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Research article

Use of copper metal balls as internal heat distributor in fixed-bed pyrolyzer of spent coffee grounds for biochar production

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Abstract

Importance of the work: Small copper balls were used as internal heat distributor in a cylindrical pyrolysis bed of spent coffee grounds (SCG) for biochar production.

Objectives: To investigate the temperatures of the SCG during pyrolysis, including the biochar properties of the SCG beds with and without copper balls.

Materials & Methods: Samples of 300 g of SCG were pyrolyzed at 500°C under a nitrogen atmosphere for 2 hr. Temperature changes and biochar properties around the axes of the beds with and without metal balls and their last positions of decomposition were investigated. Two placements of metal balls (MBs) were considered: as layers in the SCG bed and mixing of the MBs with the same weight throughout the bed.

Results: With two layers of 8 mm MBs in the SCG bed, the temperature rate around the bed center during decomposition at 200-450°C was 21.32% greater than without the MBs. This improvement was better than that of 4 mm MBs, which produced a temperature rate increase of 9.64% over the normal bed. Mixing the MBs throughout the bed produced the opposite result, due to the high total heat capacity of the MBs and the SCG bed. The biochar properties from the first case were investigated and compared with those from the normal bed. With the MBs, the product properties were similar to those without MBs, except for the porosity and cation exchange capacity (CEC), which were significantly higher. The biochar was suitable for soil amendment, especially in an acidic soil.

Main finding: Placement of 8 mm copper ball layers could be used as an internal heat distributor in the SCG bed. The temperature around the bed axis was closer to that around the heating surface, resulting in a more rapid decomposition rate which produced higher values for porosity, pH and CEC, which are the main parameters for soil amendment.

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Introduction

Biomass is organic material from plants and animals that can be utilized as fuel for cooking and heating or transformed into solid, liquid or gas fuel for electricity generation and transportation by thermal conversion such as torrefaction, pyrolysis and gasification (Lim et al., 2012; Kumar et al., 2020; Bhatia et al., 2021). The solid product or biochar after torrefaction or pyrolysis is utilized in many fields, such as high heating value solid fuel or mixed with acidic soil for neutralization. Due to its porous structure, biochar could increase the water retention capacity in soil, absorb nutrients and become habitat for microorganisms that in turn could benefit plant growth. Furthermore, biochar could be used as an adsorber in water and air treatments to remove some heavy metal and toxic pollutants, which otherwise may cause environmental problems. In addition, biochar could be applied as precursor to produce an electric conductor or battery electrodes (Huggins et al., 2014; Andrade et al., 2020).

Slow pyrolysis is a simple transformation process of biomass into a higher thermal value fuel by thermochemical reaction in a fixed bed reactor (Yuan et al., 2020). The resulting products, such as biochar, bio-oil and non-condensable light gas, can be generated by heating at high temperatures of 500–700°C in the absence of oxygen (Hu and Gholizadeh, 2019). The proportion of products from the pyrolysis depends on various factors, such as the reaction temperature, type of raw materials used, holding time and type of reactor (Tan et al., 2015; Chen et al., 2020a). Temperature is the main factor in determining the product properties, especially for the biochar. An increase in the temperature results in an increase in the carbon content, which is a measure of the fuel heating content and electrical conductivity for electrodes or capacitors in the case of battery applications. In addition, the functional group, porosity and adsorption ability also change with the temperature used in the pyrolysis (Zhao et al., 2017).

Biochar from spent coffee grounds (SCG) is an attractive topic for many researchers since coffee is one of the most traded agricultural commodities globally and the increasing demand for coffee beans results in higher amounts of SCG (Jagdale et al., 2019), which also causes bio-waste in the environment (Fernandesa et al., 2006). The SCG material is dried before using in a pyrolysis reactor. With slow pyrolysis in a fixed bed reactor, since the bed is stationary and the dried SCG is in powder-like form with low thermal conductivity, the temperature distribution from the outer heating surface to the center of the bed is retarded, resulting in the biomass near the reactor surface being exposed to high temperature heat for a longer period than for material in the center of the bed. Consequently, the biochar properties are not uniform and a long holding time for pyrolysis at a given temperature throughout the bed is needed.

There have been many designs of fixed bed reactors to achieve a more uniform temperature distribution throughout the bed. Nakaso (2009) used a brush made of carbon fiber with high thermal conductivity, which enhanced the reaction heat in a packed bed. Mei et al. (2012) investigated the temperature distribution in a microreactor with micro-pin-fin arrays; the enhanced heat transfer unit reduced the non-uniform temperature distribution that caused a non-isothermal reaction in the bed. Zhang et al. (2022) designed an internal heating pipe with helical fins in a tubular fixed bed reactor; the reaction temperature was more uniform and the yield increased after the reaction. Chen et al. (2020b) demonstrated designs of highly conductive fins for heat transfer enhancement in a multi-tube thermochemical heat storage unit, where the dehydration process of $Ca(OH)_2$ was considered as the baseline to perform topology optimization. Gabriele et al. (2022) proposed designs of tree-like heat exchanger structures with high thermal conductivity embedded in a closed thermochemical energy storage system that obtained better thermal and chemical levels of performance.

From the above literature, most studies attempted to overcome the heat transfer limitation by introducing inserts of highly conductive materials, such as metallic fins or inner tubes with fins and a chemical coating, to generate more heat in the packed bed. Even better results in the temperature distribution in the bed were achieved by loading in and out raw material and products, respectively, although this was quite complicated. In addition, less raw material could be placed in the reactor because of the additional extensions to the reactor's internal volume.

The current study utilized small copper metal balls not only as heat distributors in a packed bed of dried spent coffee grounds, but also investigated simplified and low-cost modifications to the reactor. Two designs were considered: layers of small metal balls in the SCG bed and mixing small metal balls throughout the SCG bed. Temperature distributions were monitored at the heating surface and at the center of the bed during pyrolysis using a set of thermocouples. The properties of the biochar products after pyrolysis, such as heating value, Brunauer-Emmett-Teller (BET) surface area and electrical conductivity, were considered and compared with those from the bed without metal balls.

Materials and Methods

Raw materials

The SCG sample was collected from the Coffee Café in Chiang Mai, Thailand and sieved through a 1 mm mesh, dried in an oven at 80°C for 24 hr. and then collected in a vacuum bag. The sample was subjected to slow pyrolysis at a controlled temperature of 500°C for 2 hr.

Experimental setup

Fig. 1 shows the experimental setup for slow pyrolysis used in this study. The unit consisted of an electric furnace, a fixed bed cylindrical reactor (10.4 cm internal diameter, 0.5 cm thickness and 16 cm height) and a water condenser. Nitrogen gas from a nitrogen tank was fed into the reactor continuously during pyrolysis and the gas carried away the volatile compounds from the SCG to the condenser to produce a liquid product. A set of thermocouples was used to monitor the furnace temperature, gas temperature inside reactor and the SCG bed around the heating surface at height of 1.7 cm and 5 cm from the bottom of the SCG bed (positions 1 and 3) and at the same level as the bed axis (positions 2 and 4). The latter two were the last positions of the SCG bed to decompose.

Biochar preparation

A sample of the dried SCG (300 g) was placed in the reactor (SCG bed height approximately 10 cm) for pyrolyzing under a nitrogen atmosphere with a nitrogen gas flow rate of 50 mL/min. The heating temperature was controlled at 500°C with a heating rate 30°C/min and the heating holding time was 2 hr. Two designs were tested using small metal balls as internal heat distributors, as shown in Fig. 2: The first design used two layers of 8 mm metal balls (760 g total weight) that were split on the SCG bed into three sections, each 3.3 cm thick, with a weight of 100 g. The second design mixed the balls of the same weight uniformly throughout the SCG bed. The first design experiment was repeated with 4 mm metal balls (470g). The properties of biochar at position 2 were investigated in terms of the heating value, specific surface area, pore volume, pore size, iodine adsorption, pH, electrical conductivity (EC) and CEC and all the results were compared with those without metal balls. Each experiment was repeated three times and the average results were presented.

Biochar analysis

Thermogravimetric analysis (TGA) and differential thermogravimetric (DTG) curves in the Thermo plus EVO2 software (Rigaku; Japan) were used to investigate the decomposition behavior of the SCG with temperature.

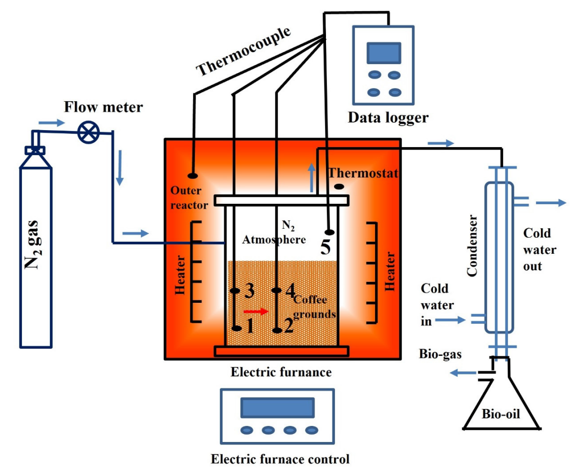

Fig. 1 Experimental setup for spent coffee grounds pyrolysis and positions of temperature measurements

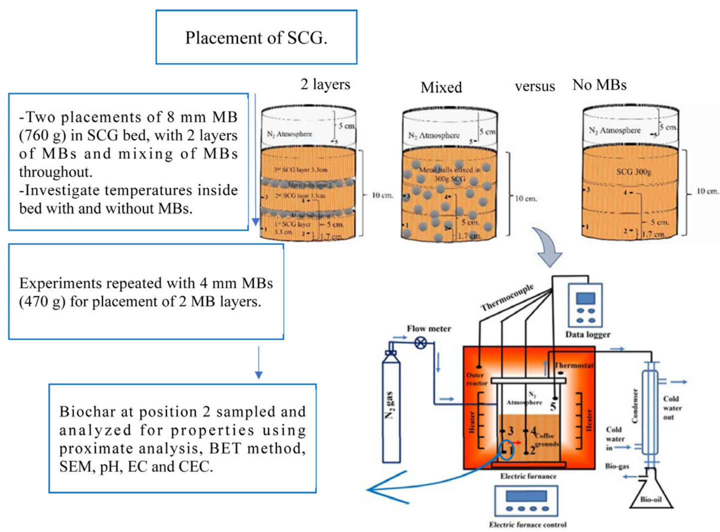

Fig. 2 Spent coffee grounds (SCG) bed with and without metal ball (MB) placements, where BET = Brunauer-Emmett-Teller, SEM = scanning electron microscopy, EC = electrical conductivity and CEC = cation exchange capacity

Each sample, approximately 1 mg, was heated at a rate of 10°C/min to raise the ambient temperature to 900°C. The TGA experiments were performed a under nitrogen atmosphere with a flow rate of 100 mL/min. Proximate analysis and the higher heating values (HHVs) of the raw material and biochar after pyrolysis were carried out using a TGA-701 Thermogravimetric Analyzer and bomb calorimeter, respectively. The specific surface area and pore size of each biochar sample was investigated using the BET technique using a surface area and pore size analyzer (Moded Autosorb 1 MP; Quantachrome; USA). In addition, the morphologies of the biochars were observed using scanning electron microscopy (SEM; JEOL JSM-5910LV; France). The pH and EC levels of each biochar sample were measured using a conductivity meter (Metrohm 914; Switzerland). The CEC were determined based on reagent NH_4OCA/distillation.

Results and Discussion

Thermal decomposition analysis of spent coffee grounds

Fig. 3 shows the TGA and DTG curves of the experimental SCG at a heating rate of 10°C/min under a nitrogen atmosphere in the range 30–900°C. The TGA curve shows the percentage weight loss while the DTG curve presents the mass rate change as a function of the temperature during pyrolysis. The SCG weight loss below 200°C was related to the evaporation of moisture and some volatile compounds (Burhenne et al., 2013), while in the range 200–450°C, the weight dropped quickly because of the high thermal decomposition into volatile substances of the hemicellulose, cellulose and lignin in the sample (Pandey and Kim, 2011). Above 500°C, the weight loss rate of the DTG curve was reported to be rather steady but lower yield of biochar (Saiyud et al., 2022). However, in the current study, the process temperature was controlled not to exceed 500°C. The total weight loss at 900°C was reported to be around 85%.

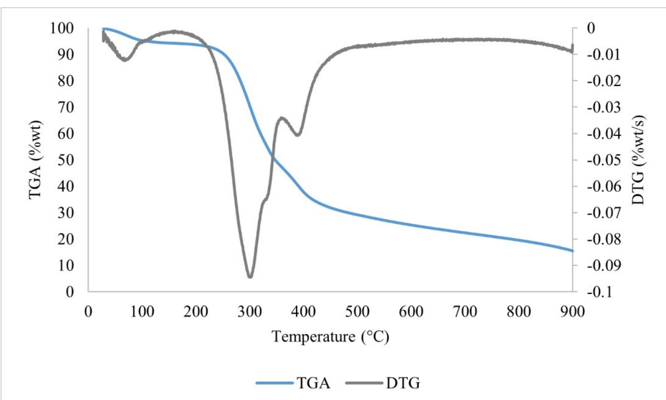

Fig. 3 Thermogravimetric analysis (TGA) and differential thermogravimetric (DTG) curve analysis from spent coffee ground

Effect of metal balls on bed temperature

Fig. 4 shows the temperature changes of the nitrogen in the reactor, the normal SCG bed at positions 1 and 3 (close to the reactor heating surface) and 2 and 4 (at the axis of the bed) in the SCG bed during pyrolysis. Nitrogen gas was fed into the reactor continuously and the flow rate was rather low; consequently, the gas temperature increased quickly due to the heat from the reactor surface wall. The gas temperature reached 450°C in 30 min, with at higher temperatures, the gas also transferred heat into the SCG bed. Since the SCG bed at positions 3 and 4 was closer to the bed surface than for positions 1 and 2, the shallow position received more heat than the deeper position.

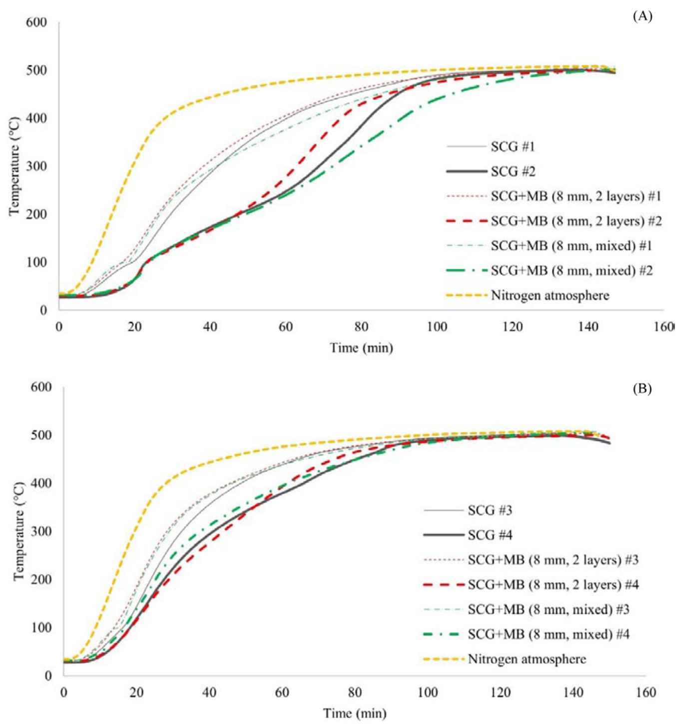

Fig. 4 Temperature profiles in spent coffee grounds (SCG) bed with two metal ball (MB) placements at: (A) positions #1 and #2; (B) positions #3 and #4

For normal operation without the metal balls, the bed temperatures around the reactor heating surface (positions 1 and 3) rapidly increased to around 450°C and after that they approached asymptotically the controlled temperature at 500°C. However, position 3 was closer to the upper bed surface that also received convective heat from the high temperature nitrogen, resulting in its temperature being slightly higher than for position 1. The bed temperatures at the axis (positions 2 and 4) were retarded due to the high thermal resistance of the bed material. Similarly, the temperature at position 4 was higher than for position 2 since the previous position also absorbed more heat from nitrogen at the upper bed surface than the latter one. At position 2, from about 80–100°C and up to 200°C, there was evaporation of moisture and some volatile matter within the bed (see Fig. 3); then, the temperature increased steadily with time at a rate of approximately 3.3°C/min. Above 200°C, the temperature rate increased to be approximately 5.9°C/min due to the exothermic change from the thermal decomposition levels of the hemicellulose, cellulose and lignin in the sample. After that, the bed was heated to 450°C and approached 500°C.

The effects of metal balls (MBs) as internal heat distributors on the bed temperatures were investigated from the results in Fig. 4. By the placement of two layers of the copper MBs with an average diameter of 8 mm (as described in Fig. 2), the bed temperatures at positions 1 (Fig. 4A) and 3 (Fig. 4B) around the heating surface were slightly higher than those without the metal balls, because the SCG in the bed had a greater area of heat transfer than from just the reactor heating surface, with the increase provided by the MBs. A similar result was found at position 4. However, at position 2, the bed temperature with MBs increased significantly more than for the normal bed during thermal decomposition in the range 200–450°C, indicating that the MB layers acted as an extended surface that carried more heat from the reactor heating surface to the SCG bed. Consequently, a more uniform bed temperature could be achieved, along with more uniform biochar product properties. In addition, the holding time to get complete pyrolysis was shortened compared to for the unit without metal balls, resulting in a lower amount of heat input for the pyrolysis. The temperature rate at position 2, with the MBs, changed from 3.33°C/min to 7.2°C/min at 200°C, while without the MBs, the value changed from 3.33°C/min to 5.9°C/min; thus, the temperature rate of the unit with MBs increased approximately 22% during thermal decomposition, compared to without the MBs.

Mixing the metal balls with the same weight throughout the SCG bed was not effective. Furthermore, the higher heat capacity of the bed covering the copper metal balls and SCG had a total heat capacity of 0.87 kJ/K plus SCG at 1.9 kJ/kgK (Cardoso et al., 2018) plus the copper metal of 0.39 kJ/kgK (Paul, 2016)), compared to the SCG only, with a total heat capacity of 0.57 kJ/K. Thu, the heat rate of the temperature at position 2 above 200°C changed slightly from the first period and was also lower than that for the normal bed. It could be concluded that the second placement was inappropriate.

The effect of MB sizing on the temperature distribution in the SCG bed was also investigated using the placement of the two MB layers. Each layer acted as an extended surface of the reactor's heating surface for transferring heat into the SCG bed, with the thickness being a key factor; the greater the thickness, the more heat was conducted from the reactor surface through the MB layer and into the SCG bed. In addition, the bigger size of metal balls provided a larger surface area and a higher heat transfer rate to the SCG bed.

Fig. 5 shows the temperature histories of position 2 in the bed for two layers of 4 mm copper balls (470 g, with total surface area 125.6 cm^2) compared to those of 8 mm copper balls (860g, with total surface area 196.4 cm^2). The smaller-sized copper balls resulted in less area of heat conduction from the reactor heating surface that could transfer heat into the SCG bed, resulting in the increase in the temperature rate at position 2 during thermal decomposition was only approximately 9.6% compared to that of the normal condition and the rate was still less than that for the 8 mm copper balls.

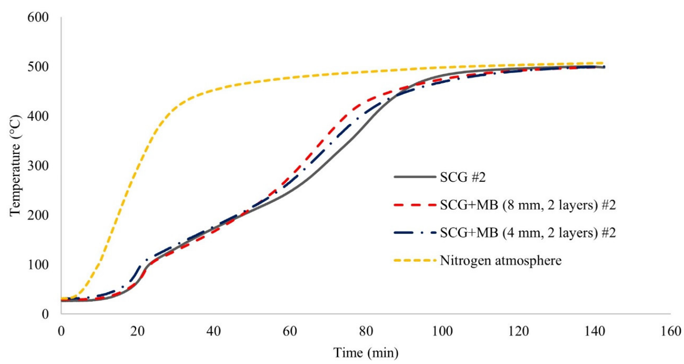

Fig. 5 Temperature profiles at position #2 with 8 mm and 4 mm metal balls (MBs) for placement of two MB layers compared with normal bed, where SCG = spent coffee grounds,

Characteristics of biochar produced from spent coffee grounds

Table 1 shows the product yields after pyrolysis at 500°C for a holding time of 2 hr. Since the holding time was sufficiently long for each experiment, there was no significant difference in the biochar yield after pyrolysis of the SCG with and without the MBs. The percentage of biochar yield was about 25.7–26%wt.

Table 2 shows the proximate analyses and higher heating values of raw SCG and biochar obtained from SCG pyrolysis with and without the MBs. During pyrolysis, there was high thermal decomposition of the components in the sample, with the percentages of moisture and volatile matter including ash of the biochar products being lower than those of the raw SCG but the amounts of fixed carbon and HHV increased. These properties of the products with and without MBs were not much different and the values were similar to those from the experiments of Tangmankongworakoon (2019).

Since the process with the MBs reached the decomposition temperature (200–450°C) more rapidly, the pyrolysis was more complete and the products from the SCG bed with the copper balls had higher values for the specific surface area, pore volume and iodine number than those without MBs, as given in Table 3. The specific surface area, pore volume and pore size, including the iodine adsorption capacity increased 1.10%, 15.76%, 14.44% and 118%, respectively, compared to those for the normal bed. In addition, based on the SEM technique, Fig. 6 shows the surface morphology analyses of the products from the beds with and without MBs. In the process with the MBs, the sample reached the thermal decomposition period (200–450°C) earlier and a longer holding time for thermal decomposition was achieved and the surface of the product from the bed without the MBs (Fig. 6A) had less porosity than with the MBs (Fig. 6B).

Table 1 Product yields from pyrolysis (%wt)

Treatment	Product		
	Biochar	Bio-oil	Non-condensable gas (100-[Char+Oil])
SCG	25.7±0.0	40.6±0.7	33.8±0.7
SCG+MB (8 mm layers)	25.9±0.6	40.7±0.3	33.6±0.5
SCG+MB (8 mm mixed)	26.0±1.0	40.6±0.7	33.4±0.5
SCG+MB (4 mm layers)	25.8±0.6	40.9±0.4	33.3±0.6

SCG = spent coffee grounds; MB = metal ball; 100-[Char+Oil] = %wt of Non-condensable gas calculate from 100%wt minus with the total %wt of biochar and bio-oil

Mean ± SD within columns derived from three independent experiments.

Table 2 Proximate analyses and higher heating values of raw spent coffee grounds (SCG) and biochar products (on as-received basis) of bed with and without metal balls (MBs)

Proximate analysis (%wt)	Biochars			
	SCG	SCG	SCG+MBs (8mm; 2 layers)	SCG_350–550°C (Tangmankongworakoon, 2019)
Moisture	6.72	0.25	0.96	4.16
Volatile matter	64.04	14.11	14.68	11.89
Ash	9.36	6.45	6.51	6.18
Fixed carbon	19.60	79.19	77.85	77.77
HHV (MJ/kg)	21.52	28.77	28.08	30.81

SCG_350–550°C = Temperature range of the SCG pyrolysis; HHV = higher heating value

Table 3 Brunauer-Emmett-Teller analysis and iodine number of raw spent coffee grounds (SCG) and produced biochars

Biochar	Specific surface area (m^2/g)	Pore volume (cc/g)	Pore size (Å)	Iodine number (mg/mL)
SCG	29.02	0.0387	26.66	270
SCG+MBs (8mm; 2 layers)	29.34	0.0448	30.51	590

MB = metal ball

Table 4 Parameters of biochar products

Biochar	pH	Electrical conductivity (mS/cm)	Cation exchange capacity (meq/100 g)
SCG	10.41	1.26	12.71
SCG+MBs (8mm; 2 layers)	10.53	1.19	16.44

SCG = spent coffee grounds; MB = metal ball

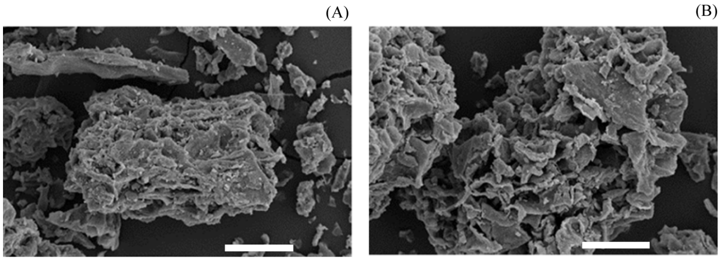

Fig. 6 Photographs of surface morphology of biochar products: (A) from bed without metal balls; (B) from the bed with metal balls, where scale bar = 50 µm

The values for the pH, EC and CEC are also main properties indicating biochar quality for soil amendment (Domingues et al., 2017). Table 3 shows the values of the biochar properties from the beds with and without MBs. With the MBs, the biochar products achieved more complete thermal decomposition than without the MBs. The longer pyrolysis period at high temperature generated greater vaporization of the volatile components, leaving the metallic elements and cations in the bed (Yuan et al., 2020; Al-Wabel et al., 2013). Enrichment of the basic ions is also associated with alkaline species, such as carbonates, oxides and hydroxides (Houben et al., 2013; Domingues et al., 2017). The results showed that the pH and EC values of the bed with the MBs did not differ significantly from those of the normal bed; however, the CEC improved significantly and therefore, the biochar was suitable for solving acidic or demineralized soil problems. In addition, the increase in CEC was related to the increase in the specific surface area (Saravanan et al., 2019), enabling the biochar to increase the nutrient and water holding capacities in the soil, leading to a reduced fertilizer requirement (Domingues et al., 2017).

Conclusion

This study proposed the placement of copper MBs for internal thermal distribution using 300 g of SGC for pyrolysis in a fixed-bed under a nitrogen atmosphere at 500°C, with a holding time of 2 hr. Two MB placements (layers of the MBs in the bed and mixing the MBs throughout the bed) were carried out and the temperature histories at the center of the bed were investigated during pyrolysis. The conclusions reached from these results were: 1) the placement of two MB layers consisting of copper balls (8 mm in diameter) improved the thermal performance as the extended surface from the bed heating area was greater than for smaller copper balls (4 mm in diameter), with the temperature rates at the bed axis during the decomposition period increasing 21.32% and 9.64%, respectively, compared to without the MBs; 2) mixing the MBs throughout the bed was not appropriate, since their role in extending the surface of the bed heating area was not as effective; in addition, the effect of the high total heat capacity of the balls and the SCG retarded the bed temperature heating rate; 3) the two layers of 8 mm copper balls achieved a longer decomposition period at high temperature, resulting in increases in the specific surface area, pore volume and pore size, as well as the CEC.

Thus, the developed technique improved the properties of the biochar for soil amendment, especially in an acidic soil. In addition, the nutrient and WHC of the biochar was improved.

Acknowledgement

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Conflict of Interest

The authors declare that there are no conflicts of interest.

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