

SUPPLEMENTARY INFORMATION FOR

Improving fast pyrolysis of lignin using three additives with different modes of action

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Used lignin and the Organosolv process

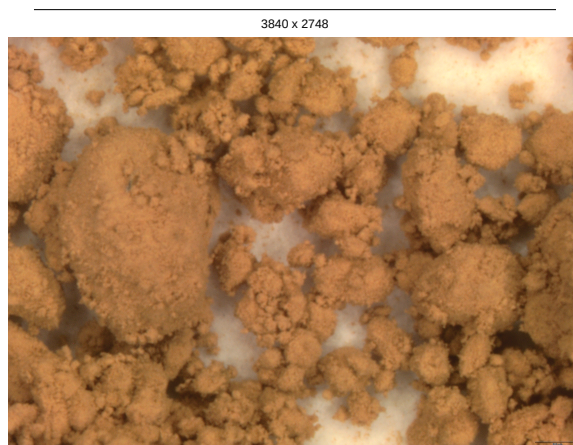


Figure 1: Magnified image of the as-received organosolv lignin (using an Olympus SZX12).

In brief, the starting material for the obtained batch of lignin was debarked beech wood (*Fagus sylvatica*) which was oven-dried. The wood chips were cooked in a solution containing equal amounts of ethanol and water (by mass), along with 0.8 wt.% H_2SO_4 (on oven-dried wood basis) as catalyst. The wood-to-water ratio was 29 on mass basis. Cooking was performed at 170 °C for 100 min, at a maintained pressure of 20 bar, using nitrogen gas. The cooking H-factor of this delignification process was 1501 [Bioresour. Technol., 2016, 199, 128 – 134].

Residues from lignin/attapulgite and lignin-calcium hydroxide



Figure 2: Residues of lignins after oxidation. Left: residues from lignin/attapulgite mixture. Right: residues from lignin with calcium hydroxide.

Evolved compounds from lignin's leachate

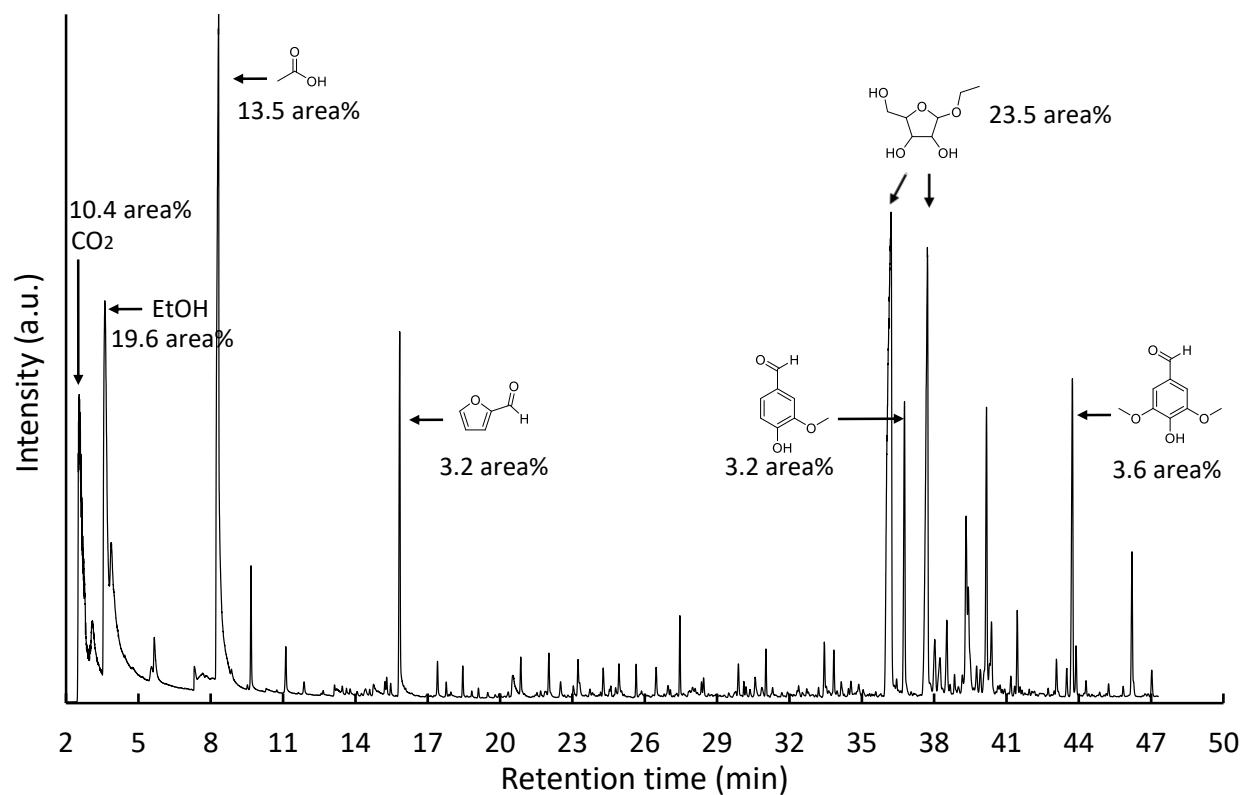


Figure 3: Low-temperature pyrogram (200 °C) to analyze volatile compounds within the minor solid fraction obtained by evaporating water from leachate of pure organosolv lignin. The chromatogram is annotated with compounds that comprise *ca.* 70% of the total area.

TGA/DSC of lignins and its additives

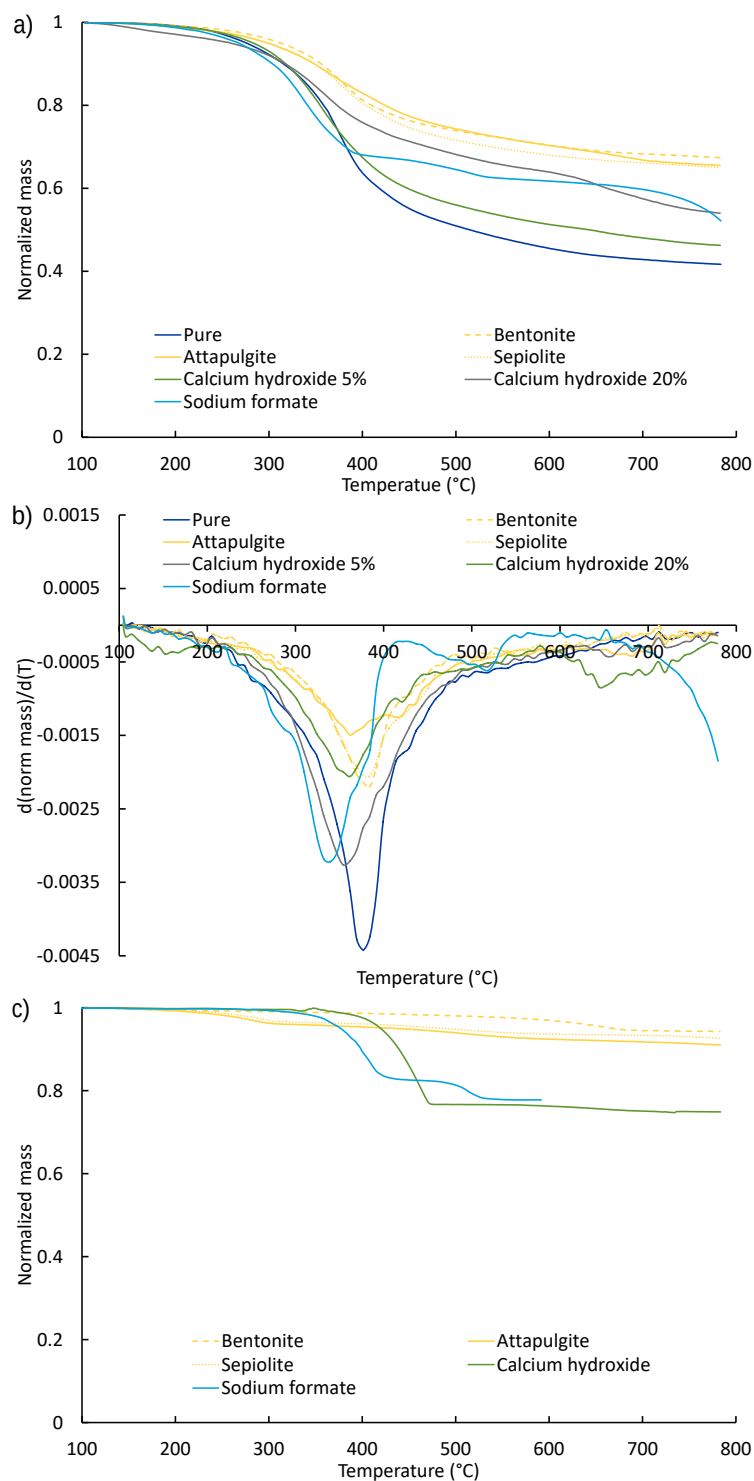


Figure 4: Results from the heating phase of TGA/DSC analysis. (a) normalized TGA from lignins with and without additives. (b) dTGA from lignins with and without additives. (c) normalized TGA from additives themselves.

Raw data for analytical pyrolysis

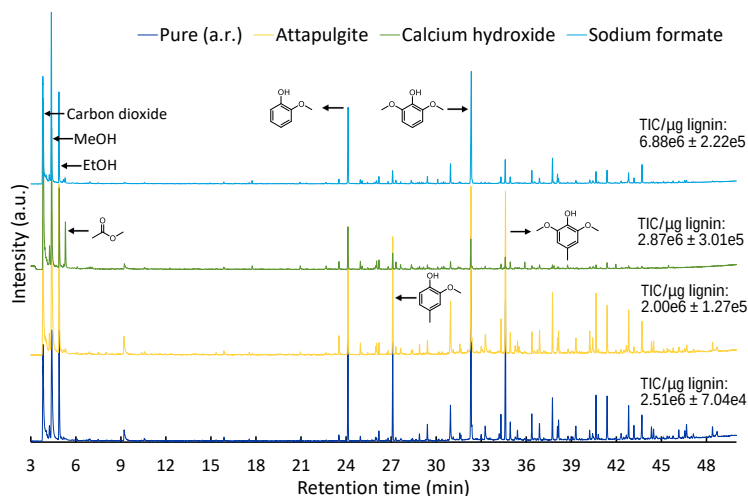


Figure 5: Representative pyrograms for pure lignin, lignin/clay (exemplified by lignin/attapulgit), lignin-calcium hydroxide and lignin/sodium formate (all at 500 °C). The pyrograms are annotated with those compounds that had largest area% and changed most remarkably among the lignins.

The TIC/μg lignin of lignin/sodium formate was between 2.5 to 3 times higher than for the other lignins. This was due to (i) the evolution of CO and H₂ for sodium formate and (ii) to the increased evolution of organic compounds during pyrolysis.

Table 1: Average and standard deviation in each compound's relative peak area upon analytical pyrolysis of lignin with and without additives.

	Pure		Attapulgite		Bentonite		Sepiolite		Calcium hydroxide		Sodium formate	
	Av	stdev	Av	stdev	Av	stdev	Av	stdev	Av	stdev	Av	stdev
Carbon dioxide	7.98	0.19	9.36	0.69	8.85	0.39	10.51	2.40	28.23	1.25	15.44	0.34
Acetaldehyde	1.35	0.04	1.76	0.19	1.44	0.08	1.81	0.14	3.81	0.17	1.44	0.07
Methanol	13.48	0.45	14.43	0.57	13.49	0.20	13.06	0.41	20.21	0.13	19.87	0.15
Ethanol	7.28	0.20	8.71	0.09	8.88	0.20	9.77	0.07	8.57	0.18	8.58	0.09
2-Propenal	0.21	0.01	0.22	0.01	0.22	0.01	0.25	0.01	0.29	0.03	0.16	0.01
Acetone	0.29	0.02	0.28	0.02	0.29	0.01	0.31	0.06	0.58	0.03	0.62	0.04
Methyl acetate	0.24	0.04	0.44	0.05	0.23	0.01	0.48	0.10	5.40	0.04	0.55	0.01
2-Methylfuran	0.09	0.00	0.10	0.00	0.12	0.00	0.17	0.02	0.23	0.01	0.07	0.01
2-Butanone	0.15	0.01	0.16	0.01	0.16	0.01	0.17	0.03	0.30	0.02	0.26	0.00
Methyl propionate	0.01	0.01	0.03	0.00	0.00	0.00	0.02	0.02	0.24	0.03	0.03	0.00
Benzene	0.17	0.07	0.16	0.07	0.13	0.06	0.12	0.04	0.05	0.08	0.14	0.01
Acetic acid	1.40	0.07	1.72	0.15	1.49	0.02	1.57	0.42	1.52	0.23	0.30	0.02
1-hydroxy-2-Propanone	0.06	0.01	0.07	0.04	0.07	0.06	0.12	0.02	0.13	0.02	0.02	0.00
Toluene	0.13	0.03	0.13	0.03	0.10	0.01	0.14	0.04	0.36	0.08	0.14	0.02
Styrene	0.06	0.01	0.08	0.03	0.07	0.01	0.09	0.04	0.00	0.00	0.05	0.02
Furfural	0.28	0.07	0.20	0.02	0.33	0.03	0.29	0.09	0.33	0.02	0.24	0.02
2-Methyl-2-cyclopentenone	0.02	0.00	0.06	0.00	0.03	0.00	0.09	0.04	0.38	0.01	0.28	0.03
3-methyl-2-Cyclopenten-1-one	0.10	0.00	0.14	0.01	0.10	0.01	0.16	0.03	0.48	0.01	0.18	0.01
2,3-Dimethyl-2-cyclopenten-1-one	0.05	0.00	0.10	0.00	0.07	0.00	0.12	0.01	0.45	0.07	0.16	0.04
Phenol	0.40	0.04	0.87	0.14	0.47	0.04	0.72	0.12	0.79	0.03	0.45	0.01
2-Methoxyphenol	5.56	0.18	4.53	0.09	4.58	0.24	4.23	0.16	4.32	0.11	8.44	0.09
2-Methylphenol	0.26	0.01	0.50	0.04	0.37	0.03	0.49	0.04	0.73	0.03	0.38	0.01
1,4-dimethoxybenzene	0.02	0.00	0.08	0.01	0.03	0.01	0.08	0.02	0.29	0.01	0.30	0.02
3-Methylphenol	0.19	0.01	0.31	0.03	0.24	0.01	0.33	0.03	0.33	0.02	0.13	0.01
4-Methylphenol	0.18	0.02	0.50	0.03	0.24	0.02	0.46	0.10	0.82	0.03	0.29	0.01
2-Methoxy-6-methylphenol	0.51	0.01	0.50	0.01	0.47	0.01	0.52	0.05	0.88	0.03	0.71	0.02
2-Methoxy-5-methylphenol	0.14	0.01	0.16	0.01	0.11	0.00	0.16	0.01	0.25	0.01	0.22	0.02
2-Methoxy-4-methylphenol	5.25	0.06	4.94	0.19	5.45	0.13	5.23	0.74	1.52	0.04	1.28	0.02
2,6-Dimethylphenol	0.23	0.01	0.40	0.04	0.31	0.02	0.41	0.03	0.82	0.04	0.39	0.02
3,4-Dimethoxytoluene	0.07	0.01	0.22	0.03	0.18	0.14	0.47	0.04	0.65	0.05	0.20	0.02
3,5-Dimethylphenol	0.10	0.01	0.22	0.01	0.13	0.00	0.22	0.04	0.58	0.02	0.40	0.01
2,6-Dimethoxytoluene	0.12	0.02	0.20	0.01	0.20	0.02	0.28	0.06	0.14	0.00	0.08	0.01
2,3-Dimethoxytoluene	0.34	0.01	0.39	0.02	0.39	0.01	0.44	0.06	0.27	0.01	0.16	0.01
3,4-Dimethylphenol	0.00	0.00	0.06	0.00	0.01	0.00	0.06	0.02	0.18	0.01	0.08	0.00

Table 1 – Continued from previous page

	Pure		Attapulgite		Bentonite		Sepiolite		Calcium hydroxide		Sodium formate	
	Av	stdev	Av	stdev	Av	stdev	Av	stdev	Av	stdev	Av	stdev
4-Ethyl-2-methoxyphenol	0.85	0.02	0.54	0.04	0.70	0.02	0.61	0.08	0.49	0.02	0.78	0.04
1,2,3-Trimethoxybenzene	0.02	0.01	0.04	0.01	0.01	0.00	0.04	0.02	0.19	0.01	0.46	0.03
2,4-Dimethoxytoluene	0.08	0.00	0.14	0.00	0.09	0.01	0.15	0.01	0.30	0.02	0.13	0.01
3,4,5-trimethylphenol	0.01	0.00	0.03	0.00	0.02	0.01	0.03	0.01	0.24	0.03	0.17	0.00
2-Methoxy-4-vinylphenol	2.45	0.13	2.90	0.44	3.13	0.15	2.87	0.09	0.84	0.02	2.00	0.13
3-Methoxyphenol	0.26	0.01	0.28	0.03	0.25	0.00	0.23	0.00	0.08	0.01	0.11	0.01
5-Ethyl-1,3-dimethoxybenzene	0.00	0.00	0.07	0.00	0.01	0.01	0.06	0.01	0.26	0.02	0.11	0.01
2-Methoxy-5-(2-propenyl)-phenol	0.38	0.01	0.42	0.02	0.42	0.01	0.42	0.03	0.17	0.01	0.22	0.01
2-Methoxy-4-propylphenol	0.25	0.01	0.18	0.01	0.19	0.02	0.18	0.03	0.07	0.01	0.11	0.01
Catechol	0.03	0.02	0.09	0.13	0.12	0.01	0.01	0.01	0.00	0.00	0.00	0.00
2,6-Dimethoxyphenol	9.43	0.27	7.25	0.30	7.41	0.45	6.49	0.61	2.92	0.17	13.66	0.10
2-Methoxy-4-(1-propenyl)-phenol	0.30	0.01	0.38	0.07	0.39	0.05	0.31	0.07	0.10	0.02	0.13	0.00
3-Methoxy-5-methylphenol	1.17	0.05	1.30	0.24	1.41	0.05	1.26	0.13	0.25	0.02	0.16	0.05
2,5-Dimethoxytoluene	0.10	0.00	0.14	0.00	0.14	0.01	0.14	0.01	0.09	0.01	0.07	0.01
Ethyl-b-D-ribose	0.50	0.26	0.13	0.04	0.13	0.01	0.17	0.23	0.07	0.03	0.22	0.03
2-Methoxy-4-(2-propenyl)-phenol	1.35	0.02	1.38	0.06	1.45	0.02	1.33	0.08	0.44	0.03	0.66	0.03
3,5-Dimethoxy-4-hydroxytoluene	7.83	0.22	7.11	0.22	7.81	0.16	7.51	1.27	1.08	0.06	2.33	0.03
4-Hydroxy-3-methoxybenzaldehyde	1.04	0.03	0.94	0.04	1.54	0.01	0.81	0.02	0.78	0.02	0.72	0.01
3,5-Dimethoxytoluene	0.29	0.01	0.54	0.04	0.40	0.02	0.61	0.03	0.25	0.02	0.10	0.04
1,2,3-Trimethoxy-5-methylbenzene-nr2	0.55	0.02	0.60	0.03	0.49	0.02	0.55	0.05	0.18	0.02	0.13	0.01
1-(4-Hydroxybenzylidene)acetone	0.09	0.01	0.36	0.14	0.21	0.05	0.46	0.02	0.17	0.05	0.06	0.01
Ethyl-b-D-ribose-nr2	0.15	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
6-Methylisoeugenol	0.12	0.00	0.14	0.00	0.13	0.00	0.14	0.01	0.75	0.05	0.11	0.01
1,2,3-Trimethoxy-5-methylbenzene	1.49	0.02	1.03	0.01	1.28	0.02	1.11	0.29	0.37	0.02	1.31	0.04
3-Methoxy-1,2-benzenediol	0.18	0.05	0.19	0.07	0.24	0.00	0.21	0.05	0.25	0.01	0.30	0.02
4-Hydroxy-3-methoxybenzoic acid methyl ester	0.12	0.01	0.21	0.02	0.12	0.00	0.22	0.09	0.13	0.01	0.01	0.00
1-(4-hydroxy-3-methoxyphenyl)-Ethanone	0.98	0.00	1.07	0.04	0.93	0.02	0.83	0.00	0.52	0.02	0.57	0.01
3-Methoxy-5-propylphenol	0.13	0.00	0.12	0.02	0.13	0.01	0.12	0.01	0.07	0.01	0.10	0.00
3,5-Dihydroxytoluene	0.08	0.01	0.11	0.02	0.12	0.00	0.13	0.02	0.07	0.01	0.01	0.00
4-Ethenyl-2,6-dimethoxyphenol	2.16	0.09	2.63	0.10	2.43	0.04	2.82	0.20	0.39	0.02	2.26	0.14
1-(3,5-dimethoxyphenyl)-ethanone	0.00	0.00	0.02	0.03	0.00	0.00	0.02	0.04	0.32	0.03	0.05	0.09
1-(4-hydroxy-3-methoxyphenyl)-2-propanone	0.67	0.01	0.66	0.02	0.65	0.00	0.69	0.05	0.22	0.03	0.96	0.04
2,6-Dimethoxy-4-(2-propenyl)-phenol	1.07	0.02	0.98	0.03	1.08	0.02	0.99	0.07	0.17	0.02	0.51	0.02
1-(4-hydroxy-3-methoxyphenyl)-1-Propanone	0.28	0.00	0.26	0.01	0.25	0.01	0.23	0.01	0.45	0.03	0.17	0.01
4-(1-Hydroxyallyl)-2-methoxyphenol	0.20	0.01	0.12	0.03	0.19	0.02	0.12	0.06	0.11	0.02	0.02	0.00
1-(4-Hydroxy-3-methoxyphenyl)butan-1-one	1.05	0.03	0.91	0.04	0.99	0.01	0.80	0.05	0.09	0.01	0.34	0.01

Table 1 – Continued from previous page

	Pure		Attapulgite		Bentonite		Sepiolite		Calcium hydroxide		Sodium formate	
	Av	stdev	Av	stdev	Av	stdev	Av	stdev	Av	stdev	Av	stdev
2-Butanone, 4-(4-hydroxy-3-methoxyphenyl)-	0.57	0.02	1.07	0.05	0.69	0.04	1.15	0.02	0.29	0.02	0.48	0.01
3-Allyl-1,5-dimethoxy-6-methyl-benzene	0.64	0.02	1.03	0.04	0.72	0.03	1.10	0.01	0.39	0.02	0.50	0.02
2,6-Dimethoxy-4-(prop-1-en-1-yl)phenol	2.35	0.05	2.38	0.10	2.54	0.05	2.40	0.14	0.39	0.03	1.16	0.01
Homovanillic acid	0.37	0.01	0.18	0.01	0.23	0.02	0.16	0.02	0.01	0.02	0.18	0.01
4-Hydroxy-3,5-dimethoxybenzaldehyde	2.55	0.10	2.23	0.10	3.30	0.06	1.84	0.05	0.65	0.04	1.40	0.02
Homosyringaldehyde	0.55	0.06	0.48	0.13	0.35	0.04	0.55	0.22	0.12	0.01	0.27	0.12
1,2,3-Trimethoxy-5-(2-propenyl)-benzene	0.21	0.01	0.21	0.01	0.20	0.01	0.21	0.02	0.07	0.01	0.15	0.01
Methyl syringate	0.40	0.00	0.54	0.04	0.39	0.00	0.50	0.10	0.18	0.08	0.11	0.01
1-(4-hydroxy-3,5-dimethoxyphenyl)-Ethanone	1.90	0.05	2.03	0.04	1.84	0.01	1.60	0.10	0.26	0.04	1.25	0.02
4-(3-Hydroxy-1-propenyl)-2-methoxyphenol	0.83	0.05	0.23	0.12	0.51	0.04	0.07	0.06	0.00	0.00	0.54	0.04
Syringylacetone	1.59	0.05	1.49	0.08	1.47	0.02	1.49	0.11	0.23	0.01	1.91	0.03
b-Hydroxypropiosyringone	0.12	0.00	0.15	0.01	0.13	0.01	0.13	0.01	0.03	0.01	0.08	0.01
1-(4-hydroxy-3,5-dimethoxyphenyl)-1-propanone	0.71	0.02	0.51	0.08	0.52	0.01	0.42	0.07	0.04	0.02	0.10	0.01
Butylsyringone	0.56	0.04	0.54	0.01	0.53	0.01	0.46	0.01	0.01	0.02	0.13	0.01
4-Acetyl-2,6-dimethoxyphenyl acetate	0.17	0.01	0.07	0.04	0.09	0.02	0.10	0.02	0.00	0.00	0.00	0.00
cis-Sinapyl alcohol	0.15	0.02	0.11	0.06	0.07	0.04	0.15	0.08	0.04	0.04	0.07	0.01
3,5-Dimethoxycinnamic acid	0.13	0.04	0.17	0.05	0.13	0.01	0.21	0.04	0.01	0.01	0.10	0.01
7,8-Dimethoxy-4-methylcoumarin	0.21	0.01	0.22	0.02	0.18	0.02	0.17	0.01	0.32	0.03	0.09	0.01
3,4,5-trimethoxybenzaldehyde	0.18	0.01	0.22	0.02	0.19	0.01	0.19	0.03	0.08	0.01	0.18	0.00
5-(3-Hydroxypropyl)-2,3-dimethoxyphenol	0.61	0.01	0.32	0.03	0.36	0.03	0.26	0.02	0.00	0.00	0.19	0.01
Undecanoic acid	0.47	0.02	0.23	0.01	0.22	0.03	0.06	0.00	0.00	0.00	0.22	0.00
dodecanoic acid	0.89	0.03	0.40	0.05	0.31	0.02	0.18	0.02	0.00	0.00	0.22	0.00
3,4,5-Trimethoxypropenylbenzene	0.27	0.02	0.19	0.02	0.21	0.02	0.15	0.01	0.00	0.00	0.08	0.00
trans-Sinapyl alcohol	0.55	0.12	0.27	0.19	0.28	0.07	0.11	0.09	0.00	0.00	0.11	0.02
3,5-Dimethoxy-4-hydroxycinnamaldehyde	0.63	0.05	0.40	0.05	0.44	0.03	0.37	0.02	0.01	0.00	0.07	0.01

Table 2: Average and standard deviation in each compound's peak area per mass lignin (area/ μg) lignin upon analytical pyrolysis of lignin with and without additives.

	Pure			Attapulgite			Bentonite			Sepiolite			Calcium hydroxide			Sodium formate		
	Av	stdev	Av	stdev	Av	stdev	Av	stdev	Av	stdev	Av	stdev	Av	stdev	Av	stdev	Av	stdev
Carbon dioxide	5.33E+06	1.81E+05	5.79E+06	1.77E+05	6.63E+06	3.73E+05	6.36E+06	1.44E+06	1.05E+07	1.06E+06	1.56E+07	1.06E+06	1.05E+07	1.06E+06	1.56E+07	4.12E+05	4.12E+05	4.12E+05
Acetaldehyde	9.04E+05	4.39E+04	1.09E+06	8.00E+04	1.08E+06	5.00E+04	1.09E+06	8.74E+04	1.42E+06	1.55E+05	1.46E+06	1.55E+05	1.42E+06	1.55E+05	1.46E+06	1.13E+05	1.13E+05	1.13E+05
Methanol	9.02E+06	4.80E+05	8.95E+06	6.30E+05	1.01E+07	6.39E+05	7.92E+06	6.01E+05	7.51E+06	4.66E+05	2.01E+07	4.66E+05	7.51E+06	4.66E+05	2.01E+07	5.59E+05	5.59E+05	5.59E+05
Ethanol	4.87E+06	2.54E+05	5.40E+06	2.68E+05	6.66E+06	3.17E+05	5.92E+06	3.06E+05	3.18E+06	1.67E+05	8.67E+06	1.67E+05	3.18E+06	1.67E+05	8.67E+06	2.10E+05	2.10E+05	2.10E+05
2-Propenal	1.39E+05	8.78E+03	1.34E+05	7.39E+03	1.65E+05	4.68E+03	1.51E+05	1.54E+04	1.08E+05	1.98E+04	1.59E+05	1.98E+04	1.08E+05	1.98E+04	1.59E+05	9.36E+03	9.36E+03	9.36E+03
Acetone	1.93E+05	1.75E+04	1.73E+05	8.66E+03	2.18E+05	1.02E+04	1.86E+05	3.19E+04	2.17E+05	2.69E+04	6.21E+05	2.69E+04	2.17E+05	2.69E+04	6.21E+05	3.42E+04	3.42E+04	3.42E+04
Methyl acetate	1.63E+05	2.75E+04	2.71E+05	2.30E+04	1.71E+05	1.38E+04	2.89E+05	6.14E+04	2.01E+06	1.38E+05	5.59E+05	1.38E+05	2.01E+06	1.38E+05	5.59E+05	1.87E+04	1.87E+04	1.87E+04
2-Methylfuran	5.79E+04	2.95E+03	6.37E+04	1.70E+03	9.28E+04	3.18E+03	1.03E+05	1.39E+04	8.69E+04	6.53E+03	7.28E+04	6.53E+03	8.69E+04	6.53E+03	7.28E+04	9.74E+03	9.74E+03	9.74E+03
2-Butanone	9.93E+04	5.71E+03	9.89E+04	6.64E+03	1.18E+05	3.66E+03	1.06E+05	1.47E+04	1.13E+05	7.76E+03	2.67E+05	7.76E+03	1.13E+05	7.76E+03	2.67E+05	8.61E+03	8.61E+03	8.61E+03
Methyl propionate	3.57E+03	6.18E+03	1.76E+04	5.34E+02	0.00E+00	0.00E+00	1.19E+04	1.07E+04	8.75E+04	1.01E+04	3.48E+04	1.01E+04	8.75E+04	1.01E+04	3.48E+04	1.07E+03	1.07E+03	1.07E+03
Benzene	1.17E+05	5.02E+04	1.02E+05	4.37E+04	9.78E+04	4.43E+04	7.21E+04	2.55E+04	1.92E+04	3.33E+04	1.40E+05	3.33E+04	1.92E+04	3.33E+04	1.40E+05	1.37E+04	1.37E+04	1.37E+04
Acetic acid	9.34E+05	2.07E+04	1.07E+06	1.20E+05	1.12E+06	5.68E+04	9.48E+05	2.56E+05	5.65E+05	1.12E+05	3.04E+05	1.12E+05	5.65E+05	1.12E+05	3.04E+05	1.60E+04	1.60E+04	1.60E+04
1-hydroxy-2-Propanone	3.79E+04	5.66E+03	4.11E+04	2.73E+04	4.83E+04	3.80E+04	7.41E+04	1.01E+04	5.00E+04	6.33E+03	2.03E+04	6.33E+03	5.00E+04	6.33E+03	2.03E+04	2.02E+03	2.02E+03	2.02E+03
Toluene	8.55E+04	2.04E+04	8.16E+04	2.40E+04	7.63E+04	6.41E+03	8.25E+04	2.71E+04	1.33E+05	3.20E+04	1.45E+05	3.20E+04	1.33E+05	3.20E+04	1.45E+05	1.39E+04	1.39E+04	1.39E+04
Styrene	4.05E+04	7.68E+03	5.01E+04	2.23E+04	5.34E+04	4.40E+03	5.22E+04	2.42E+04	0.00E+00	0.00E+00	5.35E+04	0.00E+00	0.00E+00	0.00E+00	5.35E+04	1.97E+04	1.97E+04	1.97E+04
Furfural	1.91E+05	5.47E+04	1.22E+05	1.41E+04	2.47E+05	1.66E+04	1.78E+05	5.64E+04	1.23E+05	1.08E+04	2.38E+05	1.08E+04	1.23E+05	1.08E+04	2.38E+05	1.13E+04	1.13E+04	1.13E+04
2-Methyl-2-cyclopentenone	1.39E+04	1.68E+03	3.50E+04	8.43E+02	2.53E+04	1.47E+02	5.57E+04	2.33E+04	1.42E+05	7.47E+03	2.82E+05	7.47E+03	1.42E+05	7.47E+03	2.82E+05	2.27E+04	2.27E+04	2.27E+04
3-methyl-2-Cyclopenten-1-one	6.93E+04	4.81E+03	8.49E+04	4.18E+03	7.20E+04	6.14E+03	9.49E+04	2.00E+04	1.78E+05	1.03E+04	1.84E+05	1.03E+04	1.78E+05	1.03E+04	1.84E+05	6.74E+03	6.74E+03	6.74E+03
2,3-Dimethyl-2-cyclopenten-1-one	3.47E+04	3.69E+03	6.04E+04	2.35E+03	5.17E+04	3.35E+03	7.10E+04	7.11E+03	1.66E+05	1.66E+04	1.60E+05	1.66E+04	1.66E+05	1.66E+04	1.60E+05	4.09E+04	4.09E+04	4.09E+04
Phenol	2.65E+05	3.10E+04	5.45E+05	1.13E+05	3.53E+05	3.47E+04	4.37E+05	7.75E+04	2.92E+05	1.56E+04	4.53E+05	1.56E+04	2.92E+05	1.56E+04	4.53E+05	7.03E+03	7.03E+03	7.03E+03
2-Methoxyphenol	3.72E+06	2.02E+05	2.81E+06	1.96E+05	3.44E+06	3.74E+05	2.57E+06	2.17E+05	1.61E+06	8.00E+04	8.53E+06	8.00E+04	1.61E+06	8.00E+04	8.53E+06	3.17E+05	3.17E+05	3.17E+05
2-Methylphenol	1.71E+05	9.65E+03	3.14E+05	3.82E+04	2.75E+05	2.25E+04	3.00E+05	3.22E+04	2.70E+05	1.15E+04	3.85E+05	1.15E+04	2.70E+05	1.15E+04	3.85E+05	2.59E+03	2.59E+03	2.59E+03
1,4-dimethoxybenzene	1.48E+04	2.40E+03	4.69E+04	7.87E+03	2.48E+04	6.94E+03	4.62E+04	1.46E+04	1.07E+05	3.68E+03	3.01E+05	3.68E+03	1.07E+05	3.68E+03	3.01E+05	1.95E+04	1.95E+04	1.95E+04
3-Methylphenol	1.26E+05	7.35E+03	1.92E+05	2.44E+04	1.79E+05	8.82E+03	1.97E+05	1.99E+04	1.22E+05	9.77E+03	1.36E+05	9.77E+03	1.22E+05	9.77E+03	1.36E+05	8.59E+03	8.59E+03	8.59E+03
4-Methylphenol	1.20E+05	1.67E+04	3.09E+05	3.47E+04	2.81E+05	1.82E+04	2.81E+05	6.16E+04	3.03E+05	1.52E+04	2.91E+05	1.52E+04	3.03E+05	1.52E+04	2.91E+05	5.02E+03	5.02E+03	5.02E+03
2-Methoxy-6-methylphenol	3.38E+05	1.68E+04	3.11E+05	2.37E+04	3.52E+05	2.59E+04	3.12E+05	3.71E+04	3.26E+05	1.30E+04	7.20E+05	1.30E+04	3.26E+05	1.30E+04	7.20E+05	3.35E+04	3.35E+04	3.35E+04
2-Methoxy-5-methylphenol	9.15E+04	5.67E+03	9.69E+04	1.09E+04	8.54E+04	6.18E+03	9.65E+04	1.09E+04	9.38E+04	4.27E+03	2.21E+05	4.27E+03	9.38E+04	4.27E+03	2.21E+05	1.80E+04	1.80E+04	1.80E+04
2-Methoxy-4-methylphenol	3.51E+06	5.09E+04	3.07E+06	2.66E+05	4.08E+06	1.95E+05	3.17E+06	4.83E+05	5.65E+05	3.03E+04	1.29E+06	3.03E+04	5.65E+05	3.03E+04	1.29E+06	4.10E+04	4.10E+04	4.10E+04
2,6-Dimethylphenol	1.52E+05	7.80E+03	2.52E+05	3.96E+04	2.29E+05	1.16E+04	2.49E+05	2.36E+04	3.05E+05	1.03E+04	3.97E+05	1.03E+04	3.05E+05	1.03E+04	3.97E+05	8.80E+03	8.80E+03	8.80E+03
3,4-Dimethoxytoluene	4.50E+04	9.85E+03	1.37E+05	1.39E+04	1.29E+05	9.61E+04	2.84E+05	2.52E+04	2.42E+05	1.17E+04	1.98E+05	1.17E+04	2.42E+05	1.17E+04	1.98E+05	1.83E+04	1.83E+04	1.83E+04
3,5-Dimethylphenol	7.00E+04	8.59E+03	1.35E+05	7.10E+03	9.79E+04	5.24E+03	1.32E+05	2.34E+04	2.15E+05	1.20E+04	4.07E+05	1.20E+04	2.15E+05	1.20E+04	4.07E+05	4.29E+03	4.29E+03	4.29E+03
2,6-Dimethoxytoluene	8.30E+04	1.23E+04	1.22E+05	1.12E+04	1.52E+05	1.20E+04	1.68E+05	3.37E+04	5.23E+04	4.41E+03	8.15E+04	4.41E+03	5.23E+04	4.41E+03	8.15E+04	3.72E+03	3.72E+03	3.72E+03
2,3-Dimethoxytoluene	2.27E+05	7.18E+03	2.40E+05	2.20E+04	2.89E+05	9.51E+03	2.66E+05	4.09E+04	1.00E+05	5.05E+03	1.60E+05	5.05E+03	1.00E+05	5.05E+03	1.60E+05	9.54E+03	9.54E+03	9.54E+03
3,4-Dimethylphenol	1.32E+03	1.36E+03	3.56E+04	3.46E+03	1.08E+04	4.57E+02	3.83E+04	1.44E+04	6.84E+04	4.12E+03	8.00E+04	4.12E+03	6.84E+04	4.12E+03	8.00E+04	2.49E+03	2.49E+03	2.49E+03

Table 2 – Continued from previous page

	Pure			Attapulgitte			Bentonite			Sepiolite			Calcium hydroxide			Sodium formate		
	Av	stdev		Av	stdev		Av	stdev		Av	stdev		Av	stdev		Av	stdev	
4-Ethyl-2-methoxyphenol	5.71E+05	2.68E+04		3.36E+05	3.12E+04		5.28E+05	3.81E+04		3.71E+05	5.62E+04		1.84E+05	9.92E+03		7.86E+05	3.53E+04	
1,2,3-Trimethoxybenzene	1.60E+04	5.82E+03		2.45E+04	4.70E+03		1.01E+04	2.61E+03		2.23E+04	1.10E+04		7.16E+04	2.20E+03		4.68E+05	4.13E+04	
2,4-Dimethoxytoluene	5.25E+04	2.36E+03		8.49E+04	4.88E+03		6.94E+04	6.51E+03		8.94E+04	7.76E+03		1.12E+05	6.60E+03		1.36E+05	9.81E+03	
3,4,5-trimethylphenol	3.87E+03	2.02E+03		2.00E+04	2.38E+03		1.18E+04	4.02E+03		2.06E+04	9.00E+03		9.05E+04	1.03E+04		1.74E+05	5.35E+03	
2-Methoxy-4-vinylphenol	1.63E+06	7.08E+04		1.81E+06	3.42E+05		2.35E+06	2.11E+05		1.73E+06	4.97E+04		3.14E+05	2.20E+04		2.02E+06	9.78E+04	
3-Methoxyphenol	1.73E+05	8.28E+03		1.75E+05	2.34E+04		1.88E+05	1.31E+04		1.40E+05	8.05E+03		3.07E+04	2.23E+03		1.12E+05	1.24E+04	
5-Ethyl-1,3-dimethoxybenzene	0.00E+00	0.00E+00		4.32E+04	9.61E+02		5.03E+03	8.72E+03		3.38E+04	4.93E+03		9.75E+04	3.16E+03		1.14E+05	1.52E+04	
2-Methoxy-5-(2-propenyl)-phenol	2.51E+05	3.51E+03		2.58E+05	2.26E+04		3.15E+05	1.32E+04		2.54E+05	2.15E+04		6.31E+04	2.99E+03		2.25E+05	1.04E+04	
2-Methoxy-4-propylphenol	1.69E+05	7.52E+03		1.12E+05	9.94E+03		1.40E+05	1.75E+04		1.06E+05	1.83E+04		2.64E+04	3.38E+03		1.10E+05	7.06E+03	
Catechol	1.89E+04	1.61E+04		5.52E+04	8.59E+04		9.02E+04	1.12E+04		4.54E+03	7.04E+03		0.00E+00	0.00E+00		0.00E+00	0.00E+00	
2,6-Dimethoxyphenol	6.30E+06	2.30E+05		4.50E+06	4.10E+05		5.57E+06	6.64E+05		3.93E+06	4.79E+05		1.09E+06	1.18E+05		1.38E+07	3.46E+05	
2-Methoxy-4-(1-propenyl)-phenol	2.03E+05	1.18E+04		2.35E+05	5.06E+04		2.94E+05	4.51E+04		1.86E+05	3.96E+04		3.89E+04	7.91E+03		1.29E+05	2.41E+03	
3-Methoxy-5-methylphenol	7.82E+05	3.53E+04		8.11E+05	1.80E+05		1.06E+06	6.23E+04		7.64E+05	6.01E+04		9.45E+04	7.16E+03		1.59E+05	5.02E+04	
2,5-Dimethoxytoluene	6.88E+04	2.15E+03		8.67E+04	6.83E+03		1.03E+05	3.47E+03		8.23E+04	9.33E+03		3.19E+04	4.09E+03		7.52E+04	8.10E+03	
Ethyl-b-D-ribose	3.38E+05	1.83E+05		8.27E+04	2.89E+04		9.43E+04	9.54E+03		1.00E+05	1.40E+05		2.44E+04	1.00E+04		2.27E+05	3.32E+04	
2-Methoxy-4-(2-propenyl)-phenol	9.04E+05	2.40E+04		8.58E+05	7.94E+04		1.09E+06	6.99E+04		8.06E+05	6.41E+04		1.64E+05	1.30E+04		6.69E+05	2.31E+04	
3,5-Dimethoxy-4-hydroxytoluene	5.23E+06	1.13E+04		4.42E+06	3.60E+05		5.85E+06	2.69E+05		4.55E+06	7.98E+05		4.01E+05	3.05E+04		2.35E+06	8.64E+04	
4-Hydroxy-3-methoxybenzaldehyde	6.95E+05	1.01E+04		5.85E+05	4.37E+04		1.16E+06	6.39E+04		4.93E+05	1.55E+04		2.88E+05	1.27E+04		7.29E+05	1.69E+04	
3,5-Dimethoxytoluene	1.95E+05	8.06E+03		3.38E+05	4.24E+04		2.99E+05	5.78E+03		3.69E+05	1.93E+04		9.13E+04	6.53E+03		1.04E+05	4.16E+04	
1,2,3-Trimethoxy-5-methylbenzene-nr2	3.66E+05	6.09E+03		3.71E+05	3.95E+04		3.69E+05	1.61E+04		3.32E+05	3.84E+04		6.63E+04	8.09E+03		1.34E+05	8.62E+03	
1-(4-Hydroxybenzylidene)acetone	6.14E+04	2.70E+03		2.23E+05	8.01E+04		1.56E+05	4.48E+04		2.79E+05	9.21E+03		6.45E+04	1.97E+04		5.78E+04	6.62E+03	
Ethyl-b-D-ribose-nr2	1.02E+05	2.49E+04		0.00E+00	0.00E+00		0.00E+00	0.00E+00		0.00E+00	0.00E+00		0.00E+00	0.00E+00		0.00E+00	0.00E+00	
6-Methylisoeugenol	8.12E+04	3.54E+03		8.86E+04	4.94E+03		9.78E+04	4.85E+03		8.36E+04	7.99E+03		2.78E+05	8.31E+03		1.14E+05	9.82E+03	
1,2,3-Trimethoxy-5-methylbenzene	9.95E+05	3.71E+04		6.37E+05	3.42E+04		9.58E+05	5.93E+04		6.74E+05	1.79E+05		1.38E+05	9.18E+03		1.33E+06	7.95E+04	
3-Methoxy-1,2-benzenediol	1.24E+05	3.70E+04		1.18E+05	4.23E+04		1.80E+05	1.28E+04		1.29E+05	2.42E+04		9.34E+04	3.32E+03		2.98E+05	2.40E+04	
4-Hydroxy-3-methoxybenzoic acid methyl ester	7.93E+04	8.05E+03		1.28E+05	6.30E+03		8.92E+04	8.16E+03		1.35E+05	5.21E+04		4.63E+04	4.28E+03		9.94E+03	6.31E+02	
1-(4-hydroxy-3-methoxyphenyl)-Ethanone	6.57E+05	1.58E+04		6.62E+05	5.24E+04		6.96E+05	4.33E+04		5.04E+05	2.44E+04		1.92E+05	1.45E+04		5.72E+05	1.30E+04	
3-Methoxy-5-propylphenol	8.43E+04	4.27E+03		7.53E+04	1.50E+04		9.45E+04	1.13E+04		7.36E+04	7.63E+03		2.55E+04	7.55E+02		1.04E+05	7.19E+03	
3,5-Dihydroxytoluene	5.29E+04	6.11E+03		6.69E+04	1.31E+04		8.96E+04	6.73E+03		7.84E+04	1.15E+04		2.60E+04	1.76E+03		1.07E+04	4.72E+03	
4-Ethenyl-2,6-dimethoxyphenol	1.44E+06	2.17E+04		1.63E+06	1.44E+05		1.82E+06	1.28E+05		1.71E+06	1.51E+05		1.45E+05	1.61E+04		2.28E+06	9.03E+04	
1-(3,5-dimethoxyphenyl)-ethanone	0.00E+00	0.00E+00		1.14E+04	1.98E+04		0.00E+00	0.00E+00		1.46E+04	2.53E+04		1.18E+05	1.24E+04		5.15E+04	8.93E+04	
1-(4-hydroxy-3-methoxyphenyl)-2-propanone	4.46E+05	7.95E+03		4.11E+05	2.71E+04		4.91E+05	3.31E+04		4.19E+05	3.38E+04		8.18E+04	1.24E+04		9.70E+05	3.65E+04	
2,6-Dimethoxy-4-(2-propenyl)-phenol	7.18E+05	6.75E+03		6.08E+05	4.41E+04		8.13E+05	5.42E+04		6.01E+05	5.09E+04		6.25E+04	9.78E+03		5.16E+05	2.95E+04	
1-(4-hydroxy-3-methoxyphenyl)-1-Propanone	1.89E+05	5.15E+03		1.63E+05	1.16E+04		1.85E+05	1.52E+04		1.42E+05	1.03E+04		1.68E+05	1.19E+04		1.73E+05	1.42E+04	
4-(1-Hydroxyallyl)-2-methoxyphenol	1.34E+05	9.14E+02		7.60E+04	2.00E+04		1.43E+05	1.56E+04		7.05E+04	3.65E+04		4.22E+04	6.58E+03		2.35E+04	3.35E+03	
1-(4-Hydroxy-3-methoxyphenyl)butan-1-one	6.99E+05	2.69E+04		5.64E+05	4.39E+04		7.46E+05	4.22E+04		4.82E+05	4.12E+04		3.33E+04	4.55E+03		3.45E+05	1.43E+04	

Table 2 – Continued from previous page

	Pure		Attapulgitte		Bentonite		Sepiolite		Calcium hydroxide		Sodium formate	
	Av	stdev	Av	stdev	Av	stdev	Av	stdev	Av	stdev	Av	stdev
2-Butanone, 4-(4-hydroxy-3-methoxyphenyl)-	3.82E+05	9.13E+03	6.65E+05	6.31E+04	5.17E+05	8.96E+03	6.94E+05	2.84E+04	1.09E+05	1.27E+04	4.89E+05	2.20E+04
3-Allyl-1,5-dimethoxy-6-methyl-benzene	4.27E+05	7.71E+03	6.38E+05	5.96E+04	5.43E+05	1.30E+04	6.64E+05	3.76E+04	1.43E+05	7.15E+03	5.05E+05	3.27E+04
2,6-Dimethoxy-4-(prop-1-en-1-yl)phenol	1.57E+06	1.19E+04	1.48E+06	1.26E+05	1.90E+06	1.28E+05	1.45E+06	1.13E+05	1.44E+05	9.87E+03	1.17E+06	2.74E+04
Homovanillic acid	2.47E+05	1.57E+03	1.12E+05	1.34E+04	1.69E+05	2.02E+04	9.85E+04	1.57E+04	3.29E+03	5.70E+03	1.83E+05	1.86E+04
4-Hydroxy-3,5-dimethoxybenzaldehyde	1.70E+06	4.67E+04	1.38E+06	9.49E+04	2.48E+06	1.94E+05	1.12E+06	2.61E+04	2.42E+05	2.12E+04	1.41E+06	6.42E+04
Homosyringaldehyde	3.66E+05	4.03E+04	2.97E+05	7.57E+04	2.62E+05	4.17E+04	3.31E+05	1.37E+05	4.41E+04	5.67E+03	2.77E+05	1.27E+05
1,2,3-Trimethoxy-5-(2-propenyl)-benzene	1.39E+05	4.90E+03	1.28E+05	9.58E+03	1.47E+05	4.19E+03	1.26E+05	1.70E+04	2.44E+04	1.78E+03	1.52E+05	1.31E+04
Methyl syringate	2.68E+05	6.15E+03	3.33E+05	9.77E+03	2.92E+05	1.74E+04	3.02E+05	6.15E+04	6.74E+04	2.97E+04	1.13E+05	1.36E+04
1-(4-hydroxy-3,5-dimethoxyphenyl)-Ethanone	1.27E+06	8.95E+03	1.26E+06	7.48E+04	1.38E+06	8.71E+04	9.66E+05	6.80E+04	9.85E+04	1.63E+04	1.26E+06	4.43E+04
4-(3-Hydroxy-1-propenyl)-2-methoxyphenol	5.57E+05	2.78E+04	1.44E+05	7.97E+04	3.83E+05	5.03E+04	4.06E+04	3.59E+04	4.02E+02	1.68E+02	5.50E+05	5.63E+04
Syringylacetone	1.06E+06	3.04E+04	9.22E+05	7.77E+04	1.10E+06	7.02E+04	9.01E+05	7.32E+04	8.51E+04	7.32E+03	1.93E+06	4.67E+04
b-Hydroxypropiosyringone	7.97E+04	1.07E+03	9.63E+04	9.79E+03	9.75E+04	3.86E+03	7.73E+04	5.48E+03	9.98E+03	1.56E+03	8.12E+04	8.05E+03
1-(4-hydroxy-3,5-dimethoxyphenyl)-1-propanone	4.74E+05	7.87E+03	3.15E+05	3.24E+04	3.86E+05	1.55E+04	2.53E+05	4.27E+04	1.55E+04	8.48E+03	1.05E+05	9.10E+03
Butylsyringone	3.74E+05	2.29E+04	3.37E+05	1.61E+04	3.95E+05	1.61E+04	2.78E+05	9.12E+03	3.93E+03	5.86E+03	1.30E+05	1.20E+04
4-Acetyl-2,6-dimethoxyphenyl acetate	1.13E+05	5.59E+03	4.36E+04	2.41E+04	6.80E+04	1.49E+04	5.82E+04	1.19E+04	0.00E+00	0.00E+00	0.00E+00	0.00E+00
cis-Sinapyl alcohol	9.71E+04	1.58E+04	7.07E+04	3.56E+04	5.23E+04	2.88E+04	8.93E+04	4.95E+04	1.41E+04	1.32E+04	6.62E+04	4.88E+03
3,5-Dimethoxycinnamic acid	8.75E+04	2.40E+04	1.05E+05	2.95E+04	9.87E+04	1.01E+04	1.29E+05	2.08E+04	2.98E+03	5.16E+03	9.87E+04	4.59E+03
7,8-Dimethoxy-4-methylcoumarin	1.38E+05	1.31E+04	1.35E+05	1.85E+04	1.36E+05	1.88E+04	1.05E+05	5.73E+03	1.19E+05	1.84E+04	9.15E+04	1.37E+04
3,4,5-trimethoxybenzaldehyde	1.19E+05	8.00E+03	1.34E+05	1.15E+04	1.45E+05	1.24E+04	1.12E+05	1.66E+04	2.87E+04	3.96E+03	1.84E+05	6.46E+03
5-(3-Hydroxypropyl)-2,3-dimethoxyphenol	4.09E+05	1.67E+04	1.97E+05	2.68E+04	2.73E+05	2.02E+04	1.59E+05	2.11E+04	8.25E+02	9.65E+02	1.96E+05	1.27E+04
Undecanoic acid	3.16E+05	1.96E+04	1.43E+05	1.04E+04	1.68E+05	2.78E+04	3.90E+04	2.58E+03	5.81E+02	1.01E+03	2.27E+05	8.71E+03
dodecanoic acid	5.96E+05	1.55E+04	2.48E+05	3.77E+04	2.30E+05	2.62E+04	1.08E+05	1.05E+04	0.00E+00	0.00E+00	2.17E+05	3.22E+03
3,4,5-Trimethoxypropenylbenzene	1.80E+05	1.13E+04	1.18E+05	1.48E+04	1.61E+05	2.04E+04	9.22E+04	3.87E+03	1.40E+03	1.06E+03	7.65E+04	2.78E+03
trans-Sinapyl alcohol	3.68E+05	7.44E+04	1.67E+05	1.21E+05	2.10E+05	6.21E+04	6.81E+04	5.52E+04	1.09E+03	1.48E+03	1.09E+05	1.99E+04
3,5-Dimethoxy-4-hydroxycinnamaldehyde	4.24E+05	2.61E+04	2.48E+05	3.57E+04	3.34E+05	3.99E+04	2.26E+05	1.20E+04	2.63E+03	1.85E+03	7.00E+04	6.07E+03

PCA analysis from py-GC/MS

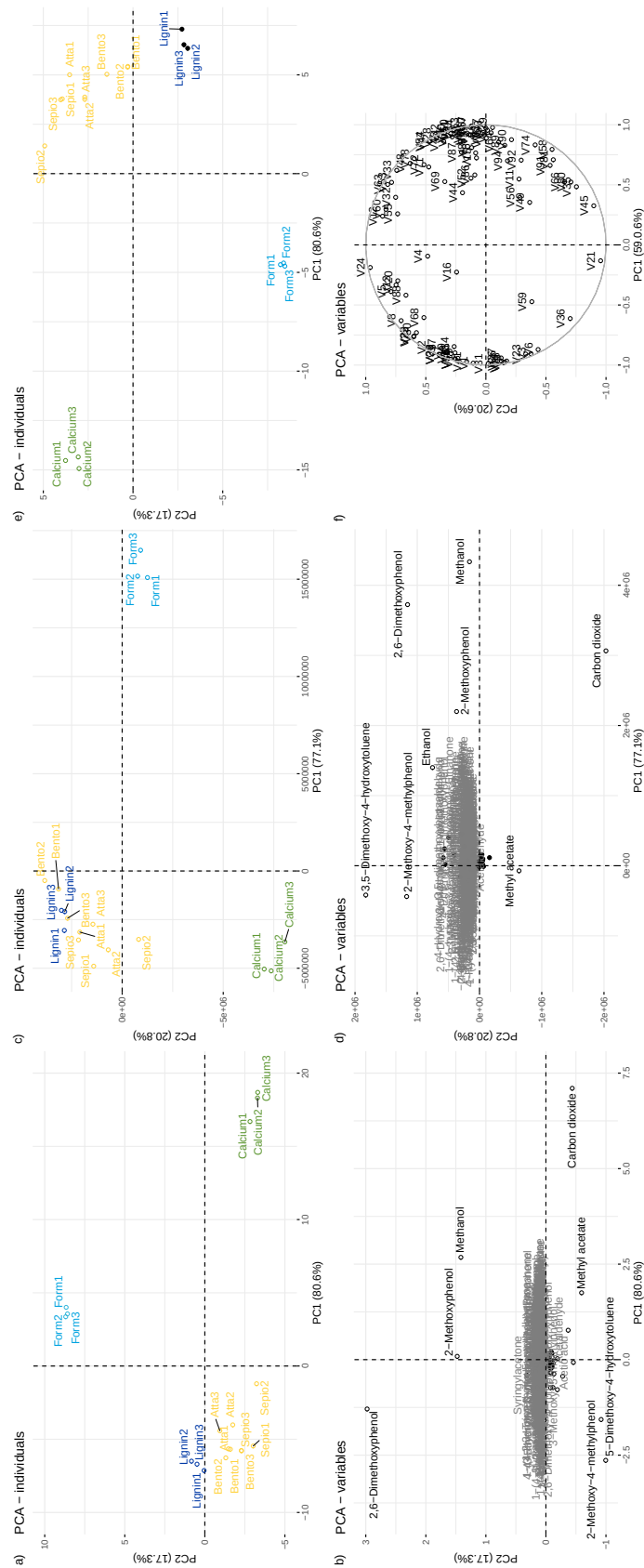


Figure 6: Individuals and variables plots from principal component analysis, using lignin with and without additives as dependent variables and unscaled area% (a, b), unscaled area/ μg lignin (c, d) and scaled area% (e, f) as independent variables.

Pre-pyrolysis softening and melting

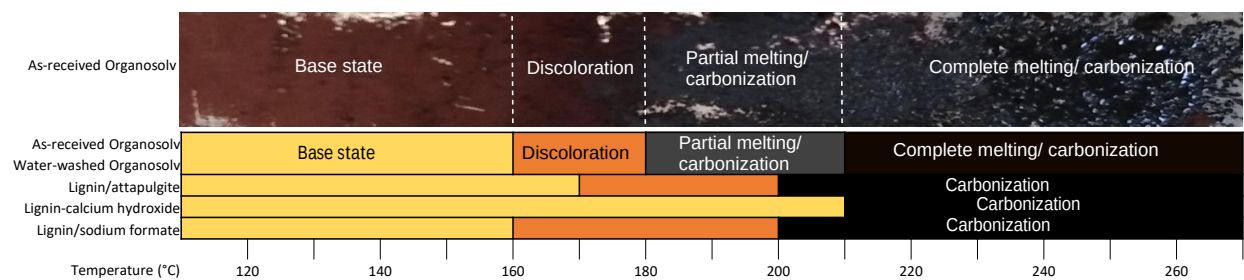


Figure 7: Visualization of the textural change in lignin and lignins with additives over a temperature range from 110 °C to 270 °C.

Practical observations during fast pyrolysis



Figure 8: Visualization of pyrolysis liquids from fast pyrolysis of lignins. From left to right: pure lignin, lignin/attapulgite, lignin-calcium hydroxide and lignin/sodium formate.

Elemental analysis of the aqueous phase

Table 3: Elemental analysis of the aqueous phase from pyrolysis of pure organosolv lignin and lignins with additives.

Aqueous phase	C (wt.%)	H (wt.%)	N (wt.%)	O (wt.%)	H/C	O/C
Lignin/attapulgate	4.23 ± 0.03	11.21 ± 0.04	0.45 ± 0.03	84.11 ± 0.02	31.80	14.91
Lignin-calcium hydroxide	1.60 ± 0.20	9.71 ± 2.07	0.55 ± 0.02	88.15 ± 2.29	72.78	41.31
Lignin/sodium formate	2.28 ± 0.03	9.71 ± 2.07	0.41 ± 0.03	86.15 ± 0.11	58.79	28.34

GCxGC-FID analysis of the aqueous phase

Table 4: Concentrations of various groups of GC-detectable compounds (wt.%, liquid basis) in the aqueous phase after pyrolysis of lignin with and without additives.

	Aqueous phase		
	Attapulgite	Ca(OH) ₂	CHOONa
Alkylphenols	0.52	0.28	0.17
Cathecols	0.37	0.01	0.00
Guaiacols	0.04	0.01	0.11
Acids	0.11	0.11	0.16
HCs (lin/branch)	0.09	0.00	0.00
Cycloalkanes	0.00	0.00	0.00
Ket./aldehy.	0.00	0.03	0.02
Aromatics	0.07	0.08	0.07
PAHCs	0.00	0.00	0.00
Total	1.19	0.52	0.52

2D GC raw chromatograms

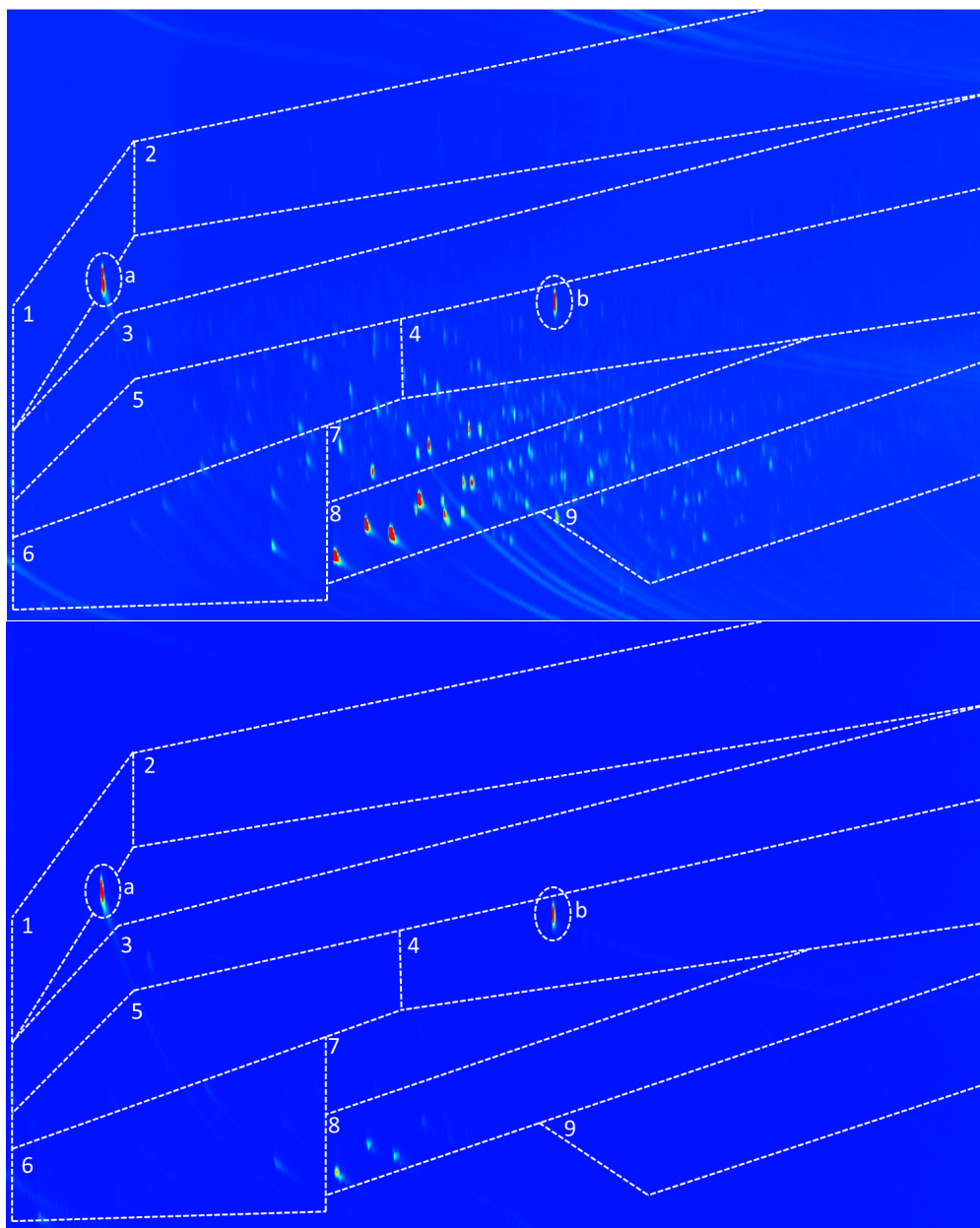


Figure 9: Representative GCxGC-FID chromatogram of a heavy pyrolysis liquid from lignin/attapulgitite pyrolysis (top) and its aqueous phase (bottom). The regions in the GCxGC-FID chromatogram have the following meaning: 1 = cycloalkanes, 2 = linear/branched alkanes, 3 = aromatics, 4 = naphthalenes and polycyclic aromatic hydrocarbons, 5 = ketones/alcohols, 6 = acids, 7 = guaiacols, 8 = alkylphenolics, 9 = catechols, a = internal standard (*di*-butylether) and b = butylated hydroxytoluene (*i.e.*, stabilizer in THF).

HSQC NMR raw spectra

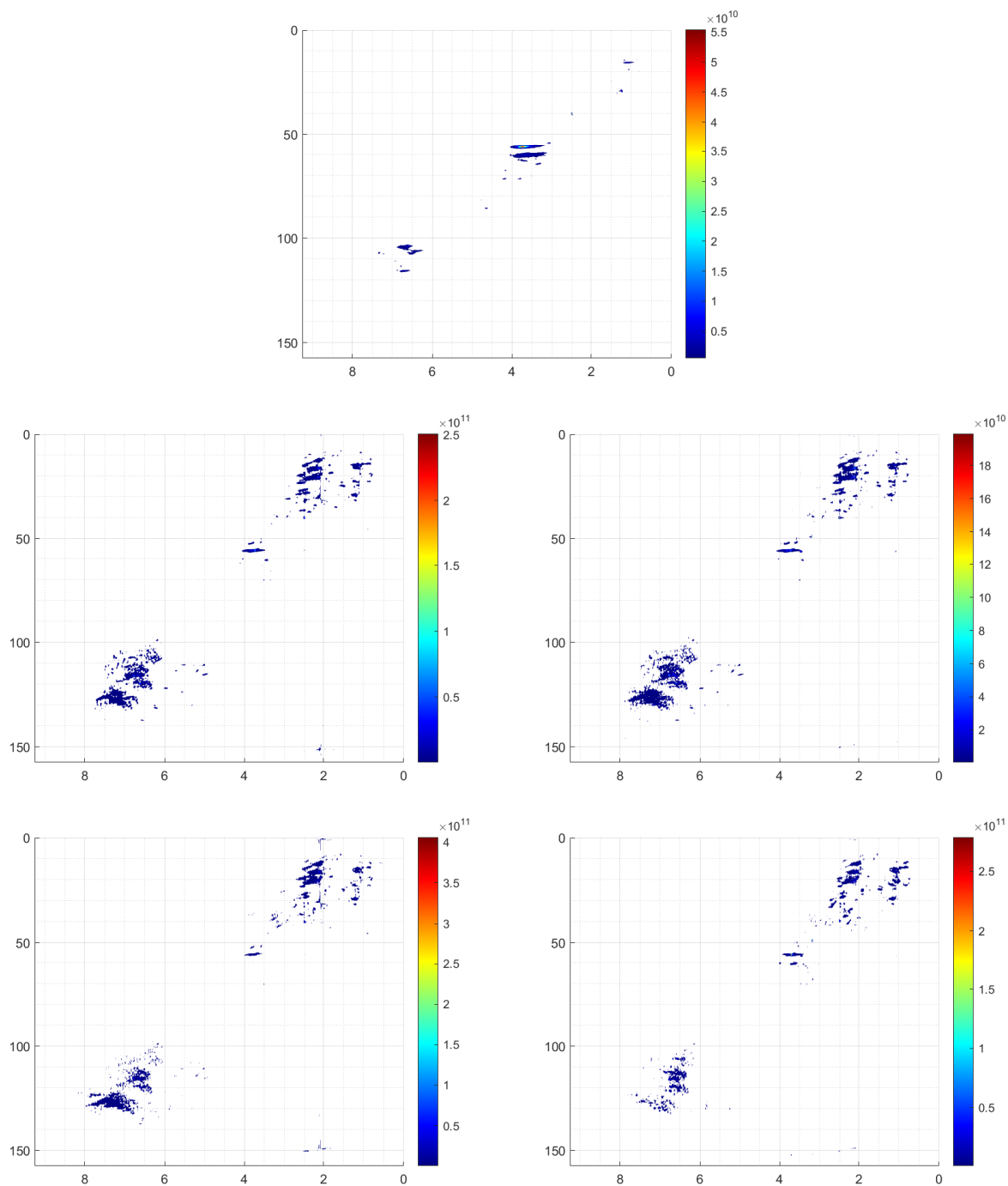


Figure 10: Raw HSQC NMR spectra (x-axis proton NMR and y-axis is carbon NMR). In order of appearance: pure organosolv lignin, heavy liquids from pure lignin, heavy liquids from lignin/attapulgitite, heavy liquids from lignin-calcium hydroxide and lignin/sodium formate.