Understanding the Cleavage of Inter- and Intra-molecular Linkages in Corncob Residue for Utilization of Lignin to Produce Monophenols

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Table S1 Assignment of absorption peaks in FTIR spectra of solid samples.[26-28]

Wavenumbers (cm^{-1})	Assignment
1709	C-C stretching vibration in aromatic skeleton (lignin)
1605	Aromatic ring vibrations (lignin)
1515	Aromatic ring vibrations (lignin)
1374	Aliphatic C-H stretching (cellulose)
1166	C-O-C stretching at β-(1-4)-glycosidic (cellulose)
1113	C＝O/C-O-C stretching glucose ring stretching vibration (cellulose)
1057	C-O stretching vibrations (cellulose)
897	C-O-C vibration at β-(1-4)-glycosidic(cellulose)

Table S2 Resonance assignment of ^{13}C CPMAS spectra of corncob residue and reaction residues.

Peak No.	δ(ppm)	Assignment
1	151	Lignin: $S_{3(e)}$, $S_{5(e)}$
2	147.5	Lignin: $S_{3(ne)}$, $S_{5(ne)}$,
		$G_{3(ne, e)}$, $G_{4(ne, e)}$
3	138	Lignin: $S_{1(e)}$, $S_{4(e)}$, $G_{1(e)}$
4	134	Lignin: $S_{1(ne)}$, $S_{4(ne)}$, $G_{1(ne)}$
5	119	Lignin: G_6
6	112	Lignin: G_5, G_6, S_2, S_6
7	108	Cellulose: C_1
8	92	Cellulose: C_4 (ordered)
9	87	Cellulose: C_4 (disordered)
		Lignin: C_β
10	78	Cellulose: C_2, C_3, C_5
		Lignin: C_α
11	74	Cellulose: C_2, C_3, C_5
12	68	Cellulose: C_6 (ordered)
13	65	C_6 (disordered)
		Lignin: C_γ
14	58	Lignin: OCH3

S: carbon in syringyls, G: carbon in guaiacyls, ne: in non-etherified arylglycerol β-aryl ethers, e: in etherified arylglycerol β-aryl ethers.

Table S3 Effect of the ratio of H_2O/THF on the molecular weights distribution of oligomers in liquid products.

The ratio of H_2O/THF	M_w	M_w	M_w/M_n
10:0	306	233	1.31
7:3	528	328	1.61
5:5	560	359	1.56
3:7	617	370	1.67
0:10	692	368	2.10

Reaction conditions: 4.0 g of corncob residue was added in 100 mL of solvent at 140 °C for 1 h.

Table S4 Assignment of main lignin ^{13}C-^{1}H correlation signals in HSQC spectra of liquid fraction.

Labels	δ_C/δ_H (ppm)	Assignment
OMe	56.0/3.74	C-H in methoyls
A_γ	59.8/3.61	C_γ-H_γ in β-O-4' structures (A)
I_γ	61.2/4.15	C_γ-H_γ in β-O-4' structures (I)
C_γ	62.6/3.71	C_γ-H_γ in phenylcoumaran substructure (C)
G_2	111.5/6.80	C_2-H_2 in guaiacyl units (G)
G'_2	111.4/7.4	C_2-H_2 in oxidized (C_α=O) guaiacyl units (G)
G_5	115.3/6.68-6.99	C_5-H_5 in guaiacyl units (G)
G_6	119.8/6.60	C_6-H_6 in guaiacyl units (G)
$S_{2,6}$	104.3/6.71	$C_{2,6}$-$H_{2,6}$ in syringyl units (S)
$S'_{2,6}$	106.5/7.26	$C_{2,6}$-$H_{2,6}$ in (C_α=O) syringyl units (S)
$S''_{2,6}$	104.7/7.30	$C_{2,6}$-$H_{2,6}$ in (carboxylic group) syringyl units (S)
$H_{2,6}$	128.2/7.19	$C_{2,6}$-$H_{2,6}$ in *p*-hydroxyphenyl units (H)
$HB_{2,6}$	130.8/7.56	$C_{2,6}$-$H_{2,6}$ in oxidized (C_α=O) *p*-hydroxyphenyl units (HB)
PCA_α	143.8/7.49	C_α-H_α in p-coumaric acid (PCA)

Table S5 Effect of different salts on the molecular weights distribution of oligomers in liquid products.

	Salts	M_w	M_w	M_w/M_n
Step-one [a]	Na_2CO_3	722	444	1.63
	NaOH	622	281	2.22
	$NaHCO_3$	676	292	2.32
	K_2CO_3	620	265	2.34
Step-two [b]	Na_2CO_3	293	253	1.16
	NaOH	290	257	1.13
	$NaHCO_3$	288	253	1.14
	K_2CO_3	283	251	1.13

Reaction conditions: [a] 4.0 g of corncob residue and salts (molar equivalent of Na^+ or CO^{3-} in 0.5 g Na_2CO_3) were added in 100 mL of solvent (H_2O-THF: 5 : 5, v/v) at 140 °C for 1 h.

[b] 100 mL of liquid fraction in step-one at 300 °C for 2 h.

Table S6 The yield[a] of monophenols by the further reaction of the liquid fraction from step-one with different salts.

Monophenols		Alkaline salts [b]			
		$NaHCO_3$ (9.4) [c]	Na_2CO_3 (12.1) [c]	K_2CO_3 (12.2) [c]	NaOH (13.6) [c]
S	2,6-Dimethoxylphenol [I]	6.5	6.0	7.1	8.7
H	Phenol [II]	7.2	7.4	7.4	7.2
	4-Ethylphenol	0.7	0.8	0.9	1.4
G	Guaiacol [III]	4.6	5.2	5.3	5.8
	4-Methylguaiacol	2.7	2.8	3.0	2.8
	4-Ethylguaiacol	0.6	0.8	0.8	1.3
2,3-Dihydrobenzofuran		0.5	0.4	0.4	0.5
Total monophenols		22.8	23.4	24.9	27.7
Selectivity (I+II+III) [b]		79.9	79.4	79.2	78.3

[a] wt%, based on the lignin content in corncob residue.

[b] In step-one: Salts (molar equivalent of Na^+ or CO_3^- in 0.5 g Na_2CO_3) was added in 100 mL solvent (H_2O-THF: 5 : 5, v/v).

[c] Initial pH value

Reaction conditions: 100 mL of liquid fraction from step-one at 300 °C for 2 h.

Figures

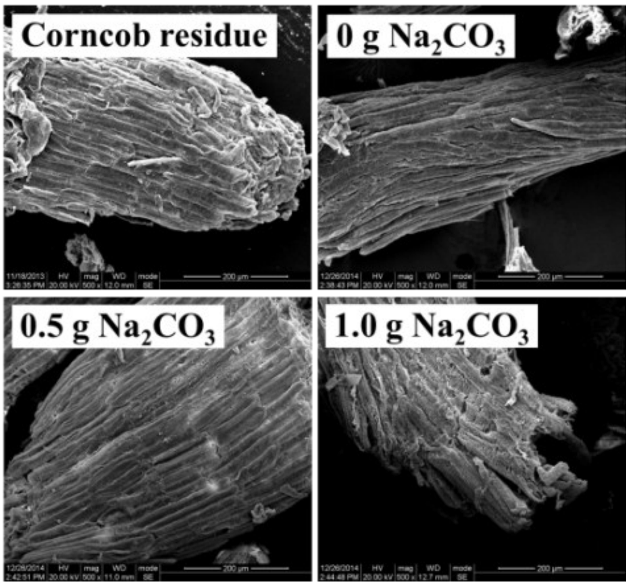

Fig. S1 SEM micrographs of corncob residue and reaction residues with different amount of Na_2CO_3 added. Reaction conditions: 4.0 g of corncob residue in 100 mL of solvent (H_2O-THF: 3 : 7, v/v) at 140 °C for 1 h.

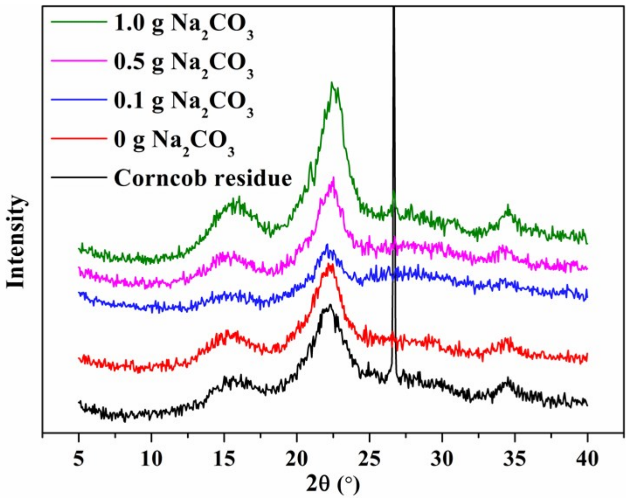

Fig. S2 XRD of corncob residue and reaction residues with different amount of Na_2CO_3 added. Reaction conditions: 4.0 g of corncob residue in 100 mL of solvent (H_2O-THF: 3 : 7, v/v) at 140 °C for 1 h.

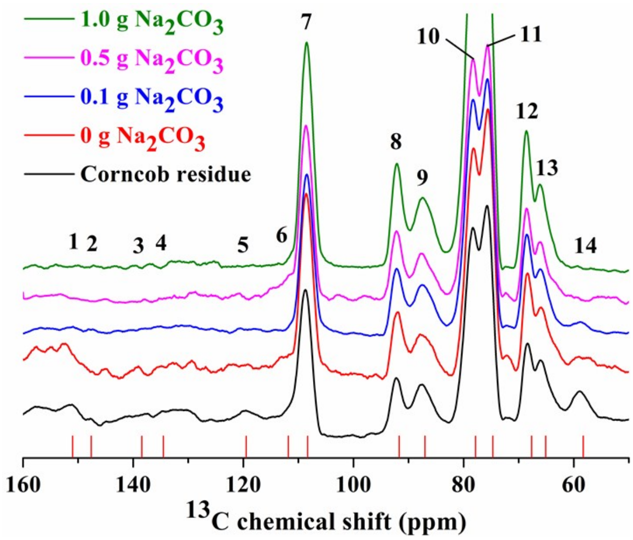

Fig. S3 ^{13}C CPMAS solid-state NMR spectra of corncob residue and reaction residues. Reaction conditions: 4.0 g of corncob residue in 100 mL of solvent (H_2O-THF: 3 : 7, v/v) at 140 °C for 1 h.

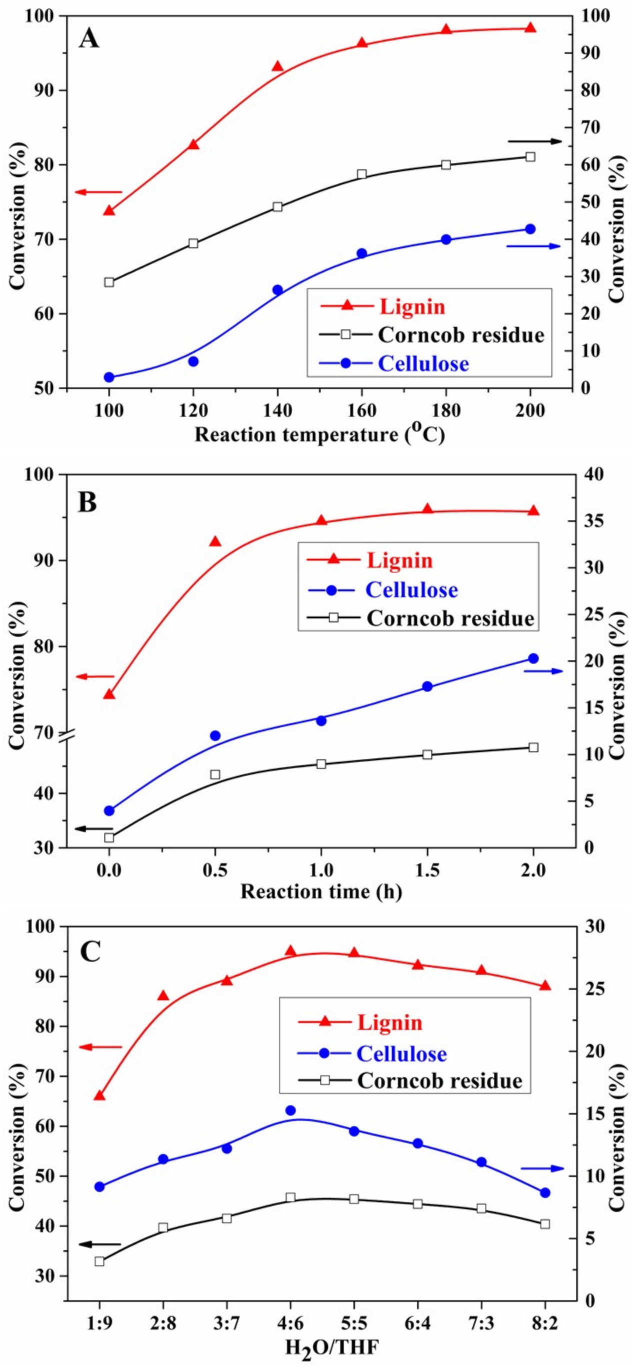

Fig. S4 Effect of reaction conditions (A. Reaction temperature; B. Reaction time; C. The ratio of H_2O/THF with Na_2CO_3) on the conversion of corncob residue. Reaction conditions: A 4.0 g of corncob residue and 1.0 g of Na_2CO_3 in 100 mL of solvent (H_2O-THF: 3 : 7, v/v) for 1 h. B 4.0 g of corncob residue and 0.5 g of Na_2CO_3 in 100 mL of solvent (H_2O-THF: 5 : 5, v/v) at 140 °C. C 4.0 g of corncob residue and 0.5 g of Na_2CO_3 in 100 mL of solvent at 140 °C for 1 h.

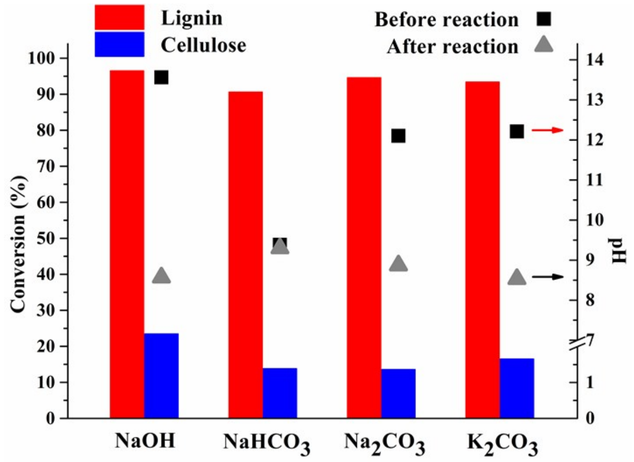

Fig. S5 Effect of alkaline salts on the conversion of lignin and cellulose in corncob residue and the pH value of the reaction solvent. Reaction conditions: 4.0 g of corncob residue and salt (molar equivalent of Na^+ or CO_3^{2-} in 0.5 g of Na_2CO_3) in 100 mL of solvent (H_2O-THF: 5 : 5, v/v) at 140 °C for 1 h.

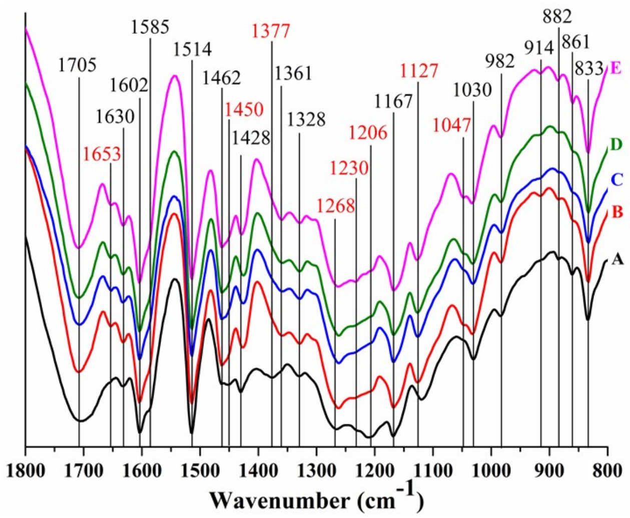

Fig. S6 FTIR spectra (1800-800 cm^{-1}) of liquid fraction influenced by the ratio of H_2O/THF without Na_2CO_3. (A) 10 : 0; (B) 7 : 3; (C) 5 : 5; (D) 7 : 3; (E) 0 : 10. Reaction conditions: 4.0 g of corncob residue was added in 100 mL of solvent at 140 °C for 1 h.

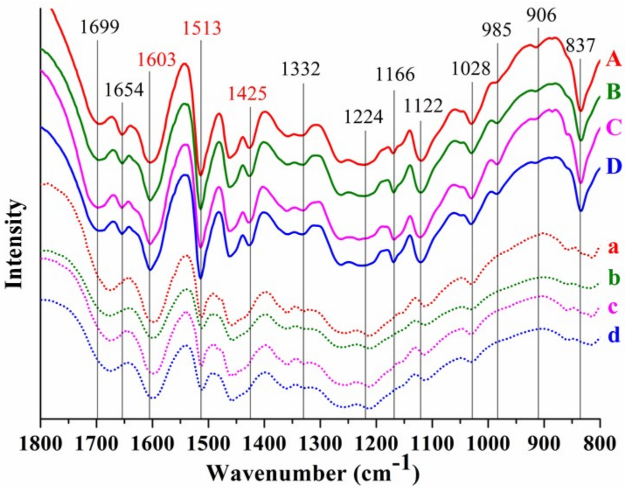

Fig. S7 FTIR spectra (1800-800 cm^{-1}) of liquid fraction influenced by different salts. After step-one: (A) Na_2CO_3; (B) NaOH; (C) $NaHCO_3$; (D) K_2CO_3. After step-two: (a) Na_2CO_3; (b) NaOH; (c) $NaHCO_3$; (d) K_2CO_3. Reaction conditions: Step-one: 4.0 g of corncob residue and salts (molar equivalent of Na^+ or CO^{3-} in 0.5 g Na_2CO_3) were added in 100 mL of solvent (H_2O-THF: 5 : 5, v/v) at 140 °C for 1 h. Step-two: 100 mL of liquid fraction in step-one at 300 °C for 2 h.

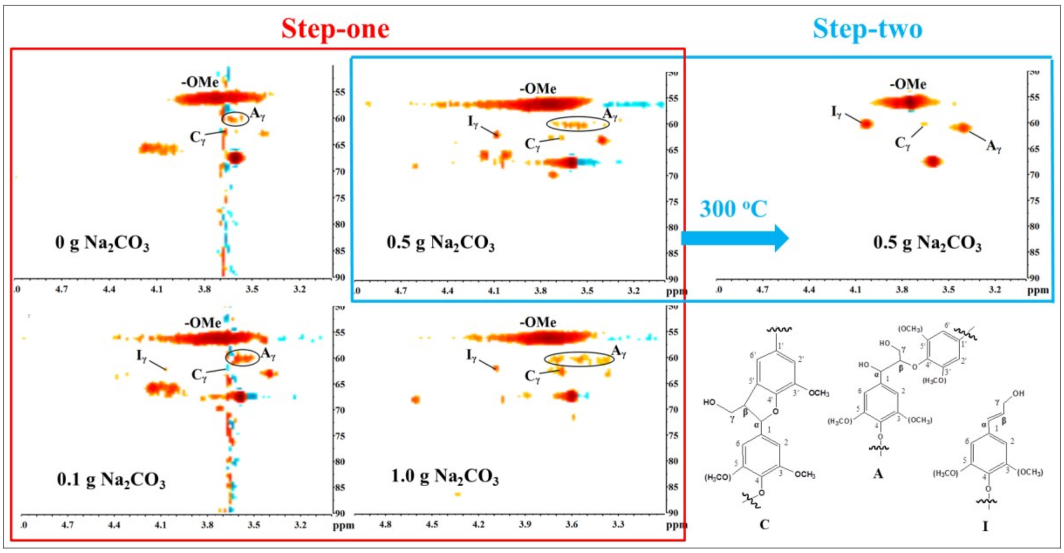

Fig. S8 2D HSQC NMR spectra (aliphatic side-chain region) of liquid fraction. Reaction conditions: Step-one: 4.0 g of corncob residue in 100 mL of solvent (H_2O-THF: 3 : 7, v/v) at 140 °C for 1 h. Step-two: 100 mL of liquid fraction in step-one at 300 °C for 2 h.

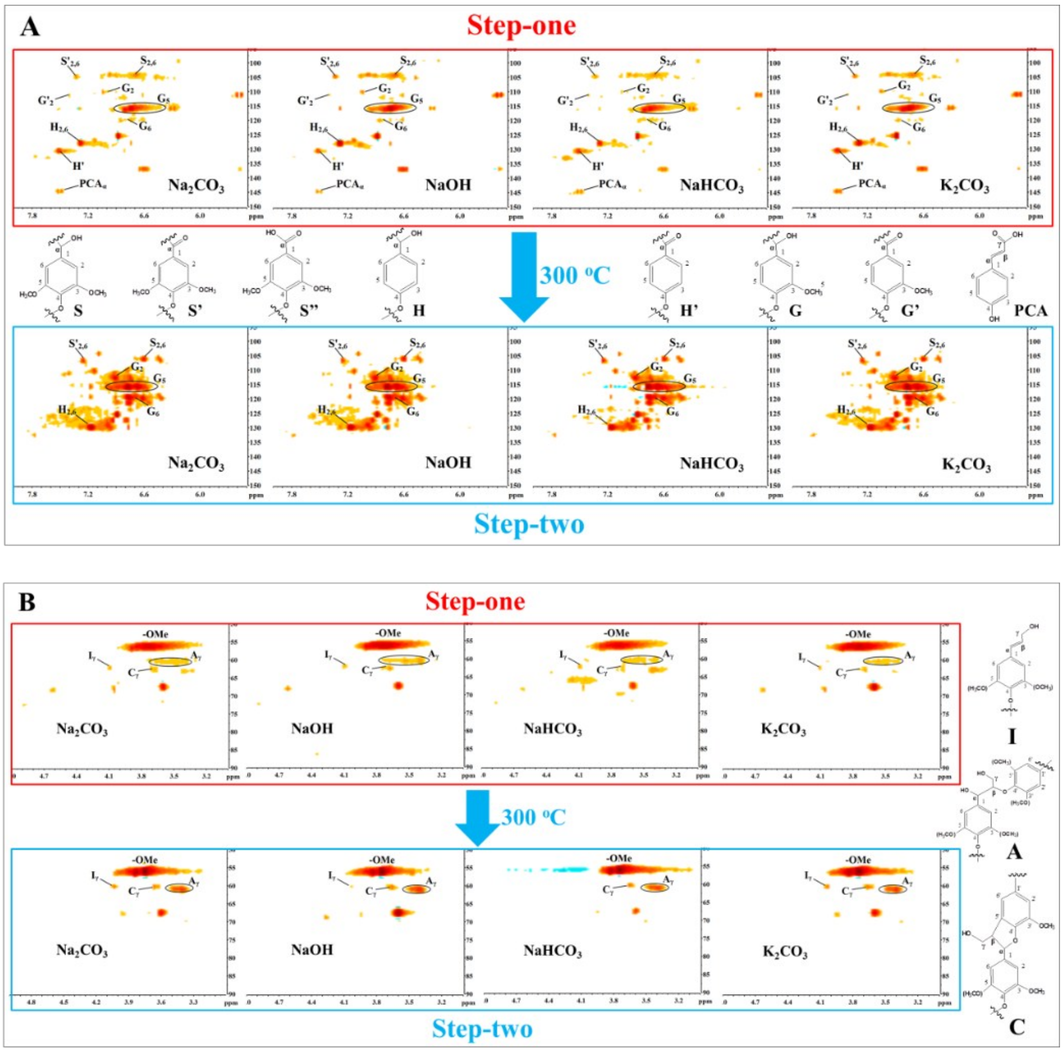

Fig. S9 2D HSQC NMR spectra (A aromatic region; B aliphatic side-chain region) of liquid fraction. Reaction conditions: Step-one: 4.0 g of corncob residue and salts (molar equivalent of Na^+ or CO^{3-} in 0.5 g Na_2CO_3) were added in 100 mL of solvent (H_2O-THF: 5 : 5, v/v) at 140 °C for 1 h. Step-two: 100 mL of liquid fraction in step-one at 300 °C for 2 h.

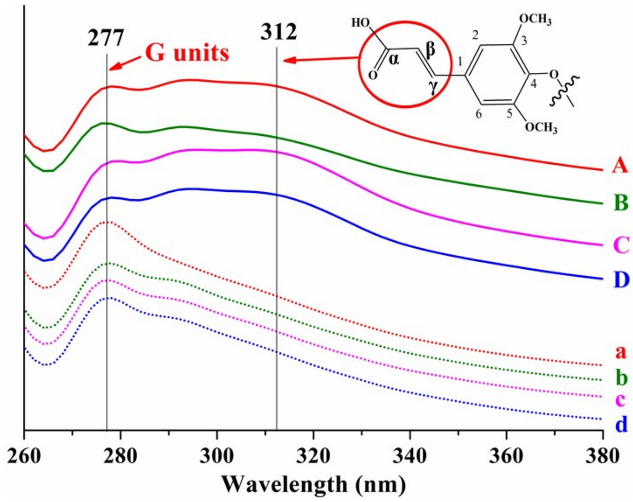

Fig. S10 UV spectra (260-380 nm) of liquid fraction influenced by different salts. After step-one: (A) Na_2CO_3; (B) NaOH; (C) $NaHCO_3$; (D) K_2CO_3. After step-two: (a) Na_2CO_3; (b) NaOH; (c) $NaHCO_3$; (d) K_2CO_3. Reaction conditions: Step-one: 4.0 g of corncob residue and salts (molar equivalent of Na^+ or CO^{3-} in 0.5 g Na_2CO_3) were added in 100 mL of solvent (H_2O-THF: 5 : 5, v/v) at 140 °C for 1 h. Step-two: 100 mL of liquid fraction in step-one at 300 °C for 2 h.