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Suitability of Different Agricultural and Urban Organic Wastes as Feedstocks for the Production of Biochar—Part 1: Physicochemical Characterisation

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Abstract: Biochar is traditionally made from clean lignocellulosic or waste materials that create no competition for land use. In this paper, the suitability of alternative feedstocks of agricultural and urban origins are explored. A range of biochars was produced from holm oak and a selection of organic wastes, such as greenhouse wastes, greenwastes, a cellulosic urban waste, municipal press cake and pig manure. They were characterized and assessed for their potential agricultural use. The physicochemical properties of biochars were mainly driven by the characteristics of feedstocks and the pyrolysis temperature. The use of pre-treated lignocellulosic residues led to biochars with a high concentration of ash, macro and micronutrients, whereas raw lignocellulosic residues produced biochars with characteristics similar to traditional wood biochars. All biochars were found to be suitable for agricultural use according to the international standards for the use of biochars as soil amendments, with the exception of a biochar from urban origin, which presented high levels of Cr and Pb. The use of these biochars as soil amendments requires a thorough agronomical evaluation to assess their impact on soil biogeochemical cycles and plant growth.

Keywords: charcoal; agriculture; proximate analysis; ultimate analysis; heavy metals

1. Introduction

The recent EU action plan for circular economy sets clear targets for the reduction of waste and establishes an ambitious, but reliable, long-term strategy for waste management and recycling [1]. The main environmental hazards associated with poor organic waste management are soil and water pollution and the release of greenhouse gases to the atmosphere, contributing to global warming. Besides, the disposal of organic wastes implies significant losses of natural resources such as organic matter, nutrients and energy [2].

Appropriate management of organic waste can help mitigate climate change by decreasing gas emission from landfills and also indirectly reducing other transport and energy efforts from poor waste management [3]. The new circular economy business model adopted by the EU [1] enforces its members to reduce the amount of biodegradable waste disposed of in landfills, including agricultural residues, and household, commercial and industrial waste. The revised legislative proposal on waste aims at reducing the environmental impact from landfilling of wastes and to ensure their valorisation,

reuse, or recycling [4]. Composting is the most common recycling option for organic waste in the EU, despite the fact that only one-third of the potentially available feedstocks are used for compost production [5]. Thus, composting and other biological treatments have an important role to play in helping the EU to move towards closing the loop of a product's lifecycle. More recently, the pyrolysis of organic waste for biochar and bioenergy co-production has gained considerable interest worldwide as an alternative recycling option.

According to the International Biochar Initiative (IBI), biochar is defined as a solid material obtained from thermochemical conversion of biomass in an oxygen-limited environment [6]. Thus, this solid product has about a third of the mass of the original biomass and contains half the original carbon (C), which is enriched in aromatic C and highly resistant to decomposition. Biochar is intended for use as an agent for soil improvement and also for a broad range of beneficial environmental functions and services, including improved resource use efficiency, soil remediation and greenhouse gas mitigation [7]. The use of biochar as a soil amendment is often considered as a mechanism to sequester organic carbon (C_{org}), which remains in the soil for centuries or millennia, depending on the degree of aromaticity and the chemical complexity (O/C_{org} ratio) of the biochar [8]. The benefits of a given biochar material vary widely on the origin of the feedstocks as well as pyrolysis conditions, which determine their physicochemical properties. The use as soil amendment also requires that biochars do not contain harmful levels of heavy metals or persistent organic contaminants [6]. Different international initiatives, such as the IBI certification [6], the Biochar Quality Mandate [9] by the British Biochar Foundation and the European Biochar Certificate (EBC) [10], among others, have recently published guidelines to identify the main qualities and characteristics of biochar and set up quality standards for its use in agriculture.

Currently, biochars are mostly produced from forestry and clean agricultural waste, and especially from woody materials. The growth of lignocellulosic crops for biochar production is being questioned, since they can compete with food production. However, there is a broad range of organic residues that could potentially be transformed to biochar, not representing a competition with food production systems. For example, the lignocellulosic residues generated after the harvesting of horticultural crops, and also clean wastes from household, commercial and industrial processes [7,11], could present favorable properties as potential feedstock for pyrolysis.

Recently, a large number of studies have been published in the scientific literature evaluating the impact of raw lignocellulosic and other feedstocks on the characteristics of biochars [12–15]. However, there is limited information on the use of alternative lignocellulosic residues of agricultural or urban origin, which could replace the traditional use of wood to produce biochar. These alternative feedstocks may have undergone biological or physicochemical pre-treatments, which may alter their lignocellulosic composition and ash content, affecting the properties of the obtained biochars.

The aim of this work is to explore the suitability of alternative residues from agricultural and urban origin as feedstock for the production of biochar. To achieve this aim, a physicochemical and agronomical characterisation was performed on a series of biochars obtained by pyrolysis from a wide range of organic wastes of different origins (with different lignocellulosic composition and ash content) and at different pyrolysis conditions (slow pyrolysis at 400 °C and 600 °C).

2. Materials and Methods

2.1. Feedstock Description

A range of organic wastes from agricultural and urban sources was chosen to provide a wide variety of feedstock for the pyrolysis process. The selection was based mainly on their origin, as well as the different concentrations of organic matter and their lignocellulosic composition:

Holm Oak (Oak) pruning is a forestry waste used as a model of typical lignocellulosic biomass that is free of any potentially hazardous elements (like heavy metals or other toxic compounds). It was supplied by Proininiso Inc. (Malaga, Spain).

Greenhouse Waste (GH) is an agricultural waste constituted of a mixture of horticultural crop residues (stalks and leaves), mainly from pepper (*Capsicum annum*) and aubergine (*Solanum melongena*), grown in a greenhouse in TECNOVA (Almería, Spain). This waste is a heterogeneous lignocellulosic biomass that also contains up to 2% plastic tags.

Greenwaste (GW) is an organic waste of municipal origin comprised of a mixture of grass, leaves, branches, small stems, tree pruning, etc. separately supplied from gardens in urban areas; it is usually shredded and chipped. It is a highly heterogeneous residue collected by Stichting Energieonderzoek Centrum Nederland (ECN) (Petten, The Netherlands) from urban parks in The Netherlands.

CellMatt (CM) is an organic waste of urban origin produced by Graphite Resources Limited (Newcastle, UK) from household, commercial and industrial wastes through steam autoclaving technology that sterilises wastes (>160 °C and 6 bar) to achieve the complete removal of pathogens. During the process, the biological fraction of the waste is broken down into a cellulose-rich biomass.

Pig Manure (PM) is an agricultural waste generated in swine-growing facilities, mainly containing the faeces and urine of the animals. It can include plant material, such as straw, typically used as bedding material. This waste was collected from farms in The Netherlands and used by ECN to produce biochar. The feedstock was not available for analysis. Physicochemical characterisation was obtained from the scientific literature [16–18].

Municipal Press Cake (PC) is an organic waste of urban origin obtained from anaerobic digestion of source-separated municipal waste. Municipal pressed cake contains largely fibrous and woody material. It was supplied by Organic Waste Systems (OWS) (Gent, Belgium).

2.2. Biochar Production

Feedstocks were converted into biochar through slow pyrolysis in a Pyromaat Auger pyrolysis reactor, as described by Fryda and Visser [19]. Pyromaat is an indirectly heated screw conveyer reactor, in which the biomass is moved along the reactor length at a fixed speed using a screw thread feeder. At the end of the reactor, the biochar is collected, while the gas and the dust are directed to an afterburner cleaning system [19]. The slow pyrolysis biochars were produced at a highest treatment temperature (HTT) of 400 °C and 600 °C and residence time of 60 min.

In addition, two commercial biochars from holm oak produced at HTT of 450 °C and 650 °C (OC450 and OC650) were obtained from Proiniso Inc. (Malaga, Spain), where biochar is produced by continuous large-scale slow pyrolysers (at residence time of about 15 h), using a mono retort reactor.

2.3. Analytical Methods

A series of analyses were conducted to evaluate the physicochemical properties of feedstocks and biochars. In the case of biochars, the analytical methodologies recommended by IBI were followed [6], whereas in the case of feedstock conventional analytical methodologies were used, as described below.

Both, feedstocks and biochars, were air-dried, ground and sieved (<1 mm) before analysis. Moisture content was obtained by drying at 105 °C for 24 h. The organic matter content in feedstocks was determined by loss on ignition at 550 °C according to UNE-CEN/TS 14775:2010. In the case of biochars, the ash and volatile content were determined at 750 °C and 950 °C, respectively, according to ASTM D1762-84, and expressed as percentage of the total weight. Fixed carbon was calculated by subtraction, as follows:

$$\text{Fixed C (\%)} = 100 - \text{ash (\%)} - \text{volatile content (\%)}, \quad (1)$$

To conduct ultimate analyses, the samples were ball milled to achieve a homogenised sample. Total nitrogen (N), total carbon (C), total organic carbon (C_{org}), total hydrogen (H) and total sulphur (S) were analysed by automatic elemental analysis (LECO CHNS-932, LECO Corporation, Saint Joseph, MI, USA) and expressed as a percentage of total dry weight. Total oxygen (O) was determined by difference, according to Enders et al. [20], as follows:

$$O (\%) = 100 - \text{ash} (\%) - C (\%) - N (\%) - H (\%), \quad (2)$$

Feedstocks were subjected to biochemical analyses to assess the concentration of lignin, cellulose and hemicellulose. Lignin was determined by Klason's method, described in ASTM D1106-96; cellulose was analysed by ASTM D1103-60 and hemicellulose concentration by subtracting the cellulose concentration from the delignified sample (hollocellulose) obtained by Browning's method [21].

The thermal analysis of the feedstock was performed by using an SDT-2960 simultaneous DSC-TGA thermal analyser (TA instruments, New Castle, DE, USA) under static-nitrogen atmosphere with the following temperature ramp: (1) temperature equilibration at 30 °C, followed by linear heating (at a rate of 5 °C min⁻¹) from 30 to 105 °C; (2) isotherm for 10 min; (3) and ramping of 5 °C min⁻¹ from 105 to 1000 °C.

Macro-, micro-nutrients and heavy metal concentrations of feedstocks and biochars were measured after microwave HNO₃/H₂O₂ digestion by Inductively Coupled Plasma spectroscopy (ICP-OES) (ICAP 6500 DUO THERMO, Cheshire, UK).

The physical characterisation of the biochars was carried out by evaluating the physical adsorption of N₂ at -196 °C using a NOVA 2200e surface area and pore size analyser (Quantachrome Instruments, Boynton Beach, FL, USA). The cation exchange capacity (CEC) of the biochars was measured by a modified NH₄⁺-acetate compulsory displacement method [22,23]. Water holding capacity (WHC) of biochars was determined via mass difference after saturating the biochar with distilled water, which was kept at atmospheric pressure, allowing the water to completely drain [24]. The electrical conductivity (EC) and pH values of feedstock samples were determined in a 1:10 (*w/v*) aqueous extract; however, in the case of biochars, they were determined in a 1:20 (*w/v*) aqueous extract according to IBI [6].

The content of water extractable organic C (TEOC) and N (TEN) was determined on biochar: distilled water mixture (1:10 *w/v*) shaken for 2 h at 120 strokes per minute and room temperature. The mixture was then centrifuged at 70,000 × *g* for 15 min and filtered (Whatman GF/F < 0.7 μm). Clear extracts were analyzed for their C and N content by means of a TOC-TN analyser (Shimadzu TOC-VCSN, Shimadzu Corporation, Kyoto, Japan).

Polycyclic Aromatic Hydrocarbons (PAHs) were measured following the method EPA TO-13A. Samples were extracted in toluene by either Soxhlet extraction or accelerated solvent extraction (Dionex ASE 350, Thermo Scientific, Sunnyvale, CA, USA), depending upon the sample and volume reduction. Samples were analysed using GC-MS in SIM mode using a Perkin Elmer Clarus GC-MS in SIM mode and full scan mode.

2.4. Calculations and Statistical Analyses

The results of the chemical analyses are expressed on an oven-dry basis (105 °C, 24 h) and presented as the mean value and standard deviation of the replicates (at least duplicate analyses). Statistical analyses of data were performed using the IBM SPSS Statistics 22 (IBM Corporation, Armonk, NY, USA). The relationships between studied parameters were addressed through a correlation analysis (Pearson correlation coefficient) and significance defined as *p* < 0.05.

3. Results and Discussion

3.1. Physicochemical Characterisation of Feedstocks

The suitability of the organic wastes as feedstocks for the production of biochar was evaluated considering their physicochemical and chemical properties (Tables 1–3), their lignocellulosic composition (Figure 1) and thermal behavior (Figure 2). Their thermal analysis gives an indication of pyrolysis behavior and can also fingerprint differences between the feedstock.

The six organic wastes from agricultural and municipal sources were selected to provide a wide variety of feedstock for the pyrolysis process. The selection included residues that had been subjected to

physico-chemical or biological treatments (pre-treated) and others which did not (raw). Pre-treatment had an impact on the lignocellulosic composition of residues and their ash concentration.

Holm oak prunings (Oak) were mostly composed of lignin, cellulose and hemicellulose, which made up about 96% of its organic matter (Figure 1). This rich lignocellulosic composition reflects the origin of this waste, a clean hard wood material, and can be considered as “raw lignocellulosic” feedstock. This residue had the highest volatile content and C_{org} concentration of all the wastes studied. It was also characterized by a high C/N ratio, low ash concentration and low EC (Table 1). The pyrolytic behavior of the waste is shown in Figure 2. The thermal analysis showed the classic thermal degradation of oak wood, characterized by a high pyrolytic decomposition assigned to celluloses and hemicelluloses below 400 °C, the thermoxidation of lignin, which takes place in the temperature range between 400 and 500 °C and a final step with an almost complete degradation, leaving a residue that is less than 0.07% of the initial weight [25].

Greenhouse waste (GH) is a heterogeneous vegetable waste with a lignocellulosic composition of over 85% of organic matter, similar to oak. However, GH has larger cellulose content (53%) and lower lignin (24%) and hemicellulose (7%) content than Oak, due to the lower amount of wood in these agricultural wastes. The rich lignocellulosic composition provides a high C_{org} , and therefore a large volatile content, similarly to Oak, and for this reason GH could also be considered as a “raw lignocellulose” waste. However, due to its horticultural origin, it contains a higher concentration of total N and K, with respect to O, and soluble elements that give rise to the highest EC of all the wastes studied (9.8 mS cm⁻¹). Thermal analysis revealed a similar degradation pattern to Oak as a consequence of a similar lignocellulosic composition, with an additional degradation step after 400 °C due to the plastic tags and a final residue that represents 14.73% of the original dry weight.

Table 1. Chemical properties of the organic waste used as feedstock for the pyrolysis process. GH: greenhouse waste, GW: green waste, CM: CellMatt, PM: pig manure and PC: municipal press cake.

Feedstock	pH ¹	EC ¹	Volatile Content	Ash	C	C_{org}	H	S	O
		(mS cm ⁻¹)							
Oak	5.7 (0.1)	0.7 (0.0)	79.6 (0.2)	2.9 (0.3)	48.7 (0.2)	46.4 (0.7)	8.1 0.0	0.00 (0.00)	39.8 (0.2)
GH	5.4 (0.0)	9.8 (1.1)	72.1 (0.1)	14.2 (0.5)	41.1 (0.0)	41.0 (0.2)	7.5 0.1	0.87 (0.07)	34.9 (0.0)
GW	n.a. n.a.	n.a. n.a.	n.a. n.a.	23.0 (0.5)	38.7 (0.2)	36.2 (0.9)	4.8 (0.1)	0.06 (0.04)	37.3 (0.0)
CM	7.1 (0.0)	4.3 (0.2)	63.8 (0.8)	25.1 (0.6)	40.9 (0.0)	39.0 (1.7)	7.5 0.1	0.87 (0.07)	24.2 (0.0)
PM	7.3 ² n.a.	6.9 ² n.a.	60.2 ³ (0.9)	18.3 ³ (2.0)	33.5 ⁴ n.a.	n.a. n.a.	6.2 ⁴ n.a.	n.a. n.a.	57.5 ⁴ n.a.
PC	8.0 (0.2)	1.8 (0.3)	29.1 (0.7)	63.8 (0.4)	20.8 (0.0)	20.4 (0.6)	2.2 (0.1)	0.26 (0.02)	11.7 (0.0)

¹ Water extract 1:10 w/v 25 °C; EC: Electrical Conductivity; ² data obtained from Santos et al. [17]; ³ data obtained from Huang et al. [16]; ⁴ data obtained from Xiu et al. [26]; n.a.: not available; standard deviation in italics within brackets (n = 2).

Green waste (GW) is also a lignocellulosic feedstock, which can be considered as rich lignocellulosic material as Oak and GH. Its composition depends on the proportion of branches, grass and leaves in the mixture, which defines the relative proportions of lignin, cellulose and hemicellulose. The presence of branches and grass increases the proportion of lignin and cellulose, whereas the presence of leaves and grass increases the proportions of cellulose and hemicellulose [27]. In addition, this residue may have higher amounts of ash than Oak and GH feedstocks, which implies high concentrations of mineral constituents, including potentially toxic heavy metals such as Cr, Ni, Pb and Zn (Table 3) as a consequence of the urban origin of this waste and the presence of treated wood. Despite the theoretical rich lignocellulosic composition of green waste, this waste presents differences from raw lignocellulosic feedstocks due to the presence of inert components. The urban origin of green

waste may be responsible for the high ash concentration of these wastes, originating from their mixing with other municipal residuals during collection.

CellMatt (CM) is an organic waste that has undergone pre-treatment, consisting of an autoclaving process that caused the partial degradation of the organic matter. CM is characterised by a lignocellulosic composition of over 74% of organic matter, so it could be defined as “pre-treated organic” feedstock. Its main difference from “raw lignocellulosic” residues is the absence of the hemicellulose fraction, which was decomposed during the pre-treatment process. However, the C_{org} concentration (40.9%) was not affected by autoclaving and was similar to GH and GW (Table 1). Another important characteristic of CM is the high mineral composition reflected by the ash content (25%). The heavy metal concentration of CM (Table 3) is the highest of all the wastes studied and could represent a limitation for its use as a soil amendment. The thermal analysis showed the characteristic degradation pattern of lignocellulosic feedstock (Figure 1) and a high amount of final residue (25.08% of the total weight).

Table 2. Concentration of nutrients in feedstocks (dry-weight basis). GH: greenhouse waste, GW: green waste, CM: CellMatt, PM: pig manure and PC: municipal press cake.

Feedstock	N	P	K	Ca	Mg	Na	Fe	Cu	Mn	Zn	Mo	B
	(g 100 g ⁻¹)						(mg kg ⁻¹)					
Oak	0.53 (0.01)	0.06 (0.00)	0.20 (0.00)	0.91 (0.05)	0.06 (0.00)	0.01 (0.00)	136 (5)	7.3 (0.9)	220 (5)	19 (1)	<0.5 (0.0)	8.5 (0.1)
GH	1.44 (0.01)	0.18 (0.01)	3.31 (0.12)	0.88 (0.02)	0.37 (0.02)	0.03 (0.00)	113 (6)	16.9 (0.2)	55 (3)	32 (1)	<0.5 (0.0)	16.6 (0.8)
GW	1.41 (0.13)	0.10 <i>n.a.</i>	0.74 <i>n.a.</i>	0.72 <i>n.a.</i>	0.13 <i>n.a.</i>	0.03 <i>n.a.</i>	2215 <i>n.a.</i>	18.6 <i>n.a.</i>	145 <i>n.a.</i>	68 <i>n.a.</i>	3.0 <i>n.a.</i>	16.62 <i>n.a.</i>
CM	1.43 (0.01)	0.22 (0.01)	0.45 (0.05)	3.35 (0.04)	0.18 (0.01)	0.64 (0.03)	7415 (1457)	146.4 (8.1)	174 (15)	835 (81)	<0.5 (0.0)	38.6 (15.3)
PM ¹	2.81 1	4.22	1.06	5.08	1.30	0.29	2055	156.2	351	623	3.7	747.0
PC	<i>n.a.</i> 1.20 (0.00)	<i>n.a.</i> 0.36 (0.02)	<i>n.a.</i> 0.74 (0.02)	<i>n.a.</i> 2.60 (0.30)	<i>n.a.</i> 0.29 (0.02)	<i>n.a.</i> 0.18 (0.01)	<i>n.a.</i> 8534 (399)	<i>n.a.</i> 46.6 (1.2)	<i>n.a.</i> 206 (8)	<i>n.a.</i> 202 (11)	<i>n.a.</i> 2.1 (0.1)	<i>n.a.</i> 22.0 (0.3)

¹ These data were obtained from Xiu et al. [26]; *n.a.*: not available; standard deviation in italics within brackets (n = 2).

Table 3. Heavy metal concentration in feedstocks. GH: greenhouse waste, GW: green waste, CM: CellMatt, PM: pig manure and PC: municipal press cake.

Feedstock	Cd	Cr	Ni	Pb
	(mg kg ⁻¹)			
Oak	<0.1 (0.0)	5.0 (0.1)	2.4 (0.6)	0.9 (0.2)
GH	0.4 (0.0)	2.8 (0.3)	2.5 (0.1)	0.9 (0.1)
GW	0.3 (0.0)	137.7 (2.3)	56.5 (3.5)	16.8 (1.2)
CM	0.9 (0.2)	163.7 (3.3)	99.1 (0.6)	119.5 (1.9)
PM ¹	<i>n.a.</i>	2.2	<i>n.a.</i>	18.8
PC	1.1 (0.0)	67.1 (8.0)	30.5 (3.8)	98.3 (16.6)

¹ These data were obtained from Xiu et al. [26]; *n.a.*: not available; standard deviation in italics within brackets (n = 2).

Pig manure (PM) cannot be considered raw lignocellulosic residue, since the lignocellulosic fraction only constituted 44% of the organic matter [16]. Thus, C_{org} concentrations are typically lower than in raw lignocellulosic residues (Table 1). The main characteristic of PM is the high N concentration (2.8%) [26] and consequently a low C/N ratio that has a marked impact on the characteristics of biochars. In general, PM is characterized by 18.3% of ash matter [16], with high EC and neutral

pH values [17]. Therefore, PM has high nutrient concentrations, especially P, Ca, Mg, Fe, Cu, Mn, Zn and B [26].

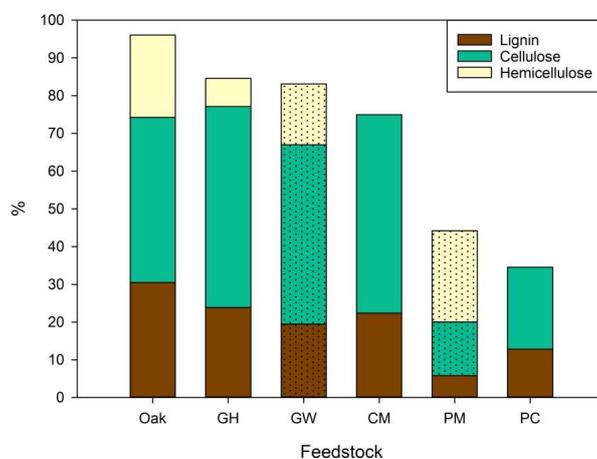


Figure 1. Lignocellulosic fractions of feedstocks: Oak: Holm Oak pruning, GH: Greenhouse waste; CM: CellMatt; PM: pig manure; PC: municipal press cake. The dotted data of GW and PM was obtained as average of studies by Donovan et al. [27] and Xiu et al. [18].

Municipal press cake (PC) is another organic waste that has undergone a pre-treatment process (anaerobic digestion), and could thus be defined as “pre-treated organic” feedstock. The lignocellulosic composition of PC constituted 33% of organic matter, with only 22% cellulose and 13% lignin. This material contained very low levels of hemicellulose, due to the partial degradation of the organic matter during anaerobic digestion. Pre-treatment also resulted in low C_{org} concentration and a high ash content (63.8%), which prevent its classification as biochar [6,20]. Therefore, PC has high EC and high concentration of inorganic elements (Ca, Fe, Cu, Mn, Zn, B, Cd, Cr, Ni and Pb), that in the case of Cd, Ni and Zn could limit its agricultural use. The thermal degradation profile reflected the presence of a large proportion of mineral elements with a massive final residue (61.09% of the initial weight).

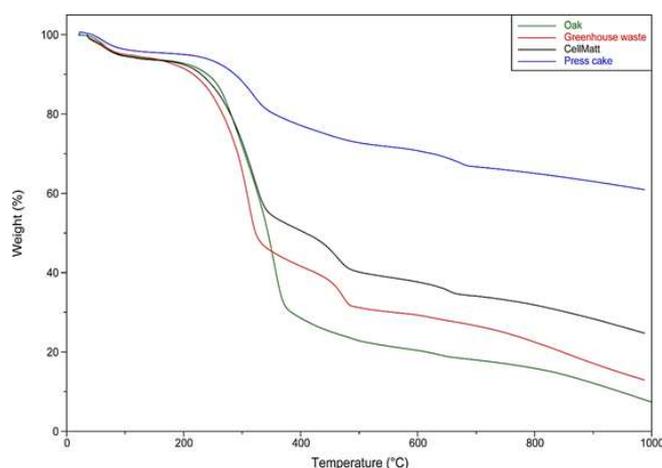


Figure 2. Weight loss profiles for four different biomass types: Oak, greenhouse waste, CellMatt and municipal press cake. The thermal analysis was performed with a DSC-TGA thermal analyser in static-nitrogen atmosphere.

The preparation of biochars from organic wastes was aimed at the recycling of these wastes as soil amendments in agriculture. Consequently, biochar characterizations include a general physicochemical

description, evaluation of their agronomical properties, and assessment of potential limitations associated with the presence of persistent pollutants.

3.1.1. Physicochemical Characterisation

Elemental Composition

The elemental composition of biochars, including C_{org}, H, N, S and O is shown in Table 4. The amount of C_{org} stored in aromatic structures is directly related to its C sequestration potential, a key feature of biochars when used as soil amendment. In this study, biochars were compared based on C_{org} rather than total C, which would also include carbonates from the ash fraction.

The amount of C_{org} is one of the most relevant parameters considered by the IBI quality standards for the classification of biochars [6]. According to these standards, biochars can be classified into three categories: Class 1 for biochars containing $\geq 60\%$ C, class 2 $\geq 30\%$ and $<60\%$ C, and class 3 $\geq 10\%$ and $<30\%$ C. Thus, the biochars obtained in this study can be classified as follows: O and GH (class 1), OC, GW, CM and PM (class 2), and PC (class 3). This classification reflects the importance of the feedstock, rather than HTT, on the concentration of C_{org} in the biochar. Only raw lignocellulosic feedstocks gave rise to class 1 biochars, whereas biochars obtained from pre-treated organic wastes or green wastes from urban origin only fell into class 2 or 3.

Table 4. Chemical properties of the biochars obtained at low (400–450 °C) and high temperature (600–650 °C). OC, commercial oak, O: Oak, GH: greenhouse waste, GW: green waste, CM: CellMatt, PM: pig manure and PC: municipal press cake.

Biochar	C _{org}	H	S	O	H/C _{org}	O/C _{org}	WEOC	WEN	WEOC/WEN
	(g 100 g ⁻¹)				(mg kg ⁻¹)				
OC450	56.6 (0.1)	3.05 (0.08)	0.0 (0.0)	16.2 (0.2)	0.64	0.21	237 (9)	6.4 (0.7)	37
OC650	59.7 (1.6)	1.39 (0.03)	0.0 (0.0)	15.7 (0.6)	0.28	0.20	609 (3)	30.0 (0.1)	20
O400	70.5 (0.6)	4.73 (0.19)	0.0 (0.0)	15.0 (0.2)	0.80	0.16	885 (19)	5.1 (0.2)	173
O600	75.8 (0.3)	2.45 (0.01)	0.0 (0.0)	6.1 (0.1)	0.39	0.06	250 (11)	2.0 (0.3)	124
GH400	61.5 (0.6)	3.27 (0.14)	0.0 (0.0)	14.9 (1.0)	0.63	0.18	4610 (11)	48.7 (0.6)	95
GH600	71.0 (0.6)	1.54 (0.02)	0.1 (0.0)	7.5 (0.1)	0.26	0.08	344 (28)	16.4 (1.0)	21
GW400	36.0 (0.4)	2.75 (0.02)	0.0 (0.0)	0.0 (0.0)	0.91	n.a.	1331 (54)	52.5 (0.7)	25
GW600	42.7 (1.4)	1.25 (0.01)	0.0 (0.0)	0.0 (0.0)	0.35	n.a.	173 (9)	67.9 (0.7)	3
CM400	36.5 (0.5)	4.01 (0.17)	0.4 (0.3)	6.3 (0.3)	1.31	0.13	952 (24)	18.9 (0.2)	50
CM600	34.6 (0.3)	1.26 (0.05)	0.7 (0.1)	0.8 (0.2)	0.43	0.02	130 (14)	14.2 (0.3)	9
PM400	52.2 (0.4)	3.26 (0.05)	0.1 (0.0)	13.0 (0.7)	0.74	0.19	3584 (2)	106.5 (0.7)	34
PM600	54.9 (0.3)	1.18 (0.05)	0.1 (0.1)	4.9 (0.3)	0.26	0.07	267 (10)	31.8 (0.8)	8
PC400	16.2 (1.4)	0.69 (0.01)	0.3 (0.0)	3.9 (0.1)	0.51	0.18	796 (33)	38.5 (1.6)	21
PC600	14.8 (0.0)	0.31 (0.01)	0.4 (0.1)	1.6 (0.4)	0.25	0.08	109 (6)	6.9 (0.4)	16

WEOC: Water extractable organic C; WEN: water extractable N; n.a.: not available; standard deviation in italics within brackets (n = 2).

Pyrolysis conditions (time of residence and HTT) also affected the characteristics of biochars. The main difference is the low surface area and total pore volume for the ECN chars compared to those from Proininso (Table 5). Both surface area and total pore volume are consistently lower for all of the chars produced from the ECN pyromat reactor and might be due to the lower residence time in this reactor. The use of long residence time in the Proininso reactor decreased the amount

of C_{org} of the OC biochar compared to the short residence time (1 h) in the Pyromat reactor for Oak (Table 4). Additionally, C_{org} increased with temperature in raw lignocellulosic biochars and PM biochar, whereas concentrations of H, S and O decreased. However, CM and PC biochars (characterized by high ash content, Figure 3) exhibited a different trend, characterized by a loss of C_{org} and a rise in S concentration with increasing temperature, which is accumulated in the ash fraction as a concentration effect from organic matter degradation.

Table 5. Physical and physicochemical properties of the biochars obtained at low (400–450 °C) and high temperature (600–650 °C). OC, commercial oak, O: oak, GH: greenhouse waste, GW: green waste, CM: CellMatt, PM: pig manure and PC: municipal press cake.

Biochar	pH ¹	EC ¹	WHC	CEC	N ₂ BET Surface Area	Total Pore Volume
		(mS cm ⁻¹)	%	(cmolc kg ⁻¹)	(m ² g ⁻¹)	(cm ³ g ⁻¹)
OC450	9.5 (0.1)	0.6 (0.0)	94 (4)	59.4 (8.1)	180.0	0.150
OC650	9.4 (0.0)	0.4 (0.0)	84 (2)	76.6 (0.7)	280.0	0.160
O400	9.6 (0.1)	0.6 (0.1)	91 (10)	105.8 (12.1)	1.0	0.005
O600	8.8 (0.0)	0.7 (0.0)	97 (4)	65.2 (20.2)	2.0	0.010
GH400	9.9 (0.0)	5.6 (0.0)	198 (8)	109.5 (21.8)	1.3	0.003
GH600	9.7 (0.0)	6.3 (0.0)	153 (6)	146.2 (32.3)	2.0	0.015
GW400	9.5 (0.0)	1.3 (0.1)	n.a.	64.8 (11.5)	2.0	0.011
GW600	10.4 (0.0)	0.7 (0.0)	55 (3)	62.7 (2.1)	2.0	0.015
CM400	9.4 (0.1)	2.2 (0.1)	82 (5)	65.7 (16.2)	2.0	0.007
CM600	10.4 (0.0)	3.5 (0.1)	68 (3)	67.9 (12.5)	4.0	0.029
PM400	9.8 (0.0)	6.6 (0.2)	n.a.	52.2 (0.4)	n.a.	n.a.
PM600	10.7 (0.0)	6.8 (0.1)	n.a.	54.9 (0.3)	n.a.	n.a.
PC400	9.9 (0.1)	1.1 (0.1)	51 (5)	16.2 (1.4)	2.0	0.004
PC600	10.4 (0.0)	0.7 (0.0)	53 (11)	14.8 (0.0)	2.5	0.017

¹ water extract 1:20 w/v 25 °C; EC: Electrical Conductivity; WHC: Water Holding Capacity; CEC: Cation Exchange Capacity; n.a.: not available; standard deviation in italics within brackets (n = 2).

The increase of C_{org} with temperature in lignocellulosic biochars is due to the aromatization of C, which mostly begins at 220 °C [28], when the decomposition of hemicelluloses (220–315 °C) and celluloses (315–400 °C) take place. The decomposition of lignins (150–900 °C) mainly occurs above 400 °C, due to its aromatic structure [29,30]. Thus, in biochars prepared at 400 °C, the hemicellulose and cellulose fractions have mostly been degraded, whereas pyrolysis at 600 °C implies also a higher decomposition of lignin [7,14,31]. However, C losses during the pyrolysis of lignin are lower than for cellulose [32]. The presence of lignin in the feedstock increases C content in the biochar through dehydration of hydroxyl groups and thermal degradation of lignocellulose structures [29].

The effect of the temperature of pyrolysis was not so evident in CM and PC biochars. The C_{org} concentrations in these biochars were similar to those found in the original feedstocks. Furthermore, the increase in the temperature of pyrolysis from 400 °C to 600 °C caused a decrease in the concentration of C_{org} (Table 4). This phenomenon could be due to the pre-treatment of both feedstocks, where the most labile fraction of the C_{org} had been partially degraded.

The concentration of the rest of the elements (N, H, O and S) was also affected by feedstock composition and temperature of pyrolysis. In the case of N, PM biochars recorded the highest concentrations of N (2.28% and 1.21% for PM400 and PM600, respectively), compared to the other biochars (Tables 4 and 6). The large amount of N in PM biochars can be explained by the high protein

content in the feedstock [33]. Oak biochars registered the lowest N concentration due to the low concentration of this element in the original feedstock (0.53%).

Knicker [32] showed that N compounds affected the thermal and chemical recalcitrance of biochar. Thus, depending on feedstock composition, biochars will have different amounts and thermally altered N components incorporated into their structure [32]. For instance, it has been revealed that N-rich biochars from GW, with a relatively high N concentration mainly due to the grass and leaves composition, are more stable to oxidation with respect to N-poor wood biochar like oak biochar [32]. These differences in the N composition would have consequences for N availability in soil [34]. In general, all biochars showed a reduction in the concentration of N with increasing temperature, which agrees with observations in previous studies [13,20]. Oak biochars were the exception, which might be explained by the inclusion of N within the aromatic C structures. Preliminary studies suggested that high temperatures of pyrolysis could preserve N in wood biochars by the formation of heterocyclic N [12,22].

The response of H and O content to changes in the HTT of pyrolysis was similar for all biochars, and tended to decline with increasing temperature. This has been reported in previous studies and it is due to the scission of weaker bonds (C-O and C-H compared to C-C) in the carbonaceous material, so that only a recalcitrant oxygen fraction remains fixed in the biochar [12,14]. This effect reduces the presence of O-containing functional groups, decreasing the surface acidity and polarity of biochars [35].

The decrease in S content during pyrolysis could be due to volatilization, even at low pyrolysis temperature [12,20].

Table 6. Total macro and micro nutrient concentrations in the studied biochars. OC, commercial oak, O: oak, GH: greenhouse waste, GW: green waste, CM: CellMatt, PM: pig manure and PC: municipal press cake.

Biochar	(g 100 g ⁻¹)						(mg kg ⁻¹)					
	N	P	K	Ca	Mg	Na	Fe	Cu	Mn	Zn	Mo	B
OC450	0.73 (0.08)	0.04 (0.00)	0.99 (0.04)	1.39 (0.11)	0.13 (0.01)	0.02 (0.00)	160 (14)	4.5 (0.4)	152 (6)	8 (1)	<0.1 (0.0)	6.8 (0.0)
OC650	1.08 (0.08)	0.20 (0.01)	0.67 (0.03)	3.82 (0.22)	0.25 (0.01)	0.02 (0.00)	542 (40)	9.9 (0.6)	463 (26)	30 (2)	<0.5 (0.0)	16.1 (0.8)
O400	0.33 (0.00)	0.07 (0.01)	0.90 (0.01)	2.14 (0.13)	0.12 (0.02)	0.09 (0.01)	1351 (152)	18.3 (2.8)	44 (5)	75 (14)	2.5 (1.1)	13.4 (0.2)
O600	0.34 (0.00)	0.08 (0.01)	1.07 (0.08)	2.64 (0.24)	0.15 (0.01)	0.15 (0.02)	1667 (372)	22.0 (2.4)	62 (5)	86 (14)	1.3 (0.6)	16.1 (0.7)
GH400	1.14 (0.05)	0.24 (0.00)	3.39 (0.00)	2.18 (0.00)	0.76 (0.00)	0.28 (0.00)	1059 (97)	17.9 (0.4)	68 (1)	38 (1)	2.0 (0.2)	24.0 (0.3)
GH600	0.88 (0.02)	0.25 (0.01)	4.13 (0.10)	2.59 (0.06)	0.91 (0.03)	0.30 (0.01)	544 (21)	16.5 (0.4)	61 (2)	26 (1)	0.8 (0.0)	27.3 (0.5)
GW400	1.39 (0.00)	0.26 (0.01)	0.82 (0.02)	2.60 (0.16)	0.43 (0.02)	0.13 (0.00)	9124 (124)	41.4 (2.9)	1804 (125)	200 (7)	3.3 (0.1)	38.8 (0.1)
GW600	0.90 (0.01)	0.32 (0.03)	0.99 (0.05)	3.23 (0.07)	0.48 (0.02)	0.15 (0.01)	9550 (264)	50.1 (0.8)	321 (18)	263 (21)	4.0 (0.3)	41.0 (2.2)
CM400	1.25 (0.00)	0.42 (0.00)	0.84 (0.00)	4.26 (0.07)	0.34 (0.00)	0.70 (0.01)	10053 (1612)	96.2 (4.0)	225 (15)	357 (13)	5.6 (0.4)	29.6 (0.2)
CM600	1.21 (0.01)	0.37 (0.03)	0.70 (0.07)	5.17 (0.54)	0.36 (0.06)	0.99 (0.14)	10182 (287)	128.2 (5.3)	276 (28)	490 (103)	3.2 (0.5)	32.3 (2.1)
PM400	2.28 (0.06)	1.96 (0.07)	2.49 (0.07)	0.92 (0.06)	0.33 (0.01)	2.44 (0.07)	3213 (116)	111.7 (3.9)	365 (16)	453 (12)	3.6 (0.1)	63.9 (1.1)
PM600	1.45 (0.12)	2.65 (0.04)	2.92 (0.09)	1.14 (0.01)	0.45 (0.01)	2.97 (0.04)	2890 (483)	138.6 (4.9)	484 (7)	654 (82)	4.5 (0.1)	76.4 (1.9)
PC400	0.90 (0.01)	0.55 (0.01)	1.07 (0.01)	3.31 (0.66)	0.45 (0.01)	0.28 (0.00)	12217 (560)	97.7 (16.7)	282 (18)	324 (85)	4.9 (0.8)	29.2 (0.1)
PC600	0.64 (0.01)	0.51 (0.01)	0.99 (0.01)	2.99 (0.07)	0.40 (0.04)	0.26 (0.01)	11399 (496)	76.0 (9.8)	260 (2)	265 (8)	3.9 (0.2)	28.8 (1.9)

Standard deviation in italics within brackets (n = 2).

Molar H/C_{org} and O/C_{org} Ratios

The comparison between the relative contribution of two different elements may provide useful information on the chemical characteristics of biochars. Thus, the molar H/C_{org} ratio has been proposed as an index of aromaticity of biochars, and also, in combination with the O/C_{org} ratio,

to classify the stability of biochars [6,20]. Molar ratios H/C_{org} and O/C_{org} are shown in Table 4 and plotted on a Van Krevelen diagram [36] in Figure 3. The molar H/C_{org} ratio shows the degree of thermochemical alteration that produces fused aromatic ring structures in the material [6]. Thus, a H/C_{org} ratio below 0.7 indicates that the biochars have been thermochemically altered or “thermochemically converted” [6] (Figure 3).

The study of the Van Krevelen diagram allows the differentiation of the properties of feedstocks and biochars prepared under different conditions. Results showed great differences between feedstocks, located in the top-right corner of the diagram, and the biochars, divided in two different groups (prepared at 400 °C and 600 °C), located in the bottom-left corner. When the temperature of pyrolysis increased, H/C_{org} and O/C_{org} ratios tended to decrease and homogenise. A negative correlation between production temperature and H/C_{org} ratio has been found ($p < 0.01$). Feedstocks that showed the largest differences in H/C_{org} ratios, were CM with the highest value (2.30) and PC with the lowest (1.31) (Table 1 and Figure 3). The differences in H/C_{org} ratios decreased in biochars at 400 °C, ranging from 0.51 to 1.31, which showed that some of them were not completely “converted” (O400, GW400, CM400 and PM400). However, at 600 °C, all biochars registered similar H/C_{org} ratios, in the range of 0.26–0.43. Thus, the highest H/C_{org} of CM400 can be explained by the large proportion of the cellulosic fraction in the feedstock, characterized by a high amount of H and O-containing functional groups [8].

According to Spokas [8] and Enders et al. [20] H/C_{org} below 0.4 or O/C_{org} below 0.2 indicate a high C sequestration potential, whereas biochar above these limits are considered to have a moderate sequestration ability. According to this, all biochars prepared at 600 °C (except CM600) can be classified as “high sequestration potential” materials, whereas the rest are classified with “moderate sequestration ability”, except GW biochars that have “no C sequestration ability” due to their high ash content. In addition, according to Spokas [8] the O/C_{org} ratio can help to predict the life time of biochar in soil. Biochars with an O/C_{org} ratio under 0.2 will possess a half-life of >1000 years. All biochars prepared at both temperatures are in this class, except OC450, which possesses a half-life between 100 and 1000 years. This effect has implications on biotic and abiotic interactions in amended soils, being that biochars with low O/C_{org} ratio values are less easily biodegradable [8]. However, the relationship between material properties, decomposers, and environmental conditions could determine the greater persistence of biochar on soil, rather than only its recalcitrance [37].

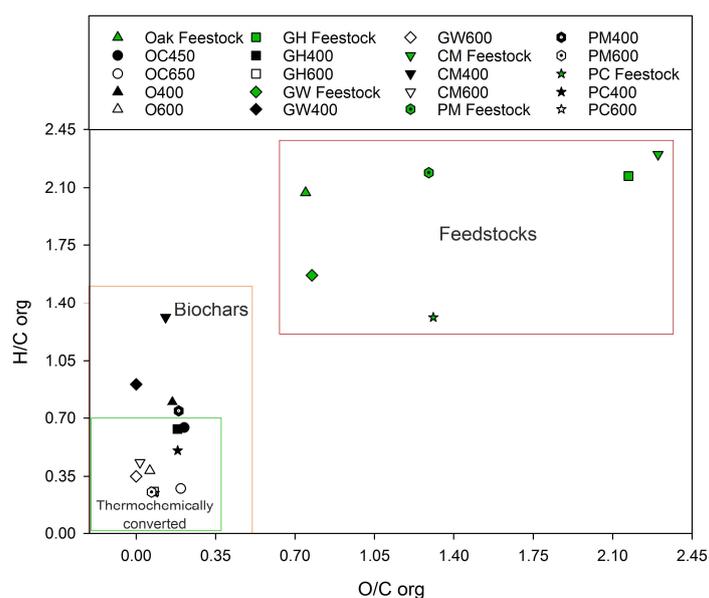


Figure 3. H/C_{org} and O/C_{org} ratios for feedstocks (red square) and pyrolysed residues in Van Krevelen diagram. The orange square contains all biochars, while the green one includes only the thermochemically converted materials ($H/C_{org} < 0.7$), according to IBI [4].

Volatile Matter, Ash and Fixed Carbon Content

The percentages of ash, fixed C and volatile matter of biochars at 400 °C and 600 °C are given in Figure 4. These three parameters define the main physicochemical properties of biochars, especially a high proportion of fixed C (>50%), low ash (<20%) and volatile content (<30%) observed in raw lignocellulosic biochars (Oak and GH), that are typical characteristics of biochars prepared from woody materials [20,28]. However, biochars prepared from other sources (PC, CM and GW biochars) showed higher ash (>50%), similar volatile content (<30%), and lower concentration of fixed C (<40%), whereas PM biochars had intermediate values (Figure 4).

A negative correlation between volatile content and production temperature was found for the studied biochars ($p < 0.01$), which reflects the dependence of fixed C and volatile content from both the chemical characteristics of feedstocks and the pyrolysis conditions. This relationship is in agreement with results found by other authors [20,38]. Cellulose, hemicellulose and lignin degrade at 150–900 °C and are affected by the mineral compounds in feedstocks [38]. Thus, increasing the pyrolysis temperature increases the carbonaceous skeleton of biochars, which is a pore structure [28] that mimics the cellular structure of wood in the original feedstock [38,39].

The largest proportions of ashes were found in PC, GW and CM and then in PM biochars, whereas, the lowest proportions were found in raw lignocellulosic biochars (Oak, GH). This effect is due to the original mineral composition of feedstocks. It should be noted that higher pyrolysis temperature increases ash content and decreases volatile content due to the losses of organic matter during the thermal decomposition and concentration of mineral constituents from feedstocks [28]. In addition, fixed C tends to increase with higher pyrolysis temperature due to the increased aromatic ring structure of C atoms and their condensation and growth into larger sheets and stacks [7]. However, PC biochars did not show an increase in fixed C at 600 °C; this could be explained by the high ash content that hinders the formation of aromatic C forms, as observed by Enders et al. [20]. Xu and Chen [40] also found that a large mineral content can prevent the diffusion of heat and therefore the release of volatile matter during pyrolysis.

According to the volatile content, ash and fixed C data, it is expected that biochars prepared at 400 °C would be more reactive in soil than biochars prepared at higher temperatures. In general, biochars at 400 °C showed a higher H/C_{org} and O/C_{org} ratio that imply more diversified organic molecules, including aliphatic and cellulose type structures and containing more O-containing functional groups, which are more easily biodegradable and also exhibit a larger ion exchange capacity [7,8].

3.1.2. Agronomical Characterisation

Macro and Micro Nutrients Composition

The mineral composition of biochars (Table 6) is an indication of their potential as a nutrient source. The presence of nutrients in biochars, which are directly related to the ash content, is governed by the composition of the original feedstocks and the pyrolysis temperature. Wood and raw lignocellulosic biochars are characterized by a low number of nutrients. On the other hand, CM, PC and also GH and PM biochars are rich in exchangeable base cations. In addition, CM, PC and PM biochars have high Fe, Cu, Mn and Zn content, as expected from the concentrations in the original feedstocks. In general, the concentration of macro and micro nutrients was enriched with increasing pyrolysis temperature, especially in the case of raw lignocellulose biochars. However, biochars from PC reversed this trend, and biochars from CM did not show a clear pattern. While CM biochars showed an opposite behavior for different nutrients (reductions in P and K and increments in the rest), PC biochars showed a reduction in the concentration of all nutrients.

As already mentioned, the level of N was low in all biochars, except in the case of PM (Table 6). Furthermore, the incorporation of N into the biochar structure reduces its availability for plants.

P tended to increase during the pyrolysis process, indicating an enrichment of this element (Table 6). It is known that P only starts to volatilise when the pyrolysis temperature is greater than 800 °C [34].

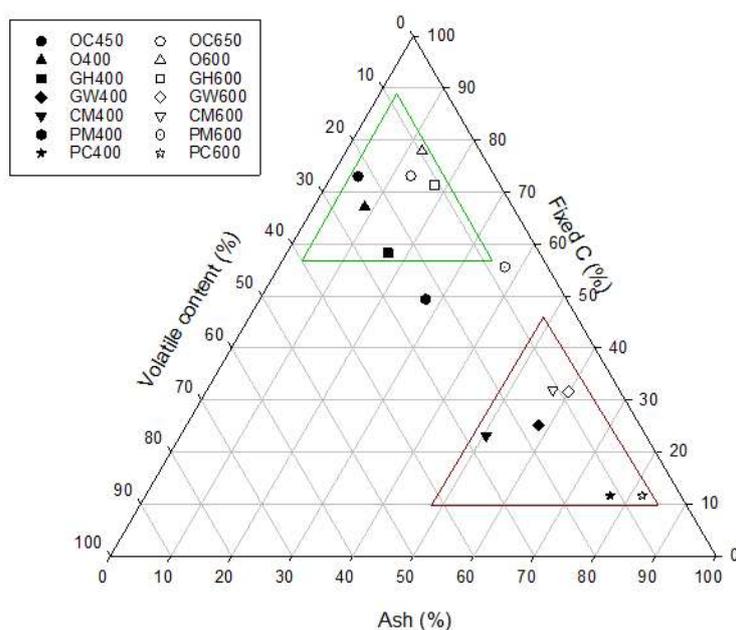


Figure 4. Triangle plot of ash, fixed C and volatile content percentages of tested biochars showing the effect of pyrolysis temperature and original feedstocks. The black symbols represent the biochars produced at low temperature and the white symbols those produced at high temperature (400 °C and 600 °C, respectively). The green triangle contains the raw lignocellulosic biochars, and the red one includes the pre-treated lignocellulosic biochars.

The sum of the cations K, Na, Ca and Mg reflected an increase with respect to the feedstocks and in relation to the temperature in both pyrolysis processes for all biochars with high lignocellulosic contents and manure, except in the case of PC biochars. The enrichment in nutrients could be due to a concentration effect, especially in raw lignocellulosic biochars, as observed by Enders et al. [20].

Water-extractable C and N showed great variability, ranging from 109 to 4610 and 2 to 106 $\mu\text{g g}^{-1}$ for WEOC and WEN, respectively (Table 4). The biochars with the highest content of WEOC and WEN derived from agricultural waste (GH400 and PM400). High values for these two variables were also recorded for GW400. The increase of pyrolysis temperature led to a general and remarkable decrease in WEOC, with the only exception of commercial biochar from holm oak (OC). On the contrary, the effect of pyrolysis temperature was less evident in the case of WEN (Table 4). As a consequence, the ratio between WEOC and WEN showed an inverse relationship with temperature, except in the case of OC biochar.

Utilization of biochar as an amendment could increase the soil content of WEOC and WEN, the importance of which for agriculture and environment has long been recognized. WEOC is the most dynamic and bioavailable fraction of C and plays an important role in plant nutrient uptake, organic matter decomposition and soil microbial activity and facilitates the transport of metals and organic pollutants in soils [41]. Soil amendment with biochar could stimulate soil microbial biomass growth and activity, as it has been demonstrated that easily available C may induce activation of microorganisms but can also be limiting for microbial growth [42]. Extractable N represents the primary source of mineralisable N and it has been used as an indicator of changes in soil and fertilizer management.

pH and EC Values

All biochars showed alkaline pH, which ranged from 8.8 to 10.7 (Table 5). Two groups of biochars could be distinguished as a function of pH values: one group, including OC, Oak and GH biochars with values lower than 9.7 and a second group, consisting of GW, CM, PM and PC biochars, with values above 10.4. Increasing pyrolysis temperature increased pH values in CM, PC, GW, and PM biochars with high-ash content, a trend that was also observed by Enders et al. [20]. The decomposition during pyrolysis removes acidic functional groups and increases the ash content [29,36], causing the hydrolysis of Ca, K and Mg salts in the presence of water [22] and leading to more alkaline biochars. In contrast, this effect was not so relevant in raw lignocellulose biochars such as Oak, OC and GH.

EC is a measurement that correlates with salinity and therefore is an important parameter to be determined in any organic amendment before its use on land. The EC values in the studied biochars ranged from 0.4 to 6.8 mS cm⁻¹ (Table 5). The EC results were correlated with the original EC values of the feedstocks. Thus, Oak and OC biochars showed the lowest EC values and PM and GH the highest. Increasing pyrolysis temperature also tended to increase EC values. This effect was clearly observed in other studies regarding biochar prepared at higher temperatures (600 °C and 800 °C) [12].

Water Holding Capacity

The hydraulic properties of biochars were evaluated by their WHC, which ranged from 47.3% to 198.3%, expressed on a dry weight basis (Table 5). Raw lignocellulosic biochars, with low-ash content, showed the highest WHC (from 84.4% to 198.3%), whereas high-ash biochars showed lower values (from 47.3% to 82.5%). In general, high temperature biochars presented greater water uptake than low temperature biochars, which is in agreement with Gray et al. [43]. In addition, Spokas et al. [44] related the WHC of biochars with the pore size of materials, which increases with the temperature of production.

Water holding capacity is a key feature of biochars that improves the agronomic quality of soils. However, the hydrological properties of biochars cannot be fully assessed until they are added to the soils, where it is possible to evaluate the actual amount of water that is accessible to plants [28,45].

Cation Exchange Capacity

The CEC of biochars was evaluated as a property for agronomical use. The values of CEC were highly dependent on the original feedstock (Table 5). Lignocellulosic materials showed higher CEC values than municipal wastes, which were characterized by lower C concentration and higher ash content. In general, temperature of pyrolysis only had a minor impact on CEC values (Table 5).

3.1.3. Potential Limitations for the Agricultural Use of Biochars: Heavy Metal and PAH Contents

The presence of heavy metals and PAH in biochar may represent a limitation for its agricultural use, especially in the case of biochars prepared from feedstocks of urban or agroindustrial origin, which may contain high levels of heavy metals. The heavy metal concentration of the different biochars is shown in Table 7.

Due to the absence of European legislation on biochar, the suitability of biochars for agricultural use was assessed depending on heavy metal concentrations according to the European Biochar Certificate (EBC), a guideline on the production of biochar developed by the European Biochar Foundation. In general, the heavy metal concentration of the biochars increased with respect to the original feedstock and with pyrolysis temperature, owing to a concentration effect.

Table 7. Heavy metal and total PAH concentration in the studied biochars. OC, commercial oak, O: oak, GH: greenhouse waste, GW: green waste, CM: CellMatt, PM: pig manure and PC: municipal press cake.

Biochar	Cd	Cr	Ni	Pb	PAH ¹
	(mg kg ⁻¹)				
OC450	<0.1	5 (1)	3.3 (0.9)	1.1 (0.2)	2.06
OC650	<0.1	3 (0)	9.2 (0.9)	1.2 (0.1)	0.10
O400	<0.1	32 (7)	26.0 (7.6)	17.9 (5.0)	1.60
O600	<0.1	58 (3)	39.1 (8.4)	27.1 (3.3)	3.87
GH400	<0.1	29 (0)	15.8 (1.3)	5.8 (0.5)	n.a.
GH600	<0.1	21 (1)	10.2 (0.4)	3.5 (0.0)	n.a.
GW400	0.8 (0.1)	93 (7)	35.4 (2.2)	66.2 (2.4)	n.a.
GW600	0.1 (0.0)	125 (6)	44.1 (1.9)	86.3 (19.0)	n.a.
CM400	1.4 (0.0)	126 (4)	72.5 (2.0)	212.4 (35.1)	2.95
CM600	1.3 (0.3)	129 (26)	66.1 (2.8)	209.5 (72.7)	3.00
PM400	<0.1	8 (1)	7.3 (0.2)	4.8 (0.1)	n.a.
PM600	<0.1	10 (1)	9.5 (0.2)	6.1 (0.0)	n.a.
PC400	1.4 (0.0)	92 (1)	46.4 (1.8)	100.0 (0.5)	2.37
PC600	1.0 (0.0)	102 (35)	48.1 (16.1)	111.5 (6.2)	8.10

¹ PAH: polycyclic aromatic hydrocarbons (sum of the 16 EPA PAHs), standard deviation in italics within brackets (n = 2), n.a.: not available.

According to EBC [10], biochars can be classified in three different quality grades: “premium”, “basic” and “not recommended”, depending on their heavy metal concentrations. Oak and GH biochars fall into the category of “premium” quality. However, the use of biochars from feedstocks of urban origins might be restricted. CM biochars would not be recommended as soil amendment in agriculture due to the high concentration of Cr, Pb and Ni. The rest of the biochars (GW and PC) fall within the category of “basic”, with the only concern of biochars prepared at high temperature (600 °C), where the concentration of Cr may exceed legal limits. Special attention should be paid to the use of Ni-Cr steel in construction of pyrolysis reactors to avoid metal contamination from abrasion of the equipment [46]. In the case of PAH, most of the analysed biochars fall within the category of “premium”, with the only exception of PC600, which can be considered “basic” grade.

4. Conclusions

A range of biochars was produced from organic wastes of agricultural and urban origins. Most of them presented suitable properties for use in agriculture. The physicochemical properties of biochars were driven by the characteristics of feedstocks and the pyrolysis temperature. The use of pre-treated lignocellulosic residues led to biochars with a high concentration of ash, macro and micronutrients, whereas raw lignocellulosic residues produced biochars with characteristics similar to traditional wood biochars. The pyrolysis temperature established differences between biochars obtained at 400 °C and 600 °C. The use of high temperatures increased the ash content and recalcitrant C and increased the

losses of N and O containing functional groups. Consequently, biochars prepared at 400 °C presented higher mineral and volatile organic matter content, which are favorable properties for their agricultural use and interaction with soil nutrient cycles.

According to national legislation for organic amendments and international standards for the use of biochars as soil amendments, all the biochars were found to be suitable for agricultural use, with the exception of CM, which presented high levels of Cr and Pb. The occurrence of heavy metals in the feedstock and contamination during pyrolysis may limit the use of certain biochars in agriculture. Before employing these biochars as soil amendments, an exhaustive agronomical evaluation should be performed to assess their impact on soil biogeochemical cycles and plant growth.

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