

Variation in the properties of biochars produced by mixing agricultural residues and mineral soils for agricultural application

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Abstract

The research and application of biochars enriched with minerals have increased in recent years; however, the mineral fraction used consists of specific minerals, such as clay minerals and synthesized compounds. In this work, the effects of adding two specific soil types (sandy and clayey) to rice and coffee husks in order to generate biochars via pyrolysis was investigated. Chemical, physical–chemical, thermal, spectroscopic and crystallographic analyses were conducted on the produced biochars. The study confirmed that the presence of mineral soils during the pyrolysis process increases the yield, C retention ratio, and specific surface area. It also decreases the pH, cation exchange capacity (CEC), nutrient content, and carbon-to-nitrogen ratio of biochars. However, the biochars produced by mixing coffee husks and mineral soils still demonstrate a capacity to increase the pH and the CEC of tropical soils. In addition, increased C retention demonstrates an environmental benefit of this biochar production method. Biomass pyrolysis combined with clayey soil results in a biochar with a higher degree of aromaticity and higher thermal stability when compared to biomass pyrolysis alone. These characteristics give the biochar a recalcitrant character, without the necessity for steps related to the synthesis of specific mineral compounds, which reduces the economic and energy cost of the process.

Keywords

Biochar properties, biomass, coffee husk, crop residues, pyrolysis, rice husk, surface chemistry, soils

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Introduction

Biochar is the carbon (C)-rich material produced by biomass pyrolysis at temperatures ranging from 300 to 900°C, forming predominantly recalcitrant and stable organic C structures (Wang and Wang, 2019).

These physicochemical properties give to biochar a series of characteristics that have attracted interest for its industrial (as adsorbent material for filters) (Liu et al., 2019), environmental (reduction of greenhouse gas emissions, wastewater treatment and soil decontamination), and agricultural use (such as fertilizer and soil conditioner) (Ding et al., 2017).

The amendment of biochar to the soil has attracted significant interest over the past decade due to a several reasons such as: (a) biochar is a good alternative for crop residues and solid waste disposal; (b) biochar improve soil quality and plant growth; and (c) biochar contributes efficiently to carbon dioxide (CO₂) capture and sequestration (Ding et al., 2017).

Nevertheless, biochar may have heterogenous properties depending on the characteristics and composition of the raw material and conditions of pyrolysis (Ding et al., 2017). For example, it was shown that biochar produced under CO₂

atmosphere has better pore structure, holds more nutrients and produces better nutrient speciation than biochar produced under nitrogen (N₂) atmosphere. It has also been shown that the best temperature range for biochar preparation is from 350°C to 400°C, as macronutrient loss is reduced and the nutrient bioavailability increases (Tian et al., 2017).

Moreover, pyrolysis temperature is a key factor determining the properties of the biochar and its behavior in soil. For that

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matter, it has been observed that the degree of aromaticity and C stability of biochars produced by low pyrolysis temperature are lower than those produced at higher temperatures and, therefore, their residence time in the soil is shorter (Zhang et al., 2020). However, it was observed that biochar stability increases when a mineral fraction such as vermiculite, is introduced into its preparation (Liu et al., 2020).

At the agronomic level, biochars enriched with clay minerals and fertilizers have been proposed to have a high cation exchange capacity (CEC), a high potential for soil acidity neutralization, a high nutrient content, and a long residence time in the soil (Chia et al., 2014). This long residence time is explained by the kind of organic mineral complex formed during heating of organic material in the presence of mineral compounds (Chia et al., 2014).

Different kinds of mineral compounds (e.g. clay minerals, synthesized compounds, and mineral fertilizers) and different methods have been used to modify biochar properties (Chia et al., 2014; Liu et al., 2020). For instance, Chia et al. (2014) first produced and activated the biochar, then mixed the biochar with the mineral compounds in an aqueous solution, then dried and torrefied the mixture to ensure the reaction of the organic and mineral molecules. Liu et al. (2020) used a simpler method, mixing vermiculite and biomass and then heating the mixture.

In this sense, simpler methods with lower economic and energy costs are highly advisable, as despite the large number of studies with biochar, its commercialization and worldwide agricultural application is still negligible (Maroušek et al., 2019).

Taking these aspects to account, the hypothesis of this study is that biochars with the functional and recalcitrant properties can be obtained by biomass pyrolysis in the presence of a mineral soils. Therefore, this study was performed to determine the effects of the presence of mineral soil during biomass pyrolysis on the physicochemical properties of biochars. For this purpose, pyrolysis of two agricultural residues (rice and coffee husks) in the presence of two kinds of soils (sandy and clayed soils) was carried out at low temperature (350°C) and their properties and agronomy quality were evaluated.

These materials and pyrolysis method were selected because they do not require the steps of activation, drying, and torrefaction, contributing to the energy efficiency of biochar production. In addition, the selected residues are typical in Brazil, and other regions of America, Africa, and Asia, with an average production of 170 and 2 million tons per year, respectively (Abbasi and Abbasi, 2010), therefore, the results derived from this study can contribute to improving the quality of agricultural soils in tropical and subtropical areas around the world.

Material and methods

Feedstock of biochars

Two types of organic waste (rice and coffee husks) and two specific soil types (sandy and clayey) were used to produce biochars. Rice and coffee husks were obtained from a grain processing

Table 1. Properties of soils used in biochar composition.

Properties	Sandy soil	Clayey soil
pH	4.20	4.50
CEC (cmol _c kg ⁻¹)	2.98	6.18
Available P (mg kg ⁻¹)	1.00	1.00
Available K (mg kg ⁻¹)	0.05	0.05
Ca ²⁺ (cmol _c kg ⁻¹)	0.15	0.48
Mg ²⁺ (cmol _c kg ⁻¹)	0.08	0.15
H ⁺ (cmol _c kg ⁻¹)	1.70	4.90
Al ³⁺ (cmol _c kg ⁻¹)	1.00	0.60
Total Al (g kg ⁻¹)	41.81	149.25
Al-ox (g kg ⁻¹)	0.50	2.32
Total Fe (g kg ⁻¹)	13.99	10.71
Fe-ox (g kg ⁻¹)	0.14	1.54
Sand (g kg ⁻¹)	784.00	292.00
Silt (g kg ⁻¹)	95.00	104.00
Clay (g kg ⁻¹)	121.00	604.00
Mineralogy	K, Gh, and Gb	K, Gh, Hm, and Gb

CEC: cation exchange capacity; Al-ox: oxalate extractable aluminum; Fe-ox: oxalate extractable iron; K: kaolinite; Gb: gibbsite; Gh: goethite; Hm: hematite.

company, dried in a forced-ventilation oven at 105°C for 48 h and milled in a Wiley knife mill (TE-340/Tecnal) with a 0.7 mm sieve.

Biomass analyses were performed in duplicate. Elemental analyses (C, N, and S) were conducted using a FLASH 1112, Macromostrat LECO TruSpec CHNO Elemental Analyzer (Thermo Finnigan) and a LECO SC-144DR. Macronutrients concentration were extracted by acid digestion at 90°C using nitric acid, hydrogen peroxide, and hydrochloric acid (5:3:5) (Kimbrough and Wakakuwa, 1989). Phosphorus (P) concentration was determined by the colorimetric method with absorbance measured at 880 nm, according to Murph and Riley (1962) modified by Drummond and Maher (1995), using a JASCO spectrophotometer model V630. The calcium (Ca) and magnesium (Mg) contents were determined with atomic absorption spectroscopy, while potassium (K) contents were determined by flame photometry (Sparks et al., 1996), using a PerkinElmer 1100B atomic absorption spectrophotometer.

Soil samples were obtained in two areas of cultivated pastures (*Urochloa brizantha*), in Rondônia, Brazil. A soil profile was opened and classified in each area, and a single sample (approximately 30 kg) was collected at the depth of 10–20 cm from each profile. The soils were dried in a forced-ventilation oven at 105°C for 48 hours and sieved in 2 mm mesh.

The soils selected belong to the order of Oxisols (Soil Survey Staff, 2014), with a similar mineralogical composition characterized by the presence of kaolinite, goethite, hematite, and gibbsite (Table 1). The soil analysis was performed in duplicate. According to their granulometric composition, the soil samples were designated as sandy (sand = 784 g kg⁻¹) or clayey (clay = 604 g kg⁻¹) (Soil Science Division Staff, 2017). Soil pH was measured in water (1:2.5) using a glass electrode. Total content (C, N, S, P, K,

Ca, Mg, iron (Fe), and aluminum (Al)) was carried out in the same way as the biomass.

The exchangeable cations, Ca^{2+} , Mg^{2+} and Al^{3+} , were extracted using 1.0 M of KCl and measured with atomic absorption spectroscopy (PerkinElmer 1100B). H^+ and Al^{3+} were extracted with calcium acetate (0.5 M) at pH 7.0 and determined by titration (NaOH at 0.025 M). Available K and P were extracted with a Mehlich-1 solution. The amorphous Fe and Al oxyhydroxides (Fe-ox and Al-ox) were obtained by extraction with ammonium oxalate (pH 3.0) in a dark environment, and the quantification of Fe and Al was performed by atomic absorption spectroscopy (PerkinElmer 1100B) (Sparks et al., 1996).

The mineralogy was determined from samples in the form of non-oriented powder. X-ray diffraction (XRD) analysis was performed using an XRD diffractometer with Cu $K\alpha$ radiation (Shimadzu 6000-XRD). The X-ray source was operated at 40 kV and 30 mA. The instrument was equipped with a graphite monochromator. The scan rate was $1^\circ 2\theta \text{ min}^{-1}$ from 3 to 70° (2θ).

Preparation of biochars

The biomass (75 g) was packed in closed Al containers (159 mL) to create a CO_2 rich atmosphere, and pyrolysis proceeded in an EDG muffle furnace equipped with microprocessor controller at 350°C for 2 hours, discounting the equipment heating time and the material cooling waiting time (room temperature) (Matoso et al., 2019).

Biochars produced by mixing biomass and mineral soils were obtained in the same way but incorporated two different types of soil (sandy and clayed soil). The biomass was mixed with mineral soil at a ratio of 3:2 (60 g of biomass: 40 g of soil). These values were chosen since the mass loss of the control feedstock during the pyrolysis process resulted in a final 2:3 dry mass ratio, approximately. Similar value has been used by Chia et al. (2014). The obtained biochars were denominated as follows:

- (a) Ri, rice husk biochar;
- (b) Ri + S, biochar produced by rice husk and sandy soil;
- (c) Ri + C, biochar produced by rice husk and clayey soil;
- (d) Cf, coffee husk biochar;
- (e) Cf + S, biochar produced by coffee husk and sandy soil; and
- (f) Cf + C, biochar produced by coffee husk and clayey soil.

Characterization of biochars

Biochar yield and C retention. The biochar yield and C retention ratio was calculated according to Liu et al. (2020). These parameters were determined considering the loss in mass of raw materials (biomass and soil) and the mixtures during heat treatment. The biochar yield (1) and C retention ratio (2) were calculated by using equations (1) and (2):

$$Y = (\text{Mbc} - \text{Ms}) / \text{Mbm} \times 100 \quad (1)$$

where Y is the biochar yield (%), Mbc is the weight of biochar after pyrolysis (g), Ms is the weight of soil residues after heat treatment (350°C) (g), and Mbm is the weight of biomass before pyrolysis (g).

$$R = (Y \times \text{Cbc} / \text{Cbm}) \times 100\% \quad (2)$$

where R is the C retention ratio of biochar (%), and Cbc and Cbm are the C contents of biochar and biomass (%), respectively.

pH, elemental composition, and cation exchange capacity. The pH in biochar was measured with a biochar-to-deionized water ratio of 1:5, after stirring for 5 minutes and waiting 1 hour for equilibrium. CEC was determined using a modified NH_4^+ acetate compulsory displacement method (Sparks et al., 1996; Gaskin et al., 2008). Sodium acetate (1 M, pH 8.2) was used to saturate the exchange sites, and ammonium acetate (1 M, pH 7.0) was used to displace sodium ions. CEC was calculated from the Na^+ displaced by NH_4^+ .

The total concentration of biochar (C, H, N, O, S, P, K, Ca, and Mg) was performed using the same methods as from the biomass samples.

Specific surface area (SSA) and crystallographic structure. The SSA was determined by physical adsorption of N_2 using the isotherm of the Brunauer–Emmett–Teller method, which describes multilayer adsorption. Analyses were performed on a Micromeritics Corporation® ASAP 2020 instrument. Readings were performed at predetermined (0.05574, 0.15000, and 0.30045) relative pressure points.

The crystallographic structure of biochars was qualitatively analyzed in samples in the form of non-oriented powder. This analysis was performed using the same equipment and calibration as from the soil samples.

Thermal analytical measurements were simultaneously performed on samples through differential scanning calorimetry (DSC) and thermogravimetry (TG) using a Netzsch STA 449 thermal analyzer. Approximately 10 mg of biochar and soil samples were heated under an N_2 atmosphere from room temperature to 1100°C at a linear heating rate of $10^\circ\text{C}/\text{minute}$.

For each biochar, a 1:100 pellet (sample: potassium bromide) was prepared, and the Fourier-transform infrared (FT-IR) spectra were recorded in the $4,000$ to 400 cm^{-1} region with a resolution of 1 cm^{-1} in a FT-IR Spectrometer PerkinElmer Spectrum Two.

Results and discussion

Biochar yield

The biochar yields of the two agricultural residues were similar (between 45 and 46%) and increased (by 9 to 16%) from Ri + S, Ri + C, Cf + S, and Cf + C samples (Table 2). Previous studies have established that the main transformations of the biomass submitted to pyrolysis at 380°C , are loss of moisture and

hydration water, and the decomposition of hemicellulose and cellulose, but the effect of pyrolysis on the biochar yield depends on the composition of the raw material (He et al., 2018; Zhang et al., 2020). In our case, the content of these compounds in rice and coffee husks is similar (Boufi, 2017; Oliveira et al., 2018), which explains the similar yields obtained. However, when the soil was incorporated into biomass and pyrolysis was carried out, in all cases a higher yield was obtained than the Ri and Cf samples, due to less thermal degradation of the mineral fraction when compared to the organic fraction (Liu et al., 2020).

Physicochemical properties of biochars

The pH of biochars ranged from 6.2 to 9.9 (Table 2), as in previous studies (Chia et al., 2014; Jindo et al., 2014). pH values were mainly influenced by the type of biomass. The highest pH values corresponded to biochars derived from coffee husk (Cf) and their

Table 2. Yield, carbon (C) retention ratio, pH, cation exchange capacity (CEC) and specific surface area (SSA) of biochars produced by mixing agricultural residues and mineral soils.

Biochar	Yield	C retention ratio	pH	CEC	SSA
	%	%		cmol _c kg ⁻¹	m ² g ⁻¹
Ri	45.26	56.76	7.6	20.81	2.08
Cf	46.42	61.44	9.9	89.27	0.63
Ri + S	52.65	69.67	7.2	8.49	2.50
Ri + C	51.49	72.86	6.2	13.38	14.45
Cf + S	50.60	78.17	9.8	40.89	2.53
Cf + C	52.85	74.13	8.9	47.11	16.80

Ri: rice husk biochar; Cf: coffee husk biochar; Ri + S: biochar produced by mixing rice husk and sandy soil; Ri + C: biochar produced by mixing rice husk and clayey soil; Cf + S: biochar produced by mixing coffee husk and sandy soil; Cf + C: biochar produced by mixing coffee husk and clayey soil.

mixtures with soils (Cf + S and Cf + C), with values ranging from 8.9 to 9.9. While Ri and their mixtures with soils (Ri + S and Ri + C) resulted in a more acidic reaction (6.2–7.6).

The SSA varied widely (0.63 to 16.80 m² g⁻¹), corresponding to the highest values to clay soil (Ri + C and Cf + C) (Table 2). These values are below those observed in previous studies (Jindo et al., 2014; Li et al., 2015). At pyrolysis temperatures below 450°C, an increased percentage of condensed volatile compounds relative to the condensed aromatic structures are present (Tarelho et al., 2020). These compounds can obstruct the pores formed during pyrolysis (Ding et al., 2017), which explain the low SSA (<17 m² g⁻¹) in our biochars.

However, when pyrolysis occurred along with the soil, the organic compounds were bound to the mineral phase, maintaining the original porosity of the soil, and thus the mixture of biomass with clayey soil resulted in a higher SSA (Table 2). Similar results were found by enriching biochar with clay minerals (Li et al., 2015; Zhao and Zhou, 2019).

The CEC of biochars was influenced by the feedstock type (Table 2). The CEC of Cf (89.27 cmol_c/kg) was higher than Ri (20.81 cmol_c/kg), because the coffee husks have a higher mineral content (P, K, Ca, Mg, and Na) than rice husks (Table 3). High concentration of P, K, Mg, and Na, can catalyze oxygen chemisorption on the surface of the coal at low temperatures (Gaskin et al., 2008; Meszaros et al., 2007). For this reason, O:C atomic ratio of Ri (O:C = 0.18) was lower than Cf (O:C = 0.26) (Table 2) suggesting a higher content of carboxylic groups in Cf. Gaskin et al. (2008) obtained similar results for a wide group of materials such as poultry litter, peanut hulls, and pine chips.

On the other side, our results showed a clear decrease of CEC in Ri + S, Ri + C, Cf + S, and Cf + C samples, ranging 36–60% when compared to Ri and Cf samples (Table 2). The Cf + C and Ri + C samples showed smaller CEC reduction. A small amount of the difference observed for CEC can be explained by the difference of 3.12 cmol_c kg⁻¹ between the clayey and sandy soil

Table 3. Elemental content (g kg⁻¹) and atomic ratios of feedstock and biochars produced by mixing agricultural residues and mineral soils.

	Rice husk	Coffee husk	Sandy soil	Clayey soil	Ri	Cf	Ri + S	Ri + C	Cf + S	Cf + C
C	400.7	423.5	4.73	13.18	502.50	560.50	228.00	249.50	281.30	267.30
H	56.27	57.13	2.30	16.10	34.81	41.14	18.07	25.09	22.90	25.97
O	307.96	316.45	–	–	121.00	193.50	67.60	124.80	97.40	126.70
H:C	1.69	1.62	5.84	14.67	0.83	0.88	0.95	1.21	0.95	1.17
O:C	0.58	0.56	–	–	0.18	0.26	0.22	0.38	0.26	0.36
C:N	74.90	30.32	12.26	15.22	130.60	33.48	60.62	77.45	25.58	30.28
N	6.24	16.29	0.45	1.01	4.49	19.53	4.39	3.76	12.83	10.30
S	0.41	1.33	0.10	0.16	0.34	0.90	0.21	0.23	0.51	0.52
P	0.39	0.88	0.16	0.30	0.71	1.64	0.40	0.47	0.93	0.91
K	2.02	28.90	0.12	0.10	3.43	42.20	2.11	1.94	27.70	22.90
Ca	0.37	6.48	0.00	0.00	1.20	13.74	0.27	0.19	6.14	5.36
Mg	0.40	1.66	0.10	0.11	0.78	0.90	0.38	0.40	1.76	1.60

Ri: rice husk biochar; Cf: coffee husk biochar; Ri + S: biochar produced by mixing rice husk and sandy soil; Ri + C: biochar produced by mixing rice husk and clayey soil; Cf + S: biochar produced by mixing coffee husk and sandy soil; Cf + C: biochar produced by mixing coffee husk and clayey soil.

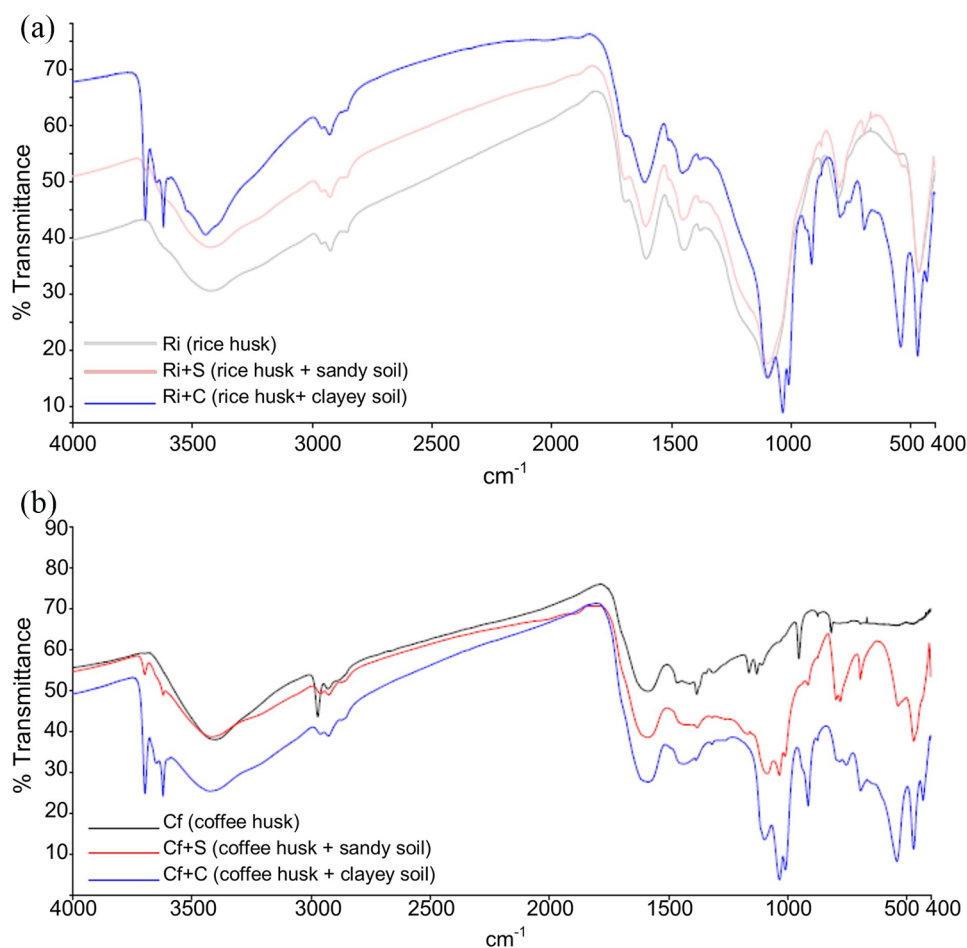


Figure 1. Fourier-transform infrared spectra of the of biochars produced by mixing agricultural residues and mineral soils: (a) rice husk biochar (Ri), biochar produced by mixing rice husk and sandy soil (Ri + S), biochar produced by mixing rice husk and clayey soil (Ri + C); and (b) coffee husk biochar (Cf), biochar produced by mixing coffee husk and sandy soil (Cf + S), and biochar produced by mixing coffee husk and clayey soil (Cf + C).

(Table 2), but the greater effect is explained by oxygen chemisorption in the organo-mineral complex formed in biochars produced by the addition of clay soil.

In this way, FT-IR spectra of the Cf, Cf + S, and Cf + C samples showed a shoulder around 1250 cm⁻¹ (Figure 1(b)), absent in biochars derived from rice husks, and that was attributed to the C–O stretching of carboxylic acids (Figure 1(a)). Carboxylic acids make up most of the total acidity of biochars (Song and Guo, 2012) and contribute to increasing CEC in relation to lactones. The lactone groups were identified in Ri, Ri + S, and Ri + C at a peak near 1695 cm⁻¹ (Figure 1(a)). In addition, the lower transmittance of peaks in the 1162–1010 cm⁻¹ region in Ri, Ri + S and Ri + C (Figure 1(a)) relative to Cf, Cf + S, and Cf + C (Figure 1(b)) was attributed to Si–O and not to OH groups of phenols.

In summary, our results indicate that biochars produced by mixing coffee husk and clayey soil resulted in a compound with a higher CEC and a lower transmittance of carboxylic groups than those formed from sandy soil. Thus, the clayey soils from other mineralogy can be better studied to compose biochars. The Cf, Cf + S, and Cf + C demonstrated a capacity to increase the pH of acidic soil and the CEC of mineral soils, mainly in tropical

regions that have a CEC close to 15 cmol_c kg⁻¹ and whose pH is characterized by acid reaction (Song and Guo, 2012).

Biochar CEC is mainly a result of acidic surface functional groups (Song and Guo, 2012). When the biochar is applied to the soil, there is an increase in the negative surface charge and oxygenated functional groups compared to the newly produced product (Joseph et al., 2010). Thus, the effect of biochars on soil CEC can be prolonged. However, positive results for pH are observed only in the first year of application (Carvalho et al., 2016).

Elemental composition of biochars

The behavior of the elements was not homogenous during the pyrolysis process (Table 3). In general, Ri and Cf samples showed an enrichment of C and loss of H, O, and S; while N behavior was different between the two plant materials.

The contents of C and H were higher in Ri (C = 502.50 g kg⁻¹ and H = 34.81 g kg⁻¹) and Cf (C = 560.50 g kg⁻¹ and H = 41.14 g kg⁻¹) compared to Ri + S, Ri + C, Cf + S, and Cf + C samples (C = 228–281 g kg⁻¹ and H 18.07–5.97 g kg⁻¹) (Table 3), because of the diluent effect of the mineral fraction (Chia et al., 2014; Zhao and Zhou, 2019). C retention ratio was higher in Ri + S, Ri + C,

Cf + S, and Cf + C samples (Table 2) due to organo-mineral interactions, which increase the stability of C, leading to lower CO₂ emission during the pyrolysis process (Liu et al., 2020; Matoso et al., 2019).

The mean concentration of N in rice and coffee husks were 6.24 and 16.3 g kg⁻¹, respectively. Ri lost (28%) N during pyrolysis, while in Cf there was an enrichment (20%) (Table 3). The loss of N is attributable to the removal of N via volatilization during pyrolysis in the form of ammonia, nitric oxide, and hydrogen cyanide (Tian et al., 2017). However, the loss of N and other elements depends fundamentally on the pyrolysis temperature, and the composition of the raw material (He et al., 2018). In biochar produced at temperatures up to 400°C, the N can form a stable C–N heterocycle, which results in the concentration of N in the biochar (Cao and Harris, 2010; He et al., 2018), but this effect has been observed only in biochars derived from raw materials rich in N (He et al., 2018; Zhang et al., 2020). Our results suggest that the type of raw material plays an essential role in the N balance before and after pyrolysis.

The C-to-nitrogen (C:N) ratio increased from 75 and 30 in rice and coffee husks to 131 and 33 in Ri and Cf samples, respectively (Table 3). A very high C:N ratio was observed for Ri, which may limit its agricultural use, due to the N immobilization process (Ameloot et al., 2015). Adding of soil to rice husks to obtain biochar resulted in a reduction of the C:N ratio by 54% with the use of sandy soil and 41% with the clay soil, which can then be an interesting strategy to increase its agronomic viability.

The content of sulfur (S) in biochars was lower when compared to the rice and coffee husks (Table 3). This result is explained by the ease of S loss during pyrolysis. The S from biomass is released as S oxides and carbonyl sulfide while pyrolyzing, and the loss can be up to 50% (He et al., 2018; Pariyar et al., 2020).

The phosphorous (P) content in the biochar was higher than the raw material, and this is in line with the conservative behavior of this element that lacks a gaseous phase during the pyrolysis process, especially at low temperatures, resulting in inorganic P concentration (Tan and Yuan, 2017; Tian et al., 2017). Xu et al. (2016) demonstrated that biomass pyrolysis at any temperature decreases the water-soluble P content in biochars, an agronomically interesting result, as it reduces the potential for P loss in the system. They also observed that the fractions considered bioavailable of P increase from 300 to 400°C in the biochars produced, demonstrating the viability of converting biomass into biochar for the P recycling.

Geogenic elements (K, Ca, and Mg) in raw materials was superior to coffee husk than rice husk (Table 3). This situation was maintained in the biochar, where we can clearly see relative enrichment because of the loss of moisture and hydration water, and the release of volatile matter (He et al., 2018; Zhang et al., 2020). In biochars produced at temperatures of 350 and 400°C, about 80% of K is present in water-soluble form, demonstrating the rapid availability of this element when the biochar is applied to soil (Tan and Yan 2017; Tian et al., 2017). Ca and Mg have less

bioavailability in biochars compared to K. Gaskin et al. (2008), working with a wide group of materials and with a pyrolysis temperature of 400°C, observed a similar bioavailability of Ca and Mg and that the increase in pyrolysis temperature leads to a reduction in its bioavailability.

Our results indicate that the elemental composition of different biochars agrees with the initial composition of the raw materials and the pyrolysis temperature. In up to 350°C, there are no significant losses of P, K, Ca, and Mg, resulting in their concentration in the final product (Tian et al., 2017). Coffee husk was the biomaterial to apply as source of nutrients to the soil in the form of biochar. The addition of mineral soils to the composition of biochars also reduced the content of N, S, P, K, Ca, and Mg, due to the low initial content in both soils and the diluting effect (Tables 1 and 3). However, in our case, at least to decrease the C:N ratio of biochars, the addition of soil was an interesting strategy.

Stability properties of biochars

No crystalline forms of C were observed in the Ri and Cf samples (Figure 2(b) and Figure 2(c)). The XRD pattern of Ri and Cf samples showed a strong noise in the region from 10 to 30 2θ°, which was attributed to the large amount of organic material that was not carbonized (Wang et al., 2012). These results were confirmed by the high mass loss up to 311°C (Tables 4 and 5) and by the high atomic ratio H:C (Table 3).

The high H:C ratio (> 0.8) (Table 3) indicates a low aromaticity and potential for C sequestration of biochars. Biochars produced by mixing biomass and soil also presented high H:C ratios, even higher than those of Ri and Cf. Nevertheless, as goethite and kaolinite were not completely disintegrated during pyrolysis (Figure 2(b) and Figure 2(c)), the H contained in the structure of these materials also contributed to the total content, and it is not appropriate to infer the degree of thermal conversion and aromaticity from this attribute (Liu et al., 2020). Thus, these aspects can be better discussed based on the thermal (TG–DSC) and FT-IR analyses.

The kaolinite and goethite observed in soils (Figure 2(a)) was maintained in biochars (Figure 2(b) and Figure 2(c)). The presence of goethite (identified by a peak at 0.269 nm) in clayey-soil modified biochars occurred because this mineral likely underwent partial substitution (up to 1/3) of Fe³⁺ by Al³⁺, leading to a higher thermal resistance (up to 400°C) (Cornell and Schwertmann, 2003).

Neoformation of magnetic Fe oxide was expected, but the magnetite and/or maghemite peaks (0.253 and 0.297 nm) (Cornell and Schwertmann, 2003) were not observed in the biochars, nor hematite peak (0.251 nm). Probably, part of the hematite was reduced to magnetite, but in an insufficient quantity to be detected by XRD. Associated to this, the increase of noise in the XRD patterns of the C-rich material made it difficult to identify the Fe oxide peaks (Cornell and Schwertmann, 2003).

For all biochars, a first mass loss region was observed up to approximately 180°C (Table 4), with an endothermic peak near 130°C (Table 5), characterized by loss of moisture and hydration

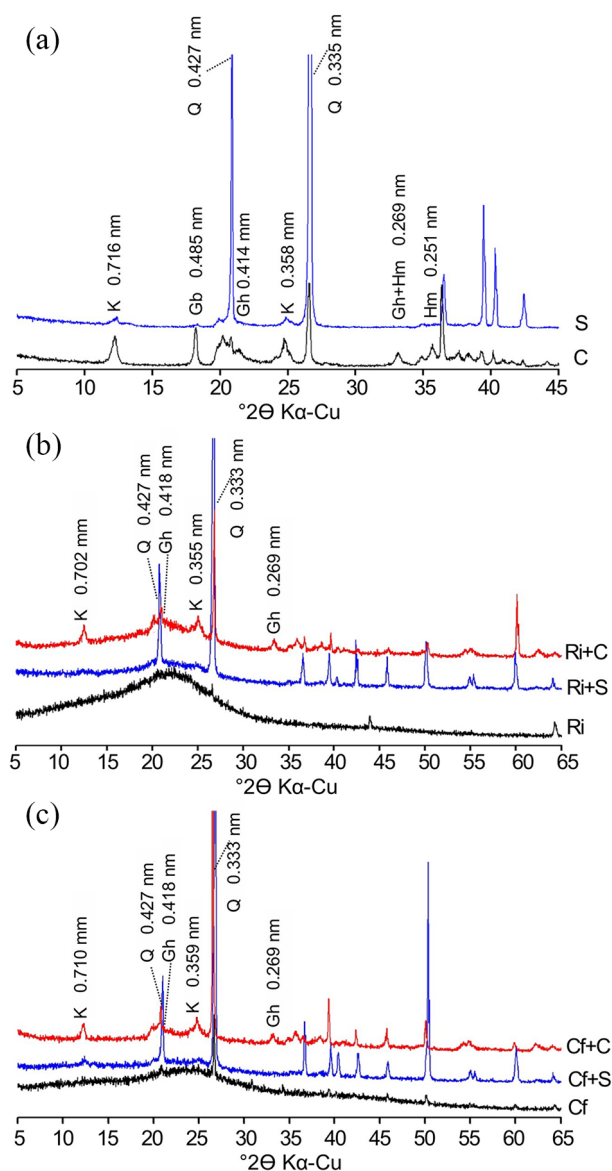


Figure 2. X-ray diffraction patterns of the mineral feedstock and the biochars produced by mixing agricultural residues and mineral soils: (a) sandy soil (S), clayey soil (C); (b) rice husk biochar (Ri), biochar produced by mixing rice husk and sandy soil (Ri + S), biochar produced by mixing rice husk and clayey soil (Ri + C); and (c) coffee husk biochar (Cf), biochar produced by mixing coffee husk and sandy soil (Cf + S), biochar produced by mixing coffee husk and clayey soil (Cf + C). K: kaolinite; Q: quartz; Gb: gibbsite; Gh: goethite; Hm: hematite.

water. In the temperature range approximately between 200 and 450°C, two primary exothermic reactions occurred, resulting from the thermal oxidation of organic compounds. The first reaction was characterized by the decomposition of aliphatic and functional groups, revealing an exothermic peak with a maximum at 311 and 268°C for Ri and Cf, respectively. The second exothermic event corresponded to the reaction of molecules containing aromatic rings and occurred at higher temperatures: 444 and 423°C, respectively (Table 5). It was found that Ri and Cf lost approximately 60% of their mass up to 669 and 700°C, respectively (Table 4).

A higher concentration of aliphatic than of aromatic compounds was found in Ri biochar, while the inverse result was observed for Cf. A higher transmittance of peaks in the 2970–2850 cm^{-1} region observed in the Cf samples indicates a small number of aliphatic groups (CH_3 and CH_2). For Ri, a lower transmittance of these peaks was observed, indicating a higher content of the aliphatic groups (Figure 1).

In Cf, mass loss up to 885°C was observed (Table 4). In this interval, an exothermic reaction (maximum temperature 756°C) and two endothermic reactions occurred (750 and 826°C) (Table 5). The exothermic reaction was characterized by the decomposition of recalcitrant organic compounds, while the endothermic reactions resulted from the dehydroxylation of amorphous silica compounds. For Ri, decomposition of silica compounds was evidenced at a lower temperature, 561°C (Table 5).

Biochars produced by mixing biomass and clayey soil presented a lower organic fraction, as observed by the lower mass loss and lower energy release during the exothermic events related to the decomposition of labile and aromatic compounds (Tables 4 and 5). As in the case of C and H contents, this result is explained by the lower relative biomass content in the composition of these biochars. The higher occurrence of exothermic peaks above 400°C (Table 5) indicates a higher degree of aromaticity of the organic compounds of these biochars. This result is corroborated by the lower transmittance of aromatic C–H groups (peaks between 873 and 805 cm^{-1}) and C=C (peaks between 1605 and 1587 cm^{-1}) of Cf + C. The peak at 695 cm^{-1} also reached a lower transmittance for biochars produced by mixing biomass and clayey soil; however, this peak may be derived from both aromatic C–C and translational O–H from kaolinite (Figure 1).

Our results of the TG–DSC and FT-IR analyses showed that the pyrolysis of biomass along with mineral soils increased the degree of aromaticity of the formed compounds, particularly with the combination of coffee husk and clayey soil. The high degree of aromaticity of biochar is interesting from the point of view of its greater resistance to biotic and abiotic decomposition processes (Chia et al., 2014; Zhang et al., 2020). Thus, biochars produced by mixing biomass and clayey soil can influence the physical–chemical processes of soil over a longer term than those that only have an organic composition.

Finally, studies should be carried out on the effect of biochars produced by mixing biomass and soil in different agronomic, edaphic, and environmental contexts to prove their potential for use. In addition, there are properties of these biochars that can be better studied, such as the stability of C, using biochar oxidation and mineralization techniques (Chia et al., 2014; Liu et al., 2020), and the adsorption power of nutrients, aiming at the enrichment of biochars (before their application to soil) with nutrients contained in liquid residues, such as waste water from agriculture or industry (Maroušek et al., 2019).

Despite the various benefits of using agricultural biochar, a high demand from the industrial and energy sector keeps the price of the product still high, which prevents its use on a commercial scale (Maroušek et al., 2017). In this context, Maroušek et al. (2019) point out that the production of biochar on a smaller

Table 4. Thermogravimetry data of the biochars produced by mixing agricultural residues and mineral soils.

Biochar or soil	Peak									
	1		2		3		4		5	
	T (°C)	Loss (%)	T (°C)	Loss (%)	T (°C)	Loss (%)	T (°C)	Loss (%)	T (°C)	Loss (%)
Ri	166	2.31	660	62.38	-	-	-	-	-	-
Cf	179	6.08	722	57.38	885	12.78	-	-	-	-
Ri + S	182	3.23	686	59.69	-	-	-	-	-	-
Ri + C	180	2.71	254	0.97	343	4.42	551	21.68	1097	28.6
Cf + S	179	2.76	674	25.00	835	4.78	-	-	-	-
Cf + C	174	4.52	474	21.36	724	20.59	-	-	-	-
Sandy soil	112	0.16	234	0.24	293	0.23	438	1.27	-	-
Clayey soil	260	3.50	327	1.26	470	3.82	-	-	-	-

Ri: rice husk biochar; Cf: coffee husk biochar; Ri + S: biochar produced by mixing rice husk and sandy soil; Ri + C: biochar produced by mixing rice husk and clayey soil; Cf + S: biochar produced by mixing coffee husk and sandy soil; Cf + C: biochar produced by mixing coffee husk and clayey soil; T: maximum peak temperature; Loss: mass loss.

Table 5. Differential scanning calorimetry data of biochars produced by mixing agricultural residues and mineral soils.

Biochar or soil	Peak	Endothermic						Exothermic				
		1	2	3	4	5	6	1	2	3	4	5
Ri	T	137	555	561	-	-	-	311	444	-	-	-
	E	-0.63	-4.7	-3.56	-	-	-	-0.38	-0.27	-	-	-
Cf	T	139	332	750	826	-	-	268	423	756	-	-
	E	-0.89	-3.81	-4.44	-2.46	-	-	-0.22	-0.28	-4.37	-	-
Ri + S	T	145	561	610	-	-	-	307	479	566	-	-
	E	-0.78	-11.08	-6.48	-	-	-	-0.48	-0.29	-0.13	-	-
Ri + C	T	146	353	454	567	737	889	261	328	487	573	886
	E	-0.28	-3.61	-4.57	-6.07	-6.92	-6.59	-0.32	-0.20	-0.23	-0.12	-6.56
Cf + S	T	132	356	566	588	676	793	199	435	571	-	-
	E	-0.18	-2.78	-5.18	-5.03	-4.36	-2.35	-0.11	-0.24	-0.1	-	-
Cf + C	T	135	352	467	679	-	-	281	427	687	-	-
	E	-0.27	-3.97	-6.03	-2.38	-	-	-0.31	-0.28	-0.23	-	-
S	T	225	574	954	-	-	-	78	236	576	940	-
	E	-0.46	-1.11	-1.90	-	-	-	0	-0.47	-1.09	-1.85	-
C	T	133	252	384	573	964	-	76	270	483	576	951
	E	-0.32	-0.50	-1.53	-1.87	-4.16	-	-0.12	-0.71	-1.61	-1.87	-4.17

Ri: rice husk biochar; Cf: coffee husk biochar; Ri + S: biochar produced by mixing rice husk and sandy soil; Ri + C: biochar produced by mixing rice husk and clayey soil; Cf + S: biochar produced by mixing coffee husk and sandy soil; Cf + C: biochar produced by mixing coffee husk and clayey soil; S: sandy soil; C: clayey soil; T (°C): maximum peak temperature; E: peak $\Delta H/\Delta t$ (mW/mg.min).

scale and close to sources of raw material and/or places of application are important aspects to reduce production costs.

In this sense, our study makes a significant contribution, because in Brazil, the production of charcoal for energy use is carried out mainly from wood (Silva et al., 2018), so agricultural residues can be an important source of biomass to produce biochar. We used a simplified biochar production process that indicates a decrease in operating costs and the possibility of reproduction in sites close to agricultural production areas. However, we emphasize that an in-depth economic analysis is recommended, as fixed and variable costs depend on each production site.

Conclusion

Our findings show that coffee husk provides better biochars for agricultural use than the rice husk. Biomass pyrolysis combined

with clayey soil results in a biochar with a higher degree of aromaticity and higher thermal stability when compared to biomass pyrolysis alone. These characteristics give the biochars a recalcitrant character, without the need for steps related to synthesis of specific mineral compounds, which reduces the economic and energy cost of the process. Thus, biochars produced by mixing coffee husk and clayey soil can be studied for agriculture application in different agronomic and environmental contexts.

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