

Supporting information for:

Catalytic hydrogenolysis of lignin under syngas: the enhancement on the C_β-O bond cleavage with CO

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1.1 Lignin separation and determination of lignin content

Organosolv lignin was extracted from sugarcane bagasse according to the reported procedure ¹. Firstly, 10.0 g dried sugarcane bagasse, 120 mL ethanol and 30 mL 0.3 M H₂SO₄ solution were placed into a 250 mL stainless steel autoclave. The autoclave was heated to 110 °C for 4 h and then cooled to room temperature. The liquor containing lignin was collected by filtration. Then, 800 mL deionized water was added to the above liquid for lignin precipitation. Finally, the lignin was collected by filtration and dried in vacuum (45 °C) for 24 h, and the obtained organosolv lignin was named lignin-110. Similarly, the organosolv lignin obtained at separation temperatures of 130, 150, and 170 °C was designated as lignin-130, lignin-150, and lignin-170, respectively.

The content of lignin in bagasse was determined by the method provided in the literature ². Firstly, bagasse powder (60-80 mesh) was treated with an ethanol/benzene mixture (1:2, v/v) in a Soxhlet extractor for 12 h to remove the impurities such as wax, fat, and resin. Next, the obtained bagasse powder was washed alternately with ethanol and water three times, dried at 80 °C for 12 h. The dried bagasse powder (1.00 g) was placed in a 50 ml flask and mixed gradually with 72 wt.% H₂SO₄ (15 mL) in an ice bath under stirring. Then, the flask was moved to a 20 °C bath for 2 h. After that, the mixture was diluted to 3 wt.% H₂SO₄ solution with deionized water, refluxed for 4 h, and then cooled down to room temperature. The solution was filtered, and the solid residue was washed with water until it was neutral. Finally, the solid was collected, dried in vacuum (45 °C) until the weight became constant, and weighted (0.1602 g). The content of lignin in bagasse powder (P) was calculated by equation (6).

$$P = \frac{W_1}{W_0} \times 100 \quad (6)$$

Where W_1 and W_0 are the weight of lignin and test bagasse powder, respectively. According to the calculation, the content of lignin in bagasse is 16 wt.%.

1.2 HPLC analysis

The conversion of p-coumaric acid was tested by high-performance liquid chromatography (HPLC, Agilent 1260) equipped with a refractive index detector (RID). The column was Guangzhou FLM Titank C18 5u (FMG-5560-EONU, 250 × 4.6 mm). An acetonitrile/H₂O (v/v=60/40) solution was used as the mobile phase at a flow rate of 0.7 mL/min. Both the column and detector temperatures were 35 °C.

1.3 GPC analysis

After the completion of reaction, the catalyst is separated firstly from the reaction mixture by filtration, and then the solvent is removed through rotary evaporation. Finally, the depolymerization products is further dried in vacuum (45 °C) for 24 h and record its mass.

The molecular weight distributions of raw lignin and re-lignin were measured by gel permeation chromatography (GPC) on an Agilent 1260 high performance liquid chromatography (HPLC) using a refractive index detector (RID) and two PL gel columns. The column temperature was set as 30 °C. 1.0 mL min⁻¹ THF (HPLC grade) was used as mobile phase. The concentration of samples (raw lignin and depolymerization products) is 30 mg mL⁻¹ in THF. Before injection, the sample is filtered through a 0.45 µm nylon membrane.

1.4 2D HSQC NMR analysis

Two-dimensional heteronuclear single quantum coherence (2D HSQC) NMR spectroscopy was recorded on a Bruker Avance III 600 MHz spectrometer. 0.07 g lignin sample was dissolved in 0.5 mL DMSO-d₆ for 2D HSQC NMR analysis. The spectral widths were 5000/20,000 Hz for ¹H/¹³C-dimension. The number of collected complex points was 1024 for ¹H-dimension with a recycle delay of 1.5 s.

1.5 The determination of hydroxyl group in lignin

³¹P NMR analysis of the lignin samples were performed using a Bruker Avance III 600 MHz spectrometer according to the method detailed in previous publications ³. Internal standard cyclohexanol (4.02 mg) and chromium acetylacetonate (3.57 mg) were added into the mixture of pyridine-d₅ and deuteriochloroform (1.6:1, v/v) to prepare the relaxation agent. The dry lignin sample (30 mg) was dissolved in the pyridine-d₅/deuteriochloroform mixture (400 µL) in an NMR tube. After absolute dissolution of the lignin, the relaxation agent (150 µL) and 2-chloro-4,4,5,5 tetramethyl-1,3,2-dioxaphospholane (TMDP, 100 µL) were added into the NMR tube. Shaking the tube to ensure well blend. The mixture was kept at room temperature for 2 h. The ³¹P NMR spectra of phosphitylated lignin sample were recorded by a Bruker Avance III HD 600 MHz spectrometer with scan number of 512 and recycle delay of 1 s. The content of hydroxyl group, C (mmol/g), was finally determined based on following equation (7).

$$C = \frac{(150 \times 10^{-3} \times \rho A_2)/(100.16 \times A_1)}{m} \quad (7)$$

Where ρ stands for the concentration of cyclohexanol, mg/mL; A_1 is the integral area of the hydroxyl group in cyclohexanol; A_2 is the integral area of the hydroxyl or carboxyl groups in the lignin structure; m is the mass of the lignin sample, g; 150 is the volume of cyclohexanol added, µL; and 100.16 is the molar mass of cyclohexanol, g/mol.

1.6 Characterization of Pd/C catalyst

The crystalline phases of Pd/C catalysts were examined by powder X-ray diffraction (XRD) patterns using a Bruker D8 Advance diffractometer equipped with Cu K α radiation at 40 kV and 20 mA in the 2 θ ranged from 5 to 90° with a step size of 0.02° and a step time of 0.1 s. X-ray

photoelectron spectroscopy (XPS) was performed on an AXIS SUPRA+ (Kratos) instrument with a monochromate Al K α anode. All binding energy calculations were calibrated using the peak position of C1s at 284.8 eV. The transmission electron microscope (TEM) images were obtained by using a Rigaku JEOL JEM-2100F (200 kV).

N₂ adsorption and desorption were measured on a Micrometric ASAP 2460 system. The samples were outgassed at 120 °C for 8 h prior to sorption measurement. The Brunauer-Emmett-Teller (BET) method was applied to calculate the total surface area from the obtained adsorption data, while the t-plot method was used to distinguish between micro- and mesoporosity. The mesopore size distribution was calculated using the Barrett-Joyner-Halenda (BJH) method on the adsorption branch of isotherm. The micropore size distribution was determined by Horvath-Kawazoe method.

The Pd contents of the catalysts were determined by an inductively coupled plasma-atomic emission spectrometry (ICP-AES).

2. Supplementary Figures & Tables

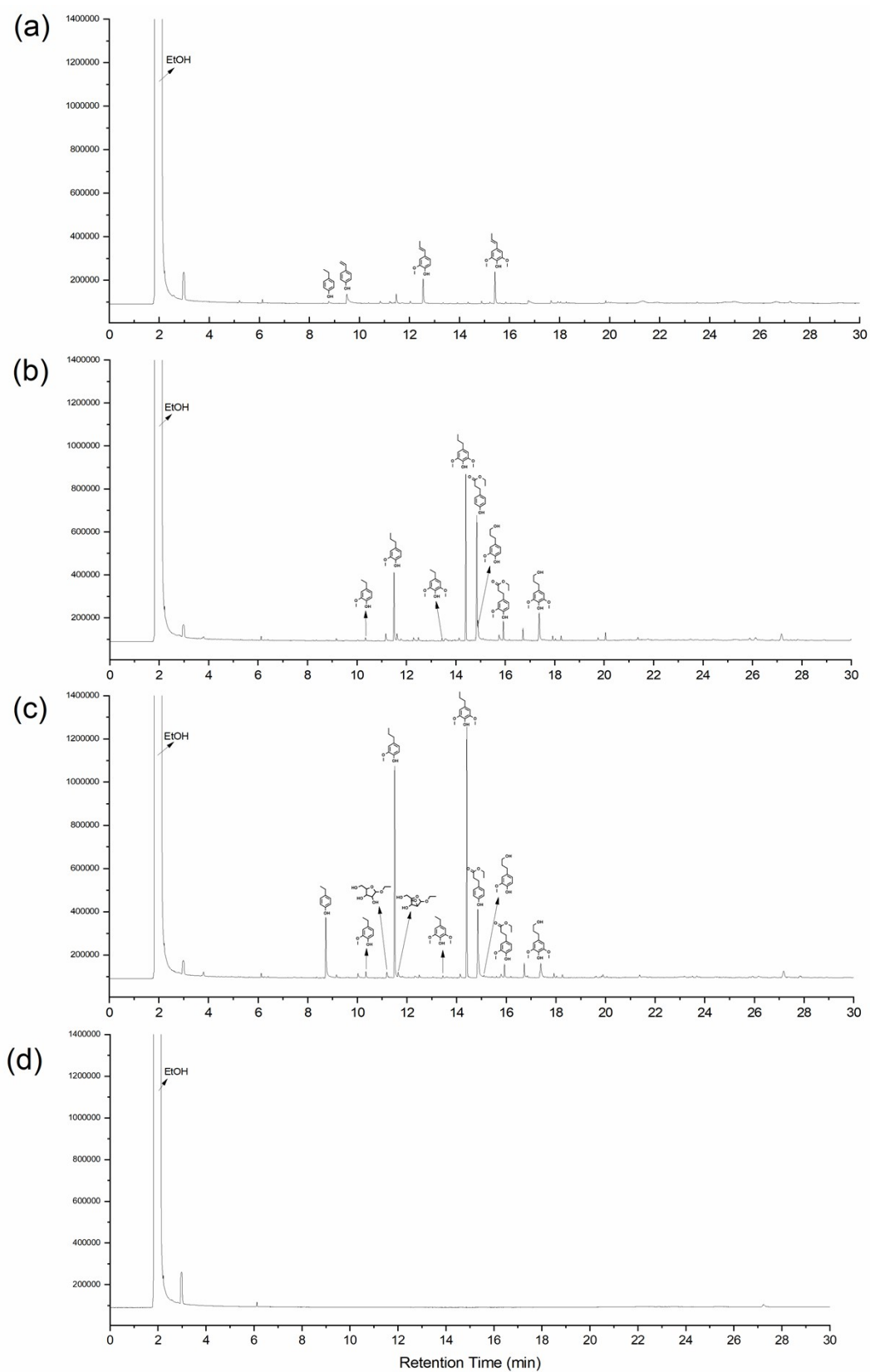
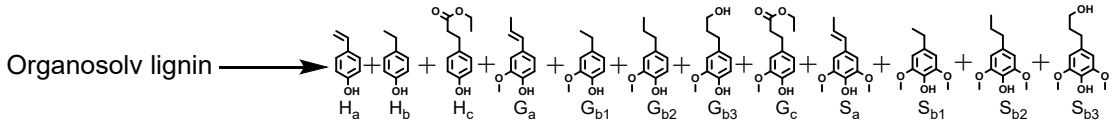


Fig. S1. GC-FID spectrum of depolymerization of lignin over Pd/C in different atmospheres.

Conditions: 0.1 g organosolv lignin-110, 0.05 g 5 wt.% Pd/C, 20 mL EtOH, 230 °C, 4 h, 3.0 MPa. (a) CO, (b) H₂, (c) syngas (CO/H₂=1/2), and (d) syngas (CO/H₂=1/2), without feedstock.

Table S1. Lignin depolymerization to monophenols in different atmospheres. ^a

Organosolv lignin 															
Entry	CO/H ₂ /Ar (MPa/MPa/MPa)	Cat.	Yield (mg/g)												Total (mg/g)
			H _a	H _b	H _c	G _a	G _{b1}	G _{b2}	G _{b3}	G _c	S _a	S _{b1}	S _{b2}	S _{b3}	
1 ^b	0/0/1	--	22.3	n.d.	n.d.	4.2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	26.5
2 ^b	0/1/0	--	20.5	n.d.	n.d.	5.1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	25.6
3 ^b	1/0/0	--	21.2	n.d.	n.d.	4.8	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	26.0
4 ^b	0/1/1	--	22.6	n.d.	n.d.	5.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	27.6
5 ^b	1/1/1	--	23.1	n.d.	n.d.	4.7	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	27.8
6	0/3/0	5 wt.% Pt/C	n.d.	1.8	33.9	n.d.	2.5	20.8	2.2	6.8	n.d.	2.0	55.0	3.5	128.5
7	1/2/0	5 wt.% Pt/C	9.5	33.7	18.1	19.5	1.1	22.0	n.d.	3.1	29.9	1.5	37.4	n.d.	175.8
8	3/0/0	5 wt.% Pt/C	29.4	13.2	n.d.	15.8	n.d.	3.5	n.d.	n.d.	28.2	n.d.	2.1	n.d.	92.2
9	0/3/0	5 wt.% Ru/C	n.d.	1.2	33.4	n.d.	1.5	25.2	4.8	8.5	n.d.	2.3	64.8	3.7	145.7
10	1/2/0	5 wt.% Ru/C	n.d.	13.6	34.8	n.d.	1.1	30.7	2.9	6.8	n.d.	3.5	70.8	1.5	165.7
11	3/0/0	5 wt.% Ru/C	12.2	25.1	n.d.	23.0	1.0	4.1	n.d.	n.d.	35.4	0.6	19.0	n.d.	120.4
12	0/3/0	5 wt.% Pd/C	n.d.	1.4	33.0	n.d.	1.2	7.0	2.5	11.0	n.d.	1.1	37.9	4.7	99.8
13	1/2/0	5 wt.% Pd/C	n.d.	18.2	26.8	n.d.	1.5	38.9	1.1	9.6	n.d.	1.0	79.0	1.5	177.6
14	3/0/0	5 wt.% Pd/C	33.6	4.0	n.d.	10.8	n.d.	2.7	n.d.	n.d.	33.4	n.d.	0.3	n.d.	84.8
15 ^c	1/2/0	10 wt.% Pd/C	3.1	17.5	24.9	3.8	2.8	36.5	2.9	3.0	4.8	0.9	53.1	7.5	160.8
16	1/2/0	10 wt.% Pd/C	n.d.	11.7	32.1	n.d.	2.7	57.5	3.1	5.4	n.d.	0.9	73.4	12.2	199.0
17	0/0/1	5 wt.% Pd/C	14.3	21.2	11.3	12.8	8.3	4.8	0.9	n.d.	35.4	4.8	14.5	1.3	129.7
18	0/0/2	5 wt.% Pd/C	12.7	23.5	12.3	11.0	9.9	7.8	1.1	0.9	32.7	4.4	13.0	1.2	130.5
19	0/0/3	5 wt.% Pd/C	11.7	24.1	13.1	12.1	8.9	8.0	1.0	2.0	29.1	4.8	14.2	1.2	130.1
20	2/0/1	5 wt.% Pd/C	23.6	10.5	n.d.	13.6	4.5	1.9	n.d.	n.d.	38.3	0.8	0.6	n.d.	93.9
21	2/0/0	5 wt.% Pd/C	23.9	10.5	n.d.	12.7	3.3	0.8	n.d.	n.d.	40.0	1.5	1.6	n.d.	94.3
22	0/2/1	5 wt.% Pd/C	n.d.	1.5	38.6	n.d.	1.8	10.4	1.5	10.5	n.d.	1.8	47.6	6.9	120.6
23	0/2/0	5 wt.% Pd/C	n.d.	1.6	38.3	n.d.	2.2	10.1	2.0	14.1	n.d.	2.2	45.2	8.1	123.9
24	0.7/1.3/1	5 wt.% Pd/C	1.4	19.4	31.6	2.4	3.4	41.6	4.0	3.8	3.4	1.0	60.7	12.0	184.7
25	0.7/1.3/0	5 wt.% Pd/C	1.4	16.6	33.1	0.8	3.1	42.2	4.0	3.8	1.8	1.0	62.5	12.0	182.4

^a 0.1 g organosolv lignin-110, 0.05 g catalyst, 20 mL EtOH, 230 °C, 4 h, ^b without catalyst, ^c 0.025 g 10 wt.% Pd/C, n.d.: not detected.

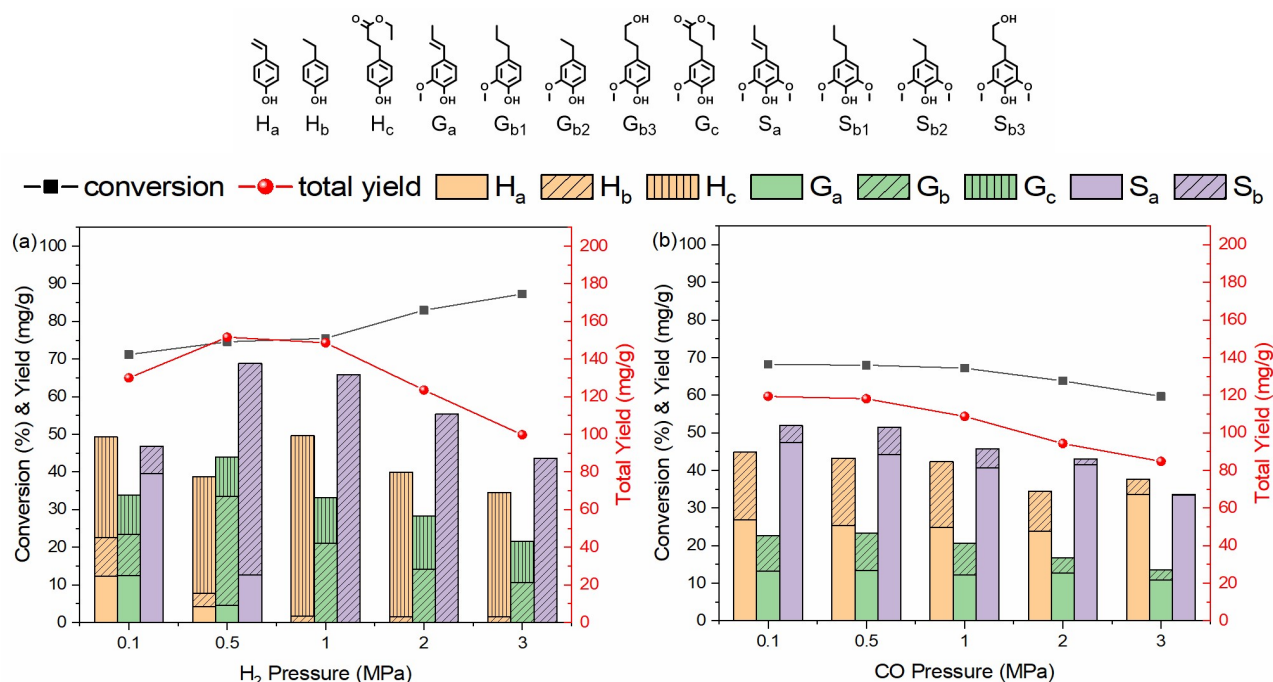
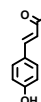
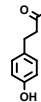
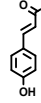


Fig. S2. Lignin depolymerization to monophenols over Pd/C in (a) H₂ and (b) CO atmospheres.

Conditions: 0.1 g organosolv lignin-110, 0.05 g 5 wt.% Pd/C, 20 mL EtOH, 230 °C, 4 h.

Table S2. Effects of atmospheres on the conversion of *p*-coumaric acid. ^a

Entry	Sub.	Atmosphere (MPa)			Conv. (%)	Yield (%)				
		CO	H ₂	Ar						
1 ^[b]		0	0	3.0	67.6	60.9	n.d.	5.1	n.d.	n.d.
2		0	0	3.0	100	n.d.	87.7	n.d.	7.3	n.d.
3		0	3	0	100	n.d.	n.d.	n.d.	n.d.	99.9
4		0.1	2.9	0	100	n.d.	9.6	n.d.	79.6	n.d.
5		0.5	2.5	0	100	n.d.	53.4	n.d.	41.8	n.d.
6		1.0	2.0	0	100	n.d.	87.4	n.d.	7.8	n.d.
7		2.0	1.0	0	100	n.d.	88.6	n.d.	7.7	n.d.
8		2.5	0.5	0	100	2.4	87.0	n.d.	6.5	n.d.
9		2.9	0.1	0	100	2.9	89.5	n.d.	6.0	n.d.
10		3.0	0	0	100	71.5	11.6	5.9	1.9	n.d.
11 ^b		0	0	3.0	100	n.d.	n.d.	n.d.	99.3	n.d.
12		0	0	3.0	100	n.d.	n.d.	n.d.	99.0	n.d.
13		0	0	3.0	100	n.d.	n.d.	/	100	n.d.
14		0	3.0	0	100	n.d.	n.d.	/	n.d.	99.0
15		1.0	2.0	0	100	n.d.	n.d.	/	99.0	n.d.
16		1.0	0	0	67.1	n.d.	n.d.	/	66.2	n.d.

^a 0.2 mmol substrate, 0.05 g 5 wt.% Pd/C, 20 mL EtOH, 230 °C, 4 h, ^b without Pd/C. R: -OH, =O, or -OCH₂CH₃, n.d.: not detected.

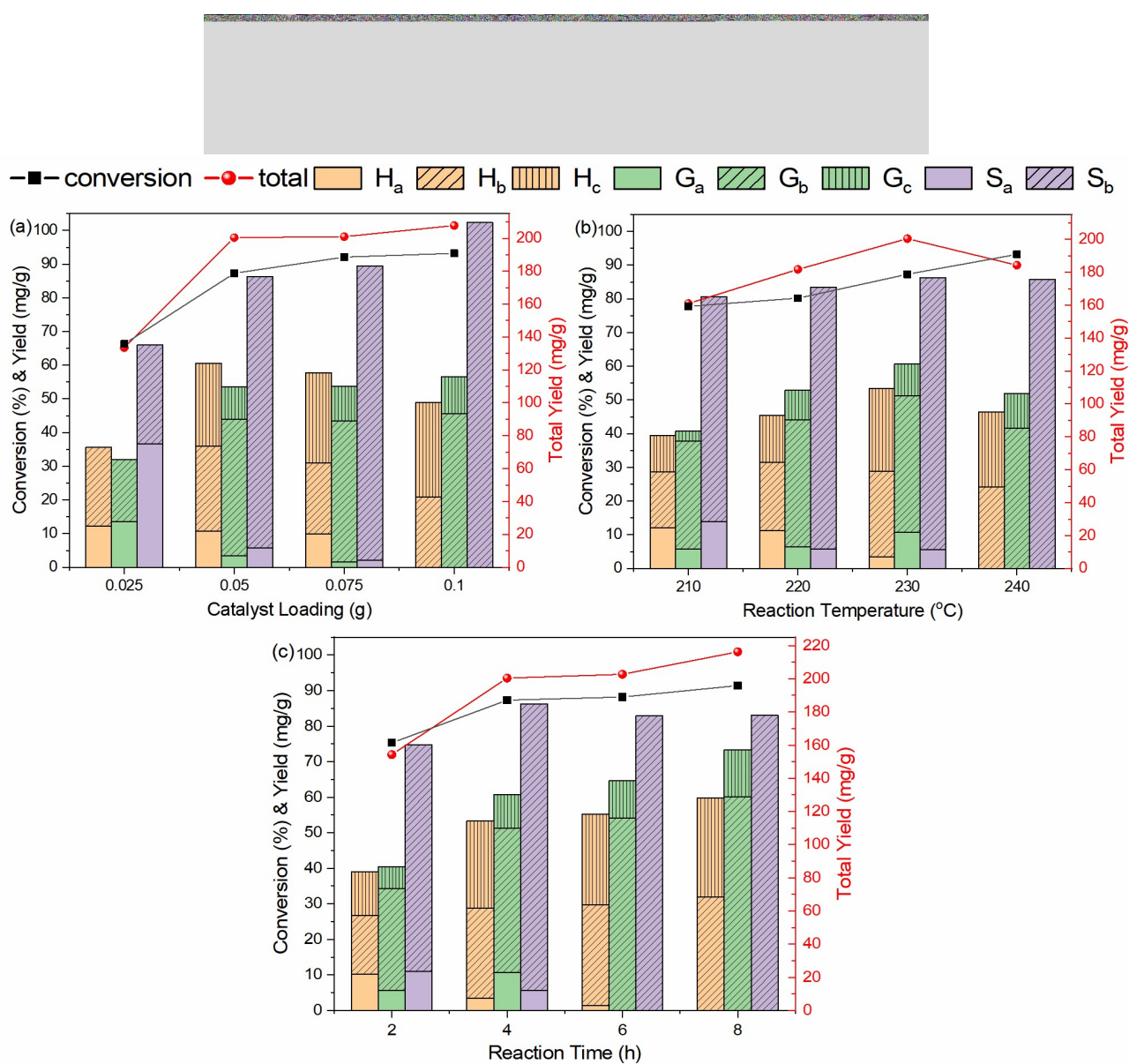
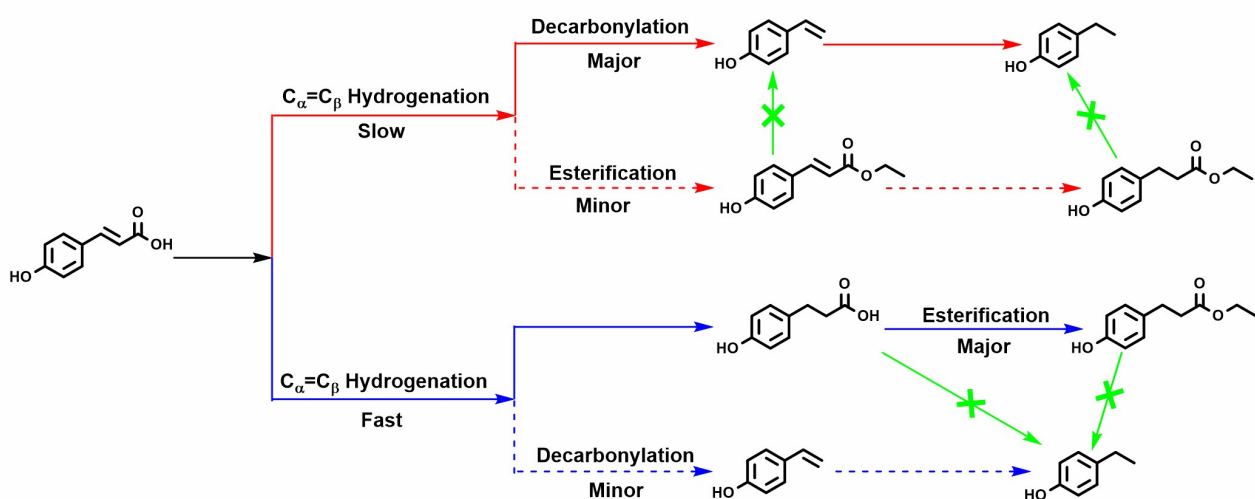


Fig. S3. Lignin depolymerization to monophenols over Pd/C in different reaction conditions.

Conditions: 0.1 g organosolv lignin-110, 20 mL EtOH, CO/H₂=2/1, (a) 4 h, 230 °C, (b) 0.05 g 5 wt.% Pd/C, 4 h, (c) 0.05 g 5 wt.% Pd/C, 230 °C.

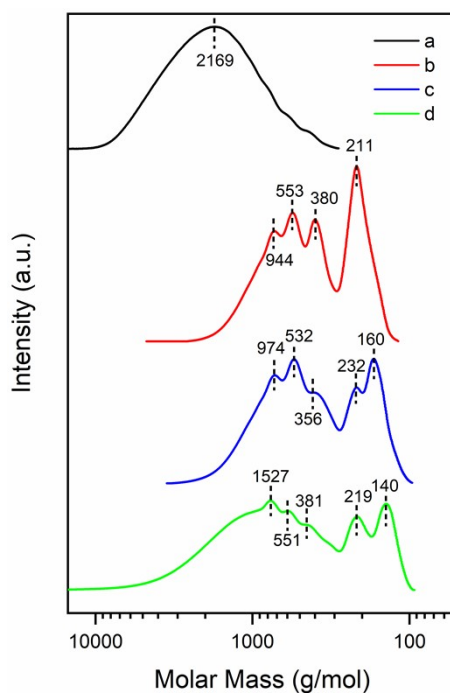


Fig. S4. Molecular weight distributions of raw lignin and its products.

Note: (a) raw lignin, sample (b), (c), and (d) were obtained from raw lignin after treatment at 3.0 MPa H₂, syngas (CO/H₂=2/1), and CO over 5 wt.% Pd/C at 230 °C in 20 mL EtOH for 4 h, respectively.

Table S3. Effect of reaction atmospheres on the molecular weight distributions and yield of depolymerization products. ^a

Entry	CO/H ₂ (MPa/MPa)	re-lignin molecular weight			Yield (mg/g)		
		M _w	M _n	M _w /M _n	Monophenol	Dimer and oligomer	Lignin oil
1	0/3	944	885	1.1	99.8	627.2	727.0
2	2/1	974	898	1.1	200.4	407.8	608.2
3	3/0	1527	1142	1.3	84.8	288.3	373.1

^a 0.1 g organosolv lignin-110, 0.05 g 5 wt.% Pd/C, 20 mL EtOH, 230 °C, 4 h, note: yield of dimer and oligomer = yield of lignin oil - yield of monophenol, yield of lignin oil = (mass of the depolymerization products – mass of re-lignin)*1000.

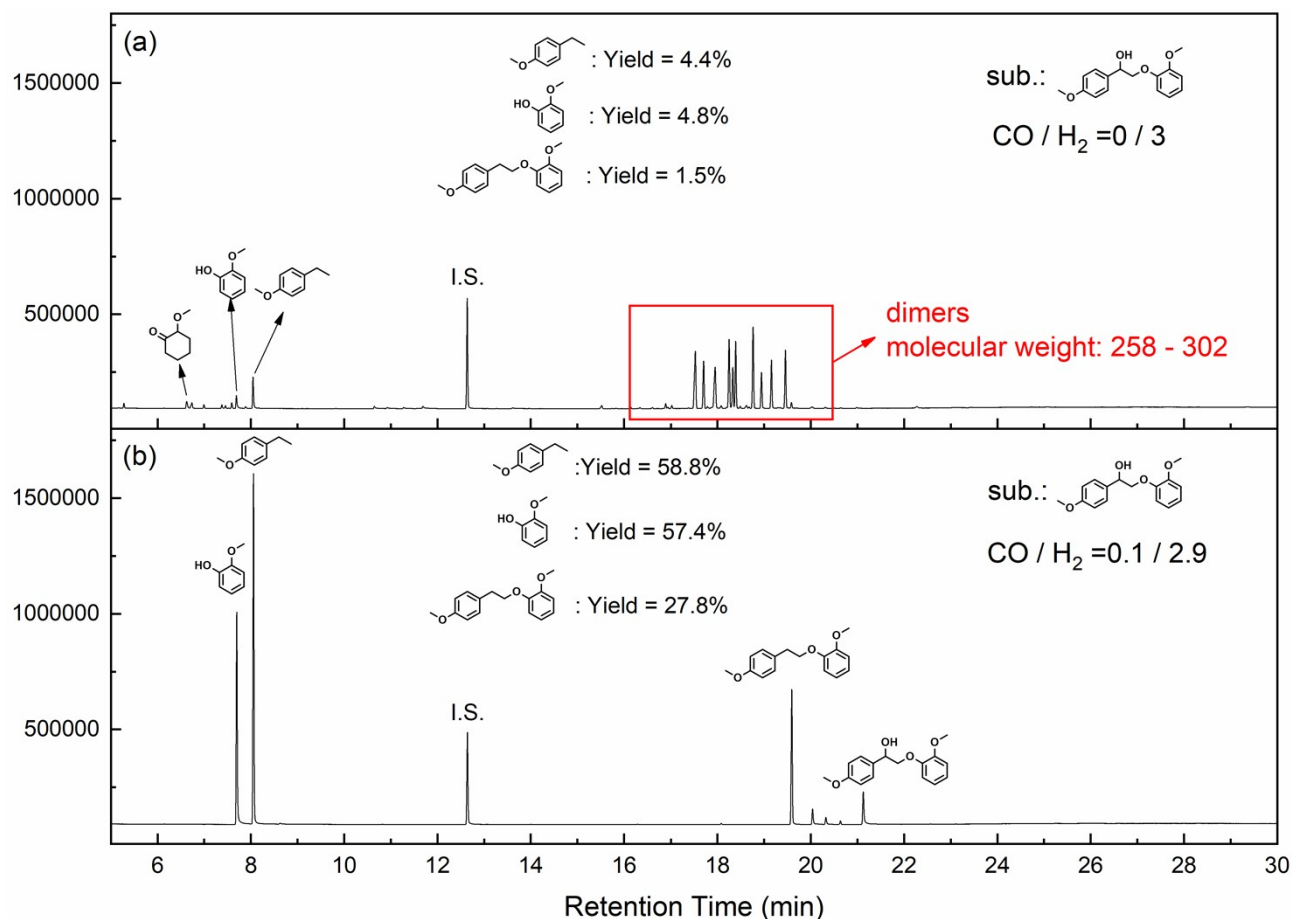


Fig. S5. GC-FID spectrum of hydrogenolysis of compound **F** over Pd/C in (a) H_2 and (b) syngas. Conditions: 0.2 mmol substrate, 0.05 g 5 wt.% Pd/C, 20 mL EtOH, 230 °C, 1 h, (a) 3.0 MPa H_2 , (b) 3.0 MPa syngas ($\text{CO}/\text{H}_2=0.1/2.9$).

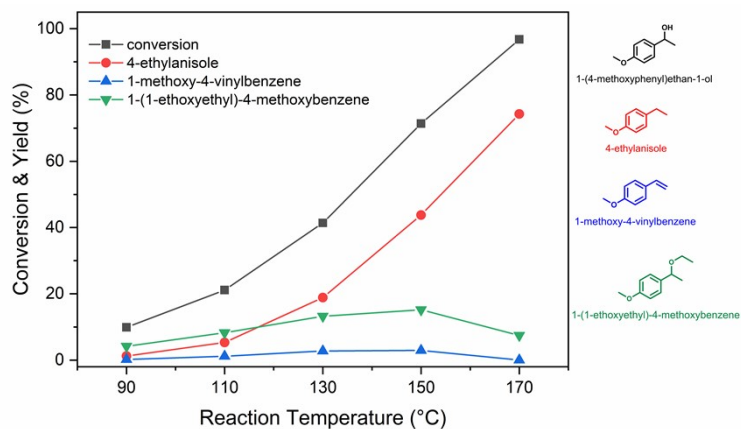


Fig. S6. The effects of reaction temperature on the conversion of 1-(4-methoxyphenyl)ethan-1-ol. Conditions: 0.2 mmol substrate, 0.05 g 5 wt.% Pd/C, 20 mL EtOH, 1 h, $\text{CO}/\text{H}_2=1/2$.

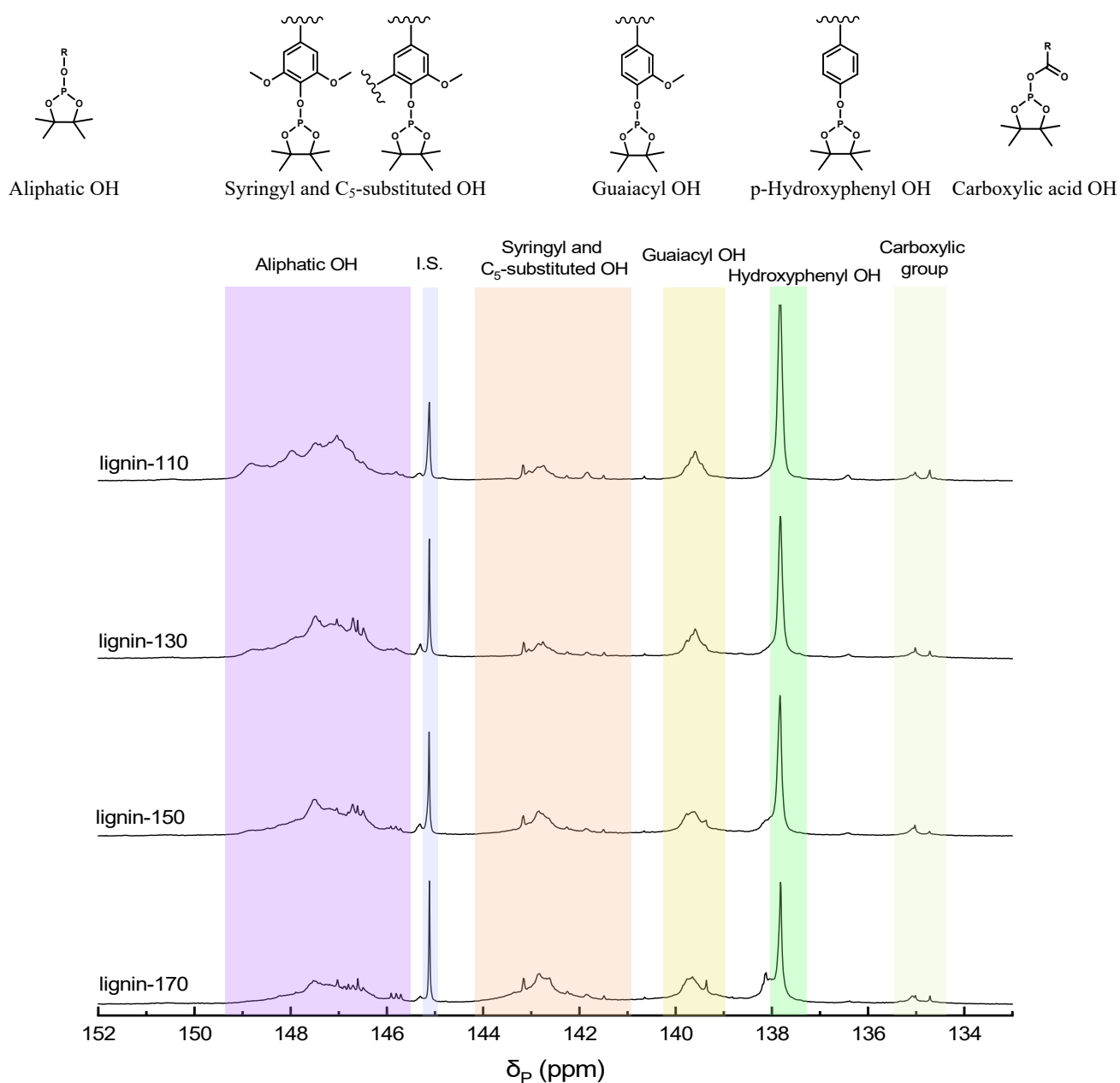


Fig. S7. A quantitative ^{31}P NMR spectrum of different organosolv lignin derivatized with TMDP using cyclohexanol as an internal standard (I.S.).

Table S4. The content of different OH groups in organosolv lignin.

Entry	Lignin	the OH groups content (mmol /g)				
		Aliphatic OH	Syringyl/ C_5 -substituted OH	Guaiacyl OH	p-Hydroxyphenyl OH	Carboxylic acid OH
1	lignin-110	2.89	0.50	0.49	1.14	0.14
2	lignin-130	2.64	0.49	0.58	0.91	0.14
3	lignin-150	2.13	0.88	0.65	0.79	0.13
4	lignin-170	1.57	1.30	0.92	0.73	0.13

Table S5. Bagasse powder depolymerization to monophenols over Pd/C under syngas. ^a

Bagasse																
Entry	Bagasse mass (g)	Yield (mg/g)														Total (mg/g)
		H _a	H _b	H _c	H _{c1}	G _a	G _{b1}	G _{b2}	G _{b3}	G _c	G _{c1}	S _a	S _{b1}	S _{b2}	S _{b3}	
1 ^b	1.0	34.8	n.d.	n.d.	14.4	14.9	n.d.	n.d.	n.d.	n.d.	5.9	12.1	n.d.	n.d.	n.d.	82.1
2	0.1	n.d.	80.6	40.4	n.d.	5.5	10.5	63.4	2.3	21.5	n.d.	3.8	3.4	119.0	6.8	357.2
3	0.2	n.d.	76.0	38.1	n.d.	8.3	10.0	59.8	2.2	19.6	n.d.	4.0	3.2	112.3	6.5	340.0
4	0.3	n.d.	70.8	35.9	n.d.	15.2	9.6	57.8	1.7	18.9	n.d.	27.3	2.7	93.3	5.0	338.3
5	0.4	0.9	66.6	33.4	2.7	20.3	9.6	56.4	1.6	15.9	2.1	32.3	2.7	85.2	4.7	334.3
6	0.5	1.0	64.5	36.2	6.8	26.3	8.6	52.0	1.9	15.4	3.9	38.3	2.4	76.6	5.6	339.3
7	0.6	1.0	62.4	37.7	8.8	32.5	8.3	46.3	1.4	12.7	4.8	48.6	2.0	69.0	4.1	339.6
8	0.8	1.1	60.2	31.5	10.2	39.1	7.7	38.9	1.1	11.0	5.4	52.3	1.8	54.6	3.4	318.2
9	1.0	1.2	59.0	28.8	11.4	44.7	7.3	32.6	0.9	9.6	5.8	56.4	1.7	44.8	2.8	307.0
10	1.2	1.6	54.8	21.5	13.6	51.0	7.3	24.1	0.8	5.2	6.6	61.5	1.6	37.0	2.4	288.9

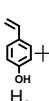
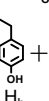
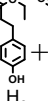
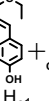
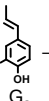
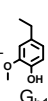
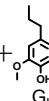
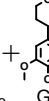
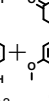
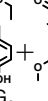
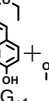
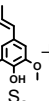
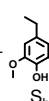
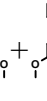
^a 0.1 g 5 wt.% Pd/C, 20 mL EtOH, 230 °C, 4 h, 3.0 MPa syngas (CO/H₂=2/1), ^b without catalyst, n.d.: not detected.

Table S6. Effects of reaction temperature on bagasse powder depolymerization. ^a

Bagasse																
Entry	Temp. (°C)	Yield (mg/g)														Total (mg/g)
		H _a	H _b	H _c	H _{c1}	G _a	G _{b1}	G _{b2}	G _{b3}	G _c	G _{c1}	S _a	S _{b1}	S _{b2}	S _{b3}	
1	210	7.7	45.9	14.3	11.2	53.5	4.6	20.4	0.9	3.8	4.5	65.7	1.1	26.7	2.4	262.7
2	220	3.2	55.9	20.1	12.8	48.7	5.9	28.6	0.9	5.9	5.6	62.0	1.3	36.4	2.4	289.7
3	230	1.2	59.0	28.8	11.4	44.7	7.3	32.6	0.9	9.6	5.8	56.4	1.7	44.8	2.8	307.0
4	240	0.5	62.2	34.1	9.3	35.1	9.3	40.2	0.9	14.4	5.0	47.3	2.1	54.8	3.3	318.7

^a 1.0 g bagasse, 0.1 g 5 wt.% Pd/C, 20 mL EtOH, 4 h, 3.0 MPa syngas (CO/H₂=2/1), n.d.: not detected.

Table S7. Effects of reaction time on bagasse powder depolymerization. ^a

Bagasse →              																
Entry	Time (h)	Yield (mg/g)														Total (mg/g)
		H _a	H _b	H _c	H _{c1}	G _a	G _{b1}	G _{b2}	G _{b3}	G _c	G _{c1}	S _a	S _{b1}	S _{b2}	S _{b3}	
1	2	4.9	54.2	18.2	11.3	54.9	5.8	23.4	0.9	4.9	4.7	67.7	1.3	30.7	2.7	285.5
2	4	1.2	59.0	28.8	11.4	44.7	7.3	32.6	0.9	9.6	5.8	56.4	1.7	44.8	2.8	307.0
3	6	1.2	64.4	40.3	11.0	38.1	8.6	41.6	1.1	14.5	5.7	47.3	1.9	56.0	3.4	335.2
4	8	0.7	65.2	49.5	9.1	28.3	9.4	46.8	1.3	18.7	4.8	38.3	2.1	64.1	4.0	342.2
5	10	0.4	68.6	50.8	9.3	22.7	10.7	52.8	1.2	20.9	4.7	33.3	2.5	70.9	3.5	350.7

^a 1.0 g bagasse, 0.1 g 5 wt.% Pd/C, 20 mL EtOH, 230 °C, 3.0 MPa syngas (CO/H₂=2/1), n.d.: not detected.

Table S8. Overview of literature data for the catalytic depolymerization of various lignin over Pd/C.

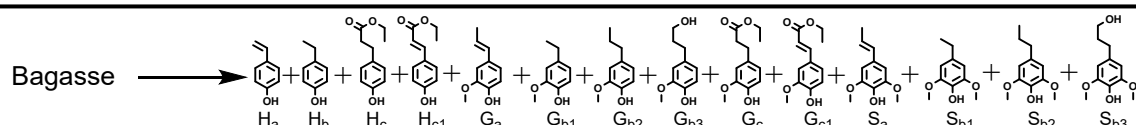
Feedstocks	Catalysts	Solvent	Feed-to-catalyst ratio	Temp. (°C)	Time (h)	H ₂ (MPa)	Yield (wt.%)	Ref.
birch wood	5 wt.% Pd/C	methanol	10	180	2	3	14	4
birch wood	5 wt.% Pd/C + Yb(III)-triflate	methanol	10	180	2	3	43	4
oak sawdust	5 wt.% Pd/C	methanol	20	180	2	3	19	5
birch sawdust	5 wt.% Pd/C	H ₂ O	13	200	4	4	25.5	6
ethanol solv M. Giganteus	10 wt.% Pd/C	dioxane	5	200	24	0.1	12	7
poplar sawdust	5 wt.% Pd/C	methanol	10	200	3	2	27	8
birch sawdust	5 wt.% Pd/C	ethanol	10	200	3	3	17.4	9
corn stover	5 wt.% Pd/C	methanol	2	220	4	3	22.8	10
fermented corn stover	5 wt.% Pd/C	methanol	2	220	4	3	28.5	10
milled poplar	5 wt.% Pd/C	methanol	10	225	12	3.4	59	11
poplar sawdust	5 wt.% Pd/C	methanol	10	250	3	2	44	8
beech sawdust	5 wt.% Pd/C	methanol	5	250	3	3.0	25.3	12
alkali lignin	5 wt.% Pd/C	methanol	5	260	5	4.0	6.8	13
alkali lignin	5 wt.% Pd/C + CrCl ₃	methanol	5	260	5	4	28.5	13
bamboo sawdust	5 wt.% Pd/C	ethanol	6.7	260	4	4	24.4	14
hydrolyzed lignin	5 wt.% Pd/C and CrCl ₃	ethanol	5	280	4	2	18.9	15
bagasse powder	5 wt.% Pd/C	ethanol	1	230	4	3 (syngas)	35.7	This work
bagasse powder	5 wt.% Pd/C	ethanol	10	230	4	3 (syngas)	30.7	This work
bagasse powder	5 wt.% Pd/C	ethanol	10	230	10	3 (syngas)	35.1	This work

Table S9. Effects of reaction solvent on bagasse powder depolymerization. ^a

|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|

^a 1.0 g bagasse, 0.1 g 5 wt.% Pd/C, 20 mL, 230 °C, 6 h, 3.0 MPa syngas (CO/H₂=2/1), n.d.: not detected.

Table S10. Investigation of Pd/C catalyst stability. ^a

																
Entry	Cat.	Yield (mg/g)														Total (mg/g)
		H _a	H _b	H _c	H _{c1}	G _a	G _{b1}	G _{b2}	G _{b3}	G _c	G _{c1}	S _a	S _{b1}	S _{b2}	S _{b3}	
1	Pd/C-fresh	1.2	64.4	40.3	11.0	38.1	8.6	41.6	1.1	14.5	5.7	47.3	1.9	56.0	3.4	335.2
2	Pd/C-2h	1.4	68.9	37.3	7.6	37.8	9.8	44.1	0.9	14.9	4.7	53.4	1.9	40.9	2.8	326.4
3	Pd/C-4h	2.4	65.1	36.4	14.2	48.8	8.4	37.2	0.7	8.2	6.9	59.1	1.7	44.3	2.1	335.6
4	Pd/C-6h	1.9	65.9	36.7	13.5	45.3	9.2	35.1	0.6	10.1	7.0	55	1.8	44.0	1.8	327.9
5	Pd/C-8h	1.2	67.7	36.9	14.5	49.3	9.6	33.6	0.7	13.2	7.5	58.9	2.1	44.6	2.0	341.7
6	Pd/C-10h	2.1	67.7	37.5	13.7	48.0	9.2	36.9	0.7	13.8	7.9	57.3	2.1	47.1	2.2	346.1

^a 1.0 g bagasse, 0.1 g catalyst, 20 mL EtOH, 230 °C, 6 h, 3.0 MPa syngas (CO/H₂=2/1), n.d.: not detected.

Note: Pd/C-fresh is the fresh 5 wt.% Pd/C catalyst; Pd/C-2h, Pd/C-4h, Pd/C-6h, Pd/C-8h, and Pd/C-10h are obtained from 5 wt.% Pd/C after treatment at 3.0 MPa syngas (CO/H₂=2/1), 230 °C in EtOH for 2, 4, 6, 8 and 10 h, respectively.

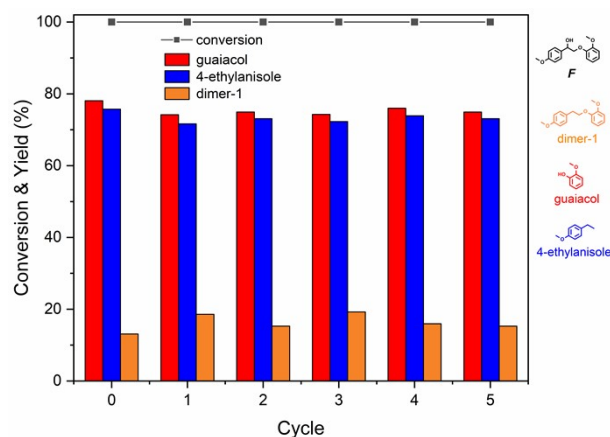


Fig. S8. The stability test of Pd/C for the catalytic conversion of model compound **F**.

Conditions: 0.4 mmol compound **F**, 0.1 g 5 wt.% Pd/C, 230 °C, 20 mL EtOH, 3.0 MPa syngas (CO/H₂=2/1), 1 h.

Note: After completion of reaction, the catalyst was recovered from the reaction mixture by simple vacuum filtration. The catalyst was washed thoroughly with EtOH to get rid of the product residue, subsequently, the separated catalyst was directly used for the subsequent run.

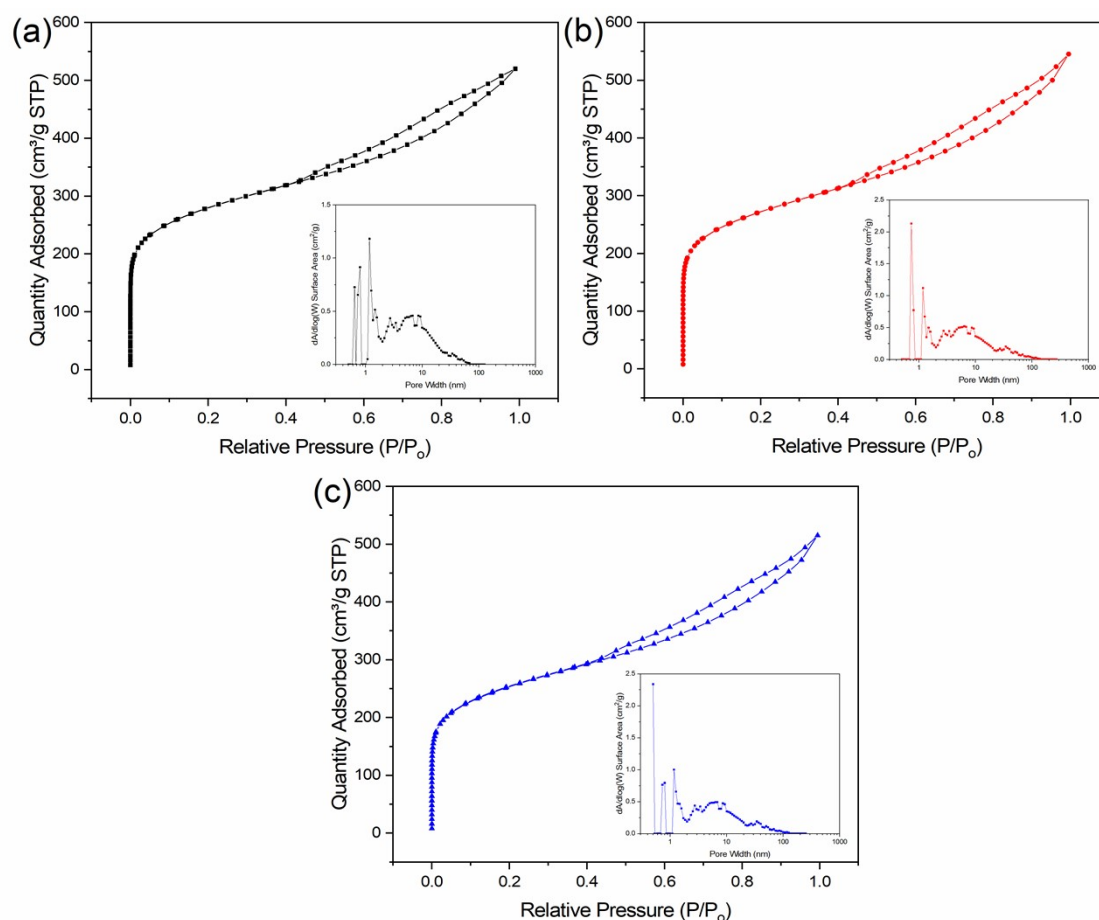


Fig. S9. N₂ adsorption-desorption isotherms and pore size distribution plots of (a) Pd/C-fresh, (b) Pd/C-4h, and Pd/C-cycle.

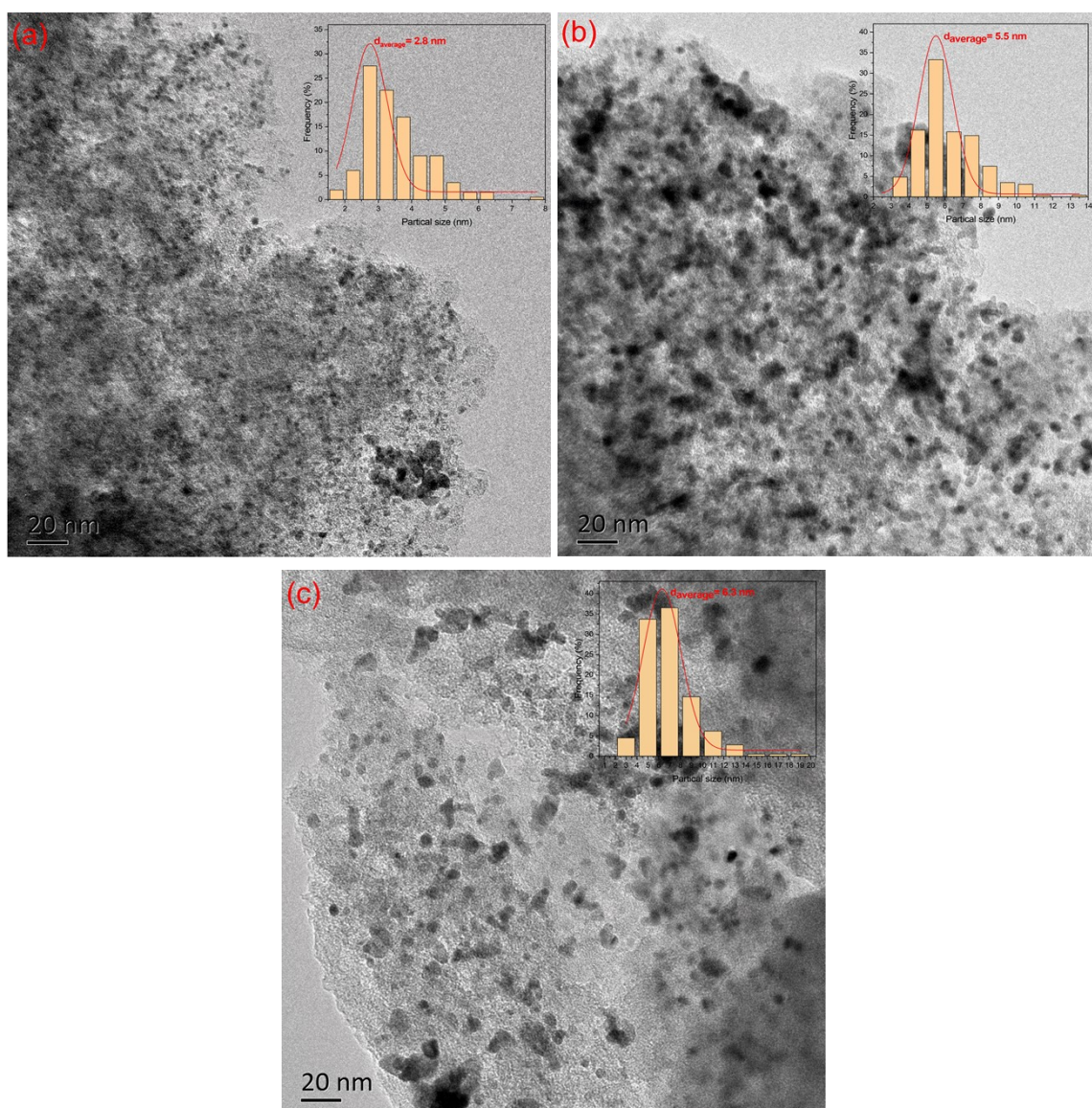
Note: Pd/C-fresh is the fresh 5 wt.% Pd/C catalyst, Pd/C-4h is obtained from 5 wt.% Pd/C after treatment at 3.0 MPa syngas (CO/H₂=2/1), 230 °C in EtOH for 4 h, and Pd/C-cycle is the catalyst recovered after 5 cycles of experiments.

Table S11. The physical properties of the samples.

Catalyst	Pd content (wt.%) ^a	Surface area m ² /g	Pore diameter (nm)	Pore volume (cm ³ /g)
Pd/C-fresh	4.81	906.3	4.7	0.78
Pd/C-4h	4.52	885.8	4.8	0.80
Pd/C-cycle	3.99	828.6	4.8	0.75

^a ICP-AES analysis.

Note: Pd/C-fresh is the fresh 5 wt.% Pd/C catalyst, Pd/C-4h is obtained from 5 wt.% Pd/C after treatment at 3.0 MPa syngas (CO/H₂=2/1), 230 °C in EtOH for 4 h, and Pd/C-cycle is the catalyst recovered after 5 cycles of experiments.

**Fig. S10.** TEM photograph of different Pd/C catalyst, (a) Pd/C-fresh, (b) Pd/C-4h, and (c) Pd/C-cycle.

Note: Pd/C-fresh is the fresh 5 wt.% Pd/C catalyst, Pd/C-4h is obtained from 5 wt.% Pd/C after treatment at 3.0 MPa syngas (CO/H₂=2/1), 230 °C for 4 h, and Pd/C-cycle is the catalyst recovered after 5 cycles of experiments.

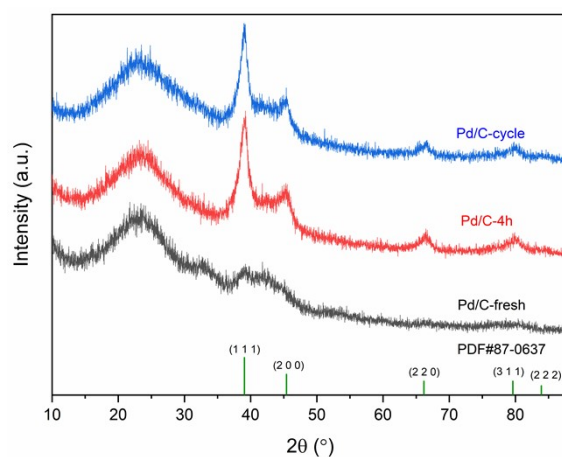


Fig. S11. XRD patterns of different Pd/C catalyst.

Note: Pd/C-fresh is the fresh 5 wt.% Pd/C catalyst, Pd/C-4h is obtained from 5 wt.% Pd/C after treatment at 3.0 MPa syngas ($\text{CO}/\text{H}_2=2/1$), 230 °C in EtOH for 4 h, and Pd/C-cycle is the catalyst recovered after 5 cycles of experiments.

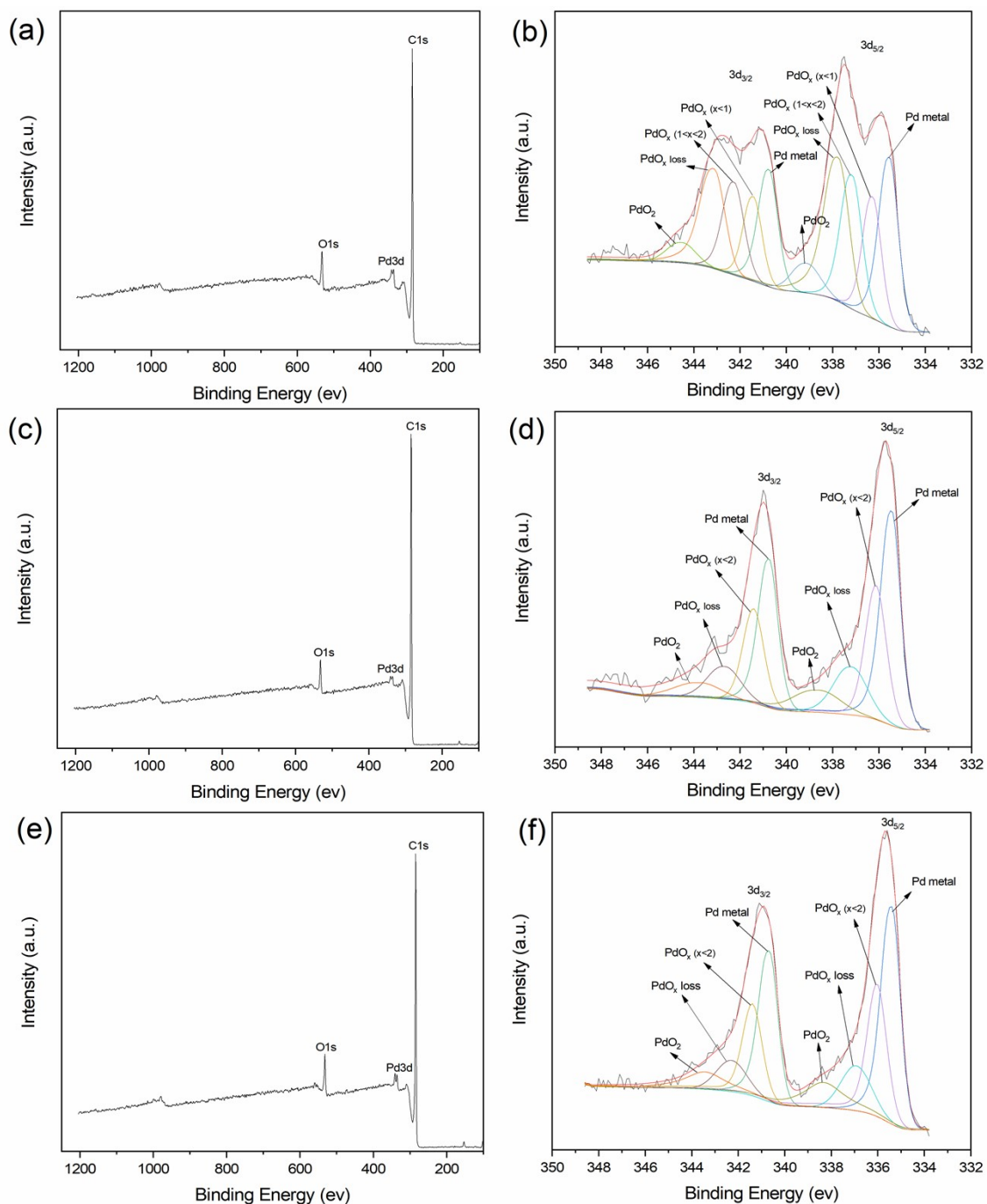


Fig. S12. XPS spectra of different Pd/C catalyst, (a, b) Pd/C-fresh, (c, b) Pd/C-4h, and (e, f) Pd/C-cycle.

Note: Pd/C-fresh is the fresh 5 wt.% Pd/C catalyst, Pd/C-4h is obtained from 5 wt.% Pd/C after treatment at 3.0 MPa syngas ($\text{CO}/\text{H}_2=2/1$), 230 °C for 4 h, and Pd/C-cycle is the catalyst recovered after 5 cycles of experiments.

Table S12. The XPS results of different samples

Catalyst	Pd metal	PdO_x	PdO_2	Pd metal/ PdO_x
Pd/C-fresh	335.61	336.43	338.87	0.7
Pd/C-4h	335.44	336.13	338.59	1.1
Pd/C-cycle	335.39	336.04	338.32	1.0

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