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ANALYSIS OF BIOCHARS PRODUCED FROM THE GASIFICATION OF *PINUS PATULA* PELLETS AND CHIPS AS SOIL AMENDMENTS

ANÁLISIS DE LOS BIOCARBONES PRODUCIDOS A PARTIR DE LA GASIFICACIÓN DE PELLETS Y ASTILLAS DE *PINUS PATULA* COMO ENMENDADORES DE SUELOS

Jonatan Gutiérrez [1,2]
https://orcid.org/0000-0001-7532-8519
Ainhoa Rubio-Clemente [2]
https://orcid.org/0000-0003-1527-260X
Juan F. Pérez [1,*]
https://orcid.org/0000-0002-3811-4471
[1] Universidad de Antioquia – UdeA, Facultad de Ingeniería, Grupo de Manejo Eficiente de la Energía – GIMEL, Medellín, Colombia.
[2] Universidad de Antioquia – UdeA, Facultad de Ingeniería, Grupo de Investigación Energía Alternativa – GEA, Medellín, Colombia.

***Corresponding author**: juanpb@udea.edu.co

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ABSTRACT

In this work, biochar (BC), a co-product of the fixed bed gasification process of *Pinus patula* wood pellets (PL) and chips (CH), was characterized as soil amendment. The physicochemical properties and the mineral content of the pellet's biochar (PL-BC) and the chips biochar (CH-BC) were analyzed following the NTC5167 Colombian technical standard. The BET surface area values of the BCs were 367,33 m^2/g and 233,56 m^2/g for the PL-BC and the CH-BC, respectively, and the pore volume was 0,20 cm^3/g for the PL-BC and 0,13 cm^3/g for the CH-BC. These characteristics favor the increase of the BCs water-holding capacity (WHC). Properties such as the pH (8,8-9,0), the WHC (219 % - 186,4 %), the total organic carbon (33,8 % - 23,9 %), the metalloid presence (Ca, Mg, K, Mn, Al, Si, and Fe), and the ash (1,92 wt% - 2,74 wt%) and moisture contents (11,13 wt% - 11,63 wt%) for both BCs were found to be within the limits set by the NTC5167 standard. Furthermore, the presence of micro and macronutrients, such as Fe and phosphorus (P), and the alkaline pH, make possible the use of these BCs as amendments for acid soils.

Keywords: Byproduct valorization, fixed-bed reactor, gasification biochar, soil amendment, wood biomass.

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Resumen

En este trabajo se caracterizó el biocarbón (BC), subproducto del proceso de gasificación en lecho fijo de pellets (PL) y astillas (CH) de madera de *Pinus patula*, como enmendador de suelos. Las propiedades fisicoquímicas y el contenido mineral de las cenizas del biocarbón de pellets (PL-BC) y del biocarbón de astillas (CH-BC) se analizaron siguiendo la norma técnica colombiana NTC5167. El área superficial BET de los BC fue de 367,33 m^2/g y 233,56 m^2/g, para el PL-BC y el CH-BC, respectivamente, y el volumen de poro fue de 0,20 cm^3/g para el PL-BC y de 0,13 cm^3/g para el CH-BC. Estas características favorecen el aumento de la capacidad de retención de agua (WHC) de los BCs. El pH (8,8-9,0), la WHC (219 % - 186,4 %), el carbono orgánico total (33,8 % - 23,9 %), la presencia de metaloides (Ca, Mg, K, Mn, Al, Si y Fe), el contenido de cenizas (1,92 wt% - 2,74 wt%) y humedad (11,13 wt% - 11,63 wt%) para ambos BCs, cumplen con lo establecido por la norma NTC5167. Además, la presencia de micro y macronutrientes, como el Fe y el fósforo (P), y el pH alcalino, hacen viable utilizar estos BCs como enmendadores de suelos con carácter ácido.

Palabras claves: Biocarbón de gasificación, biomasa, enmendador de suelos, reactor de lecho fijo, valorización de subproducto.

INTRODUCTION

In 2019, the study "Carga de Enfermedad Ambiental en Colombia" (Environmental disease load in Colombia) stated that water, air and soil pollution cause diseases, some among which are harmful and lethal for the inhabitants from the country (Instituto Nacional de Salud 2019). The pollution of water and soil quality is attributed to toxic organic and inorganic substances with an anthropogenic origin such as commercial, industrial and residential activities, as well as the monoculture of foreign or illegal species, illegal mining, deforestation, and the use of fertilizers and pesticides. All these activities have harmful consequences on the surrounding ecosystems and mainly affect the soil (Lim *et al.* 2013). As a consequence, the exploration of solutions which contribute to mitigate and remedy the damage to edaphic resources, and in general, the environmental damage has become a priority. A mitigating alternative is the study of materials that reduce the polluting load, while at the same time provide the soil with nutrients. Among these materials, the biochar (BC) derived from biomass thermochemical processes is highlighted. The relevance of BC is associated with the physicochemical properties enabling this material to reduce the bioavailability, accumulation, and toxicity of the pollutants contained in soils (Sohi 2012).

According to the *International Biochar Initiative* (IBI), BC is a "solid material obtained from the thermochemical conversion of biomass in a low-oxygen environment" (International Biochar Initiative 2019) and, considering that the biomass is widely used as an energy source due to its availability, low cost and neutrality in carbon emissions, there is a current availability of this carbonaceous material (Kamal Baharin *et al.* 2020). According to the IBI, BC can help solve the world food safety crisis and guarantee a good quality of the soil because it improves aspects such as fertility and agricultural and agroforestry productivity. Furthermore, BC has positive effects on the climate change crisis by reducing both safely and effectively greenhouse gas emissions (GGE) caused by agricultural systems. BC contributes to sustainability of agricultural production at every scale by keeping the productivity, while at the same time reducing the use of chemical fertilizers and allowing for the recycling of agricultural and organic waste. Moreover, water quality is improved through the reduction of leachates of soil nutrients to water bodies (International Biochar Initiative 2019).

BC produced in the gasification is a byproduct of the thermochemical process (Hernández *et al.* 2016) whose properties and potential applications are determined by the feedstock, technology and gasification conditions (Qian *et al.* 2013, 2015). For medium-high temperatures such as the ones reached during biomass gasification, the properties of the resulting BC, such as the pore structure, surface area, pH, fixed carbon (FC) and ash contents (AC) are improved. While the pore average size, the mass production yield, the acid functional groups, the hydrogen (H) and oxygen (O) mass fractions, and the volatile matter content (VM) are adversely affected (Zhao *et al.* 2018). Al-Wabel *et al.* (2013) found that at high gasification temperatures, the basic functional groups, carbon stability and the content of carbon (C), nitrogen (N), phosphorous (P), potassium (K), calcium (Ca), and magnesium (Mg) increased, while the O/C and H/C ratios tended to decrease. Keiluweit *et al.* (2010) concluded that at high temperatures, the formation of ashes with alkaline minerals in the BC increased. Besides, the BC produced contains a lower density of acid functional groups (phenolic and carboxyl compounds), which leads to an increase in the BC pH up to values between 8 and 10.

Among the main properties for the classification of BC as a soil amendment, the proximate (FC, VM, AC, and moisture content –MC–) and ultimate analyses (C, H, O, and N), the pore volume, the surface area, the pH, the water-holding capacity (WHC), the cation exchange capacity (CEC), the total oxidizable organic carbon (TOC), and the mineral content of the ashes, are highlighted (Buss *et al.* 2018, Qian *et al.* 2015). For the application of the BC to the soil, the H/C atomic ratio is related to BC stability (Hansen *et al.* 2015), being the long-term stability a key factor to decrease carbon dioxide (CO_2) emissions to the atmosphere (Singh *et al.* 2012). On the other hand, the BC derived from the gasification usually shows a pH between neutral and basic (Almaroai *et al.* 2014), inducing a limestone effect on acid soils by increasing the soil pH to values between 8 to 9, which in turn increases the productivity of plants (van Zwieten *et al.* 2010).

Among the soil properties improved by means of the application of BCs, the following are worth noted: i) the increase of microbial and enzymatic activity (Abbas *et al.* 2018), which favors the rise in microorganisms in the soil; ii) resistance to plagues and diseases (Zhang *et al.* 2021); iii) increase in the capacity of water retention and improvement of the water use by the plants (Tanure *et al.* 2019), which is of great use in areas with reduced water resources (Fischer *et al.* 2019); iv) removal of pesticides (Yang *et al.* 2010); and v) elimination of inorganic pollutants present in the soil such as chrome (Cr), arsenic (As) and copper (Cu), among others (Paz-Ferreiro *et al.* 2014).

The BCs produced at high temperatures, such as the ones reached in the gasification process, are more effective for treating organic pollutants because they have a large surface area and developed pore structures (Ahmad *et al.* 2014). While the BCs, obtained at low temperatures, are more efficient for the adsorption or inorganic pollutants due to the presence of a higher number of functional compounds in the surface with elemental O and the higher release of cations. As a consequence, the BCs can be designed to selectively improve their chemical and physical properties through the modification of raw materials and process temperatures, depending on the type of pollutant to be removed (Novak *et al.* 2009).

On the other hand, energy production with forest biomass through thermochemical processes like combustion, pyrolysis and gasification is highlighted to primarily use chips (CH) and pellets (PL) (Pérez and Ramírez 2019). Particularly, in 2018, Colombia produced ~$7{,}1\times10^6$ m^3 of wood to be used as fuel (FAO 2019). In addition, the country has a forest potential of 24 million ha for a sustainable commercial exploitation (Minagricultura 2015); such potential area is located outside the jungle and tropical rain forest and does not compete with cattle farming nor with agriculture (Pérez and Ramírez 2019), being patula pine (*Pinus patula*) one of the species with a higher dendroenergetic potential in Colombia due to its silvicultural properties (annual volumetric yield of ~20 m^3/ha-year, harvest time of ~13 years, and planted area of ~38500 ha) (Pérez *et al.* 2019). Thereby, patula pine is a reference as an energy forest crop and as a raw matter for energy production through thermochemical processes (Ramos-Carmona *et al.* 2017), with the ensuing BC production.

In this work, the BCs derived from the gasification of *Pinus patula* wood pellets (PL-BC) and chips (CH-BC) are characterized and compared between them as possible soil amendments. From the authors' knowledge, these BCs have not been studied nor compared previously in the scientific literature as material to be used for soil amendment. In this regard, this study contributes to the sustainability of the energy recovery from forest biomass and gives an added value to the solid waste derived from thermochemical processes in order to be used in other productive processes. Thus, the physical and chemical properties and the mineral content of PL-BC and CH-BC are assessed under the NTC5167 standard (ICONTEC 2011).

MATERIALS AND METHODS

PL-BC and CH-BC properties were assessed in order to determine the potential use of these BCs as soil amendments following the NTC5167 standard (ICONTEC 2011). The BCs were produced using an atmospheric concurrent fixed-bed reactor (reverse downdraft, or top-lit updraft – TLUD), with a constant air flow as a gasifying agent. Both BCs (PL-BC and CH-BC) and the biomasses used as raw materials for gasifying (PL and CH) were physicochemical characterized through the Brunauer, Emmett and Teller (BET) surface area, pore volume, scanning electron microscope (SEM), ultimate and proximate analyses, pH, TOC, WHC, CEC, and X-ray fluorescence (XRF). The measurements for the BC characterization were replicated twice in order to verify the results obtained.

Materials

The *Pinus patula* PL used in the current study were acquired from a wood vending site located in Medellín city (Colombia). The PL (Figure 1a) produced had a length between 10 mm and 15 mm and a diameter of 8 mm. In turn, the CH (Figure 1b) produced in a *Bandit 95XP* equipment had sizes between 4 mm and 20 mm.


(a) (b)
(c) (d)

Figure 1: Raw biomasses and biochars produced through the gasification process. (a) PL, (b) CH, (c) BC derived from pellets (PL-BC) and (d) BC derived from chips (CH-BC).

Methods

BC production

PL-BC (Figure 1c) and CH-BC (Figure 1d) were produced in a reverse downdraft gasifier (cylindrical reactor with a diameter of 160 mm and a height of 280 mm). The gasifying agent supplied was air with a mass flow of 0,12 kg/m^2·s ± 3,58×10^{-3} kg/m^2·s (fixed for both biomasses), which was supplied by a reciprocating compressor (2,6 kW, 1,88×10^4 rad/min, up to 254 L/min) and fitted with a manometer and a rotameter to regulate the air pressure and flow, respectively. Fresh biomass, ~1300 g of PL for the production of PL-BC or ~550 g of CH for the production of the CH-BC, was loaded through the top of the gasifier. The fuel was ignited, and the air was supplied through the bottom of the reactor in order to activate gasification reactions (drying, pyrolysis, oxidation, and reduction) for obtaining the producer gas and the BC.

The PL gasification process for the production of PL-BC reached a fuel-air equivalence ratio of 1,52 (± 0,19) and an average temperature of 391 °C (± 81,68 °C) on the reactor walls.

Meanwhile, the production of CH-BC associated with CH gasification reached a fuel-air equivalence ratio of 1,85 (± 0,25) and an average temperature of 230 °C (± 30,77 °C) on the reactor walls. The experimental installation and characterization of the gasification process for the PL and the CH in the reverse downdraft reactor is described in detail by Gutiérrez *et al.* (2021).

Physicochemical characterization of BCs

Physical properties

The surface morphology of the raw biomasses (PL and CH) and of the BCs (PL-BC and CH-BC) was assessed through the surface area and pore volume (Pv); furthermore, the surface of samples was analyzed by the scanning electron microscope (SEM). The surface area and the Pv were quantified using an *ASAP 2020* (Micromeritics Instrument Corp., USA) equipment, by means of adsorption isotherms with nitrogen. Surface area calculation was carried out through the BET method, which was applied to the adsorption data of N_2 in the relative pressure interval (P/P_0) 0,05-0,35 to –196 °C. The samples were degassed at 1,33 Pa during 18 h at a temperature of 250 °C. The Pv was obtained with the *Barret, Joyner and Halenda* (BJH) method (Qian *et al.* 2013). The observations made through the SEM were carried out in a *JEOL JSM-6490* microscope (Jeol Ltd., Japan) working at an acceleration voltage of 20 kV. Samples were covered by a gold film before being entered to the equipment and observations were made at ×250.

Chemical properties

Raw biomasses and BCs were characterized through the ultimate analysis, C, H, N, sulfur (S), and O contents. The characterization was carried out under the ASTM D5373-08 standard (ASTM 2008) and a *Leco Truspec micro* (Leco®,USA) equipment was used. The elemental contents of C, H and N were determined at 1050 °C in a helium (He) atmosphere, while the S content was quantified at 1350 °C using also a He atmosphere. The O concentration was obtained by difference (Protásio *et al.* 2013). The MC, VM, FC and AC contained in the PL, CH, PL-BC and CH-BC were measured in a *TGA Q50* (TA Instruments, USA) equipment, in accordance with the modified ASTM D5142-04 standard (Medic *et al.* 2012).

The functional groups on the surface of raw biomasses and the BCs were determined through Fourier-transform infrared spectroscopy (FTIR) in a *IRAffinity-1* (Shimadzu, Japan) equipment and with a detector operated in a wave number range of 4000 cm^{-1} to 400 cm^{-1}. For qualitative FTIR, a KBr pellet was prepared at 2 wt% of sample (wood or biochar). The baselines of the FTIR spectra were superimposed for qualitative comparison. The functional group evolution can support the change analysis in biomass samples after gasification and the assessment and characterization of the BC properties. The aromaticity is among the most significant changes in the BC chemical structure (Fang *et al.* 2014), and it is determined through the aromaticity index (A, dimensionless), calculated by means of Eq. (1) (Brewer *et al.* 2011), where FC (wt%) and VM (wt%) are the fixed carbon and volatile matter contents, respectively, of the sample.

$$\mathrm{A} = \frac{\mathrm{FC}}{\mathrm{FC} + \mathrm{VM}} \qquad (1)$$

BC properties as soil amendments

The main characteristics that have to be assessed in order to determine the suitability of a material as a soil amendment are the pH, the TOC, the WHC, the CEC, and the ash mineral composition (Qian *et al.* 2015; Buss *et al.* 2018). The NTC5167 standard (ICONTEC 2011) was the basis to determine the pH of the BCs through potentiometry and the TOC was measured by titration. The WHC and the CEC were quantified through gravimetry and volumetry, respectively. In all cases, a sample of dry BC (105 °C for 24 h), ground and sieved (150-300 μm) was used. The WHC was measured by pressing 100 g of BC and adding distilled water until reaching the saturation point (thick substance that does not absorb nor drips water). The WHC was calculated through Eq. (2), where W_{BC} (g) is the BC sample weight, V (mL) is the water volume necessary to reach the saturation point, and MC (%) is the BC moisture content obtained in the proximate analysis. The pH of the PL-BC and CH-BC samples was determined by introducing a calibrated potentiometer in the saturated paste that was obtained for the calculation of the WHC. The TOC was determined by the Walkley Black method based on the dichromate ion reduction, and the CEC was measured by the 1 N pH 7 ammonium acetate method (Gunarathne *et al.* 2020). Both methods are described in detail in the NTC5167 standard (ICONTEC 2011).

$$\mathrm{WHC} = \frac{\mathrm{V} \cdot 100}{\mathrm{W_{BC}}} \cdot \frac{100 - \mathrm{MC}}{100} \quad (2)$$

The BC ash mineral composition was measured through XRF analysis, under the ASTM D4326-94 standard (Vamvuka *et al.* 2009) using a *Thermo ARL Optim'X WDXRF* (Thermo Fisher Scientific Inc., USA) equipment. The BC sample was dried during 24 h at 110 °C then stabilized in a desiccator and calcined at 950 °C. The XRF analysis was carried out in a He atmosphere at a room temperature during 25 min. The oxides present in the ashes and quantified were CaO, MgO, P_2O_5, K_2O, MnO, SO_3, SiO_2, Al_2O_3, Na_2O, BaO, CuO, TiO_2, Fe_2O_3, NiO, and SrO.

RESULTS AND DISCUSSION

BC physicochemical characterization

The results of the physical and chemical properties of the PL, CH, PL-BC and CH-BC are shown in Table 1. The ash mineral composition of the four samples, on absolute base and without considering losses by ignition, is shown in Table 2. The parameters, presented in this section, were measured in duplicate with a variation below 3 %, thus the average value is presented.

Table 1: Physicochemical properties of the raw biomasses (PL and CH) and the produced BCs (PL-BC and CH-BC).

Properties	**PL**	**CH**	**PL-BC**	**CH-BC**	**Standard**
Physical properties					
BET surface area [m^2/g]	1,16	4,66	367,33	233,56	-
Pore volume, Pv [cm^3/g]	0,0006	n.d.	0,20	0,13	-
Ultimate analysis (wt% dry ash free)					
Carbon	46,83	47,38	97,94	97,06	ASTM D5373-08
Hydrogen	5,67	6,08	0,97	0,85	ASTM D5373-08
Oxygen	47,48	46,38	0,90	1,66	By difference
Nitrogen	0,02	0,16	0,19	0,43	ASTM D5373-08
Proximate analysis (wt% dry base)					
Volatile matter	84,64	83,83	20,59	24,36	ASTM D5142-04
Fixed carbon	14,09	15,85	77,49	72,90	By difference
Ash content	1,27	0,32	1,92	2,74	ASTM D5142-04
Moisture content, M [wt%]	7,91	11,12	11,13	11,63	ASTM D5142-04
Aromaticity index, A [-]	0,14	0,16	0,79	0,75	Eq. 1
Soil amendment					
pH [-]	n.m.	n.m.	8,80	9,00	NTC5167
Total oxidizable organic carbon, TOC [%]	n.m.	n.m.	33,80	23,90	NTC5167
Water-holding capacity, WHC [%]	n.m.	n.m.	219,00	186,40	NTC5167
Cation exchange capacity, CEC [meq/100 g]	n.m.	n.m.	21,70	22,60	NTC5167
n.m.: not measured; n.d.: not detected.					

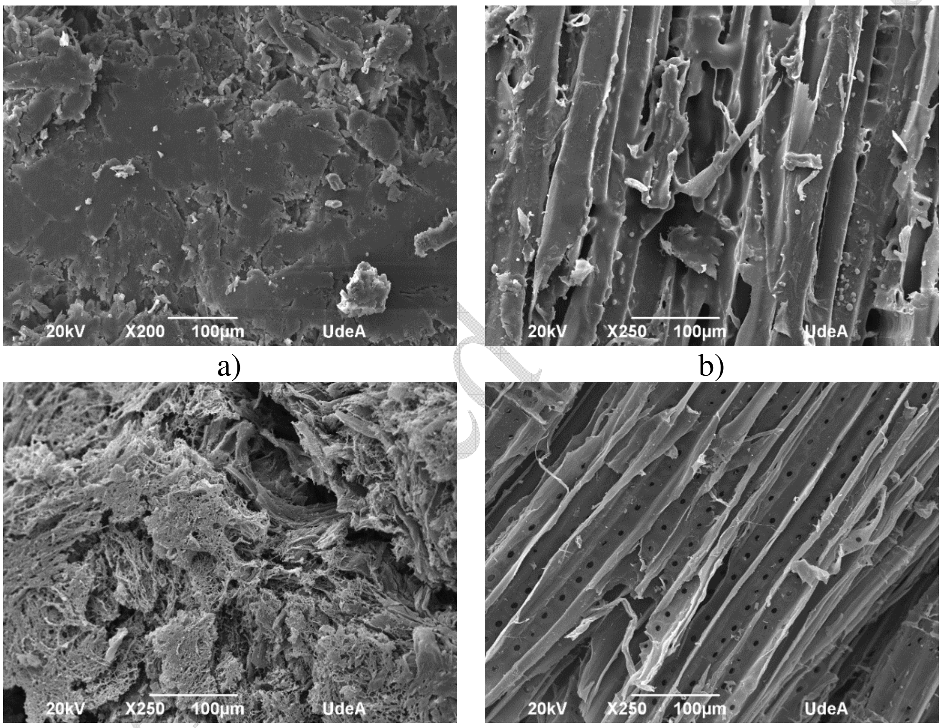
Table 2: Ash mineral composition of the raw biomasses (PL and CH) and the produced BCs (PL-BC and CH-BC).

Mineral content (AC%)	**PL**	**CH**	**PL-BC**	**CH-BC**
CaO	55,90	46,13	53,42	55,53
MgO	14,86	16,97	15,41	16,70
P_2O_5	10,86	15,31	9,23	9,52
K_2O	0,00	0,97	6,91	2,98
MnO	6,23	6,13	6,17	5,76
Al_2O_3	3,04	1,25	2,58	2,03
SO_3	4,10	7,24	2,43	2,87
SiO_2	2,66	3,74	1,99	2,60
Fe_2O_3	0,96	1,61	0,74	1,01
Na_2O	0,00	0,00	0,46	0,45
SrO	0,59	0,65	0,33	0,19
BaO	0,00	0,00	0,21	0,17
CuO	0,00	0,00	0,12	0,12
TiO_2	0,00	0,00	0,00	0,07
NiO	0,80	0,00	0,00	0,00

The difference in the BET surface area between the raw biomasses and the BCs was ~97 % (Table 1), due to the opening of the closed pores and the widening of the open pores during the gasification process (Hernández *et al.* 2016). The BET surface area for the PL-BC was ~36 % higher than that of CH-BC, with values of 367,33 m^2/g and 233,56 m^2/g, respectively. This result was attributed to the lower fuel-air ratio reached during pellet gasification to produce the PL-BC (BC production section), which favored a higher process temperature (~41 % higher gasification temperature for the PL-BC when compared to the CH-BC). The higher temperature in the gasification process fosters hemicellulose and cellulose degradation, which is reflected in the lower VM content. The release of VM caused changes in BC morphology and gave way to a porous carbonaceous structure (González and Pérez 2019), which allows to consider the use of PL-BC and CH-BC in the amendment of degraded soils without having the need for a process of additional activation (Trigo *et al.* 2016). Furthermore, the Pv (0,20 cm^3/g) of the PL-BC was ~35 % higher than that of the Pv found for the CH-BC (0,13 cm^3/g), which is also ascribed to the higher temperatures reached during the gasification process for obtaining the PL-BC.

In Figure 2a and 2b, the SEM images for the PL and the CH, respectively, are shown. A compact structure is observed for the PL as a result of the densification process (González *et al.* 2020), while the CH showed a fibrous structure, which is distinctive of ligneous biomasses (Nanda *et al.* 2013). The PL-BC (Figure 2c) showed an amorphous porous structure as a consequence of the higher gasification temperatures; and in the CH-BC (Figure 2d) the pores opening is observed due to the gasification process. The higher BET and Pv values reached for the PL-BC (Table 1) match the observations made in the SEM images, where it is evident that from the pellet gasification a more porous carbonaceous coproduct is obtained. Therefore, it is worth noting that the PL-BC has more reactive sites for alternate uses. Nevertheless, both BCs show a porous structure with a high surface area and a considerable pore diameter. These features improve the soil characteristics regarding the decrease in its apparent density, the increase in the WHC, which favors the aggregate formation, and the increase in organic matter content (Zhang *et al.* 2021).

Concerning the ultimate and proximate analyses reported in Table 1, the VM content of the BCs decreases with regard to the raw woods. The VM of the raw woods went from 83,83 % - 84,64 % to 20,59 % - 24,36 % for the BCs. VM reduction is attributed to the reactions involved in the gasification stages (drying, pyrolysis, oxidation, and reduction). Therefore, it is concluded that a high percentage of VM present in the raw matter went on to form the producer gas (González *et al.* 2018, Gutiérrez *et al.* 2021).



a) b)

c) d)

Figure 2: Surface morphology through SEM images × 250 for (a) PL, (b) CH, (c) PL-BC and (d) CH-BC.

This process of solid-gas conversion is reflected in the low content of H and O, and the high content of C in the BCs, which has a direct relation with the formation of a FC-rich material (77,49 wt% and 72,9 wt% for the PL-BC and the CH-BC, respectively) (Dunnigan *et al.* 2018). The FC is ~5 times higher for the BCs with regard to the raw biomasses (Table 1). The C content reached for the PL-BC (97,94 wt%) and the CH-BC (97,06 wt%) meets the values set by the European Biochar Certificate (EBC); where a minimum C content of 50 % allows to use a BC as a soil amendment (EBC 2019). Furthermore, Bayu *et al.* (2017) stated that a high concentration of C in the BC favors the properties of the material to be used as a soil amendment since the C availability in the treated soil increases. Additionally, it is highlighted that during the gasification process, the N is transformed into water-soluble compounds, such as the ammonium nitrate (De la Rosa *et al.* 2016), which benefits the fixation of microbial and vegetable N. This favors the biogeochemical cycle of N and reduces nitrous oxide emissions (N_2O) through nitrification and denitrification (Wang *et al.* 2019).

The differences in the contents of VM, FC and AC between the PL-BC and CH-BC (Table 1) were the result of the higher temperatures reached during the PL gasification (Gutiérrez *et al.* 2021). The VM content was 15,5 % lower for the PL-BC than that of the CH-BC, with values of 20,59 wt% and 24,36 wt%, respectively, which allowed to obtain a FC concentration 6 % higher for the PL-BC. The AC reached for the BCs (1,92 wt% for the PL-BC and 2,74 wt% for the CH-BC) matches the AC of the lignocellulosic biomasses, which is less than 2,5 wt% (Díez and Pérez 2017). The slight increase in the AC of the BCs, when compared to the raw biomasses, was attributed to the thermal degradation of biomass constituents (hemicellulose and cellulose) during the gasification process (Wang *et al.* 2014). The difference in the MC between PL-BC and CH-BC was lower than 5 %. Even though the temperatures during the gasification process were higher than 700 °C inside the reactor (González and Pérez 2019), the MC of 11,13 wt% for the PL-BC and 11,63 wt% for the WC-BC was ascribed to the steam produced from the oxidation reactions, which condenses on the solid carbonaceous matrix of the BC due to the gasification reactor settings (Díez and Pérez 2019).

The high temperatures inside the reactor associated with the gasification process favored the decrease in the functional groups onto the surface of the BCs. Figure 3 shows the functional groups on the surface of the raw biomasses and the BCs. The decrease in the hydroxyl (-OH) and aliphatic (-CH) groups, which correspond to the peaks between 3700 cm^{-1} – 3000 cm^{-1}, and 2980 cm^{-1} - 2800 cm^{-1}, respectively, resulted from the release of the MC, and the biomass hemicellulose and cellulose degradation. Furthermore, the A index ~5 higher for the BCs in comparison to the raw biomasses -PL and CH- (Table 1) reflects the decrease in the OH and CH functional groups (Qian *et al.* 2013). As a consequence of the peaks reduction, between 1800 cm^{-1} and 1600 cm^{-1} (C=O and C=C), between 1200 cm^{-1} and 1000 cm^{-1} (C-O-C), and between 850 cm^{-1} and 650 cm^{-1} (C-H) in the BCs regarding to the raw biomasses, the BCs reached an aromatic structure. Hence, the aromaticity of BCs is related to its basic pH and a lower CEC (Lee *et al.* 2010), see BCs as soil amendments section.

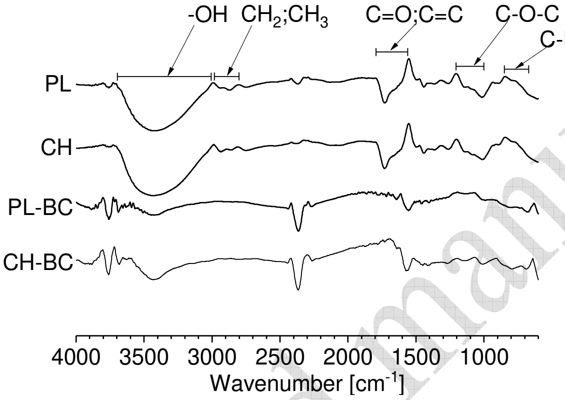


Figure 3: FTIR spectrum for PL, CH, PL-BC and CH-BC.

BCs as soil amendments

Table 3 shows the standards that materials must fulfill to be classified as a soil amendment according to the NTC5167 standard (ICONTEC 2011). It is worth noting that the properties of the BCs analyzed herein, met the requirements of the standard, with the exception of the CEC. The CEC is a property that favors the plants nutrition and growth, since the soil absorbs ammonium (NH_4^+) and K^+, calcium (Ca^{2+}) and magnesium (Mg^{2+}) ions (Ok *et al.* 2016). Here, the CEC reached values of 21,70 meq/100 g for the PL-BC and 22,60 meq/100 g for the CH-BC, which might be attributed to the high temperatures of the gasification process. These caused a reduction in the carboxyl (-COOH), hydroxyl (-OH) and carbonyl (-CO) functional groups (Lee *et al.* 2010). Consequently, the BC has a more stable structure (aromatic structure) that promoted the Na^+, K^+ and Mg^{2+}cation bonds through cation-π interactions; these bonds are directly related to the decrease in the CEC (Gomez-Eyles *et al.* 2013). Besides, the low AC in the BCs entails low mineral contents such as Mg, K and sodium (Na), which are in charge of increasing the CEC (Mia *et al.* 2015). In Table 2, the PL-BC was found to exhibit a mineral content of 15,41 % Mg, 6,91 % K, and 0,46 % Na; while the CH-BC reached concentrations of 16,70 % Mg, 2,98 % K, and 0,45 % Na.

Table 3: Required specifications by the NTC5167 standard (ICONTEC 2011) to use a material as a soil amendment. Adapted from (ICONTEC 2011).

Property	Value
AC	< 60 %
MC	< 35 %
TOC	> 15 %
CEC	> 30 meq/100 g
WHC	Minimum own weight of BC
pH	4 – 9
Maximum content of heavy metals	
Arsenic (As)	< 41 mg/L
Cadmium (Cd)	< 39 mg/L
Chromium (Cr)	< 1200 mg/L
Mercury (Hg)	< 17 mg/L
Nickel (Ni)	< 420 mg/L
Lead (Pb)	< 300 mg/L

The TOC was 33,8 % for the PL-BC and 23,9 % for the CH-BC (Table 1), meeting the NTC5167 standard (ICONTEC 2011). These TOC values are ascribed to the high PL-BC and CH-BC recalcitrant fraction (FC), which was produced by the biomass thermal degradation during the gasification process (Ok *et al.* 2016). The WHC is an especially important property for the use of BC as a soil amendment, because WHC helps to increase crop water and nutrient absorption (Yu *et al.* 2017). In this case, the WHC reached values of 219 % and 186,4 % for the PL-BC and the CH-BC, respectively, which meet the NTC5167 requirement (ICONTEC 2011). This result was attributed to the opening of the closed pores and the widening of the open pores in the BCs due to the VM release during the biomass gasification process. Consequently, the surface area rose because of the increased number of pores and their average radius (Hernández *et al.* 2016), which favors the WHC (Díez and Pérez 2019). It is worth noting that both properties, TOC and WHC, were higher for the PL-BC when compared to the CH-BC (~29 % higher TOC and ~15 % higher WHC for the PL-BC). Therefore, better results for the BC derived from PL as a soil amendment are expected.

Concerning the pH, the PL-BC reached a pH of 8,8 and the CH-BC pH was of 9,0, which meet the NTC5167 standard (ICONTEC 2011). The basic character of both BCs was attributed to the presence of basic functional groups that capture inorganic minerals and alkali compounds such as hydroxides, nitrates and carbonates during the gasification process. According to Zhang *et al.* (2021), the BC from lignocellulosic biomass has a pH between 7,0 and 10,4 because during the gasification process, the organic acid volatilization and the acid functional groups decomposition (-COOH, -OH and phenolic functional groups) occur; as it was described in the FTIR spectrum in BC physicochemical characterization section. The PL-BC and CH-BC can be suitable to improve acid soils properties because they would promote the proton (H^+) interchange with the soil, favoring the rise in the soil pH and, consequently, improving the nutrient bioavailability such as Mg, Ca and P for the plants (van Zwieten *et al.* 2010).

Finally, heavy metals contents were not found in the PL-BC and CH-BC, as it was indicated by the NTC5167 (ICONTEC 2011). Similar results were reported by Díez and Pérez (2019) when characterized BCs derived from the gasification of different forest species (wood chips). Therefore, according to the properties of PL-BC and CH-BC, these BCs can be used as soil amendments, mainly acid ones (Bayu *et al.* 2017). Concerning the CEC, there are alternatives to improve this property, among which it is highlighted the mixing with compost (Nsamba *et al.* 2015).

Mineral content of PL-BC and CH-BC

Table 2 shows the mineral content of ashes for the PL, CH, PL-BC and CH-BC. No significant differences between the raw biomasses and the BCs were found. Thereby, it is stated that the gasification process did not generate a significant change in the mineral ash composition between the biomasses gasified here. The BCs coming from lignocellulosic biomasses generally contain macronutrients such as Ca, K and P, secondary macronutrients such as Mg, and micronutrients such as manganese (Mn), zinc (Zn), copper (Cu), iron (Fe), molybdenum (Mo), and boron (B). Whereby, the application of BC to the soil represents an important nutrient reserve (Baptista *et al.* 2013), which leads to improve the plant growth (Zhang *et al.* 2021). Herein, both BCs (PL-BC and CH-BC) showed a similar composition regarding their ash mineral content since they came from the same forest species (*Pinus patula*). The BCs studied have a significant amount of macronutrients, from which Ca is the most abundant with 53,41 % for PL-BC and 55,53 % for the CH-BC, followed by P with 9,23 % for the PL-BC and 9,52 % for the CH-BC, and K with 6,91 % for the PL-BC and 2,98 % for the CH-BC. This mineral content allows to infer a positive behavior of the BCs generated here to be used in soil amendment because plants require high levels of Ca, P and K (Baptista *et al.* 2013). The produced BCs also contribute to the improvement of the geochemical cycle and effectiveness of P, silicon (Si) and N in the soil; increasing the agricultural productivity. Besides, Si is a mineral that helps with carbon stability, improves crops resistance to disease and plagues and inhibits the adsorption of heavy metals from the plants roots (Detmann *et al.* 2012).

Mg (a secondary macronutrient) content was 15,41 % for the PL-BC and 16,70 % for the CH-BC. Alternatively, micronutrients present in the PL-BC reached values of 6,17 %, 0,12 % and 0,74 % for Mn, Cu and Fe, respectively. Meanwhile, for the CH-BC, they reached values of 5,76 % Mn, 0,12 % Cu, and 1,01 % Fe. It is worth noting that the presence of Fe and aluminum (Al) in the BCs is important for the soil amendment because these elements allow for the retention of P, especially in acid soils (Bayu *et al.* 2017). The stability of the soil structure, particularly, the stability of secondary pores is favored by several substances with binding effects such as the organic substances and Al and Fe oxides. The binding effect of these substances increases the resistance to shearing both between primary particles as well as between soil aggregates (Blume *et al.* 2016). The maximum levels allowed for the Al content in the BCs are not specified in the NTC5167 standard (ICONTEC 2011). On the other hand, it is highlighted that in the BCs studied in the current work (PL-BC and CH-BC) no traces of heavy metals such as lead (Pb), cadmium (Cd), and mercury (Hg) were found, which are highly toxic for the soil, fauna and flora (Godlewska *et al.* 2021). This is another point in favor for the application of BCs coming from the gasification of patula pine in soil amendment.

CONCLUSIONS

Both produced BCs (PL-BC and CH-BC) were found to be materials with a porous structure and a suitable BET surface area. These properties are adequate for the application of the referred BCs in the improvement of soil characteristics, such as the decrease in the apparent density and the increase in the WHC. The obtained BCs met the specifications of the NTC5167 standard, including the pH, MC, and the heavy metals content, which were non-detected in the BCs studied here. Nevertheless, better results are expected to be achieved for the PL-BC when compared to the CH-BC as a soil amendment, since the PL-BC has a more porous structure, higher surface area, pore diameter, FC and TOC contents, and a better WHC. The CEC was the only property that did not meet the standard because of a reduction in the functional groups COOH, -OH and -CO, as a result of the high temperatures reached during the gasification process. The basic pH of the BCs (PL-BC and CH-BC) makes them suitable for the treatment of acid soils and generates an increase in the nutrient bioavailability. Furthermore, the mineral content in the ashes, among which the presence of micro and macro nutrients is noted, and metals, such as Fe, would allow for the retention of P in acid soils through the application of the BCs assessed.

In this regard, further researches are required by implementing the BCs analyzed in degraded and eroded soils in order to validate their capacity as soil amendment.

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