G > Mal - Ph**	**2**	459
$FeCl_3$	cornstalk SEP-EH-AE lignin	water + NaOH (2 N)	120	5 O_2 / N_2 / 20 tot (at OT)	30 min	10 wt%	Mal - S > Mal - G > Mal - Ph		
$LaCoO_3$	cornstalk SEP-EH-AE lignin	water + NaOH (2 N)	120	5 O_2 / N_2 / 20 tot (at OT)	50 min	16 wt%	Mal - S > Mal - G > Mal - Ph		461
$LaCo_{0.9}Cu_{0.1}O_3$	cornstalk SEP-EH-AE lignin	water + NaOH (2 N)	120	5 O_2 / N_2 / 20 tot (at OT)	40 min	17 wt%	Mal - S > Mal - G > Mal - Ph		
$LaCo_{0.8}Cu_{0.2}O_3$	**cornstalk SEP-EH-AE lignin**	**water + NaOH (2 N)**	**120**	**5 O_2 / N_2 / 20 tot (at OT)**	**40 min**	**20 wt%**	**Mal - S > Mal - G > Mal - Ph**	**2**	
$CuSO_4$	cornstalk SEP-EH-AE lignin	water + NaOH (2 N)	120	5 O_2 / N_2 / 20 tot (at OT)	30 min	15 wt%	Mal - S > Mal - G > Mal - Ph		
$LaMnO_3$	straw extracted lignin	water + NaOH (2 N)	140	5 O_2 (at OT)	*n.i.*	12 wt%	Mal - S > Mal - G, Mal - Ph		463
$La_{0.8}Sr_{0.2}MnO_3$	straw extracted lignin	water + NaOH (2 N)	140	5 O_2 (at OT)	*n.i.*	19 wt%	Mal - S > Mal - G, Mal - Ph		
$LaMn_{0.8}Cu_{0.2}O_3$	**straw extracted lignin**	**water + NaOH (2 N)**	**140**	**5 O_2 (at OT)**	***n.i.***	**23 wt%**	**Mal - S > Mal - G, Mal - Ph**	**3**	
$LaFeO_3$, $LaMnO_3$, $LaFe_xMn_yO_3$, $La_xSr_yMnO_3$ hollow nanospheres	cornstalk AH-AE lignin (HCl)	water + NaOH (2 N)	120	2 O_2	1 h	2.6-3 wt%	Mal - G (only quantified compound)		464
$LaMnO_3$ hollow nanospheres	**cornstalk AH-AE lignin (HCl)**	**water + NaOH (2 N)**	**120**	**2 O_2**	**2 h**	**3.4 wt%**	**Mal - G (only quantified compound)**	**1**	
$LaMnO_3$ (citric acid method)	cornstalk AH-AE lignin (HCl)	water + NaOH (2 N)	120	2 O_2	2 h	1.9 wt%	Mal - G (only quantified compound)		
/	cornstalk AH-AE lignin (HCl)	water + NaOH (2 N)	120	2 O_2	1 h	1.2 wt%	Mal - G (only quantified compound)		
/	bamboo SEP-AE lignin	water + NaOH (2 N)	170	1.5 O_2 / 8.5 tot (at OT)		7 wt%	Mal - S/G > Eoxo - S/G		470
$CuSO_4$	**bamboo SEP-AE lignin**	**water + NaOH (2 N)**	**170**	**1.5 O_2 / 8.5 tot (at OT)**		**10 wt%**	**Mal - S/G > Eoxo - S/G**	**1**	
Cu Phenanthroline	**pine MWL**	**water + NaOH (0.5M)**	**80**	**2.7 O2**	**24 h**	**16 wt%**	**Mal - G > Mooh - G**	**2**	471
/ or $CuSO_4$	spruce lignosulfonate (Na, Borregaard)	water + NaOH (3M)	160	N_2 / 11.5 tot (at OT)	25 min	4 wt%	Mal - G > Mooh - G		472
$CuSO_4$ (fed-batch, continuous feeding of oxygen)	**spruce lignosulfonate (Na, Borregaard)**	**water + NaOH (3M)**	**160**	**2.6-6 O_2 (at OT)**	**25-50 min**	**8 wt%**	**Mal - G > Mooh - G**	**1**	
CuO, $Fe_2(SO_4)_3$	wheat alkali lignin	water + NaOH (3M) + H_2O_2	150	*n.i.*	1 h	13 wt%	Mal - S/G > Mooh - S/G > Eoxo - S/G > Mooh, Mal, Eoxo - Ph		473
CuO, $Fe_2(SO_4)_3$	wheat alkali lignin	methanol + NaOH (3M) + H_2O_2	150	*n.i.*	1 h	11 wt%	Mal - S/G > Mooh - S/G > Eoxo - S/G > Mooh, Mal, Eoxo - Ph		
CuO, $Fe_2(SO_4)_3$	wheat alkali lignin	dioxane + NaOH (3M) + H_2O_2	150	*n.i.*	1 h	9 wt%	Mal - S/G > Mooh - S/G > Eoxo - S/G > Mooh, Mal, Eoxo - Ph		
CuO, $Fe_2(SO_4)_3$	wheat alkali lignin	THF + NaOH (3M) + H_2O_2	150	*n.i.*	1 h	7 wt%	Mal - S/G > Mooh - S/G > Eoxo - S/G > Mooh, Mal, Eoxo - Ph		
CuO, $Fe_2(SO_4)_3$	wheat alkali lignin	ethanol + NaOH (3M) + H_2O_2	150	*n.i.*	1 h	4 wt%	Mal - S/G > Mooh - S/G > Eoxo - S/G > Mooh, Mal, Eoxo - Ph		
CuO, $Fe_2(SO_4)_3$	**wheat alkali lignin**	**methanol/water (1:1 v/v) + NaOH (3M) + H_2O_2**	**150**	*n.i.*	**1 h**	**18 wt%**	**Mal - S/G > Mooh - S/G > Eoxo - S/G > Mooh, Mal, Eoxo - Ph**	**2**	
CuO, $Fe_2(SO_4)_3$	wheat alkali lignin	dioxane/water (1:1 v/v) + NaOH (3M) + H_2O_2	150	*n.i.*	1 h	15 wt%	Mal - S/G > Mooh - S/G > Eoxo - S/G > Mooh, Mal, Eoxo - Ph		

Table S6 continued

Catalyst & system specifications	Lignin[a]	Solvent	T (°C)	p (bar) at RT[b]	Reaction time	Monomer yield	Monomer structure	MYC	Ref
CuO, $Fe_2(SO_4)_3$	wheat alkali lignin	ethanol/water (1:1 v/v) + NaOH (3M) + H_2O_2	150	*n.i.*	1 h	16 wt%	Mal - S/G > Mooh - S/G > Eoxo - S/G > Mooh, Mal, Eoxo - Ph		473
CuO, $Fe_2(SO_4)_3$	wheat alkali lignin	THF/water (1:1 v/v) + NaOH (3M) + H_2O_2	150	*n.i.*	1 h	8 wt%	Mal - S/G > Mooh - S/G > Eoxo - S/G > Mooh, Mal, Eoxo - Ph		
$CuSO_4/FeCl_3$	**spruce kraft lignin**	**water + NaOH (3M)**	**170**	**5 O_2**	**20 min**	**1.58 wt%**	**Mal - G > Eoxo - G**	**1**	474
$CuSO_4/FeCl_3$	Protobind 1000 / Granit lignin	water + NaOH (3M)	170	5 O_2	20 min	1.38 wt%	Mal - G > Mal - S; Eoxo - S/G		
$CuSO_4/FeCl_3$	**Protobind 1000 / Granit lignin**	**water + NaOH (3M) + MeOH (40 vol%)**	**170**	5 O_2	**20 min**	**1.62 wt%**	**Mal - G > Mal - S; Eoxo - S/G**	**1**	

[a] For commercial lignin substrates, the commercial name (Indulin AT, Alcell lignin, etc.) or provider (Sigma-Aldrich, TCI, SEKAB, etc.) is usually indicated. [b] When A / B / C format is used, A represents the partial oxygen pressure, B the inert makeup gas and C the total reaction pressure, either at room temperature (RT) or operation temperature (OT). [c] E. A. Borges da Silva, M. Zabkova, J. D. Araújo, C. A. Cateto, M. F. Barreiro, M. N. Belgacem and A. E. Rodrigues, *Chemical Engineering Research and Design*, 2009, **87**, 1276-1292.

Table S7 Oxidative depolymerisation - Acidic and pH-neutral lignin oxidation to phenolic compounds									*In support of Figure 17 in the main article*
Catalyst & system specifications	**Lignin[a]**	**Solvent**	**T (°C)**	**p (bar) at RT**	**Reaction time**	**Monomer yield**	**Monomer structure**	**MYC**	**Ref**
Acidic lignin oxidation									
$H_3PMo_{12}O_{40}$	spruce kraft lignin (Sigma-Aldrich)	water	170	5 O_2	20 min	0.2 wt%	Mal - G > Eoxo - G		474
$H_3PMo_{12}O_{40}$	spruce kraft lignin (Sigma-Aldrich)	methanol/water (4:1 v/v)	170	5 O_2	20 min	2.92 wt%	MooMe, Mal - G > Eoxo - G		
$H_3PMo_{12}O_{40}$	**poplar organosolv lignin**	**methanol/water (4:1 v/v)**	**170**	**5 O_2**	**20 min**	**3.25 wt%**	**MooMe, Mal - S/G > Eoxo - S/G**	**1**	
$H_3PMo_{12}O_{40}$	spruce kraft lignin (Sigma-Aldrich)	water	170	5 O_2	20 min	2.45 wt%	Mal - G (other quantification method)		
$H_3PMo_{12}O_{40}$	**spruce kraft lignin (Sigma-Aldrich)**	**methanol/water (4:1 v/v)**	**170**	**5 O_2**	**20 min**	**5.18 wt%**	**MooMe, Mal - G (other quantification method)**	**1**	
H_2SO_4	spruce kraft lignin (Sigma-Aldrich)	water	170	5 O_2	20 min	1.18 wt%	Mal - G (other quantification method)		
H_2SO_4	spruce kraft lignin (Sigma-Aldrich)	methanol/water (4:1 v/v)	170	5 O_2	20 min	2.76 wt%	MooMe, Mal - G (other quantification method)		
$H_3PMo_{12}O_{40}$	spruce kraft lignin (Sigma-Aldrich)	water	170	10 O_2	20 min	5.86 wt%	Mal - G		475
$H_3PMo_{12}O_{40}$	**spruce kraft lignin (Sigma-Aldrich)**	**methanol/water (4:1 v/v)**	**170**	**10 O_2**	**20 min**	**8.79 wt%**	**MooMe, Mal - G**	**1**	
HCl	spruce kraft lignin (Sigma-Aldrich)	water	170	10 O_2	20 min	2.77 wt%	Mal - G		
HCl	spruce kraft lignin (Sigma-Aldrich)	methanol/water (4:1 v/v)	170	10 O_2	20 min	7.17 wt%	**MooMe, Mal - G**		
$H_3PMo_{12}O_{40}$	softwood lignosulfonate (Ca, Borresperse, Borregaard)	water	170	10 O_2	20 min	5.48 wt%	Mal - G		
$H_3PMo_{12}O_{40}$	**softwood lignosulfonate (Ca, Borresperse, Borregaard)**	**methanol/water (4:1 v/v)**	**170**	**10 O_2**	**20 min**	**10.03 wt%**	**MooMe, Mal - G**	**1**	
$H_3PMo_{12}O_{40}$	softwood lignosulfonate (Na, Ultrazine NA, Borregaard)	water	170	10 O_2	20 min	6.59 wt%	Mal - G		
$H_3PMo_{12}O_{40}$	**softwood lignosulfonate (Na, Ultrazine NA, Borregaard)**	**methanol/water (4:1 v/v)**	**170**	**10 O_2**	**20 min**	**12.7 wt%**	**MooMe, Mal - G**	**2**	
$H_3PMo_{12}O_{40}$	**pine kraft lignin (Indulin AT)**	**methanol/water (4:1 v/v)**	**170**	**10.8 O_2**	**20 min**	**7 wt%**	**MooMe, Mal - G**	**1**	476
H_2SO_4	pine kraft lignin (Indulin AT)	methanol/water (4:1 v/v)	170	10 O_2	20-120 min	4.7 wt%	MooMe, Mal - G		477
$H_3PMo_{12}O_{40}$	pine kraft lignin (Indulin AT)	methanol/water (4:1 v/v)	170	10 O_2	20-120 min	5.8 wt%	MooMe, Mal - G		
$CuCl_2$, $FeCl_3$ + H_2SO_4	pine kraft lignin (Indulin AT)	methanol/water (4:1 v/v)	170	10 O_2	20-120 min	5.3-5.5 wt%	MooMe, Mal - G		
$CuSO_4$, $CoCl_2$ + H_2SO_4	**pine kraft lignin (Indulin AT)**	**methanol/water (4:1 v/v)**	**170**	**10 O_2**	**20-120 min**	**6.3 wt%**	**MooMe, Mal - G**	**1**	
peracetic acid	corn stover DAP-EH-AE lignin	water	60	1 air	1 h	22 wt%	Mooh -G; oh - Ph > Mooh - S/Cat/Ph		481
peracetic acid	spruce SEP-EH-AE lignin	water	60	1 air	1.5 h	18 wt%	Mooh - G/Cat > oh - G		
peracetic acid + Nb_2O_5	**corn stover DAP-EH-AE lignin**	**water**	**60**	**1 air**	**1.5 h**	**47 wt%**	**Mooh -G; oh - Ph > Mooh - S/Cat/Ph**	**5**	
peracetic acid + Nb_2O_5	**spruce SEP-EH-AE lignin**	**water**	**60**	**1 air**	**5 h**	**35 wt%**	**Mooh - G/Cat > oh - G**	**4**	

Table S7 continued

Catalyst & system specifications	Lignin[a]	Solvent	T (°C)	p (bar) at RT	Reaction time	Monomer yield	Monomer structure	MYC	Ref
Co/Mn/Zr/Br catalyst[b]	hardwood acetosolv lignin (Sigma-Aldrich)	acetic acid/water (92:8 wt/wt)	180	138 air (at OT)	2 h	10.9 wt%	Mooh, Mal - S/G	2	479
Co/Mn/Zr/Br catalyst[b]	hardwood acetosolv lignin (Sigma-Aldrich)	acetic acid	140	69 air (at OT)	2 h	4.5 wt%	Mooh, Mal - S/G		
Co/Mn/Zr/Br catalyst[b]	sugarcane bagasse hydrolytic lignin (Sigma-Aldrich)	acetic acid	140	69 air (at OT)	2 h	7.5 wt%	Mooh, Mal - S/G/Ph	1	
Co/Mn/Zr/Br catalyst[b]	hardwood acetosolv lignin, acetylated (Sigma-Aldrich)	acetic acid	140	69 air (at OT)	2 h	2.2 wt%	Mooh, Mal - S/G	1	
Co/Mn/Zr/Br catalyst[b]	lignosulfonate, acetylated (Sigma-Aldrich)	acetic acid	140	69 air (at OT)	2 h	0.2 wt%	Mooh, Mal - G	1	
Co/Br catalyst[c]	spruce Organocell lignin (methanol/water/NaOH/anthraquinone pulping)	acetic acid	210	5-15 O_2	15 min	4.5 wt%	Mooh, Mal - G	1	480
Co/Br catalyst[c]	eucalyptus acetosolv lignin (acetic acid/water/HCl pulping)	acetic acid	210	5-15 O_2	15 min	1 wt%	Mooh, Mal - G	1	
Co/Br catalyst[c]	sugarcane bagasse acetosolv lignin	acetic acid	210	5-15 O_2	15 min	0.2 wt%	Mooh, Mal - G	1	
Co/Br catalyst[c]	sugarcane bagasse acetonosolv lignin (acetone/water/$FeCl_3$ pulping)	acetic acid	210	5-15 O_2	15 min	1 wt%	Mooh, Mal - G	1	
pH-neutral lignin oxidation									
Pd/CeO_2	organosolv lignin	methanol	185	10 O_2	24 h	8.5 wt%	Mal - G/Ph > H- G	1	482
$Mn(NO_3)_2$	beech organosolv lignin (Fraunhofer)	$[C_2C_1im][CF_3SO_4]$	100	17.5 O_2 / N_2 / 84 tot[d]	24 h	11.5 wt%	2,6-dimethoxybenzoquione (only quantified compound)	2	486
$H_6PMo_{10}V_2O_x$	willow ionosolv lignin	$[HC_4im][HSO_4]$	100	oxygen flow	5 h	0.5 wt%	Mal, H - S/G/Ph > Eoxo - S/G	1	484
$H_6PMo_{10}V_2O_x$	pine ionosolv lignin	$[HC_4im][HSO_4]$ + H_2O_2	100	*n.i.*	5 h	0.3 wt%	Mal, H - G	1	
$CuSO_4$	Alcell lignin	$[C_1C_1im][Me_2PO_4]$/MIBK	175	25 O_2	1.5 h	30 wt%	Mal - S/G/Ph	3	487

[a] For commercial lignin substrates, the commercial name (Indulin AT, Alcell lignin, etc.) or provider (Sigma-Aldrich, TCI, SEKAB, etc.) is usually indicated. [b] Catalyst system: $Co(Ac)_2/Mn(Ac)_2/Zr(Ac)_4/HBr$ (1:1:0.1:2 molar ratio). [c] catalyst system: $Co(Ac)_2/NH_4Br$ (1:5 molar ratio). [d] Partial oxygen pressure / inert makeup gas / total reaction pressure.

Table S8 Oxidative depolymerisation - Lignin oxidation to non-phenolic carboxylic acids									*In support of Figure 17 in the main article*
Catalyst & system specifications	**Lignin[a]**	**Solvent**	**T (°C)**	**p (bar) at RT**	**Reaction time**	**Monomer yield**	**Monomer structure**	**MYC**	**Ref**
/	**poplar FT-DAP lignin (70% of lignin, precipitates when cooling down)**	**water + NaOH (1 M) + H_2O_2**	**120**	***n.i.***	**10 min**	**56 wt%**	**oxalic & formic acid > acetic & malonic acid**	**6**	179
/	poplar FT-DAP lignin	water + H_2SO_4 (5 mM) + H_2O_2	140	*n.i.*	30 min	41 wt%	formic acid > acetic acid > succinic & malonic acid		
/	**softwood kraft lignin**	**water + H_2O_2 (in flow reactor)**	**200**	***n.i.***		**45 wt%**	**formic, acetic & succinic acid**	**5**	489
/	**softwood organosolv lignin (Sigma-Aldrich)**	**water + H_2O_2 (in flow reactor)**	**160**	***n.i.***		**20 wt%**	**formic, acetic & succinic acid**	**2**	
chalcopyrite ($CuFeS_2$)	**corn stover DAP-EH-AE lignin**	**acetic acid/sodium acetate/water (buffer solution, pH 4) + H_2O_2**	**60**	***n.i.***	**5 h**	**14 wt%**	**succinic & malonic acid > malic & maleic acid**	**2**	488
chalcopyrite ($CuFeS_2$)	**spruce SEP-EH-AE lignin**	**acetic acid/sodium acetate/water (buffer solution, pH 4) + H_2O_2**	**60**	***n.i.***	**5 h**	**11 wt%**	**succinic & malonic acid > malic & maleic acid**	**2**	
/	**softwood kraft lignin (Sigma-Aldrich)**	**water + NaOH (0.1 M)**	**225**	**10 O_2 (at OT)**	**10-15 min**	**44 wt%**	**formic, acetic, succinic, oxalic & glutaconic acid**	**5**	490
Vanadium pyrophosphate	softwood kraft lignin (FPInnovations)	water + NaOH (1.75 M) in fluidisedbed	377	0.7 C/O_2; Ar/O_2 mixture	9 min	2.2 wt%	malonic acid > maleic anhydride > acrylic acid		491
Al-V-Mo	softwood kraft lignin (FPInnovations)	water + NaOH (1.75 M) in fluidised bed	377	0.7 C/O_2; Ar/O2 mixture	9 min	7 wt%	lactic acid >> maleic anhydride > acetic acid > acrylic acid		
Vanadium pyrophosphatee (forced concentration cycling)	softwood kraft lignin (FPInnovations)	water + NaOH (1.75 M) in fluidised bed	377	0.7 C/O_2; Ar/O_2 mixture	9 min	4 wt%	maleic anhydride > acrylic acid		
Al-V-Mo (forced concentration cycling)	**softwood kraft lignin (FPInnovations)**	**water + NaOH (1.75 M) in fluidised bed**	**327**	**0.7 C/O_2; Ar/O_2 mixture**	**9 min**	**23 wt% (17 C%)**	**lactic & formic acid > acetic & phthalic acid > maleic anhydride, acrylic acid**	**3**	

[a] For commercial lignin substrates, the commercial name (Indulin AT, Alcell lignin, etc.) or provider (Sigma-Aldrich, TCI, SEKAB, etc.) is usually indicated.

Table S9 Base-catalysed depolymerisation (BCD) *In support of Figure 18 in the main article*

Catalyst & system specifications	Lignin[a]	Solvent	T (°C)	p (bar) at RT	Reaction time	Monomer yield	Monomer structure	MYC	Ref
NaOH	**Alcell lignin**	**ethanol/water (1:3 v/v)**	**240**	***n.i.***	**30 min**	**4 wt%**	**E, M, H - S/G/Cat/Ph**	**1**	497
NaOH	**hemp SEP-AE lignin**	**water**	**330**	**35 N_2**	**45 min**	**11 wt%**	**M, H - Cat > M, Mal, H - G**	**2**	493
NaOH	**softwood SEP-AE lignin**	**water**	**330**	**35 N_2**	**45 min**	**10 wt%**	**M, H - G/Cat**	**1**	
NaOH, continuous mode	**softwood kraft lignin (Indulin AT)**	**water**	**315**	**130 (at OT)**	**0.7 (LHSV of 1.4 h^{-1})**	**8 wt%**	**M, H - Cat > M, Mal, H - G**	**1**	494
NaOH, continuous mode	**hardwood organosolv lignin (Sigma-Aldrich)**	**water**	**300**	**250 (at OT)**	**4.2 min**	**15 wt%**	**Eoxo, Mal, H - S/G**	**2**	492
NaOH, KOH, $Ca(OH)_2$, LiOH, K_2CO_3	olive tree pruning ethanosolv lignin	water	300	90 (at OT)	40 min	1-4 wt%	M, H - Cat > H - S/G/Ph		495
NaOH, K_2CO_3	**olive tree pruning ethanosolv lignin**	**water**	**300**	**90 (at OT)**	**40 min**	**4 wt%**	**M, H - Cat > H - S/G/Ph**	**1**	
NaOH	**olive tree pruning organosolv lignin**	**water**	**300**	**90 (at OT)**	**80 min**	**4 wt%**	**E, M, H - Cat > M, H - Ph**	**1**	498
MgO	pine ethanosolv lignin	methanol	250	1 N_2	30 min	9 wt%	P, E, M, H - S/G/Ph		503
MgO	pine ethanosolv lignin	ethanol	250	1 N_2	30 min	8 wt%	P, E, M, H - S/G/Ph		
MgO	pine ethanosolv lignin	ethanol/water	250	1 N_2	30 min	11 wt%	P, E, M, H - S/G/Ph		
MgO	**pine ethanosolv lignin**	**THF**	**250**	**1 N_2**	**30 min**	**13 wt%**	**P, E, M, H - S/G/Ph**	**2**	
MgO	pine ethanosolv lignin	water	250	1 N_2	30 min	2 wt%	P, E, M, H - S/G/Ph		
HTC, Ni-HTC, HTC($NO_{3,ex}$)	**corn stover DAP-EH lignin**	**water**	**275**	***n.i.***	**1 h**	**7 wt%**	**Eoxo, Mal, H - S/G/Ph**	**1**	501
HTC, Ni-HTC, HTC($NO_{3,ex}$)	corn stover DMR-EH lignin	water	275	*n.i.*	1 h	8 wt%	Eoxo, Mal, H - S/G/Ph		
HTC, Ni-HTC, HTC($NO_{3,ex}$)	corn stover DAP-EH lignin	3-methyl-3-pentanol	275	*n.i.*	1 h	5-6 wt%	V- Ph > V- G; Pene, H -S		
HTC, Ni-HTC, HTC($NO_{3,ex}$)	**corn stover DMR-EH lignin**	**3-methyl-3-pentanol**	**275**	***n.i.***	**1 h**	**7-9 wt%**	**V- Ph > V- G; Pene, H -S**	**1**	
Na_2CO_3	**bamboo HWP-AE lignin**	**water**	**250**	**10 N_2**	**1.5 h**	**8 C%**	**H, Ox - S/G/Ph**	**1**	499
NaOH	**pine ethanosolv lignin**	**methanol**	**260**	**40 H_2**	**4 h**	**8 wt%**	**phenols & guaiacols**	**1**	387
Na-X	**softwood kraft lignin (TCI)**	**ethanol/water (1:2 wt/wt)**	**250**	**1 N_2**	**1 h**	**18 wt%**	**Eoxo, M, Mal, H - G**	**2**	502

[a] For commercial lignin substrates, the commercial name (Indulin AT, Alcell lignin, etc.) or provider (Sigma-Aldrich, TCI, SEKAB, etc.) is usually indicated.

Table S10 Acid-catalysed depolymerisation (ACD) *In support of Figure 18 in the main article*

Catalyst & system specifications	Lignin[a]	Solvent	T (°C)	p (bar) at RT	t (h)	Monomer yield	Monomer structure	MYC	Ref
$NiCl_2$, $FeCl_2$	**Alcell lignin**	**water**	**305**	**1 N_2**	***n.i.***	**2-3 wt%**	**H - Cat > H - G/Ph**	**1**	505
$ZnCl_2$	**softwood kraft lignin (Sigma-Aldrich)**	**ethanol**	**300**	**10 H_2**	**2 h**	**34 wt%**	**H - G > H - Cat > E, M, H - G/Cat/Ph**	**4**	506
$NiCl_2$, $ZnCl_2$, $AlCl_3$, $CuCl_2$	softwood kraft lignin (Sigma-Aldrich)	water	260	10 H_2	2 h	4-5 wt%	H - G > E, Eoxo, Eooh, M, Mal - G; M, H - Ph		
$NiCl_2$, $ZnCl_2$, $AlCl_3$, $CuCl_2$	softwood kraft lignin (Sigma-Aldrich)	ethanol	260	10 H_2	2 h	9-14 wt%			
H_3PO_4	**softwood kraft lignin (Sigma-Aldrich)**	**water**	**260**	**10 H_2**	**2 h**	**11 wt%**	**H - G > E, Eoxo, Eooh, M, Mal - G; M, H - Ph**	**2**	
$ZnCl_2$	softwood kraft lignin (Sigma-Aldrich)	methanol, ethanol, butanol, octane	260	10 H_2	2 h	14-19 wt%			
MCl_x (Fe, Cu, Co, Ni, Al), $M(Oac)_2$ (Fe, Cu, Co, Ni)	Protobind 1000	water	400	1 air	4 h	5-7 wt%	phenols > catechols		508
MCl_x (Fe, Cu, Co, Ni, Al), $M(Oac)_2$ (Fe, Cu, Co, Ni), $M(OTf)_x$ (Cu,Ni, Al)	Protobind 1000	ethanol	400	1 air	4 h	4-13 wt%	phenols > guaiacols		
$Cu(Oac)_2$, $Co(Oac)_2$	**Protobind 1000**	**ethanol**	**400**	**1 air**	**4 h**	**11-13 wt%**	**phenols > guaiacols**	**2**	
$M(OTf)_2$ (Al, Ni, Cu, Sc)	Protobind 1000	ethanol/water (3.5:3 v/v)	400	1 air	4 h	13-21 wt%	phenols, gauiacols (mainly phenols)		507
$Al(OTf)_3$	**Protobind 1000**	**ethanol/water (3.5:3 v/v)**	**400**	**1 air**	**4 h**	**21 wt%**	**phenols > guaiacols**	**3**	
$CrCl_3$	**softwood kraft lignin (Sigma-Aldrich)**	**methanol**	**260**	**40 H_2**	**5 h**	**24 wt%**	**phenols & guaiacols**	**3**	386
2-step process: (1) SiO_2-Al_2O_3; batch (2) ZrO_2-Al_2O_3-FeO_x; continuous in fixed bed (catalytic cracking of butanol phase)	**organosolv lignin propionate (Sigma-Aldrich)**	**(1) butanol/water (1:4 v/v); (2) butanol**	**(1) 300; (2) 400**	**(1) 1 N_2; (2) 1 N_2**	**(1) 2 h; (2) 2 h**	**7 wt%**	**APh > AG**	**1**	515
	softwood kraft lignin	**(1) butanol/water (1:4 v/v); (2) butanol**	**(1) 300; (2) 400**	**(1) 1 N_2; (2) 1 N_2**	**(1) 2 h; (2) 2 h**	**9 wt%**	**APh > AG**	**1**	
2-step process: (1) SiO_2-Al_2O_3; batch (2) CeO_2-ZrO_2-Al_2O_3-FeO_x; continuous in fixed bed (catalytic cracking of butanol phase)	**softwood kraft lignin**	**(1) butanol/water (1:4 v/v); (2) butanol/water (steam)**	**(1) 350; (2) 400**	**(1) 1 N_2; (2) 150 (at OT)**	**(1) 2 h; (2) 2-4 h**	**(1) 12 wt%; (2) 17 wt%**	**(1) guaiacols & catechols; (2) APh**	**2**	516
H_2SO_4	softwood kraft lignin (TCI)	methanol/water (5:1 v/v)	250	7 N_2	30 min	39 wt%	Mal, P(2-oxo) - G > Eooh, MooMe, Pene(al), Eoxo, V - G		509
HCl	softwood kraft lignin (TCI)	methanol/water (5:1 v/v)	250	7 N_2	30 min	29 wt%	Mal, P(2-oxo) - G > Eooh, MooMe, Pene(al), Eoxo, V - G		
SO_4/ZrO_2, Nb_2O_5, H-Beta, silica-alumina, $MoO3/SiO_2$	softwood kraft lignin (TCI)	methanol/water (5:1 v/v)	250	7 N_2	30 min	18-30 wt%	Mal, P(2-oxo) - G > Eooh, MooMe, Pene(al), Eoxo, V - G		
clay (K10), Al-pillared clay, H-Mor	softwood kraft lignin (TCI)	methanol/water (5:1 v/v)	250	7 N_2	30 min	40 wt%	Mal, P(2-oxo) - G > Eooh, MooMe, Pene(al), Eoxo, V - G		
H-ZSM-5, H-USY	**softwood kraft lignin (TCI)**	**methanol/water (5:1 v/v)**	**250**	**7 N_2**	**30 min**	**55-60 wt%**	**Mal, P(2-oxo) - G > Eooh, MooMe, Pene(al), Eoxo, V - G**	**6**	
silica-alumina (500 rpm SR)	softwood kraft lignin (TCI)	methanol/water (5:1 v/v)	250	7 N_2	30 min	29 wt%	Mal, MooMe, Eoxo, Eooh, Poxo, Pene, Pene(al) - G		514
silica-alumina	softwood kraft lignin (TCI)	water	250	7 N_2	30 min	/	/		

Table S10 continued

Catalyst & system specifications	Lignin[a]	Solvent	T (°C)	p (bar) at RT	t (h)	Monomer yield	Monomer structure	MYC	Ref
silica-alumina	softwood kraft lignin (TCI)	methanol/water (5:1 v/v)	250	7 N_2	30 min	29 wt%	Mal, MooMe, Eoxo, Eooh, Poxo, Pene, Pene(al) - G		514
silica-alumina	softwood kraft lignin (TCI)	methanol/water (5:1 v/v)	250	7 N_2	30 min	56 wt%	Mal, MooMe, Eoxo, Eooh, Poxo, Pene, Pene(al) - G		
silica-alumina (1000 rpm SR)	softwood kraft lignin (TCI)	methanol/water (5:1 v/v)	250	7 N_2	30 min	59 wt%	Mal, MooMe, Eoxo, Eooh, Poxo, Pene, Pene(al) - G		
silica-alumina	**softwood kraft lignin (Sigma-Aldrich)**	**methanol/water (5:1 v/v)**	**250**	**7 N_2**	**30 min**	**58 wt%**	**Mal, MooMe, Eoxo, Eooh, Poxo, Pene, Pene(al) - G**	**6**	
silica-alumina	**organosolv lignin (Sigma-Aldrich)**	**methanol/water (5:1 v/v)**	**250**	**7 N_2**	**30 min**	**33 wt%**	**Mal, MooMe, Eoxo, Eooh, Poxo, Pene, Pene(al) - G**	**4**	
silica-alumina	**industrial organosolv lignins**	**methanol/water (5:1 v/v)**	**250**	**7 N_2**	**30 min**	**55-62 wt%**	**Mal, MooMe, Eoxo, Eooh, Poxo, Pene, Pene(al) - G**	**7**	
silica-alumina	**methanosolv bagasse lignin**	**methanol/water (5:1 v/v)**	**250**	**7 N_2**	**30 min**	**61 wt%**	**Mal, MooMe, Eoxo, Eooh, Poxo, Pene, Pene(al) - G**	**7**	
H-USY, H-Beta	**bamboo EH-AE lignin**	**methanol/water (5:2 v/v)**	**270**	**1 N_2**	**30 min**	**3-5 wt%**	**Eooh - G; Pene - S > Eooh, Pene, P, E - S/G**	**1**	421
formic acid	**Protobind 1000**	**ethanol**	**360**	**1 N_2**	**1 h**	**3 wt%**	**E - S/G/Ph > P, M, H - S/G/Ph**	**1**	512
formic acid	**softwood kraft lignin (Sigma-Aldrich)**	**water**	**264**	**1 N_2**	**6 h**	**33 wt%**	**H - Cat > P, E, M, H - G**	**4**	432
formic acid	**Alcell lignin**	**acetone/water (8:2 v/v)**	**300**	**100 CO_2 (at OT)**	**3.5 h**	**10 wt%**	**H - S > M, H - G > E, Mal, Eoxo - G**	**1**	513
formic acid	**wheat straw ethanosolv lignin (ECN)**	**acetone/water (8:2 v/v)**	**300**	**100 CO_2 (at OT)**	**3.5 h**	**12 wt%**	**Mooh, Mal, Eoxo, E, H - S/G**	**2**	
HOTf	**walnut dioxasolv lignin (reflux, 24 h)**	**dioxane**	**140**	***n.i.***	**4 h**	**2 wt%**	**P(oxo)2, Mal, Mooh - S/G**	**1**	97
HOTf + ethylene glycol (acetal formation)	**walnut dioxasolv lignin (reflux, 24 h)**	**dioxane**	**140**	***n.i.***	**4 h**	**6 wt%**	**E(acetal) - S/G/Ph > Poh(acetal) - S/G**	**1**	
HOTf	**walnut dioxasolv lignin (reflux, 24 h)**	dioxane	120	*n.i.*	24 h	1 wt%	P(oxo)2, Mal, Mooh - S/G		
HOTf +Ir/PPh_3 (decarbonylation)	**walnut dioxasolv lignin (reflux, 24 h)**	dioxane	120	*n.i.*	24 h	2 wt%	M - S/G/Ph > P(oxo)2, H - S/G/Ph		
HOTf + ethylene glycol (acetal formation)	**pine methansolv lignin (170 °C, 24 h)**	**dioxane**	**140**	***n.i.***	**30 min**	**4.5 wt%**	**E(acetal) - G/Ph > Poh(acetal) - G**	**1**	376
HOTf + ethylene glycol (acetal formation)	**beech ethanosolv lignin (ECN)**	**dioxane**	**140**	***n.i.***	**30 min**	**7.4 wt%**	**E(acetal) - S/G/Ph**	**1**	
HOTf + ethylene glycol (acetal formation)	**walnut methanosolv lignin (170 °C, 24 h)**	**dioxane**	**140**	***n.i.***	**30 min**	**11.3 wt%**	**E(acetal) - S/G/Ph > Poh(acetal) - S/G**	**2**	
HOTf + ethylene glycol (acetal formation)	**walnut methanosolv lignin (170 °C, 24 h)**	**dioxane**	**140**	***n.i.***	**15 min**	**14 wt%**	**E(acetal) - S/G/Ph**	**2**	375
$Bi(OTf)_3$ + ethylene glycol (acetal formation)	**walnut methanosolv lignin (170 °C, 24 h)**	dioxane	140	*n.i.*	15 min	15 wt%	E(acetal) - S/G/Ph		
$Fe(OTf)_3$ + ethylene glycol (acetal formation)	**walnut methanosolv lignin (170 °C, 24 h)**	**dioxane**	**140**	***n.i.***	**15 min**	**19 wt%**	**E(acetal) - S/G/Ph**	**2**	
$Hf(OTf)_3$ + ethylene glycol (acetal formation)	**walnut methanosolv lignin (170 °C, 24 h)**	dioxane	140	*n.i.*	15 min	12 wt%	E(acetal) - S/G/Ph		

Table S10 continued

Catalyst & system specifications	Lignin[a]	Solvent	T (°C)	p (bar) at RT	t (h)	Monomer yield	Monomer structure	MYC	Ref
$Bi(OTf)_3$ + ethylene glycol (acetal formation)	**beech ethanosolv lignin (ECN)**	**dioxane**	**140**	***n.i.***	**15 min**	**2.1 wt%**	**E(acetal) - S/G**	**1**	204
$Bi(OTf)_3$ + ethylene glycol (acetal formation)	**walnut ethanosolv lignin (reflux, 5% water, 0.2 M HCl, 6 h)**	**dioxane**	**140**	***n.i.***	**15 min**	**18.1 wt%**	**E(acetal) - S/G/Ph**	**2**	
$Bi(OTf)_3$ + ethylene glycol (acetal formation)	**beech ethanosolv lignin (reflux, 5% water, 0.2 M HCl, 6 h)**	**dioxane**	**140**	***n.i.***	**15 min**	**17 wt%**	**E(acetal) - S/G**	**2**	
$Bi(OTf)_3$ + ethylene glycol (acetal formation)	**douglas fir ethanosolv lignin (reflux, 5% water, 0.2 M HCl, 6 h)**	**dioxane**	**140**	***n.i.***	**15 min**	**11.3 wt%**	**E(acetal) - G/Ph**	**2**	
$Bi(OTf)_3$ + ethylene glycol (acetal formation)	**walnut butanosolv lignin (reflux, 5% water, 0.2 M HCl, 6 h)**	**dioxane**	**140**	***n.i.***	**15 min**	**10 wt%**	**E(acetal) - S/G/Ph**	**1**	
$Bi(OTf)_3$ + ethylene glycol (acetal formation)	**beech butanosolv lignin (reflux, 5% water, 0.2 M HCl, 6 h)**	**dioxane**	**140**	***n.i.***	**15 min**	**9.8 wt%**	**E(acetal) - S/G**	**1**	
$Bi(OTf)_3$ + ethylene glycol (acetal formation)	**douglas fir butanosolv lignin (reflux, 5% water, 0.2 M HCl, 6 h)**	**dioxane**	**140**	***n.i.***	**15 min**	**8.4 wt%**	**E(acetal) - G/Ph**	**1**	
methanesulfonic acid + ethylene glycol (acetal formation)	walnut butanosolv lignin (reflux, 5% water, 0.2 M HCl, 6 h)	dioxane	140	*n.i.*	3 h	8.2 wt%	E(acetal) - S/G/Ph		
toluenesulfonic acid + ethylene glycol (acetal formation)	walnut butanosolv lignin (reflux, 5% water, 0.2 M HCl, 6 h)	dioxane	140	*n.i.*	3 h	7.4 wt%	E(acetal) - S/G/Ph		
$Bi(OTf)_3$ + ethylene glycol (acetal formation)	walnut butanosolv lignin (reflux, 5% water, 0.2 M HCl, 6 h)	2-methylTHF	140	*n.i.*	15 min	6 wt%	E(acetal) - S/G/Ph		
$Fe(OTf)_3$ + ethylene glycol (acetal formation)	**walnut methanosolv lignin (170 °C, 24 h)**	**dioxane**	**140**	***n.i.***	**15 min**	**11.7 wt%**	**E(acetal) - S/G/Ph > Poh(acetal) - S/G/Ph**	**2**	**205**
$Fe(OTf)_3$ + ethylene glycol (acetal formation)	**walnut methanosolv lignin (90 °C, 5% water, 0.2 M HCl, 6 h)**	**dioxane**	**140**	***n.i.***	**15 min**	**38.2 wt%**	**E(acetal) - S/G/Ph > Poh(acetal), Pene(ketal) - S/G/Ph**	**4**	
$Fe(OTf)_3$ + ethylene glycol (acetal formation)	**pine methanosolv lignin (170 °C, 24 h)**	**dioxane**	**140**	***n.i.***	**15 min**	**11.2 wt%**	**E(acetal) - G > Poh(acetal), Pene(ketal) - G**	**2**	
$Fe(OTf)_3$ + ethylene glycol (acetal formation)	**walnut ethanosolv lignin (reflux, 5% water, 0.2 M HCl, 6 h)**	**dioxane**	**140**	***n.i.***	**15 min**	**20.3 wt%**	**E(acetal) - S/G/Ph > Poh(acetal), Pene(ketal) - S/G/Ph**	**2**	
$Fe(OTf)_3$ + ethylene glycol (acetal formation)	**douglas fir ethanosolv lignin (reflux, 5% water, 0.2 M HCl, 6 h)**	**dioxane**	**140**	***n.i.***	**15 min**	**17.5 wt%**	**E(acetal) - G/Ph > Poh(acetal), Pene(ketal) - G/Ph**	**2**	
$Fe(OTf)_3$ + ethylene glycol (acetal formation)	**walnut butanosolv lignin (reflux, 5% water, 0.2 M HCl, 6 h)**	**dioxane**	**140**	***n.i.***	**15 min**	**26.1 wt%**	**E(acetal) - S/G/Ph > Poh(acetal), Pene(ketal) - S/G/Ph**	**3**	
$Fe(OTf)_3$ + ethylene glycol (acetal formation)	**beech butanosolv lignin (reflux, 5% water, 0.2 M HCl, 6 h)**	**dioxane**	**140**	***n.i.***	**15 min**	**20.8 wt%**	**E(acetal) - S/G > Poh(acetal), Pene(ketal) - S/G**	**3**	
$Fe(OTf)_3$ + ethylene glycol (acetal formation)	**douglas fir butanosolv lignin (reflux, 5% water, 0.2 M HCl, 6 h)**	**dioxane**	**140**	***n.i.***	**15 min**	**12.5 wt%**	**E(acetal) - G/Ph > Poh(acetal), Pene(ketal) - G/Ph**	**2**	
$Fe(OTf)_3$ + ethylene glycol (acetal formation)	**walnut dioxasolv lignin (reflux, 24 h)**	**dioxane**	**140**	***n.i.***	**15 min**	**18.5 wt%**	**E(acetal) - S/G/Ph > Poh(acetal) - S/G/Ph**	**2**	
$Fe(OTf)_3$ + ethylene glycol (acetal formation)	**pine dioxasolv lignin (reflux, 10% water, 0.2 M HCl, 1 h)**	**dioxane**	**140**	***n.i.***	**15 min**	**17.3 wt%**	**E(acetal) - G/Ph > Poh(acetal), Pene(ketal) - G/Ph**	**2**	

Table S10 continued

Catalyst & system specifications	Lignin[a]	Solvent	T (°C)	p (bar) at RT	t (h)	Monomer yield	Monomer structure	MYC	Ref
$Fe(Otf)_3$ + ethylene glycol (acetal formation)	**oak dioxasolv lignin (reflux, 10% water, 0.2 M HCl, 1 h)**	**dioxane**	**140**	***n.i.***	**15 min**	**14.1 wt%**	**E(acetal) - S/G > Poh(acetal), Pene(ketal) - S/G**		**205**
$Fe(OTf)_3$ + ethylene glycol (acetal formation)	**barley straw dioxasolv lignin (reflux, 10% water, 0.2 M HCl, 1 h)**	**dioxane**	**140**	***n.i.***	**15 min**	**15.6 wt%**	**E(acetal) - S/G/Ph > Poh(acetal), Pene(ketal) - S/G/Ph**	**2**	
$Fe(OTf)_3$ + ethylene glycol (acetal formation)	**birch dioxasolv lignin (reflux, 10% water, 0.2 M HCl, 1 h)**	**dioxane**	**140**	***n.i.***	**15 min**	**20.2 wt%**	**E(acetal) - S/G > Poh(acetal) - S/G**	**2**	
$Fe(OTf)_3$ + ethylene glycol (acetal formation)	**oak CIMV lignin (formic acid/acetic acid/water pulping, 104 °C)**	**dioxane**	**140**	***n.i.***	**15 min**	**20.2 wt%**	**E(acetal) - S/G > Poh(acetal), Pene(ketal) - S/G**	**2**	
$Fe(OTf)_3$ + ethylene glycol (acetal formation)	**beech ethanosolv lignin (ECN)**	**dioxane**	**140**	***n.i.***	**15 min**	**6 wt%**	**E(acetal) - S/G > Poh(acetal), Pene(ketal) - S/G**	**1**	
$Fe(OTf)_3$ + ethylene glycol (acetal formation)	**poplar ethanosolv lignin (ECN)**	**dioxane**	**140**	***n.i.***	**15 min**	**1 wt%**	**E(acetal) - S/G > Poh(acetal), Pene(ketal) - S/G**	**1**	
$Fe(OTf)_3$ + ethylene glycol (acetal formation)	**spruce ethanosolv lignin (ECN)**	**dioxane**	**140**	***n.i.***	**15 min**	**2.2 wt%**	**E(acetal) - G > Pene(ketal) - G**	**1**	
$Fe(OTf)_3$ + ethylene glycol (acetal formation)	**Alcell lignin**	**dioxane**	**140**	***n.i.***	**15 min**	**4.1 wt%**	**E(acetal) - S/G**	**1**	
$Fe(OTf)_3$ + ethylene glycol (acetal formation)	**Indulin AT**	**dioxane**	**140**	***n.i.***	**15 min**	**0.5 wt%**	**E(acetal) - G > Pene(ketal) - G**	**1**	
$Fe(OTf)_3$ + ethylene glycol (acetal formation)	**softwood kraft lignin**	**dioxane**	**140**	***n.i.***	**15 min**	**2.6 wt%**	**E(acetal) - G**	**1**	
$Fe(OTf)_3$ + ethylene glycol (acetal formation)	**softwood kraft lignin (sigma-aldrich)**	**dioxane**	**140**	***n.i.***	**15 min**	**0.5 wt%**	**E(acetal) - G**	**1**	
$Fe(OTf)_3$ + ethylene glycol (acetal formation)	**Protobind 1000**	**dioxane**	**140**	***n.i.***	**15 min**	**2.4 wt%**	**E(acetal) - S/G/Ph**	**1**	
$Fe(OTf)_3$ + ethylene glycol (acetal formation)	**lignosulfonate (Na, sigma-aldrich)**	**dioxane**	**140**	***n.i.***	**15 min**	**0.5 wt%**	**E(acetal) - S/G**	**1**	
$Rh(cod)Cl_2$ + dppp (decarbonylation)[b]	poplar dioxasolv lignin	dioxane/water (9:1)	175	1 Ar	2 h	2.6 wt%	Pene - S/G > M, E - S/G		377
HOTf + $Rh(cod)Cl_2$ + dppp (decarbonylation)	poplar dioxasolv lignin	dioxane/water (9:1)	175	1 Ar	2 h	10.6 wt%	Pene- S/G > M - S/G > Poxo - S/G > E - S/G		
$M(OTf)_3$ (M:Yb, Sc, Ln, Ga) + $Rh(cod)Cl_2$ + dppp (decarbonylation)	poplar dioxasolv lignin	dioxane/water (9:1)	175	1 Ar	2 h	9.4-11.4 wt%	Pene, M, Poxo, E - S/G		
$Ga(OTf)_3$ + $Rh(cod)Cl_2$ + dppp (decarbonylation)	poplar dioxasolv lignin	dioxane/water (9:1)	175	1 Ar	2 h	9.4 wt%	M - S/G > Poxo - S/G > Pene, E - S/G		
$Sc(OTf)_3$ + $Rh(cod)Cl_2$ + dppp (decarbonylation)	poplar dioxasolv lignin	dioxane/water (9:1)	175	1 Ar	2 h	9.5 wt%	M, Pene, Poxo - S/G > E - S/G		
$Yb(OTf)_3$ + $Rh(cod)Cl_2$ + dppp (decarbonylation)	**poplar dioxasolv lignin**	**dioxane/water (9:1)**	**175**	**1 Ar**	**4 h**	**12.4 wt%**	**Pene - S/G > M, Poxo, E - S/G**	**2**	
$Sc(OTf)_3$ + $Rh(cod)Cl_2$ + dppp (decarbonylation)	**brewers spent grain dioxasolv lignin**	**dioxane/water (9:1)**	**175**	**1 Ar**	**2 h**	**5.2 wt%**	**M - S/G > Pene - S/G**	**1**	
$Sc(OTf)_3$ + $Rh(cod)Cl_2$ + dppp (decarbonylation)	**pine dioxasolv lignin**	**dioxane/water (9:1)**	**175**	**1 Ar**	**2 h**	**6.8 wt%**	**M - G > Pene - G**	**1**	

[a] For commercial lignin substrates, the commercial name (Indulin AT, Alcell lignin, *etc.*) or provider (Sigma-Aldrich, TCI, SEKAB, *etc.*) is usually indicated. [b] cod = 1,5-cyclooctadiene; dppp = bis-1,3-(diphenylphosphino) propane.

Table S11 Solvolytic depolymerisation							*In support of Figure 20 in the main article*		
Lignin[a]	**Solvent**	**T (°C)**	**p (bar) at RT**	**Reaction time**	**Monomer yield**	**Monomer structure**		**MYC**	**Ref**
softwood kraft lignin (Indulin AT)	**acetone**	**430**	***n.i.***	**30 min**	**3 wt%**	**M, DM - Ph; M, H - G**		**1**	526
softwood kraft lignin (Indulin AT)	butanol	400	*n.i.*	50 min	2 wt%	M, DM - Ph; M, H - G			
softwood kraft lignin (Sigma-Aldrich)	**ethanol/water (1:1 wt/wt)**	**300**	***n.i.***	**30 min**	**7 wt%**	**Poxo, Pene, Eooh, Eoxo, E, Mal, M, H - G/Ph**		**1**	519
softwood kraft lignin (Sigma-Aldrich)	ethanol	300	*n.i.*	30 min	7 wt%	Poxo, Pene, Eooh, Eoxo, E, Mal, M, H - G/Ph			
softwood kraft lignin (Sigma-Aldrich)	water	300	*n.i.*	30 min	3 wt%	Poxo, Pene, Eooh, Eoxo, E, Mal, M, H - G/Ph			
softwood kraft lignin (Sigma-Aldrich)	ethanol	350	*n.i.*	30 min	4 wt%	Poxo, Pene, Eooh, Eoxo, E, Mal, M, H - G/Ph			
softwood kraft lignin (Sigma-Aldrich)	water	350	*n.i.*	30 min	4 wt%	H - Cat; Poxo, Pene, Eooh, Eoxo, E, Mal, M, H - G/Ph			
Alcell lignin	**acetone/water (8:2 v/v)**	**300**	**100 CO_2 (at OT)**	**3.5 h**	**7 wt%**	**E, Eoxo, M, Mal, H - S/G**		**1**	513
softwood kraft lignin (Tokyo Kasei Kogyo Co. Ltd., Japan)	**water**	**350**	**1 Ar**	**30 min**	**37 wt%**	**M, H - Cat, Ph**		**4**	521
softwood kraft lignin (Tokyo Kasei Kogyo Co. Ltd., Japan)	water	400	1 Ar	15 min	33 wt%	M, H - Cat, Ph			
softwood kraft lignin (Sigma-Aldrich)	**water**	**280-380**	***n.i.***	**0**	**11 wt%**	**Poxo, Eoxo, E, Mal, M, H - G/Ph; M, H - Cat**		**2**	522
softwood kraft lignin (Sigma-Aldrich)	**water**	**300-450**	***n.i.***	**2-10 s**	**10 wt%**	**M, H - G; Cat, Ph**		**1**	520
bamboo HWP-AE lignin	**water**	**250**	**10 N_2**	**1.5 h**	**3.2 C%**	**Eoxo, E, M, H - S/G/Ph**		**1**	499
softwood kraft lignin (Sigma-Aldrich)	**water**	**264**	**1 N_2**	**6 h**	**22 wt%**	**P, E, M, H - G; H - Cat/Ph**		**3**	432
Protobind 1000	**ethanol**	**300**	**10 N_2**	**4 h**	**5 wt%**	**E, M, H - S/G/Ph**		**1**	416
Protobind 1000	methanol	300	10 N_2	4 h	4 wt%	E, M, H - S/G/Ph			
softwood kraft lignin (Sigma-Aldrich)	water	260	10 H_2	2 h	3 wt%	Poxo, Eoxo, Mal, H - G/Ph			506
softwood kraft lignin (Sigma-Aldrich)	methanol, ethanol	260	10 H_2	2 h	7 wt%	Poxo, Eoxo, Mal, H - G/Ph			
softwood kraft lignin (Sigma-Aldrich)	octane	260	10 H_2	2 h	5 wt%	Poxo, Eoxo, Mal, H - G/Ph			
softwood kraft lignin (Sigma-Aldrich)	**butanol**	**260**	**10 H_2**	**2 h**	**11 wt%**	**Poxo, Eoxo, Mal, H - G/Ph**		**2**	
corn stover DAP-EH lignin	**water**	**275**	***n.i.***	**1 h**	**5 wt%**	**Eoxo, Mal, H - S/G/Ph**		**1**	501
corn stover DMR-EH lignin	water	275	*n.i.*	1 h	4 wt%	Eoxo, Mal, H - S/G/Ph			
corn stover DAP-EH lignin	3-methyl-3-pentanol	275	*n.i.*	1 h	1 wt%	Pene, V - S/G/Ph			
corn stover DMR-EH lignin	**3-methyl-3-pentanol**	**275**	***n.i.***	**1 h**	**4 wt%**	**Pene, V - S/G/Ph**		**1**	
olive tree pruning ethanosolv lignin	**water**	**300**	**90 (at OT)**	**40 min**	**3 wt%**	**H - S/G**		**1**	495
Protobind 1000	**water**	**400**	**1 air**	**4 h**	**8 wt%**	**phenols > catehols**		**1**	508
Protobind 1000	ethanol	400	1 air	4 h	1 wt%	phenols, guaiacols			

Table S11 continued

Lignin[a]	Solvent	T (°C)	p (bar) at RT	Reaction time	Monomer yield	Monomer structure	MYC	Ref
olive tree pruning acetosolv lignin	**acetone, methanol, ethanol,**	**300**	**2 N_2**	**40 min**	**2 wt%**	**H - S/Goh/G/Cat; Poxo, Eoxo - S/G**	**1**	527
olive tree pruning formasolv lignin	**acetone, methanol, ethanol,**	**300**	**2 N_2**	**40 min**	**1 wt%**	**H - S/Goh/G/Cat; Poxo, Eoxo - S/G**	**1**	
olive tree pruning acetosolv/formasolv lignin	**acetone, methanol, ethanol,**	**300**	**2 N_2**	**40 min**	**1 wt%**	**H - S/Goh/G/Cat; Poxo, Eoxo - S/G**	**1**	
Protobind 1000	methanol, ethanol, 2-propanol	350	30 H_2	40 min	9-11 wt%	P, Pene, E, Eoxo, M, H - S/G/Ph; H - Cat		383
Protobind 1000	**2-propanol**	**350**	**30 H_2**	**40 min**	**11 wt%**	**P, Pene, E, Eoxo, M, H - S/G/Ph; H - Cat**	**2**	
softwood kraft lignin (Sigma-Aldrich)	**methanol**	**260**	**40 H_2**	**5 h**	**6 wt%**	**phenols & guaiacols**	**1**	386
pine ethanosolv lignin	**methanol**	**260**	**40 H_2**	**4 h**	**2 wt%**	**phenols & guaiacols**	**1**	387
softwood kraft lignin (TCI)	**methanol/water (5:1 v/v)**	**250**	**7 N_2**	**30 min**	**10 wt%**	**Mal, MooMe, Eoxo, Eooh, Poxo, Pene, Pene(al) - G**	**1**	509
switchgrass ILP-EH lignin (58 wt% KL)	**isopropanol**	**300**	**20 N_2**	**3 h**	**10 wt%**	**Pene, Poxo, P, E, M, H - S/G/Ph**	**1**	309
corncob residue organosolv lignin (THF/water pulping)	**THF**	**300**	**20 N_2**	**8 h**	**27 wt% (24 wt%)[b]**	**E, H - S/G/Ph**	**3**	524
bamboo ethanosolv lignin (*Phyllostachys heterocycla cv. Pubescens*)	**ethanol**	**300**	**20 N_2**	**2 h**	**16 wt% (7 wt%)[c]**	**E, H - S/G/Ph**	**2**	525
cornstover organosolv lignin	**tetralin**	**400**	**1 N_2**	**15 min**	**11 wt%**	**P, E, V, M, H - S/G/Ph**	**2**	528
cornstover organosolv lignin	isopropanol	400	1 N_2	15 min	11 wt%	P, E, V, M, H - S/G/Ph		
cornstover organosolv lignin	naphtalene	400	1 N_2	50 min	8 wt%	P, E, V, M, H - S/G/Ph		
spruce kraft lignin (Sigma-Aldrich)	**dihydroanthracene/dioxane (1:1 wt/wt)**	**303**	**0.004[d]**	**2 h**	**3 wt%**	**P, Pene, E, Eoxo, M, Mal, H - S/G/Ph**	**1**	529
sugarcane bagasse hydrolysis-solvent extracted lignin (Sigma-Aldrich)	**dihydroanthracene/dioxane (1:1 wt/wt)**	**303**	**0.004[d]**	**2 h**	**1 wt%**	**P, Pene, E, Eoxo, M, Mal, H - S/G/Ph**	**1**	
softwood kraft black liquor (Cellardennes, Belgium)	**dihydroanthracene/dioxane (1:1 wt/wt)**	**303**	**0.004[d]**	**2 h**	**2 wt%**	**E, M, H - S/G/Ph**	**1**	
spruce MWL	dihydroanthracene/dioxane (1:1 wt/wt)	303	0.004[d]	2 h	5 wt%	P, Pene, Pene(oh), E, Eoxo, M, Mal, H - S/G/Ph		
Alcell lignin	dihydroanthracene/dioxane (1:1 wt/wt)	303	0.004[d]	2 h	2 w%	P, Pene, Pene(oh), E, Eoxo, M, Mal, H - S/G/Ph		
spruce MWL	**dihydroanthracene/dioxane (1:1 wt/wt)**	**352**	**0.004[d]**	**4 h**	**11 wt%**	**P, Pene, Pene(oh), E, Eoxo, M, Mal, H - S/G/Ph**	**2**	
Alcell lignin	**dihydroanthracene/dioxane (1:1 wt/wt)**	**352**	**0.004[d]**	**4 h**	**7 wt%**	**P, Pene, Pene(oh), E, Eoxo, M, Mal, H - S/G/Ph**	**1**	

[a] For commercial lignin substrates, the commercial name (Indulin AT, Alcell lignin, *etc.*) or provider (Sigma-Aldrich, TCI, SEKAB, *etc.*) is usually indicated. [b] Monomer yield based on lignin in corncob residue. [c] Monomer yield based on native lignin in bamboo. [d] After filling the reactor (sealed pyrex tube) with lignin and solvent, the air was removed by three freeze-pump-helium-thaw-cycles, and the reactor was placed in liquid nitrogen, evacuated (to 400 Pa) and sealed.

Table S12 Fast pyrolysis							*In support of Figure 20 in the main article*	
Lignin[a]	**Set-up**	**T (°C)**	**Residence time**	**Gas**	**Monomer yield**	**Monomer structure**	**MYC**	**Ref**
pine dioxasolv lignin	**micropyrolyser (batch; 0.5 mg; sandwich method)[b]**	**500**	**4 s**	**He**	**6 wt%**	**Pene, E, Eoxo, V, M, Mal, H - G**	**1**	542
pine dioxasolv lignin	micropyrolyser (batch; 0.5 mg)	500	4 s	He	4 wt%	Pene, E, Eoxo, V, M, Mal, H - G		
cedar dioxasolv lignin	**micropyrolyser (batch; 0.5 mg; sandwich method)**	**500**	**4 s**	**He**	**8 wt%**	**Pene, E, Eoxo, V, M, Mal, H - G**	**1**	
cedar dioxasolv lignin	micropyrolyser (batch; 0.5 mg)	500	4 s	He	7 wt%	Pene, E, Eoxo, V, M, Mal, H - G		
cypress dioxasolv lignin	**micropyrolyser (batch; 0.5 mg; sandwich method)**	**500**	**4 s**	**He**	**7 wt%**	**Pene, E, Eoxo, V, M, Mal, H - G**	**1**	
cypress dioxasolv lignin	micropyrolyser (batch; 0.5 mg)	500	4 s	He	6 wt%	Pene, E, Eoxo, V, M, Mal, H - G		
douglas fir kraft lignin	**micropyrolyser (batch; 0.2 g)**	**550-650**	**120 s**	**He**	**3 wt%**	**E, M, H - G/Ph**	**1**	544
Alcell lignin	micropyrolyser (batch; 1 mg)	400-800	15 s	*n.i.*	12-17 wt%	Pene, Poxo, E, Eoxo, V, M, Mal, H - S/Goh/G/Cat/Ph		533
Alcell lignin	**micropyrolyser (batch; 1 mg)**	**600**	**15 s**	***n.i.***	**17 wt%**	**Pene, Poxo, E, Eoxo, V, M, Mal, H - S/Goh/G/Cat/Ph**	**2**	
Protobind 1000	micropyrolyser (batch; 1 mg)	400-800	15 s	*n.i.*	11-16 wt%	Pene, Poxo, Pene(ooh), E, Eoxo, V, M, Mal, H - S/Goh/G/Cat/Ph		
Protobind 1000	**micropyrolyser (batch; 1 mg)**	**600**	**15 s**	***n.i.***	**16 wt%**	**Pene, Poxo, Pene(ooh), E, Eoxo, V, M, Mal, H - S/Goh/G/Cat/Ph**	**2**	
cornstover organosolv lignin	**micropyrolyser (batch; 0.5 mg)**	**500**	***n.i.***	**He**	**18 wt%**	**Pene, Pene(ol), E, Eoxo, V, M, Mal, H - S/G/Ph**	**2**	115
maple HWP-EH lignin (81% KL)	**micropyrolyser (batch)**	**600**	**240 s**	**He**	**8 wt% (11 C%)**	**Pene, V, M, H - S/G**	**1**	324
softwood kraft lignin (TCI)	**micropyrolyser (batch; 1.5 mg)**	**650**	**20 s**	**He**	**27 wt% (29 C%)[c]**	**Eoxo, V, M, Mal, H - G/Ph; H - Cat**	**3**	535
Protobind 1000 / Granit lignin	**micropyrolyser (batch; 1 mg)**	**650**	**20 s**	**He**	**5 wt%**	**Pene, E, V, M, H - S/G/Ph**	**1**	539
organosolv lignin (Lignol Innovations Inc.)	**micropyrolyser (batch; 1 mg)**	**650**	**20 s**	**He**	**4 wt%**	**Pene, E, V, M, H - S/G/Ph**	**1**	
sugarcane bagasse lignin (from pretreatment for bio-ethanol production)	**micropyrolyser (batch; 1 mg)**	**650**	**20 s**	**He**	**4 wt%**	**Pene, E, V, M, H - S/G/Ph**	**1**	
softwood DAP-EH lignin (Etek lignin; Sekab Sweden, 50 wt% lignin)	**micropyrolyser (batch; 1 mg)**	**650**	**20 s**	**He**	**2 wt%**	**Pene, E, V, M, H - S/G/Ph**	**1**	
aspen butanosolv lignin	**micropyrolyser (batch; 0.5 mg)**	**600**	**8 s**	**He**	**10 wt%**	**Pene, Eoxo, V, M, Mal, H - S/G/Ph**	**1**	541
prairie cordgrass organosolv lignin (MIBK/EthOH/water)	**micropyrolyser (batch; 0.5 mg)**	**600**	**8 s**	**He**	**6 wt%**	**V, M, H - S/G/Ph**	**1**	540
softwood kraft lignin (Sigma-Aldrich)	**micropyrolyser (batch; 1 mg)**	**700**	**60 s**	**He**	**30 wt%**	**Pene, E, V, M, H - G/Ph**	**3**	532
beech MWL	**micropyrolyser (batch; 0.5 mg)**	**600**	**10 s**	**He**	**18 wt%**	**Pene, Pene(ol), Pene(al), Poxo, E, Eoxo, V, M, Mal, H - S/G; M, H - Goh/Cat**	**2**	381
spruce MWL	**micropyrolyser (batch; 0.5 mg)**	**600**	**10 s**	**He**	**16 wt%**	**Pene, Pene(ol), Pene(al), E, Eoxo, V, M, Mal, H - G/Ph; M, H - Goh/Cat**	**2**	
bamboo MWL	**micropyrolyser (batch; 0.5 mg)**	**600**	**10 s**	**He**	**13 wt%**	**Pene, Pene(ol), Pene(al), Poxo, E, Eoxo, V, M, Mal, H - S/G/Ph; M, H - Goh/Cat**	**2**	

Table S12 continued

Lignin[a]	Set-up	T (°C)	Residence time	Gas	Monomer yield	Monomer structure	MYC	Ref
spruce MWL	**micropyrolyser (batch)**	**450**	**10 s**	**He**	**20 wt%**	**Pene, Pene(ol), Pene(al), Poxo, E, Eoxo, V, M, Mal, H - G**	**2**	408
spruce Organocell lignin (methanol/water/NaOH/anthraquinone pulping)	**micropyrolyser (batch)**	**450**	**10 s**	**He**	**13 wt%**	**Pene, Pene(ol), Pene(al), Poxo, E, Eoxo, V, M, Mal, H - G**	**2**	
spruce Organocell lignin	**semi-continuous reactor (36 g)**	**400**	**6 h**	**H_2 (140 bar)**	**6 wt%**	**P, E, DM, M, H - G/Ph**	**1**	
bamboo EMAL	**tubular reactor (batch; 0.25 g)**	**600**	**3-4 min**	**N_2**	**11 wt%**	**Pene, M, Mal, Mooh, H - S/G/Ph**	**2**	543
rice husk pyrolytic lignin (precipitated by water additions)	**tubular reactor (batch; 0.5 g)**	**600**	***n.i.***	**N_2**	**37 wt% (40 C%)[c]**	***n.i.***	**4**	545
rice husk pyrolytic lignin (glycerol assisted destillation followed by precipitation through water addition)	**tubular reactor (batch; 0.5 g)**	**600**	***n.i.***	**N_2**	**34 wt% (37 C%)[c]**	**E, M, H - Ph**	**4**	
softwood kraft lignin (alkaline lignin, Sigma-Aldrich)	**tubular reactor (batch; 0.5 g)**	**600**	***n.i.***	**N_2**	**6 wt% (6 C%)[c]**	***n.i.***	**1**	
softwood kraft lignin (Sigma-Aldrich)	**tubular reactor (batch; 0.5 g)**	**600**	***n.i.***	**N_2**	**7 wt% (7 C%)[c]**	***n.i.***	**1**	
cornstover acetosolv lignin (mixed with $Ca(OH)_2$)	fluidised bed reactor (continoous)	450-600	*n.i.*	N_2	4-7 wt%	Pene, E, Eoxo, V, M, Mal, H - S/G/Ph		549
cornstover acetosolv lignin (mixed with $Ca(OH)_2$)	**fluidised bed reactor (continoous)**	**450**	***n.i.***	**N_2**	**7 wt%**	**Pene, E, Eoxo, V, M, Mal, H - S/G/Ph**	**1**	
cornstover acetosolv lignin (mixed with $Ca(OH)_2$)	**micropyrolyser (batch; 0.5 mg)**	**500**	***n.i.***	**He**	**12 wt%**	***n.i.***	**2**	
Alcell lignin (pellets, fed together with natural mineral additive)	bubbling fluidised bed, batch (50 g)	400	~ 1 s	Ar	3 wt%	Pene, E, Eoxo, M, Mal, H - S/G/Ph; H - Goh/Cat		547
Protobind 1000 / Granit lignin (pellets, fed together with natural mineral additive)	bubbling fluidised bed, batch (50 g)	400	~ 1 s	Ar	5 wt%	Pene, E, Eoxo, M, Mal, H - S/G/Ph; H - Goh/Cat		
Alcell lignin (pellets, fed together with natural mineral additive)	**bubbling fluidised bed, continuous (100 g/h)**	**400**	**~ 1 s**	**Ar**	**7 wt%**	**Pene, E, Eoxo, M, Mal, H - S/G/Ph; H - Goh/Cat**	**1**	
Protobind 1000 / Granit lignin (pellets, fed together with natural mineral additve)	**bubbling fluidised bed, continuous (100 g/h)**	**400**	**~ 1 s**	**Ar**	**9 wt%**	**Pene, E, Eoxo, M, Mal, H - S/G/Ph; H - Goh/Cat**	**1**	
wheat straw ethanosolv lignin (pellets, fed together with natural mineral additve)	**bubbling fluidised bed, batch (40 g)**	**500**	**1-3 s**	**Ar**	**7-8 wt%**	**Pene, E, Eoxo, V, M, Mal, H - S/G/Ph; H - Goh/Cat**	**1**	548
Protobind 1000 / Granit lignin (pellets, fed together with natural mineral additive)	**bubbling fluidised bed, batch (40 g)**	**500**	**1-3 s**	**Ar**	**11 wt%**	**Pene, E, Eoxo, V, M, Mal, H - S/G/Ph; H - Goh/Cat**	**2**	
Alcell lignin (pellets, fed together with natural mineral additive)	**bubbling fluidised bed, batch (40 g)**	**500**	**1-3 s**	**Ar**	**9 wt%**	**Pene, E, Eoxo, V, M, Mal, H - S/G/Ph; H - Goh/Cat**	**1**	
Alcell lignin (pelletised together with natural mineral additive)	**bubbling fluidised bed, fed-batch (150 g)**	**500**	***n.i.***	***n.i.***	**6 wt% (2 wt%)[d]**	**catechols, APh, syringols, guaiacols, unidentified monomers**	**1**	546
wheat straw formasolv/acetosolv lignin (from CIMV process, Biolignin; pelletised together with natural mineral additive)	bubbling fluidised bed, fed-batch (150 g)	500	*n.i.*	*n.i.*	6 wt% (1 wt%)[d]	catechols, APh, syringols, guaiacols, unidentified monomers		
softwood kraft lignin (pelletised together with natural mineral additive)	**bubbling fluidised bed, fed-batch (150 g)**	**500**	***n.i.***	***n.i.***	**7 wt% (3 wt%)[d]**	**catechols, APh, guaiacols, unidentified monomers**	**1**	

Table S12 continued

Lignin[a]	Set-up	T (°C)	Residence time	Gas	Monomer yield	Monomer structure	MYC	Ref
wheat straw formasolv/acetosolv lignin (from CIMV process, Biolignin; pelletised together with natural mineral additive)	**bubbling fluidised bed, continuous (600 g/h, 1 kg)**	**500**	***n.i.***	***n.i.***	**8 wt%**	***n.i.***	**1**	546
beech ethanosolv lignin (pelletised together with stearic acid and polyvinylpyrrolidon)	**fluidised bed reactor (continuous) (> 30 g)**	**597**	***n.i.***	***n.i.***	**14 wt%**	**M - S/G**	**2**	550
spruce ethanosolv lignin (pelletised together with stearic acid and polyvinylpyrrolidon)	**fluidised bed reactor (continuous) (> 30 g)**	**497**	***n.i.***	***n.i.***	**10 wt%**	**M - G**	**1**	
beech kraft lignin (pelletised together with stearic acid and polyvinylpyrrolidon)	**fluidised bed reactor (continuous) (> 30 g)**	**497**	***n.i.***	***n.i.***	**3 wt%**	***n.i.***	**1**	
spruce kraft lignin (pelletised together with stearic acid and polyvinylpyrrolidon)	**fluidised bed reactor (continuous) (> 30 g)**	**497**	***n.i.***	***n.i.***	**5 wt%**	***n.i.***	**1**	
wheat straw EH lignin (Inbicon; 79 wt% KL)	**pyrolysis centrifuge reactor (200-500 g)**	**550**	**0.8 s**	**N_2**	**4 wt%[e]**	**Pene, Pene(ol), E, Eoxo, V, M, Mal, H - S/G/Ph**	**1**	551
maple HWP-EH lignin	**micropyrolyser (slow pyrolysis)**	**500**	**0 s (HR: 150 °C/min)**	**He**	**4 wt% (4 C%)[c]**	**Pene, E, Eoxo, M, Mal, Mooh, H - S/G; H - Goh**	**1**	534
maple ethanosolv lignin	**micropyrolyser (slow pyrolysis)**	**500**	**0 s (HR: 150 °C/min)**	**He**	**1 wt% (1 C%)[c]**	**Pene, E, Eoxo, M, Mal, Mooh, H - S/G; H - Goh**	**1**	
softwood kraft lignin (FP innovations, Canada; mixed with char)[f]	**microwave pyrolysis oven (300 g; slow pyrolysis)**	**877**	**800 s total time (HR: ~ 75 °C/min)**	**N_2**	**7 wt%**	**Pene, E, V, M, H - G; Pene, E, EM, DM, M, H - Ph; M, H - Cat**	**1**	552
softwood kraft lignin (FP innovations, Canada; mixed with char)	**microwave pyrolysis oven (slow pyrolysis)**	**777**	**800 s total time (HR: 110 °C/min)**	**N_2**	**10 wt%**	**Pene, E, V, M, H - G; Pene, E, EM, DM, M, H - Ph; M, H - Cat**	**1**	553
softwood kraft lignin (FP innovations, Canada; mixed with char)	microwave pyrolysis oven (50 g; slow pyrolysis)	800	10 min (HR: 50 °C/min)	N_2	7 wt%	Pene, E, V, Eoxo, M, Mal, H - G/Ph; M, H - Cat		554
softwood kraft lignin (FP innovations, Canada)	**furnace (batch, 50 g; slow pyrolysis)**	**800**	**10 min (HR: 50 °C/min)**	**N_2**	**7 wt%**	**Pene, E, V, Eoxo, M, Mal, H - G/Ph; M, H - Cat**	**1**	

[a] For commercial lignin substrates, the commercial name (Indulin AT, Alcell lignin, *etc.*) or provider (Sigma-Aldrich, TCI, SEKAB, *etc.*) is usually indicated. [b] Sample sandwiched between two pieces of glass fiber paper. [c] The reported carbon yield (C%) is converted to mass yield (wt%) by suggesting that softwood kraft lignin is composed of coniferyl alcohol units (MW: 180,2 g/mol, #C's: 10) and by taking 4-vinylguaiacol (MW: 150.18 g/mol, #C's: 9) as representative product for fast pyrolysis. The following conversion factor is used: X wt% = Y C% x 0.926 (= 10/9 * 150.18/180.2). [d] Yield of identified compounds (catechols, alkylphenols, syringols and guaiacols) in brackets. [e] The combined yield of quantified compounds, *viz*. syringol, guaiacol and vinylguaiacol, is about 1.5 wt% at 550 °C. As these compounds represent about 41% of all phenolic monomers, a total monomer yield of 4 wt% was suggested. [f] As lignin does not interact well with electromagnetic waves, it was mixed with the char obtained from lignin microwave pyrolysis, which is a strong microwave-to-heat convertor.

Table S13 Catalytic fast pyrolysis (CFP)									*In support of Figure 20 in the main article*
Catalyst & system specifications	Lignin[a]	Set-up[b]	T (°C)	Residence time	Gas	Monomer yield	Monomer structure	MYC	Ref
H-ZSM-5 (*in situ*, mixed)	**maple HWP-EH lignin**	**micropyrolyser (19 C:F)**	**600**	**240 s**	**He**	**10 wt% (23 C%)**	**naphth > tol, Ebenz, xyl > benz**	**1**	324
H-ZSM-5 (*in situ*, mixed)	**maple HWP-AH lignin (H_2SO_4)**	**fluidised bed reactor**	**600**	**0.2 WHSV (OT: 30 min)[c]**	**N_2**	**2 wt% (2 C%)[d]**	**benz > tol, napth, xyl**	**1**	563
H-ZSM-5 (*in situ*, mixed)	softwood kraft lignin (TCI)	micropyrolyser (batch; 1.5 mg lignin; 4 C:F)	650	20 s	He	32 wt% (44 C%)[d]	aromatics > phenols		535
silicalite (*in situ*, mixed)	softwood kraft lignin (TCI)	micropyrolyser (batch; 1.5 mg lignin; 4 C:F)	650	20 s	He	37 wt% (40 C%)[e]	methoxyphenols > phenols > aromatics		
H-USY (*in situ*, mixed)	**softwood kraft lignin (TCI)**	**micropyrolyser (batch; 1.5 mg lignin; 4 C:F)**	**650**	**20 s**	**He**	**34 wt% (47 C%)[d]**	**aromatics (tol, xyl > benz, TMbenz, napth) > phenols (DM, M, H - Ph)**	**4**	
H-ZSM-5 (*in situ*, mixed)	**switchgrass MWL**	**micropyrolyser (batch; 0.5 mg lignin; 20 C:F)**	**600**	***n.i.***	**He**	**5 wt% (7 C%)[d]**	**aromatics (C10+ arom > xyl, tol > benz)**	**1**	558
H-ZSM-5 (*in situ*, mixed)	**Protobind 1000 / Granit lignin**	**micropyrolyser (batch; 1 mg lignin; 1-3 C:F)**	**650**	**20 s**	**He**	**12 wt%**	**aromatics (tol, xyl > benz, Ebenz, napth), phenols (Pene, E, V, M, H - S/G/Ph)**	**2**	539
H-ZSM-5 (*in situ*, mixed)	**organosolv lignin (Lignol Innovations Inc.)**	**micropyrolyser (batch; 1 mg lignin; 1-3 C:F)**	**650**	**20 s**	**He**	**9 wt%**	**aromatics (tol, xyl > benz, Ebenz, napth), phenols (Pene, E, V, M, H - S/G/Ph)**	**1**	
H-ZSM-5 (*in situ*, mixed)	**sugarcane bagasse lignin (from pretreatment for bio-ethanol production)**	**micropyrolyser (batch; 1 mg lignin; 1-3 C:F)**	**650**	**20 s**	**He**	**8 wt%**	**aromatics (tol, xyl > benz, Ebenz, napth), phenols (Pene, E, V, M, H - S/G/Ph)**	**1**	
H-ZSM-5 (*in situ*, mixed)	**softwood DAP-EH lignin (Etek lignin; Sekab Sweden, 50 wt% lignin)**	**micropyrolyser (batch; 1 mg lignin; 1-3 C:F)**	**650**	**20 s**	**He**	**8 wt%**	**aromatics (tol, xyl > benz, Ebenz, napth), phenols (Pene, E, V, M, H - S/G/Ph)**	**1**	
H-ZSM-5	**Protobind 1000 / Granit lignin**	**micropyrolyser (batch; 1 mg lignin; 5 C:F)**	**550**	**18 s**	**He**	**9 wt%**	**aromatics (benz, tol, xyl, napth) > phenols (H - S/G/Ph)**	**1**	560
H-ZSM-5	**softwood DAP-EH lignin (Etek lignin; Sekab Sweden, 50 wt% lignin)**	**micropyrolyser (batch; 1 mg lignin; 5 C:F)**	**550**	**18 s**	**He**	**12 wt%**	**aromatics (benz, tol, xyl, napth) > phenols (H - S/G/Ph)**	**2**	
H-Beta	Protobind 1000 / Granit lignin	micropyrolyser (batch; 1 mg lignin; 5 C:F)	550	18 s	He	6 wt%	aromatics (benz, tol, xyl, napth) > phenols (H - S/G/Ph)		
H-Beta	softwood DAP-EH lignin (Etek lignin; Sekab Sweden, approx 50% lignin)	micropyrolyser (batch; 1 mg lignin; 5 C:F)	550	18 s	He	6 wt%	aromatics (benz, tol, xyl, napth) > phenols (H - S/G/Ph)		
H-ZSM-5 (*in situ*, mixed)	**aspen butanosolv lignin**	**micropyrolyser (batch; 0.5 mg lignin; 3 C:F)**	**600**	**8 s**	**He**	**28 wt%**	**aromatics (tol, xyl > benz, Ebenz, napth) > phenols (Pene, V, Eoxo, M, H - S/G/Ph)**	**3**	541
H-Y (*in situ*, mixed)	**aspen butanosolv lignin**	**micropyrolyser (batch; 0.5 mg lignin; 2 C:F)**	**600**	**8 s**	**He**	**17 wt%**	**phenolics (Pene, E, Eoxo, V, M, Mal, H - S/G/Ph) > aromatics (tol, xyl > benz, Ebenz, napth**	**2**	
H-ZSM-5 (*in situ*, mixed)	prairie cordgrass organosolv lignin (MIBK/EtOH/water pulping)	micropyrolyser (batch; 0.5 mg lignin; 5 C:F)	600	8 s	He	10 wt%	aromatics (tol, xyl > benz, Ebenz, napth) > phenols (V, M, H - S/G/Ph)		540
H-ZSM-5 (*in situ*, mixed)	**prairie cordgrass organosolv lignin (MIBK/EtOH/water pulping)**	**micropyrolyser (batch; 0.5 mg lignin; 5 C:F)**	**650**	**8 s**	**He**	**14 wt%**	**aromatics (tol, xyl > benz, Ebenz, napth) > phenols (V, M, H - S/G/Ph)**	**2**	

Table S13 continued

Catalyst & system specifications	Lignin[a]	Set-up[b]	T (°C)	Residence time	Gas	Monomer yield	Monomer structure	MYC	Ref
H-ZSM-5 (*in situ*, mixed)	**softwood kraft lignin (Sigma-Aldrich)**	**micropyrolyser (batch; 0.4 mg lignin; 20 C:F)**	**650**	**10 s**	**He**	**5 wt%**	**aromatics (tol, benz, xyl, naphtn) > phenols (M, H - Ph)**	**1**	559
$Mo_2N/y-Al_2O_3$ (*ex situ*)	**softwood kraft lignin (Sigma-Aldrich)**	**micropyrolyser (batch; 1 mg lignin; 4 C:F)**	**700**	**60 s**	**He**	**18 wt%**	**benz > tol > xyl, napth, Ebenz**	**2**	532
H-Y (*ex situ*, 2 separate ovens)	corn stover acetosolv lignin	micropyrolyser (batch; 0.5 mg lignin; 20 C:F)	500/600[f]		He	4 wt% (6 C%)[d]	tol, xyl, benz, napth		562
H-ZSM-5 (*ex situ*, 2 separate ovens)	**corn stover acetosolv lignin**	**micropyrolyser (batch; 0.5 mg lignin; 20 C:F)**	**500/600[f]**		**He**	**8 wt% (10 C%)[d]**	**tol, xyl, benz, napth, ind**	**1**	
ZSM-5, H-ZSM-5, Beta, MCM-41, SBA15 (*ex situ*)	rice husk pyrolytic lignin (precipitated by water additions)	tubular reactor (batch; 0.5 g lignin; 1 C:F)	600		N_2	9-28 wt% (12-39 C%)[d]	aromatics, polycyclic aromatics, phenols		545
ZSM-5 (*ex situ*)	**rice husk pyrolytic lignin (precipitated by water additions)**	**tubular reactor (batch; 0.5 g lignin; 1 C:F)**	**600**		**N_2**	**28 wt% (39 C%)[d]**	**aromatics (tol, napth > benz, Ebenz) > phenols (E, M, H - Ph)**	**3**	
ZSM-5, H-ZSM-5, Beta, MCM-41, SBA-15 (*ex situ*)	rice husk pyrolytic lignin (glycerol assisted destillation followed by precipitation through water addition)	tubular reactor (batch; 0.5 g lignin; 1 C:F)	600		N_2	9-28 wt% (12-38 C%)[d]	aromatics, polycyclic aromatics, phenols		
ZSM-5 (*ex situ*)	**rice husk pyrolytic lignin (glycerol assisted destillation followed by precipitation through water addition)**	**tubular reactor (batch; 0.5 g lignin; 1 C:F)**	**600**		**N_2**	**28 wt% (38 C%)[d]**	**aromatics (tol, napth > benz, Ebenz) > phenols (E, M, H - Ph)**	**3**	
H-ZSM-5 (*ex situ*, separate configurations)	**wheat straw EH lignin (Inbicon, Denmark, 56 wt% KL)**	**pyrolysis centrifuge reactor (25-45 g; 1.1-1.8 g/min for 25 min) / catalytic fixed-bed reactor (30 g catalyst)**	**500/600[f]**	**1.8 s (OT: 25 min)[c]**	**N_2**	**4 wt%**	**benz, tol > xyl, naphth, Ebenz**	**1**	564

[a] For commercial lignin substrates, the commercial name (Indulin AT, Alcell lignin, *etc.*) or provider (Sigma-Aldrich, TCI, SEKAB, *etc.*) is usually indicated. [b] C:F is the catalyst-to-feedstock ratio. [c] OT = operation time. [d] The reported carbon yield (C%) is converted to mass yield (wt%) by suggesting that softwood kraft lignin is composed of coniferyl alcohol units (MW: 180,2 g/mol, #C's: 10) and by taking toluene (MW: 92.14 g/mol, #C's: 7) as representative product for CFP. The following conversion factor is used: X wt% = Y C% x 0.73 (= 10/7 * 92.14/180.2). [e] Since CFP with silicalite yields similar products as noncatalysed fast pyrolysis, a conversion factor of 0.926 was used to convert the monomer yield in C% to wt% (see explanation in footnote c of Table S12). [f] Pyrolysis temperature / Catalytic upgrading temperature.

Part C. References

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