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

Supplementary Information

Thermochemical Behavior of Alkali Pretreated Biomass – a Thermogravimetric and Py-GC/FID study

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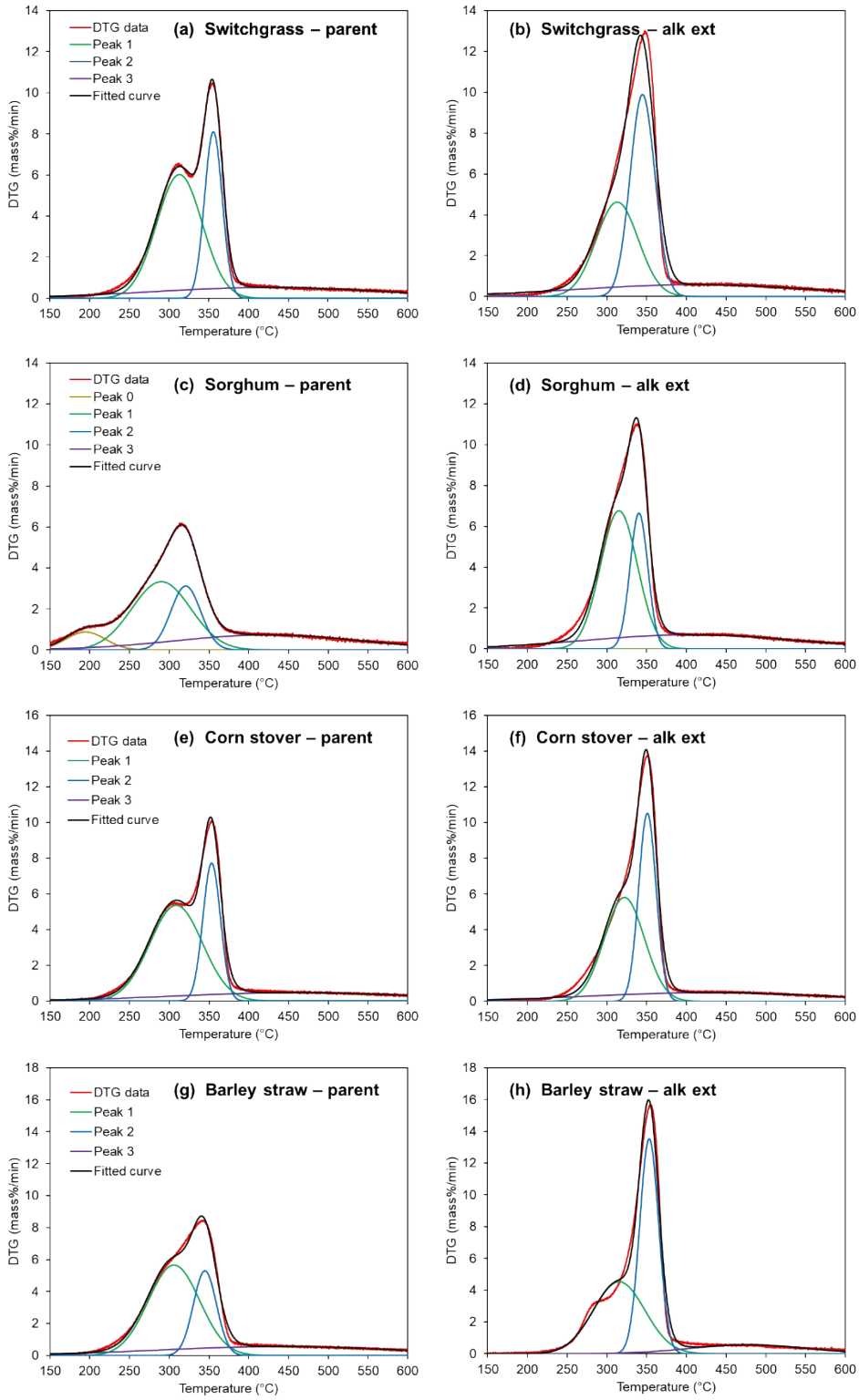

Figure S1: Deconvoluted DTG curves for each parent and alkali extracted biomass. Peak 1, 2, and 3 represent decomposition of hemicellulose, cellulose, and lignin, respectively. For sorghum biomass a peak attributed to protein decomposition was observed, which is denoted as Peak 0.

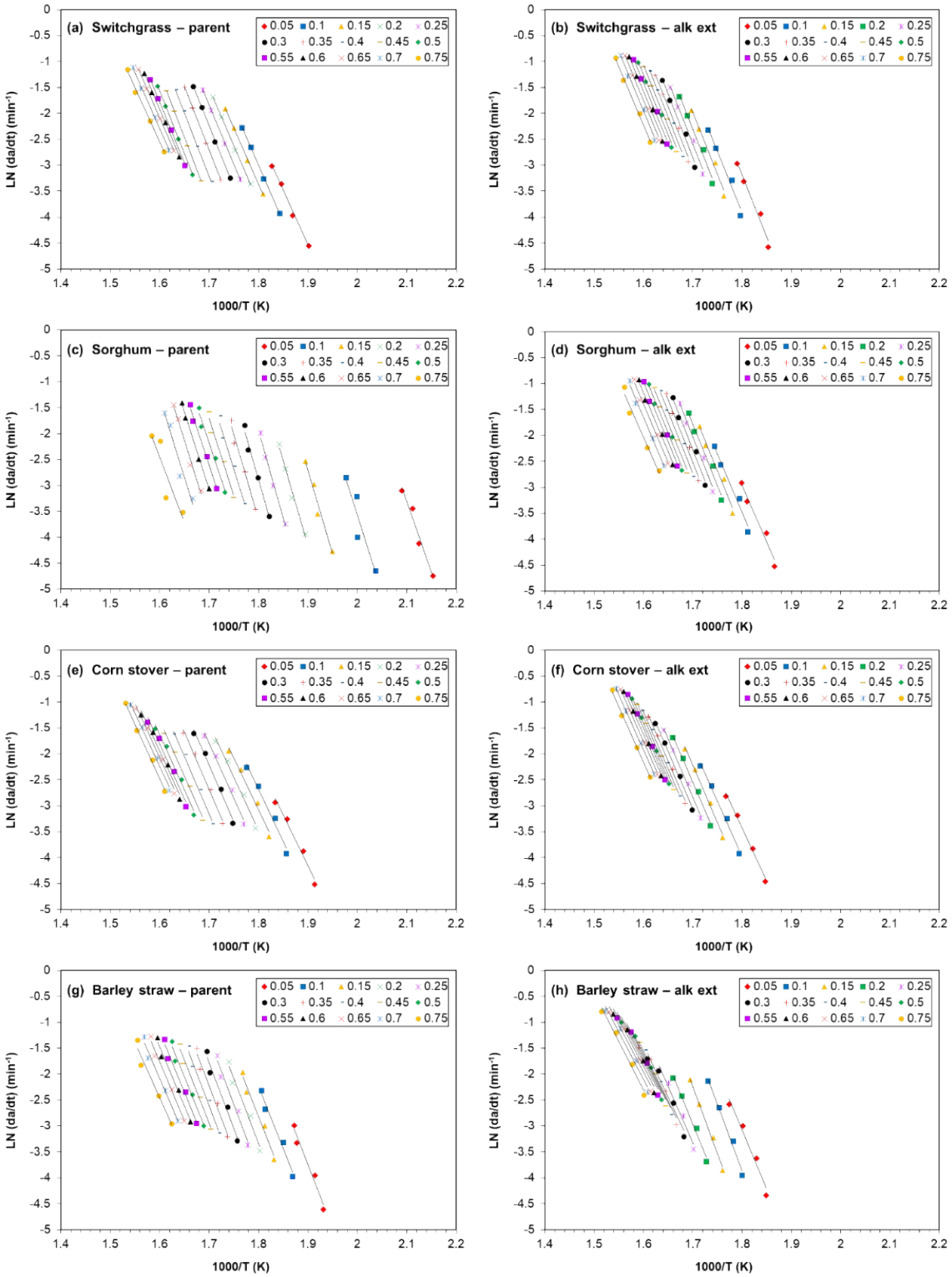

Figure S2: Ln(da/dt) vs 1000/T plots used for kinetic analysis by the Freidman method for each parent biomass (a, c, e, and g) and alkali extracted biomass (b, d, f, and h) sample.

Table S1: Compounds quantified by Py-GC/FID analysis (yields reported in g / 100 g dry biomass) for switchgrass. Normalized yields are normalized to the original biomass basis.

Peak no.	RT	Compound	Parent	Alkali PT	Alkali PT (normalized)
1	4.669	2,3-Butanedione	0.2	0.2	0.1
2	5.266	1,5-Hexadien-3-ol	1.1	1.3	0.7
3	5.605	Benzene	0.4	0.6	0.3
4	6.467	2,5-Dimethylfuran	1.8	3.1	1.8
5	7.020	2-Butenal	0.4	0.5	0.3
6	7.559	Acetic acid	6.8	2.2	1.3
7	8.907	Acetol	3.5	5.5	3.2
8	9.960	3-Penten-2-one	0.2	N.D.	N.D.
9	13.139	1-Hydroxy-2-butanone	0.7	1.2	0.7
10	13.473	Acetic acid, methyl ester	1.5	1.1	0.6
11	14.582	3-Pentyn-1-ol	0.3	0.2	0.1
12	15.493	2-Methylpentanal	0.7	1.5	0.9
13	15.703	Pyruvic acid, methyl ester	1.2	1.3	0.7
14	16.100	Cyclopentenone	0.4	0.4	0.2
15	16.236	Furfural	1.2	1.1	0.6
16	19.086	Acetol acetate	0.9	0.7	0.4
17	19.321	2-Butanone	0.3	0.3	0.2
18	22.030	3-Methylcyclopentanone	0.9	1.2	0.7
19	22.938	2-Furanmethanol	0.2	0.2	0.1
20	23.319	5-Methylfurfural	0.2	N.D.	N.D.
21	24.048	3-Methylcyclopent-2-enone	0.2	0.2	0.1
22	24.371	Butyrolactone	0.2	0.3	0.2
23	24.937	2(5H)-Furanone	0.6	0.9	0.5
24	25.603	2-Acetyl-5-methylfuran	0.2	0.2	0.1
25	25.798	4-Pentyn-1-ol	0.4	0.2	0.1
26	27.025	3-Methyl-1,2-cyclopentanedione	0.6	0.9	0.5
27	27.124	2-Hydroxy-3-methylcyclopentenone	0.2	0.2	0.1
28	28.809	Phenol	0.3	0.2	0.1
29	29.360	2-Methoxyphenol	0.4	0.3	0.2
30	31.122	o-Cresol	N.D.	N.D.	N.D.
31	31.740	3-Ethyl-2-hydroxy-2-cyclopenten-1-one	0.2	0.4	0.2
32	32.033	3,5-Dihydroxytoluene	0.2	0.2	0.1
33	32.629	m-Cresol	0.1	0.2	0.1
34	32.817	p-Cresol	0.2	N.D.	N.D.

35	33.2	2-Methylcyclopentanone	N.D.	0.2	0.1
36	34.307	p-Creosol	0.2	0.2	0.1
37	34.51	Pentanal	0.3	0.6	0.3
38	38.28	3-Methylbutanal	0.4	0.4	0.2
39	38.61	2-Pyranone	0.3	0.3	0.2
40	40.1	Propylene carbonate	0.5	0.4	0.2
41	40.68	4-Vinylphenol	0.7	0.3	0.2
42	40.785	4-Vinylguaiacol	1.4	N.D.	N.D.
43	42.5	HMF	0.3	0.3	0.2
44	42.881	Catechol	0.1	0.2	0.1
45	42.9	Syringol	0.4	0.2	0.1
46	43.499	2-Pentanone	0.1	N.D.	N.D.
47	46.226	4-Methylcatechol	0.2	N.D.	N.D.
48	46.4	Isoeugenol	0.5	0.4	0.2
49	47.128	Vanillin	0.3	0.1	0.1
50	47.611	Hydroquinone	0.2	0.1	0.1
51	56.28	Levoglucosan	3.3	3.2	1.9
Total			36.0	33.5	19.2

Table S2: Compounds quantified by Py-GC/FID analysis (yields reported in g / 100 g dry biomass) for sorghum. Normalized yields are normalized to the original biomass basis.

Peak no.	**RT**	**Compound**	**Parent**	**Alkali PT**	**Alkali PT (normalized)**
1	4.669	2,3-Butanedione	0.2	0.2	0.1
2	5.266	1,5-Hexadien-3-ol	1.1	1.4	0.5
3	5.605	Benzene	0.2	0.5	0.2
4	6.467	2,5-Dimethylfuran	1.0	2.6	1.0
5	7.020	2-Butenal	0.4	0.5	0.2
6	7.559	Acetic acid	7.7	2.9	1.1
7	8.907	Acetol	3.3	5.0	2.0
8	9.960	3-Penten-2-one	N.D	N.D.	N.D.
9	13.139	1-Hydroxy-2-butanone	0.6	1.3	0.5
10	13.473	Acetic acid, methyl ester	1.3	1.0	0.4
11	14.582	3-Pentyn-1-ol	0.2	0.2	0.1
12	15.493	2-Methylpentanal	0.5	1.6	0.6
13	15.703	Pyruvic acid, methyl ester	0.9	1.2	0.5
14	16.100	Cyclopentenone	0.4	0.5	0.2

15	16.236	Furfural	1.4	1.2	0.5
16	19.086	Acetol acetate	0.9	0.7	0.3
17	19.321	2-Butanone	0.2	0.3	0.1
18	22.030	3-Methylcyclopentanone	0.6	1.2	0.5
19	22.938	2-Furanmethanol	0.1	0.2	0.1
20	23.319	5-Methylfurfural	0.2	N.D.	N.D.
21	24.048	3-Methylcyclopent-2-enone	0.2	0.2	0.1
22	24.371	Butyrolactone	0.3	0.4	0.2
23	24.937	2(5H)-Furanone	0.5	0.9	0.3
24	25.603	2-Acetyl-5-methylfuran	0.1	0.2	0.1
25	25.798	4-Pentyn-1-ol	0.2	N.D.	N.D.
26	27.025	3-Methyl-1,2-cyclopentanedione	0.6	0.9	0.4
27	27.124	2-Hydroxy-3-methylcyclopentenone	N.D	N.D.	N.D.
28	28.809	Phenol	0.5	0.2	0.1
29	29.360	2-Methoxyphenol	0.4	0.2	0.1
30	31.122	o-Cresol	0.1	N.D.	N.D.
31	31.740	3-Ethyl-2-hydroxy-2-cyclopenten-1-one	0.2	0.3	0.1
32	32.033	3,5-Dihydroxytoluene	0.1	0.2	0.1
33	32.629	m-Cresol	N.D	0.1	0.1
34	32.817	p-Cresol	0.2	N.D.	N.D.
35	33.2	2-Methylcyclopentanone	0.1	0.2	0.1
36	34.307	p-Creosol	N.D	N.D.	N.D.
37	34.51	Pentanal	0.3	0.5	0.2
38	38.28	3-Methylbutanal	0.3	N.D.	N.D.
39	38.61	2-Pyranone	0.2	0.2	0.1
40	40.1	Propylene carbonate	0.3	0.4	0.2
41	40.68	4-Vinylphenol	0.6	0.1	0.1
42	40.785	4-Vinylguaiacol	2.0	N.D.	N.D.
43	42.5	HMF	0.5	0.2	0.1
44	42.881	Catechol	N.D	N.D.	N.D.
45	42.9	Syringol	0.3	N.D.	N.D.
46	43.499	2-Pentanone	0.2	N.D.	N.D.
47	46.226	4-Methylcatechol	N.D	N.D.	N.D.
48	46.4	Isoeugenol	0.3	0.3	0.1
49	47.128	Vanillin	0.1	N.D.	N.D.
50	47.611	Hydroquinone	0.2	0.2	0.1
51	56.28	Levoglucosan	1.3	1.7	0.7
Total			31.6	30.2	11.9

Table S3: Compounds quantified by Py-GC/FID analysis (yields reported in g / 100 g dry biomass) for corn stover. Normalized yields are normalized to the original biomass basis.

Peak no.	RT	Compound	Parent	Alkali PT	Alkali PT (normalized)
1	4.669	2,3-Butanedione	0.2	0.3	0.1
2	5.266	1,5-Hexadien-3-ol	1.1	1.3	0.7
3	5.605	Benzene	0.4	0.5	0.3
4	6.467	2,5-Dimethylfuran	2.2	3.4	1.8
5	7.020	2-Butenal	0.7	0.5	0.3
6	7.559	Acetic acid	8.2	2.3	1.2
7	8.907	Acetol	2.9	2.8	1.5
8	9.960	3-Penten-2-one	0.2	0.1	0.1
9	13.139	1-Hydroxy-2-butanone	0.6	1.1	0.6
10	13.473	Acetic acid, methyl ester	1.7	1.1	0.6
11	14.582	3-Pentyn-1-ol	0.2	0.3	0.2
12	15.493	2-Methylpentanal	1.0	1.4	0.7
13	15.703	Pyruvic acid, methyl ester	1.5	1.5	0.8
14	16.100	Cyclopentenone	0.3	0.4	0.2
15	16.236	Furfural	1.1	1.1	0.6
16	19.086	Acetol acetate	0.8	0.7	0.3
17	19.321	2-Butanone	0.3	0.3	0.1
18	22.030	3-Methylcyclopentanone	1.0	1.3	0.7
19	22.938	2-Furanmethanol	0.2	0.2	0.1
20	23.319	5-Methylfurfural	N.D.	0.2	0.1
21	24.048	3-Methylcyclopent-2-enone	0.2	0.2	0.1
22	24.371	Butyrolactone	0.3	0.3	0.2
23	24.937	2(5H)-Furanone	0.9	1.0	0.5
24	25.603	2-Acetyl-5-methylfuran	0.2	0.3	0.1
25	25.798	4-Pentyn-1-ol	0.3	0.2	0.1
26	27.025	3-Methyl-1,2-cyclopentanedione	0.5	0.8	0.4
27	27.124	2-Hydroxy-3-methylcyclopentenone	0.2	0.3	0.1
28	28.809	Phenol	0.3	0.1	0.1
29	29.360	2-Methoxyphenol	0.3	N.D.	N.D.
30	31.122	o-Cresol	N.D.	N.D.	N.D.
31	31.740	3-Ethyl-2-hydroxy-2-cyclopenten-1-one	0.2	0.3	0.2
32	32.033	3,5-Dihydroxytoluene	N.D.	0.2	0.1
33	32.629	m-Cresol	0.1	0.2	0.1
34	32.817	p-Cresol	0.1	N.D.	N.D.

35	33.2	2-Methylcyclopentanone	0.2	0.3	0.2
36	34.307	p-Creosol	0.1	N.D.	N.D.
37	34.51	Pentanal	0.4	0.5	0.2
38	38.28	3-Methylbutanal	0.3	0.5	0.2
39	38.61	2-Pyranone	0.4	0.4	0.2
40	40.1	Propylene carbonate	0.4	0.3	0.2
41	40.68	4-Vinylphenol	0.8	N.D.	N.D.
42	40.785	4-Vinylguaiacol	3.1	N.D.	N.D.
43	42.5	HMF	N.D.	0.4	0.2
44	42.881	Catechol	N.D.	N.D.	N.D.
45	42.9	Syringol	0.6	N.D.	N.D.
46	43.499	2-Pentanone	N.D.	N.D.	N.D.
47	46.226	4-Methylcatechol	N.D.	N.D.	N.D.
48	46.4	Isoeugenol	0.4	0.4	0.2
49	47.128	Vanillin	0.2	N.D.	N.D.
50	47.611	Hydroquinone	N.D.	N.D.	N.D.
51	56.28	Levoglucosan	3.1	5.2	2.7
Total			38.4	32.6	17.0

Table S4: Compounds quantified by Py-GC/FID analysis (yields reported in g / 100 g dry biomass) for barley straw. Normalized yields are normalized to the original biomass basis.

Peak no.	**RT**	**Compound**	**Parent**	**Alkali PT**	**Alkali PT (normalized)**
1	4.669	2,3-Butanedione	0.2	0.3	0.2
2	5.266	1,5-Hexadien-3-ol	1.1	1.4	0.8
3	5.605	Benzene	0.5	0.4	0.3
4	6.467	2,5-Dimethylfuran	2.9	2.7	1.6
5	7.020	2-Butenal	0.6	0.5	0.3
6	7.559	Acetic acid	7.3	2.7	1.6
7	8.907	Acetol	3.4	3.2	1.9
8	9.960	3-Penten-2-one	0.2	0.3	0.2
9	13.139	1-Hydroxy-2-butanone	0.7	0.8	0.5
10	13.473	Acetic acid, methyl ester	1.5	1.3	0.8
11	14.582	3-Pentyn-1-ol	0.2	0.4	0.2
12	15.493	2-Methylpentanal	1.6	0.6	0.3
13	15.703	Pyruvic acid, methyl ester	1.3	1.5	0.9
14	16.100	Cyclopentenone	0.4	0.4	0.2
15	16.236	Furfural	1.0	1.5	0.9

16	19.086	Acetol acetate	0.7	0.8	0.4
17	19.321	2-Butanone	0.3	0.2	0.1
18	22.030	3-Methylcyclopentanone	1.1	1.2	0.7
19	22.938	2-Furanmethanol	0.2	0.2	0.1
20	23.319	5-Methylfurfural	0.1	0.2	0.1
21	24.048	3-Methylcyclopent-2-enone	0.2	0.2	0.1
22	24.371	Butyrolactone	0.3	N.D.	N.D.
23	24.937	2(5H)-Furanone	0.9	0.8	0.5
24	25.603	2-Acetyl-5-methylfuran	0.2	0.3	0.2
25	25.798	4-Pentyn-1-ol	0.3	0.8	0.5
26	27.025	3-Methyl-1,2-cyclopentanedione	0.6	0.8	0.5
27	27.124	2-Hydroxy-3-methylcyclopentenone	0.4	0.6	0.3
28	28.809	Phenol	0.2	0.2	0.1
29	29.360	2-Methoxyphenol	0.5	0.2	0.1
30	31.122	o-Cresol	N.D.	N.D.	N.D.
31	31.740	3-Ethyl-2-hydroxy-2-cyclopenten-1-one	0.3	0.4	0.2
32	32.033	3,5-Dihydroxytoluene	0.2	0.2	0.1
33	32.629	m-Cresol	0.1	0.2	0.1
34	32.817	p-Cresol	N.D.	N.D.	N.D.
35	33.2	2-Methylcyclopentanone	0.3	0.2	0.1
36	34.307	p-Creosol	0.2	N.D.	N.D.
37	34.51	Pentanal	0.6	0.4	0.2
38	38.28	3-Methylbutanal	0.2	1.1	0.7
39	38.61	2-Pyranone	0.4	0.5	0.3
40	40.1	Propylene carbonate	0.3	0.4	0.3
41	40.68	4-Vinylphenol	0.6	0.2	0.1
42	40.785	4-Vinylguaiacol	0.9	0.3	0.2
43	42.5	HMF	0.2	0.7	0.4
44	42.881	Catechol	N.D.	N.D.	N.D.
45	42.9	Syringol	0.5	0.4	0.2
46	43.499	2-Pentanone	N.D.	N.D.	N.D.
47	46.226	4-Methylcatechol	0.2	N.D.	N.D.
48	46.4	Isoeugenol	0.3	0.9	0.6
49	47.128	Vanillin	0.3	N.D.	N.D.
50	47.611	Hydroquinone	0.2	N.D.	N.D.
51	56.28	Levoglucosan	2.0	10.2	6.1
Total			36.6	40.6	24.2