
Supporting Information

Enhancing H_2 yield from photoreforming of natural lignocellulose feedstock by two-stage thermo-alkaline hydrolysis pretreatment

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Materials and methods

1.1 Catalyst synthesis.

$SrTiO_3$-0.5 wt.%Pt were synthesized following a previous report[1, 2]. In a typical synthesis, 1000 mg of $SrTiO_3$ and 250 ml deionized water were added into a 500 ml beaker with. After ultrasonic 20 min, 125 μl H_2PtCl_8 solution was dropwise added into the beaker and stirred for 30 min. The solution was then stirred and dried at 80 °C. Finally, the samples were calcined in air at 500 °C for 3 h to remove the residual chlorine. It was then cooled naturally to room temperature.

1.2 Ion chromatography analysis.

Organic acids in TAH/TS-TAH of natural lignocellulose waste were tested by Ion chromatography with gradient elution method[1]. The column temperature and flow rate were set to 35 °C and 1 ml/min respectively.

1.3 Gas chromatography-mass spectrometry analysis.

Other components in TAH/TS-TAH of natural lignocellulose feedstock were analyzed by gas chromatography-mass spectrometry (GC-MS, Agilent 7890A-5975C, USA)[1]. The carrier gas was He and the GC column oven was 45 °C holding for 5 min. Then the column temperature was raised to 250 °C at a rate of 5 °C/min. All samples were extracted with dichloromethane before tested.

Supporting Figures

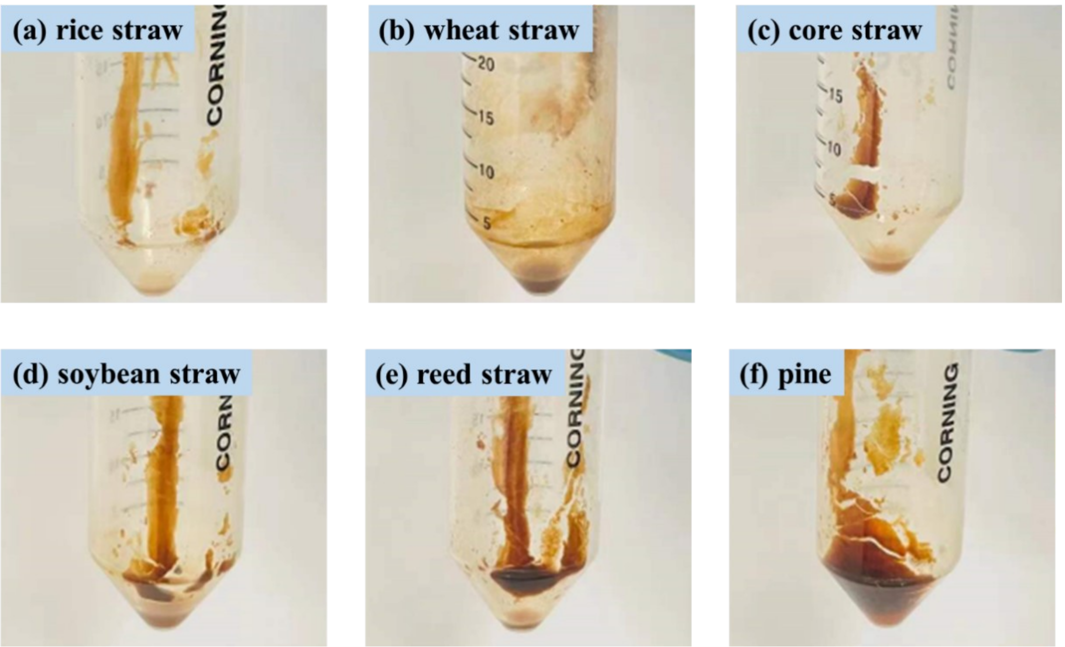
(a) rice straw
(b) wheat straw
(c) core straw
(d) soybean straw
(e) reed straw
(f) pine

Fig. S1 TAH-AS of natural lignocellulose waste.

The calculation of carbon balance

In the calculation, the chemical formulas of cellulose, hemicellulose and lignin are $(C_6H_{10}O_5)_n$, $(C_5H_8O_4)_n$, $(C_{81}H_{92}O_{28})_n$. The relevant formulas are shown below.

$$C_{cellulose} = \frac{M_C \times 6}{M_C \times 6 + M_H \times 10 + M_O \times 5}$$

$$C_{hemicellulose} = \frac{M_C \times 5}{M_C \times 5 + M_H \times 8 + M_O \times 4}$$

$$C_{cellulose} = \frac{M_C \times 81}{M_C \times 81 + M_H \times 92 + M_O \times 28}$$

$$C_{lactic} = \frac{M_C \times 3}{M_C \times 3 + M_H \times 6 + M_O \times 3}$$

$$C_{acetic} = \frac{M_C \times 2}{M_C \times 2 + M_H \times 4 + M_O \times 2}$$

$$C_{propionic} = \frac{M_C \times 3}{M_C \times 3 + M_H \times 5 + M_O \times 2}$$

$$C_{formic} = \frac{M_C \times 1}{M_C \times 1 + M_H \times 2 + M_O \times 2}$$

$$C_{tartaric} = \frac{M_C \times 4}{M_C \times 4 + M_H \times 6 + M_O \times 6}$$

$$C_{oxalic} = \frac{M_C \times 2}{M_C \times 2 + M_H \times 2 + M_O \times 4}$$

In the formulas, CX means the content of element C in certain substance X. Natural lignocellulose feedstocks were fixed at 8,000 mg/L in the research. We could calculate the amount of element C in natural lignocellulose feedstocks since the proportion of cellulose, hemicellulose and lignin were given. We could also calculate the element C in small-molecule acid. Then we could verify the carbon balance between natural lignocellulose feedstocks and small-molecule acid.

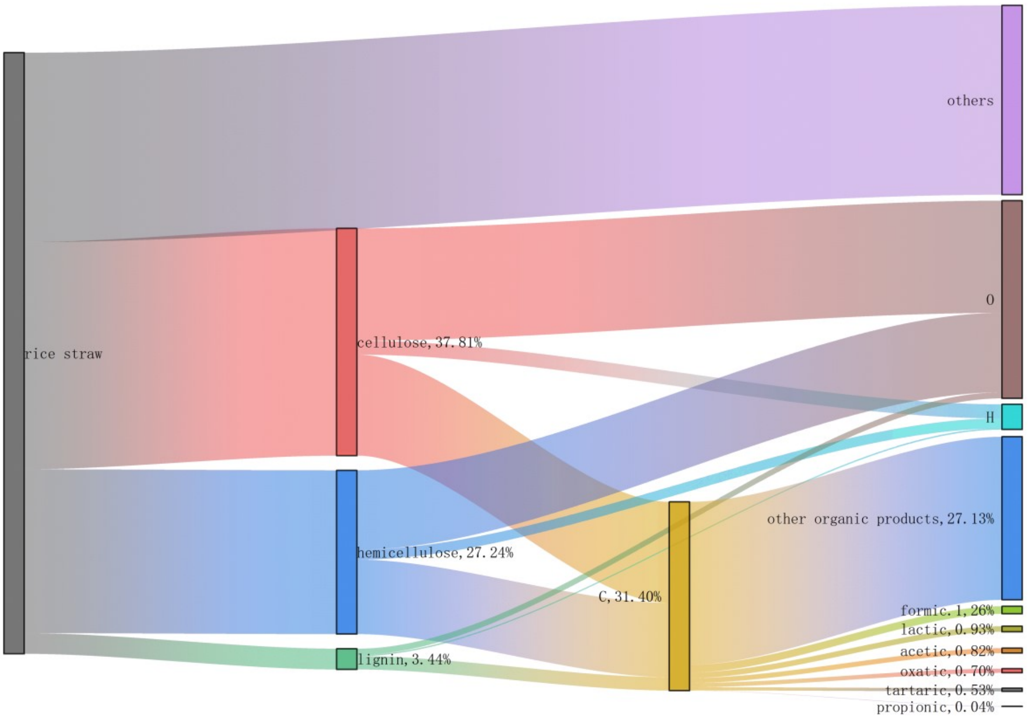

Fig. S2 Fate of element C in rice straw.

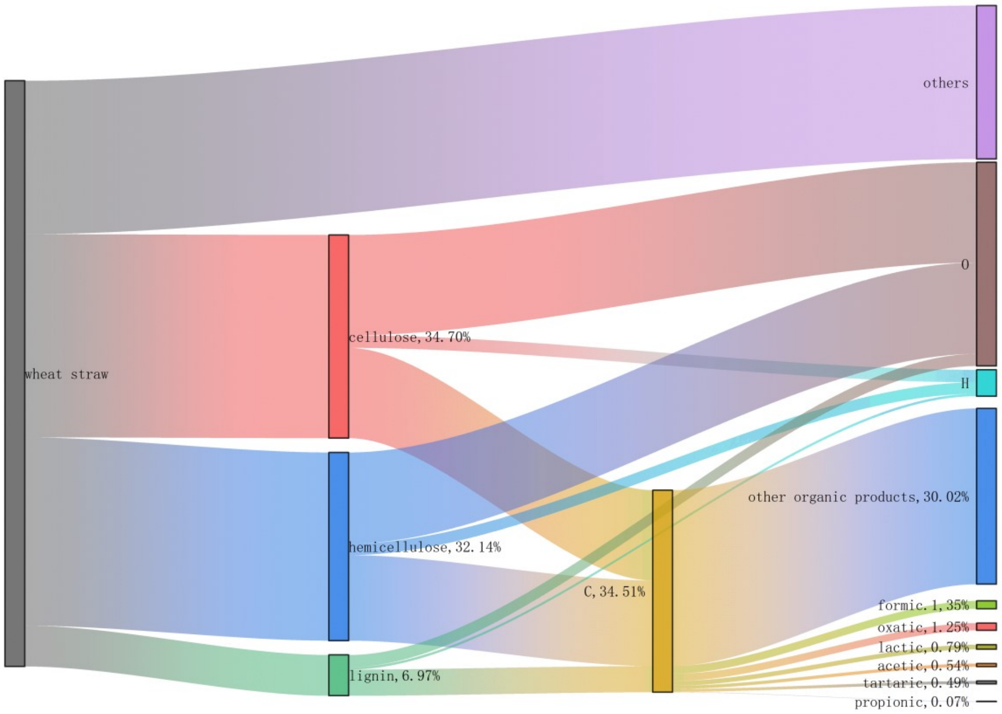

Fig. S3 Fate of element C in wheat straw.

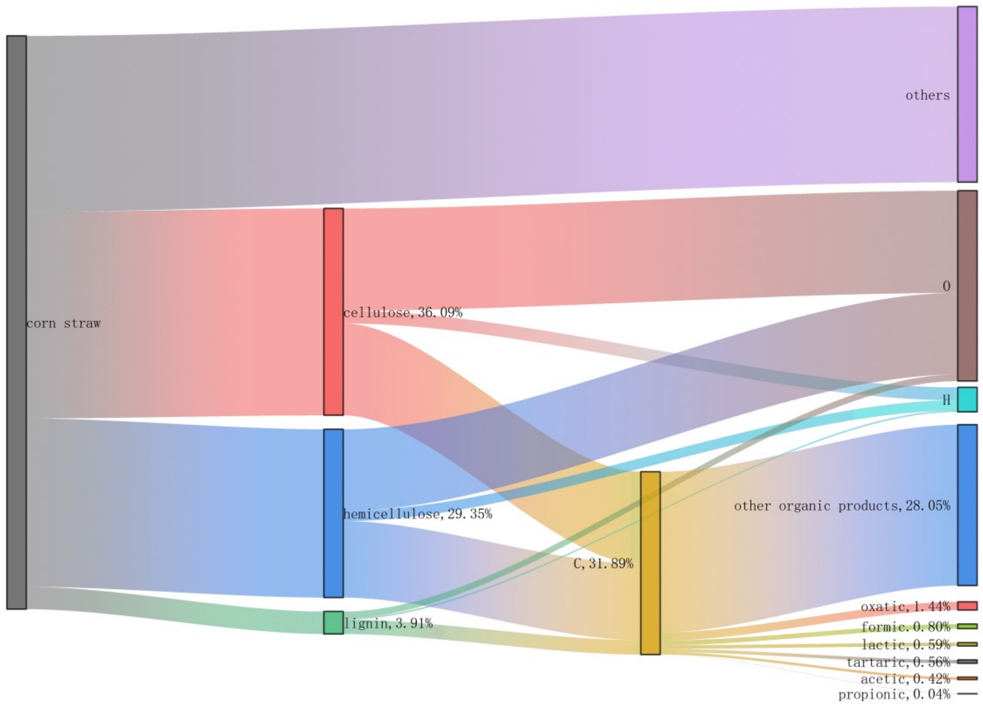

Fig. S4 Fate of element C in corn straw.

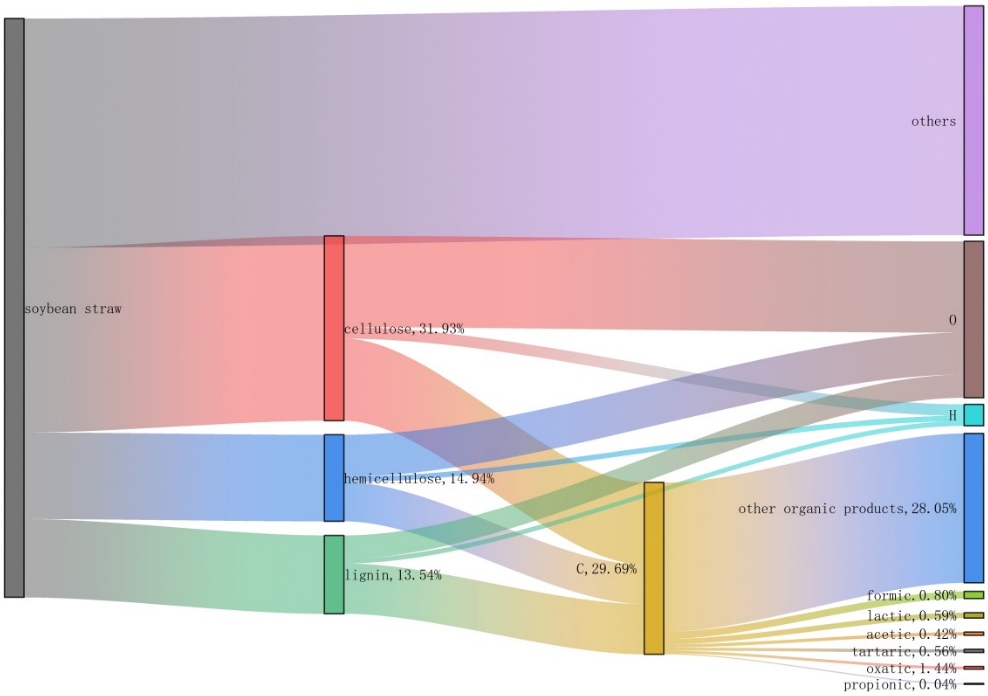

Fig. S5 Fate of element C in soybean straw.

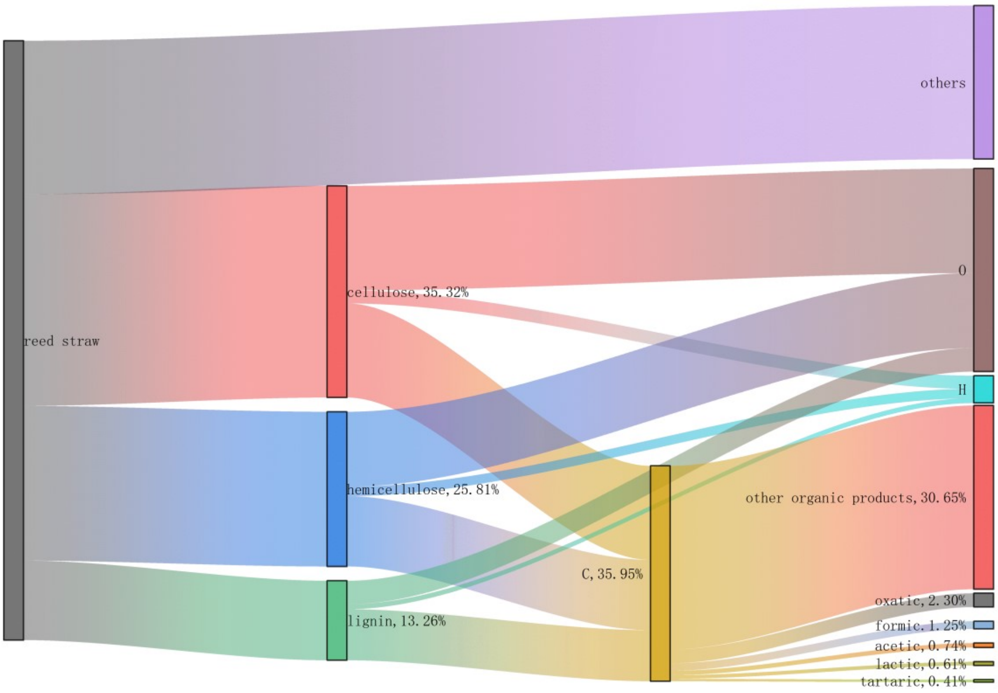

Fig. S6 Fate of element C in reed straw.

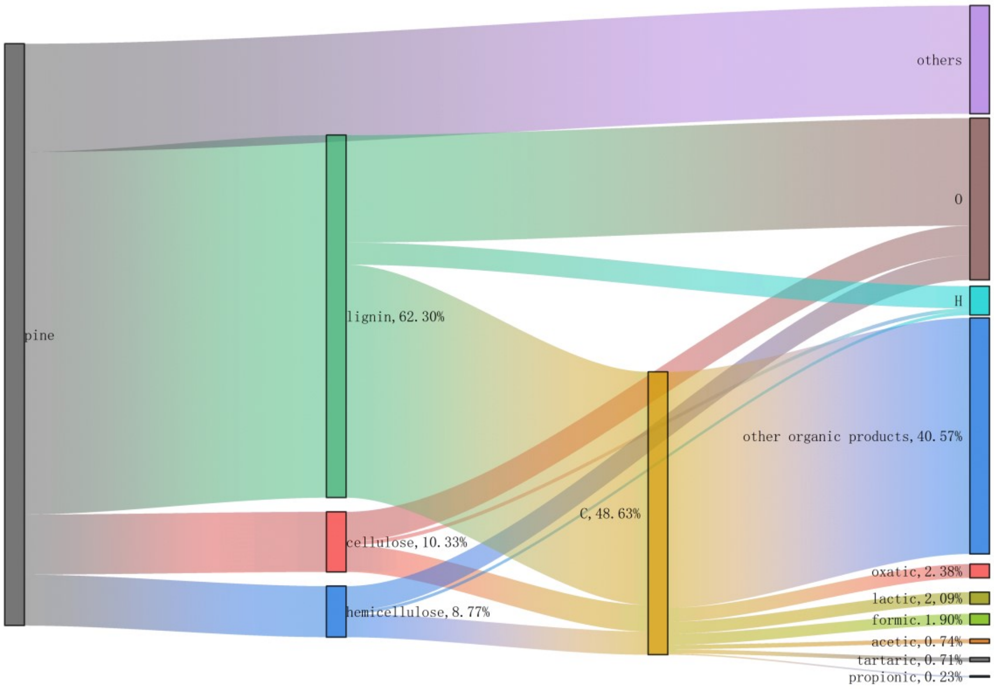

Fig. S7 Fate of element C in pine.

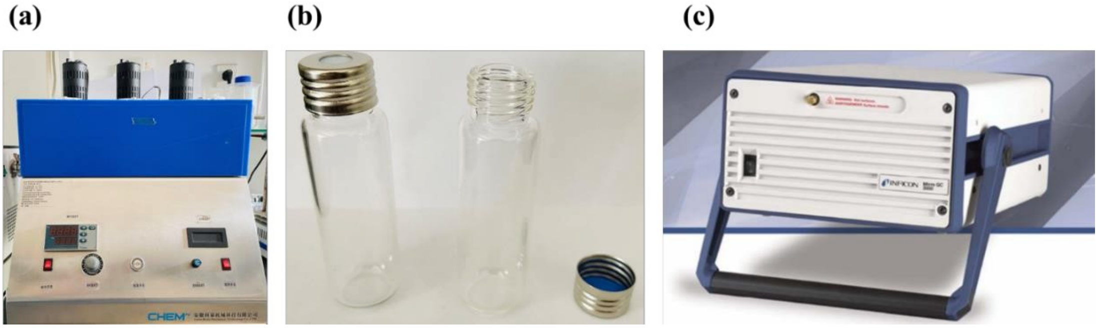

Fig.S8 (a)customized photoreactor;(b)customized reaction bulb;(c)Micro GC

Supporting Tables

Table S1 Elemental analysis of natural lignocellulose waste

Samples	C (wt.%)	H (wt.%)	O (wt.%)	N (wt.%)	S (wt.%)	Si (wt.%)	Total (%)
rice straw	38.75	5.31	38.23	0.82	0.10	6.43	89.64
wheat straw	42.11	5.50	41.27	0.78	0.13	2.13	91.92
corn straw	41.81	5.64	42.20	1.17	0.12	2.43	93.37
soybean straw	41.94	5.59	39.89	1.17	0.13	0.79	89.51
reed straw	43.60	5.69	37.90	2.06	0.19	1.98	91.42
pine	46.92	5.99	42.55	0.21	0.02	0.70	96.39

Table S2 Industrial analysis of natural lignocellulose waste

Samples	Moisture (wt%.)	Ash (wt.%)	Volatiles (wt.%)	Fixed carbon (wt.%)
rice straw	7.38	11.87	63.32	17.44
wheat straw	7.18	5.15	68.37	19.30
corn straw	7.15	6.87	66.78	19.20
soybean straw	8.29	3.83	69.80	18.09
reed straw	6.55	7.66	67.65	18.14
pine	7.23	0.11	74.68	17.99

Table S3 Distribution of main organic products in TAH solution of natural lignocellulose wastes

TAH	Detected Species	Molecular Formula	Area Pct (%)
rice straw	Undecane	$C_{11}H_{24}$	34.89
	6-ethyloct-3-yl-propyl ester-Oxalic acid	$C_{15}H_{28}O_4$	10.58
	2-cyano-Acetamide	$C_3H_4N_2O$	6.62
	4-aminocarbonyl-methyl ester-Benzoic acid	$C_9H_9NO_3$	6.02
wheat straw	2,3,4-trimethyl-Hexane	C_9H_{20}	33.96
	2-methyl-Decane	$C_{11}H_{24}$	6.68
	5-Aminoisoxazole	$C_3H_4N_2O$	6.10
	2-ethyl-1-methyl-Pyrrolidine	$C_7H_{15}N$	5.30
	Piperidine	$C_5H_{11}N$	3.93
corn straw	Undecane	$C_{11}H_{24}$	28.08
	Octacosane	$C_{28}H_{58}$	11.93
	2-Propenamide	C_3H_5NO	6.59
	2,4,4-trimethyl-Hexane	C_9H_{20}	4.65
	ethyl-1-methyl-Pyrrolidine	$C_7H_{15}N$	4.18
soybean straw	2-methyl-Octane	C_9H_{20}	32.23
	Heptadecane	$C_{17}H_{36}$	11.06
	3-ethylhexane	C_8H_{16}	7.03
	hexyl pentyl ester-Sulfurous acid	$C_{11}H_{24}O_3S$	5.78
	2-ethyl-2-methyl-Oxazolidine	$C_6H_{13}NO$	4.59
reed straw	1,8-Nonadien-3-ol	$C_9H_{16}O$	28.51
	3-methyl-5-propyl-Nonane	$C_{13}H_{28}$	11.00
	Piperazine	$C_4H_{10}N_2$	9.11
pine	Undecane	$C_{11}H_{24}$	25.94
	2,3,6-trimethyl-Decane	$C_{13}H_{28}$	12.79
	2,3-dimethoxy-Benzamide	$C_9H_{11}NO_3$	10.83
	5,6-dimethyl-Decane	$C_{12}H_{26}$	6.33
	2,6-Dimethyldecane	$C_{12}H_{26}$	5.67
	3,4,5,6-tetramethyl-Octane	$C_{12}H_{26}$	5.21

Table S4 Distribution of organic products in TAH-AS of natural lignocellulose

wastes

TAH-AS	Detected Species	Molecular Formula	Area Pct (%)
rice straw	1,3-bis(1,1-dimethylethyl)-Benzene	$C_{14}H_{22}$	9.46
	2,4-bis(1,1-dimethylethyl)-Phenol	$C_{14}H_{22}O$	4.52
	2,2'-methylenebis[6-(1,1-dimethylethyl)-4-methyl-Phenol	$C_{23}H_{32}O_2$	3.16
	1,3-bis(1-methylethenyl)-Benzene	$C_{12}H_{14}$	2.67
wheat straw	2,4-bis(1,1-dimethylethyl)-Phenol	$C_{14}H_{22}O$	12.24
	1,3-bis(1,1-dimethylethyl)-Benzene	$C_{14}H_{22}$	3.95
	2,4,6-trimethyl-Decane	$C_{13}H_{28}$	2.20
	2,6,10-trimethyl-Tetradecane	$C_{17}H_{36}$	1.59
corn straw	1,3-bis(1,1-dimethylethyl)-Benzene	$C_{14}H_{22}$	12.52
	2,2'-methylenebis[6-(1,1-dimethylethyl)-4-methyl-Phenol	$C_{23}H_{32}O_2$	5.81
	2,4-bis(1,1-dimethylethyl)-Phenol	$C_{14}H_{22}O$	3.74
	Eicosane	$C_{20}H_{42}$	1.12
soybean straw	1,3-bis(1,1-dimethylethyl)-Benzene	$C_{14}H_{22}$	12.63
	2,4-bis(1,1-dimethylethyl)-Phenol	$C_{14}H_{22}O$	6.05
	Eicosane	$C_{20}H_{42}$	4.54
	2,2'-methylenebis[6-(1,1-dimethylethyl)-4-methyl-Phenol	$C_{23}H_{32}O_2$	1.95
reed straw	2,4-bis(1,1-dimethylethyl)-Phenol	$C_{14}H_{22}O$	10.92
	1,3-bis(1,1-dimethylethyl)-Benzene	$C_{14}H_{22}$	5.02
	2,2'-methylenebis[6-(1,1-dimethylethyl)-4-methyl-Phenol	$C_{23}H_{32}O_2$	4.98
	Cyclohexasiloxane dodecamethyl	$C_{12}H_{36}O_6Si_6$	2.20
pine	1,3-bis(1,1-dimethylethyl)-Benzene	$C_{14}H_{22}$	12.56
	2,4-bis(1,1-dimethylethyl)-Phenol	$C_{14}H_{22}O$	5.77
	Eicosane	$C_{20}H_{42}$	5.32

	2,2'-methylenebis[6-(1,1-dimethylethyl)-4-methyl-Phenol	$C_{23}H_{32}O_2$	1.89

Table S5 Distribution of other organic products in TS-TAH solution of natural lignocellulose wastes

TS-TAH	Detected Species	Molecular Formula	Area Pct(%)
rice straw	3-ethyl-Hexane	C_8H_{16}	38.23
	Butylated Hydroxytoluene	$C_{15}H_{24}O$	27.03
	2,2'-methylenebis[6-(1,1-dimethylethyl)-4-methyl-Phenol	$C_{23}H_{32}O_2$	13.11
wheat straw	Octane	C_8H_{18}	49.05
	Butylated Hydroxytoluene	$C_{15}H_{24}O$	18.04
	2,2'-methylenebis[6-(1,1-dimethylethyl)-4-methyl-Phenol	$C_{23}H_{32}O_2$	8.21
corn straw	Octane	C_8H_{18}	56.42
	Butylated Hydroxytoluene	$C_{15}H_{24}O$	36.42
	2,2'-methylenebis[6-(1,1-dimethylethyl)-4-methyl-Phenol	$C_{23}H_{32}O_2$	5.32
soybean straw	Octane	C_8H_{18}	40.10
	Butylated Hydroxytoluene	$C_{15}H_{24}O$	26.64
	2,2'-methylenebis[6-(1,1-dimethylethyl)-4-methyl-Phenol	$C_{23}H_{32}O_2$	18.79
reed straw	Octane	C_8H_{18}	53.56
	Butylated Hydroxytoluene	$C_{15}H_{24}O$	33.23
	2,2'-methylenebis[6-(1,1-dimethylethyl)-4-methyl-Phenol	$C_{23}H_{32}O_2$	7.00
pine	Butylated Hydroxytoluene	$C_{15}H_{24}O$	26.87
	2,2'-methylenebis[6-(1,1-dimethylethyl)-4-methyl-Phenol	$C_{23}H_{32}O_2$	24.31
	Octane	C_8H_{18}	6.20
	5-Eicosene	$C_{20}H_{40}$	3.36

Table S6 Distribution of other organic products in TS-TAH-30 solution of natural lignocellulose wastes

TS-TAH-30	Detected Species	Molecular Formula	Area Pct（%）
rice straw	2,2'-methylenebis[6-(1,1-dimethylethyl)-4-methyl-Phenol	$C_{23}H_{32}O_2$	35.16
	2,4-dimethyl-Hexane	C_8H_{18}	24.44
	Butylated Hydroxytoluene	$C_{15}H_{24}O$	18.04
wheat straw	Octane	C_8H_{18}	48.01
	Butylated Hydroxytoluene	$C_{15}H_{24}O$	32.80
	2,2'-methylenebis[6-(1,1-dimethylethyl)-4-methyl-Phenol	$C_{23}H_{32}O_2$	9.11
corn straw	Octane	C_8H_{18}	49.51
	Butylated Hydroxytoluene	$C_{15}H_{24}O$	33.89
	2,2'-methylenebis[6-(1,1-dimethylethyl)-4-methyl-Phenol	$C_{23}H_{32}O_2$	8.02
soybean straw	2,2'-methylenebis[6-(1,1-dimethylethyl)-4-methyl-Phenol	$C_{23}H_{32}O_2$	31.19
	Octane	C_8H_{18}	30.75
	Butylated Hydroxytoluene	$C_{15}H_{24}O$	18.75
reed straw	2,2'-methylenebis[6-(1,1-dimethylethyl)-4-methyl-Phenol	$C_{23}H_{32}O_2$	35.16
	2,4-dimethyl-Hexane	C_8H_{18}	24.44
	Butylated Hydroxytoluene	$C_{15}H_{24}O$	18.04
pine	Octane	C_8H_{18}	30.24
	Butylated Hydroxytoluene	$C_{15}H_{24}O$	19.65
	2,2'-methylenebis[6-(1,1-dimethylethyl)-4-methyl-Phenol	$C_{23}H_{32}O_2$	19.31

Table S7 Estimation PR hydrogen enhancement efficiency of organic acids in TS-TAH of corn stover

TS-TAH	Organic acids as a share of TSC (wt.%), **a**	PR hydrogen yield for different single organic acids derived from TS-TAH (μmol，12 h), **b**	Actual contribution of hydrogen yield in TS-TAH (μmol，12 h), **c**
lactic acid	1.5	11.68	0.17
acetic acid	1.1	0.25	0.0026
propionic acid	0.8	1.00	0.008
formic acid	3.1	8.33	0.25
tartaric acid	1.8	22.24	0.39
oxalic acid	5.4	0.22	0.012
Totol	13.7	-	0.83
PR TS-TAH of core straw	-	4.7	4.7

Note: c= a×b

Table S8 Quantity of organic acid generated from TS-TAH

Samples	Cellulose (wt.%)	Hemicellulose (wt.%)	Lignin (wt.%)	Cellulose (mg/L)	Hemicellulose (mg/L)	Lignin (mg/L)	Lactic (mg/L)	Acetic (mg/L)	Propionic (mg/L)	Formic (mg/L)	Tartaric (mg/L)	Oxatic (mg/L)
rice straw	37.81	27.24	3.440	3025	2179	275.2	185.1	164.0	6.014	387.2	132.2	209.2
wheat straw	34.70	32.14	6.970	2776	2571	557.6	157.0	108.4	11.18	415.2	123.7	374.5
corn straw	36.09	29.35	3.910	2887	2348	312.8	118.3	84.54	6.426	244.1	140.3	430.8
soybean straw	31.93	14.94	13.54	2554	1195	1083	185.8	108.6	30.20	378.7	132.8	139.2
reed straw	35.32	25.81	13.26	2826	2065	1061	121.4	148.8	0.000	382.3	103.3	688.7
pine	10.33	8.770	62.30	826.4	701.6	4984	417.0	148.5	37.01	582.6	178.5	715.3

References

[1] W. Wang, B. Cheng, M. Zhao, E. Anthony, R. Luque, D.D. Dionysiou, Boosting H_2 yield from photoreforming of lignocellulose by thermo-alkaline hydrolysis with selective generation of a key intermediate product: Tartaric acid, Energ Convers. Manage. 257 (2022) 115444. https://doi.org/https://doi.org/10.1016/j.enconman.2022.115444.

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