Assessment of the surface chemistry of wood-derived biochars using wet chemistry, Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy

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Considerations about biochar pre-treatment for analysis of carbonaceous surfaces

Acid-washing was chosen as possible biochar pre-treatment. Acid-washing is a key step for analysing the oxygen-containing surface functionalities by potentiometric titration, a methodology applied for studying soil organic matter (Cooke *et al.* 2006; López *et al.* 2008). Acid-washing allows a gentle acidification that provides a carbonaceous surface free of inorganic cations and anions, except for H⁺ (Cooke *et al.* 2006). In this study, concentrated nitric acid was used, which could affect biochar surfaces (Chen and Wu 2004) by introducing structures containing N–O bonds and/or altering surface area. However, a harsh acid attack was avoided by using low acid concentration, by working always at room temperature and also by limiting contact time of biochar with acid solution. Consequently, neither a major surface change nor any production of additional black carbon (Kuhlbusch 1995) were expected.



Fig. S1. X-ray photoelectron spectra of the O 1s region for both untreated (continuous line) and acid-washed (dashed line) biochar from pine, poplar and willow produced at contrasted HHT. The optimum fitting was obtained by resolving two peaks: (i) O double bounded to C (C=O) groups (carbonyl, carboxyl) (≈532.0 eV); and (ii) singly bonded O (-O-) in C-O groups in esters, ethers and oxygen atoms in hydroxyls (≈533.7 eV). The latter peak could include some contribution of chemisorbed O and water, not resolved as individual peak (Biniak *et al.* 1997; Nahil and Williams 2012). Other differences (untreated vs. acid-washed biochar) are mentioned in the manuscript.



Fig. S2. Derivative thermogravimetric (DTG) curve for both untreated and acidwashed biochar produced from poplar at 550 °C (PO-550). x- and y-axes scales are the same for both curves. Thermal analysis is described elsewhere (Calvelo Pereira *et al.* 2011; Sevilla and Fuertes 2010).

Table S1. Assignments of peaks and bands in FTIR spectra, indicating functional

groups associated.

Absorbance,	Assignation	References
cm ⁻¹		
3800 - 3300	Broad overlap band of vibration of O-H in C-OH or water	Bandosz and Petit (2009); Petit <i>et al.</i> (2009)
≈2960	asymmetric and symmetric C-H stretching vibrations in aliphatic – CH, –CH ₂ , –CH ₃ ,	Biniak <i>et al.</i> (1997); Elizalde-González <i>et al.</i> (2007); Nguyen <i>et al.</i> (2008); (1999)
2850	asymmetric and symmetric C-H stretching vibrations in aliphatic – CH, –CH ₂ , –CH ₃ ,	Biniak <i>et al.</i> (1997); Nguyen <i>et al.</i> (2008); Pradhan and Sandle (1999)
1600 - 1580	aromatic ring stretching; highly conjugated carbonyl groups (C=O)	Moreno-Castilla <i>et al.</i> (2000); Pradhan and Sandle (1999)
1460 - 1470	O-H deformation in carboxyl groups; C-H bending vibrations	Biniak <i>et al.</i> (1997); Moreno-Castilla <i>et al.</i> (2000)
1430 - 1410	COOH and CHO stretching; as broad band, OH bound typical of cellulose	Chun <i>et al.</i> (2004); Elizalde-González <i>et al.</i> (2007)
pprox 1370	C–C in aromatic rings	Francioso et al. (2011)
pprox 1310	syringyl ring with C-O stretching	Wang <i>et al.</i> (2009)
1070 - 1060	C-O vibrations; hydroxyl groups	Elizalde-González <i>et al.</i> (2007); Petit <i>et al.</i> (2009)
pprox 870	Carbonate ion	Tatzber <i>et al.</i> (2007)
830 - 820	aromatic CH out of plane	Artz <i>et al.</i> (2008)
pprox 785	CH out-of-plane aromatic bending	Francioso et al. (2011)
pprox 720	Carbonate ion	Tatzber <i>et al.</i> (2007)

Table S2. Amount of oxygenated acidic functional groups (mmol kg⁻¹, determined by Boehm titration) of untreated biochars from pine, poplar and willow produced at contrasted HHT.

Sample	Feedstock	HHT °C	Strong acid fraction ^A (mmol kg ⁻¹)	Moderately acid and Lactone fraction ^B (mmol kg ⁻¹)	Weak acid fraction ^C (mmol kg ⁻¹)
PI-400	Pine	400	10.1	69	465
PO-400	Poplar		0.2	126	941
WI-400	Willow		0.0	158	813
PI-550	Pine	550	8.1	10	21
PO-550	Poplar		0.2	22	179
WI-550	Willow		0.0	27	295

^A mainly carboxylic acids; ^B low pK_a phenols and hydrolysis of lactones; ^C mainly high pK_a phenols.

1 Table S3. Distribution of carbon (C 1s), oxygen (O 1s) and nitrogen (N 1s) moieties (at.%, obtained from XPS analysis) for untreated

Element			С						0			N	
Energy, eV			285.0	286.5	288.0	289.2	290.8	293.1	531.8	532.8	533.6	399.0	400.9
Assignment			$C \ 1s \ I$	C 1s II	C 1s III	C 1s IV	C 1s V	C 1s VI	O~1s~I	O~1s Ib	O 1s II	m N~1s~I	m N~1s~II
Untreated	Feedstock	HHT °C	C-C, C=C	C-OR	C=O	COOR	CaCO3/π-π	π-π	C=O	C=O	-0-	≈pyridine	Quaternary N
PI-400	Pine	400	63.3	15.6	2.6	1.5	0.5	0.0	4.0	0.0	12.0	0.3	0.5
PO-400	Poplar		64.9	12.8	2.5	1.9	1.0	0.0	5.8	0.0	10.1	0.3	0.7
WI-400	Willow		58.3	17.9	2.8	2.2	1.0	0.0	5.7	0.0	10.7	0.4	1.1
PI-550	Pine	550	75.3	8.4	2.6	1.6	1.1	0.0	4.3	0.0	6.1	0.2	0.4
PO-550	Poplar		72.7	9.2	2.3	1.6	1.3	0.0	5.5	0.0	6.5	0.4	0.6
WI-550	Willow		66.0	11.7	1.9	1.0	4.0	1.3	6.2	0.0	6.8	0.5	0.6
Acid-washed													
PI-400	Pine	400	57.3	18.1	2.9	1.8	2.5	0.7	4.8	0.0	11.1	0.1	0.8
PO-400	Poplar		62.1	14.3	2.8	2.3	1.3	0.0	5.2	0.0	10.9	0.2	1.0
WI-400	Willow		58.8	17.4	2.9	2.4	0.8	0.0	4.9	0.0	11.3	0.4	1.1
PI-550	Pine	550	68.2	11.8	2.1	1.3	3.4	1.6	1.2	6.1	3.6	0.2	0.5
PO-550	Poplar		64.7	13.1	2.2	1.5	3.0	2.0	1.9	7.0	3.6	0.3	0.8
WI-550	Willow		68.6	12.0	2.3	1.9	1.2	0.0	5.3	0.0	7.4	0.4	0.8

2	and acid-wahsed bio	ochars from pine	, poplar and willow	produced at c	ontrasted HHTp.
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