Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Table S1 Hexoses yield (% cellulose) and total sugars yield (% dry matter) from enzymatic hydrolysis supplied with +/- 1% Tween-80 in raw material and steam-exploded residues of rapeseed stalks.

Sample	Pretreatment	Hexoses yield		Total sugars yield	
		- 1%Tween-80	+ 1%Tween-80	- 1%Tween-80	+ 1%Tween-80
Bn13	Raw material	50.63±0.49	51.19±0.11	19.96±0.14	20.53±0.19
	Steam-exploded	58.51±1.03**	84.56±0.81**	28.07±0.4**	41.18±0.58**
		16%	65%	41%	101%
Bn08	Raw material	47.44±0.58	54.28±0.48	22.32±0.24	22.6±0.05
	Steam-exploded	50.91±1.98*	81.71±0.34**	25.71±0.95**	41.09±0.19**
		7%	51%	15%	82%
Bn15	Raw material	43.16±0.83	46.03±1.14	19.36±0.34	21.45±0.5
	Steam-exploded	50.49±0.05**	68.07±1.71**	26.27±0.03**	36.62±0.93**
		17%	48%	36%	71%

* And** indicated significant differences between raw material and SE residues by *t*-test at $p < 0.05$ and $p < 0.01$ (n=3). # Percentage of increased rates between the raw material and SE residues by subtraction of two values divided by the raw material. Data indicated mean ± SD (n=3).

Table S2 Monosaccharides proportion released from enzymatic hydrolysis.

Smaples	% hexoses			% pentoses	
	Mannose	**Glucose**	Galactose	Arabinose	**Xylose**
Bn13	1.64±0.13	**97.81±0.15**	0.36±0.03	3.09±0.27	**96.9±0.27**
Bn08	1.81±0.17	**97.67±0.22**	0.33±0.03	3.43±0.29	**96.56±0.29**
Bn15	2.05±0.35	**97.29±0.50**	0.43±0.13	3.25±0.15	**96.74±0.15**

Monosaccharides proportion analysis (hexoses and pentoses) of supernatant from enzymatic hydrolysis supplied with 1% Tween-80 after pretreatment with 5% CaO in steam-exploded residues of three rapeseed stalks by GC-MS. Data indicated mean ± SD (n=3).

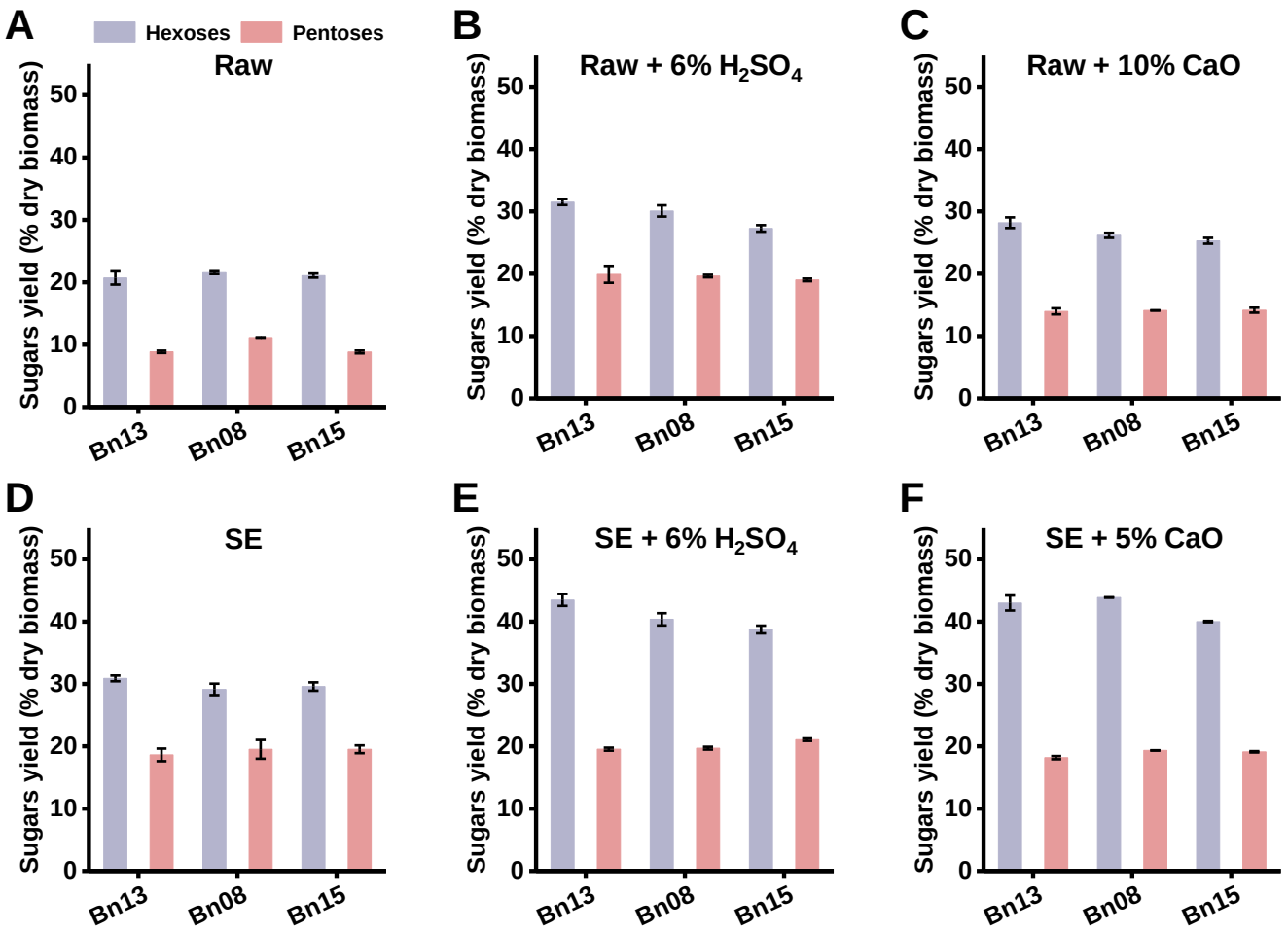

Fig. S1 Sugars yield (hexoses and pentoses, respectively) released from pretreatment and enzymatic hydrolysis supplied with 1% Tween-80 in raw materials and steam-exploded residues. (A) Raw material. (B) Raw material with 6% H_2SO_4. (C) Raw material with 10% CaO. (D) Steam-exploded residues. (E) SE residues with 6% H_2SO_4. (F) SE residues with 5% CaO. Data indicated mean ± SD (n=3).

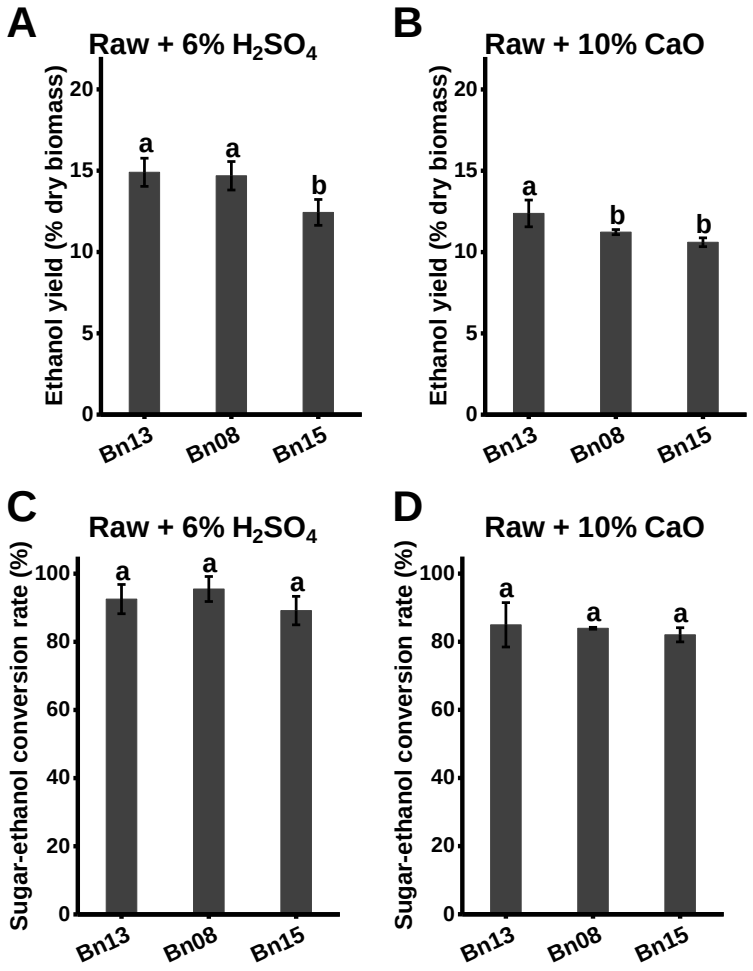

Fig. S2 Bioethanol yields released from yeast fermentation using total hexoses obtained from pretreatment and enzymatic hydrolysis. (A and C) Raw material with 6% H_2SO_4. (B and D) Raw material with 10% CaO. Different Letters (a, b, c) indicated significant difference by LSD-test at $p < 0.05$. Data indicated mean ± SD (n=3).

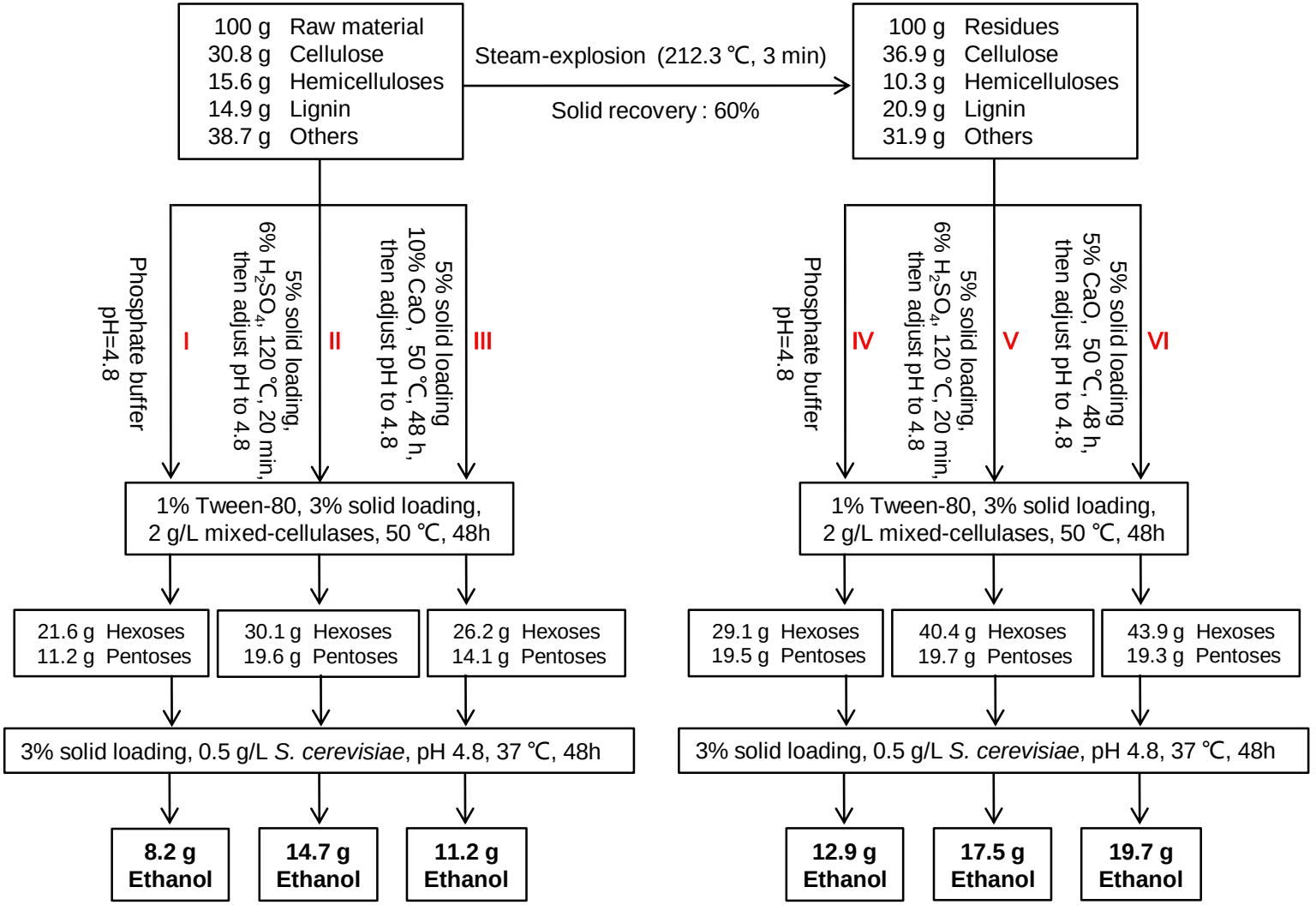

Fig. S3 Mass balance analysis for bioethanol production in rapeseed stalk (Bn08).

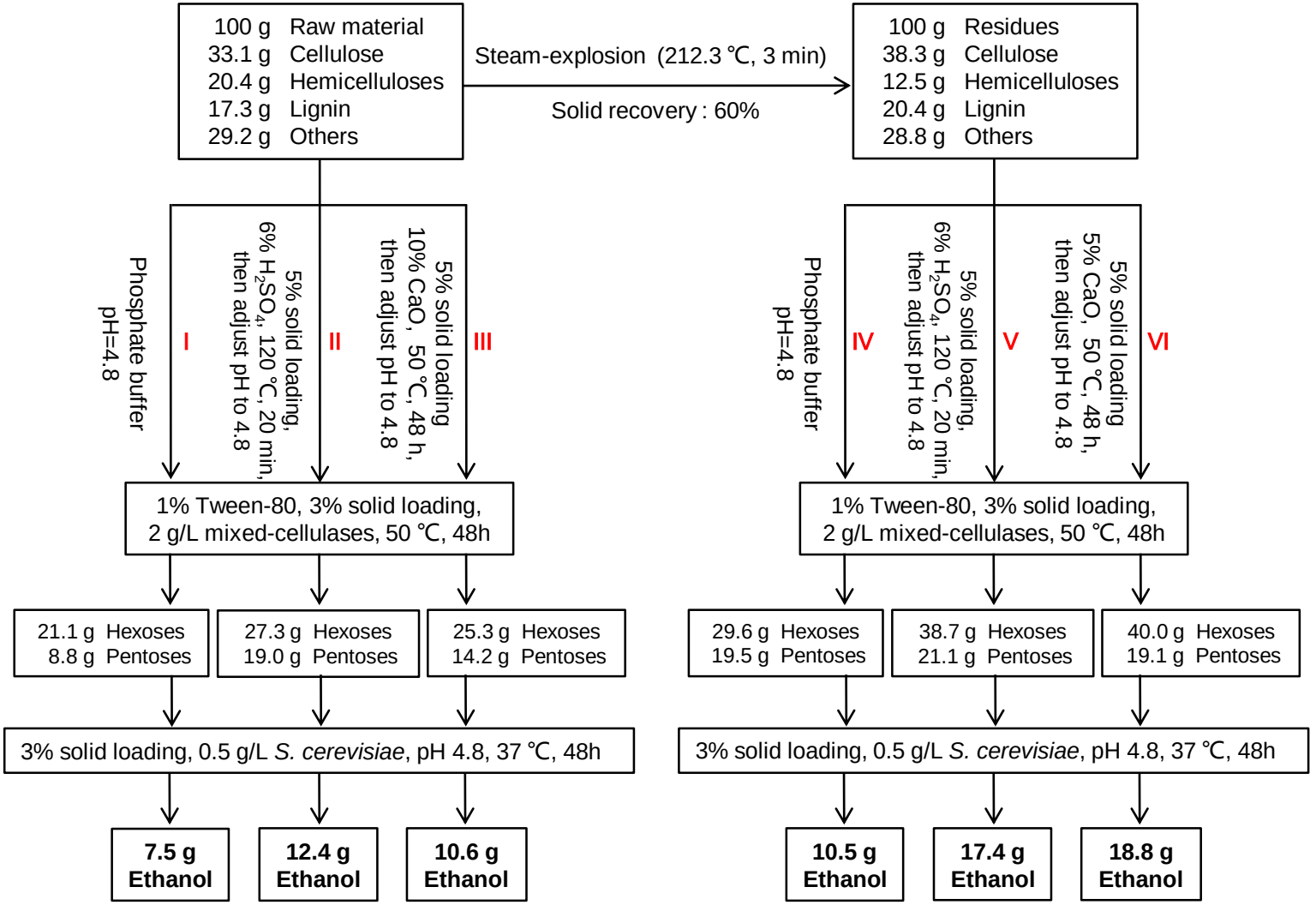

Fig. S4 Mass balance analysis for bioethanol production in rapeseed stalk (Bn15).

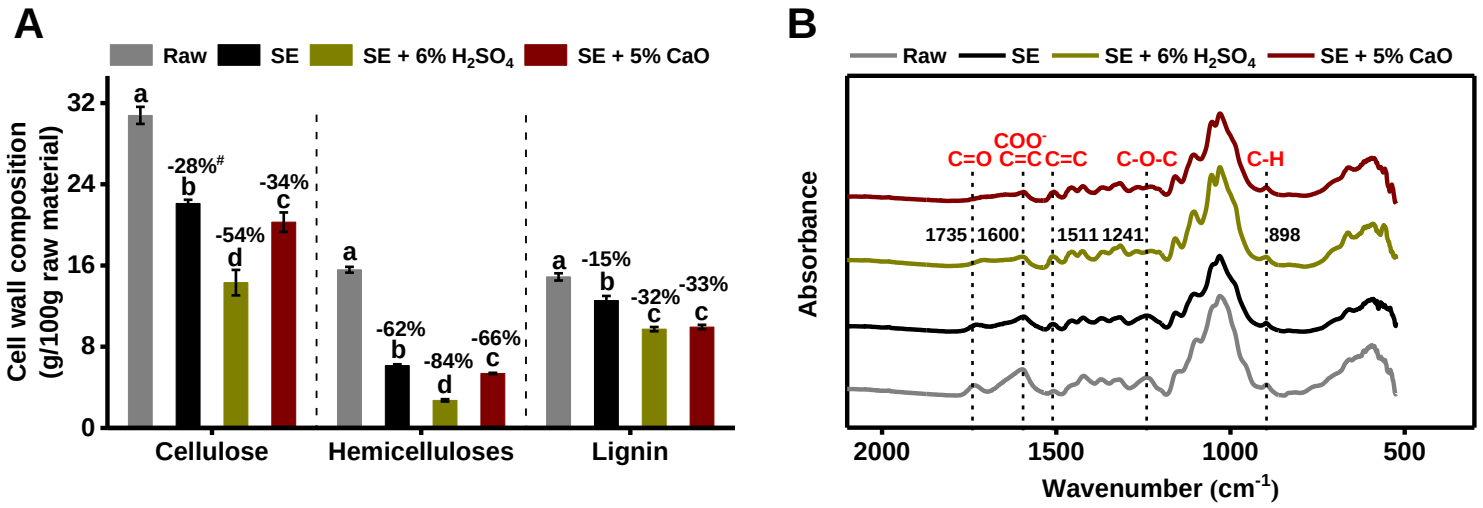

Fig. S5 Characterization of wall polymer extraction under three optimal pretreatments in rapeseed sample (Bn08). (A) Cell wall composition (based on 100 g raw material of rapeseed stalk). (B) Fourier transform infrared spectroscopic profiling among raw material and three pretreated residues of Bn08. Different letters (a, b, c, d) indicated multiple significant difference by LSD-test at $p < 0.05$. # indicated percentage of decreased rates between the raw material and pretreated residues by subtraction of two values divided by the raw material. Data indicated mean ± SD (n=3).

Table S3 Characteristic bands of the FTIR spectra in biomass residues as referred from previous studies.

Observed Wavenumber (cm^{-1})	Functional group	Assignment	Reference
898	**C–H vibration**	**Cellulose**	1
1051	C–O–C ring skeletal vibration	Hemicelluloses	2
1163	C–O–C asymmetric stretching	Cellulose	3
1241	**C-O-C stretching of aryl-alkyl ether**	**Lignin**	4
1371	C-H_2 scissoring	Cellulose	3
1460	C-H_3 asymmetric bending	Lignin	5
1511	**C=C stretching of the aromatic ring**	**Lignin**	2
1600	**COO^- symmetric stretching** **C=C stretching**	**Pectin, lignin**	5,6
1735	**C=O stretching of acetyl or carboxylic acid**	**Hemicelluloses, pectin, lignin**	6,7

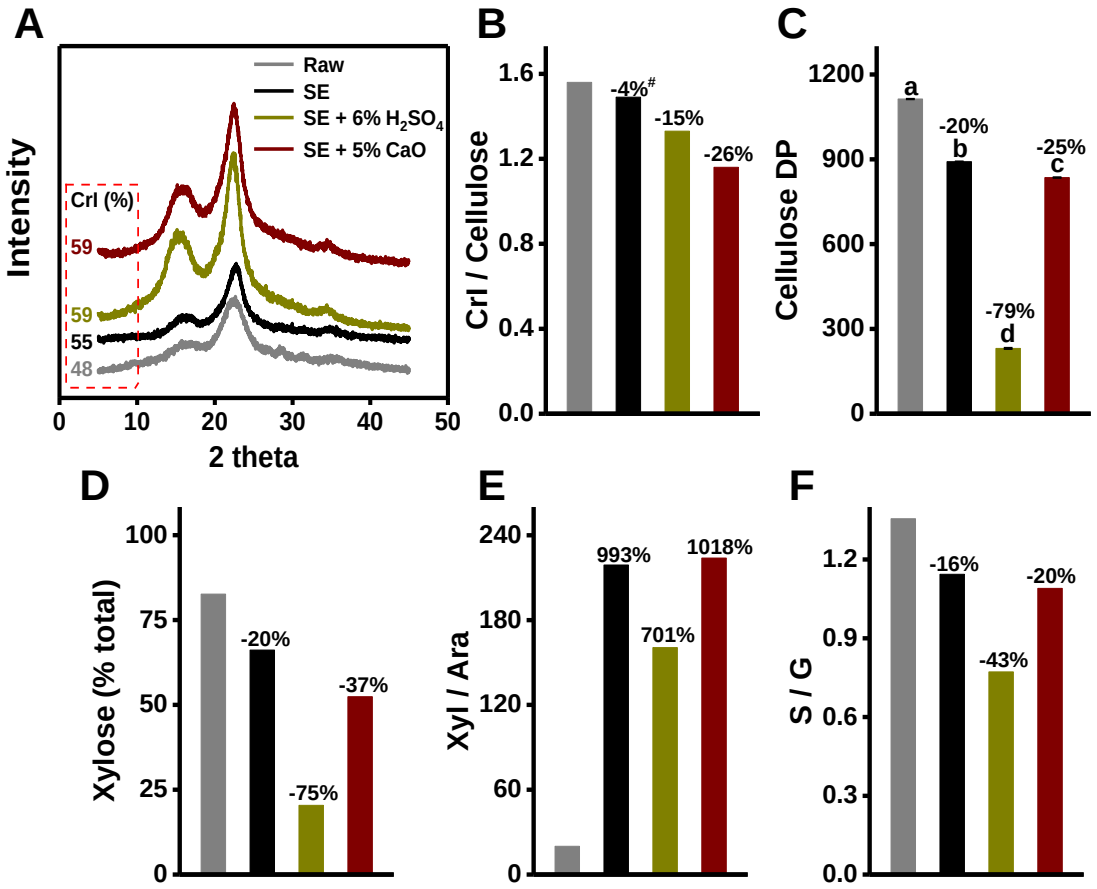

Fig. S6 Detection of wall polymer features in three pretreated-residues of rapeseed sample (Bn08). (A) Cellulose crystallinity index (%). (B) Ratio of CrI value against cellulose level. (C) Cellulose DP. (D) Xylose proportion of hemicelluloses. (E) Xyl/Ara (xylose/arabinose) ratio of hemicellulose. (F) S/G ratio of lignin. Letters (a, b, c, d) indicated multiple significant difference by LSD-test at $p < 0.05$. # indicated percentage of increased or decreased rates between the raw material and pretreated residues by subtraction of two values divided by the raw material, respectively. Data indicated mean ± SD (n=3).

Table S4 Monosaccharides composition of hemicellulose in raw material and pretreated residues.

Sample	Pretreatment	Monosaccharide of hemicelluloses (% total)							
		Rha	Fuc	Ara	Xyl	Man	Glc	Gal	Xyl / Ara
Bn13	Raw	0.59	0.23	2.59	81.94	2.33	7.68	4.64	32
	SE	0.07	0.02	0.29	54.50	2.71	40.19	2.22	190
	SE + 6% H_2SO_4	0.03	0.02	0.12	20.18	3.25	76.40	0.00	173
	SE + 5% CaO	0.03	0.05	0.29	51.87	3.54	41.98	2.25	176
Bn08	Raw	1.47	0.16	4.12	82.64	2.10	5.60	3.91	20
	SE	0.15	0.05	0.30	66.16	2.68	28.92	1.74	219
	SE + 6% H_2SO_4	0.02	0.02	0.13	20.41	2.63	76.79	0.00	161
	SE + 5% CaO	0.04	0.03	0.23	52.41	3.16	42.10	2.03	224

Raw: raw material; **SE**: steam explosion;
Rha: rhamnose; **Fuc**: fucose; **Man**: mannose; **Glc**: glucose;
Gal: galactose; **Xyl**: xylose; **Ara**: arabinose; **Xyl/Ara**: ratio of xylose and arabinose.

Table S5 Monomer proportion of lignin in raw material and pretreated residues.

Sample	Pretreatment	Lignin monolignols(% total)					
		H	G	S	H/G	S/G	H/S
Bn13	Raw	2.59	48.97	48.44	0.05	0.99	0.05
	SE	2.09	49.43	48.48	0.04	0.98	0.04
	SE + 6% H_2SO_4	2.06	55.13	42.81	0.04	0.78	0.05
	SE + 5% CaO	1.63	51.18	47.19	0.03	0.92	0.03
Bn08	Raw	1.97	41.62	56.41	0.05	1.36	0.03
	SE	2.58	45.44	51.97	0.06	1.14	0.05
	SE + 6% H_2SO_4	2.15	55.22	42.63	0.04	0.77	0.05
	SE + 5% CaO	1.95	46.92	51.14	0.04	1.09	0.04

H: *p*-hydroxyphenyl alcohol; **G**: guaiacyl alcohol; **S**: sinapyl alcohol;
S/G: ratio of sinapyl alcohol and guaiacyl alcohol.

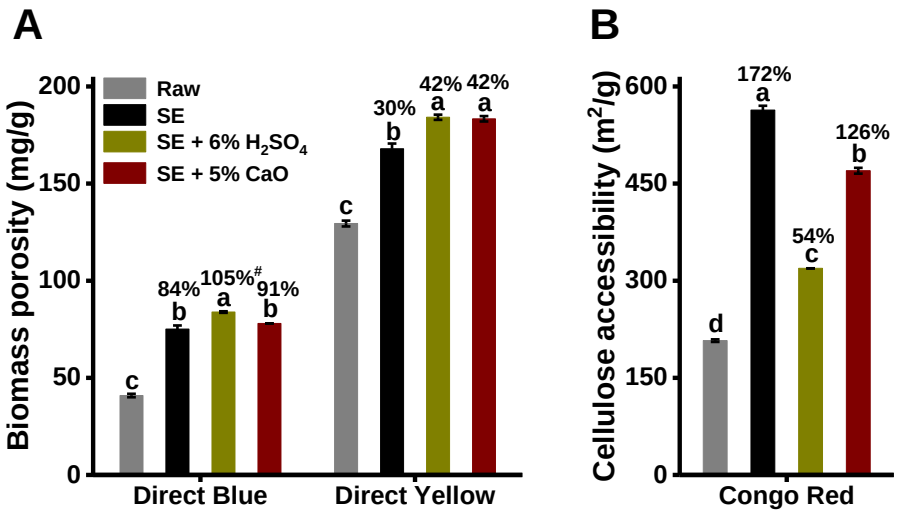

Fig. S7 Detection of biomass porosity and cellulose accessibility in three pretreated-residues of rapeseed sample (Bn08). (A) Biomass porosity detected by Simons' stain; Direct Blue and Direct Yellow measured as small pores and large pores, respectively. (B) Cellulose accessibility detected by Congo Red Stain. Letters (a, b, c, d) indicated multiple significant difference by LSD-test at $p < 0.05$. # indicated percentage of increased rates between the raw material and pretreated residues by subtraction of two values divided by the raw material. Data indicated mean ± SD (n=3).

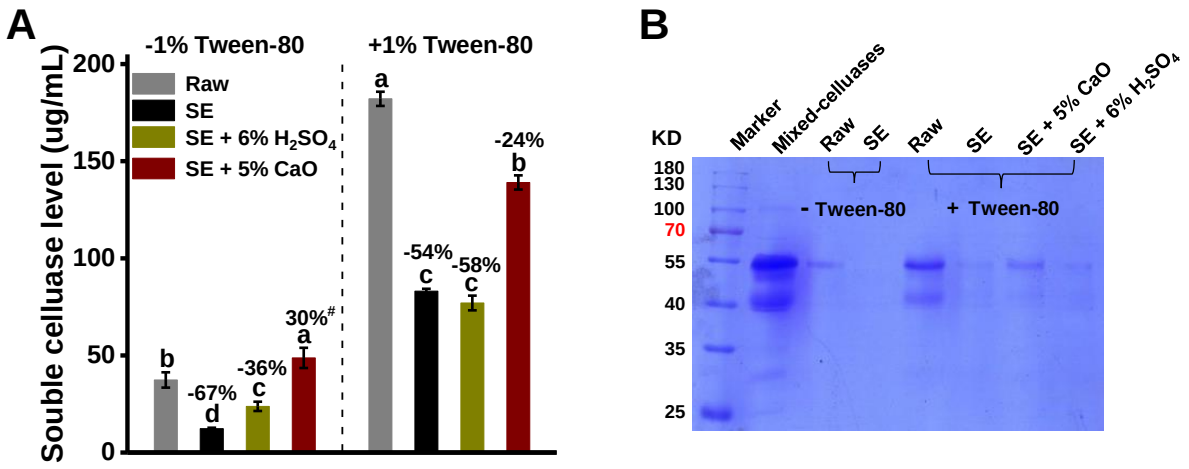

Fig. S8 Characterization of Tween-80 roles in biomass enzymatic saccharification. (A) Soluble celluase level (ug /mL) of the supernatant collected from enzymatic hydrolysis of diverse lignocellulose substrates supplied with/without 1% Tween-80 in rapeseed cultivar (Bn08). (B) SDS-PAGE separation of soluble celluases. Letters (a, b, c, d) indicated multiple significant difference by LSD-test at $p < 0.05$. # Percentage of increased or decreased rates between the raw material and pretreated residues by subtraction of two values divided by the raw material. Data indicated mean ± SD (n=3).

Reference

1. N. A. Boakye-Boaten, S. Xiu, A. Shahbazi, L. Wang, R. Li, M. Mims and K. Schimmel, *Bioresour. Technol.*, 2016, **204**, 98-105.
2. X. Zhou, Q. Li, Y. Zhang and Y. Gu, *Bioresour. Technol.*, 2017, **224**, 721-726.
3. M. A. Haque, D. N. Barman, T. H. Kang, M. K. Kim, J. Kim, H. Kim and H. D. Yun, *Biosyst. Eng.*, 2013, **114**, 294-305.
4. R. Ravindran, S. Jaiswal, N. Abu-Ghannam and A. K. Jaiswal, *Bioresour. Technol.*, 2018, **248**, 272-279.
5. A. Goshadrou, K. Karimi and M. Lefsrud, *Carbohydr. Polym.*, 2013, **96**, 440-449.
6. M. Szymanska-Chargot and A. Zdunek, *Food biophys.*, 2013, **8**, 29-42.
7. Q. Wang, W. Wei, G. P. Kingori and J. Sun, *Cellulose*, 2015, **22**, 3559-3568.