### **Supplementary Materials**

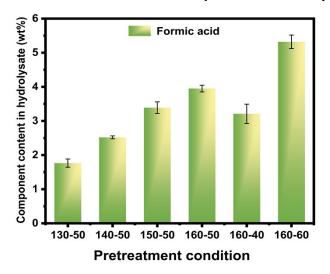
# Sustainable biorefinery for cascade fractionation of moso bamboo into furfural, glucan oligomers and less-condensed lignin

#### 1. Toluene-ethanol extraction

- a. Sample preparation: Weigh a known amount of dried sample and place it in the extraction bag. Insert the bag into the Soxhlet extractor, ensuring uniform distribution of the sample and preventing any leakage during extraction.
- b. Extraction solvent preparation: Prepare a toluene-ethanol mixture with a 2:1 volume ratio and perform distillation to remove impurities, ensuring the solvent achieves analytical-grade purity.
- c. Assembly of the extraction apparatus: Connect the round-bottom flask to the Soxhlet extractor, add 150 mL of the prepared toluene-ethanol solvent mixture to the round-bottom flask, attach the condenser, and ensure that the apparatus is securely sealed to prevent solvent evaporation during the extraction process.
- d. Reflux extraction: Heat the round-bottom flask in a water bath maintained at 90±2 °C to initiate reflux extraction, with the extraction cycle frequency controlled at 6–8 cycles per hour over a total duration of 6 hours.
- e. Post-extraction processing: Following extraction, the extraction bag was removed, and the residue was transferred onto a glass plate, then dried in a vacuum oven at 60 °C for 4 h to eliminate residual solvent.
- f. Recovery and reuse: Collect the mixed solvent in the round-bottom flask and transfer it to a rotary evaporator. Ethanol and toluene are separately recovered by adjusting the vacuum levels and water bath temperatures accordingly. The recovered ethanol and toluene can be directly reused in subsequent biomass extraction processes.

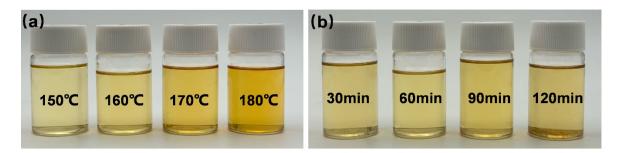
This recovery process not only reduces solvent consumption and minimizes environmental pollution, but also simplifies operations through low energy input, thereby aligning with the principles of green and sustainable biorefineries.

## 2. Impact of pre-extraction conditions on the separation efficiency of hemicellulose



**Fig. S1** The content of formic acid in the hydrolysate during p-TsOH pretreatment.

## 3. Preparation of furfural from biphasic system





**Fig. S2** The color and state of the organic phase under different reaction conditions (temperature, time and MIBK/filtrate ratios)

**Table. S1** 2D HSQC NMR data for the signal assignments in moso bamboo lignin samples in DMSO-d6

Label	δC/δH (ppm)	Assignments
$A_{\alpha}$	71.8/4.86	$C_{\alpha}$ – $H_{\alpha}$ in $\beta$ –O–4 unit (A) (Erythro)
OMe	56.63/3.72	C-H in Methoxy
$A_{\beta}(S)$	85.8/4.12	$C_{\beta}$ – $H_{\beta}$ in $\beta$ –O–4 linked to S (A)
$A_{\beta}(G)$	83.4/4.38	$C_{\beta}$ – $H_{\beta}$ in $\beta$ –O–4 linked to G (A)
$A_{\gamma}$	59.9/3.35-3.80	$C_{\gamma}$ – $H_{\gamma}$ in $\beta$ – $O$ –4 substructures (A)
Α',	63.0/4.36	$C_{\gamma}$ – $H_{\gamma}$ in $\gamma$ -acylated $\beta$ – $O$ –4 (A')
$BD_{lpha}$	76.0/4.81	Cα-Hα in benzodioxane substructures
$HK_{lpha}$	44.5/3.67	Cα-Hα in Hibbert ketone
$HK_{\gamma}$	67.1/4.19	Cγ-Hγ in Hibbert ketone
$B_{\alpha}$	84.8/4.66	$C_{\alpha}$ – $H_{\alpha}$ in $\beta$ - $\beta$ resinol (B)
$B_{\beta}$	53.5/3.07	$C_{\beta}$ – $H_{\beta}$ in $\beta$ - $\beta$ (resinol) (B)
S <sub>2,6</sub>	103.9/6.70	C <sub>2,6</sub> —H <sub>2,6</sub> in syringyl units (S)
S' <sub>2,6</sub>	106.3/7.32	$C_{2,6}$ – $H_{2,6}$ in oxidized S units (S')
$G_2$	110.8/6.97	C <sub>2</sub> –H <sub>2</sub> in guaiacyl units (G)
G <sub>5</sub>	114.5/6.70	C <sub>5</sub> –H <sub>5</sub> in guaiacyl units (G)
$G_6$	119.0/6.78	C <sub>6</sub> –H <sub>6</sub> in guaiacyl units (G)
PCE <sub>2,6</sub>	130.2/7.48	C <sub>2,6</sub> —H <sub>2,6</sub> in p-coumarate (p-CE)
PCE <sub>7</sub>	144.8/7.51	C <sub>7</sub> —H <sub>7</sub> in p-coumarate (p-CE)
PCE <sub>8</sub>	113.7/6.24	C <sub>8</sub> –H <sub>8</sub> in p-coumarate (p-CE)