Supplementary Material for:

Towards Biochar and Hydrochar Engineering—Influence of Process Conditions on Surface Physical and Chemical Properties, Thermal Stability, Nutrient Availability, Toxicity and Wettability

Alba Dieguez-Alonso[1,*], Axel Funke[2], Andrés Anca-Couce[3], Alessandro Girolamo Rombolà, Gerardo Ojeda[5] , Jörg Bachmann[6] and Frank Behrendt[1]
[1]Technische Universität Berlin, Institute of Energy Engineering, Chair for Energy Process Engineering and Conversion Technologies for Renewable Energies, Fasanenstr. 89, 10623 Berlin, Germany; alba.dieguezalonso@tu-berlin.de
[2] Institute of Catalysis Research and Technology (IKFT), Karlsruhe Institute of Technology, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany; axel.funke@kit.edu
[3] Institute of Thermal Engineering, Graz University of Technology, Inffeldgasse 25b, 8010 Graz, Austria; anca-couce@tugraz.at
[4] Department of Chemistry "Giacomo Ciamician", C.I.R.I. Energia Ambiente and C.I.R.S.A., Università di Bologna, Ravenna Campus, Via S. Alberto 163, 48123 Ravenna, Italy; alessandro.rombola@unibo.it
[5] CREAF Ecological and Forestry Applications Research Centre, 08193 Cendanyola del Vallès, Spain; g.ojeda@creaf.uab.cat
[6] Institute of Soil Science, Leibniz University of Hannover, Herrenhaeuser Str. 2, 30419 Hannover, Germany; bachmann@ifbk.uni-hannover.de

* Correspondence: alba.dieguezalonso@tu-berlin.de; Tel.: +49-(30)-314-24381

1. Materials and Methods

CD and PW biochars were produced at the Technische Universität Berlin (Berlin, Germany), in a technical-scale fixed-bed pyrolysis reactor. In each batch, 1500 g of dry pine wood chips or dry corn digestate were used. The temperatures were measured inside the bed at four different heights: 0, 5, 10, 30 cm from the bottom of the reactor and at three different radial positions, 0, 5 and 10 cm from the reactor wall. The reference temperature was taken at 10 cm from the bottom of the bottom of the reactor and 10 cm from the container wall, i.e., in the central axis of the cylindrical bed.

The hydrothermal carbonization experiments for PW and CD hydrochars production were performed at the Leibniz Institute for Agricultural Engineering and Bioeconomy (Potsdam, Germany). Distilled water was added to the dry digestate in each experiment to achieve the desired solid content of 20 % by mass. The experiments were conducted in a 1 L autoclave (Series 4520 from Parr Instruments, stainless steel T 316) equipped with a temperature controller. The pressure was monitored and rose above saturated pressure of the process liquor due to developed gases. After the desired reaction time, the reactor was cooled down to room temperature. Gases were collected in a gas bag made of aluminum composite (Tesseraux GmbH, Germany) and analyzed within 15 min in a SSM6000 analyser (Pronova Analysentechnik GmbH & Co. KG, Germany).
The reactor contents were filtered through folded paper (ROTH Type 113P filter) for twenty minutes and dried with the filter at 105 °C overnight. In case of washing, the char was rinsed with 100 ml distilled water before it was dried. The influence of maximum temperature, time at this temperature and washing effect on the char properties was evaluated for the case of CD. For that, a full factorial 2^3 design analysis was performed. Three different temperatures (200, 220 and 240 °C), three different times at maximum temperature (10, 185 and 360 min) and three different number of washings (0, 3 and 6) were the considered parameters. HTC experiments with PW were reduced to the parameters reaction temperature and time in a full factorial 2^3 design at the same level as for the CD experiments. Experiments were conducted in duplicates.

2. Analytical methods

The determination of oxygen-containing functional groups on the char surface was done applying the Boehm titration method [Boehm1964]. The experimental procedure is based on the description by Goertzen et al. [Goertzen2010], including the sample pretreament proposed by Tsechansky and Graber [Tsechansky2014]. Due to the presence of inorganic basic and acidic components, which can condense on the biochar surface but not be part of the biochar structure, false results from the Boehm titration could be obtained caused by the solubilisation of these components in the Boehm solutions [Tsechansky2014]. Consequently, they were removed prior titration. This washing was performed first with HCl (0.05 M) and NaOH (0.05 M), during 24 h each, to remove basic and acidic species respectively. After this, a final washing with HCl was performed to protonate the acidic species on the char surface again. After each washing and before the next one, the biochar was rinsed with deionized water until a conductivity lower than 10 µS/cm was reached. The final step before titration was the degassing using N_2.

3. Results

mg/kg	**Al_{sol}**	**Al_{liq}**	**Fe_{sol}**	**Fe_{liq}**	**Na_{sol}**	**Na_{liq}**
PW400-20	-	-	-	-	-	-
PW400-40	-	-	-	-	-	-
PW600-20	-	-	-	-	-	-
PW600-40	-	-	-	-	-	-
CD400-20	1518±95	-	3175±249	-	1926±322	-
CD400-40	1699±236	-	3512±444	-	2150±238	-
CD600-20	1636±219	-	3446±273	-	1880±292	-
CD600-40	1651±135	-	3290±248	-	1966±271	-
PW240-360	24.6±1.8	0.1±0.0	33.0±4.3	3.6±1.4	42.7±6.7	16.7±0.1
PW240-10	16.2±2.6	0.1±0.1	15.0±1.2	1.2±0.1	24.7±3.9	17.3±0.3
PW200-360	20.4±3.8	0.1	19.3±9.5	1.6±1.8	29.5±3.3	16.6±0.1
PW200-10	14.4±2.6	0.7±0.0	14.4±0.4	1.5±0.2	27.7±6.2	18.6±2.5
CD240-360-0	1623	-	2797	0.2	375.8	110.3
CD240-10-0	1555	0.9	2280	1.2	310.8	129.5
CD240-10-6	1204	0.1	2476	3.0	115.7	157.4
CD220-185-3	1346±14	0.3±0.1	2657±153	1.8±0.7	168±2.1	141.6±37.7
CD200-360-0	1264	0.5	2341	2.8	574.8	156.8
CD200-360-6	1115	0.1	2540	2.3	133.2	173.1
CD200-10-0	968	-	1931	4.4	605.8	99.1
CD200-10-6	1036	0.2	2186	4.9	223.2	119.3

Table S1: Inorganic elemental composition (Al, Fe and Na) for pine wood and corn digestate biochars and hydrochars. In the case of hydrochars, both the composition of the solid (sol) and the liquid (liq) fraction are included.

t(s)	PW600-40	CD600-40	PW600-20	PW400-40	CD400-40
2-10	73.7°	66.2°	77.2°	81.4°	70.1°
10-20	83.1°	57.1°	89.3°	88.8°	88.3°
20-30	81.3°	66.8°	89.8°	89.8°	89.4°
30-40	79.5°	73.1°	89.8°	89.9°	88.8°
40-50	77.7°	74.9°	89.9°	90.0°	88.4°
50-60	77.3°	73.8°	89.8°	89.9°	88.0°
60-70	77.0°	73.6°	89.7°	89.9°	87.5°
70-80	74.7°	74.0°	89.7°	89.9°	87.1°

Table S2: Contact angle for PW and CD biochars obtained from comparison of water and hexane absorption curves, according to [Ojeda2015].

References

[Boehm1964] H. P. Boehm, E. Diehl, W. Heck, R. Sappok, Angew. Chem. internat. Edit. 3 (1964) 669-677.

[Goertzen2010] S. L. Goertzen, K. D. Theriault, A. M. Oickle, A. C. Tarasuk, H. A. Andreas, Carbon 48 (2010) 1252-1261.

[Tsechansky2014] l. Tsechansky, E. R. Graber, Carbon 66 (2014) 730-733.

[Ojeda2015] G. Ojeda, S. Mattana, A. Avila, J.M. Alcaniz, M. Volkmann, J. Bachmann, Geoderma 249–250 (2015) 1–11.