Electronic Supplementary Material (ESI) for RSC Advances

Revealing the chemistry of biomass pyrolysis by means of tunable synchrotron photoionisation - mass spectrometry

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Supplementary material

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1. Mass spectra

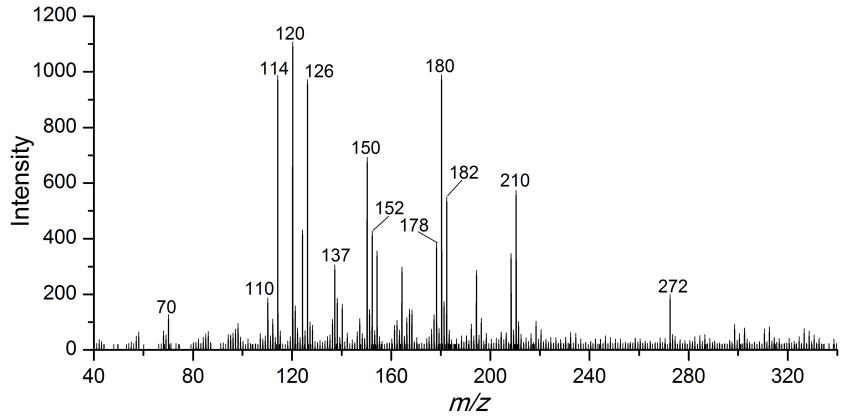


Figure S.1. Mass spectrum of volatile products from miscanthus pyrolysis with photon energy set at 9.5eV and pyrolysis reactor at 350°C

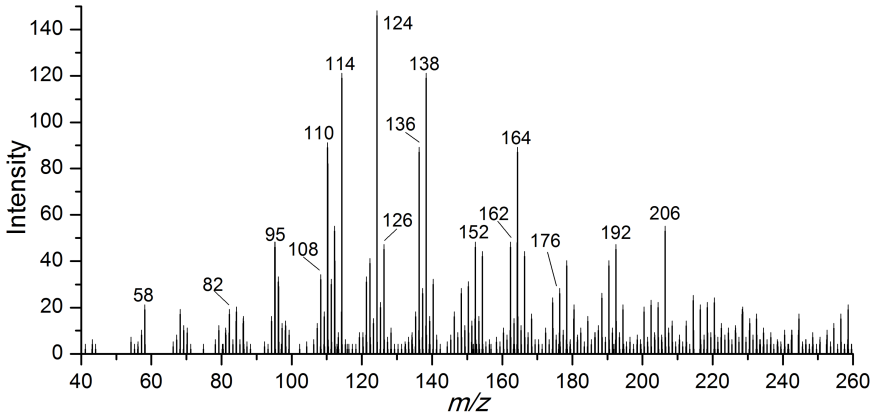


Figure S.2. Mass spectrum of volatile products from the pyrolysis of xylan (birch, Sigma Aldrich) with photon energy set at 9.5eV and pyrolysis reactor at 350°C

Deeper works are needed to solve the chemical structures of the major species produced from xylan pyrolysis from m/z 124 (124, 136, 138, 152, 162, 164, 178, 192, 206). To the best of our knowledge, these species have never been reported from MBMS with higher ionisation energy [4a,d,21,22b] or from Pyrolysis-GC/MS [19,20]. These highly reactive species (rich in oxygen) are detected here probably thanks to the low vacuum (reducing secondary reactions) and to the soft ionisation.

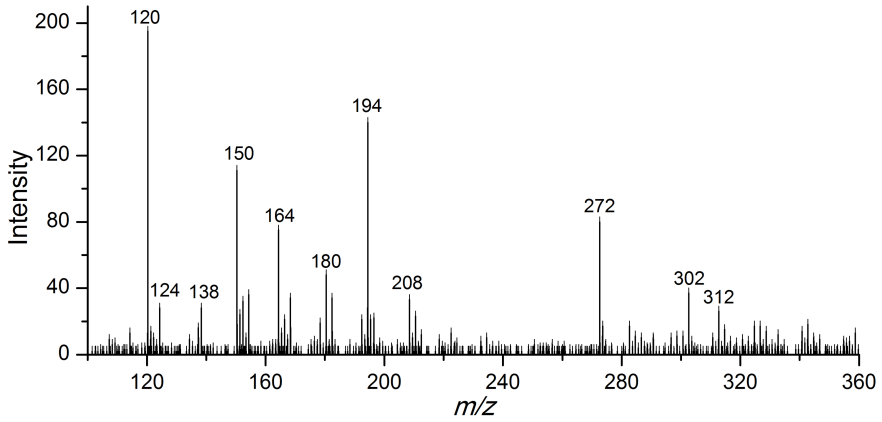


Figure S.3. Mass spectrum of volatile products from the pyrolysis of organosolv lignin extracted from miscanthus with photon energy set at 9.5eV and pyrolysis reactor at 350°C

The experimental procedure for organosolv lignin extraction was previously presented in ref. [5a].
The compound at m/z 272 (lignin dimer) is a major species for miscanthus organosolv lignin, native lignin in miscanthus and oak. m/z 332 has also been detected for oak pyrolysis. A stylben link between the two aromatic rings (see table S.2.) seems more probable in agreement with Hosoya et al. [20a] because enol ether link (proposed by Evans & Milne [4a]) is less stable and much less probable to occur in lignins and very few benzofuran type links were analysed in miscanthus lignin [24].

2. MSMS of key ions

A new potential major intermediate compound from microcrystalline cellulose pyrolyse has been evidenced (m/z=128 in figure 1 of the manuscript). Its molecular structure (or position isomers) could be deduced from the following MSMS spectrum of the m/z 128 isolated from a microcrystalline cellulose pyrolysis experiment by means of the QTOF-MS. The species at m/z 128 could be 5-methyl-4-oxotetrahydrofuran-2-carbaldehyde (or other position isomers) from its MSMS fragmentation. m/z 128 may also represent multiple isomer products.

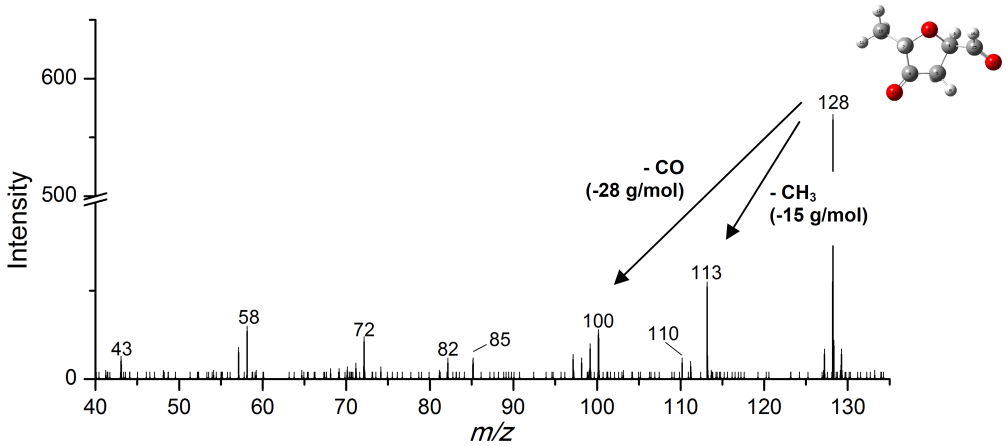


Figure S.4. MSMS of m/z=128, a new potential major intermediate compound from cellulose primary pyrolysis

Other compounds with an elemental formula of $C_6O_3H_8$ (m/z = 128 g/mol) were presented in ref. [19], but at minor yield and with a chemical structure not compatible with the MSMS. The compound at m/z 128 could also be a dihydro-hydroxymethyl-pyran-4-one but such a compound would exhibit a closer MSMS spectra than m/z=114. MSMS of m/z=114 does not produce m/z 82 and does produce m/z 104, 96 and 68 (see below). Moreover, the proposed chemical structure could be a precursor of methylfuranones detected at major yield in many studies [4a,19,20] and in this work (m/z=98g/mol).

The MSMS of m/z=114, one of the major markers for xylan pyrolysis and also produced during cellulose pyrolysis, is presented in Figure S.5.

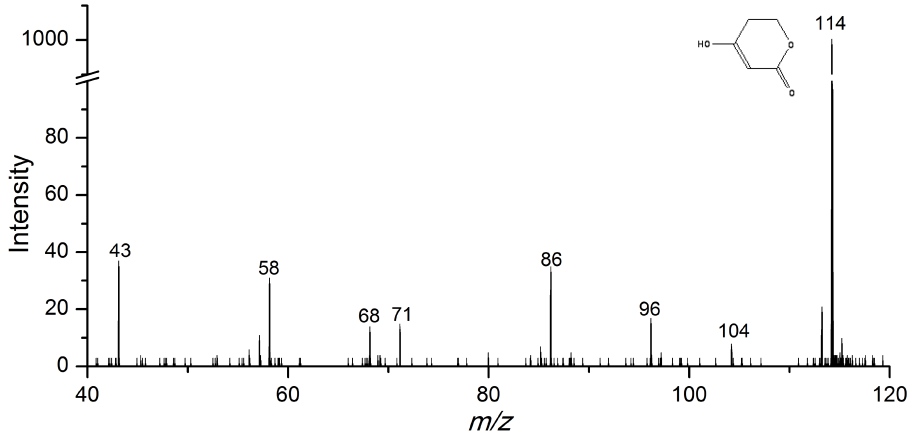
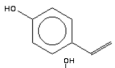
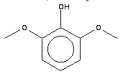
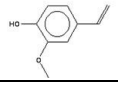


Figure S.5. MSMS of m/z=114, a major marker from xylan pyrolysis

The MSMS of m/z 114 (Figure S.5.) shows fragments at m/z = 96 and 68 that could be furfural and furan respectively. The compound at m/z = 114 could thus be a C_5 carbohydrate (furfural + H_2O) partly dehydrated. The proposed chemical structure (4-Hydroxy-5,6-dihydro-(2H)-pyran-2-one) has been evidenced as the main m/z =114 species in ref. [20b] for Miscanthus pyrolysis and is in agreement with Evans & Milne [4a]. Its structure also matches with CO elimination to give a fragment at m/z=86 (114-28).

3. Ionisation thresholds of some lignin markers and effect of photon energies on peak areas

Table S.1. Molecular structure and adiabatic ionization threshold of some major lignin primary tars calculated from CBS-QB3 method [11]

Molecular structure	Name	Molar mass (g/mol)	Adiabatic ionization threshold (eV)
	guaiacol	124.14	7.99
	4-vinylphenol	120.15	7.98
	syringol	154.16	7.76
	4-vinylguaiacol	150.17	7.65

It can be noticed that theoretical adiabatic ionization threshold of methoxyl-phenols are similar.

Aromatic functionalized compounds produced from lignin devolatilisation are less sensitive than levoglucosan for dissociative photoionisation. Their peak areas increase with a similar pattern as a function of photon energy (Figure S.6.). Nevertheless, MS spectra for organosolv lignin become a little noisier from 10eV. 9.5eV could be optimum photon energy.

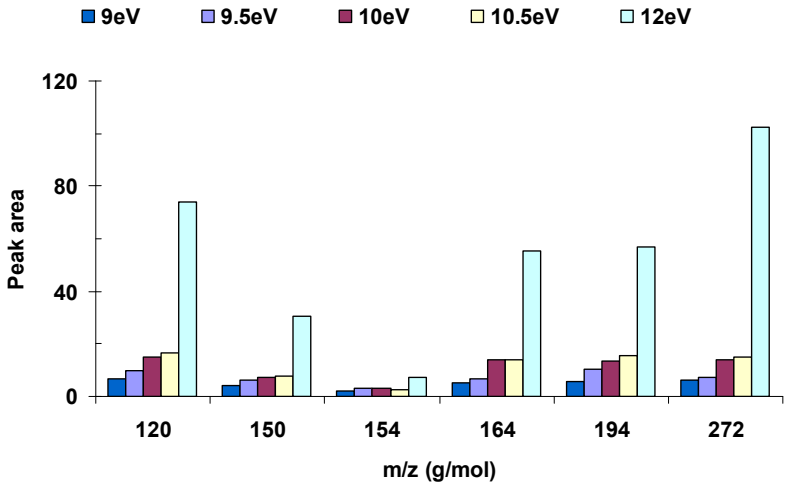
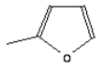
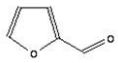
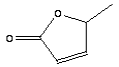
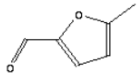
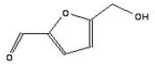
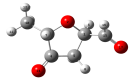
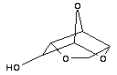
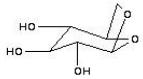
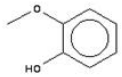
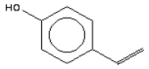
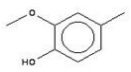
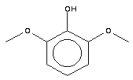
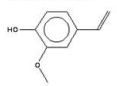
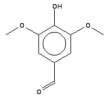
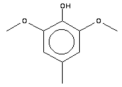
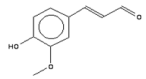
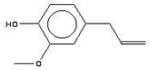
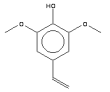
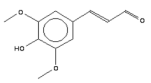
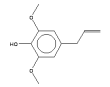
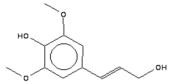
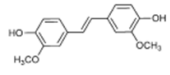


Figure S.6. Evolution of peak areas of some ions from organosolv lignin pyrolysis as a function of photon energy

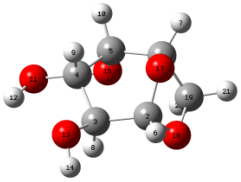
4. Main identified species ranked by elemental formula

Table S.2. Main identified species for biomass primary pyrolysis based on MSMS analysis, lignin advanced analysis of functional groups [5a,24] and comparison with literature data.

Formula	Chemical structure	Products name	CAS N°	Molecular weight (g/mol)	Origin (cellulose, xylan, lignin). Comments on formation mechanisms and differenciation from some isomers.
C_5H_6O		2-methylfuran	534-22-5	82.10	major from cellulose 2methyl-furan rather than cyclopentenone based on MSMS
$C_5H_4O_2$		furfural (2-furancarboxaldehyde)	98-01-1	96.08	major from cellulose, from MSMS
$C_5H_6O_2$		5-methyl 2-(5H)furanone (and position isomers)	591-11-7	98.10	Based on MSMS. major from cellulose (in agreement with ref. [20]). 3 isomers of di-hydro-methyl-furanone detected by Faix et al. [19].
$C_5H_6O_3$		4-Hydroxy-5,6-dihydro-2H-pyran-2-one	-	114.10	major from cellulose and xylan, from MSMS (also in ref. [4a,20b]).
$C_6H_6O_2$		5-methylfurfural	620-02-0	110.11	major from cellulose, from MSMS (CO and CH3 elimination), in agreement with [4a]. Also major from xylan.
$C_6H_6O_3$		5-hydroxymethylfurfural (HMFU, 2 furancarboxaldehyde, 5-hydroxymethyl)	67-47-0	126.11	Major, based on MSMS and in agreement with [4a,20a]
$C_6H_8O_3$		5-methyl-4-oxotetrahydrofuran-2-carbaldehyde (and position isomers)	not in Nist	128.12	Potentially a new compound, from MSMS spectra, see paper. Could be a precursor of methylfuranones.
$C_6H_8O_4$		1,4: 3,6-Dianhydro-glucopyranose	not in Nist	144.13	based on ref. [19,20b], and from ab-initio calculation for levoglucosan dissociative photoionisation (dehydration).
$C_6H_{10}O_5$		levoglucosane (LVG, 1,6 anhydro-β - glucopyranose)	498-07-7	162.14	Main compound for microgranular cellulose (Sigma). Minor for cellulose extracted from Miscanthus (higher ash content).
$C_7H_8O_2$		guaiacol	90-05-1	124.14	minor for organosolv lignin of miscanthus.
C_8H_8O		4-ethenylphenol or 4-vinyl-phenol	2628-17-3	120.15	major in miscanthus organosolv lignin and miscanthus in agreement with [20b]

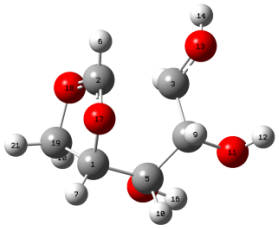
$C_8H_{10}O_2$		4methylguaiacol (Phenol, 2-methoxy-4-methyl-)	93-51-6	138.16	minor for miscanthus organosolv lignin
$C_8H_{10}O_3$		syringol (2,6 dimethoxy-phenol)	91-10-1	154.16	major in oak pyrolysis, mainly formed at high conversion time or temperature (with m/z 168). Some also in Miscanthus and organosolv miscanthus lignin.
$C_9H_{10}O_2$		4-vinylguaiacol	7786-61-0	150.17	major for miscanthus organosolv lignin and for miscanthus
$C_9H_{10}O_4$		Syringaldehyde (Benzaldehyde, 4-hydroxy-3,5-dimethoxy-)	134-96-3	182.17	major in oak and mischantus, rather than 4-ethyl syringol, ethyl link less probable in lignin
$C_9H_{12}O_3$		4-methylsyringol (4-methyl-2,6-dimethoxyphenol)	6638-05-7	168.19	major in oak, mainly formed at high conversion time or temperature (with m/z 154).
$C_{10}H_{10}O_3$		Coniferylaldehyde	458-36-6	178.18	major for miscanthus
$C_{10}H_{12}O_2$		Eugenol	97-53-0	164.20	From in miscanthus organosolv lignin and in miscanthus
$C_{10}H_{12}O_3$		4-vinylsyringol (Phenol, 4-ethenyl, 2,6-dimethoxy)	In NIST, no CAS N°	180.20	major in miscanthus organosolv lignin and miscanthus in agreement with ref. [20b]
$C_{11}H_{12}O_4$		Sinapic aldehyde (3,5-Dimethoxy-4-hydroxycinnamaldehyde)	In Nist, no CAS N°	208.21	major for miscanthus and oak, in agreement with ref. [4a,22b]
$C_{11}H_{14}O_3$		methoxyeugenol (2,6dimethoxy-4-(2-propenyl)-phenol)	6627-88-9	194.23	major in miscanthus organosolv lignin but less major in miscanthus
$C_{11}H_{14}O_4$		sinapyl alcohol (2-Propen-1-ol, 3-(4-hydroxy-3,5-dimethoxyphenyl))	In NIST, no CAS N°	210.23	major in Miscanthus, in agreement with ref. [4a], but much less in miscanthus organosolv lignin than in Miscanthus (due to extraction process)
$C_{16}H_{16}O_4$		4,4' - dihydro 3,3' - dimethoxy stylben	not in Nist	272.29	Example of lignin dimer, from Hosoya et al. [20a]. A stylben link between the two aromatic rings seems more probable because enol ether link (proposed by Evans & Milne [4a]) is less stable and much less probable to occur in lignins and very few benzofuran type links were analysed in miscanthus lignin [24].

5. Cartesian coordinates of the optimised geometry of levoglucosan and mass 128 (5-methyl-4-oxotetrahydrofuran-2-carbaldehyde) obtained at the CBS-QB3 level of theory



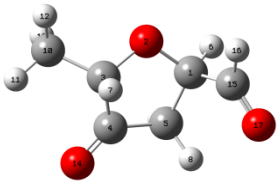
Levoglucosan

1	C	1.3355	0.583652	0.746963
2	C	0.586058	-1.3773	0.052882
3	C	-0.826603	-0.87769	-0.357104
4	C	-1.16182	0.371911	0.450566
5	C	0.010802	1.36555	0.492716
6	H	0.604106	-2.45633	0.217034
7	H	1.9495	1.07359	1.49986
8	H	-0.805258	-0.634892	-1.4242
9	H	-1.3744	0.041298	1.47246
10	H	-0.163645	2.05813	1.32589
11	O	-2.281	1.06981	-0.089174
12	H	-2.97774	0.417068	-0.221798
13	O	-1.87445	-1.80981	-0.073667
14	H	-1.85921	-2.50048	-0.743225
15	O	0.098913	2.09505	-0.721726
16	H	-0.813275	2.29649	-0.970373
17	O	1.01121	-0.731114	1.23991
18	O	1.53167	-1.01563	-0.944001
19	C	2.11773	0.232676	-0.525964
20	H	2.00528	0.976297	-1.31133
21	H	3.17401	0.069663	-0.295408



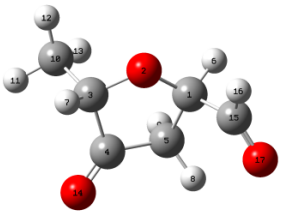
Ionized levoglucosan

1	C	-1.30519	-0.687286	0.743281
2	C	-0.924969	1.3916	0.127502
3	C	1.01817	0.885233	-0.434903
4	C	1.23071	-0.314156	0.477637
5	C	0.075422	-1.33893	0.442347
6	H	-0.781393	2.46274	0.226893
7	H	-1.8498	-1.20601	1.52605
8	H	0.827853	0.689753	-1.48891
9	H	1.3819	0.050782	1.49745
10	H	0.294488	-2.08194	1.21575
11	O	2.36053	-1.01666	-0.012907
12	H	3.17264	-0.600804	0.299454
13	O	1.81039	1.91849	-0.137709
14	H	1.94111	2.50961	-0.89348
15	O	-0.008253	-1.94663	-0.828534
16	H	0.813957	-2.42733	-0.989019
17	O	-1.05016	0.678476	1.23794
18	O	-1.64346	0.943766	-0.883764
19	C	-2.15271	-0.384687	-0.4912
20	H	-1.99049	-1.0669	-1.31793
21	H	-3.21122	-0.260058	-0.264468



5-methyl-4-oxotetrahydrofuran-2-carbaldehyde (or position isomers) (mass 128)

1	C	0.99407	-0.382746	0.731181
2	O	-0.098255	-1.25885	0.408369
3	C	-1.0385	-0.548099	-0.40498
4	C	-0.853897	0.929911	-0.034587
5	C	0.435007	1.03742	0.776107
6	H	1.3903	-0.722638	1.69393
7	H	-0.769639	-0.649083	-1.46942
8	H	1.11398	1.77028	0.336419
9	H	0.188726	1.36044	1.79044
10	C	-2.44438	-1.06954	-0.172652
11	H	-3.15293	-0.462083	-0.739237
12	H	-2.5276	-2.10924	-0.493331
13	H	-2.69866	-1.01	0.887794
14	O	-1.60156	1.82274	-0.331248
15	C	2.1137	-0.567628	-0.296707
16	H	2.21961	-1.6158	-0.648626
17	O	2.82484	0.316388	-0.69564



Ionized mass 128

1	C	0.856503	-0.611608	0.49743
2	O	-0.071361	-1.24947	-0.349922
3	C	-1.24329	-0.490299	-0.558879
4	C	-0.82961	0.953102	-0.091163
5	C	0.291689	0.733547	0.929
6	H	1.13153	-1.27207	1.33262
7	H	-1.49635	-0.534513	-1.61869
8	H	1.02338	1.54171	0.932089
9	H	-0.198905	0.689711	1.90676
10	C	-2.42491	-0.938363	0.319935
11	H	-3.28314	-0.297758	0.109422
12	H	-2.6697	-1.96749	0.050896
13	H	-2.1924	-0.895913	1.3851
14	O	-1.33122	1.95605	-0.466945
15	C	2.21508	-0.50263	-0.312056
16	H	2.44228	-1.36064	-0.96804
17	O	2.9089	0.447731	-0.162604