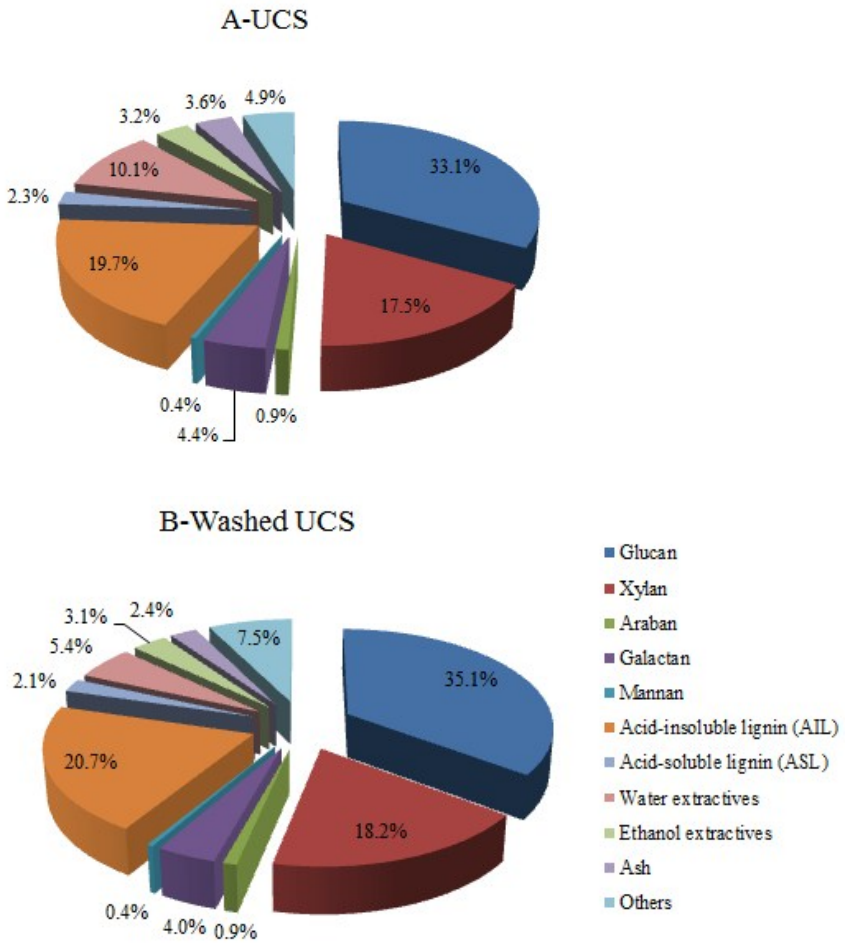
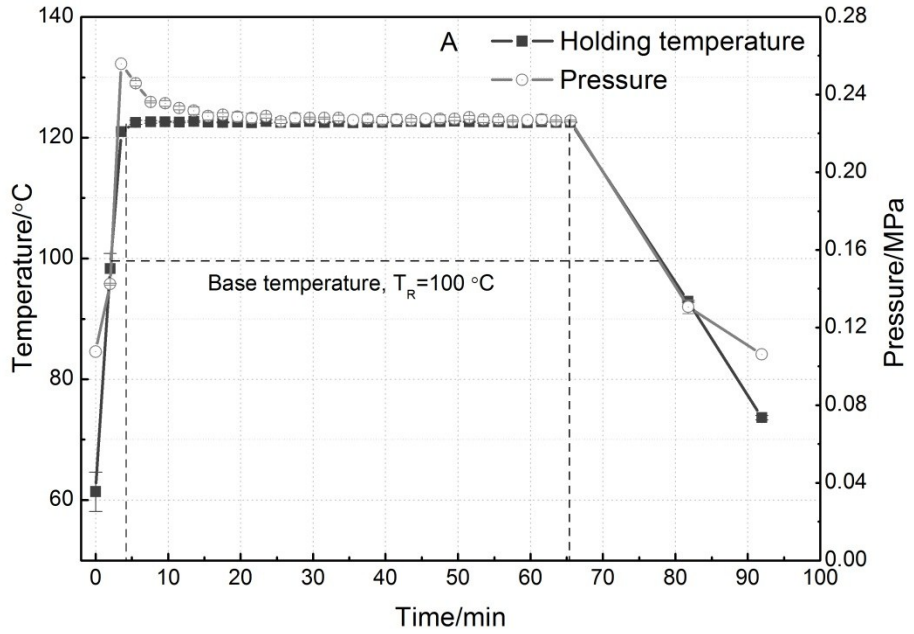
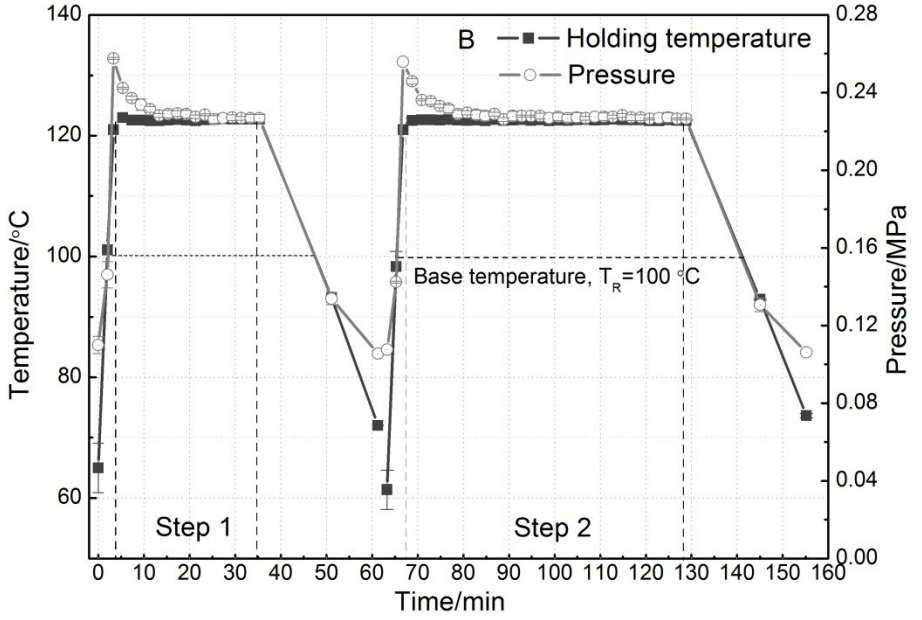


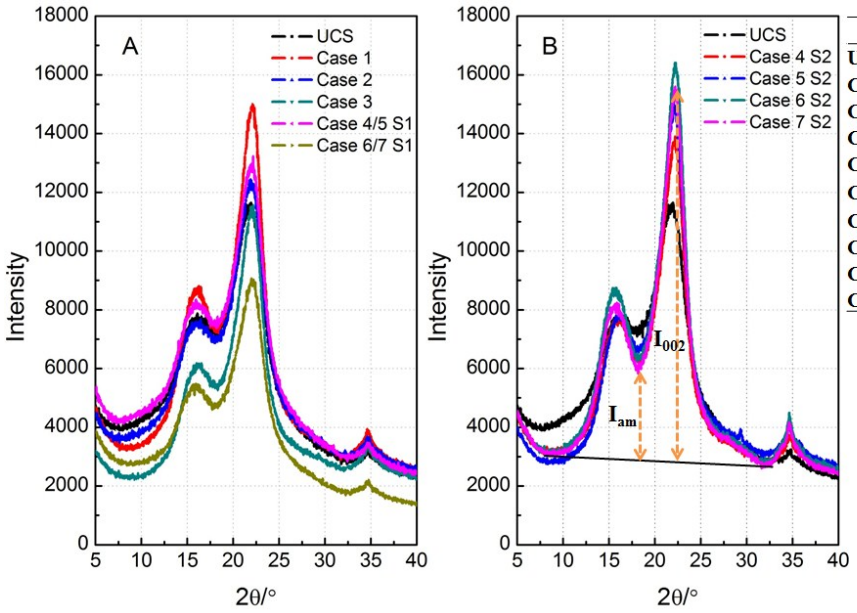
Electronic supplemental information 1 Composition analysis of corn stover without or with pre-washing. UCS, untreated corn stover. Washed UCS, UCS after pre-washing with deionized water. The composition of washing stream was calculated based on the dry weight of UCS. All data are mean values of duplicate experiments.





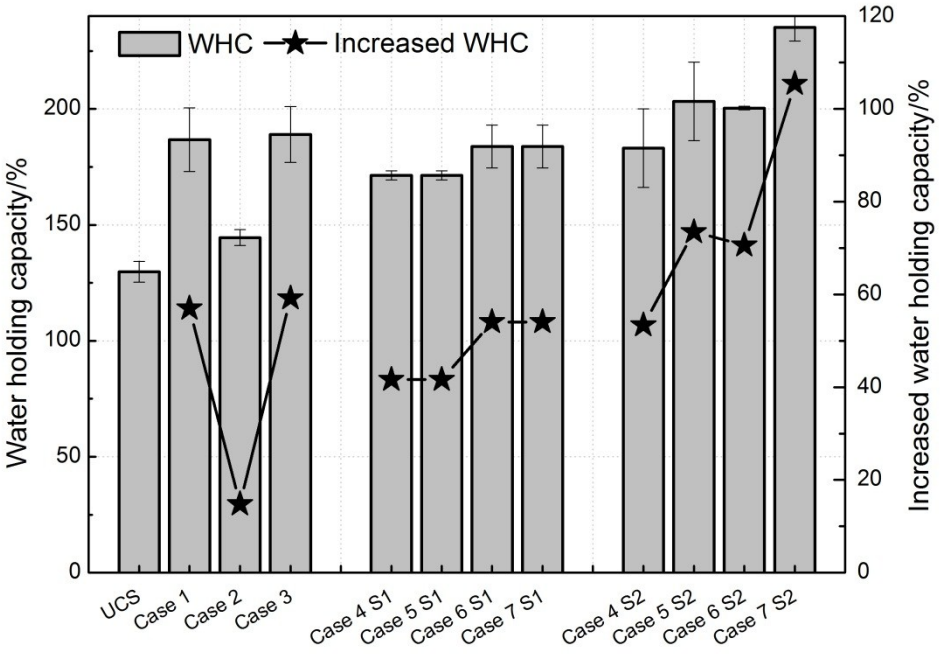
Electronic supplemental information 2 Holding temperature and pressure profiles in (A) single pretreatments (Cases 1-3) and (B) combinatorial pretreatments (Cases 4-7) of corn stover

Electronic supplemental information 3 Morphological structure of untreated and pretreated corn stover by different combinatorial pretreatment strategies. A, untreated corn stover; B, pretreated corn stover in Case 1; C, pretreated corn stover in Case 2; D, pretreated corn stover in Case 3; E, pretreated corn stover in Case 4 Step 1; F, pretreated corn stover in Case 5 Step 1; G, pretreated corn stover in Case 6 Step 1; H, pretreated corn stover in Case 7 Step 1; I, pretreated corn stover in Case 4 Step 2; J, pretreated corn stover in Case 5 Step 2; K, pretreated corn stover in Case 6 Step 2; J, pretreated corn stover in Case 7 Step 2.

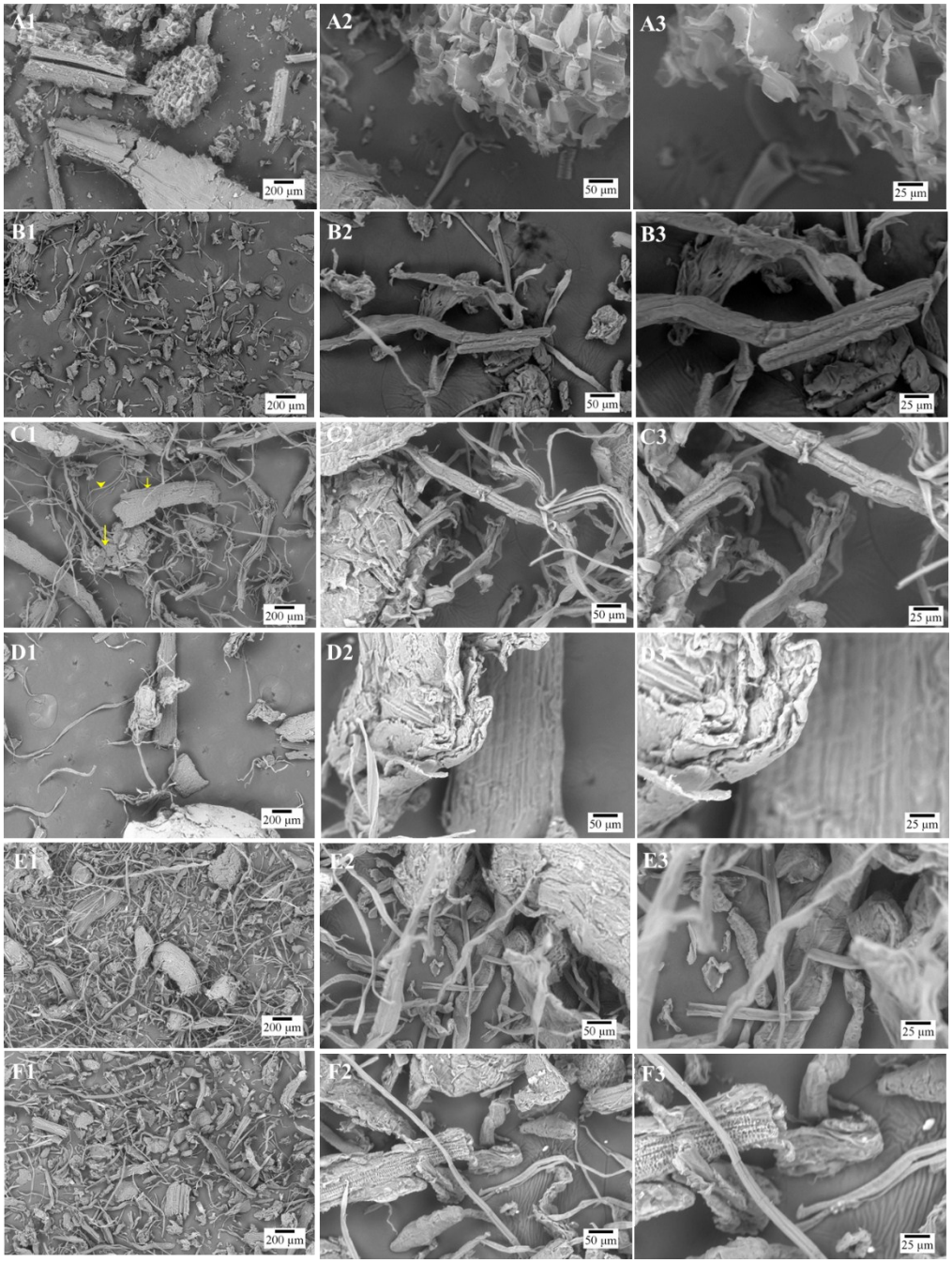


	CrI%	SD
UCS	57.9	0.1
Case 1	66.5	0.1
Case 2	62.3	0.2
Case 3	67.7	1.0
Case 4/5 S1	63.1	0.1
Case 6/7 S1	68.8	2.4
Case 4 S2	70.9	0.1
Case 5 S2	70.1	0.4
Case 6 S2	76.9	0.1
Case 7 S2	77.5	0.2

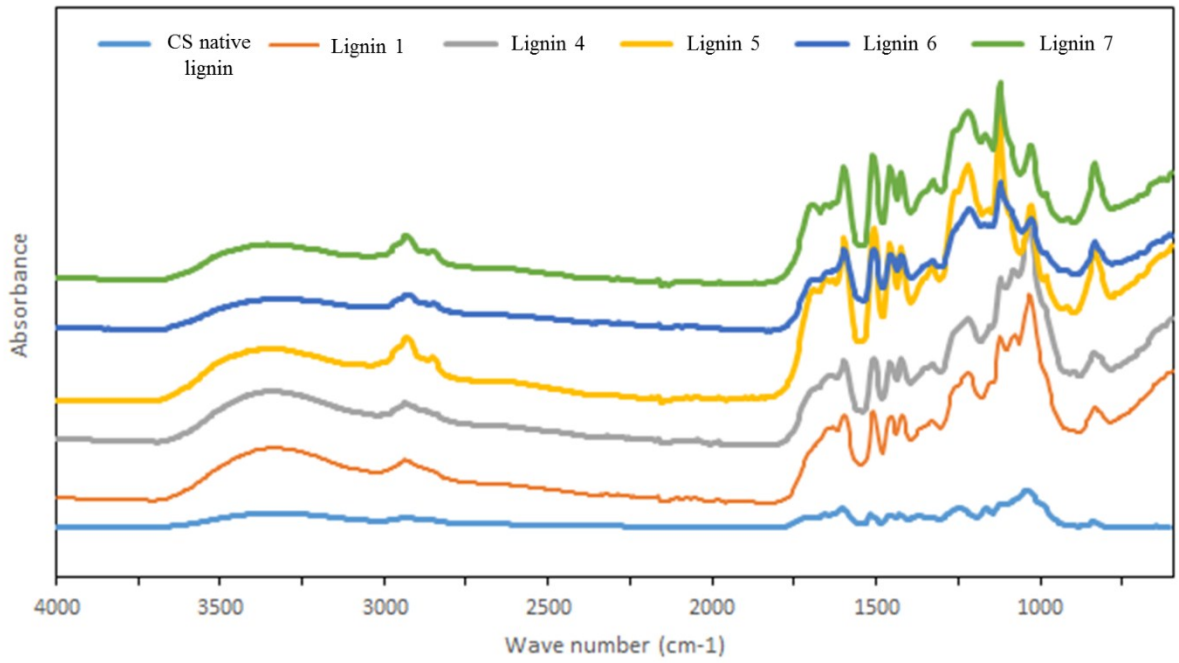
Electronic supplemental information 4 X-ray diffraction profiles of untreated corn stover (UCS) and pretreated corn stover produced from each single and combinatorial pretreatment strategy. The profiles were used to calculate CrI by the peak height method. S1 stands for Step 1; S2 stands for Step 2.



Electronic supplemental information 5 Water holding capacity (WHC) of untreated corn stover (UCS) and pretreated corn stover produced from each single and combinatorial pretreatment strategy. Increased water holding capacity indicates an increase in WHC for pretreated corn stover as compared to that for UCS. S1 stands for Step 1; S2 stands for Step 2.



Electronic supplemental information 6 SEM images of untreated and pretreated corn stover. A1-3, untreated corn stover; B1-3, corn stover pretreated in NaOH (Case 1); C1-3 liquid hot water followed by NaOH (Case 4); D1-3, liquid hot water followed by EtOH+NaOH (Case 5); E1-3, H_2SO_4 followed by NaOH (Case 6); F1-3, H_2SO_4 followed by EtOH+NaOH (Case 7). Pretreatment strategies were described in Table 1. Figure C1 shows fiber strands, cuboid and ellipsoid structures as arrowheads, short arrow and long arrow, respectively.



Electronic supplemental information 7 FTIR spectra of corn stover (CS) native lignin and fractionated lignin produced from different pretreatments. “Lignin 1” represents the fractionated lignin produced by pretreatment Case 1 described in Table 1.

Electronic supplemental information 8 the relative abundance of the derivatives generated from carbohydrates and lignin fractions by different pretreatments of corn stover as determined by GC-MS

	Compounds	Chemical formula	Case 1	Case 2	Case 3	Case 4/5S1	Case 6/7S1	Case 4S2	Case 5S2	Case 6S2	Case 7S2
	Acids										
1	Glycolic acid	C2H4O3	0.0006	-	0.0892	0.0004	0.0009	0.0188	0.0432	0.0549	0.1150
2	Oxalic acid	C2H2O4	0.0382	-	0.0890	0.0095	0.0064	-	0.2099	-	0.0521
3	Lactic acid	C3H6O3	0.0037	-	0.1518	0.0004	0.0026	0.1250	0.1523	0.0353	0.1548
4	Malonic acid	C3H4O4	-	-	0.0512	-	-	-	0.0745	-	0.0952
5	Butanoic acid	C4H8O2	0.0024	-	0.0035	0.0028	0.0013	0.0063	0.0028	0.0171	0.2627
6	Isobutyric acid	C4H8O2	-	-	-	-	-	-	1.0617	-	0.3289
7	Hydroxybutyric acid	C4H8O3	0.0878	-	0.2163	-	-	0.1651	0.4519	0.2173	0.6146
8	Malic Acid	C4H6O5	0.4572	-	1.6629	0.0126	0.0179	0.6594	1.3687	0.7714	1.5315
9	Valeric acid	C5H10O2	0.0012	-	0.2206	-	0.1765	-	0.1205	-	0.1050
	Total		**0.8587**	**0.0000**	**3.4730**	**0.0386**	**0.2226**	**0.9983**	**4.5937**	**1.4344**	**4.1630**
	Furans										
10	Butyrolactone	C4H6O2	0.0070	-	0.0738	-	-	0.1641	0.1782	0.0765	0.1248
11	Maleic anhydride	C4H2O3	0.0023	-	0.1149	0.0314	0.0479	0.0755	0.3454	0.3445	0.0440
12	Succinic anhydride	C4H4O3	-	-	-	-	-	0.0653	0.0848	0.1224	0.1039
13	Furfural	C5H4O2	-	-	-	0.0145	0.0924	0.0116	0.0178	0.0239	0.0345
14	Methyl furoate	C6H6O3	-	-	-	-	0.0110	-	-	-	-
15	5-Hydroxymethyl-furfural	C7H8O3	-	-	-	0.0021	0.0508	-	-	-	-
16	5-(Hydroxymethyl)-2(3H)-furanone	C9H16O2	0.0464	-	0.3460	-	-	0.0316	0.2069	0.0551	0.1851
	Total		**0.0558**	**0.0000**	**0.5348**	**0.0479**	**0.2021**	**0.3481**	**0.8331**	**0.6224**	**0.4923**
	Phenols										
17	Phenol	C6H6O	0.0118	-	0.0491	0.0169	0.0360	0.0234	0.0668	0.0448	0.0760
18	Benzaldehyde	C7H6O	0.0208	-	0.0359	0.0067	0.0082	0.0262	0.0363	0.0329	0.0419
19	4-Hydroxybenzaldehyde	C7H6O2	0.0570	0.0002	0.5616	0.0509	0.0617	0.3446	0.3988	0.3132	0.4012
20	Guaiacol	C7H8O2	0.0559	-	0.0953	0.0121	0.0426	0.0369	0.0770	0.0652	0.1238
21	Benzoic acid	C7H6O2	-	-	-	-	-	-	0.0564	-	0.0656
22	*p*-Anisic acid	C8H8O3	0.0032	-	0.0142	0.0154	0.0252	0.0129	0.0230	0.0153	0.0262
23	Isovanillic acid	C8H8O4	0.0122	-	0.1521	-	-	0.0373	0.2455	0.0669	0.2723
24	Vanillic acid	C8H8O4	0.3161	-	0.5194	0.0209	0.0224	0.1116	0.1653	0.1370	0.2319
25	Vanillin	C8H8O3	0.0446	-	0.8494	0.0580	0.0132	0.4881	0.1952	0.2377	0.2715
26	Coumarone	C8H6O	0.5912	0.0124	2.2042	0.1283	0.1764	2.4800	2.9846	2.4119	2.1412
27	Piceol	C8H8O2	0.1367	-	0.1874	-	-	0.0687	0.1063	0.1013	0.1519
28	Benzeneacetic acid	C8H8O2	-	-	-	-	-	0.0079	-	0.1386	-
29	4-Hydroxybenzeneacetic acid	C8H8O2	-	-	0.1229	-	-	-	0.1216	-	0.1095
30	4-Methoxyphenylacetic acid	C9H10O3	0.0613	-	0.1832	-	-	0.1733	0.2324	0.2026	0.3597
31	Homovanillate	C9H10O4	0.0447	-	0.2547	-	-	0.0527	0.2509	0.0664	0.2980
32	m-Phthalaldehyde	C8H6O2	-	-	-	0.0048	0.0052	-	-	-	-
33	Phthalic acid	C8H6O4	-	0.0002	-	-	-	-	-	-	-
34	4-Vinylguaiacol	C9H10O2	0.3768	-	0.6600	0.0188	0.2215	0.4265	0.7406	0.6604	0.8603
35	4-Hydroxy-3-methyl-acetophenone	C9H10O2	0.8876	0.0028	1.6411	-	-	1.9917	2.6481	0.7850	2.2760
36	2,4'-Dihydroxy-3'-methoxy-acetophenone	C9H10O4	-	-	-	-	-	-	0.0745	-	0.1266
37	*p*-Coumaric acid	C9H8O3	0.1400	-	5.8445	0.1958	0.2271	3.6473	4.1269	1.9027	3.3337
38	Apocynin	C9H10O3	0.0095	-	0.3605	0.0085	0.0153	0.1315	0.3020	0.1581	0.2037
39	Syringaldehyde	C9H10O4	0.0232	-	0.0557	0.0257	0.0335	0.0628	0.0965	0.0722	0.1099
40	4-sec-Butylphenol	C10H14O	-	-	-	-	-	-	-	0.1190	0.2752
41	(1,2-Dimethoxyethyl)benzene	C10H14O2	-	-	-	-	-	-	-	0.0724	0.0767
42	Ferulic acid	C10H10O4	0.0566	-	1.6143	0.1997	0.2232	1.1326	3.2582	0.2229	0.6242
43	Acetosyringone	C10H12O4	0.0695	-	0.6674	-	-	0.6621	0.7998	0.4844	0.2884
44	Acetoxycinnamic acid	C11H10O4	-	-	-	-	-	-	1.6191	-	1.8340
45	4-Acetoxy-3-methoxystyrene	C11H12O3	-	-	-	0.0001	0.0008	-	-	-	-
46	4-tert-Amylphenol	C11H16O	0.0144	-	-	0.0127	0.0080	0.0149	-	0.0606	-
47	Ethyl ferulate	C12H14O4	-	-	1.5587	-	-	-	1.1000	-	0.5765
48	(1-Methoxy-4-methyl-3-pentenyl)-benzene	C13H18O	-	-	-	-	-	-	0.0658	-	0.0733
49	3,5-Di-tert-butylphenol	C14H22O	0.0066	-	0.0197	0.0691	0.0686	0.1094	0.1961	0.1652	0.1937
50	Butylated hydroxytoluene	C15H24O	0.0055	-	0.9586	0.0789	0.0525	0.1215	0.0857	0.2533	0.1925
51	2,2'-Methylenebis(6-tert-butyl-4-ethylphenol)	C25H36O2	-	-	-	0.1002	0.0734	0.0993	0.0811	0.0827	0.1090
	Total		**3.00097**	**0.01559**	**19.1446**	**1.07139**	**1.51693**	**12.6111**	**20.9874**	**9.49522**	**16.2168**