Table S1

Current status of research on lignin Biotransformation Technology,Thermochemical Conversion Technology and Pretreatment Technology

Technology classification	Publish time	Processing method	Research Content
Biotransformation Technology	2016	Bioenzyme degradation technology	Rahman et al. explored whether Dyp-type biotinase has peroxidase activity towards lignin and reported the kinetic characteristics of biotinase towards lignin substrates [1].
	2020	Bacterial decomposition enzyme depolymerization	Prakram explored the improvement of lignin depolymerization by three bacterial ligninolytic enzymes and reviewed the bacterial sources, production conditions, enzyme properties, incentive structures, and industrial applications [2].
Thermochemical Conversion Technology	2022	Pyrolysis technology	Fan et al. explored the free radical footprint of coke and bio-oil produced from industrial lignin during pyrolysis and elucidated the relationship between free radical concentration and pyrolysis products [3].
	2023	Pyrolysis Technology and Catalysts	Wang et al. investigated the role of catalysts in assisting catalytic hydrolysis during pyrolysis by using the intermediate products formed by lignin pyrolysis together with Pd/C catalysts, aiming to elucidate the catalytic mechanism of catalysts on lignin pyrolysis process and the conversion path of lignin pyrolysis products [4].

	2017	Hydrothermal carbonization technology	Emmanuel et al. performed hydrothermal carbonization of industrial lignin and physicochemical characterization of the obtained hydrothermal coke to determine the optimal hydrothermal carbonization temperature of industrial lignin [5].
	2020	Fractionation process and hydrothermal carbonization	Renan et al. produced acidic sulfonated carbon from two Kraft lignins by a combination of fractionation process and hydrothermal carbonization and developed a simple and optimized method to obtain acidic sulfonated carbon [6].
	2021	Hydrothermal carbonization technology	Li et al. used enzymatic lignin as a carbon source to prepare three-dimensional multistage porous carbon by hydrothermal carbonization and investigated the operating parameters of the hydrothermal carbonization process to enhance the specific capacitance performance of carbon materials [7].
	2022	Hydrothermal carbonization technology	Tian et al. produced hydrochar by hydrothermal carbonization of amine-modified black liquor lignin and characterized its physicochemical properties using various analytical techniques, which revealed a significant effect of hydrochar on the adsorption of Cr from wastewater [8].
	2022	Pyrolysis and hydrothermal carbonization technology	Lukas et al. hydrothermally carbonized Kraft lignin and pyrolyzed the obtained hydrothchar with the feedstock by mixing it with a eutectic salt mixture, aiming to investigate the effect of the eutectic salt mixture on the coke conversion and to reveal the typical characteristics of the material [9].

	2022	Hydrothermal carbonization technology	Lin et al. used bio-oil as a medium for hydrothermal carbonization of lignin, aiming to investigate the effect of organic matter in bio-oil on the properties of hydrochar, and found that bio-oil can effectively improve the combustion performance of hydrochar [10].
	2022	Hydrothermal carbonization technology	Kenneth et al. investigated the effect of hydrothermal carbonization temperature and holding time on the physicochemical properties of different extracted lignin, and found that the extraction conditions of lignin affected the physicochemical properties of hydrothchar [11].
Pretreatment Technology	2019	Fenton oxidation and sulfonylation pretreatment	Ying et al. performed sequential Fenton oxidation with sulfomethylation pretreatment of lignin to reduce the negative effects of lignin during enzymatic saccharification, demonstrating that Fenton pretreatment as a pre-step followed by sulfomethylation pretreatment of lignin would help accelerate lignin depolymerization [12].
	2020	$ZnCl_2$ pretreatment and hydrothermal technology	Wu et al. obtained multistage porous carbon by hybrid hydrothermal carbonization of $ZnCl_2$ as an activator and catalyst with lignin, and found that the porous carbon material has excellent high electrochemical properties using various characterization techniques [13].
	2020	Alkali pretreatment and hydrothermal technology	Xue et al. used a combination of alkali pretreatment and hydrothermal pretreatment in their study for experiments on lignocellulosic organisms, and the results showed that the method accelerated the lignin depolymerization time [14].

	2020	Fenton Pretreatment	Wu et al. investigated the structural changes of lignin during pyrolysis and the changes of methoxy content in pyrolysis by-products using different concentrations of Fenton's solution for pretreatment of lignin [15].
	2022	Multi-phase Fenton catalysis	An et al. explored the extent of degradation of lignin pollutants by making composites of iron sulfide by a solvothermal method and then subjecting them to mixed Fenton catalysis with lignin model pollutants [16].
	2023	Mechanical catalysis, photocatalysis and Fenton oxidation	Dominic et al. subjected lignin to mechanical pretreatment or Fenton pretreatment in combination with photocatalysis to depolymerize lignin into aromatic building blocks and explored the synergistic effect of both pretreatments with photocatalysis to enhance the degree of photocatalytic depolymerization of lignin [17].

Note on the depth of penetration of XPS and FTIR on samples.

The performance and penetration depth of XPS and FTIR are different. XPS penetrates to a depth of about 10 nm and is used to characterize the surface structure of the sample[18] ; FTIR penetrates to a range of 0.5-5 μm and is used to characterize the internal structure of the sample[19].

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Table S2

The yield data of three sets of parallel experimental samples of HL and DAL after Fenton pretreatment.

	1-FHL	2-FHL	3-FHL	1-FDAL	2-FDAL	3-FDAL
Initial mass (g)	10.00	10.00	10.00	10.00	10.00	10.00
Final mass (g)	5.89	6.22	6.94	6.08	6.91	7.45

Table S3

The yield data of three parallel sets of experimental samples for the formation of hydrochar by HL, FHL, DAL and FDAL.

	1-HL-H	2-HL-H	3-HL-H	1-FHL-H	2-FHL-H	3-FHL-H	1-DAL-H	2-DAL-H	3-DAL-H	1-FDAL-H	2-FDAL-H	3-FDAL-H
Initial mass (g)	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00
Final mass (g)	0.97	1.02	1.28	1.32	1.36	1.55	1.02	1.11	1.38	1.49	1.54	1.71

Table S4

Experimental sample group 1: Elemental analysis, Sample yield, HHV and Energy recovery efficiency of two lignin feedstocks and their hydrochars at various stages of treatment.

Sample group 1	Ultimate analysis (wt%, dry basis)				LY(%)[a]	HY (%)[b]	HHV (MJ/kg)[c]	ER (%)[d]
	C	H	Fe	Ash				
1-HL	56.92	4.31	-	0.69	-	-	20.33	-
1-HL-H	71.76	4.15	-	0.44	-	32.33	25.73	40.92
1-FHL	68.44	4.03	0.33	0.72	69.40	-	25.06	-
1-FHL-H	83.99	3.86	-	0.51	-	44.00	29.71	52.16
1-DAL	56.07	4.86	-	0.66	-	-	20.46	-
1-DAL-H	79.83	4.61	-	0.34	-	34.00	27.84	46.26
1-FDAL	72.88	4.03	0.19	0.72	69.10	-	25.54	-
1-FDAL-H	88.76	3.04	-	0.43	-	49.67	31.65	61.55

[a] LY, lignin yield after Fenton pretreatment.

[b] HY, hydrochar yield.

[c] HHV, high heating value.

[d] ER, energetic recovery efficiency.

Experimental sample group 2: Elemental analysis, Sample yield, HHV and Energy recovery efficiency of two lignin feedstocks and their hydrochars at various stages of treatment.

Sample group 2	Ultimate analysis (wt%, dry basis)				LY(%)[a]	HY (%)[b]	HHV (MJ/kg)[c]	ER (%)[d]
	C	H	Fe	Ash				
2-HL	57.44	4.25	-	0.83	-	-	20.50	-
2-HL-H	72.13	4.03	-	0.63	-	34.00	27.88	46.24
2-FHL	69.47	4.12	0.24	0.84	58.90	-	25.32	-
2-FHL-H	84.40	3.92	-	0.74	-	45.33	30.60	54.78
2-DAL	57.11	4.74	-	0.85	-	-	20.63	-
2-DAL-H	79.88	4.57	-	0.51	-	37.00	28.36	50.86
2-FDAL	73.21	4.14	0.16	0.55	60.80	-	25.83	-
2-FDAL-H	89.43	2.96	-	0.57	-	51.33	31.99	63.57

[a] LY, lignin yield after Fenton pretreatment.

[b] HY, hydrochar yield.

[c] HHV, high heating value.

[d] ER, energetic recovery efficiency.

Experimental sample group 3: Elemental analysis, Sample yield, HHV and Energy recovery efficiency of two lignin feedstocks and their hydrochars at various stages of treatment.

Sample group 3	Ultimate analysis (wt%, dry basis)				LY(%)[a]	HY (%)[b]	HHV (MJ/kg)[c]	ER (%)[d]
	C	H	Fe	Ash				
3-HL	59.13	4.07	-	1.27	-	-	22.95	-
3-HL-H	72.32	4.09	-	0.91	-	42.67	28.29	52.60
3-FHL	70.62	3.88	0.39	0.87	62.20	-	27.14	-
3-FHL-H	85.02	3.80	-	0.52	-	51.67	32.51	61.89
3-DAL	55.27	4.89	-	0.65	-	-	21.07	-
3-DAL-H	80.01	4.50	-	0.89	-	46.00	29.15	63.64
3-FDAL	73.39	4.34	0.22	0.53	74.50	-	27.02	-
3-FDAL-H	90.10	2.76	-	0.41	-	57.00	32.87	69.34

[a] LY, lignin yield after Fenton pretreatment.

[b] HY, hydrochar yield.

[c] HHV, high heating value.

[d] ER, energetic recovery efficiency.

Table S5

The additional basic information for comparing samples before and after the treatment of FP and HTC.

Sample	Alkly (0-50ppm)	Methoxy (50-60ppm)	Aliphatic hydroxyl (70-75ppm)	O-Alkly (50-95ppm)	Aromatic (95-135ppm)	phenolic hydroxyl (150-158ppm)	O-Aromatic (135-165ppm)	Carbonyl (165-185ppm)
HL	9.41	6.94	3.37	22.39	28.65	2.41	17.77	3.84
HL-H	12.82	5.21	2.14	20.22	31.83	1.94	24.48	3.08
FHL	12.60	6.17	2.88	20.10	28.94	2.20	17.40	3.21
FHL-H	14.48	4.64	1.93	18.31	32.57	1.75	25.22	2.81
DAL	7.93	5.03	3.01	14.94	40.33	2.03	18.64	6.66
DAL-H	10.22	4.09	1.99	10.79	46.71	1.66	34.47	3.34
FDAL	8.07	4.88	2.54	12.57	44.18	1.83	16.31	4.39
FDAL-H	11.73	3.35	1.83	12.44	49.12	1.37	36.92	3.70

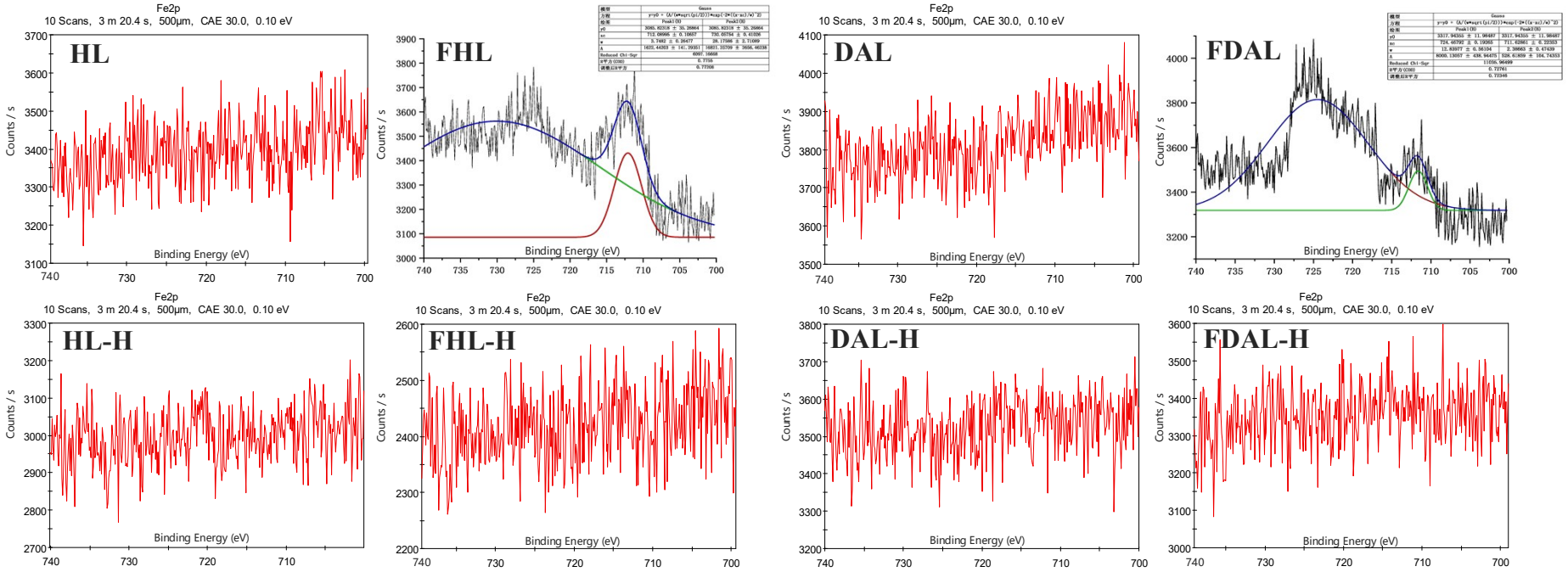

Fig. 1 The XPS spectra of four types of lignin and their hydrochars for the quantitative analysis of elemental Fe.

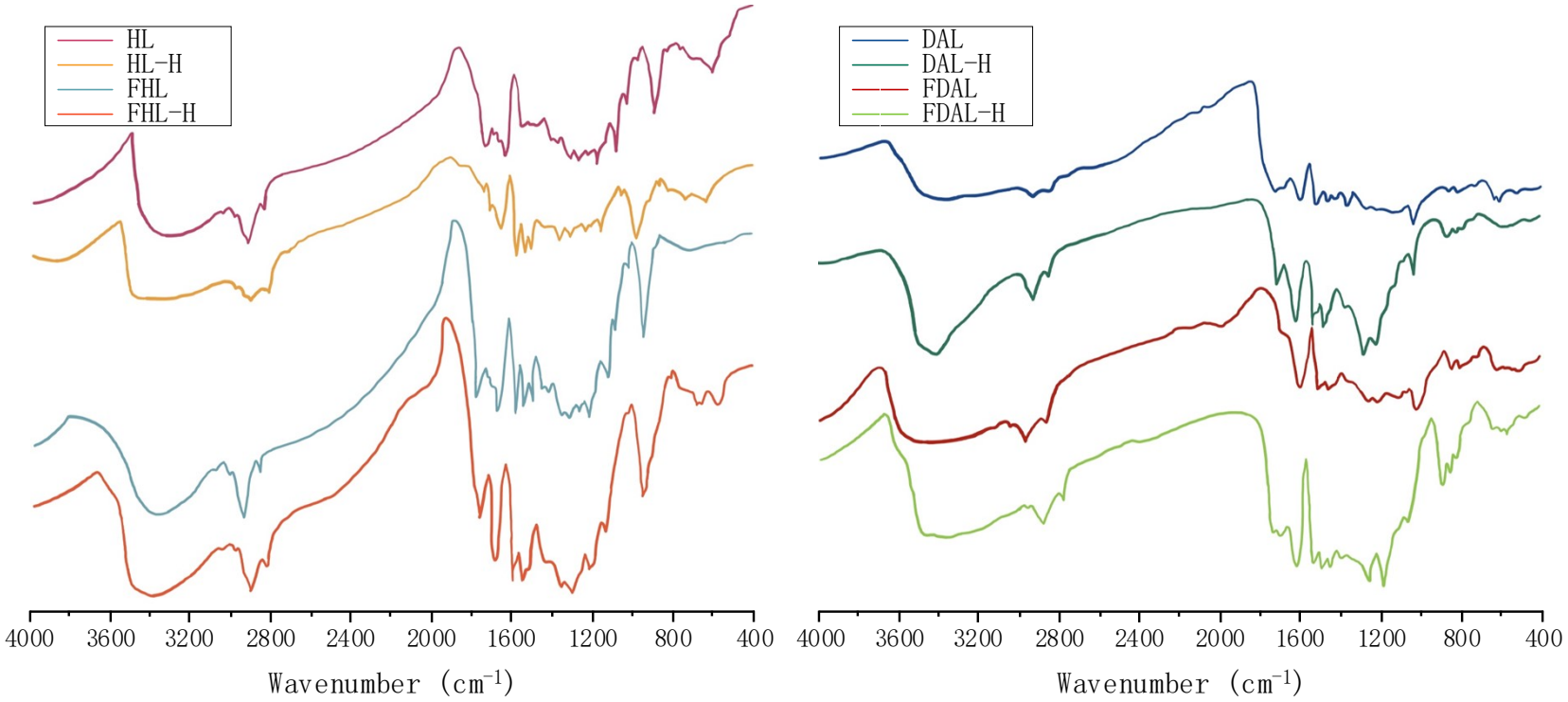

Fig. 2 The untreated lignin and its hydrochar FTIR spectra.

Abbreviations

FP	Fenton pretreatment	HTC	hydrothermal carbonization
FP-HTC	first FP of lignin followed by HTC	G	guaiacyl unit
S	syringyl unit	H	p-hydroxyphenyl unit
HL	herbal lignin	HL-H	hydrochar of HL
FHL	Fenton pretreated HL	FHL-H	hydrochar of FHL
DAL	de-alkalized lignin	DAL-H	hydrochar of DAL
FDAL	Fenton pretreated DAL	FDAL-H	hydrochar of FDAL