Electronic Supplementary Material (ESI) for Green Chemistry.

Supplementary Figures and Tables

Elucidating mechanism of Densifying Lignocellulosic biomass with acidic Chemicals (DLC) for lignocellulosic biorefinery

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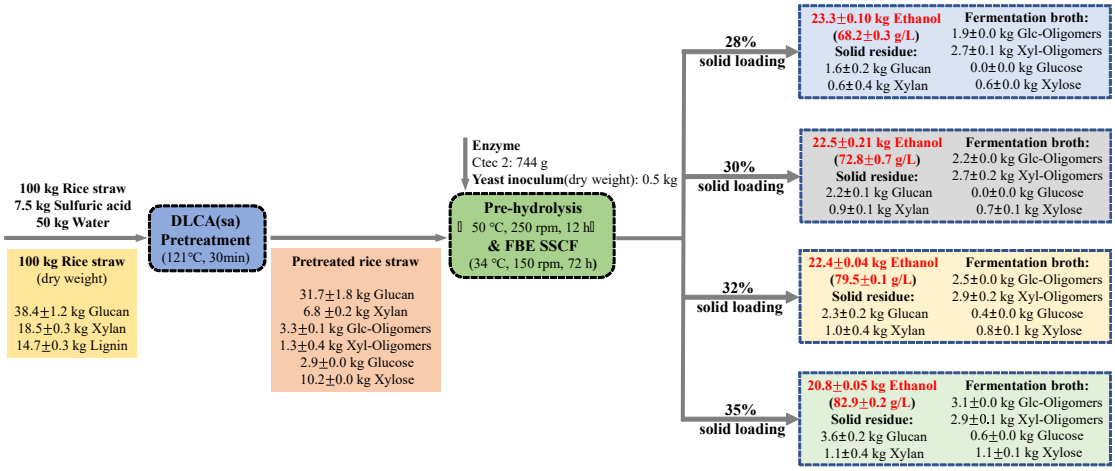

Fig. S1. Mass flow of glucan and xylan during DLCA(sa) pretreatment and SSCF for ethanol production. The mass balances were conducted based on 28%-35% solid loadings.

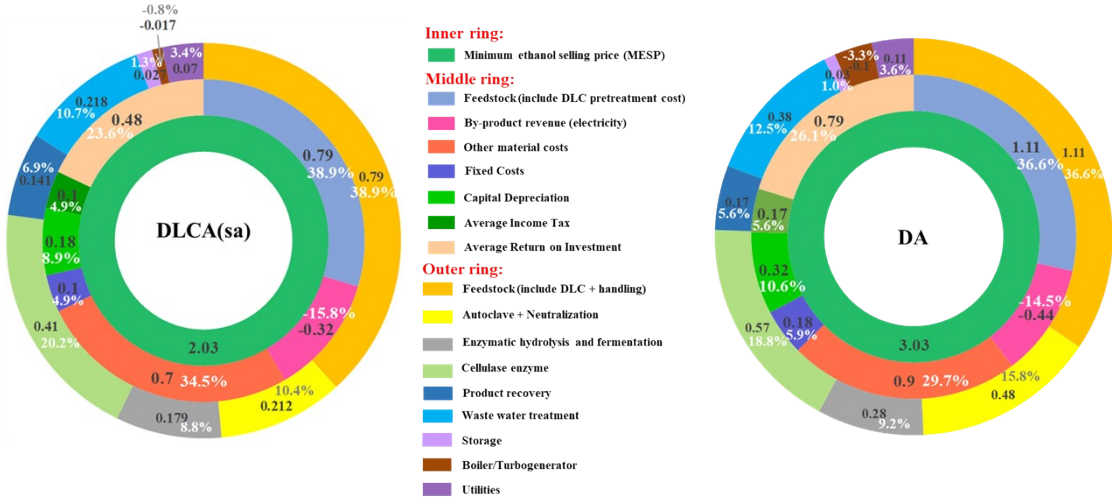

Fig. S2. Techno-economic analysis for the ethanol production from DLCA(sa) pretreatment and DA pretreatment. The TEA was performed based on NREL model with modifications [1]. The black font represents the costs of the component, unit is US$/per gallon, the white/gray font represents the relative contribution of the components of the MESP. TEA data related to DA pretreatment was adopted from previous publication [2].

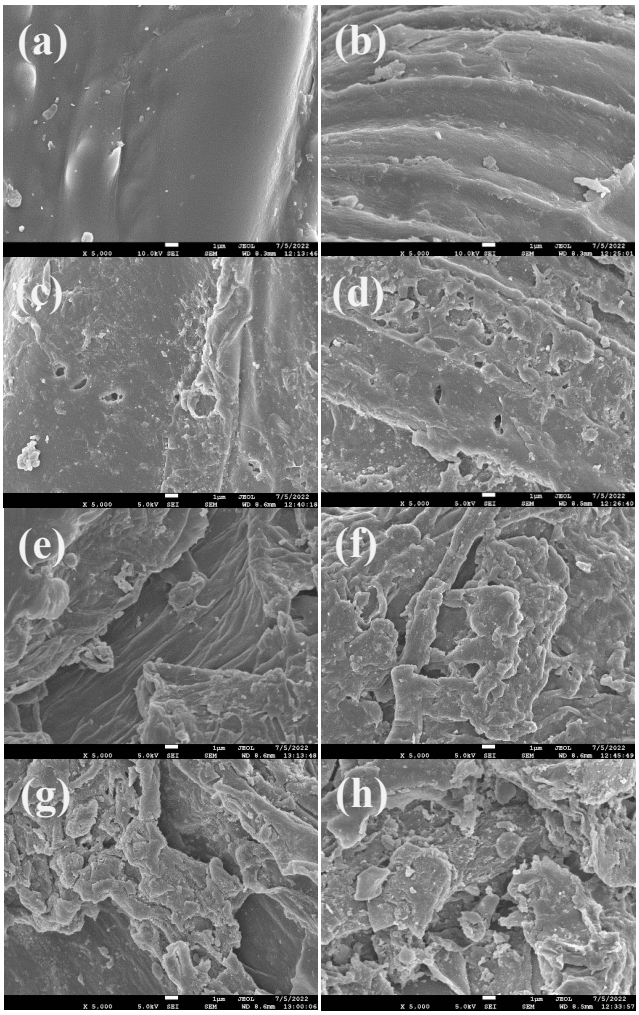

Fig. S3. SEM images of untreated RS (a), mDRS (b), DLC*-RS 20 ℃ (c), DLC*-RS 70 ℃ (d), DLC-RS (e), DLCA*-RS (f) DLCA-RS (g) and DA-RS (h). DLC* 20 ℃/70 ℃: DLC treatment by laboratory pelleting device under the temperature of 20 ℃/70 ℃.

Table S1 The information of all chemicals used in this study

Chemical reagent	Purity	Manufacturer
Sulfuric acid	AR, 95%-98%	Sinopharm Chemical Reagent Co., Ltd
Calcium hydroxide	AR, 95%	Sinopharm Chemical Reagent Co., Ltd
D-glucose	GC, ≥99.5%	Aladdin Reagent (Shanghai) Co., Ltd.
D-xylose	AR, 98%	Aladdin Reagent (Shanghai) Co., Ltd.
Avicel®PH-101	AR	Sigma-Aldrich Co., Ltd.
Citric acid	T, ≥99.5%	Shanghai Macklin Biochemical Co., Ltd.
Sodium citrate dihydrate	AR, 99%	Shanghai Yuanye Bio-Technology Co., Ltd.
Ethanol	HPLC, ≥99.8%	Aladdin Reagent (Shanghai) Co., Ltd.
Glycerol	AR, 99%	Shanghai Macklin Biochemical Co., Ltd.
5- Hydroxymethylfurfural	AR, 99%	Aladdin Reagent (Shanghai) Co., Ltd.
Levulinic acid	AR, 99%	Shanghai D&B biological science and technology Co., Ltd.

Furfural	GC, ≥99.5%	Aladdin Reagent (Shanghai) Co., Ltd.
Formic acid	HPLC, ≥98%	Aladdin Reagent (Shanghai) Co., Ltd.
Acetic anhydride	AR, 98.5%	Sinopharm Chemical Reagent Co., Ltd
Deuterated dimethyl sulfoxide	99.90%	Cambridge Isotope labratories, Inc.
Direct Red 28	BS	Shanghai Macklin Biochemical Co., Ltd.
Yeast Extract	AR, 99%	Thermo Fisher Oxoid Co., Ltd.
Tryptone	AR, 99%	Thermo Fisher Oxoid Co., Ltd.
Copper ethylenediamine hydroxide	AR, 98%	Acros Organics co., Ltd.
Chicago Sky Blue 6B (Birect Blue)	BS	Nanjing Duly Biotech Co., Ltd
Pyridine	AR, 99%	Shanghai Macklin Biochemical Co., Ltd.
Tetrahydrofuran	AR, 99%	Aladdin Reagent (Shanghai) Co., Ltd.
1,4-Dioxane	AR, 99%	Aladdin Reagent (Shanghai) Co., Ltd.
Vanillin	AR, 99%	Aladdin Reagent (Shanghai) Co., Ltd.
Sodium carbonate	GR, ≥99.9%	Shanghai Macklin Biochemical Co., Ltd.
Tetrahydrofuran	AR, 99%	Aladdin Reagent (Shanghai) Co., Ltd.
Methyl alcohol	HPLC, ≥99.9%	Aladdin Reagent (Shanghai) Co., Ltd.

Table S2 Detailed experimental parameters of various acid pretreatments

Experimental parameter chart	Type of treated biomass	Treat temperature	Treat time	Biomass loading of pretreatment (w/w)	Sulfuric acid dosage (g/g RS)	sulfuric acid conc. (g/L)
	DLC(sa)-RS	RT	3 days	75%	0.075	209.3
	DLCA(sa)-RS	121 ℃	30 min	25%	0.075	23.3
Figure 1	DA-RS	121 ℃	60 min	10%	0.05	5.6
		142 ℃	12 min	8.3%	0.145	13.2
		160 ℃	10 min	9.1%	0.11	11
Figure 2a-b	CA-RS	RT	3 days	75%	0.075	209.3

	CA-mDRS	RT	3 days	75%	0.075	209.3
	(CA+DA)-RS	121 ℃	30 min	25%	0.075	23.3
	(CA+DA)-mDRS	121 ℃	30 min	25%	0.075	23.3
	CA(70 ℃ 10 min)-mDRS	RT	3 days	75%	0.075	209.3
	(CA(70 ℃ 10 min)+DA)-mDRS	121 ℃	30 min	25%	0.075	23.3
Figure 2c-d	DA-DRS	121 ℃	30 min	25%	0.075	23.3
	D-DARS	121 ℃	30 min	25%	0.075	23.3
Figure 3&4	DLC*-RS	RT	3 days	75%	0.075	209.3
	DLC*-mDRS	RT	3 days	75%	0.075	209.3
	DLCA*-RS	121 ℃	30 min	25%	0.075	23.3
	DLCA*-mDRS	121 ℃	30 min	25%	0.075	23.3

Table S3. Schemes of biomass addition and enzyme addition for SSCF process

Process operation	Solid loading (w/w)	Process time				
		0h	12h	24h	36h	48h
Biomass addition (w/w)	28%	15%	5%	4%	4%	-
	30%	15%	5%	5%	5%	-
	32%	15%	5%	4%	4%	4%
	35%	15%	5%	5%	5%	5%
Enzyme addition (mg/g glucan)	28%	4	4	4	4	4
	30%	4	4	4	4	4
	32%	4	4	4	4	4

	35%	10	4	2	2	2

Table S4. Typical degradation inhibitors and their contents in pretreated RS

Type of Pretreatment		Content of inhibitors (mg/g pretreated biomass)					
		Formic acid	Levulinic acid	Furfural	HMF	Acetic acid	Phenols
Dillute acid (DA)	121℃ 60min	1.91±0.05	0.23±0.02	0.02±0.00	0.07±0.02	3.47±0.18	2.07±0.14
	142℃ 12min	2.14±0.04	1.08±0.05	0.09±0.01	0.19±0.01	5.22±0.20	6.15±0.29
	160℃ 10min	4.58±0.28	2.80±2.08	0.11±0.02	0.46±0.04	7.46±0.27	9.45±0.20
DLCA(sa)		1.47±0.06	0.18±0.04	0.00±0.00	0.17±0.02	8.81±0.62	2.94±0.32

Table S5. Relative changes of functional groups/chemical bonds for pretreated biomass

Bond position (cm^{-1})	Assignment	%Relative change of UT/pretreatd biomass					
		UT-RS	DLC*-mDRS 20 ℃	DLC*-mDRS 70 ℃	DLC(sa)-RS	DLCA*-mDRS	DLCA(sa)-RS
3340	O–H stretching of cellulose hydrogen bonds	-	7.25	11.70	15.92	31.05	34.42
2916	C–H stretching of methyl/methylene in cellulose	-	4.67	10.74	7.20	16.19	15.01
1720	Carboxylic acids/ester groups	-	6.71	7.62	8.33	10.62	10.58
1240	C–O adsorption of acetyl groups	-	14.26	17.47	19.56	28.46	34.28
898	Related to amorphous cellulose	-	3.69	8.36	6.03	15.17	16.27
1098/898	Ratio of amorphous cellulose to crystalline cellulose	0.83	0.86	0.89	0.89	0.9	0.91

%Relative change = 100*(intensity of UT-RS ─ intensity of pretreated RS)/intensity of UT-RS; where positive number indicates reduction.

Table S6. Subpeaks of C1s and O1s from XPS analysis for untreated and treated RS

Samples	C1s			O1s		
	C1(%) (~284.7 eV)	C2(%) (~286.6 eV)	C3(%) (~288.4 eV)	O1(%) (~531.3 eV)	O2(%) (~532.4 eV)	O3(%) (~533.3 eV)
LRS	67.49	23.96	8.55	13.89	67.24	18.87
DLC(sa)-RS	61.95	29.72	8.33	11.61	66.66	21.73
DLCA(sa)-RS	61.53	28.55	9.92	11.03	62.89	26.08
DA-RS	73.48	21.92	4.6	4.11	55.05	40.84

Subpeaks in C1s correspond to C1 (C-C), C2 (C-OH or C-O-C) and C3 (O-C-O or C=O), respectively. Subpeaks in O1s correspond to O1 (O-C=O and Ar-O-Ar), O2 (C-O-, C=O, C-O-C and O-C=O), O3 (Ph-O), respectively.

1. R. D. D. Humbird, L. Tao, C. Kinchin, D. Hsu, A. Aden, P. Schoen, J. Lukas, B. Olthof, M. Worley, D. Sexton, D. Dudgeon, *National Renewable Energy Laboratory, Golden, CO*, 2011.
2. J. Yu, Z. Xu, S. Chen, Y. Yu, C. Zhang, X. Chen and M. Jin, *Fuel*, 2021, DOI: 10.1016/j.fuel.2021.122603, 122603.