Supporting information

A sustainable and profitable biorefinery strategy: Efficiently converting lignocellulose to furfural, glucose and phenolic compounds

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1. Experimental section

1.1 Chemicals

Bamboo was obtained from a farm (Sichuang, China), which was ground to average size of 50 μm before use. The chemical composition (wt%) of the bamboo was 43.6 % cellulose, 28.3 % hemicellulose, 22.4 % acid insoluble lignin and 3.1 % acid soluble lignin. The composition (wt%) of the bamboo was determined according the method of National Renewable Energy Laboratory (NREL, 2008a, Preparation of samples for Compositional Analysis; 2008b, Determination of Structural Carbohydrates and Lignin in Biomass.). LiCl, $Al_2(SO_4)_3$, formic acid and microcrystalline cellulose were purchased from Sinopharm Chemical Reagent Co. γ-valerolactone and isopropanol were got from Aladdin Reagent Co. Guaiacol, 4-ethylguaiacol, 2-methoxy-4-methylphenol, syringic acid, 2,6-dimethoxy-4-methylphenol, 2,6-dimethoxyphenol, 4-methylphenol, phenol, syringaldehyde, 2-methoxy-4-propylphenol, 4-ethylphenol, eugenol and 4-hydroxy-3-methoxyacetophenone were supplied by Sigma-Aldrich company. Commercial 5 wt% Ru/C, Pt/C, Pd/C and Rh/C catalyst were purchased from Shanghai Macklin Biochemical Co., Ltd. All chemicals were analytical grade and used as received without further purification.

1.2 Product analysis

FAL and 5-HMF in the GVL was analyzed by gas chromatography (GC, 2010Plus, Shimadzu) for qualitative and quantitative tests. The gas chromatograph uses the SH-RTX-5 column (30m×0.32mm×0.5um), and the flame ionization detector (FID) were used to determine the volatile components with 0.43 mL min^{-1} of gaseous helium as the carrier gas. The temperature of the injector was set to 260 °C, and the temperature of

the detector was 280 °C. The column temperature programming was adopted as follows: The initial temperature of the chromatographic column was set at 100 °C for 2 min, then heated up to 280 °C at the rate of 8.0 °C min^{-1}, and held at 280 °C for 10 min. Likewise, phenolic monomers are detected with the above-mentioned gas phase equipment. The initial temperature of the chromatographic column was set at 50 °C for 2 min, and the oven temperature program was raised with a ramp of 20 °C min^{-1} from 50 °C to 280 °C for 5 min. The injector and detector temperatures was kept at 275 °C and 280 °C, respectively. Besides, the FAL, 5-HMF and sugars in water phase were measured by HPLC (Agilent 1200 series) equipped with an amines column (Model HPX-87H, 300 mm×7.8 mm, Bio-Rad), a variable-wavelength detector (Model VWD-3×00(RS)), and a refractive index (RI) detector (Model RI-101, Shodex). The mobile phase was 5 mM H_2SO_4 at a flow rate of 0.6 mL/min. The temperature of the detector and column oven was maintained at 35 °C and 50 °C, respectively. Moreover, the chemical composition of HDO is determined by Anion Exchange Chromatography (HPACE, Dionex ICS-3000) equipped with a Carbopac PA-100 column (4×250 mm, Dionex), the mobile phase is 150 mM sodium hydroxide solution containing 100 mM sodium acetate, the flow rate is 0.4 mL/min, and the column temperature is 30 °C.

1.3 Preparation of molten salt hydrate

The purchased LiCl and deionized water were mixed according to the water/salt molar ratio = 3/1, then added to a 500 ML 316L stainless steel autoclave with Teflon lining, followed by stirring (800 rpm) at 60 °C for 30 min. The LiCl·$3H_2O$ was obtained after cooling to room temperature.

1.4 Dissolution of hemicellulose and lignin

Typically, 2.5 g bamboo, 30.0 g LiCl·3H$_2$O, 20.0 g isopropanol, 1.5 g formic acid were added into a 100 mL 316L stainless steel autoclave with Teflon lining, followed by stirring at 1000 rpm. Then, the reactor was pressurized by 2 Mpa of N$_2$ and heated at 140 °C for 1.5 h. Upon completing the reaction, the reactor was rapidly cooled in an ice bath, and the mixture was filtered through a 0.45 μm membrane to collect the solid and liquid products. The solid product was defined as **Solid-1** (rich in cellulose, 1.04 g). The solid products were washed 3-5 times with deionized water, freeze-dried, and stored in a constant temperature drying oven for further treatment. The main components of the liquid products are hemicellulose and lignin, defined as **Liquid-1**. After extraction distillation, **Liquid-1** is divided into a portion rich in lignin fragments (**Liquid-2**) and a portion rich in hemicellulose derivatives (**Liquid-3**).

1.5 Cellulose enzymatic hydrolysis

The enzymatic hydrolysis of the obtained **Solid-1**, microcrystalline cellulose and raw bamboo biomass was carried out at 50 °C for 72 h in a culture flask at 150 r/min, with 2% (w/v) solid loading in the 100 mL bottle containing 50 mM sodium acetate buffer (50 mL, pH = 4.8) and cellulase (Onozuka R-10, 25 FPU/g).

1.6 Lignin depolymerization

The above-obtained **Liquid-2** and 0.2 g commercial catalyst (*e.g.*, Ru/C) were put together in a 50 mL 316L stainless steel autoclave with Teflon lining, followed by stirring speed was fixed at 1000 rpm. Then, the reactor was pressurized by 2 Mpa of H$_2$ and heated at 220 °C for 4.0 h. After reaction, the reactor was rapidly cooled down in an ice bath, and the mixture was filtered through a 0.45 μm membrane to collect the

catalyst and liquid products. The liquid product is qualitatively and quantitatively analyzed by GC-MS and GC.

1.7 Hemicellulose-to-furfural conversion

Additionally, the obtained **liquid-2**, 15.0 g GVL and 0.15 g $Al_2(SO_4)_3 \cdot 18H_2O$ were added to a 100 mL 316L stainless steel autoclave with Teflon lining. N_2 was charged into the reactor at an initial pressure of 2.0 MPa to remove air, followed by programmed heating (heating rate =7.5 °C/min) up to the target temperature and stirring with 1000 rpm for a period of time (20~160 min). The products were analyzed by GC-MS and HPLC.

$$Furfural\ yield = \frac{mole\ of\ furfural}{mole\ of\ hemicellulose/xylan} \times 100\%$$

$$Energy\ consumption\ (kWh) = p\ (kW) \times t\ (h)$$

1.8 Computational simulations

Forcite and CASTEP module of the Materials Studio software was employed for the quantum chemistry calculations. The Van der Waals interaction is calculated by atom-based method with a cutoff radius of 18.5 Å to avoid the errors of relatively short-range non-bond interactions, while electrostatic summation is calculated by Ewald method to avoid the errors of long-range non-bond energy in periodic systems. The interactions of liquid-liquid molecular systems were calculated by blends module, and the molecular configurations of each system were equilibrated using COMPASSII forcefield. Flory-Huggins model were used to simulate the thermodynamics of mixing systems. The energy bin width is 0.02 kcal/mol, and selected 1×10^7 pair configurations to find the 100 lowest energy frames and the reference temperature is set at 423 K.

In traditional Flory-Huggins model, each component occupies a lattice site. For a lattice with coordination number Z, the mixing energy (E_{mix}) and interaction parameter (x) can be calculated by eq. (1-2).

$$E_{mix} = 0.5Z(E_{bs}+E_{sb}-E_{bb}-E_{ss}) \qquad \text{eq. (1)}$$
$$x = E_{mix}/RT \qquad \text{eq. (2)}$$

where E_{ij} is the binding energy between a unit of component i and a unit of component j. Blends distinguishes the components by using the role property: one component has a base role, the other has a screen role. A given base-screen combination can give four potentially different pairs, each of which will have an associated binding energy value: base-base pair (Ebb)，screen-screen pair (Ess)，base-screen pair (Ebs)，screen-base pair (Esb)

1.9 Characterization of solid-1 and microcrystalline cellulose

The crystallinity of the sample was analyzed with an X-ray diffractometer (XRD) at 30 mA and 40 kV, respectively, the scanning rate was 5 °/min, and the scanning range was 5° to 50°. The crystallinity index (CrI) is calculated as follows:

$$CrI = \frac{I002 - Ia}{I002} \times 100\%$$

I_{002} represents the diffraction intensity of the crystalline region ($2\theta = 22.5°$) of cellulose in the biomass component; Ia represents the diffraction intensity of the amorphous region ($2\theta = 18.5°$) of cellulose in the biomass component.

The composition and structure of the substrates and residues were determined by a PerkinElmer Spectrum One Fourier transform infrared spectroscope (FTIR). The attenuated total reflectance (ATR) method was adopted here over the scan area range

from 4000 to 500 cm^{-1} with resolution of 4 cm^{-1} and accumulation of 4 times.

1.10 Characterization of liquid-2 and hydrogenolysis products

Molecular weights of the Liquid-1 and hydrogenolysis products were measured by gel permeation chromatography (GPC). The instrumentused was a Waters high-performance liquid chromatography with a refractive index (RI) detector. The mobile phase is THF, and the constant column temperature is 30 °C. A calibration curve was acquired by polystyrene as standards. The electrospray ionization mass spectra (ESI-MS) was operated in positive ion mode with 1.60 kV detector voltage, 1.56 kV ionization voltage, and 100 kPa gas drying pressure. The source temperature and solvent removal temperature were set as 200 °C, and N_2 was used as carrier gas with the flow rate of 1.5 L /min.

**1.11 Life cycle assessment**

The LCA modeling software used was Gabi, and the CML2001 Characterization model was selected. It focuses on the following four environmental factors: HTP (Human Toxicity Potential), ADP (Abiotic Depletion Potential), AP (Acidification Potential) GWP (Global Warming Potential). The normalization benchmark, normalization factor and proportion are shown in Table S4.

2. Supporting Figures
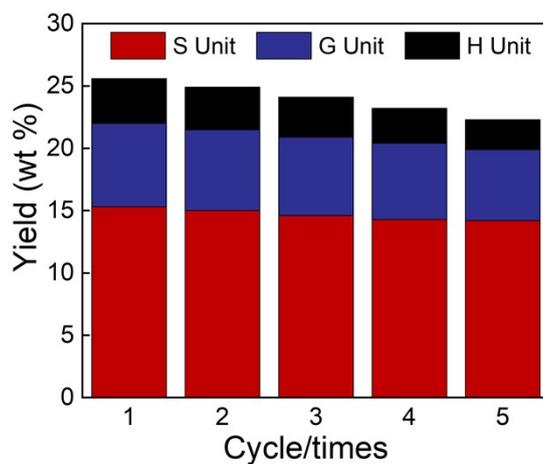
Figure. S1. Experiment on RU/C recycling of catalyst. Reaction conditions: 220 °C for 4.0 h.
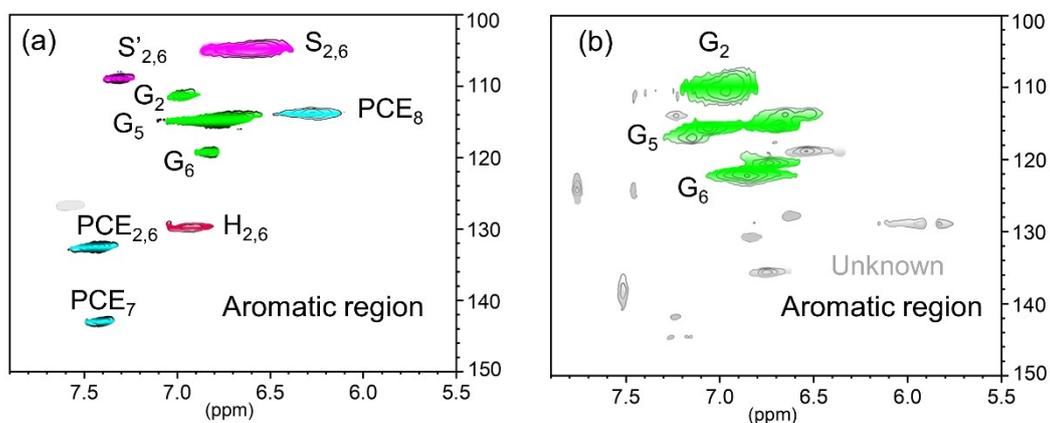
Figure. S2. 2D HSQC NMR spectrum of a: liquid-2 and b: reaction at 220 °C for 4 h.

3. Supporting tables

Table S1. The yield of phenolic monomers obtained over different catalysts.

	Pt/C	Pd/C	Ru/C	Rh/C
Guaiacol	0.95	1.21	2.51	1.57
4-Methl guaiacol	0.33	0.93	2.16	0.92
4-Ethyl guaiacol	0.61	0.82	1.03	0.29
Vanillin	0.46	0.21	0.32	0.35
4-Propyl guaiacol	1.01	0.53	0.24	1.04
Isoeugenol	0.29	0.20	0.44	0.16
Syringaldehyde	2.72	3.74	4.68	2.34
Syringol	2.59	3.28	4.75	2.52
4-Methy syringol	2.31	2.92	3.44	1.38
Syringic acid	1.88	1.87	2.43	0.46
Phenol	1.14	0.46	2.23	1.66
4-Methy phenol	0.96	0.64	1.37	1.24
Total yield (wt%)	15.25	16.81	25.60	13.93

Reaction conditions: 220 ℃, 4.0 h, 0.2 g catalysts, 22.1 g liquid-2 (20.0 g isopropanol, 1.5 g formic acid, 0.6 g lignin fragment)

Table S2. Assignments of ^{13}C-^{1}H signals in the HSQC spectra of Liquid-2 and lignin oil.

Label	δC/δH (ppm)	Assignments
B$_β$	53.51/3.05	Cβ-Hβ in β-β (resinol) (B)
Ar-OCH$_3$	56.22/3.71	C-H in methoxyls
P γ-OCH$_3$	58.41/3.28	C-H in methoxyls of 4-(3-methoxypropyl)
Aγ	59.99/3.57	Cγ–Hγ in β-O-4 substructures (A)
Cγ	62.23/3.78	Cγ-Hγ in phenylcoumaran (C)
A′γ	63.72/4.38	Cγ-Hγ in γ-acylated β-O-4 (A′)
P γ-OH	64.52/3.51	C-H in 4-Propanol
Bγ	71.19/3.79-4.16	Cγ-Hγ in β-β resinol (B)
β-β	75.33/3.80	Cβ-Hβ in resinol (B)
A$_{β(G)}$	83.50/4.39	Cβ-Hβ in β-O-4 linked to G units (A)
Bα	85.03/4.65	Cα-Hα in β-β resinol (B)
Aβ(S)	86.57/4.00	Cβ-Hβ in β-O-4 linked to S units (A)
S$_{2,6}$	104.23/6.62	C$_{2,6}$-H$_{2,6}$ in syringyl units (S)
S′$_{2,6}$	106.42/7.29	C$_{2,6}$-H$_{2,6}$ in oxidized syringyl units (S′)
G$_2$	111.40/6.96	C$_2$-H$_2$ in guaiacyl units (G)
PCE$_8$	114.25/6.31	C$_8$–H$_8$ in *p*-coumarate (*p*-CE)
G$_5$	115.81/6.73	C$_5$–H$_5$ in guaiacyl units (G)
G$_6$	119.47/6.74	C$_6$–H$_6$ in guaiacyl units (G)
H$_{2,6}$	128.27/7.15	C$_{2,6}$–H$_{2,6}$ in *p*-hydroxyphenyl units (H)
PCE$_{2,6}$	130.66/7.43	C$_{2,6}$–H$_{2,6}$ in *p*-coumarate (*p*-CE)
PCE$_7$	144.87/7.47	C$_7$–H$_7$ in *p*-coumarate (*p*-CE)

Table S3. Simple economic performance evaluation of the 100 kg waste bamboo fractionation and conversion process.

	Item	Quantity	Unit	Unit price (USD)	Unit price reference	Total (USD)
Cost	Formic acid	1.2[a]	kg	13	Alibaba[a], 2022	15.600
	Water	33.6[b]	kg	0.00048	NANJING WATER[b], 2022	0.016
	Power-1[e]	153.3[c]	kWh	0.09	SGCC[c],2022	12.841
	Power-2[f]	225.6	kWh	0.09	SGCC[c],2022	20.304
	Labor [e]	60.0[d]	h	2.24	MOHRSS[d], 2022	134.40
	Labor [f]	24.0	h	2.24	MOHRSS[d], 2022	53.760
	Equipment depreciation	1.0	times	13.0	An assumed price [g]	13.0
	Product storage	5.0	day	4.0	An assumed price [h]	20.0
Revenue	Glucose	27.20	kg	5.0	Alibaba[a], 2022	136.000
	Furfural	14.40	kg	15	Alibaba[a], 2022	216.000
	Lignin oil	23.32	kg	1.74	Minimum selling price[i]	40.577
				Balance= Revenue - Cost=122.66 (USD)		

[a]Alibaba 2022, http://www.alibaba.com. [b] Approximately 2% quality of formic acid loss during solvent recovery.

[b]Approximately 5% quality water loss during water recovery. NANJING WATER 2022, http://shuiwu.nanjing.gov.cn.

[c]Energy consumption of was calculated according to a lab-scale stainless steel reactor. SGCC 2022, http://www.sgcc.com.cn.

[d]Labor costs were calculated for 5 labors and 12 h per worker. MOHRSS 2022, http://www.mohrss.gov.cn.

[e] The power and manpower required for the operation of equipment.

[f] The power and manpower required for the separation step.

[g]The price distribution for the reaction and separation units is $10,000 and $3,000, with an estimated minimum of 1000 runs.

[h]The product weighs 64.92 kg and is expected to be stored for 5 days at $4 per day.

[i]The price of lignin oil is quoted from *Energy Environ. Sci*., 2021, 14, 4147.

Table S4. Data sheet for the proposed biorefinery strategy

		Materials	Quantity
Pretreatment (P1)	Input	Bamboo	100.0 kg
		LiCl·3H$_2$O	1200.0[a] kg
		Formic acid	60.0[b] kg
		Isopropanol	800.0[a] kg
		Electricity	50.6 kWh
	Output	Solid-1 (Cellulose)	52.0 kg
		liquid-2 (Lignin)	883.3 kg
		liquid-3 (Hemicellulose)	1232.4 kg
Fermentation (P2)	Input	Cellulase	8.1 kg
		Sodium acetate buffer	4000.0[b] kg
		Solid-1 (Cellulose)	52.0 kg
		Electricity	5.4 kWh
	Output	Saccharification liquid	4043.0 kg
Hydrolysis (P3)	Input	liquid-3 (Hemicellulose)	1232.4 kg
		Al$_2$(SO$_4$)$_3$	6.0[b] kg
		GVL	600.0[a] kg
		Electricity	20.8 kWh
	Output	Furfural-GVL	614.4 kg
		LiCl-H$_2$O	1207.2 kg
		Sugars derived	10.8
Hydrogenolysis (P4)	Input	liquid-2 (Lignin)	883.3 kg
		Ru/C	8.0[b] kg
		Hydrogen	0.25 kg
		Electricity	76.5 kWh
		Waste gas	0.11 kg
	Output	Lignin oil-Isopropanol	883.3 kg
Products separation (P5)	Input	Saccharification liquid	4043.0 kg
		Furfural-GVL	614.4 kg
		Lignin oil-Isopropanol	883.8 kg
		Activated carbon[a]	1.9[a] kg
		Diatomite[a]	1.5[a] kg
		Electricity	225.6 kwh
	Output	Glucose	27.2 kg
		Cellulase buffer	4015.8 kg
		Lignin oil	83.8 kg
		GVL	600.0 kg
		Furfural	14.4 kg
		Ru/C	7.8 kg
		Formic acid	58.8 kg
		Isopropanol	800.0 kg

a: Chemicals that are assumed to have negligible losses in the recycling process.

b: The loss or deactivation of chemicals in the recycling process cannot be ignored.

Table S5. Normalized factors and proportion of environmental impact types under model CML 2001.

Index	Unit	Total quantity	Normalized factor	Proportion
GWP	kg CO2-equiv	5.22E+12	1.92E-13	0.29
AP	kg SO2-equiv	1.68E+10	5.95E-11	0.18
ADP	kg Sb-equiv	1.62E+08	6.17E-09	0.43
HTP	kg DCB-equiv	5.00E+11	2.00E-12	0.10

Table S6. LCA characterization results of the proposed biorefinery strategy.

	Unit	P1	P2	P3	P4	P5	Sum
GWP	kg CO2-equiv	1.59E-01	3.01E-01	7.14E-02	1.03E-02	4.26E-01	9.68E-01
AP	kg SO2-equiv	1.52E-02	1.18E-03	5.31E-03	3.83E-04	5.29E-04	2.26E-02
ADP	kg Sb-equiv	7.23E-05	2.91E-05	1.01E-05	1.85E-05	5.56E-05	1.86E-04
HTP	kg DCB-equiv	2.86E-02	1.77E-03	1.88E-04	1.24E-05	1.57E-05	3.06E-02

Table S7. LCA weighting results of the proposed biorefinery strategy.

	GWP	AP	ADP	HTP	Sum
Characterization	9.68E-01	2.26E-02	1.86E-04	3.06E-02	
Normalization	1.86E-13	1.34E-12	1.15E-12	6.12E-14	
Weighting	5.39E-14	2.42E-13	4.93E-13	6.12E-15	7.96E-13