Supporting Information

Enhanced mass defect filtering to simplify and classify complex mixtures of lignin degradation products

Tobias K.F. Dier,[†] Kerstin Egele,[†] Verlaine Fossog,[‡] Rolf Hempelmann,[‡] Dietrich A. Volmer[†,*]

[†]*Institute of Bioanalytical Chemistry, Saarland University, 66123 Saarbrücken, Germany*
[‡]*Institute of Physical Chemistry, Saarland University, 66123 Saarbrücken, Germany*

*Corresponding author:

Prof. Dr. Dietrich A. Volmer
Saarland University
Institute of Bioanalytical Chemistry
D-66123 Saarbrücken, Germany
Tel +49 681 302 3433; Fax +49 681 302 2963
Email: Dietrich.Volmer@mx.uni-saarland.de

Table of content:

Table S1. Instrumental parameters for ESI, APCI and APPI

	ESI	**APCI**	**APPI**
Flow rate [µL/min]	2.0	5.83	150.0
Dry gas temperature [°C]	200	350	350
Vaporizer temperature [°C]	-	350	350
Nebulizer gas pressure [bar]	1.0	2.5	2.5
Dry gas flow rate [L/min]	4.0	4.0	6.0
Capillary voltage [kV]	4.5	2.0	2.0
Corona needle current [nA]	-	40,000	-

Table S2. Observed product ions for selected *m/z* ratios after collision-induced dissociation (compound class O_6; DBE 14)

Elemental composition	MS² product ion (*m/z*)	Calculated exact mass	Measured accurate mass	Error [ppm]	Elemental compositio n	MS² product ion (*m/z*)	Calculated exact mass	Measured accurate mass	Error [ppm]
		***m/z* 391**					***m/z* 419**		
$C_{23}H_{19}O_6$		391.118165	391.11795	-0.55	$C_{25}H_{23}O_6$		419.149465	419.15054	2.56
$C_{22}H_{16}O_6$	391-CH_3 (376)	376.09469	376.09523	1.44	$C_{24}H_{20}O_6$	419-CH_3 (404)	404.12599	404.12637	0.94
$C_{21}H_{13}O_6$	376-CH_3 (361)	361.071215	361.0716	1.07	$C_{23}H_{17}O_6$	404-CH_3 (389)	389.102515	389.10297	1.17
$C_{21}H_{16}O_5$	376-CO (348)	348.099775	348.10008	0.88	$C_{23}H_{20}O_5$	404-CO (376)	376.131075	376.13061	-1.24
$C_{20}H_{13}O_5$	361-CO (333)	333.0763	333.07683	1.59	$C_{22}H_{17}O_5$	389-CO (361)	361.1076	361.10832	1.99
	348-CH_3 (333)	333.0763	333.07683	1.59		376-CH_3 (361)	361.1076	361.10832	1.99
$C_{19}H_{10}O_5$	333-CH_3 (318)	318.052825	318.05382	3.13	$C_{21}H_{14}O_5$	361-CH_3 (346)	346.084125	346.08468	1.6
$C_{20}H_{13}O_4$	361-CO_2 (317)	317.081385	317.08178	1.25	$C_{22}H_{17}O_4$	389-CO_2 (345)	345.112685	345.11229	-1.14
$C_{19}H_{13}O_4$	333-CO (305)	305.081385	305.08195	1.85	$C_{21}H_{17}O_4$	361-CO (333)	333.112685	333.11207	-1.85
$C_{19}H_{13}O_3$	333-CO_2 (289)	289.08647	289.08700	1.83	$C_{16}H_{11}O_4$	345-C_6H_6 (267)	267.065735	267.06637	2.38
$C_{14}H_7O_4$	317-C_6H_6 (239)	239.034435	239.03494	2.11		333-C_5H_6 (267)	267.065735	267.06637	2.38
	305-C_5H_6 (239)	239.034435	239.03494	2.11					
		***m/z* 405**					***m/z* 433**		
$C_{24}H_{21}O_6$		405.133815	405.13441	1.47	$C_{25}H_{22}O_6$	433-CH_3 (418)	418.14164	418.14118	-1.1
$C_{23}H_{18}O_6$	405-CH_3 (390)	390.11034	390.11087	1.36	$C_{24}H_{19}O_6$	418-CH_3 (403)	403.118165	403.11693	-3.06
$C_{22}H_{15}O_6$	390-CH_3 (375)	375.086865	375.08735	1.29	$C_{23}H_{16}O_6$	403-CH_3 (388)	388.09469	388.09477	0.21
$C_{22}H_{18}O_5$	390-CO (362)	362.115425	362.11599	1.56	$C_{23}H_{19}O_5$	403-CO (375)	375.12325	375.12448	3.28
$C_{21}H_{12}O_6$	375-CH_3 (360)	360.06339	360.06404	1.81	$C_{22}H_{16}O_5$	388-CO (360)	360.099775	360.09946	-0.87
$C_{21}H_{15}O_5$	362-CO (347)	347.09195	347.09241	1.33	$C_{23}H_{19}O_4$	403-CO_2 (359)	359.128335	359.12821	-0.35
	375-CO (347)	347.09195	347.09241	1.33	$C_{22}H_{19}O_4$	375-CO (347)	347.128335	347.12918	2.43
$C_{20}H_{12}O_5$	360-CO (332)	332.068475	332.06914	2	$C_{18}H_{13}O_4$	359-C_5H_6 (293)	293.081385	293.08183	1.52
$C_{21}H_{15}O_4$	375-CO_2 (331)	331.097035	331.09736	0.98	$C_{17}H_{13}O_4$	347-C_5H_6 (281)	281.081385	281.08205	2.37
$C_{20}H_{15}O_4$	347-CO (319)	319.097035	319.09764	1.9	$C_{16}H_{10}O_4$	360-C_6H_6O (266)	266.05791	266.05862	2.67
$C_{20}H_{15}O_3$	347-CO_2 (303)	303.10212	303.10263	1.68		281-CH_3 (266)	266.05791	266.05862	2.67
$C_{15}H_9O_4$	331-C_6H_6 (253)	253.050085	253.05073	2.55	$C_{17}H_{13}O_3$	293-CO (265)	265.08647	265.08669	0.83
	319-C_5H_6 (253)	253.050085	253.05073	2.55					
$C_{14}H_9O_3$	303-C_6H_6 (225)	225.05517	225.05578	2.71					
	253-CO (225)	225.05517	225.05578	2.71					

Table S3. Observed product ions for selected *m/z* ratios after collision-induced dissociation (compound class O_7; DBE 14)

Elemental composition	MS^2 product ion (*m/z*)	Calculated exact mass	Measured accurate mass	Error [ppm]	Elemental composition	MS^2 product ion (*m/z*)	Calculated exact mass	Measured accurate mass	Error [ppm]
		***m/z* 421**					***m/z* 449**		
$C_{24}H_{21}O_7$		421.128730	421.12940	1.59	$C_{26}H_{25}O_7$		449.160030	449.16052	1.09
$C_{23}H_{18}O_7$	421-CH_3 (406)	406.105255	406.10588	1.54	$C_{25}H_{22}O_7$	449-CH_3 (434)	434.136555	434.1371	1.26
$C_{22}H_{15}O_7$	406-CH_3 (391)	391.081780	391.08237	1.51	$C_{24}H_{19}O_7$	434-CH_3 (419)	419.113080	419.11366	1.38
$C_{21}H_{12}O_7$	391-CH_3 (376)	376.058305	376.0589	1.58	$C_{23}H_{16}O_7$	419-CH_3 (404)	404.089605	404.0901	1.22
$C_{21}H_{15}O_6$	391-CO (363)	363.086865	363.08748	1.69	$C_{23}H_{19}O_6$	419-CO (391)	391.118165	391.11876	1.52
$C_{22}H_{18}O_5$	406-CO_2 (362)	362.115425	362.11598	1.53	$C_{24}H_{22}O_5$	434-CO_2 (390)	390.146725	390.14733	1.55
$C_{20}H_9O_7$	376-CH_3 (361)	361.034830	361.03557	2.05	$C_{22}H_{13}O_7$	404-CH_3 (389)	389.066130	389.06689	1.95
$C_{20}H_{12}O_6$	376-CO (348)	348.063390	348.06400	1.75	$C_{22}H_{16}O_6$	404-CO (376)	376.094690	376.09521	1.38
	363-CH_3 (348)	348.063390	348.06400	1.75	$C_{23}H_{19}O_5$	419-CO_2 (375)	375.123250	375.12384	1.57
$C_{21}H_{15}O_5$	362-CH_3 (347)	347.091950	347.09257	1.79	$C_{22}H_{16}O_5$	404-CO_2 (360)	360.099775	360.10031	1.49
$C_{20}H_{12}O_5$	376-CO_2 (332)	332.068475	332.06905	1.73		375-CH_3 (360)	360.099775	360.10031	1.49
$C_{20}H_{15}O_4$	347-CO (319)	319.097035	319.09762	1.83	$C_{21}H_{16}O_5$	376-CO (348)	348.099775	348.10037	1.71
$C_{19}H_{12}O_4$	348-CO_2 (304)	304.073560	304.07414	1.91	$C_{21}H_{16}O_4$	376-CO_2 (332)	332.104860	332.10505	0.57
$C_{15}H_7O_5$	332-C_5H_5 (267)	267.029350	267.02992	2.13		360-CO (332)	332.104860	332.10505	0.57
$C_{15}H_9O_4$	319-C_5H_6 (253)	253.050085	253.05073	2.55	$C_{20}H_{16}O_4$	348-CO (320)	320.104860	320.10549	1.97
$C_{14}H_7O_4$	332-C_6H_5O (239)	239.034435	239.03498	2.28	$C_{16}H_{11}O_5$	348-C_5H_5 (283)	283.060650	283.06123	2.05
	304-C_5H_5 (239)	239.034435	239.03498	2.28	$C_{16}H_{11}O_4$	332-C_5H_5 (267)	267.065735	267.06629	2.08
	267-CO (239)	239.034435	239.03498	2.28	$C_{15}H_{11}O_3$	332-C_6H_5O (239)	239.070820	239.0714	2.43
						267-CO (239)	239.070820	239.0714	2.43
		***m/z* 435**					***m/z* 463**		
$C_{25}H_{23}O_7$		435.144380	435.14492	1.24	$C_{27}H_{27}O_7$		463.17568	463.17638	1.51
$C_{24}H_{20}O_7$	435-CH_3 (420)	420.120905	420.12147	1.34	$C_{26}H_{24}O_7$	463-CH_3 (448)	448.152205	448.15287	1.48
$C_{23}H_{17}O_7$	420-CH_3 (405)	405.097430	405.09804	1.51	$C_{25}H_{21}O_7$	448-CH_3 (433)	433.128730	433.12931	1.34
$C_{22}H_{14}O_7$	405-CH_3 (390)	390.073955	390.07460	1.65	$C_{24}H_{21}O_6$	433-CO (405)	405.133815	405.13437	1.37
$C_{23}H_{20}O_5$	420-CO_2 (376)	376.131075	376.13161	1.42	$C_{25}H_{24}O_5$	448-CO_2 (404)	404.162375	404.16296	1.45
$C_{21}H_{14}O_6$	390-CO (362)	362.079040	362.07954	1.38	$C_{24}H_{21}O_5$	404-CH_3 (389)	389.138900	389.13949	1.52
$C_{22}H_{17}O_5$	376-CH_3 (361)	361.107600	361.10813	1.47	$C_{23}H_{18}O_5$	389-CH_3 (374)	374.115425	374.11599	1.51
$C_{21}H_{14}O_5$	390-CO_2 (346)	346.084125	346.08476	1.83	$C_{22}H_{15}O_5$	374-CH_3 (359)	359.091950	359.09254	1.64

$C_{20}H_{14}O_5$	362-CO (334)	334.084125	334.08465	1.57	$C_{18}H_{15}O_5$	389-C_6H_6 (311)	311.091950	311.09248	1.7
$C_{18}H_{15}O_5$	376-C_5H_5 (311)	311.091950	311.09243	1.54	$C_{17}H_{13}O_5$	374-C_6H_5 (297)	297.076300	297.07688	1.95
$C_{17}H_{12}O_5$	311-CH_3 (296)	296.068475	296.06908	2.04	$C_{16}H_{13}O_4$	297-CO (269)	269.081385	269.08194	2.06
$C_{16}H_{11}O_5$	361-C_6H_6 (283)	283.060650	283.06120	1.94	$C_{15}H_{13}O_2$	269-CO_2 (225)	225.091555	225.09211	2.47
$C_{15}H_8O_5$	334-C_5H_6 (268)	268.037175	268.03771	2	$C_{14}H_{10}O_2$	225-CH_3 (210)	210.06808	210.06866	2.76
$C_{14}H_9O_4$	334-C_6H_5O (241)	241.050085	241.05064	2.3					

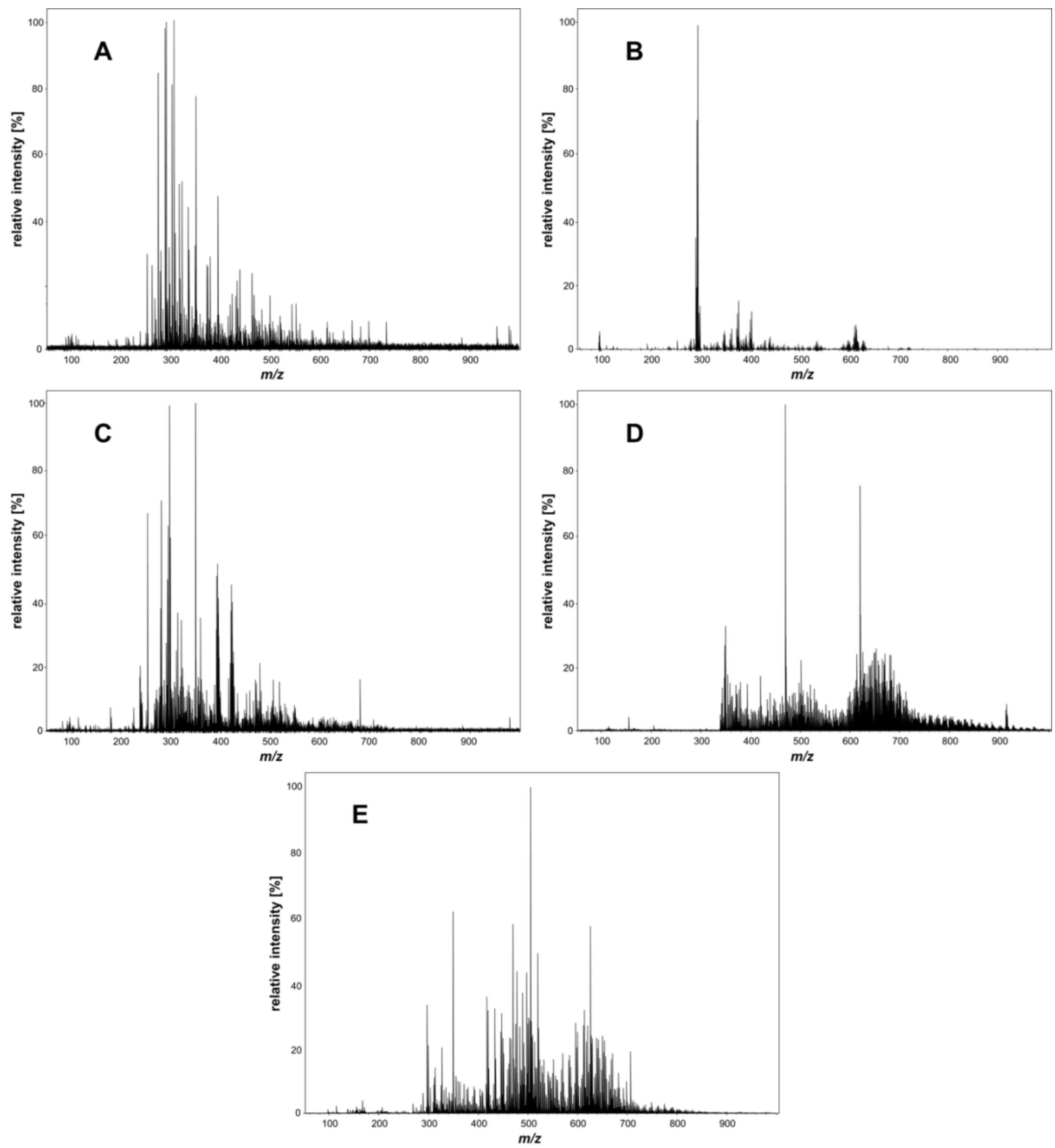

Figure S1. Mass spectra of lignin degradation products in negative ion-mode using (A) ESI at pH 3; (B) ESI at pH 7; (C) ESI at pH 10; (D) APCI; (E) dopant-assisted APPI

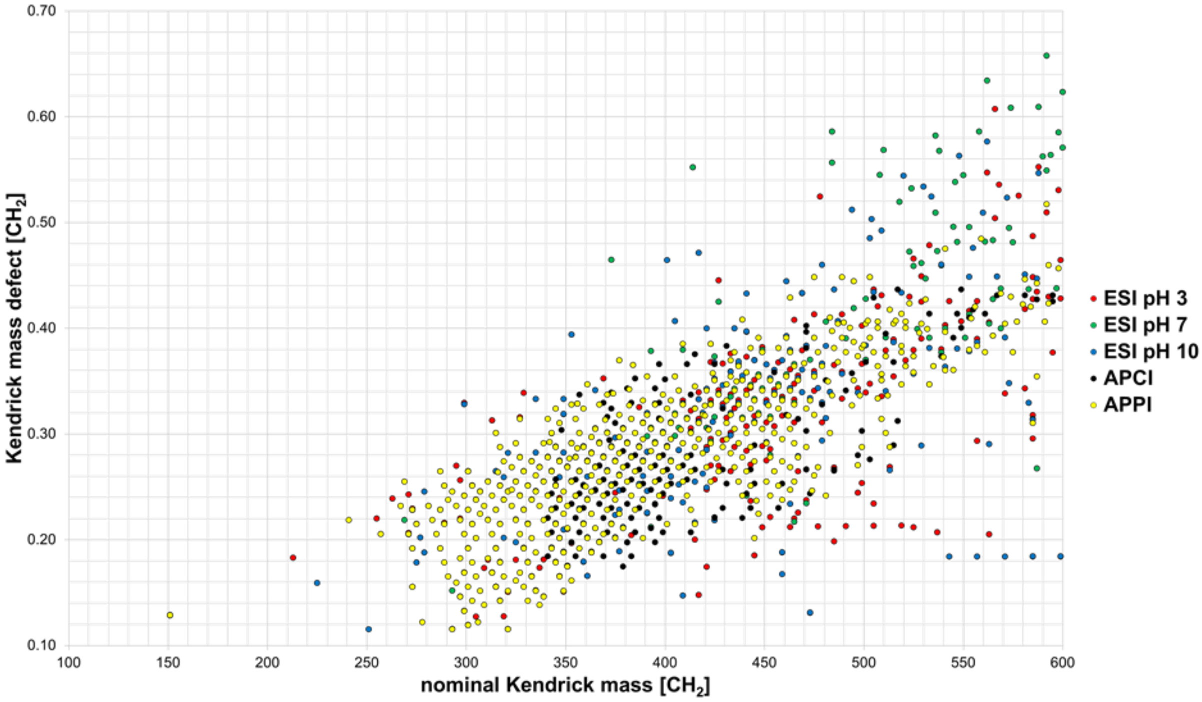

Figure S2. Enlarged areas of Kendrick mass defect plot.

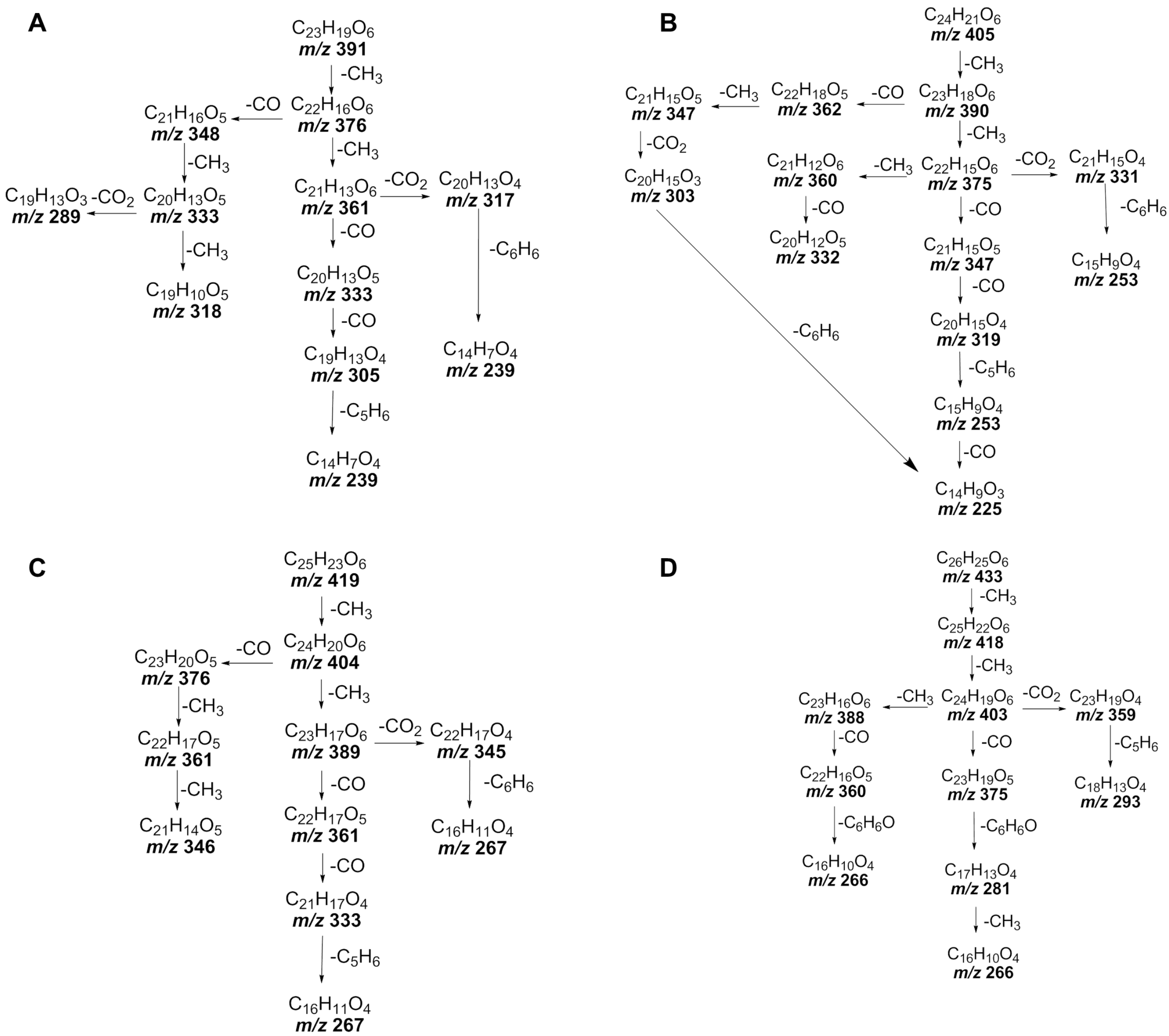

Figure S3. Linked fragmentation reactions for **A** *m/z* 391.11795, **B** *m/z* 405.13441, **C** *m/z* 419.15054, (D) *m/z* 433.16617.

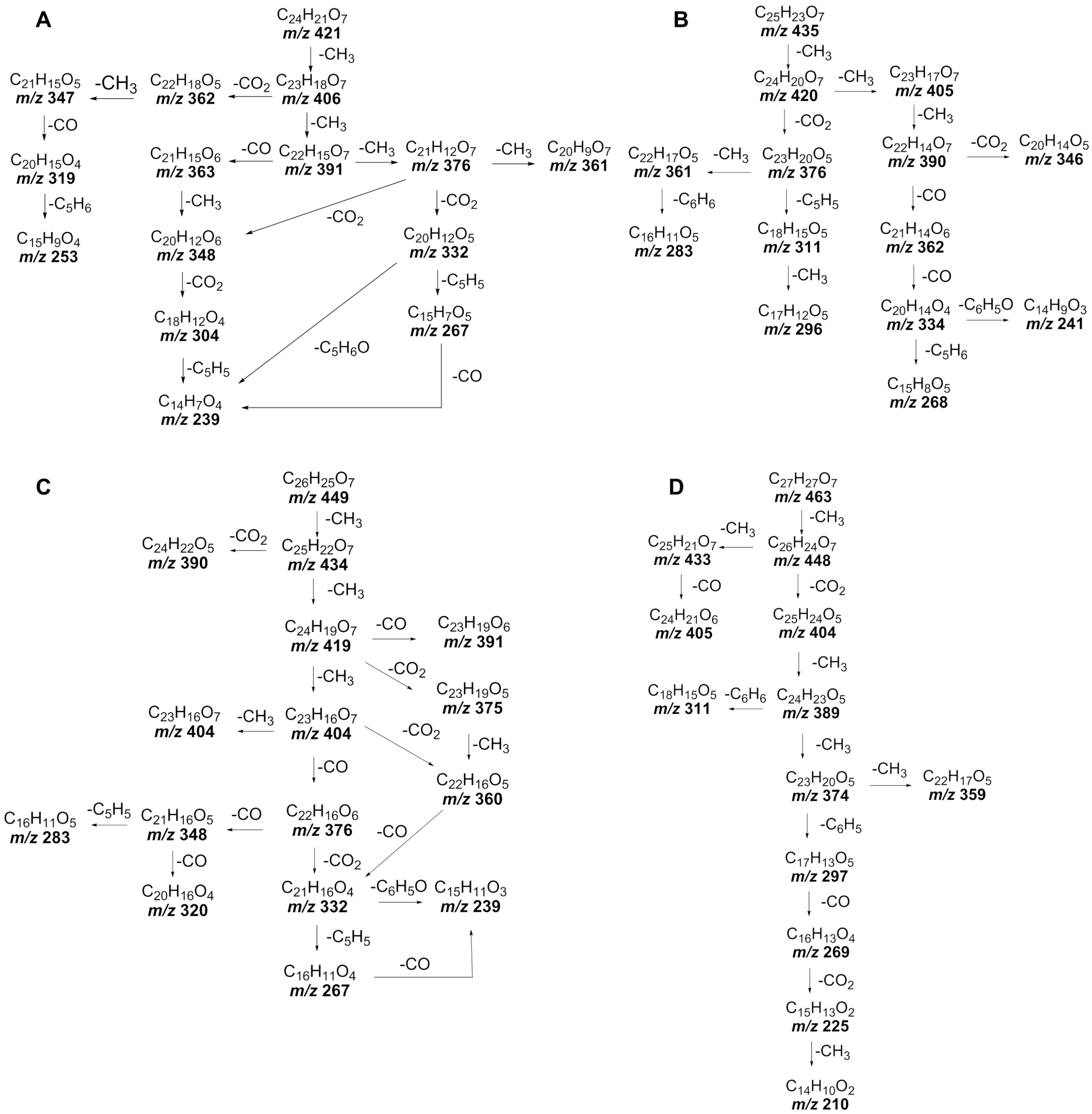

Figure S4. Linked fragmentation reactions for **A** *m/z* 421.12940, **B** *m/z* 435.14492, **C** *m/z* 449.16052, **D** *m/z* 463.17638

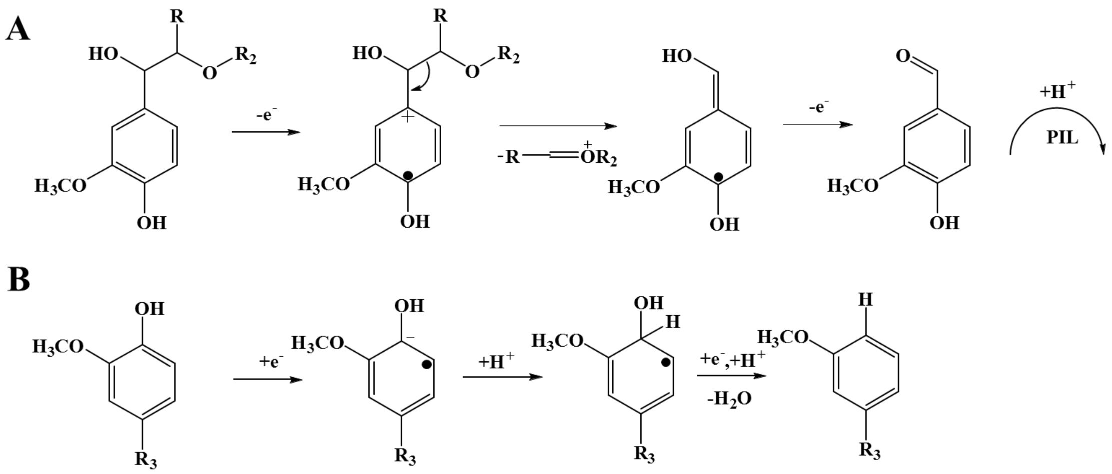

Figure S5. Proposed lignin degradation reactions by **A** electrochemical oxidation (adapted from Reichert, E.; Wintringer, R.; Volmer, D. A.; Hempelmann, R. *Phys. Chem. Chem. Phys.* **2012**, *14* (15), 5214-5221; reprinted with permission) and **B** electrochemical reduction.

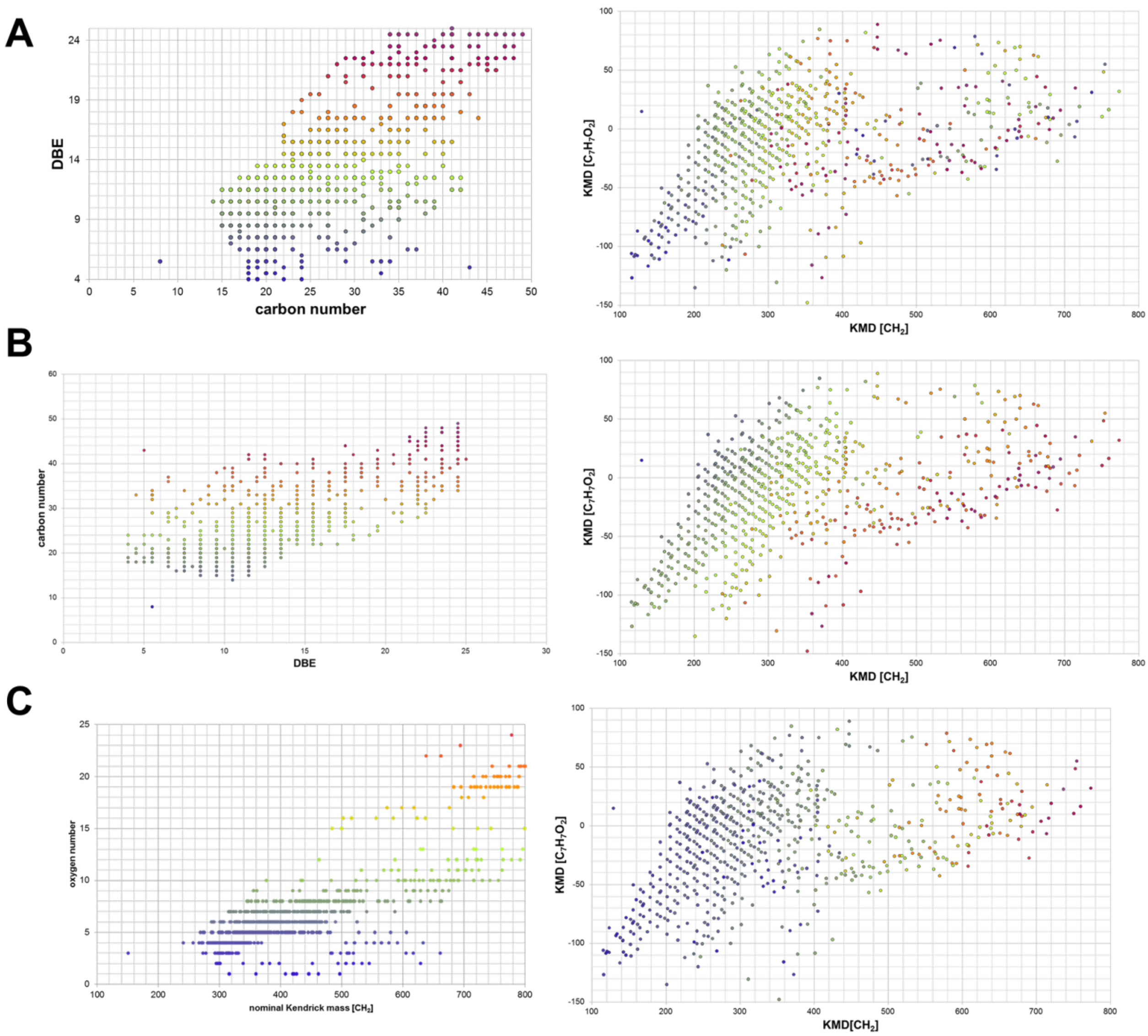

Figure S6. Comparison of enhanced mass defect filtering and **A** DBE, **B** carbon number, and **C** oxygen-content.