Supporting Information

Direct Infusion Mass Spectrometric Analysis of Bio-Oil Using ESI-Ion Trap MS

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Table S1. MS methods that have been used in characterization of bio-oils.

Ionization mode	Ion Mode	Mass analyzer	Sample	Ref
APCI	-ve	liner quadrupole Ion Trap (LQIT)	carbohydrates**	**13**
APPI	*	Liner ion trap-Orbitrap	toluene extract from Biochar**	**7**
ESI	+ve	liner quadrupole Ion Trap (LQIT)	model compounds from lignin degradtion products**	**14**
		Triple-quadrupole	Chicken manure	**9**
	+ve/-ve			**11**
		Quadrupole	lignin	**15**
	-ve	FT-ICR	pine and peanut hulls pellets	**3**
			red oak	**12**
			red pine	**2**
		Liner ion trap-Orbitrap	Water/Methanol extract from Biochar**	**7**
		liner quadrupole ION TRAP (LQIT)	carbohydrates**	**13**
			model compounds from lignin degradtion products**	**14**
		Orbitrap	red oak	**12**
		Q-TOF		**12**
FD	*	Double focussing	Chicken manure	**10**
FI	*			**10**
			pyrolytic lignin**	
LDI	*	Liner ion trap-Orbitrap	loblolly pine	**5**
		TOF	pyrolytic lignin**	**6**
	+ve	Liner ion trap-Orbitrap	Toluene extract from Biochar**	**7**
MALDI	*	TOF	pyrolytic lignin**	**6**

* N/A, **Not bio-oil sample.

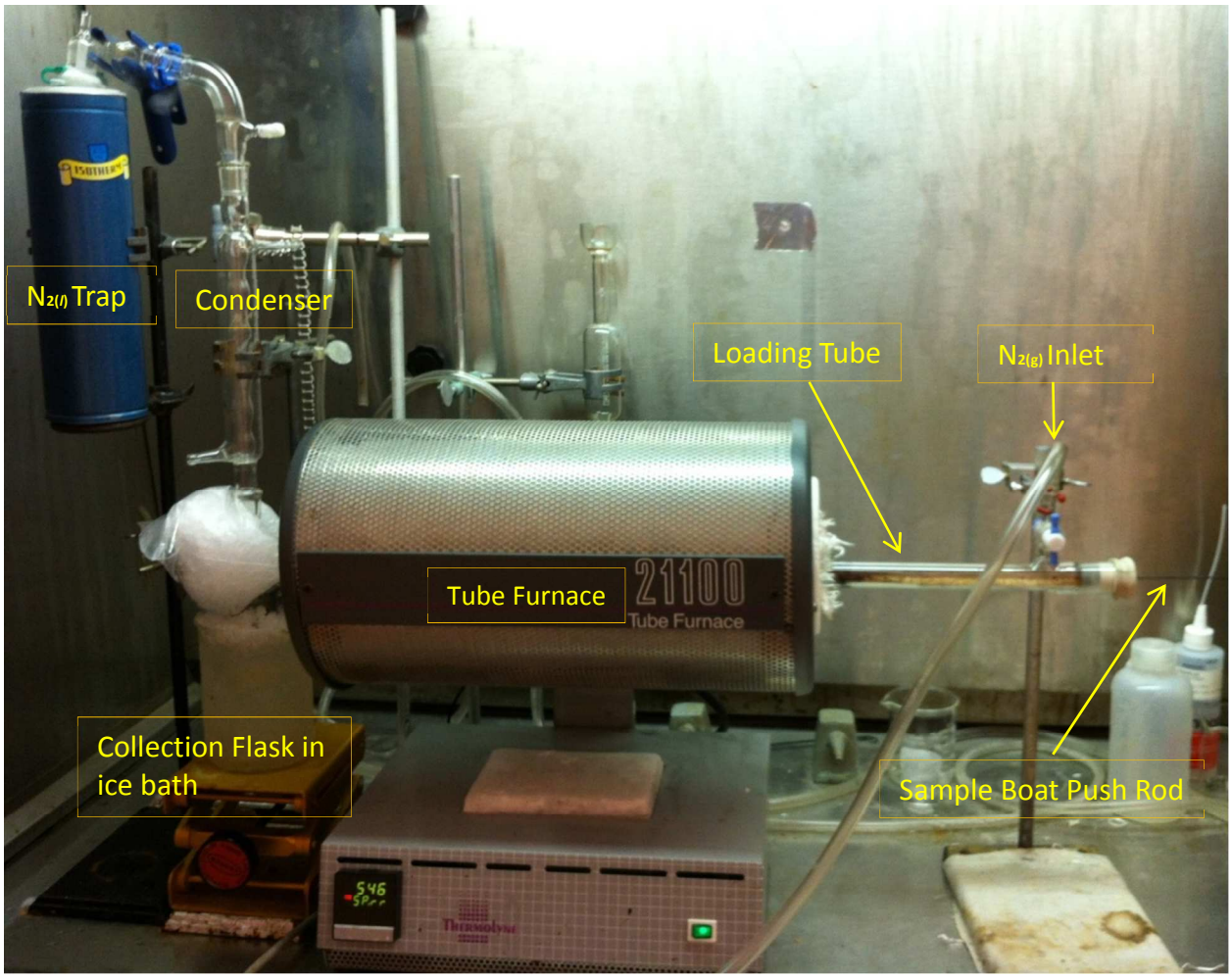

Figure S1. Small scale tube-furnace pyrolysis unit.

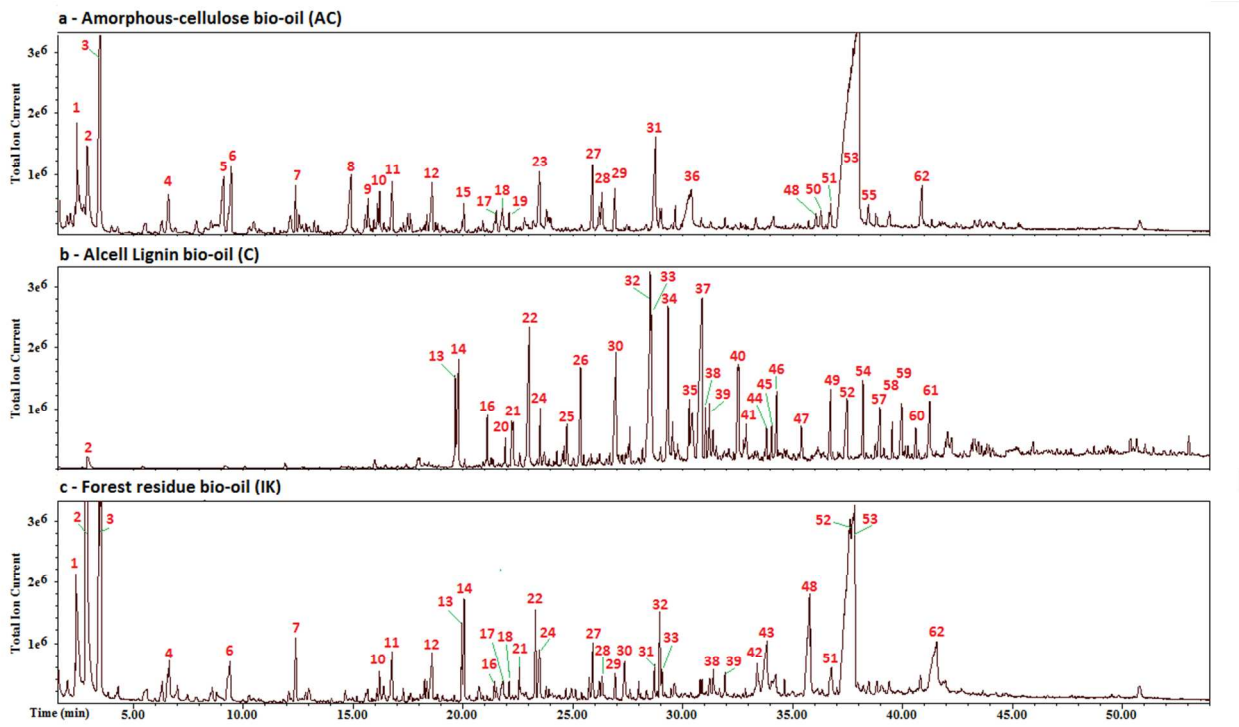

Figure S2. GC-MS: Individual products in bio-oils from a) cellulose, b) lignin and c) Forest residue.

Table S2. Products identified in bio-oil samples shown in Figure S2.

	Bio-oil feedstock	Cellulose (C)	Alcell Lignin (L)	Forest residue (FR)
Peak No.	**Compound**	**detected peaks**		
1	2-hayroxyacetaldehyde	*		*
2	acetic acid	*	*	*
3	Hydroxypropanone	*		*
4	propanoic acid	*		*
5	Pyruvic acid	*		
6	2-furaldehyde	*		*
7	Tetrahydro-4-pyrone	*		*
8	2-methyl-2-cyclopentene-1-one	*		
9	5-methyl-2-furaldehyde	*		
10	4-methyl-Cyclohexanol	*		*
11	2(5H)-Furanone	*		*
12	2-Cyclopenten-1-one, 2-hydroxy-3-methyl-	*		*
13	Phenol		*	*
14	Guaiacol		*	*
15	2,3-Dihydro-5-hydroxy-6-methyl-4H-pyran-4-one	*		
16	phenol, 2-methyl		*	*
17	4H-Pyran-4-one, 3-hydroxy-2-methyl-	*		*
18	2,5-Furandicarboxaldehyde	*		*
19	2(3H)-Furanone, dihydro-3-methylene-	*		
20	guaiacol, 3-methyl-		*	*
21	phenol, 4-methyl-		*	*
22	guaiacol, 4-methyl-		*	*
23	2,3 - dihydroxy - 1- hexen - 4 – one	*		
24	phenol, dimethyl-		*	*
25	guaiacol, 4-ethyl-		*	
26	guaiacol, dimethyl-		*	
27	(1R)-1-hydroxy-3,6-dioxabicyclo[3.2.1]octan-2-one	*		*
28	3,4-anhydro-d-galactosan	*		*
29	1,4:3,6-dianhydro-a-d-glucopyranose	*		*
30	1,2-Benzenediol, 3-methoxy-		*	*
31	5-(Hydroxymethyl)-2-furanecarboxaldehyde	*		*
32	1,2-Benzenediol	*	*	*
33	Syringol		*	*
34	1,2-Benzenediol, 6-methoxy-		*	
35	Isoeugenol		*	
36	2 - hydroxymethyl - 5 - hydroxy - 2,3 - dihydro - (4H) - pyran	*		
37	syringol, 4-methyl-		*	
38	Vanillin		*	*
39	Hydroquinone		*	*

40	syringol, 4-ethyl-		*	
41	Methyl vanillate		*	
42	Acetoguaiacone			*
43	1,6-Anhydro-β-d-talopyranose	*		*
44	syringol, 4-vinyl-		*	
45	Guaiacylacetone		*	
46	syringol, 4-propanyl		*	
47	syringol, 4-allyl-		*	
48	1,6-Anhydro-β-d-mannopyranose	*		*
49	syringol, 4-propenyl		*	
50	1,6-dianhydro-a-d-galactofuranose	*		
51	3,4-Altrosan	*		*
52	Syringaldehyde		*	
53	Levoglucosan	*		*
54	Unknown		*	
55	1,6-Anhydro-α-d-talopyranose	*		*
56	Methyl syringate		*	
57	acetosyringone		*	
58	Unknown		*	
59	syringyl acetone		*	
60	propio - syringone		*	
61	Unknown			
62	Unknown	*		*

Table S3. Model compound: Positive ion mode ESI MS, with and without dopants.

#	Compound	Mwt (g/mol)	None	Formic Acid	NaCl	NH_4Cl
3	LG	162	$[M+Na]^+$ (100%, 1.5e7), $[2M+Na]^+$ (10%)	$[M+Na]^+$ (100%, 7e6) $[2M+Na]^+$ (10%)	$[M+Na]^+$ (100%, 1.25e7), $[2M+Na]^+$ (10%)	$[M+NH4]^+$ (100%, 2.1e6), $[M+Na]^+$ (75%), $[2M+Na]^+$ (15%)
4	Glu	180	$[M+Na]^+$ (100%, 1.2e7), $[2M+Na]^+$ (20%)	$[M+Na]^+$ (100%, 9e6), $[2M+Na]^+$ (20%)	$[M+Na]^+$ (100%, 9e6), $[2M+Na]^+$ (15%)	$[M+NH4]^+$ (100%, 3e6), $[M+Na]^+$ (80%) $[LG+NH4]^+$ (40%), [LG+H]+ (10%)
5	Cbio	342.3	$[M+Na]^+$ (100%, 1e6), $[2M+Na]^+$ (10%), $[M+H]^+$ (5%), $[M-H_2O+H]^+$ (70%)	$[M+Na]^+$ (5%), $[M+H]^+$ (10%), $[M-H_2O+H]^+$ (100%, 5e5).	$[M+Na]^+$ (100%, 2e6), $[2M+Na]^+$ (5%)	$[M+NH4]^+$ (100%, 2.5e6), $[M+H]^+$ (15%), [M-H2O+H]$^+$ (90%)
8	G	124	$[M+Na]^+$ (100%, 2e5)	$[M+Na]^+$ (50%, 2e5), $[M+H]^+$ (25%)	$[M+Na]^+$ (100%, 3e5)	ND
9	S	154	$[M+Na]^+$ (100%, 3e7), $[M+H]^+$ (10%), $[2M+Na]^+$ (15%).	$[M+Na]^+$ (100%, 3e7), $[M+H]^+$ (15%), $[2M+Na]^+$ (10%).	$[M+Na]^+$ (100%, 4e7), $[2M+Na]^+$ (10%).	$[M+H]^+$ (100%, 1e7), $[M+Na]^+$ (50%)
10	V	152	$[M+Na]^+$ (100%, 1e7), $[M+H]^+$ (20%), $[2M+Na]^+$ (5%)	$[M+Na]^+$ (100%, 4.7e6), $[M+H]^+$ (95%)	$[M+Na]^+$ (100%, 2e7)	$[M+H]^+$ (100%, 6e6), $[M+Na]^+$ (5%)

Table S4. Model compound: Negative ion mode ESI MS, with and without dopants.

#	Compound	Mwt (g/mol)	None	NaOH	NH_4Cl
3	LG	162	$[M-H]^-$ (80%), $[2M-H]^-$ (100%, 6e5)	$[M-H]^-$ (100%, 5e5), $[2M-H]^-$ (50%)	$[M+Cl]^-$ (100%, 4e5)
4	Glu	180	$[M-H]^-$ (100%, 7e5), $[2M-H]^-$ (15%)	$[M-H]^-$ (100%, 4e5), $[2M-H]^-$ (25%)	$[M+Cl]^-$ (100%, 7e5)
5	Cbio	342.3	$[M-H]^-$ (95%), $[LG-H]^-$ (100%, 2e5), $[Glu-H]^-$ (15%)	$[M-H]^-$ (40%), $[LG-H]^-$ (100%, 7e5), $[Glu-H]^-$ (15%)	$[M+Cl]^-$ (100%, 8e5)
8	G	124	$M-H]^-$ (100%, 1.4e4)	$[M-H]^-$ (100%, 4e4)	poor
9	S	154	$[M-H]^-$ (70%), $[2M-H]^-$ (100%, 1.6e5)	$[M-H]^-$ (50%,2.5e5)	$[M-H]^-$ (40%, 1.5e4)
10	V	152	$[M-H]^-$ (100%, 1.4e6)	$[M-H]^-$ (100%, 1.6e6)	$[M-H]^-$ (100%, 1e6)

Table S5. Tandem mass spectra in positive and negative modes for model compounds.

Tandem mass spectra in negative mode for model compounds		
Compound (m/z of $[M–H]^-$)	MS^2 fragmentation (product ions' m/z) relative abundance	MS^3 fragmentations (product ions' m/z) relative abundance
Guaiacol (123)	123-CH_3 (108) 100%	
Vanilline (151)	151-CH_3 (136) 100%	136-CO (108) 100%
		136-CO_2 (96) 80%
Syringol (153)	153-CH_3 (138) 100%	138-CH_3 (123) 100%
	153-CO (125) 5%	
Levogulcosan (161)	161-H_2O (143) 40%	143-H_2O (125) 30%
		143-CO (113) 100%
		143-CH_2O_2 (97) 60%
		143-CH_6O_2 (71) 50%
	161-2H_2O (125) 5%	
	161-CH_4O_2 (113) 75%	113-H_2O (95) 100%
		113-CO (85) 80%
		113-CH_4O (71) 20%
	161-$C_2H_4O_2$ (101) 100%	
	161-$C_3H_4O_3$ (73) 40%	
	161-$C_3H_6O_3$ (71) 20%	
Glucose (179)	179-H_6O (161) 90%	161-H_2O (143) 50%
		161-CH_2O (131) 40%
		161-2H_2O (125) 10%
		161-CH_4O_2 (113) 100%
		161-$C_2H_4O_2$ (101) 100%
		161-$C_3H_4O_3$ (73) 40%
	179-2H_2O (143) 100%	
	179-CH_2O (149) 20%	
	179-CH_4O_2 (131) 50%	
	179-$C_2H_4O_2$ (119) 70%	119-H_2O (101) 100%
		119-CH_2O (89) 10%
	179-CH_6O_3 (113) 60%	
	179-$C_2H_6O_3$ (101) 20%	
	179-$C_3H_6O_3$ (89) 90%	
Cellobiose (341)	341-$C_6H_{10}O_5$ (Glu, 179) 25%	179-H_6O (161) 95%
		179-2H_2O (143) 100%
		179-CH_2O (149) 25%
		179-CH_4O_2 (131) 50%
		179-$C_2H_4O_2$ (119) 65%
		179-CH_6O_3 (113) 60%
		179-$C_2H_6O_3$ (101) 25%
		179-$C_3H_6O_3$ (89) 80%

	341-$C_6H_{12}O_6$ (LG, 161) 100%	161-H_2O (143) 30%
		161-CH_4O_2 (113) 75%
		161-$C_2H_4O_2$ (101) 100%
		161-$C_3H_4O_3$ (73) 40%
	341-$C_7H_{12}O_6$ (149) <5%	
	341-$C_8H_{16}O_8$ (101) <5%	
Tandem mass spectra in positive mode for model compounds		
Compound (m/z of $[M+Na]^+$)	MS^2 fragmentations (product ions' m/z) relative abundance	MS^3 fragmentations (product ions' m/z) relative abundance
Guaiacol (147)	147 (100%), No fragments	
Vanilline (175)	(175) 100%, No fragments	
Syringol (177)	(177) 100%, No fragments	
Levogulcosan (185)	(185) 100%, No fragments	
Glucose (203)	(203) 25%	
	203-H_2O (185) 20%	
	203-$C_2H_4O_2$ (143) 100%	
	203-$C_3H_6O_3$ (113) 10%	
Cellobiose (365)	365-H_2O (347) 80%	347-CH_2O (317) 60%
		347-$C_6H_8O_4$ (Glu, 203) 100%
		347-$C_6H_{10}O_5$ (LG, 185) 10%
	365-CH_2O (335) <5%	
	365-$C_2H_4O_2$ (317) <5%	
	365-$C_2H_4O_2$ (305) 100%	305-$C_2H_4O_2$ (245) 100%
	365-$C_4H_8O_4$ (245) 10%	
	365-$C_6H_{10}O_5$ (Glu, 203) 20%	
	365-$C_6H_{12}O_6$ (LG, 185) 10%	

Table S6. Negative mode MS^2 product ions resulting from ESI-Ion Trap MS of selected ions from the mass spectra of cellulose-bio-oil (C).

m/z of parent ions in full mass spectra	*m/z* values of product ions																	
	Relative ion abundance (%)																	
161	143	129	127	113	101	97												
	25	25	50	95	100	20												
173	155	145	141	129	113	111	97											
	5	20	100	80	10	10	80											
177	159	149	143	139	133	131	117	115										
	40	100	18	10	30	30	15	20										
191	173	171	163	157	147	135	131	113										
	10	10	100	40	50	10	20	20										
197	179	165	153	151	135	125	121	109	97									
	40	40	100	30	10	15	15	20	<5									
205	185	177	171	161	159	145	127	115										
	15	15	25	50	30	100	10	15										
213	195	181	169	151	127	87												
	10	10	100	60	20	70												
221	203	191	187	177	175	161	145											
	25	25	30	100	20	40	30											
235	217	215	205	203	191	189	175	161	145	137	125	115						
	20	20	20	25	100	70	15	20	20	15	15	20						
237	219	217	205	193	191	177	175	163	161									
	20	15	50	50	100	20	20	20	25									
251	233	218	207	191	177	163	161	149	139	123	113							
	50	85	90	25	100	20	10	50	15	15	5							
263	245	243	233	231	229	219	217	203	191	175	173	161	145	135	133	123	115	
	10	30	30	30	100	40	70	35	15	15	15	45	30	30	10	5	10	
277	259	257	247	245	243	233	231	215	203	189	177	161	153	145				
	30	40	25	25	40	45	100	15	30	10	10	40	30	30				
279	261	259	247	245	235	233	217	215	205	191	179	161	145					
	60	50	100	40	40	90	20	20	20	20	20	40	15					
293	289	275	273	263	261	259	255	249	247	231	229	219	203	191	179	167	161	
	50	40	80	20	70	75	25	75	100	30	30	40	30	20	25	75	60	
307	289	275	263	247	234	219	205	191	161	145	133	115	101					
	30	50	40	10	10	10	10	10	100	10	10	10	5					
323	305	303	301	291	289	279	277	265	245	219	203	179	161	145				
	40	35	40	50	100	35	40	80	40	35	20	20	60	5				
335	317	305	289	275	261	245	233	217	205	177	161	143	131	113	101			
	15	40	30	10	20	10	10	10	10	10	100	15	10	5	5			
353	335	321	309	295	277	249	219	205	189	161	149	131	115					
	40	10	90	30	20	20	15	15	15	40	20	10	5					

341	323	309	307	297	295	281	279	179	161	143								
	30	25	40	20	25	10	15	100	30	30								
365	347	333	321	305	289	277	263	249	233	219	203	189	175	161	143	125		
	30	40	50	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	100	5	<5		

Table S7. Postive mode MS^2 product ions resulting from ESI-Ion Trap MS of selected ions from the mass spectra of cellulose-bio-oil (C)

m/z of parent ions in full mass spectra	*m/z* values of product ions																	
	Relative ion abundance (%)																	
127	109	99	81															
	100	10	10															
149	131	129	121	115	101	87	71											
	100	30	10	20	10	5	25											
161	143	141	131	129	127	115	101	99	85	71								
	50	55	30	100	80	30	75	50	15	20								
171	153	151	143	141	139	137	123	111	109									
	50	100	20	20	60	40	20	30	60									
185	167	163	139	125	111	99												
	40	100	10	25	10	5												
193	175	173	165	163	161	151	147	131	123									
	100	100	30	50	20	25	40	50	20									
199	181	169	167	151	139	127	109	97										
	70	75	100	5	10	10	5	5										
201	183	169	155	141	127	117	109											
	40	100	<5	<5	<5	<5	<5											
203	185	183	171	169	159	143	129											
	30	25	10	100	25	20	10											
215	197	183	173	165	155	141	125	109										
	50	100	<5	<5	<5	<5	<5	<5										
217	197	185	183															
	10	100	50															
229	211	197	183	169	155	143	127	109										
	50	100	<5	5	<5	<5	<5	<5										
231	211	199	197	167														
	10	100	50	5														
245	227	213	203	185	177	163	153	143	127	117	109	101						
	40	100	20	20	15	10	10	5	5	5	5	10						
257	239	225	207	197	189	155	147	109										
	30	100	10	10	5	5	5	5										

287	269	267	255	253	225	211	185	169	139									
	20	20	100	80	5	5	15	5	5									
281	263	249	245	231	221	213	203	189	175	161	143	129	117	101				
	90	100	80	40	20	20	20	20	20	20	30	5	5	5				
289	271	257	239	225														
	25	100	5	5														
301	283	269	251	241	227	209	199	185	173	157								
	40	100	10	10	10	10	10	30	5	5								
317	299	285	267	257	243	225	207	173										
	30	100	<5	<5	<5	<5	<5	<5										
331	313	299	281	271	257	239	229	205	185									
	20	100	<5	<5	<5	<5	<5	<5	10									
343	325	311	307	293	283	261	251	233	215	201	185	163	145					
	566	298	<5	<5	<5	<5	<5	<5	<5	<5	5	<5	<5					
347	329	327	315	313	297	287	261	245	231	219	201	191	185	167	165	151	127	111
	80	100	80	100	40	30	20	20	20	30	25	20	40	10	10	5	5	5
359	341	327	297	297	259	241	231	213	197	185	173	149	127					
	30	100	<5	<5	<5	<5	<5	<5	<5	20	<5	<5	<5					
365	361	359	347	345	333	331	329	301	259	225	303	195	185					
	5	5	25	100	10	<5	<5	<5	<5	<5	<5	<5	20					
401	383	369	341	327	299	285	257	243	225	210	173	158	186					
	25	100	10	10	10	<5	<5	<5	<5	<5	<5	<5	<5					
413	407	395	393	391	381	379	377	351	301	281	249	185						
	40	20	20	60	45	100	60	20	25	25	15	20						

Table S8. Negative mode MS^2 product ions resulting from ESI-Ion Trap MS of selected ions from the mass spectra of Lignin-bio-oil (L)

m/z of parent ions in full mass spectra	*m/z* values of product ions																		
	Relative ion abundance (%)																		
123	108																		
	100																		
137	122	109	93																
	100	25	60																
151	136	123	107																
	100	<5	5																
165	150	137	121																
	100	20	40																
167	152	137	135	123															
	100	20	30	20															
181	166	149	137																
	100	99	20																
195	180	178	163	161	151	149	136	123											
	100	50	80	25	20	25	5	<5											
197	182	180	165	163	153	138	121												
	100	40	95	50	50	20	10												
209	194	192	177	165	163	150	137												
	100	30	75	40	40	<5	<5												
241	226	223	213	209	208	197	196	185	153	121	110	95							
	65	50	20	50	100	40	40	45	20	10	50	20							
255	253	251	240	239	238	237	235	227	223	221	211	209	193	185	166	152	139	111	95
	40	100	80	40	75	45	50	30	95	90	70	70	20	25	20	10	<5	50	<5
293	289	276	273	259	247	232	219	189	167	153									
	100	30	25	35	60	10	15	40	<5	<5									
311	294	291	277	265	247	233	209	195	185	171									
	100	95	75	50	15	20	20	20	15	10									
317	302	300	285	283	273	271	257	241	191	179	163	149	137						
	50	100	50	85	40	50	20	25	10	15	40	30	20						
325	310	308	295	293	291	279	255	247											
	15	100	15	15	70	50	20	15											
339	324	322	319	309	307	305	293	275	261	247	>>								
	20	100	20	30	30	90	60	25	30	25	<5								
345	330	328	315	313	311	301	299	281	269	241	231	219	205	191	179	163			
	40	100	20	50	70	40	70	20	20	20	20	15	20	35	35	20			

355	340	322	309	295	277														
	100	50	60	10	15														
365	350	349	332	320	305														
	65	70	100	50	10														
367	352	351	338	334	322	309	290												
	100	80	20	70	50	10	<5												
383	368	367	351	350	337	307	293	276	259	246	231	215	179						
	100	50	50	60	60	20	<5	<5	<5	<5	<5	<5	10						
389	374	373	356	344	329	312	298	283	268	235	222	191	178						
	100	50	50	25	10	<5	<5	<5	<5	<5	<5	5	<5						
393	378	377	360	348	335														
	100	50	50	30	10														
417	402	385	384	373	357	341													
	100	30	40	40	20	<5													

Table S9. Positive Negative mode MS^2 product ions resulting from ESI-Ion Trap MS of selected ions from the mass spectra of Lignin-bio-oil (L)

m/z of parent ions in full mass spectra	*m/z* values of product ions																		
	Relative ion abundance (%)																		
169	154	149	141	139	137	125	109												
	5	<5	20	5	100	<5	20												
177	195	177	160	159	149	147	143												
	50	100	30	40	90	20	50												
183	168	163	155	151	137	123	95												
	15	10	35	100	5	10	10												
191	191	174	173	163	147														
	100	5	45	30	15														
205	205	189	187	185	177	175	173	171	157	149	143								
	100	30	45	35	20	30	50	35	35	90	35								
219	219	203	201	199	191	189	187	173	171	161	159	157							
	50	50	60	80	20	40	100	20	40	20	25	20							
233	233	218	215	213	203	201	191	185	171	159									
	50	50	70	60	60	100	65	50	40	40									
253	221																		

	100																		
269	237	235	163																
	100	95	10																
283	251	249																	
	100	30																	
301	283	269	240	237	191	177													
	25	100	20	25	30	30													
331	313	299	298	297	205	191	177	167											
	5	10	10	100	10	15	50	15											
345	327	325	313	312	311	207	191	177											
	<5	<5	10	5	20	5	100	30											
345	327	325	313	311	297	283	219	205	191	189	177	175	167						
	15	30	15	30	20	20	10	10	100	20	35	50	20						
359	344	342	341	339	327	325	205	191	189	177									
	<5	<5	<5	<5	5	5	30	100	10										
359	341	325	311	297	233	219	205	207	191	189	175								
	20	20	10	10	10	10	30	25	100	35	20								
359>191	191	174	131	121	105														
	100	30	30	10	10														
373	355	341	339	219	217	205	203	191	189	177									
		15	15	20	30	100	30	90	20	15									
391	373	371	357	235	221	205	191	177											
	10	10	50	50	70	70	100	30											
401	384	383	369	367	355	339	325	247	245	233	231	219	217	205	204	191	175		
	20	20	25	25	10	10	10	20	30	90	70	70	70	100	65	70	20		
413	395	381	379	339	301	287	257	243	229	217	205	191	175						
	15	40	40	10	20	5	60	100	40	50	40	50	20						

Table S10. Negative mode MS^2 product ions resulting from ESI-Ion Trap MS of selected ions from the mass spectra of Forest residue-bio-oil (FR)

m/z of parent ions in full mass spectra	*m/z* values of product ions																				
	Relative ion abundance (%)																				
151	136	123	107	103																	
	100	10	10	<5																	
161	143	129	113	101	99	97	87	85	73	71											
	40	35	50	100	10	10	15	15	10	10											
177	162	159	149	131	115	103	97														
	100	20	5	<5	<5	<5	<5														
191	173	176	159	157	151	147	145	131	129	127											
	60	75	55	55	40	45	100	50	45	60											
221	203	201	191	189	187	177	175	161	159	157	145										
	25	330	20	75	40	80	100	50	40	30	40										
259	244	241	226	215	196	186															
	100	50	50	60	40	20															
265	247	245	235	233	231	221	219	203	191	153	131	97									
	50	40	40	60	70	100	100	50	60	40	40	80									
299	284	282	281	279	269	267	265	255	253	237	235	223	209	193	179	167	161	151	137	125	109
	60	60	30	70	30	50	75	45	100	40	50	35	20	20	20	20	20	20	20	15	10
313	298	296	295	293	281	279	269	267	251	250	249	237	221	203	191	179	167	151			
	40	20	10	50	30	50	50	55	20	20	100	10	10	5	5	5	5	10			
323	319	307	303	291	289	279	277	263	261	249	247	245	233	223	205	179	161	143			
	5	25	50	75	80	40	70	30	50	20	40	40	35	20	15	20	100	10			
325	310	309	307	306	292	280	262	248	221	205	189	179	161	145							
	70	40	40	80	90	100	50	40	20	20	15	15	10	30							

Table S11. Positive Negative mode MS^2 product ions resulting from ESI-Ion Trap MS of selected ions from the mass spectra of Forest residue-bio-oil (FR)

m/z of parent ions in full mass spectra	*m/z* values of product ions													
	Relative ion abundance (%)													
171	153	139	125	111	97									
	40	100	20	30	20									
185	167	153	125	111										
	25	100	5	5										

199	181	167	153	139	125	111	97							
	50	100	10	5	10	5	5							
201	183	181	169	167	153	139	125							
	20	25	100	60	5	5	5							
215	197	183	155	137	127									
	20	100	<5	<5	<5									
227	209	195	191	181	167	152	109	98						
	50	100	10	5	10	<5	<5	<5						
247	229	228	215	214	197	186	172	154	137	123	112			
	30	50	95	100	5	10	5	70	10	5	20			
259	241	240	227	226	208	195	185	145	151	140	122	95		
	60	70	80	100	10	15	10	15	25	10	5	5		
273	255	254	241	240	222	212	198	181	155	140	121	112	100	
	50	70	100	95	10	20	5	5	10	5	10	5	5	
301	283	282	269	268	255	237	227	215	199	187	176	150	136	
	50	30	100	70	<5	<5	<5	<5	<5	35	<5	<5	<5	
301	283	282	281	280	269	268	267	253	227					
	25	25	50	25	80	40	100	10	20					
315	297	296	283	282	269	255	227	205	187	176	164	151	137	
	40	50	100	60	<5	<5	<5	<5	<5	<5	<5	<5	<5	
347	343	329	327	315	313	185	163							
	20	10	15	35	100	10	20							
379	361	360	359	358	357	356	345	317	275	215	185			
	50	40	90	40	70	50	100	20	20	25	25			