



JEFFERSON SANTANA DA SILVA CARNEIRO

**CARBON STABILITY OF ENGINEERED BIOCHAR-BASED
PHOSPHATE FERTILIZERS**

**LAVRAS – MG
2018**

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Dissertation presented to the Federal University of Lavras, as part of the requirements of the graduate program in Soil Science, area of concentration in Soil Fertility and Plant Nutrition, to earn the title of Master.

Dr. Leônidas Carrijo Azevedo Melo
Advisor

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I DEDICATE

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ABSTRACT

Increasing soil organic carbon contents is important to increase soil quality and mitigate CO₂ emissions. Thus, pyrolysis of biomass to produce biochar has been investigated worldwide aiming to add stable carbon (C) to the soil and to improve its functional properties. In Brazil, large amounts of agro-industrial residues are produced show potential for this purpose. Although in the last decade a research efforts have advanced, there is still a long way to make biochar application viable at large scale. More recently, phosphate enriched-biochar has been proposed in order to be used as enhanced efficiency fertilizer with higher C stability as compared to regular biochars. But, due to the high acidity of some phosphate enriched-biochars, magnesium oxide (MgO) has also been proposed as additive to produce biochar-based fertilizers (BBFs). However, C stability in such materials is still poorly known. The general objective of this work was to evaluate how phosphoric acid (H₃PO₄) and MgO impregnation in the biomass will affect the thermal and chemical stability of the synthesized BBF. Phosphoric acid with and without MgO were premixed with coffee husk and poultry litter biomasses to produce BBFs by pyrolysis. The biomasses were also pyrolysed individually to produce simple biochar. The materials were chemically characterized and the C stability was thermally (thermogravimetric analysis and muffle oxidation) and chemically (H₂O₂ and K₂Cr₂O₇ oxidation) evaluated. All materials were characterized by Fourier transform infrared (FTIR) and Raman spectroscopic analysis. Results show that H₃PO₄ and H₃PO₄-MgO pretreatment increased yield and C retention in the BBFs, which showed higher thermal stability measured by TGA analysis and muffle oxidation as compared to simple biochars, causing lower mass loss and higher C remaining. Conversely, H₂O₂ oxidation was higher in the H₃PO₄-MgO treatment and K₂Cr₂O₇ oxidation in both H₃PO₄ and H₃PO₄-MgO treatments as compared to biochars, decreasing their chemical stability. The higher thermal stability of the BBFs was likely due to formation phosphorus complexes, such as C–O–PO₃ or (CO)₂PO₂ on BBFs. On the other hand, lower chemical stability was due to the high specific surface area (SSA) and lower crystallinity of C compounds of the BBFs caused mainly by MgO addition. This study indicates that co-pyrolysis of biomasses with H₃PO₄ + MgO increase yield (reduced C loss during pyrolysis) and thermal stability, but also increase chemical oxidation due to higher reactivity.

Keywords: Residues treatment. Pyrolysis. C sequestration. Tropical soil.

RESUMO

O aumento do conteúdo de carbono orgânico no solo é importante para aumentar a qualidade do solo e mitigar as emissões de CO₂. Assim, a pirólise da biomassa para produzir biocarvão tem sido investigada em todo o mundo com o objetivo de adicionar carbono (C) estável ao solo e melhorar suas propriedades funcionais. No Brasil, grandes quantidades de resíduos agroindustriais são produzidos e apresentam potencial para este propósito. Embora na última década os esforços de pesquisa tenham avançado, ainda há um longo caminho para viabilizar a aplicação de biocarvão em larga escala. Mais recentemente, o biocarvão enriquecido em fosfato foi proposto para ser usado como fertilizante de eficiência aumentada com maior estabilidade do C em comparação aos biocarvões regulares. Mas, devido à alta acidez de alguns biocarvões enriquecidos com fosfato, o óxido de magnésio (MgO) também tem sido proposto como aditivo para a produção de fertilizantes à base de biocarvão (BBFs). Entretanto, a estabilidade do C nesses materiais ainda é pouco conhecida. O objetivo geral deste trabalho foi avaliar como a impregnação com ácido fosfórico (H₃PO₄) e MgO na biomassa iria afetar a estabilidade térmica e química do BBF sintetizado. Ácido fosfórico com e sem MgO foram pré-misturados com biomassa de casca de café e de cama de frango para produzir BBFs por pirólise. As biomassas também foram pirolisadas individualmente para produzir biocarvões simples. Os materiais foram quimicamente caracterizados e a estabilidade do C foi termicamente (análise termogravimétrica e oxidação em forno mufla) e quimicamente (oxidação de H₂O₂ e K₂Cr₂O₇) avaliada. Todos os materiais foram caracterizados por análise espectroscópica de infravermelho com transformada de Fourier (FTIR) e Raman. Os resultados mostram que o pré-tratamento de H₃PO₄ e H₃PO₄-MgO aumentou a produção e retenção de C nos BBFs, que apresentaram maior estabilidade térmica mensurada pela análise de TGA e oxidação em forno mufla em comparação aos biocarvões simples, causando menor perda de massa e maior C remanescente. Por outro lado, a oxidação de H₂O₂ foi maior no tratamento com H₃PO₄-MgO e K₂Cr₂O₇ nos tratamentos H₃PO₄ e H₃PO₄-MgO em relação aos biocarvões, diminuindo sua estabilidade química. A maior estabilidade térmica dos BBFs provavelmente ocorreu devido à formação de complexos de fósforo, como C–O–PO₃ ou (CO)₂PO₂ nos BBFs. Por outro lado, a menor estabilidade química deveu-se à alta área superficial específica (ASE) e menor cristalinidade dos compostos de C dos BBFs causados principalmente pela adição de MgO. Este estudo indica que a co-pirólise de biomassas com H₃PO₄ + MgO aumenta a produção (redução da perda de C durante a pirólise) e estabilidade térmica, mas também aumenta a oxidação química devido a maior reatividade.

Palavras-chave: Tratamento de resíduos. Pirólise. Sequestro de carbono. Solos tropicais.

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PART I

INTRODUCTION

Highly weathered tropical soils are naturally of low fertility. In such environments, soil organic matter is the largest source of cation exchange capacity and therefore plays a crucial role in nutrient availability and crop yield and it is considered the main indicator of soil quality (CARMEIS FILHO et al., 2017). The increase in soil organic matter levels can be achieved by the adopted management as well as by application of organic residues or pyrogenic organic matter derived from the residues (WANG et al., 2017). In this sense, recycling organic waste is important from an environmental and agronomic point of view.

Brazil's agricultural production has grown rapidly in the last decades, driven mainly by technological advances. However, this rapid growth is responsible for the generation of large amounts of residues. For instance, Brazil is the first and second world producer of coffee and poultry, respectively (USDA, 2017a; USDA, 2017b). Thus, the disposal of residues their production has become a concern for the agricultural sector that increasingly seeks sustainable alternatives to the use of these residues (DALÓLIO et al., 2017; FERREIRA et al., 2018).

In 2017, the estimated production in Brazil of processed coffee was 2.69 million tons, and for poultry 13.3 million tons of meat (5.64 billion heads) (USDA, 2017a; USDA, 2017b). It is estimated that for each 1.0 ton of processed coffee, 1.0 ton of coffee husk is produced (DOMINGUES et al., 2017), and for each chicken about 1.75-1.80 kg of poultry litter is generated (DALÓLIO et al., 2017; ROGERI et al., 2016). Therefore, in 2017, about 2.7 million tons of coffee husk and 10.2 million tons of poultry litter were generated.

Coffee husks and poultry litter are nutrient-rich residues (NUNES et al., 2017; ROGERI et al., 2017). However, they have compounds which can limit their use *in natura* in soils. The coffee husk may contain compounds such as caffeine, tannins and polyphenols (NUNES et al., 2017) and an excess of potassium (BAÊTA et al., 2017). The problem with poultry litters is even greater because of its heterogeneous character, since it is composed of different materials. The poultry litter may contain residues of antibiotics, pesticides and herbicides, pathogens and phytotoxic substances that cause air and soil pollution and increase greenhouse gases emissions (DALÓLIO et al., 2017).

The indiscriminate disposal of this organic residues may cause environmental pollution, especially to groundwater and rivers (DALÓLIO et al., 2017; FERREIRA et al., 2018; NUNES et al., 2017; ROGERI et al., 2017). A widely used and efficient way of treating waste and avoiding such problems is composting, a natural process of aerobic decomposition by microorganisms (LIMA et al., 2017) marked by converting complex organic matter into simpler forms, with the benefits of mass and volume reduction, as well as the generation of an organic fertilizer (FERREIRA et al., 2018; MENG et al., 2017; YUAN et al., 2017). Composting is an efficient system for treating solid waste, since it is time-efficient and allows for recycling of nutrients (FERREIRA et al., 2018).

Despite the advantages of composting, such as improvement of soil physical, chemical and biological properties and increase of organic carbon (DARBY et al., 2016; SINGH; NAIN, 2014), some negative impacts can occur in the soil and environment during the preparation and application of compost. When improperly performed, soil and groundwater contamination by leaching of nutrients and heavy metals can occur, as well as emission of greenhouse gases (DARBY et al., 2016; FERREIRA et al., 2018; LIMA et al., 2017; YUAN et al., 2017). In addition, organic compost is not stable in a medium to long-term, thus significant improvements in soil organic matter, require regular reapplications for prolonged periods (BASS et al., 2016), a relatively long time (from 90 - 180 days) to complete its maturation and a large physical space for its processing and storage.

In this context, pyrolysis appears as an alternative for the treatment of these organic residues, producing more stable materials such as biochar in a shorter period of time. Pyrolysis is a process of thermochemical decomposition of organic materials under low or oxygen-free conditions in a range of higher temperatures (300-900 °C), generating the biochar (solid), bio-oil (liquid) and gaseous components (CHA et al., 2016; NANDA et al., 2016). The gas and bio-oil can be used as fuels and extensive research is being conducted on their formation, upgrading and applications (KO et al., 2012; RICHARDSON; BLIN; JULBE, 2012).

Biochar is a heterogeneous substance rich in aromatic and recalcitrant carbon (C) (CZEKAŁA et al., 2015; CORNELISSEN et al., 2016; LI et al., 2014), and thus is not readily returned to the atmosphere as CO₂ (NANDA et al., 2016). Biochar application to some soils can improve physical, chemical and biological parameters by increasing stable forms of C in soil (SINGH; COWIE; SMERNIK, 2012; SONG et al., 2016), increase crop production, reduce heavy-

metal pollution (PUGA et al., 2015; CHEN et al., 2016) and reduce greenhouse gases emissions (LI et al., 2014; SINGH; COWIE; SMERNIK, 2012).

The biochar properties, effects and stability vary widely with type of biomass, pyrolysis temperature, heating rate, residence time and potential pre- or post-processing treatments (CHA et al., 2016; CHEN et al., 2016; LI et al., 2014; NANDA et al., 2016). Despite the benefits of biochar, the low yields and low carbon retention are still limitations for its production to be profitable. In general, nearly half of the C of the biomass is immediately released during pyrolysis due to thermal decomposition and volatilization (ZHAO et al., 2014; ZHAO et al., 2016). Therefore, there is a need to develop alternatives to produce biochar with a higher yield and higher C stability.

The addition of mineral components to biochar production has shown to be an alternative to increase these properties. Researchers have recently verified that co-pyrolysis of biomass with additives, especially phosphate, increase the yield and cause greater chemical, biological and thermal stability of biochar (LI et al., 2014; XU et al., 2017; ZHAO et al., 2014; ZHAO et al., 2016). It has been proposed that addition of P-containing materials generates carbon-phosphorus complexes on the surface of biochar, which act as a physical barrier for oxygen diffusion into micropores, forming protective layers (ZHAO et al., 2014; ZHAO et al., 2016).

Despite the improved biochar stability, co-pyrolysis of biomass with phosphate compounds (e.g. phosphoric acid - H_3PO_4 ; triple superphosphate – TSP monoammonium phosphate - MAP) generates acidic biochar materials (LUSTOSA FILHO et al., 2017; ZHAO et al., 2014), that are inappropriate for use in acidic tropical soils. To overcome this limitation, Lustosa Filho et al. (2017) studied the co-pyrolysis of poultry litter biomass with phosphate compounds (H_3PO_4 , TSP and MAP) with and without MgO addition. The use of MgO caused slower release of P and alkaline reaction of the biochars, showing thus a potential for these materials to be used also as enhanced P fertilizers.

Phosphate rock is the main source of soluble phosphate fertilizers and finite resource (CHIEN; PROCHNOW; CANTARELLA, 2009). Additionally, P fixation in tropical soils causes low efficiency of phosphate fertilizers (EDELSTEIN; TONJES, 2012). In this scenario, developing more efficient phosphate fertilizers and recycling P from residues is strategic. The pretreatment of raw biomass material with phosphate and magnesium generates a biochar-based fertilizer (BBF) with high concentration of P and slow release (LUSTOSA FILHO et al., 2017), which may be an alternative to improve P use efficiency in agriculture and proper disposal of residues. Moreover,

enriching biochar with phosphate and magnesium for fertilizer use is beneficial to plants due to the synergistic effect among these nutrients in the acquisition of P (GONZALEZ-PONCE; LOPEZ-DE-SÁ; PLAZA, 2009).

The addition of MgO in co-pyrolysis for the production of biochar can also act as an *in situ* mold to form the porous structure and increase the specific surface area of the biochar (SHAHKARAMI; DALAI; SOLTAN, 2016). However, the effect of MgO and P compounds impregnation on the C stability of the resulting biochar is not yet known. Thus, we aimed at studying how the addition of H₃PO₄ and MgO in co-pyrolysis with poultry litter and coffee husk biomasses will affect yield, and thermal and chemical stability of C in these biochar materials.

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PART II

ARTICLE

Carbon stability of engineered biochar-based phosphate fertilizers

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Abstract

Converting abundant agricultural residues into valuable products such as biochar is a pressing challenge for society. Here, we aimed to produce biochar-based fertilizers (BBFs), by adding H_3PO_4 with and without MgO for co-pyrolysis with coffee husk and poultry litter. Biochar yield, C retention, thermal and chemical C stability were assessed. Biochar yield increased up to 65% when treated with H_3PO_4 and $\text{H}_3\text{PO}_4\text{-MgO}$, resulting in up to 78% higher C retention. BBFs showed higher thermal stability, by thermogravimetric analysis and muffle oxidation, when compared to corresponding pristine biochars. Conversely, addition $\text{H}_3\text{PO}_4\text{-MgO}$ decreased chemical stability (higher H_2O_2 and $\text{K}_2\text{Cr}_2\text{O}_7$ oxidation) as compared to the biochars due to the increase in surface area and reactivity. We concluded that co-pyrolysis of biomasses with H_3PO_4 and MgO promote thermal stabilization and increase chemical oxidation of the BBFs, which can be advantageous for both increasing biochar production and enrichment with plant-available nutrients.

Keywords: Biomass cycling. Carbon sequestration. Phosphate fertilizer.

1. Introduction

Converting organic residues into valuable products is a challenge for society, since large quantities of organic residues are generated worldwide through agricultural, animal and industrial activities. The disposal of these residues in landfills or their inadequate disposal on soils, may cause environmental pollution and thus not contribute to the recycling of C and nutrients within the modern concept of circular economy, that aims to optimize the use of by-products and residues to reduce pollution (Sauvé et al., 2016).

Brazil is a major producer of coffee beans and chicken, generating nearly 2.7 and 10.2 million tons of coffee husk and poultry litter residues, respectively (Dalólio et al., 2017; Domingues et al., 2017; Rogeri et al., 2016). Both materials are nutrient-rich organic residues that can be used as organic fertilizers. However, these residues typically need to be treated by composting prior to soil application. Conversion of these residues into biochar through pyrolysis is an alternative to stabilize their C through conversion into aromatic and recalcitrant forms (Cornelissen et al., 2016; Czekala et al., 2016; Li et al., 2014) and also to sanitize their material (Meng et al., 2017).

The ability of biochar to retain C in relatively stable forms is considered as one of its most important properties, either for purposes of C sequestration or soil conditioner use. However, despite the widespread expectation of high biochar stability in the environment, a considerable part of its C is in many cases labile, and can be decomposed relatively quickly, especially under tropical conditions (Sagrilo et al., 2015).

Currently, there is a trend to produce nutrient-enriched biochars aiming to reach enhanced fertilizers, also called biochar-based fertilizers (BBFs) or biochar compound fertilizer (BCF) (Joseph et al., 2013; Lustosa Filho et al., 2017; Qian et al., 2014; Yao et al.,

2015). BCFs and BBFs have significantly increased the productivity of some crops such as rice (Qian et al., 2014) and green pepper (Yao et al., 2015), respectively. In addition to the fertilizer effects obtained when adding inorganic nutrients to the process of biochar production, improvements in the properties of biochars or BBFs were observed.

In this regard, the addition of phosphate compounds to the biomass prior to pyrolysis was shown to increase yield, chemical, biological, and thermal stability of biochars (Xu et al., 2017; Zhao et al., 2016, 2014). It was proposed that co-pyrolysis of biomass with phosphate generates thermally stable phosphorus complexes on the surface of biochar, such as C–O–PO₃ or (CO)₂PO₂ (Zhao et al., 2017). These complexes are likely to decrease the reactivity of the biochar and form protection layers on its surface, reducing its oxidation (Zhao et al., 2016, 2014).

Despite the improved yield and C retention, the addition of phosphate compounds to the biomass generates acidic BBFs (pH ~ 1.51-5.12) (Lustosa Filho et al., 2017; Zhao et al., 2016, 2014), which are unsuitable for land application, especially in acidic soils. Therefore, Lustosa Filho et al. (2017) proposed the co-pyrolysis of poultry litter biomass with phosphates and MgO and noted a slower release of P and alkaline reaction (pH ~ 6.1 – 9.1), showing great potential for its use as enhanced P fertilizers in P-fixing oxide-rich tropical soils. Moreover, the production of BBF enriched with phosphate and magnesium is beneficial to plants due to the synergistic effect among these nutrients in the acquisition of P (González-Ponce et al., 2009). However, the effect of phosphate and MgO addition on the C stability of the resulting BBFs is unknown. In this study, we evaluated the effect of co-pyrolysis of coffee husk and poultry liter with H₃PO₄, with and without MgO addition on yield, C loss during pyrolysis, and thermal and chemical stability of the BBF. We hypothesized that simultaneous

addition of MgO and H₃PO₄ will increase yield and C stability as compared to the pristine biochars.

2. Material and Methods

2.1 Sample preparation and production of biochars and BBFs

Coffee husk and poultry litter biomasses were collected from farms near Lavras, Minas Gerais, Brazil (21°13'34" S and 44°58'31" W) in August 2016. Samples were air-dried at room temperature, and ground to pass through a 1.00 mm sieve. Part of the biomass was mixed with concentrated H₃PO₄, with and without MgO addition. The reagents used were of analytical grade. H₃PO₄ and MgO were mixed to achieve a P:Mg molar ratio of 1:1, and the ratio of biomass:H₃PO₄ was 1:0.5 (w/w), as described elsewhere (Lustosa Filho et al., 2017). Briefly, the pretreated samples were moistened for better homogenization, remaining for 16 h at rest. After this period the treated raw materials were oven-dried at 60 °C to a constant mass to be pyrolysed.

The treated and untreated samples were placed into stainless-steel cylinders (10.6 cm diameter and 42 cm height), which were sealed and accommodated in an adapted furnace that allows the release of gases during pyrolysis and collection of the bio-oil, as described in Lustosa Filho et al. (2017). The pyrolysis was performed by raising the temperature up to 500 °C at a heating rate of 10 °C min⁻¹, maintaining this temperature for 2 h to provide enough time for complete carbonization (Zhao et al., 2014).

The produced biochars were identified as follows: CHB = coffee husks biochar; PLB = poultry litter biochar; and BBFs were: CHB-H₃PO₄ = coffee husks biochar + phosphoric acid; PLB-H₃PO₄ = poultry litter biochar + phosphoric acid; CHB-H₃PO₄-MgO = coffee

husks biochar + phosphoric acid + magnesium oxide; and PLB-H₃PO₄-MgO = poultry litter biochar + phosphoric acid + magnesium oxide.

The yield and C retention for the pyrolysis were calculated according to equations 1 and 2.

$$\text{Yield (\%)} = \left(\frac{W_{\text{biochar}}}{W_{\text{biomass}} + W_{\text{additive}}} \right) \times 100 \quad (1)$$

$$\text{C retention (\%)} = \left(\frac{C_{\text{biochar}} \times W_{\text{biochar}}}{C_{\text{biomass}} \times W_{\text{biomass}}} \right) \quad (2)$$

Where W and C are the dry weight (g) and the contents of C (%) of the biochars, biomass and additive (H₃PO₄ and/or MgO).

2.2 Characterization of the biomasses, biochars and BBFs

A proximate analysis was carried out using a thermogravimetric analyser (model DTG - 60AH) for the determination of the volatile solids, fixed C and ashes of the biomasses, biochars and BBFs. A differential thermal analysis was also performed. Briefly, each sample was inserted into the reactor under inert (N₂) atmosphere and heated at a heating rate of 10 °C min⁻¹ until reaching 800 °C. The volatile solids and ash contents were calculated as the mass loss at 500 °C and remaining mass at 800 °C, respectively. The fixed carbon was calculated by equation 3 (Reckamp et al., 2014).

$$\text{FC(\%)} = 100 - \text{VS(\%)} - \text{ASH(\%)} \quad (3)$$

Where FC and VS are the carbon fixed and volatile solids of the biomasses, biochar and BBFs, respectively.

For the chemical characterization of the biomasses, biochars and BBFs, the pH was determined after adding 1.00 g of dry sample to 20.0 mL of deionized water (Rajkovich et al., 2012). Elemental composition (C, H and N) was measured using an elemental analyzer (model Vario TOC cube, Elementar, Germany). Total P was analyzed using a ICP-OES spectrometer (Model Blue, Germany) under argon gas, after ashing for 8 h at 500 °C in a muffle furnace, followed by nitric acid digestion at 120 °C and H₂O₂ addition in the final digestion step, to oxidize organic carbon (Enders and Lehmann, 2012). Finally, the digested material was dissolved in 20.0 mL of 5% (v/v) HCl solution using sonication for highest recovery rate of nutrients in biochars and BBFs samples (Enders and Lehmann, 2012). The specific surface area (SSA) was estimated by the methylene blue method according to Nunes and Guerreiro (2011) and Stavropoulos and Zabaniotou (2005).

The Fourier transform infrared (FTIR) spectroscopic characterization of the biomasses, biochars and BBFs was performed with a Digilab Excalibur spectrometer with a spectral range 4000-400 cm⁻¹. Oven-dried samples were ground to a powder, and the FTIR spectra with a resolution of 4 cm⁻¹ were collected over an average of 32 scans.

Raman analysis were performed with a LabRAM HR Evolution spectrometer. The backscattering configuration was used, with a 50x objective lens in an Olympus BX41 microscope. The samples were excited by a 532 nm green laser, and the power at the sample was kept lower than 5 mW to avoid sample heating and degradation. Each spectrum was collected point-by-point in a backscattering configuration, from 100 cm⁻¹ to 3200 cm⁻¹, with acquisition time of 10 s and with 10 accumulations. The Raman measurements were performed at three different points on each sample. For statistical analysis, the procedure for the exclusion of baseline used to all spectra was the exclusion of a linear baseline between

800 cm^{-1} and 2000 cm^{-1} according to the procedure described by Ribeiro-Soares et al. (2013). The data were analyzed by determining the area ratio between the D and G bands (I_D/I_G), and also the relation of the G band full width at half maximum (Γ_G) with the estimated crystallite size of these carbonaceous materials. The fitting procedure was performed by using two Lorentzian peaks. The crystallite size was estimated by equation 4 (Ribeiro-Soares et al., 2013).

$$L_a(\text{nm}) = \frac{496}{(\Gamma_G - 15)} \quad (4)$$

Where L_a is the estimated crystallite size and Γ_G is the full-width at half maximum. Optical microscopy images were also acquired from the samples by, using the Olympus Raman microscope, with a 20x magnification.

2.3 Evaluation of C stability of biochars and BBFs

2.3.1 Thermal stability

Thermal stability was evaluated by TGA analysis under inert (N_2) and oxidation (synthetic air) environments at 800 $^\circ\text{C}$ as described by Zhao et al. (2014). Moreover, thermal stability was also evaluated in a muffle furnace, in which 1.00 g of each sample was heated in open crucibles at 375 $^\circ\text{C}$ for 24 h to eliminate non-pyrogenic organic material and to determine the stable aromatic organic C, simulating combustion processes that occur naturally in fires at forest environments (Qi et al., 2017). The mass loss and remaining C were recorded in both TGA and muffle analysis. C content was determined in an elemental analyzer (model Vario TOC cube, Elementar, Germany).

2.3.2 Chemical Stability

Chemical stability of C for the biomasses, biochars and BBFs was evaluated as described by Li et al. (2014) and Yang et al. (2016). Firstly, the mass of each sample was measured to correspond to 100 mg of C and were put into a glass tube and 7.0 mL of 5% H₂O₂ (v/v) were added. The tubes were kept at 80 °C for 48 h. Also, 100 mg of C of each sample was weighed into a glass tube and 40.0 mL of a 0.1 mol L⁻¹ K₂Cr₂O₇ + 2.0 mol L⁻¹ H₂SO₄ solution was added, which was maintained at 55 °C for 60 h. After the oxidation, in both methods the samples were washed several times with distilled water to remove oxidants used and slowly filtered using filter paper (Unifil C42, blue band of slow filtering) (Song et al., 2002). The material was then placed in an oven for 72 h at 55 °C, the mass loss was recorded, and the C content was determined.

Chemical stability of C (\mathcal{A}) of the biochars and BBFs, which represents the remaining C after the chemical oxidation, was calculated according to equation 5 (Cross and Sohi, 2013):

$$\mathcal{A} (\%) = \left(\frac{M_r \times C_r}{M_i \times C_i} \right) \times 100 \quad (5)$$

Where M_r is the residual mass of biochar or BBF after chemical oxidation and C_r is its content of C (%); M_i is the initial mass of biochar or BBF prior to chemical oxidation and C_i is the original C (%) content of the biochar or BBF.

2.4 Statistical analyses

The analyzes were performed in a completely randomized design with 3 replicates with the exception of yield, C retention and thermogravimetric analyzes (proximate analysis

and thermal stability). The data were submitted to analysis of variance (ANOVA) and, when significant ($p < 0.05$), the means were compared by the Tukey test at $p < 0.05$, using the ExpDes.pt package (Ferreira et al., 2011) of the software R 3.4.1 (R Core Team, 2017).

3. Results and Discussion

3.1 Chemical, elemental and proximate analyses

The selected properties of the biomasses, biochars and BBFs are presented in Table 1. The C content of BBFs (either with H_3PO_4 or $\text{H}_3\text{PO}_4\text{-MgO}$ addition) were relatively low when compared to biochars due to the increase in the inorganic fraction caused by the additives, as indicated by the high ash contents. Co-pyrolysis of coffee husk and poultry litter biomasses with H_3PO_4 reduced the C content in 49.7% and 44.1%, respectively, as compared to coffee husk biochar and poultry litter biochar. On the other hand, the treatment of coffee husk and poultry litter with $\text{H}_3\text{PO}_4\text{-MgO}$ reduced the C content even more by 65.1% and 46.2%, respectively. A similar trend was also observed for wheat straw biochar as reported by Zhao et al. (2014). As expected, the H/C ratio was lower in biochars and BBFs as compared to the biomasses (Table 1), suggesting a higher C aromaticity (Li et al., 2014), due to formation of aromatic structures with the pyrolysis. However, the treatment with H_3PO_4 without MgO addition promoted an increase of H and H/C ratio as compared to pristine biochars, probably due to hydration reaction caused by the phosphoric acid (Fig. S1c, d). However, this result was the opposite of those found by other researchers, that observed that the addition of H_3PO_4 promotes dehydration through the removal of oxygen (O) and hydrogen (H) during pyrolysis of Pine tree sawdust (Zhao et al., 2017).

The pristine biochars were strongly alkaline ($\text{pH} > 11$) whereas the addition of H_3PO_4 resulted in a strong acidity ($\text{pH} \sim 2.00$) and adding $\text{H}_3\text{PO}_4 + \text{MgO}$ resulted in slightly acids BBFs ($\text{pH} \sim 6.0$). Lustosa Filho et al. (2017) tested the poultry litter biochar + phosphoric acid and poultry litter biochar + phosphoric acid + magnesium oxide as phosphate fertilizers in an acid tropical soil, and noted an increased soil pH after maize cultivation in pots when poultry litter biochar + phosphoric acid + magnesium oxide was used.

The volatile solids contents reduced substantially with the additives, whereas the fixed carbon increased from 10.2% in the coffee husk biochar to 35.3% in the coffee husk biochar + phosphoric acid, and from 5.04% in the poultry litter biochar to 24.3% in the poultry litter biochar + phosphoric acid. Such increase in the fixed carbon fraction after the impregnation with H_3PO_4 prior to pyrolysis is in agreement with other researchers that indicate P compounds stabilize the C fraction in the biochar (Rosas et al., 2012; Zhao et al., 2014, 2017). Conversely, the fixed carbon decreased to $< 3.0\%$ in both biomasses when H_3PO_4 plus MgO were added. Fixed carbon represents a relatively stable C fraction, derived from alteration of pristine C, during pyrolysis, which enables it to be called sequestered C (Zhao et al., 2014). These results indicate that MgO as an additive in the biomass prior to pyrolysis can cause a reduction in the C stability of the biochar product. This may occur as a function of a possible formation of the P-O-Mg bond, when the MgO is added, replacing in parts the direct bond between P-O-C and leaving the C available to be readily oxidizable.

Total P contents in BBFs ranged from 146 to 206 g kg^{-1} , much higher than the pristine biochars (3.49 - 24.4 g kg^{-1} - Table 1) and reached total P contents as high as in conventional P fertilizers, indicating a potential use as phosphate fertilizer. H_3PO_4 addition increased the specific surface area (SSA) by 38.7 to 71.2%, and $\text{H}_3\text{PO}_4 + \text{MgO}$ by 82.0 to 101.4%,

compared to coffee husk biochar and poultry litter biochar, respectively. Other studies also reported an increase in the SSA of biochar co-pyrolysed with H_3PO_4 treatment (Zhao et al., 2017) or with MgO (Jung and Ahn, 2016), but to the best of our knowledge this is the first study to report the influence of both compounds added together on biochar SSA. The H_3PO_4 addition promote an increased formation of small pores in BBFs, favoring a dramatic increase in SSA (Zhao et al., 2017). Magnesium can also act as an *in situ* mold to form the porous structure and increase the specific surface area of the biochar (Shahkarami et al., 2016). This may justify the increase in SSA with addition of MgO and H_3PO_4 .

3.2 FTIR and Raman analysis

The FTIR spectra of the biomasses (coffee husk and poultry litter), respective biochars and BBFs are presented in Fig. 1.

The broad peak observed around 3286 cm^{-1} ($3100\text{-}3500\text{ cm}^{-1}$) in coffee husk and poultry litter is characteristic of the stretching vibration of hydrogen-bonded hydroxyl (-OH) groups from carboxyls, phenols or alcohols, and water (Li et al., 2018; Xu et al., 2014; Xu et al., 2017). In many cases it may also correspond to the N-H stretching vibration in amino compounds (Lustosa Filho et al., 2017). This peak disappear after pyrolysis due to dehydration, decomposition, conversion or breakdown of these functional groups.

The peak observed at 2919 cm^{-1} probably indicates the presence of saturated symmetric and asymmetric aliphatic C-H stretching vibration (Taherymoosavi et al., 2017; Xu et al., 2014). The peak at 2746 cm^{-1} observed in the PLB- H_3PO_4 can be attributed to aldehyde groups (-CHO) and/or primary amino acid (Taherymoosavi et al., 2017). The peak observed in the biomasses, biochars, and BBFs at 2351 cm^{-1} were more pronounced in

poultry litter and its products and most likely correspond to stretching vibrations of CO₂ (Liang et al., 2018; Tian et al., 2014).

The three peak at 1637, 1600 and 1531, can be attributed to C=C and C=N vibrations (Movasaghi et al., 2008; Sahin et al., 2017), and -COO antisymmetric stretching of amino acids and C=O stretching vibrations in ketones, quinones, aldehydes, lactones, and carboxylic groups and esters (Zhao et al., 2017), and also to the N-H band (Taherymoosavi et al., 2017). The peak observed at 1435 cm⁻¹ can be due to the presence of carbonyl or carbonates (CO₃²⁻) (Lustosa Filho et al., 2017; Zhao et al., 2015) and C=C or/and saturated C-H bending vibration (Taherymoosavi et al., 2017). Coffee husk and poultry litter biomasses present a peak at 1319 and 1232 cm⁻¹ that can represent the C-N stretching in aromatic amines (Movasaghi et al., 2008) and C-O stretching in carboxylic acids (Bekiaris et al., 2016), respectively.

The peaks in the spectral region between 1150-1010 cm⁻¹ are attributed to polysaccharides, alcohols, and phosphates (Lustosa Filho et al., 2017). The peak at 1097 cm⁻¹ observed in biochar treated with H₃PO₄-MgO and the peak at 1078 cm⁻¹ in biochar treated with H₃PO₄ can be attributed to the symmetric phosphate (PO₂) stretching (Movasaghi et al., 2008), the vibration of P-O-C stretching (Zhao et al., 2016), P⁺-O⁻ in acid phosphate esters and to the symmetrical vibration in polyphosphate chain P-O-P (Xu et al., 2014). The peak at 1020 cm⁻¹ in coffee husk and poultry litter can be assigned to the C-O stretching vibrations of polysaccharide or polysaccharide-like substances (Bekiaris et al., 2016; Li et al., 2018). The peaks at 943, 875 and 750 cm⁻¹ were attributed to P-O-P stretching and the peaks at 557

and 540 cm^{-1} to P-O or P=O stretching (Bekiaris et al., 2016; Lustosa Filho et al., 2017). Finally, the peak at 470 cm^{-1} was attributed to P-O⁻ (PO_4^{3-}) (Lustosa Filho et al., 2017).

The Raman spectra, the mean area ratio between D-band and G-band, and mean crystallite size are presented in Fig. 2. All curves exhibited two relatively broad bands at the frequency ranges of 1356-1370 and 1582-1598 cm^{-1} , which correspond to the D-band and G-band, respectively (Fig. 2a). The D band's Raman activity is related to the breathing-like motion of aromatic C structures, being activated by the presence of amorphous or disordered carbon (Ribeiro-Soares et al., 2013; Zhang et al., 2015). The G-band is assigned to the tangential stretching vibrational mode among C atoms, typically found in C materials with different disorder degrees and, thus, it will be treated as an indicative of the presence of C crystallites (Ribeiro-Soares et al., 2013; Zhang et al., 2015). For highly disordered carbonaceous materials, the G-band is generally assigned to the aromatic symmetric stretching, and the D-band to aromatics with more than six rings or to C-C vibration of aromatic ring. In the case of amorphous C, the D-band can be attributed to benzene or condensed benzene amorphous rings or to the disordered or distorted structure (Elmay et al., 2015).

The I_D/I_G ratios (Fig. 2b) calculated by the Lorentzian function and crystallite size (L_a) (Fig. 2c) of each sample were more variable for H_3PO_4 -MgO treatment. Zhang et al. (2015) relate that an increase in the I_D/I_G ratio indicated a conversion of amorphous C to graphene-like domains. However, the area ratios I_D/I_G observed in our study were very similar and did not allow us to conclude if there was a reduction in amorphous C.

MgO addition caused a reduction in the crystallite size, which can indicate an increase of amorphous C. The reduction in the crystallite size is in agreement with the observed SSA increase of BBFs treated with MgO, which also might have caused oxygen atoms to crosslink the C microstructure, yielding a non-graphitizing hard C (Zhang et al., 2015) and thus decreasing the crystallite size of the BBFs. The higher disorder in the C structure is an important characteristic of biochar for soil fertility improvement, since it can increase the oxidation of aromatic rings, which gives rise to broken links enhancing the cation exchange capacity of soils by the chemical bond with nutrients (Ribeiro-Soares et al., 2013). In fact, Lustosa Filho et al. (2017) noted an increase in the cation exchange capacity in BBFs with addition of MgO, probably due to the greater amount of defects and the smaller size of crystallites. Moreover, the small crystallite sizes allow Ca, O and P to diffuse in the carbonaceous structure, while the aromatic structure is responsible for the prolonged stability against microbial degradation and leaching (Ribeiro-Soares et al., 2013).

3.3 Yield and carbon retention

The addition of H_3PO_4 prior pyrolysis increased the yield in 98% and 54% as compared to the yield of pristine biochar for coffee husk and poultry litter, respectively (Fig. 3a). Addition of MgO in complement to H_3PO_4 also increased the yield of the BBFs very similarly. Such increases have been reported earlier for the biomasses. Co-pyrolysis of H_3PO_4 with biomasses increased the yield of biochar from wheat straw in 80% (Zhao et al., 2014) and increased the yield of biochar from sawdust by 62 - 92% (Zhao et al., 2017).

H_3PO_4 addition to coffee husk and poultry litter increased the C retention after pyrolysis by 78% and 74%, respectively, as compared to pristine biochars (Fig. 3b). When MgO was also added, C retention was increased by 51% and 20% in biochar of the coffee

husk end poultry litter treated with H_3PO_4 -MgO, respectively. Although the yields in BBFs containing H_3PO_4 or H_3PO_4 -MgO were similar (Fig. 3a), the C retention in BBFs containing H_3PO_4 -MgO was lower as compared to BBFs with H_3PO_4 only (Fig. 3b). These results support the idea of reduced fixed carbon with MgO addition, as observed in the proximate analysis. Probably, P-O binds preferentially to Mg at the expense of P-O-C bonds and thus more free C is lost during pyrolysis.

The increased C retention as a result of H_3PO_4 addition to the biomass prior to pyrolysis is attributed to the formation of P-O-C-type groups, since the possible existence of such groups [i.e., $(\text{CO})_3\text{PO}$, $(\text{CO})_2\text{PO}_2$, and $(\text{CO})\text{PO}_3$] may physically protect the C structure, which reduces C loss during pyrolysis (Zhao et al., 2017, 2014). The impregnation of MgO probably had an effect on such bonds, as explained later.

3.4 Thermal stability

3.4.1 Thermogravimetric (TGA) and muffle analysis

The TGA patterns varied considerably among biomasses, biochars and BBFs (Fig. 4), indicating a strong effect of pretreatment by addition of H_3PO_4 and MgO on pyrolysis. In general, the lower the mass loss of biochars and BBFs under air atmosphere (within a temperature range from 25 °C to 800 °C) the higher their oxidative stability (Zhao et al., 2014). Additionally, the higher the inorganic fraction of the material the lower is the mass loss in TGA analysis in both oxidant (synthetic air) and inert (N_2) environments, since only a small portion of the inorganic material is vaporized during combustion (Zolin et al., 2001). Biochars and BBFs showed a higher stability as compared to their raw biomasses either in oxidant or inert conditions (Fig. 4a and 4b), proving that pyrolysis increases C stability. All BBFs started a significant mass loss at higher temperatures ($> 450^\circ\text{C}$) than the biochars (~

300 °C), especially BBFs of the coffee husk and poultry litter treated with H₃PO₄ (~ 600 °C). Prior to these inflection points, the BBFs treated with H₃PO₄ presented higher mass loss over a range of temperatures when compared to biochars, which can be attributed to the decomposition of either organic fractions of the carbon skeleton or some combination of carbon and additive (Zhao et al., 2014), and the loss of OH groups due to the presence of H₃PO₄ (Zhao et al., 2017). This trend was shifted when MgO was also added, reducing the mass loss in lower temperatures.

Overall, our TGA results indicate that H₃PO₄ addition promoted the highest increase in oxidative stability of BBFs, followed by H₃PO₄ and MgO. This result also can be seen by differential thermal analysis (Fig. 4c and 4d), which shows the exothermic peaks disappearing in the heat flow curves when the biomass was treated with H₃PO₄.

The exothermic reaction observed in the biomasses and biochars (Fig. 4c and 4d) could be ascribed to the decomposition of nitro and nitrate groups by oxidation (300 °C) and to the conversion of oxygenous groups and aliphatic carbons to CO₂ and to the breakdown of carboxyl, carbonyl and hydroxide groups (400-550 °C) (Gunes et al., 2015; Sahin et al., 2017). The H₃PO₄ addition favors the removal of O and H during biomass pyrolysis (Zhao et al., 2017), resulting in the esterification of -OH and -COOH groups, increasing the binding of phosphate groups to the carbon chains (Sahin et al., 2017), which may explain why exothermic reactions were weakened or disappeared. These findings result in the higher stability of BBFs observed here.

The FTIR analysis confirms that compost and functional groups were present in the biomasses (coffee husk and poultry litter) and disappeared with H₃PO₄ and H₃PO₄-MgO addition (as shown in the FTIR spectra in Fig. 1). When H₃PO₄-MgO was added, a small

peak at 500 °C was observed. Zhao et al. (2017) also noted that H₃PO₄ addition increases the thermal stability and decreases mass loss of sawdust biochar. Conversely, Zhao et al. (2014) did not observe an increase in thermal stability of wheat straw biochar treated with H₃PO₄, indicating that the composition of each biomass play a major role in the final biochar thermal stability following H₃PO₄ treatment.

The oxidation method involving the combustion of biochars and BBFs at 375 °C for 24 h in muffle furnace was adopted to simulate the natural combustion processes that can occur in areas with application of these materials (Qi et al., 2017) and to evaluate the (thermal) stability of organic phases, as shown in the mass loss and remaining C analysis for the different materials presented in Fig. 5.

Results showed that coffee husk biochar and poultry litter biochar were not thermally stable and lost 72.3% and 54.9% of its mass, respectively (see Fig. 5). Therefore, it is expected that these biochars can be burnt by fires in the natural environment. On the other hand, H₃PO₄ and H₃PO₄-MgO addition decreased the mass loss (<40%) during combustion at muffle furnace, suggesting a potential increase in their stability to fires under natural conditions. Poultry litter and its co-products (PLB, PLB-H₃PO₄ and PLB-H₃PO₄-MgO) presented higher stability to combustion with lower mass losses as compared to coffee husk and its co-products (CHB, CHB-H₃PO₄ and CHB-H₃PO₄-MgO). This probably occur due to the higher content of inorganic materials in poultry litter as compared to coffee husk.

The original C content of the coffee husk biochar (64.8%) was reduced to 5.8% while that of poultry litter biochar (43.3%) was reduced to 2.49%. When the biomasses were treated with H₃PO₄ the remaining C content was 24% in the coffee husk and 33% in the poultry litter biochars after combustion, which were reduced to 14% and 18%, respectively in the

treatments with H_3PO_4 and MgO . These results show that MgO addition reduced C stability as compared to H_3PO_4 treatments, although both increases C stability when compared to pristine biochars.

It is known that low-temperature poultry litter biochar has very low thermal stability and contain only small amounts of stable carbonized organic carbon (OC) (Qi et al., 2017), which is in agreement with our results. Hence, these biochars can readily lose the OC phase in wildfires in the field, leaving only the mineral components. Thus, the addition of H_3PO_4 and MgO for the confection of BBFs can provide nutrients to plants and remain longer in the environment, even when applied to the soil surface.

Aromatic compounds with C-C and C=C bonds, as well as phosphate compounds with P-O-P bonds can persist on BBFs, increasing their resistance to combustion at muffle furnace and reducing C loss. This effect occurs due to the high thermal stability of P-compounds linked to carbon, forming complexes such as P-O-CO₂ (Rosas et al., 2012; Zhao et al., 2017, 2014). Valero-Romero et al. (2017) reported that C-O-P and C₃PO bonds formed in activated charcoal treated with H_3PO_4 addition are thermally stable and decompose only at temperatures higher than 700 °C and 1000 °C, respectively, being resistant to natural fires.

The addition of inorganic compounds to biomass prior to pyrolysis can change the relative importance of the different C functional groups of biochar, leading to a decrease of biochar reactivity (Yang et al., 2016). For instance, addition of phosphates could promote hydroxyl groups to transform into ether, which is one of the most stable groups among the oxygen-containing groups in biochar, resulting in an improvement of biochar's thermal stability (Zhan et al., 2011). The FTIR spectrum (see Fig. 1) shows peaks between 1100 and 800 cm^{-1} that present phosphate groups on BBFs, including esters. Moreover, peaks of -OH

in the biomass or C-O or C=O in biochars disappear with H_3PO_4 and $\text{H}_3\text{PO}_4\text{-MgO}$ addition prior to pyrolysis, reducing their reactivity. This probably contributed to higher thermal and oxidation stability of BBFs by TGA and muffle furnace analysis.

3.4 Chemical Stability

Mass loss and C stability (ΔE) following H_2O_2 and $\text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4$ oxidation are shown in Fig. 6. The mass loss of coffee husk biochar and poultry litter biochar after H_2O_2 oxidation were 4.76% and 10.9%, respectively. However, the mass loss of BBFs with H_3PO_4 were 50.9% and 58.1%, while BBFs with $\text{H}_3\text{PO}_4\text{-MgO}$ lost 31.7% and 19.1% for coffee husk and poultry litter biomasses, respectively (Fig. 6a). Under $\text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4$ oxidation the biochars from coffee husk and poultry litter lost 15.9% and 41.3% of their initial mass, respectively (Fig. 6b). However, the mass loss in the BBFs with H_3PO_4 were 60.1% and 71.9%, while BBFs prepared from coffee husk and poultry litter biomasses with $\text{H}_3\text{PO}_4\text{-MgO}$ lost 71.1% and 73.4%, respectively. $\text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4$ is a stronger oxidizing agent than H_2O_2 , which explains the higher mass loss after this type of oxidation.

The C stability (ΔE) after oxidation with H_2O_2 of the biochars from coffee husk and poultry litter was 92.1% for both biomasses and to BBFs with H_3PO_4 it was 95.1% and 92.6%, respectively, showing no differences between the stability of these materials (Fig. 6a). However, with $\text{H}_3\text{PO}_4\text{-MgO}$ addition the ΔE were reduced to 44.9% and 48.2%, respectively. With $\text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4$ oxidation, the ΔE of biochars from coffee husk and poultry litter, that were of 83.5% and 68.6%, were reduced to 71.7% and 49.5% with H_3PO_4 addition, respectively (Fig. 6b), and they did not differ from the BBFs treated with $\text{H}_3\text{PO}_4\text{-MgO}$.

There was no difference among the biochars and the BBFs of coffee husk and poultry litter in the oxidation with H_2O_2 . However, with oxidation by $\text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4$ the biochars and BBFs of coffee husk presented higher AE . The AE in all biochars and BBFs with H_3PO_4 were higher by H_2O_2 oxidation in comparison to $\text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4$ oxidation, mainly because of its low oxidizing capacity (Xu et al., 2017).

Is it intriguing that despite the lower mass loss in $\text{H}_3\text{PO}_4\text{-MgO}$ treatments as compared to pristine biochars there was a lower chemical stability in these treatments, especially under H_2O_2 oxidation. As discussed previously, this behavior was most likely due to the higher specific surface area of $\text{H}_3\text{PO}_4\text{-MgO}$ -treated BBFs (see Table 1) and also due to smaller crystallite size on BBFs (Fig. 2c). This can be seen as a result of the MgO reaction that took place during pyrolysis. Moreover, with oxidation some C-O-P bonds become saturated and favor the oxidation of the carbonaceous substrate, with production of oxygen surface groups less stable than those of P type (Valero-Romero et al., 2017).

4. Environmental implications

The present study demonstrated that H_3PO_4 and $\text{H}_3\text{PO}_4\text{-MgO}$ addition strongly affected the pyrolysis process in terms of yield, C retention, stability, and properties. The oxidation and thermal decomposition in TGA analysis were greatly reduced in both BBFs. Co-pyrolysis with H_3PO_4 and $\text{H}_3\text{PO}_4\text{-MgO}$ not only greatly improved the C retention, but also significantly enhanced the thermal C stability as measured by TGA analysis and muffle furnace combustion at $375\text{ }^\circ\text{C}$, which can be beneficial to improve soil C sequestration. In addition, acidic BBFs (treated with H_3PO_4) can be used also to correct alkaline soils and increase their soil fertility, while near neutral BBFs (treated with $\text{H}_3\text{PO}_4\text{-MgO}$) can be used

in acidic tropical soils, providing functional stable C and a fertilizer effect. Overall, our results indicated that H_3PO_4 addition to biomass was an effective way for the formation of BBFs with enhanced properties. In previous studies our group verified that the BBFs are efficient to supply P and Mg to maize plants in P-fixing tropical soil (Lustosa Filho et al., 2017). It must be pointed out that the biomass type plays a key role in the BBF formation, and thus field tests must be undertaken with different biomasses prior to large scale BBF production. In addition, the biological stability of biochar and BBFs needs be evaluated under field soil conditions to measure its C sequestration capacity and stability, as well as in its capability to supply P and Mg to plants its subsequent impact on the environment.

5. Conclusions

This study is pioneer in studying the effects of the simultaneous additions of H_3PO_4 and MgO. The addition of H_3PO_4 -MgO increases the pH of the BBF favoring its use in acid soils; however, decreases the fixed C during pyrolysis when compared to the addition of only H_3PO_4 . Another feature is that the addition of MgO increases the specific surface area and increases the occurrence of structural defects (amorphous carbon) in BBFs and reduces crystallite size. This resulted in lower chemical stability of these BBFs when oxidized with H_2O_2 and $\text{K}_2\text{Cr}_2\text{O}_7$. However, the higher specific surface area and smaller size of crystallites, besides reducing the chemical stability of BBFs, is a favorable feature to improve soil fertility, since it can increase the reactivity and cation exchange capacity of BBFs, essential for the efficient use of nutrients in tropical soils.

In general, BBFs presented higher thermal stability when compared to BCs, showing potential to withstand natural fires when applied in the field to improve soil fertility and other soil properties.

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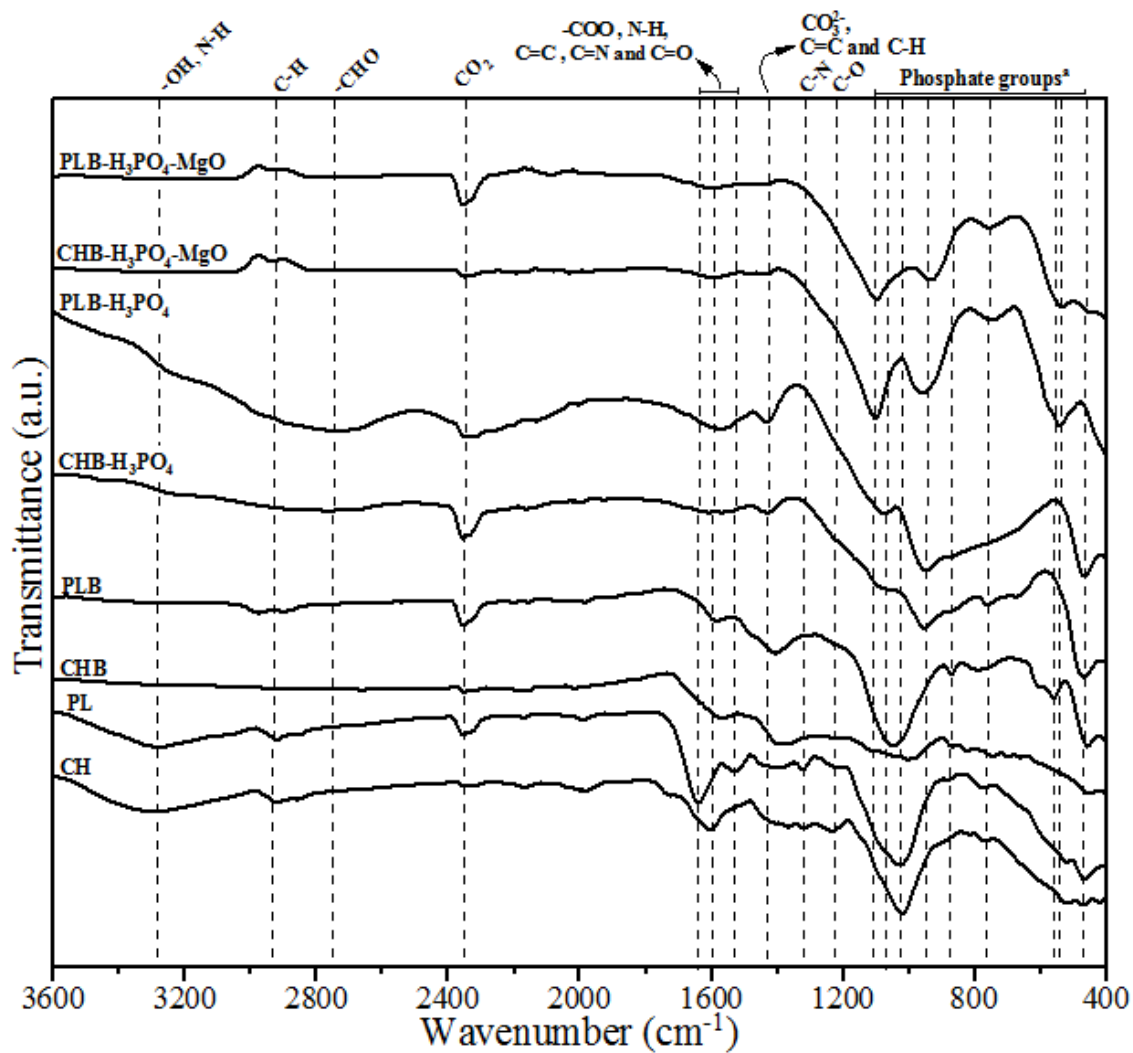


Figure 1 - (A) FTIR spectra (3600-400 cm^{-1}) of biomasses, biochars and BBFs.

Notes: *phosphate groups: P-O-P, P-O-C, P^+-O^- , P-O, P=O and PO_4^{3-} .

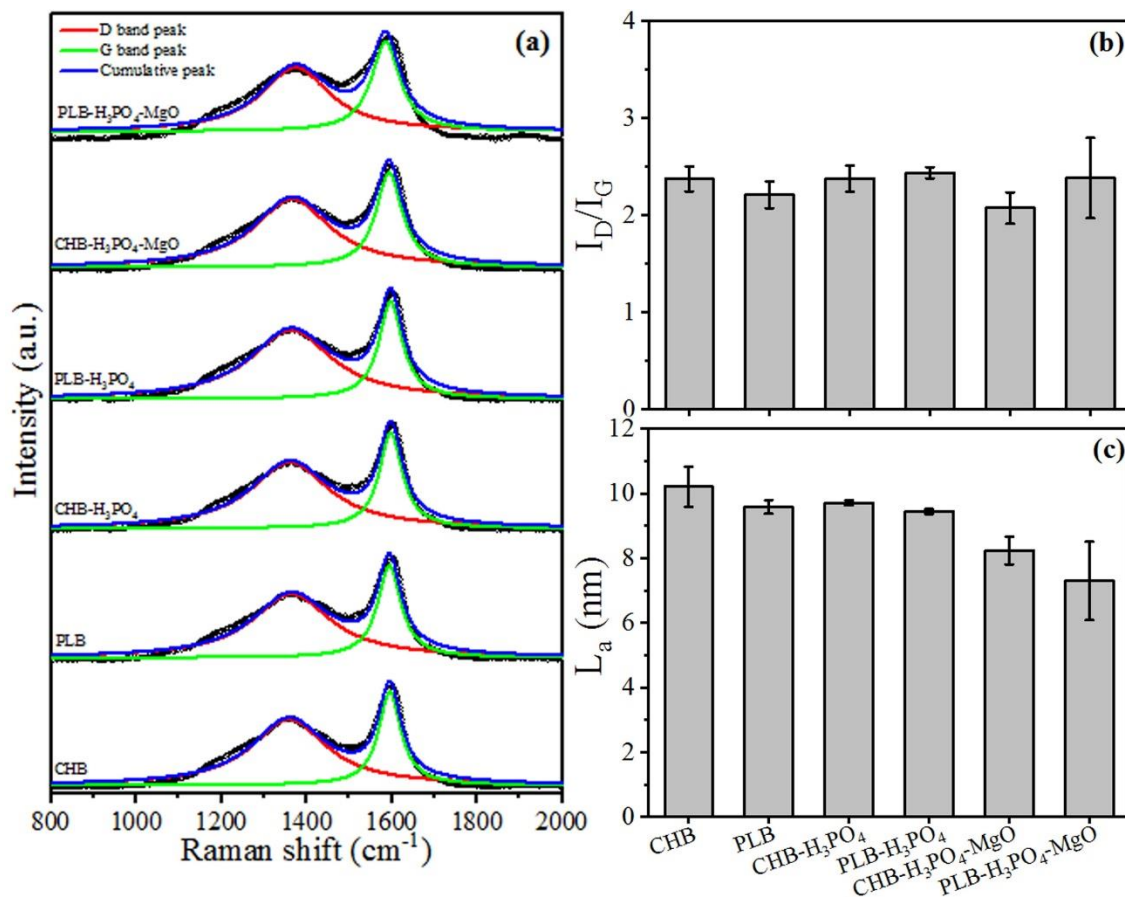


Figure 2 - Raman spectra of biochars and BBFs (a), calculated integrated area ratio of the D and G bands (I_D/I_G) (b), and estimated crystallite size (L_a) of carbonaceous materials (c).
Notes: Error bars represent the standard deviations of the treatment mean replicates (n=3).

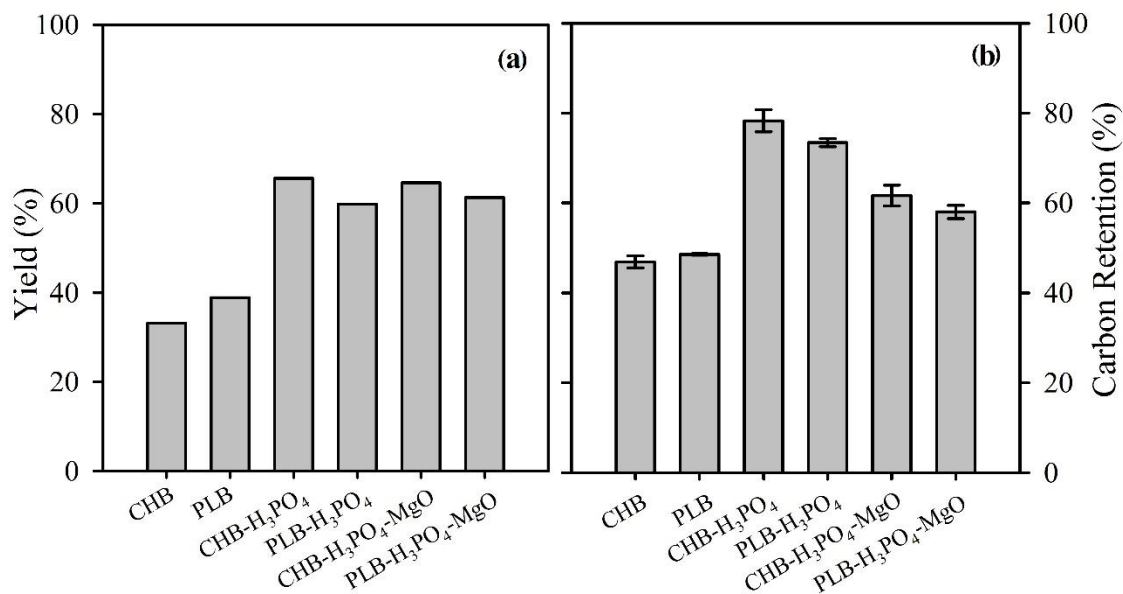


Figure 3 – Yield (a) and carbon retention (b) of biochars and BBFs produced by pyrolysis of the coffee husk and poultry litter biomasses pretreated with H_3PO_4 with or without MgO .
Notes: Error bars represent the standard deviations of the treatment mean replicates (n=2).

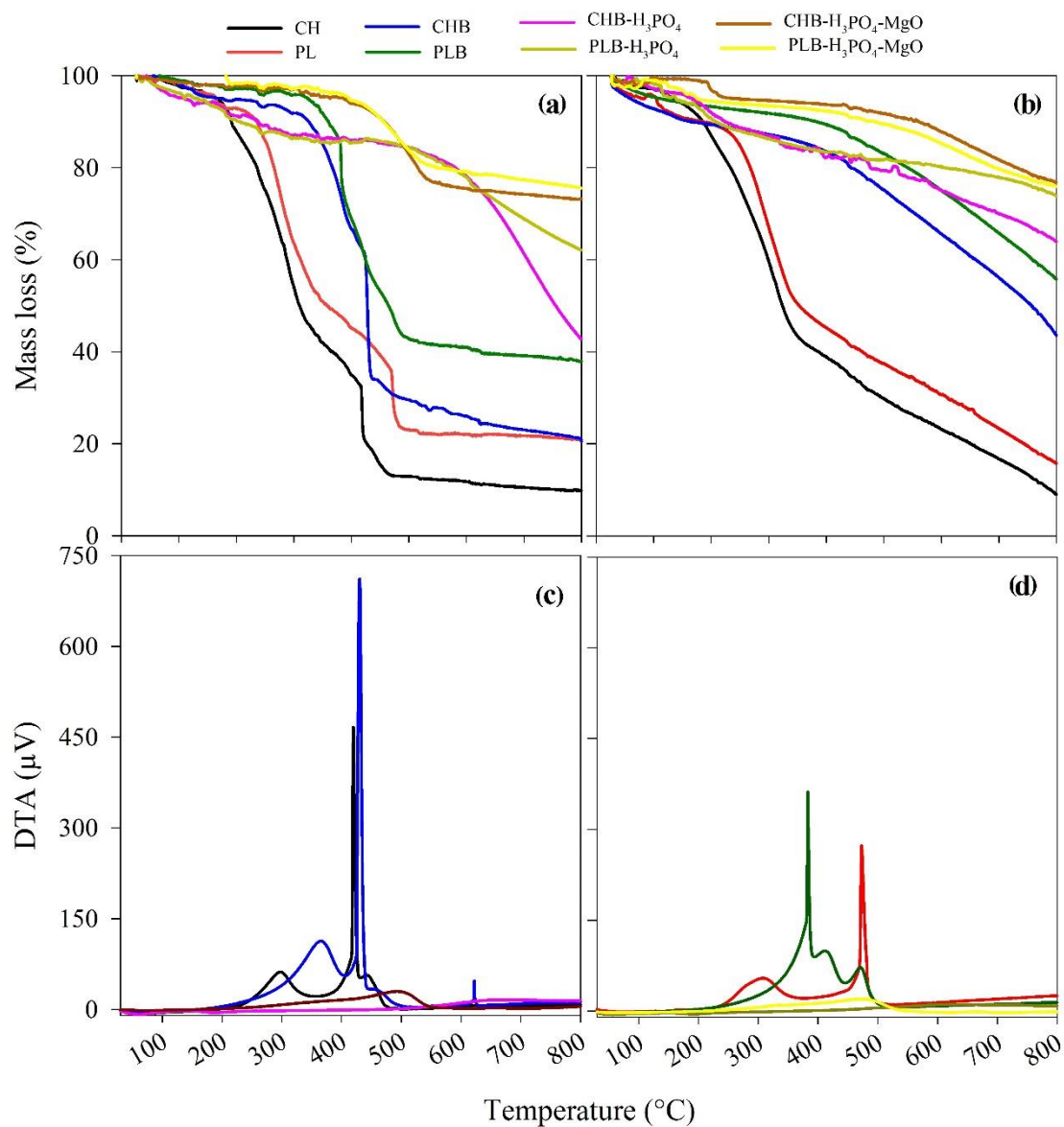


Figure 4 – Thermogravimetric analysis under synthetic air (a) and N_2 (b) atmosphere and DTA analysis (c and d).

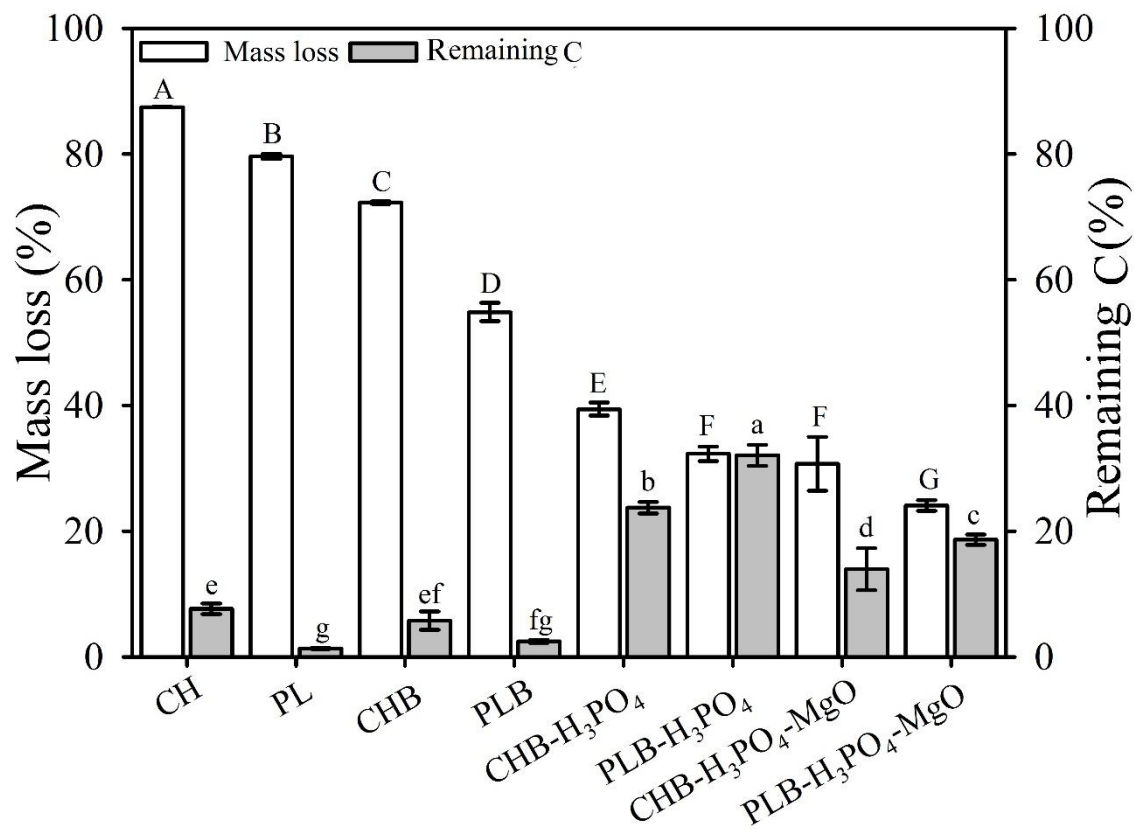


Figure 5 – Mass loss and remaining C (c) after combustion at muffle furnace combustion. Notes: Means followed by the same letter do not differ among themselves by the Tukey test ($p < 0.05$). Capital letters compare the means of mass loss and lowercase letters to remaining carbon. Error bars represent the standard deviations of the treatment mean replicates ($n=3$).

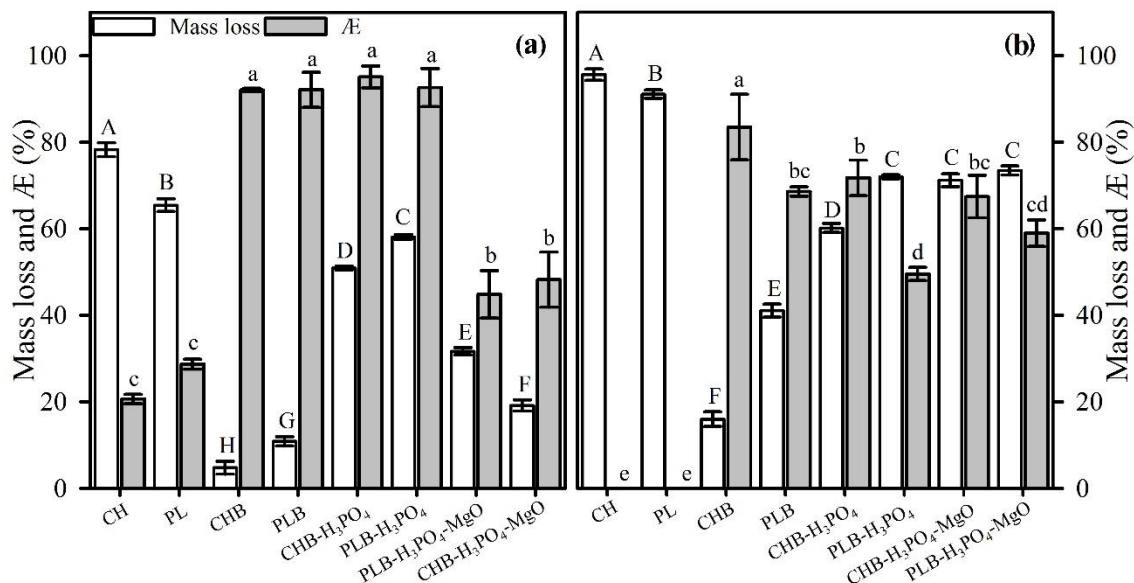


Figure 6 – Mass loss and carbon stability (\mathcal{A}) of biomasses, biochars and BBFs due to chemical oxidation with 5% H₂O₂ (a) and mass loss and stability of carbon (\mathcal{A}) of biomasses, biochars and BBFs due to chemical oxidation with 0.1 mol L⁻¹ K₂Cr₂O₇ + 2.0 mol L⁻¹ H₂SO₄ (b), respectively.

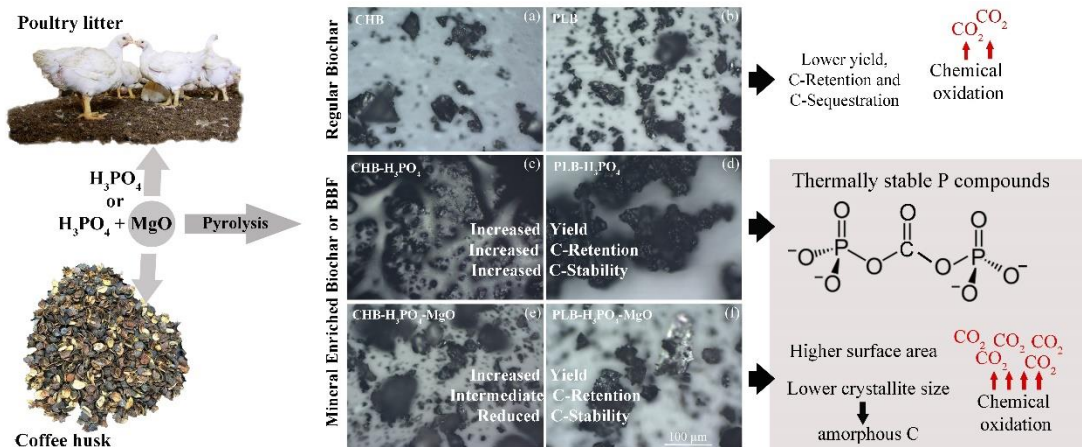
Notes: Means followed by the same letter do not differ among themselves by the Tukey test ($p < 0.05$). Capital letters compare the means of mass loss and lowercase letters to carbon stability (\mathcal{A}). Error bars represent the standard deviations of the treatment mean replicates (n=3).

Table 1 – Selected properties (mean value \pm standard deviation) of biomasses, biochars, and BBFs

Materials	C	H	H/C	VS	FC	ASH	pH	P	SSA ^a
	------(%)-----			------(%)-----				(g kg ⁻¹)	(m ² g ⁻¹)
CH	43.4 \pm 0.28	6.22 \pm 0.25	0.143	87.0	3.12	9.84	5.13 \pm 0.04	1.15 \pm 0.03	-
PL	36.1 \pm 0.18	5.75 \pm 0.00	0.159	76.4	2.26	21.4	8.25 \pm 0.02	15.6 \pm 0.39	-
CHB	64.8 \pm 3.29	2.67 \pm 0.05	0.041	70.4	10.2	19.4	11.5 \pm 0.09	3.49 \pm 0.07	68.4
PLB	43.3 \pm 0.92	2.15 \pm 0.05	0.050	57.2	5.04	37.8	11.1 \pm 0.01 ^b	24.4 \pm 0.50 ^b	56.6
CHB-H ₃ PO ₄	32.6 \pm 1.42	3.32 \pm 0.00	0.101	18.5	35.3	46.3	1.95 \pm 0.05	146 \pm 3.8	94.9
PLB-H ₃ PO ₄	24.2 \pm 0.43	2.83 \pm 0.12	0.117	14.7	24.3	61.1	2.00 \pm 0.03 ^b	206 \pm 17 ^b	96.9
CHB-H ₃ PO ₄ -MgO	22.6 \pm 3.27	1.26 \pm 0.01	0.056	22.2	2.10	75.7	5.85 \pm 0.02	177 \pm 20	124.5
PLB-H ₃ PO ₄ -MgO	20.0 \pm 0.55	1.38 \pm 0.05	0.069	25.0	2.79	72.3	6.10 \pm 0.02 ^b	162 \pm 16 ^b	114.0

Notes: VS: volatile solid, FC: fixed carbon and SSA: specific surface area; P: Total P. ^aEstimated by methylene blue method; ^bAdapted from by Lustosa Filho et al. (2017).

Graphical abstract



Highlights

- First report of co-pyrolysis of biomass with $\text{H}_3\text{PO}_4+\text{MgO}$ on changes in C stability.
- $\text{H}_3\text{PO}_4+\text{MgO}$ decreases the C chemical stability of BBFs as compared to H_3PO_4 only.
- $\text{H}_3\text{PO}_4+\text{MgO}$ increases surface area and reduce crystallinity of C compounds.
- Enriched biochar can provide stable C and functional properties as fertilizer.

Supplementary material

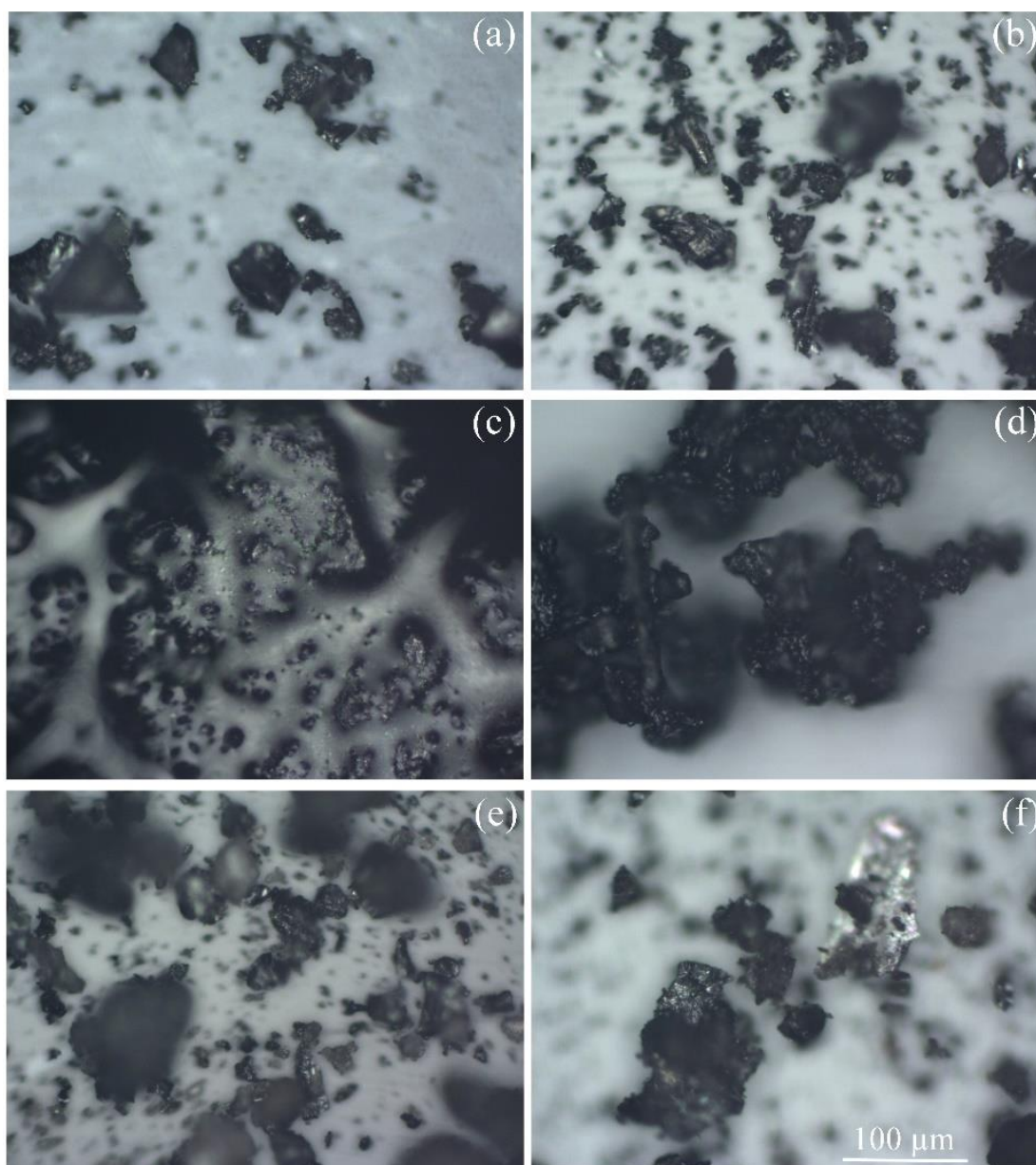


Figure S1 – Microscopy images of samples with 20x magnification: CHB (a), PLB (b), CHB-H₃PO₄ (c), PLB-H₃PO₄ (d), CHB-H₃PO₄-MgO (e) and PLB-H₃PO₄-MgO (f).
 Notes: CH – coffee husk; PL – poultry litter; CHB – Biochar of coffee husk; PLB – Biochar of poultry litter;
 CHB-H₃PO₄ – BBF of coffee husk with H₃PO₄; PLB-H₃PO₄ – BBF of poultry litter with H₃PO₄; CHB-H₃PO₄-MgO – BBF of coffee husk with H₃PO₄ + MgO; PLB-H₃PO₄-MgO – BBF of poultry litter with H₃PO₄ + MgO.