# Supporting Information for

Efficient hydrogenolysis of lignocellulose into phenolic monomers over a

CuO/m-ZrO<sub>2</sub> catalyst

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### **1** Experimental section

### **1.1 Materials**

All reagents and solvents were purchased from Accela, Adamas, Innochem, Psaitong and Aladdin. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. In addition, the commercial cellulase (Cellic@ CTec2, 100 FPU/mL) and hemicellulase (shearzyme 500 L, 100,000 IU/mL) were kindly provided from Novozymes (Beijing, China). All commercially available chemical reagents were used without further unification unless especially noted. Larch (6 years old), Poplar (5 years old), Beech (5 years old) and Pinus (5 years old) were used as raw materials in this work, which were extracted, crushed and screened into powders in size of 40 ~ 60 meshes ( $0.5 \sim 1.0 \text{ mm}$ ), and dried vacuum at 50 °C for 72 h before used. Lignin model was synthesized according literatures.<sup>1</sup> All commercially available compounds were used as received, unless otherwise noted.

# 1.2 General characterizations

The Brunauer-Emmett-Teller (BET) surface area computed by multipoint BET analysis of  $N_2$  adsorption constant temperature line and  $N_2$  adsorption–desorption constant temperature line was performed using a Kubo-X1000 equipment (Beijing Builder Co. Ltd., China) by liquid  $N_2$  (-196 °C). Samples were allowed to degas under vacuum prior to measurement for 5 h at 300 °C.

X-ray photoelectron spectra (XPS) were obtained using a scanning X-ray microprobe (PHI 5000 Verasa, ULAC-PHI, Inc.) with Al Ka emission and a 284.80 eV C1s peak used as an internal standard. After the catalyst samples were dissolved in hydrogen fluoride (HF) solution, the Cu and Zr contents were measured by inductively coupled plasma optical emission spectrometer (ICP-AES) using Thermos IRIS Intrepid II XSP emission spectroscopy.

Transmission electron microscope (TEM) was performed by a JEM-2100F FETEM fitted with energy dispersive X-ray spectrometer (EDS) for analysis at 100 kV, and the high-angle annular dark-field scanning TEM (HAADF-STEM). EDS elemental mapping was carried out at 200 kV.

The NH<sub>3</sub>-TPD was tested on Micromeritics AutoChem II 2920 apparatus to

determine the number of acid sites. Typically, about 100 mg of catalyst was restored in the H<sub>2</sub> stream at 500 °C for 60 min, and before being cooled down to room temperature in the He stream. NH<sub>3</sub>-TPD was allowed to increase in temperature from 50 °C to 800 °C at 10 °C min<sup>-1</sup> for 30 min. CO<sub>2</sub>-TPD assays were made on Micromeritics Autochem 2920 apparatus. A sample was restored at 300 °C then purged for 1 h in a 10% H<sub>2</sub>/Ar stream, and chilled to 50 °C in a He flow. After being exposed to a 5% CO<sub>2</sub>/He flows (1 h, 50 °C) and purged with He (1 h, 50 °C), the sample was treated to 500 °C at 5 °C min<sup>-1</sup> at a 30 cm/min He streams, and the dehydrogenated gas was examined by TCD.

The Nuclear Magnetic Resonance Spectroscopy (NMR) spectra were acquired on a Bruker Ascend-400 MHz spectrometer instrument (Bruker, Germany). Lignin, oily products and synthetic lignin polymer were dissolved in DMSO- $d_6$ , whereas lignin models were dissolved in CDCl<sub>3</sub>. As for 2D HSQC NMR experiment, the solvent peak (DMSO- $d_6$ ) at  $\delta_C/\delta_H$  39.5/2.49 was used as an internal reference. The standard Bruker implementations of 2D HSQC NMR experiments were used for structural characterization and the authentication were assigned according to previously reported papers.<sup>2-5</sup>

X-ray diffraction (XRD) analysis was carried out using a Shimadzu Lab XRD-6100 diffractometer with a Cu K $\alpha$  radiation source operated at 15 mA and 40 kV. XRD patterns were collected in the 2 $\theta$  range of 10° to 90° at a scan speed of 10°/min with a step of 0.02°.

GPC analyses were performed on a Water System (Sunnyvale, CA) equipped with an isocratic pump (Waters 1515), an automatic injector (Waters 717), and a Dual Absorbance UV detector (Waters 2487) with an Agilent PLgel 3  $\mu$ m 100 Å 300 × 7.5 mm column. THF was used as the mobile phase with a column flow rate and temperature of 1.0 mL/min and 30 °C, respectively. GPC samples were prepared by dissolving 2 mg of lignin in 1 mL of THF and filtered with a 0.45  $\mu$ m PTFE filter prior to injection. The filtered solution (20.0  $\mu$ L) was injected into the GPC system and detected using an UV detector set at 280 nm.<sup>6</sup> Seven GPC polystyrene standards (124 ~ 26520 g/mol) purchased from Agilent (Agilent Technologies, Inc., Santa Clara, CA) were used for calibration.<sup>7</sup> Gas chromatography (GC) and Gas chromatography-mass spectrometry (GC-MS) analyses were performed on a Shimadzu Model 2010 plus with a HP-5 column (30 m  $\times$  0.25 mm  $\times$  0.25 m) employing a flame ionization detector (FID) and a Shimadzu GCMS-QP2010SE with a HP-5MS (30 m  $\times$  0.25 mm  $\times$  0.25 mm) column, respectively. Injecting temperature was 250 °C column temperature procedure of 50 °C in 3 min, and 8 °C/min to 280 °C. The injection temperature of FID was 200 °C. The characterization and quantification lignin monomers within oil-based products has been estimated by reference to real samples obtained from commercial sourcing or independent synthesis.

### 2 Catalysts preparation and characterization

### 2.1 Synthesis of m-ZrO<sub>2</sub>

The m-ZrO<sub>2</sub> was synthesized with a modification according to previous report.<sup>8, 9</sup> The ammonium hydroxide solution was gradually introduced into an aqueous solution of zirconium nitrate tetrahydrate (Zr(NO<sub>3</sub>)<sub>4</sub>·5H<sub>2</sub>O) under continuous stirring. The mixture was vigorously agitated for 30 minutes until reaching pH 7, followed by 24 h aging at room temperature. The resulting precipitate was subsequently filtered, washed with deionized water, and dried at 110 °C for 12 h. Finally, the m-ZrO<sub>2</sub> support was obtained through calcination in air at 500 °C for 3 h.

### 2.2 Synthesis of t -ZrO<sub>2</sub>

The t-ZrO<sub>2</sub> support was synthesized via a reflux-assisted precipitation method. Specifically, 32 g of zirconyl chloride octahydrate (ZrOCl<sub>2</sub>·8H<sub>2</sub>O) was dissolved in 200 mL deionized water, followed by the gradual addition of 400 mL ammonium hydroxide solution (1 M) under vigorous stirring until pH 10 was attained. The resulting precipitate was maintained in its mother liquor at 105 °C for one week under reflux conditions with the pH = 10. The product was then thoroughly washed with deionized water until chloride ions were undetectable by AgNO<sub>3</sub> testing. After filtration, the material was dried at 110 °C for 12 h and subsequently calcined in air at 800 °C for 3 h to obtain the t-ZrO<sub>2</sub> support. For the preparation of Cu/t-ZrO<sub>2</sub> catalyst, Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O was dissolved in the suspension. The mixture was stirred at room temperature, followed by drying at 80 °C for 12 h and calcination at 500 °C for 3 h to yield the final catalyst.

### 2.3 Synthesis of CuO/x-ZrO<sub>2</sub>

The CuO/m-ZrO<sub>2</sub> and CuO/t-ZrO<sub>2</sub> catalysts were synthesized through a facile impregnation method. In a typical procedure, an aqueous solution containing a  $Cu(NO_3)_2 \cdot 3H_2O$  was introduced to the ZrO<sub>2</sub> support. The mixture was continuously stirred at 80 °C until complete evaporation of the solvent. The resulting material was subsequently dried at 80 °C for 12 h, followed by calcination in air at 500 °C for 3 h to obtain the final CuO/x-ZrO<sub>2</sub> catalysts.

# 2.4 Synthesis of CuO/SiO<sub>2</sub>, CuO/TiO<sub>2</sub> and CuO/Al<sub>2</sub>O<sub>3</sub>

 $\label{eq:cuO/SiO2} CuO/TiO2 \mbox{ and } CuO/Al2O3 \mbox{ samples were prepared with the similar} synthesis methods of CuO/x-ZrO2 \mbox{ samples, respectively.}$ 

# $2.5\ Characterization\ of\ CuO/m-ZrO_2$

Sample	Cu content (%)	Zr content (%)
Fresh CuO/m-ZrO <sub>2</sub>	28.3	42.7
Spent CuO/m-ZrO <sub>2</sub>	22.5	34.6

**Table S1.** ICP-AES analyses for the fresh CuO/m- $ZrO_2$  and spent catalysts.

:	Sample	Specific surface a	area $(m^2/g)^a$	Р	Pore Size (nm) <sup>b</sup>			
Cu	O/m-ZrO <sub>2</sub>	83.8			5.18			
1	m-ZrO <sub>2</sub>	162.3			4.39			
a	BET	surface	area,	b	Pore	Size.		

Table S2.  $N_2$  adsorption-desorption of CuO/m-ZrO\_2 and m-ZrO\_2 catalyst.



Figure S1.  $N_2$  adsorption-desorption isotherms of m-ZrO<sub>2</sub> catalyst.





Figure S3. SEM analysis of catalysts. (a) fresh CuO/m-ZrO<sub>2</sub>; (b) spent CuO/m-ZrO<sub>2</sub>.



Figure S4. XPS of the spent catalysts. (a) survey; (b) O 1s; (c) Cu 2p and (d) Zr 3d.

### **3** Chemical composition of sawdust

Firstly, the sawdust (particles size:  $0.5 \sim 1.0$  mm) was extracted with toluene/ethanol (2:1, v/v) in a Soxhlet instrument for 12 h, and then dried at 50 °C under vacuum for 8 h. The chemical compositions of woody sawdust were analyzed according to the National Renewable Energy Laboratory (NREL) standard analytical procedure (NREL/TP-510-42618).<sup>10</sup> Typically, woody sawdust (300 mg) was hydrolyzed with 72 wt% sulfuric acid solution (3.0 mL) at 30 °C for 1 h. Deionized water (84.0 mL) was then added to dilute sulfuric acid (ca. 3%). This mixture was heated at 120 °C for 1 h in an autoclave. After cooling, the mixture was filtered through a mixed cellulose ester (MCE) membrane filter (0.2 µm). The amount of acid insoluble lignin (AIL, Klason lignin) was determined by measurement the weight of residue after drying. The concentration of acid soluble lignin (ASL) was determined by UV spectra by measuring the absorbance of the soluble fraction at 205 nm. The concentrations of the determined by high performance monosaccharides were anion exchange (HPAEC-PAD).11 chromatography pulsedamperometry detection with

Entry	Cool at the to	<b>A II</b> (+0/)b		Cellulose	Hemicellulose
Entry	Substrate	AIL $(Wt\%)^{0}$	ASL (Wt%) <sup>c</sup>	(wt%)	(wt%)
1	Larix	26.9	0.3	36.7	26.6
2	Pinus	26.5	0.7	44.3	28.4
3	Poplar	22.4	2.5	42.7	19.7
4	Beech	20.3	2.8	42.1	26.8

Table S3. The composition of softwood and hardwood sawdust.<sup>a</sup>

<sup>*a*</sup> The compositions of biomass were analyzed according to the procedures of the NREL method. <sup>*b*</sup> AIL: acid insoluble lignin (Klason lignin). <sup>*c*</sup> ASL: acid soluble lignin.

### 4 Catalytic hydrogenolysis of woody biomass

In a typical reaction, woody sawdust (50 mg), CuO/m-ZrO<sub>2</sub> (25 mg) and MeOH (10 mL) were charged into a 50 mL Parr autoclave. The reactor was sealed, purged with nitrogen, and then was pressured to H<sub>2</sub> (3 MPa) at room temperature. The reaction was carried out at different temperatures for a certain time with a magnetic stirring at 800 rpm. After completion, the autoclave was cooled ( $2.8 \sim 2.9$  MPa) and depressurized carefully. Then the reaction mixture was filtered, and the insoluble fraction was washed with dichloromethane. Subsequently, the solution fraction was extracted with dichloromethane (DCM) and the resulting lignin oily product was obtained after removing all volatiles under vacuum condition. An external standard was added to the lignin oil solution in dichloromethane, which was subjected to GC and GC-MS for analysis. The identification and quantification of lignin monomers in the oily product were assessed by comparison with authentic samples acquired from commercial purchase or independent synthesis. In the case of commercial catalysts, 25 mg Ru/C (Ru content: 5 wt%) or 25 mg Pd/C (Pd content: 5 wt%) were used for the hydrogenolysis of Larch sawdust (50 mg).

### 5 Scale-up of catalytic processes

Larch sawdust (5 g), CuO/ m-ZrO<sub>2</sub> catalyst (1 g) and MeOH (30 mL) were mixed into a 100 mL Parr autoclave, which was then flushed with N<sub>2</sub> for three times and pressurized with 3 MPa H<sub>2</sub> at room temperature. Subsequently, the mixture was stirred at 500 rpm and maintained at 240 °C for 4 h. After completion of the reactions, the autoclave was cooled in water and depressurized at room temperature. The solid pulp and catalyst were filtered and thoroughly washed with dichloromethane. The combined organic phase of dichloromethane was concentrated and analyzed by GC and GC-MS. Moreover, the corresponding products were purified by a column chromatography (silica, petroleum ether–ethyl acetate) and characterized by NMR and GC-MS analysis.

### 6 Lignin products analysis

### 6.1 Monomers analysis

Gas chromatography (GC) and Gas chromatography-mass spectrometry (GC-MS) analyses were performed on a Shimadzu Model 2010 plus with a HP-5 column (30 m  $\times$  0.25 mm  $\times$  0.25 mm) employing a flame ionization detector (FID) and a Shimadzu GCMS-QP2010SE with a HP-5MS (30 m  $\times$  0.25 mm  $\times$  0.25 mm) column, respectively. Injecting temperature was 250 °C. A column temperature procedure of 50 °C in 3 min, and 8 °C min<sup>-1</sup> to 280 °C. The injection temperature of FID was 200 °C. The characterization and quantification lignin monomers within oil-based products has been estimated by reference to real samples obtained from commercial source or independent synthesis. The monomer yields were calculated using the formula:

Monomer yield 
$$(wt\%) = \frac{Mass (monomer)}{Mass (initial lignin)} \times 100\%$$
 (1)  
Monomer yield  $(wt\%) = \frac{Mole (monomer)}{Mole (initial lignin)} \times 100\%$  (2)

### 6.2 Delignification

For the soluble fraction, the dichloromethane was removed under vacuum to give crude "lignin oil", which was weighted to determine the degree of delignification (based on Klason lignin weight).

Delignification (wt%) = 
$$\frac{Mass (Lignin oil)}{Mass (initial lignin)} \times 100\%$$



**Figure S5.** Gas chromatogram of the monomers from RCF reaction of  $\beta$ -*O*-4' model compounds over different catalysts.



Figure S6. Catalytic performance of the different catalysts from RCF reaction of β-O-4'modelcompounds.

	MeO HO	OH OH OH 3 MPa H <sub>2</sub> , Me	-ZrO <sub>2</sub>	Me + Pr-G	Pe-G Po	H OMe I-G	
Entry	Pup	Phenolic	monomers yi	eld (wt%)	,	Total monomer	
	Kuli	2	Pr-G	Pe-G		(wt%)	
1	1	43.1	27.6	2.4		73.1	
2	2	28.7	4.6	20.1		53.4	
3	3	20.3	5.5	12.1		37.9	
4	4	12.8	3.5	9.4		25.7	

Table S4. Products distribution of CuO/m-ZrO<sub>2</sub>-catalyzed hydrogenolysis of β-O-4' model compounds at different recycle times.<sup>a</sup>

<sup>a</sup> Reaction condition: β-O-4' model compounds (10 mg), CuO/m-ZrO<sub>2</sub> (25 mg), MeOH (10 mL), 240 °C, H<sub>2</sub> (3 MPa), and 4 h.



Figure S7. Gas chromatogram of the different recycle times from RCF reaction of  $\beta$ -O-4' model compounds over a CuO/m-ZrO<sub>2</sub> catalyst.



Figure S8. Catalytic performance of the different recycle times from RCF reaction of  $\beta$ -*O*-4' model compounds over a CuO/m-ZrO<sub>2</sub> catalyst.



**Figure S9.** GPC of lignin monomer (Pol-G), dimer, trimer, and lignin oily product from catalytic hydrogenolysis of Larch sawdust over a CuO/m-ZrO<sub>2</sub> catalyst.

	Larch	Ca sawdust 3 MPa H <sub>2</sub> , Me	talyst OH, 240 °C, 4 h	OMe + OMe OH	OH OMe + OMe OM	e OH OMe	
			Pr-G Phenolic	Pol-G	eld (wt%)	Al-G	Total
Entry	Catalyst						- monomer
		Pr-G	Pol-G	Et-G	Pe-G	Al-G	(wt%)
1	CuO/m-ZrO <sub>2</sub>	2.9	15.4	0.3	$ND^b$	ND	18.6
2	Pd/C	2.4	12.2	3.2	ND	ND	17.8
3	Ru/C	11.6	2.5	0.6	ND	ND	14.7
4	CuO/Al <sub>2</sub> O <sub>3</sub>	6.5	0.4	0.3	5.2	ND	12.4
5	CuO/TiO <sub>2</sub>	6.7	3.6	0.4	ND	ND	10.7
6	CuO/t-ZrO <sub>2</sub>	7.4	3.4	0.2	ND	ND	10.9
7	CuO/SiO <sub>2</sub>	0.3	ND	ND	7.8	0.7	8.8
8	m-ZrO <sub>2</sub>	0.5	ND	ND	7.3	0.6	8.4

Table S5. Products distribution catalyzed hydrogenolysis of Larch sawdust under different catalysts.<sup>a</sup>

<sup>a</sup> Reaction condition: Larch sawdust (50 mg), catalyst (25 mg), solvent (10 mL), 240 °C, H<sub>2</sub> (3 MPa), and 4 h.

ND,

b

detectable.

not



**Figure S10.** Gas chromatogram of the different catalysts from RCF reaction of Larch sawdust.



**Figure S11.** GPC of lignin oil products from RCF reaction of Larch sawdust under different catalysts.



**Figure S12.** Catalytic performance of the different catalysts from RCF reaction of Larch sawdust.

CuO/m-ZrO₂ Larch sawdust → 3 MPa H₂, MeOH, 240 °C, 4 h		OH OMe +	OH OMe + OH	OH OMe +	OH OMe +	OH OMe		
			Pr-G	Pol-G	Et-G	Pe-G	Al-G	
		Phenolic m	nonomers	yield (wt	t%)			Total
Catalyst			D. C	n		41.0		monomer
	Pr-G	Pol-G	Et-G	Р	'e-G	Al-G		(wt%)
10%Cu/m-ZrO <sub>2</sub>	0.5	$ND^b$	ND		4.1	4.8		9.4
20%Cu/m-ZrO <sub>2</sub>	3.6	1.7	ND		6.2	2.9		14.5
30%Cu/m-ZrO <sub>2</sub>	5.3	8.4	0.4		0.6	ND		14.7
40%Cu/m-ZrO <sub>2</sub>	7.4	8.6	0.5	]	ND	ND		16.5
45%Cu/m-ZrO <sub>2</sub>	2.9	15.4	0.3	]	ND	ND		18.6
50%Cu/m-ZrO <sub>2</sub>	2.6	12.6	0.4	]	ND	ND		15.6
60%Cu/m-ZrO <sub>2</sub>	2.1	8.0	0.4	]	ND	ND		10.5

Table S6. Products distribution of CuO/m-ZrO<sub>2</sub>-catalyzed hydrogenolysis of Larch sawdust at various mass fraction.<sup>a</sup>

<sup>a</sup> Reaction condition: Larch sawdust (50 mg), CuO/m-ZrO<sub>2</sub> (25 mg), solvent (10 mL), 240 °C, H<sub>2</sub> (3 MPa), and 4 h.

<sup>*b*</sup> ND, not detectable.



**Figure S13.** Gas chromatogram of the monomers from RCF reaction of lignin from Larch sawdust over a CuO/m-ZrO<sub>2</sub> catalyst under different various mass fraction.



**Figure S14.** GPC of lignin oil products from RCF reaction of lignin from Larch sawdust over a CuO/m-ZrO<sub>2</sub> catalyst under different various mass fraction.

	Larch sawdust-	CuO/m-ZrO₂ 3 MPa H₂, 240 °C, 4 h	OH OMe +	OH OMe + OH	OH OMe +	OH OMe		
			Pr-G	Pol-G	Et-G	Pe-G		
Solvent		Phenolic monomers yield (wt%)						
Solvent	Pr-G	Pol-G	Et-G	Pe	-G	(wt%)		
MeOH	2.9	15.4	0.3	NI	$D^b$	18.6		
EtOH	3.8	ND	3.6	3.	.6	11.6		
<sup>i</sup> PrOH	2.5	ND	ND	6.	4	8.9		
Dioxane	e 1.5	ND	ND	6.	.1	7.6		

Table S7. Products distribution of CuO/m-ZrO<sub>2</sub>-catalyzed hydrogenolysis of Larch sawdust under different solvents.<sup>a</sup>

<sup>a</sup> Reaction condition: Larch sawdust (50 mg), CuO/m-ZrO<sub>2</sub> (25 mg), solvent (10 mL), 240 °C, H<sub>2</sub> (3 MPa), and 4 h.

ND,

b

detectable.

not



**Figure S15.** Gas chromatogram of the monomers from RCF reaction of lignin from Larch sawdust over a CuO/m-ZrO<sub>2</sub> catalyst under different solvents.



Figure S16. GPC of lignin oil products from RCF reaction of lignin from Larch sawdustoveraCuO/m-ZrO2catalystunderdifferentsolvents.

Larch sawdu	CuO ust 3 MPa H <sub>2</sub>	CuO/m-ZrO <sub>2</sub> Pa H <sub>2</sub> , MeOH, 4 h		OH OMe + OH	OH OMe	
			Pr-G	Pol-G	Et-G	_
Temperatur	Phenolic	monomers	yield (wt	%) To	tal monomer	
e (°C)	Pr-G	Pol-G	Et-C	J	(wt%)	
200	2.1	8.0	0.3		10.4	-
220	3.1	12.4	0.4		15.9	
240	2.9	15.4	0.3		18.6	
260	5.2	14.8	0.9		20.9	

Table S8. Products distribution of CuO/m-ZrO<sub>2</sub> catalyzed hydrogenolysis of Larch sawdust under different reaction temperatures.<sup>a</sup>

<sup>a</sup> Reaction condition: Larch sawdust (50 mg), CuO/m-ZrO<sub>2</sub> (25 mg), MeOH (10 mL), H<sub>2</sub> (3 MPa), 4 h.

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**Figure S17.** Gas chromatogram of the monomers from RCF reaction of lignin from Larch sawdust over a CuO/m-ZrO<sub>2</sub> catalyst under different catalyst temperatures.



**Figure S18.** GPC of lignin oil products from RCF reaction of lignin from Larch sawdust over a CuO/m-ZrO<sub>2</sub> catalyst under different catalyst temperatures.

Larch sa	Cu wdust 3 MPa H <sub>2</sub>	uO/m-ZrO <sub>2</sub> ➤ ₂, MeOH, 240 °C	OH OMe +	OH OMe + OH	OHOM	e OH + OMe	
			Pr-G	Pol-G	Et-G	Pe-G	
Time (h)	Phe	Phenolic monomers yield (wt%)					
Time (h) $-$	Pr-G	Pol-G	Et-G	Pe	-G	(wt%)	
1	1.0	7.9	$ND^b$	1.	.0	9.9	
2	1.0	9.4	0.3	Ν	D	10.7	
4	2.9	15.4	0.3	Ν	D	18.6	
6	3.9	15.1	0.4	Ν	D	19.4	

Table S9. Products distribution of CuO/m-ZrO<sub>2</sub> catalyzed hydrogenolysis of Larch sawdust with different reaction times.<sup>a</sup>

<sup>a</sup> Reaction condition: Larch sawdust (50 mg), CuO/m-ZrO<sub>2</sub> (25 mg), MeOH (10 mL), 240 °C, H<sub>2</sub> (3 MPa).

ND,

b

detectable.

not



**Figure S19.** Gas chromatogram of the monomers from RCF reaction of lignin from Larch sawdust over a CuO/m-ZrO<sub>2</sub> catalyst under different reaction times.



**Figure S20.** GPC of lignin oil products from RCF reaction of lignin from Larch sawdust over a CuO/m-ZrO<sub>2</sub> catalyst under different reaction times.

Larch sawdust	CuO/r 3 MPa H <sub>2</sub> , Me	n-ZrO <sub>2</sub> ────────────────────────────────────	OH OMe +	OH OMe + OH	OH OMe +	OH OMe + OMe
			Pr-G	Pol-G	Et-G	Pe-G Al-G
Catalyst	P	henolic m	onomers y	vield (wt%	<b>(</b> 0)	Total monomer
dosage (mg)	Pr-G	Pol-G	Et-G	Pe-G	Al-G	(wt%)
10	$ND^b$	0.9	ND	4.4	1.7	7.0
15	0.6	3.8	ND	4.2	2.3	10.9
20	1.9	6.6	ND	3.5	ND	12.0
25	2.9	15.4	0.3	ND	ND	18.6
30	2.2	13.4	0.4	ND	ND	16.0

Table S10. Products distribution of CuO/m-ZrO<sub>2</sub> catalyzed hydrogenolysis of Larch sawdust at different catalyst dosages.<sup>a</sup>

<sup>a</sup> Reaction condition: Larch sawdust (50 mg), MeOH (10 mL), H<sub>2</sub> (3 MPa), and 4 h.

<sup>*b*</sup> ND, not detectable.



**Figure S21.** Gas chromatogram of the monomers from RCF reaction of lignin from Larch sawdust over a CuO/m-ZrO<sub>2</sub> catalyst under different reaction dosages.



**Figure S22.** GPC of lignin oil products from RCF reaction of lignin from Larch sawdust over a CuO/m-ZrO<sub>2</sub> catalyst under different reaction dosages.

Source	CuO/m-ZrO <sub>2</sub> → 3 MPa H <sub>2</sub> , MeOH, 240 °C, 4 h		OH OMe	OH OMe	OH	)Me	OH OMe	OH MeO	OH e MeO	OH Me MeO
Sawdusi			+	OH		+ U	+		+	+ (
			Pr-G	Pol-G	Et-G	3	Pe-G	Pr-S	Pol-S	Et-S
										Total
	Construct			Phenolic monomers yield (wt%)						
	Sawuus	ot.								(wt%)
			Et-G	Pe-G	Pr-G	Et-S	Pr-S	Pol-G	Pol-S	
Hor	dwood	Beech	$ND^b$	ND	ND	0.8	3.7	10.5	18.0	33.0
	uwood	Poplar	ND	ND	2.6	1.9	8.1	8.6	14.6	35.8
Sof	twood	Larch	0.3	ND	2.9	ND	ND	15.4	ND	18.6
501	iwoou	Pinus	0.8	2.2	2.0	ND	ND	10.8	ND	15.8

Table S11. Products distribution of CuO/m-ZrO<sub>2</sub> catalyzed hydrogenolysis of various wood sawdust.<sup>a</sup>

<sup>a</sup> Reaction condition: Wood sawdust (50 mg), CuO/m-ZrO<sub>2</sub> (25 mg), MeOH (10 mL), H<sub>2</sub> (3 MPa), 240 °C, and 4 h.

<sup>*b*</sup> ND, not detectable.



Figure S23. Gas chromatogram of the monomers from RCF reaction of lignin from various wood sawdust over CuO/m-ZrO<sub>2</sub> catalysts.



Figure S24. GPC of lignin oil products from RCF reaction of lignin from various woodsawdustoverCuO/m-ZrO2catalysts.

# 7 Identification and quantitation of phenolic monomers

More details could be found in our previous work.<sup>12</sup>

CAS: 2305-13-7, 4-*n*-propylguaiacol (**Pr-G**) was prepared following previously reported procedures.<sup>13</sup>



Figure S25. Standard curve of compound Pr-G. Mass spectra of standard sample Pr-G. GC spectra of product derived from lignin depolymerization and standard sample Pr-G.



CAS: 2785-87-7, 4-n-guaiacol (Pol-G) was commercially available.14

Figure S26. Standard curve of compound Pol-G. Mass spectra of standard sample Pol-G. GC spectra of product derived from lignin depolymerization and standard sample Pol-G.

CAS: 97-54-1, 2-methoxy-4-[(1E)-prop-1-en-1-yl] phenol (**Pe-G**) was prepared following previously reported procedures.<sup>15</sup>



Figure S27. Standard curve of compound Pe-G. Mass spectra of standard sample Pe-G. GC spectra of product derived from lignin depolymerization and standard sample Pe-G.





Figure S28. Standard curve of compound Al-G. Mass spectra of standard sample Al-G. GC spectra of product derived from lignin depolymerization and standard sample Al-G.



CAS: 2785-89-9, 4-ethylguaiacol (Et-G) was commercially available.

Figure S29. Standard curve of compound Et-G. Mass spectra of standard sample Et-G. GC spectra of product derived from lignin depolymerization and standard sample Et-G.



CAS: 6766-82-1, 4-n-propanolsyringol (Pol-S) was commercially available.<sup>16</sup>

Figure S30. Standard curve of compound Pol-S. Mass spectra of standard sample Pol-S. GC spectra of product derived from lignin depolymerization and standard sample Pol-S.

CAS: 20736-25-8, 4-*n*-propylsyringol (**Pr-S**) was prepared following previously reported procedures.<sup>17</sup>



Figure S31. Standard curve of compound Pr-S. Mass spectra of standard sample Pr-S.GC spectra of product derived from lignin depolymerization and standard sample Pr-S.S.



CAS: 6766-82-1, 2,6-Dimethoxy-4-ethylphenol (Et-S) was commercially available.

**Figure S32.** Standard curve of compound **Et-S**. Mass spectra of standard sample **Et-S**. GC spectra of product derived from lignin depolymerization and standard sample **Et-S**.



CAS: 90-05-1, guaiacol (2) was commercially available.

**Figure S33.** Standard curve of compound **2**. Mass spectra of standard sample **2**. GC spectra of product derived from lignin depolymerization and standard sample **2**.



Figure S34. <sup>1</sup>H and <sup>13</sup>C NMR spectra of 4-*n*-propylguaiacol (Pr-G).



Figure S35. <sup>1</sup>H and <sup>13</sup>C NMR spectra of 4-*n*-guaiacol (Pol-G).

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