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Production and characterization of slow pyrolysis biochar: influence of feedstock type and pyrolysis conditions

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Abstract

Biochar was produced by fixed-bed slow pyrolysis from various feedstock biomasses under a range of process conditions. Feedstocks used were pine wood, wheat straw, green waste and dried algae. Process conditions varied were the highest treatment temperature (HTT) and residence time. The produced chars were characterized by proximate analysis, CHN-elemental analysis, pH in solution, bomb calorimetry for higher heating value, N_2 adsorption for BET surface area and two biological degradation assays (oxygen demand, carbon mineralization in soil). In proximate analysis, it was found that the fixed carbon content (expressed in *wt%* of dry and ash-free biochar) in the biochar samples strongly depended on the intensity of the thermal treatment (i.e. higher temperatures and longer residence times in the pyrolysis process). The actual yield in fixed carbon (i.e. the biochar fixed carbon content expressed as *wt%* of the dry and ash-free original feedstock biomass weight) was practically insensitive to the highest treatment temperature or residence time. The pH in solution, higher heating value and BET surface positively correlated with pyrolysis temperature. Finally, soil incubation tests showed that the addition of biochar to the soil initially marginally reduced the C-mineralization rate compared against the control soil samples, for which a possible explanation could be that the soil microbial community needs to adapt to the new conditions. This effect was more pronounced when adding chars with high fixed carbon content (resulting from more severe thermal treatment), as chars with low fixed carbon content (produced through mild thermal treatment) had a larger amount of volatile, more easily biodegradable, carbon compounds.

Keywords: biochar, biological degradation, characterization, feedstock, packed bed reactor, pyrolysis, pyrolysis conditions, slow pyrolysis

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Introduction

Rising energy costs, concerns over greenhouse gas emissions and the nonrenewable nature of fossil fuels have prompted significant research into the conversion of biomass into biofuels and other value-added renewable products (Hossain *et al.*, 2011). Among the array of biomass conversion technologies, pyrolysis is a relatively simple technique in which organic material is heated in the absence of oxygen. During the pyrolysis process, the natural polymeric constituents (i.e. lignin, cellulose, fats and starches) are thermally broken down into three different fractions: bio-oil (condensed vapours), char (solid fraction) and noncondensable gases (Mohan *et al.*, 2006). Depending on the heating rate and temperature, different distributions and yields of the aforementioned fractions can be obtained (Bridgwater & Peacocke, 2000; Lu *et al.*, 2009). To date, most biomass pyrolysis research has focused on selecting process conditions to maximize the yield of the bio-oil fraction, as it is a crude liquid biofuel that can be used without modification in stationary heat and power applications, or can be further upgraded to a drop-in biofuel (Czernik & Bridgwater, 2004; Balat *et al.*, 2009; Bridgwater, 2012). Conversely, the solid or char fraction obtained from biomass pyrolysis is often considered a waste product and consequently combusted to provide the necessary heat for the pyrolysis process. However, recent research suggests that char from pyrolysis can be used as a soil amendment, hence termed biochar, to substantially increase soil fertility (Chan *et al.*, 2007; Laird *et al.*, 2009; Novak *et al.*, 2009; Major *et al.*, 2010; Jeffery *et al.*, 2011).

At present, the mechanisms by which biochar increases soil fertility are not fully understood. Research has demonstrated that biochar application to soil increases the soil organic carbon, improves water holding capacity and soil aeration, increases the cation exchange capacity, neutralizes the pH of acidic soils and improves the soil microbial ecology (Sohi *et al.*,

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2010). In addition to these purported benefits, biochar largely consists of a recalcitrant carbon fraction which has been demonstrated to be very stable, with a half-life of over 1000 years in the soil (Lehmann *et al*., 2006; Kuzyakov *et al*., 2009; Lehmann & Joseph, 2009; Zimmerman, 2010). Consequently, biochar production by pyrolysis of biomass effectively removes carbon from the atmospheric carbon cycle, transferring it to long-term storage in soils. Biochar therefore could help in the global challenge of carbon dioxide (CO_2) mitigation, as it results in a net removal of carbon from the atmosphere (Lehmann *et al*., 2006; Lehmann & Joseph, 2009; Roberts *et al*., 2010; Matovic, 2011).

Biochar can be produced from various types of processes including slow and fast pyrolysis, and gasification. Each type of process is distinguished by different ranges of temperatures, heating rates, biomass and vapour residence times. Given this variability in pyrolysis processes and their accompanying process conditions, in combination with a wide range of available biomass feedstocks for biochar production (including wood, energy crops, agricultural waste residues, sewage sludge, anaerobic digestate, municipal wastes, etc.), large variability is to be expected in the physicochemical properties of the biochars, and ultimately, in their performance as a soil amendment and/or in their ability to store carbon permanently in the soil (Antal & Gronli, 2003). Consequently, the challenge for biochar science is to predict and assure product quality, agronomic benefits and environmental effects of any given biochar produced from any given feedstock by any given pyrolysis technology and process conditions (Masek *et al*., 2011).

To produce high-quality biochars intended for agricultural use with reliable and consistent product qualities, slow pyrolysis is often considered as the most feasible production process (Song & Guo, 2012). In slow pyrolysis, the biomass is heated in an oxygen limited or oxygen free environment, with typical heating rates between 1 and 30 °C min^{-1} (Lua *et al*., 2004). Slow pyrolysis is usually carried out at atmospheric pressure, and the process heat is typically supplied from an external energy source – generally from combustion of the produced gases or by partial combustion of the biomass feedstock (Laird *et al*., 2009). Under these circumstances biochar yields are usually up to 30 *wt%*, on dry feedstock weight basis. However, yield and the properties of the resulting biochar are dependent on several factors including the biomass feedstock, heating rate, pyrolysis temperature and vapour residence time. Of these parameters, it has been established that the highest treatment temperature (HTT; the maximum temperature which the biomass is subjected to in the pyrolysis reactor) has the greatest overall influence on the final product characteristics (Antal & Gronli, 2003; Lua *et al*., 2004; Özçimen & Ersoy-Meriçboyu, 2008).

To address the variability in biochar production techniques (other than slow pyrolysis), the wide selection of process parameters within each production technique, and the variability in feedstock selection – all of which may affect biochar performance in soils – a large number of biochar quality parameters have been described (Schimmelpfennig & Glaser, 2012; Song & Guo, 2012; Sun *et al*., 2012). More recently, attempts have been made to define a set of assays and relevant characteristics for assessing and comparing the quality of biochars (International Biochar Initiative (IBI), 2012; Schmidt *et al*., 2012). These parameters include (apart from toxicity testing): biochar particle size distribution, elemental and proximate analysis, pH and liming effect, as well as more analytically advanced properties including BET surface area, porosity and plant available nutrient content (IBI, 2012). However, it should be noted that the identification of the ranges or values of these parameters which classify biochars according to their quality is still ongoing. Furthermore, these quality parameters alone do not warrant the agronomic benefits of biochar by themselves, as soil type and climate properties also determine the net effect of biochar use.

This study is an experimental investigation of the production of biochar by slow pyrolysis and aims to relate the various feedstock and process parameters to the yield and physicochemical characteristics of biochar. Once the relationships between feedstock, production process and biochar properties are known, this knowledge will permit the production of tailor-made biochar. More specifically, an appropriate selection of biomass feedstock and pyrolysis parameters could be made that yields a biochar optimized for a specific behaviour within the soil both in terms of soil fertility improvement and enlarging the pool of stable carbon within the soil.

Materials and methods

Feedstock materials

Four biomass input materials were selected for this study: wood (pine), green waste, wheat straw, and spray-dried algae. To ensure more comparable conditions (i.e. biomass heating rate) in the pyrolysis reactor for the used different feedstocks, the materials were all pelletized.

Both the pine wood (Stelmet, Poland) and straw (Strovan, Belgium) were acquired commercially in a pelletized form (6 mm pellet diameter). Prior to the pyrolysis experiments, pine wood and straw pellets were stored at ambient temperature and ambient air humidity.

Green waste was obtained from a local garden contractor and consisted of shredded leaves, twigs and branches of

mainly coniferous trees and shrubs. Green waste feedstock material was ground in a cutting mill passing over a 2 mm screen and then cold pelletized in a laboratory pellet press (6 mm diameter). The green waste pellets were then air dried at 105 °C for 1 h, before finally being stored at −18 °C due to their sensitivity to microbial decay. Spray-dried algae were acquired commercially (SBAE Industries, Sleidinge, Belgium), and manually pelletized to a diameter of 15 mm.

Slow pyrolysis set-up

The slow pyrolysis reactions were carried out in a vertical, tubular, stainless steel reactor ($d \times L = 3.8 \times 30$ cm) which was heated by an electric furnace (schematic in Fig. 1). The maximum temperature ramp rate for the reactor was ca. 17 °C min^{-1} and the reactor was continuously swept with nitrogen (800 ml min^{-1}) to remove the produced gases and tars produced during pyrolysis.

For each slow pyrolysis experiment, biomass pellets were loosely packed in the reactor to form a bed height of 25 cm. Because of the differences in bulk density between feedstocks, the actual mass of biomass in the reactor differed: ca. 135, 100, 70, and 70 g of wood, straw, green waste and algae were respectively used in each pyrolysis experiment. Each pyrolysis experiment consisted of heating the reactor at the maximum heating rate (17 °C min^{-1}) until the HTT was reached, which ranged between 300 and 750 °C depending on the experiment. The reactor was then kept at the nominated HTT for a specific duration (residence time), before the furnace was shut off and the reactor ambiently cooled. The nitrogen flow was continued during cooling to purge the reactor of any remaining pyrolysis gases and to prevent any oxygen exposure to the char while still above ignition temperature. In total 32 experiments were performed, testing combinations of four highest treatment temperatures (HTT = 300, 450, 600, and 750 °C) and two different residence times (10 and 60 min). An overview of all experiments, including used feedstock and pyrolysis conditions, is given in Table 1.

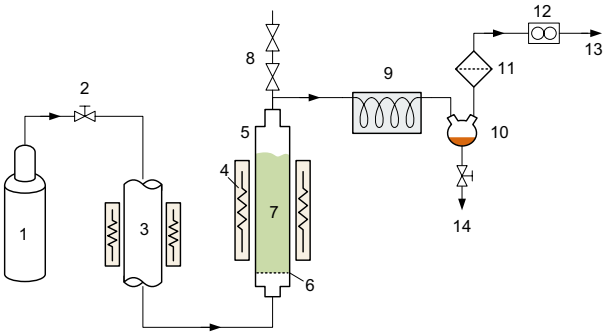

Fig. 1 Slow pyrolysis set-up for the batch production of biochar: (1) nitrogen gas supply, (2) flow control, (3) gas preheater, (4) electric tube furnace, (5) pyrolysis reactor, (6) sintered base plate, (7) packed biomass bed, (8) biomass lock hopper, (9) condenser, (10) condensate/gas separator, (11) cotton filter, (12) diaphragm gas flow meter, (13) gas vent and (14) bio-oil recovery.

Biochar characterization

Biochar yield. The yields (η) of the recovered biochar were expressed as weight percentages of dry ash-free biochar recovered to dry ash-free initial biomass. Dry ash-free (daf) basis for yield expression was chosen to avoid positive bias in yield in case of using biomass samples with a high mineral (ash) content. The yields were calculated by Eqn (1):

$$\eta = \frac{M_c - M_{ash,c}}{M_{dry,b} - M_{ash,b}} \cdot 100\% \quad (1)$$

where M_c is the weight of the char recovered from the pyrolysis reactor (kg) which after the pyrolysis process was considered to be oven dry (see below), $M_{dry,b}$ is the oven-dry mass of raw biomass material, and $M_{ash,c}$ and $M_{ash,b}$ represent the respective ash contents (i.e. weight in kg) in the biochar and raw biomass samples. More details regarding ash content determination are given in the section below.

Proximate analysis. Moisture, volatile matter and ash content were determined according to D1762-84 (ASTM, 2007). In brief, biochar samples of ca. 1 g – in duplicate – were heated in porcelain crucibles and the sample weight differences before and after heating were determined. For moisture content, samples were dried at 105 °C for 2 h (i.e. oven dry); for volatile matter samples were heated to 950 °C for 11 min (covered crucible) and for ash content 750 °C for a minimum of 2 h (uncovered crucible). The weight of the original sample, subtracted by its moisture content, ash content and volatile matter content (as determined by the aforementioned proximate analysis) corresponds to the stable carbon fraction of that sample and hence, this fraction is termed 'fixed carbon or fixed-C fraction'. In this study, the fixed carbon fraction is expressed on dry ash-free basis, or:

$$\%M_{fc} = 100 \cdot \frac{M_{dry} - M_{vm} - M_{ash}}{M_{dry} - M_{ash}} \quad (2)$$

where $\%M_{fc}$ is the fraction of fixed carbon (in *wt%*), M_{vm} is the weight of volatile matter in the sample (kg), M_{dry} is the oven dry weight of the sample (kg) and M_{ash} is the weight of the ash residue of the sample (kg).

In this study, ratio (in *wt%*) of weight of fixed carbon in a biomass sample to the weight of the original biomass feedstock on a dry and ash-free basis is defined as the fixed carbon yield, or

$$\%Y_{fc} = \frac{\%M_{fc,c} \cdot (M_{dry,c} - M_{ash,c})}{M_{dry,b} - M_{ash,b}} \quad (3)$$

where $\%Y_{fc}$ is the fixed carbon yield (in *wt%*), $M_{dry,c}$ and $M_{dry,b}$ are the dry weights (kg) of the biochar and the biomass feedstock respectively. Furthermore, $M_{ash,c}$ and $M_{ash,b}$ and are the weights (kg) of the ash in the biochar and in the original biomass feedstock out of which the biochar was produced, respectively.

Elemental analysis. The elemental (CHN) analysis was performed in duplicate using a Flash 2000 Elemental Analyser

Table 1 Overview of the tested properties of the biochars from different feedstocks, and using different HTTs and residence times in the pyrolysis process

Process conditions		Proximate analysis					Elemental analysis						Biological tests	
HTT (°C)*	Residence time (min)	Biochar yield (*wt%*)†	Volatile matter (*wt%*)†	Fixed carbon (*wt%*)†	Ash content (*wt%*)‡	Fixed carbon yield (*wt%*)§	Total C content (*wt%*)†	Total H content (*wt%*)†	H/C-ratio	HVV (MJ kg^{-1} db)	pH in solution	BET surface area (m^2 g^{-1})	BOD_{14} (mg O_2 l^{-1})*	Soil incubation performed?
Wood														
300	10	89.8	78.0	22.0	0.3	19.8	54.1	5.9	1.30	n.d.¶	4.5	n.d.	n.d.	
	60	43.7	42.6	57.4	0.5	25.1	71.3	4.7	0.79	n.d.	5.7	6	n.d.	x‖
450	10	29.2	21.4	78.6	1.0	23.0	82.5	3.8	0.56	32.5	6.6	4	79.3	
	60	27.0	16.8	83.2	1.2	22.5	86.3	3.5	0.49	32.9	6.7	23	54.8	x
600	10	24.4	8.2	91.8	1.2	22.4	90.0	2.6	0.35	34.4	6.7	196	40.5	
	60	23.3	6.4	93.6	1.3	21.8	92.3	2.3	0.30	34.4	9.1	127	25.9	x
750	10	23.0	2.6	97.4	1.1	22.4	92.5	1.4	0.19	n.d.	10.2	128	n.d.	
	60	22.7	2.6	97.4	1.1	22.1	92.5	1.1	0.15	n.d.	10.4	n.d.	n.d.	x
Straw														
300	10	94.8	76.3	23.7	8.0	22.5	50.3	6.2	1.47	n.d.	6.1	n.d.	n.d.	
	60	36.8	33.5	66.5	19.1	24.5	76.2	5.0	0.79	n.d.	9.4	n.d.	n.d.	
450	10	28.5	19.4	80.6	22.4	23.0	84.1	3.6	0.51	25.1	9.8	n.d.	41.6	
	60	27.5	15.9	84.1	22.9	23.1	86.4	3.5	0.49	25.5	10.1	16	42.0	x
600	10	25.4	8.8	91.2	24.5	23.2	90.1	2.4	0.32	25.6	10.9	n.d.	32.4	
	60	25.2	7.4	92.6	24.5	23.3	90.3	2.1	0.28	25.5	11.3	22	65.1	
750	10	23.7	4.2	95.8	26.2	22.7	92.2	1.6	0.20	n.d.	12.1	n.d.	n.d.	
	60	24.4	4.1	95.9	25.8	23.4	93.7	1.2	0.16	n.d.	11.9	n.d.	n.d.	
Green waste														
300	10	98.4	74.3	25.7	3.6	25.3	53.2	6.2	1.41	n.d.¶	7.4	n.d.	n.d.	
	60	48.6	48.6	51.4	6.8	25.0	69.3	5.4	0.94	n.d.	8.1	n.d.	n.d.	
450	10	31.3	25.3	74.7	11.1	23.4	78.8	4.2	0.63	27.5	9.6	n.d.	65.1	
	60	27.8	18.5	81.5	12.0	22.7	82.9	3.5	0.51	27.9	10.0	17	60.8	x‖
600	10	24.9	11.5	88.5	13.2	22.0	87.7	2.3	0.32	27.9	10.4	n.d.	57.4	
	60	24.4	8.8	91.2	13.4	22.3	88.4	2.0	0.27	28.0	11.3	46	31.4	
750	10	26.4	3.5	96.5	13.9	25.5	87.5	1.5	0.21	n.d.	11.4	n.d.	n.d.	
	60	23.7	1.9	98.1	13.4	23.2	93.2	1.3	0.16	n.d.	11.6	n.d.	n.d.	
Dry algae														
300	10	72.8	70.0	30.0	46.3	21.8	62.7	7.2	1.38	n.d.	4.9	n.d.	n.d.	
	60	50.1	55.2	44.8	55.8	22.4	69.5	6.9	1.19	n.d.	7.7	n.d.	n.d.	
450	10	28.4	27.5	72.5	68.6	20.6	74.5	4.5	0.72	9.22	9.1	n.d.	97.0	
	60	25.0	19.1	80.9	71.8	20.2	78.7	4.0	0.61	8.68	9.3	14	70.8	x
600	10	24.1	18.9	81.1	72.2	19.5	80.1	2.7	0.41	8.29	11.1	n.d.	71.5	
	60	22.9	15.7	84.3	73.0	19.3	83.4	2.0	0.29	8.17	11.9	19	65.2	
750	10	21.0	10.1	89.9	74.8	18.9	86.4	1.5	0.21	n.d.	12.4	n.d.	n.d.	
	60	19.3	3.9	96.1	76.4	18.5	90.6	1.4	0.19	n.d.	12.5	n.d.	n.d.	

*HTT, Highest treatment temperature; BOD, Biological oxygen demand.

†Biochar on dry and ash-free basis.

‡Biochar on dry basis.

§Expressed on dry and ash-free feedstock weight basis.

¶For HVV (higher heating value), BET surface area and biological tests, only selected samples were subjected to analysis (n.d. = not determined).

‖Indicates that for these samples a soil incubation test was performed.

(Thermo Fisher Scientific, Waltham, MA, USA). Oxygen content was not measured or calculated because of the interference of inorganic oxides in the ash, especially as the ash contents in the biochar varied from less than 1 to more than 40 *wt%* depending on the feedstock material used (see also Table 1).

Higher heating value. The HHV (higher heating value) of chars and input materials were determined by bomb calorimetry, in duplicate (Parr model 6200 calorimeter with a model 1108 oxygen bomb, Parr Instrument Company, Moline, IL) according to the instructions of Parr sheet no. 205M, 207M, and 442M.

pH in solution. Biochar samples were suspended in a 0.1 N KCl solution in a 1 : 10 (*wt/wt*) ratio. After 10 min of stirring, the pH of the biochar suspension was measured using a Model 420 Thermo Orion (Thermo Fisher Scientific). The analyses of pH were performed in duplicate.

BET surface area. The BET specific surface area of the biochars were calculated by measuring nitrogen gas adsorption at -196 °C using a Ströhlein Areameter II (CIS Ingenieurbüro Seifert, Dresden, Germany) according to the single-point method DIN66132 (Deutsches Institut für Normung, 1975). Samples were degassed at 100 °C under continuous nitrogen flow for 24 h prior to analysis. Analyses were performed in duplicate.

Biological degradation experiments. Two short-term biological degradation tests were performed: a biological oxygen demand (BOD) test and a soil incubation test. In the first, the BOD of each biochar sample was measured over 14 days in a 2.6 g l^{-1} dispersion containing a microbial inoculum obtained from a soil sample. The soil sample from which the microbial inoculum was prepared was the same as the one used in the soil incubation test (see below). The dispersion was incubated at 20 °C and buffered at a pH of 7.2. The amount of oxygen consumed by biological oxidation of each biochar sample was measured using an Oxitop Respirometer (WTW Gmbh, Weilheim, Germany). The oxygen consumption metering principle is based on absorbing evolved CO_2 by soda lime pellets – the consumption of oxygen (biological demand) is then calculated from measuring the headspace pressure drop in the container of the biochar dispersion (Veeken *et al.*, 2003). Apart from the 14-day measuring period and the use of a soil-derived microbial inoculum, the procedure was similar to ISO (1999).

The second biological degradation test consisted of measuring the respired CO_2 from incubated biochar–soil mixtures using a method adapted from Anderson & Ineson (1982). A sandy loam soil, retrieved from the area of Lendelede (Belgium) was used in the incubations. The soil sample contained 7.1 g organic carbon per kg of soil and had a pH-H_2O of 5.33. The soil was sampled from an arable farming plot and its average composition was 50 *wt%* sand, 43 *wt%* silt and 7 *wt%* clay. To prepare the incubations, the soil was thoroughly mixed, passed through a 2 mm sieve, and for each individual experiment 3.5 g of biochar was mixed with 250 g of soil (dry basis) and placed in a 6.9 cm diameter PVC tube. Next, water was added to achieve a moisture content of 50% water filled pore space. The biochar–soil preparations were then incubated for 42 days at 25 °C within sealed glass jars. The CO_2, evolved from each incubation, was trapped by a 15 ml 0.5 N NaOH solution. Periodically the lye solutions were replaced and titrated with 0.5 N HCl to a pH of 8.24 (702 SM Titrino, Metrohm, Herisau, Switzerland). Evolved CO_2 was therefore determined by subtracting the amount of titrant used in a solution from a given biochar treatment from the average amount required to neutralize the solution of the blank control; the difference being attributable to soil respired CO_2 reacting with OH^- in solution to form CO_3^{2-}. Although it has to be remarked that a part of the evolved CO_2 could be attributed to abiotic processes. The time elapsed between titrations (and replacement of the NaOH solutions) was varied during the incubation period according to the expected respiration rate. Measurements were taken on days 2, 4, 6, 10, 14, 18, 25, 36, and 42.

Results

A summary of all tests performed on the different types of biochar produced along with the results is given in Table 1. A more detailed analysis of each physicochemical or biological test is given below.

Biochar yield

The effects of pyrolysis residence time and HTT on biochar yield are illustrated in Fig. 2. The char yields (daf basis) are negatively correlated with increasing pyrolysis severity (i.e. increased HTT and longer residence times). Of the various feedstocks tested, algae had the lowest biochar yield (daf basis), with the exception for the treatment at 300 °C and with a residence time of 60 min. This could be due to a different composition in terms of extractives and cell wall components in comparison with terrestrial biomass. Also, the algae sample used had a high ash content (38.4 *wt%* daf) which may act catalytically during the pyrolysis process and alter the product distribution in terms of yield of gas, char and bio-oil (Patwardhan *et al.*, 2010). Generally, the yields in this study were lower than results reported in literature (e.g. Özçimen & Ersoy-Meriçboyu, 2008; Masek *et al.*, 2011), where biochar yield above 30 *wt%* are reported. The low biochar yields in this study can be attributed to the high nitrogen sweeping rate used in our production experiments (800 ml min^{-1}). The sweep gas reduces the vapour residence time and therefore partially inhibits secondary char forming reactions (Özçimen & Ersoy-Meriçboyu, 2008).

Proximate analysis

Proximate analysis was performed to measure the moisture, volatile matter, fixed carbon and ash contained

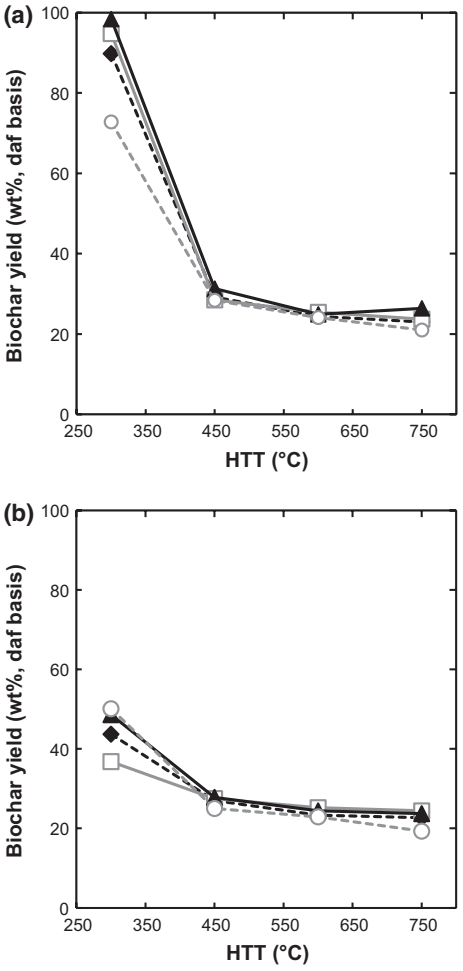

Fig. 2 The effect of HTT on biochar yield, expressed in *wt%* of biomass feedstock, on dry and ash-free basis (daf), for two different residence times: (a) 10 min and (b) 60 min. Biochar samples prepared from wood (♦), straw (□), green waste (▲) and algae (○).

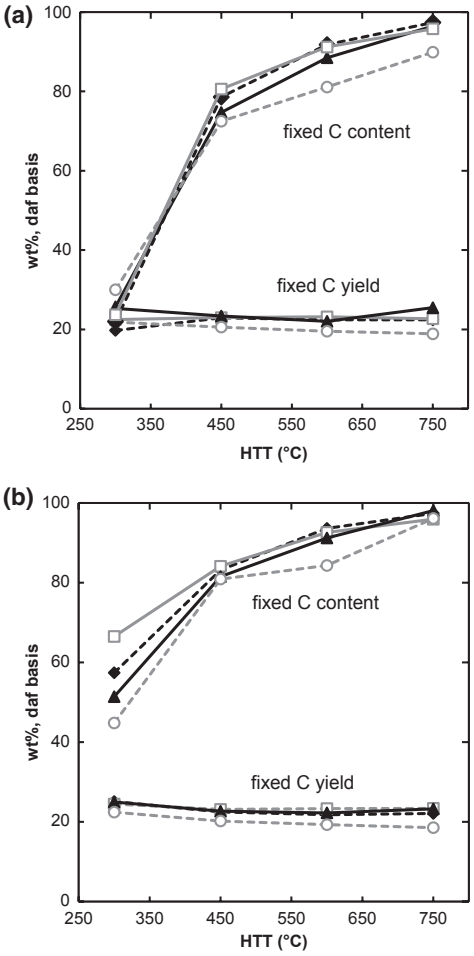

Fig. 3 The effect of HTT on fixed carbon content and on the fixed carbon yield, both expressed in *wt%* of biomass feedstock on dry and ash-free basis (daf), for two different residence times: (a) 10 min and (b) 60 min. Biochar samples prepared from wood (♦), straw (□), green waste (▲) and algae (○).

within the produced biochars and raw biomasses. The moisture contents of the input materials were 5.84, 7.99, 31.64, and 5.32 *wt%* for wood, straw, green waste and algae respectively. The relative ash content of the biochar samples shows an important increase with increasing pyrolysis severity (i.e. residence time and HTT), which is expected as ash remains in the solid fraction whereas the organic matter undergoes thermal decomposition, resulting in weight loss in the C-containing fraction. The calculated ash yields – i.e. the ratio (in per cent) of the weight of ash in the biochar to the weight of ash in the original biomass feedstock sample – were >98% for wood, green waste and algae and >95% for straw biochar. The minor losses in ash content after the pyrolysis process are likely due to lost potassium, which can volatilize at pyrolysis temperatures (Long *et al.*, 2012). In Fig. 3, the fixed carbon content is plotted against HTT for two different residence times (10 and 60 min). To allow comparison and to exclude bias from the ash content figures, the fixed carbon results are expressed on a dry ash-free basis.

As the severity of pyrolysis increases, the fixed carbon content in the produced biochars similarly increases, with HTT having a more notable impact than residence time in these experiments. However, the overall fixed carbon yield – the total fixed carbon content expressed as *wt%* of the original feedstock biomass used to produce the biochar (daf basis) – was seen to be independent of both process variations as well as of the feedstocks used. The increase in the fixed carbon content is thus a result of the reduction in the overall biochar mass rather than additional 'carbon-fixing' reactions. Conceptually, this is unsurprising as the method used to measure fixed carbon is itself also a pyrolytic process (devolatilization

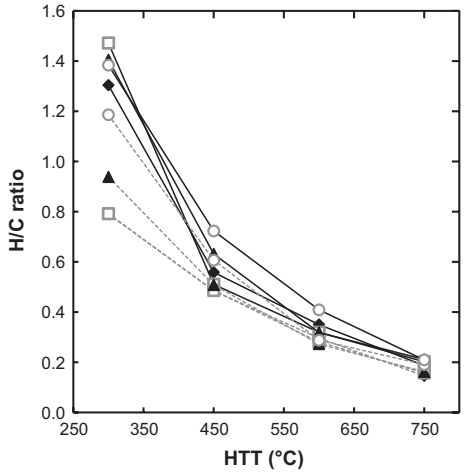

Fig. 4 The relationship between HTT and measured H/C ratio of the biochar samples. Biochar samples prepared from wood (♦), straw (□), green waste (▲) and algae (○), samples produced with a residence time of 10 min connected with solid black lines, and grey dotted lines for residence times of 60 min.

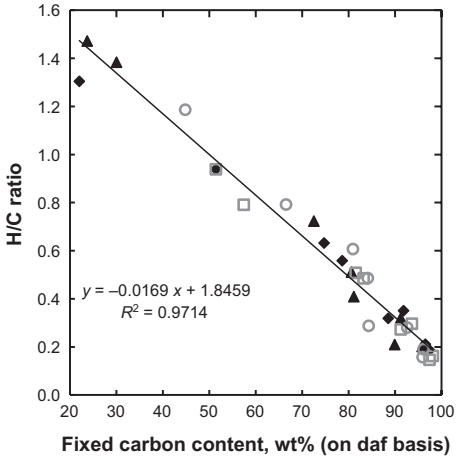

Fig. 5 The measured H/C ratio of the biochar samples plotted against fixed carbon content (in *wt%* and expressed on dry ash-free basis). Biochar samples prepared from wood (♦), straw (□), green waste (▲) and algae (○).

at 950 °C). Considering the consistency of the fixed carbon yields and the fact that all the biochar production experiments in this study were subject to HTTs much lower than 950 °C, we conclude that the proximate analysis had the overall net effect of subjecting all the biochars to the same pyrolysis process – 950 °C treatment for 6 min – in essence overriding the lower temperature pyrolysis that previously occurred in the actual biochar production process. This observation further supports the notion that HTT is the fundamental process parameter in slow pyrolysis. Slow pyrolysis can therefore be understood as a series of devolatilization reactions that progressively leave behind an increasingly condensed carbonaceous matrix.

Elemental analysis

The elemental composition of the produced biochars shift from that of the feedstock biomass to high-carbon, low-hydrogen compounds as a function of pyrolysis process intensity (HTT, residence time). These results are summarized in Fig. 4, where the H/C ratio is plotted against the HTT of production. Although large differences in elemental composition were observed between the biochars produced from the different feedstocks at lower HTTs, there was a convergence of the H/C ratio to 0.18 for all biomass types at a HTT of 750 °C.

The H/C ratios measured in this research, as demonstrated in Fig. 5, are similar to the values published by Brown *et al.* (2005), Keiluweit *et al.* (2010), Schimmelpfennig & Glaser (2012) and Sun *et al.* (2012). The H/C ratio can be considered a basic proxy for the average number of H–C bonds per carbon atom, which can be used to make an estimate for the average size of the polyaromatic graphene clusters in the biochars – which is likely to be an indicative measure of the overall biochar stability in the soil. For instance, for a biochar with an H/C ratio of 0.37, in its simplest construction, could be composed of carbon graphene clusters having an average of 22 aryl rings per cluster. In reality, the cluster formation and aryl ring consistency is unlikely to be well defined – with an extensive inhomogeneous network more probable – but such estimations may be useful in developing a better understanding of the molecular structure of biochar. The linear correlation between H/C ratio and fixed carbon content indicates that fixed carbon has a very low H content and also that volatile matter released during pyrolysis is composed of compounds with higher H/C ratios than the remaining biochar (fixed carbon). Hence the devolatilization removes most of the H from the biomass as the pyrolysis conversion reaction takes place.

Higher heating value

The calorific data are plotted in Fig. 6. The higher heating values (HHV) of the produced biochars increased with increasing pyrolysis residence time and HTT for all feedstocks except algae. This anomalous observation is explained by the fact that energy densification from pyrolysis only occurs in the organic fraction of the feedstock. For algae, the reduction of the HHV in pyrolysis is caused by the high ash content of the algae, which was 38.2 *wt%* (dry basis), whereas the ash contents of wood, straw and green waste were 0.2, 7.9 and 3.5 *wt%* respectively. Similarly, the differences in HHV of the

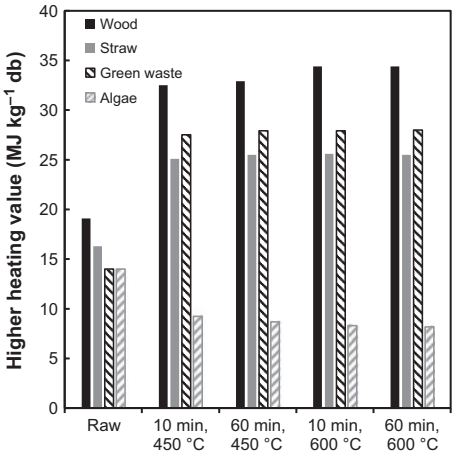

Fig. 6 The biochar higher heating value (MJ kg^{-1} – expressed on dry, i.e. ash-containing, biomass feedstock basis) of the different feedstocks tested, with varying intensity of the slow pyrolysis process (residence time, HTT).

biochars formed from other feedstocks are also attributable to relative ash contents. As pyrolysis occurs, the char slowly trends towards pure carbon (graphitic structure) which carries a HHV of 32.8 kJ kg^{-1} (Soares *et al*., 1997). Ash contained within char will therefore 'dilute' the energy content, meaning the limited value of the HHV for completely carbonized materials will be lower than that of pure C (as seen in the HHVs of biochars from straw and green waste). However, the HHV of the biochars derived from wood is higher than the HHV of pure carbon (up to almost 35 MJ kg^{-1}). This is due to the presence of C–H, C–O, and perhaps O –H bonds remaining in the carbonaceous mass. Considering biochars with carbon contents from 90% to 100%, one expects the HHV to peak and slowly decline as the heterogeneous bonding is sequentially eliminated, and the carbon molecular structures become increasingly energetically stabilized by aromatic resonances and π-π stacking of graphitic sheets.

Biochar pH in solution

The solution pH of biochar in suspension (Fig. 7) increases with intensification of the thermochemical treatment (i.e. longer pyrolysis processes with higher HTT produce more alkaline biochars). Differences in pH can be observed for the biomass types: biochar produced from wood has an average pH in solution that is in general 2 pH units lower than the values for the three other feedstocks produced at similar pyrolysis conditions. The pH of the biochar, next to its ash content, is likely to be correlated with the presence of oxygen functionalities in the biochar: during thermochemical conversion with lower process intensity, more

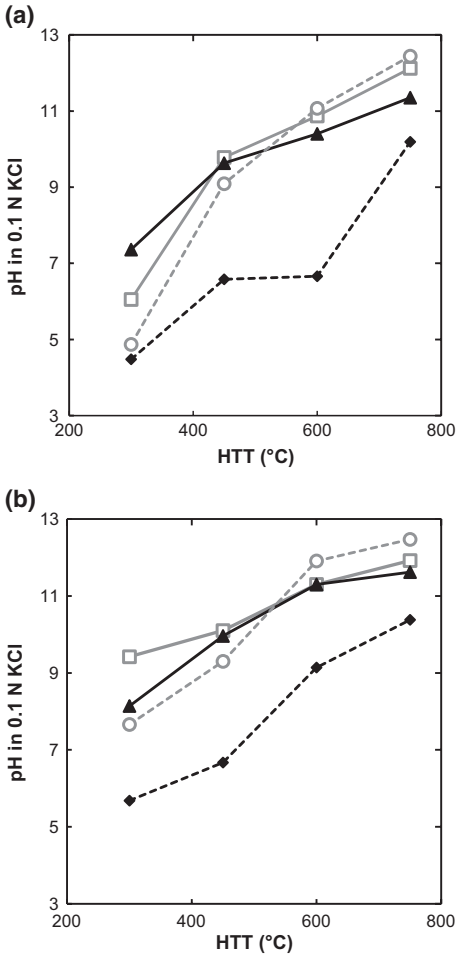

Fig. 7 The pH of biochar in solution vs. HTT and using a residence time of 10′ (a) and 60′ (b) of the different biomass feedstocks tested: wood (♦), straw (□), green waste (▲) and algae (○).

labile – and more oxygenated – carbon is retained. Consequently, at higher pyrolysis severity, the amount of carboxyl groups in the resulting biochar has been reduced and/or the acidic groups have become deprotonated to the conjugate bases resulting in more alkaline pH of the biochar in suspension. Another contributing factor to the rise in pH at more severe pyrolysis conditions is the relative increase of ash content in the biochar.

Specific surface area

The results of the BET surface analysis are given in Table 2. Two series of analyses were performed: one that included most of the pine wood-derived biochars (to evaluate the effect of HTT and residence time) and one where different feedstocks were compared at two given HTT/residence time combinations. The highest

Table 2 The BET surface area of (a) woody biochar produced at varying highest treatment temperatures (HTTs) and residence times and (b) of different feedstock materials pyrolysed with a HTT of 450 and 600 °C and a residence time of 60 min.

(a) Wood biochar

	Highest treatment temperature (°C)			
Residence time (min)	300	450	600	750
10	–	4	196	128
60	6	23	127	–

(b) Residence time = 60 min

	Biomass input material			
HTT (°C)	Wood	Straw	Green waste	Algae
450	23	16	17	14
600	127	22	46	19

–, No data recorded.

BET specific surface (196 $m^2\ g^{-1}$) was observed for biochar produced from wood at an HTT of 600 °C and a shorter residence time of 10 min. At lower pyrolysis temperatures (300 and 450 °C), the biochar surface area was generally low, but gradually increased in biochars produced with longer residence times. Pyrolysis at 600 °C produced the most accessible surface in the chars for all feedstock biomasses tested, but an inverse relationship between specific surface and residence time was also observed. When the pyrolysis temperature was increased further, the BET surface area reduced again, which is likely due to restructuring taking place in the biochar or due to the onset of ash melting at higher temperatures.

When comparing the different biomass feedstocks in Table 2b, woody biochar offers the highest potential of surface area as all other biochar types had a BET specific surface below 50 $m^2\ g^{-1}$. Also, wood had the lowest ash content of all feedstocks used (0.2, 7.9, 3.5, and 38.4 *wt%* for wood, straw, green waste and algae, respectively). From these observations, higher amount of inorganics (i.e. ash content) in the biomass feedstock negatively correlate with specific surface area in the produced biochar. This is possibly explained by fusion of molten ash filling up pores in the biochar, thereby decreasing accessible surface area.

Biological degradation

Figure 8 shows the results of the cumulative BOD for biochars produced from wood under different pyrolysis intensities (residence time, HTT). These data show that the rate of oxygen demand during the 2-week incubation period decreased exponentially, with a logarithmic relationship existing between incubation time and cumulative BOD. In case of wood, the R^2 in the logarithmic regression analysis varied between 0.899 and 0.956. Similar logarithmic trends were seen with biochars produced from feedstocks other than wood.

Total cumulated BOD was found to be directly proportional to the volatile content of biochar with a correlation of $R^2 = 0.728$ (Fig. 9). Higher carbon mineralization rates in soils amended with biochars

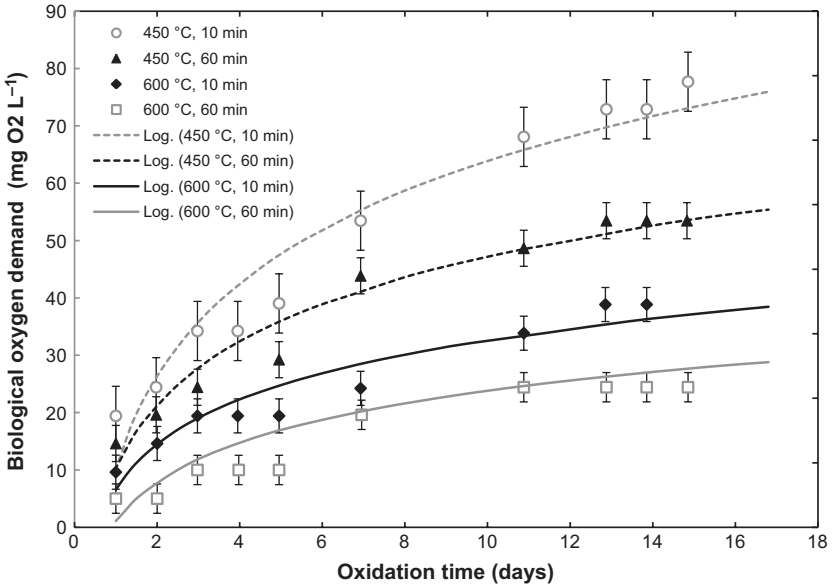

Fig. 8 Cumulative biological oxygen demand (BOD), measured over a 14-day period with regular sampling and for wood-based biochar, treated at different HTTs and different residence times.

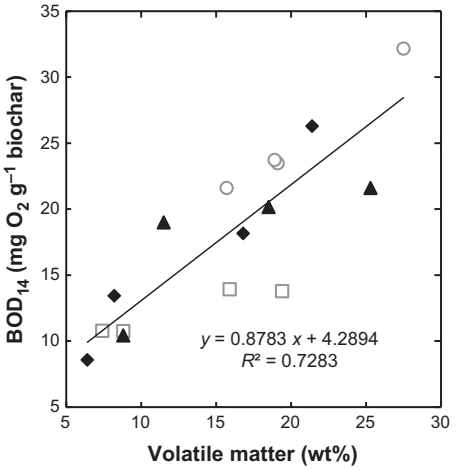

Fig. 9 Cumulative biological oxygen demand (BOD), measured over a 14-day period plotted against volatile matter content, for wood (♦), straw (□), green waste (▲) and algae (○) and under varying HTTs and residence times.

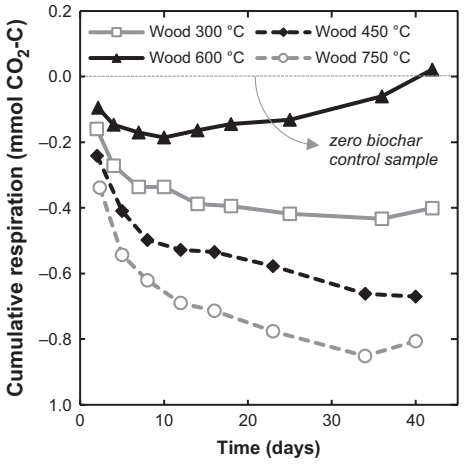

Fig. 10 Cumulative respiration, relative to the untreated control soil sample and expressed as mol CO_2-C produced per day, recorded during a 42-day incubation period in a biochar-treated soil sample. Biochar samples were all produced with a residence time of 60 min.

produced from low-temperature pyrolysis processes have also been previously observed by Zimmerman (2010) and Cross & Sohi (2011). The high-volatile matter content of these chars was identified as the main cause of the higher carbon mineralization.

Given the results in Table 1, assuming exponential decay of the volatile matter in the biochar and by taken into account the pool of volatile matter in the biochar, then extrapolation indicates that all 'volatile carbon' should be consumed after 7 months (algae, HTT = 600 °C and t_r = 60 min) to 2.3 years (wood, HTT = 750 °C and t_r = 60 min). However, these crude estimates are based on the assumption that the volatile matter and stable carbon fraction as determined by the proximate analysis method correspond respectively to the labile and recalcitrant carbon fractions in the soil, which not necessarily holds true.

In the second biological degradation test, biochar was mixed with an actual soil sample and the CO_2 production was measured during a 42-day incubation period. The tests were only limited to the woody biochar samples produced using a residence time of 60 min. In Fig. 10, the cumulative respiration, relative to the untreated control soil sample (i.e. cumulative respiration biochar-amended sample minus cumulative respiration control soil), for the different-tested woody biochars is plotted for a 42-day incubation period. It is important to stress that in this test, no distinction can be made between the mineralization of preexisting C already present in the soil sample and the C from biochar itself. The results show that the initial carbon mineralization rates are suppressed by the addition of biochar, which is clearly seen by the negative slopes of the relative carbon respiration curves in Fig. 10. After their initial reduced values, respiration rates were seen to restore to a level above that of the control (untreated) soil sample – as can be seen by the positive slope of the relative respiration curve near the end of the 42-day measurement period of most of the biochar-amended soil samples. Also, the depression of initial carbon mineralization is proportional to the intensity of thermal treatment during pyrolysis – although the sample produced at 600 °C does not follow trend. Chars produced at higher HTT tend to have lower, more suppressed, initial carbon mineralization rates. The initial depression of the respiration rate could be attributed to the time needed for the soil microculture to adapt to the new conditions. The changes brought upon the soil sample by the addition of biochar occur on different levels: for instance, the pH and soil texture will be altered; biochar could have the ability to adsorb certain compounds – i.e. nutrients or phytotoxic compounds (Beesley *et al.*, 2010; Borchard *et al.*, 2012) – or release additional nutrients; there may be a mild toxicity associated with 'fresh' biochar; perhaps the added biochars alters the soil structure and/or water-holding capacity in a way that disrupts the soil biota. Regarding the effect of biochar addition to the initial CO_2 respiration in soils, some researchers have found an opposite effect, i.e. an increase in evolved CO_2 in biochar-amended soil samples – an effect also know as positive 'priming effect' (Novak *et al.*, 2010; Jones *et al.*, 2011; Zimmerman *et al.*, 2011). However, this positive priming effect has not always been observed to significant extent (Cross & Sohi, 2011; Case *et al.*, 2012) or a negative priming effect, a reduction in initial CO_2 soil respiration in

biochar-amended soil samples could be observed (Zimmerman *et al.*, 2011). Clearly, the outcome of changes in CO_2 respiration in biochar supplemented soil samples depends on a large number of variables, including biochar type (feedstock, pyrolysis conditions), soil type, biochar loading in the soil (i.e. *wt%* biochar in soil) and physical conditions during the soil incubation tests (temperature, air humidity, soil moisture content, etc.). Consequently, it is difficult to interpret and compare the C mineralization observations in this study. Longer soil incubation tests, with different biochar loadings, are needed to clarify the overall effects biochar has on overall mineralization in the soil.

Discussion

The fixed-bed pyrolysis experiments in this study tested a range of biomass feedstocks and variable process parameters. Analysis of the produced biochars provided significant data and increased the overall understanding of slow pyrolysis. Raw biochar yield was seen to decrease with both the intensity of the pyrolysis process (i.e. residence time and highest treatment temperature) and by the ash content of the feedstock biomass. The volatile matter content of the produced biochars also declined with pyrolysis severity, whereas ash and fixed carbon contents increased. If, however, the fixed carbon content of the different biochars is corrected for ash content (i.e. reported on daf basis), it was found that whereas the fixed carbon content of the biochars strongly depended on the intensity of the thermal treatment, the actual overall yield in fixed carbon was practically insensitive to the treatment temperature and residence time. This observation could result in the faulty conclusion that the thermochemical conversion that occurs in the organic fraction of biomasses during slow pyrolysis is largely invariant across the tested range of HTTs and residence times. However, the observed constant fixed carbon yields were merely the result of the method employed for measuring 'fixed carbon', as this method itself is a pyrolysis process (up to 950 °C) and in effect, supersedes any previous slow pyrolysis production. This conclusion is further supported by the consistent linear relationship between fixed carbon and H/C atomic ratio found across the produced biochars.

The HHV of the produced chars was largely consistent for any given feedstock material beyond a moderate pyrolysis treatment. The HHV of the biochars trended towards a consistent limit for each feedstock with increasing pyrolysis intensity. The actual HHVs of the produced biochars were largely determined by the amount of 'dilution' of the combustible fraction by ash content. Thus, the energy densification in pyrolysis is confined to the C fraction and was consistent across the tested feedstocks.

The pH in dispersion of the produced biochars was governed by feedstock type, ash content and pyrolysis intensity, with more increased pyrolysis temperature and duration generally increasing the solution pH. Specific BET surface areas of the biochars produced in this study were generally low, with the exception of those produced from wood and high HTT which had comparatively moderate specific surfaces. Higher HTT increased the BET specific surface across all feedstocks, whereas longer residence times reduced the BET specific surfaces in biochars produced at high temperatures, possibly due to ash fusion filling micropores.

In the biological degradation experiments, the volatile matter content of biochar correlated positively with initial BOD. Whereas in the soil incubation carbon mineralization tests, the addition of biochar to the soil initially reduced the C-mineralization rate. Hence indicating that the soil microculture needs to adapt to the new conditions. This effect was more pronounced when adding chars with high fixed carbon content, as chars with low C-content had a larger amount of volatile, presumably, more easily biodegradable, C-compounds. The extent to which labile and stable C-fraction is present is greatly determined by the intensity of the pyrolysis process, both in terms of residence time and highest treatment temperature (HTT).

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