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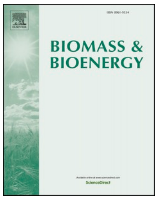

Effects of wood ash on physicochemical and morphological characteristics of sludge-derived hydrochar pellets relevant to soil and energy applications

Ali Mohammadi [a,*], Anthony Ike Anukam [b], Karin Granström [a], Samieh Eskandari [a], Martyna Zywalewska [a], Maria Sandberg [a], Elizabeth Bosede Aladejana [c]

[a] *Department of Engineering and Chemical Sciences, Karlstad University, 65188, Karlstad, Sweden*
[b] *Biochemical Process Engineering, Division of Chemical Engineering, Department of Civil, Environmental and Natural Resources Engineering, Luleå University of Technology, 97187, Sweden*
[c] *Electron Microscopy Unit, Central Analytical Laboratory, Faculty of Science and Agriculture, University of Fort Hare, Alice, 5700, South Africa*

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ABSTRACT

Hydrochar is produced through a process called hydrothermal carbonization (HTC) and constitutes a carbon-rich solid material with different remarkable applications. This study investigated the effects of wood ash on the physicochemical and morphological properties of biosludge-derived hydrochar in pelleted form relevant to the use of the pellets as a soil nutritional and liming agent and as a biofuel source. The hydrochar was mechanically compressed into uniformly-sized pellets under applied pressures of 4 and 8 kN after blending with varying percentages of wood ash in the order 0, 20 and 50%. The pure and blended pellets were characterized to determine the impact of wood ash on key properties, correlated to the two applications mentioned above. Results demonstrated a strong relationship between key features of the pellets and ash proportion. The wood ash-blended hydrochar pellets showed good hydrophobicity as a consequence of increased contents of alkali and alkaline earth metals, but were low in aromatic functional groups compared to the pure hydrochar pellet. Furthermore, the heating value of the pure hydrochar pellet was about 4% higher than that of its parent material and indicates that this pellet has the capacity to serve as a source of energy. The study generally reveals that blending hydrochar produced from biosludge under HTC conditions with up to 20%–50% of wood ash and mechanically compressing into homogeneous pellets has promising potential for a nutrient-rich material that can enhance soil fertility.

1. Introduction

Sweden is one of the world's largest exporters of pulp and paper products. The water consumption rate of the production processes generates substantial amounts of wastewater and biosludge [1]. Biosludge is normally considered as a waste product mostly disposed of by incineration. Biosludge is very difficult to dewater due to its high moisture content, making it arduous to use the material as a source of energy [2,3]. However, with hydrothermal carbonization (HTC), biosludge can be transformed into a valuable resource when striving toward a resource-efficient recovery.

In comparison to other techniques such as pyrolysis and torrefaction, HTC has distinct advantages: including high conversion efficiency, simplicity, and ease of operation as relatively mild reaction conditions eliminates the need for feedstock drying (the process uses the moisture content of the feedstock as its reaction medium [4–6]). HTC saves over 50% of thermal energy and around 70% of electrical energy in comparison to conventional methods of drying sludge [7]. The hydrochar (HC) produced is dewaterable, hygienic and has some coal-like properties. Depending on the feedstock, the HC may have high energy density [8,9].

Using HC as a source of biofuel may be the first choice that comes in mind. However, HC also has good qualities as a soil amendment especially if enhanced with wood ash and compressed into pellets. The physicochemical properties of HC pellets with and without ash addition, and the consequences thereof for the possibility to use HC for fuel and soil improvement, were examined in this study.

The need for soil improvement in forestry is due to the fact that continuous wood harvesting removes significant amounts of nutrients and alkali cations from forest soils. This increases the bioavailability of

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[*] Corresponding author.
E-mail addresses: ali.mohammadi@kau.se, mohammadia2011@gmail.com (A. Mohammadi).

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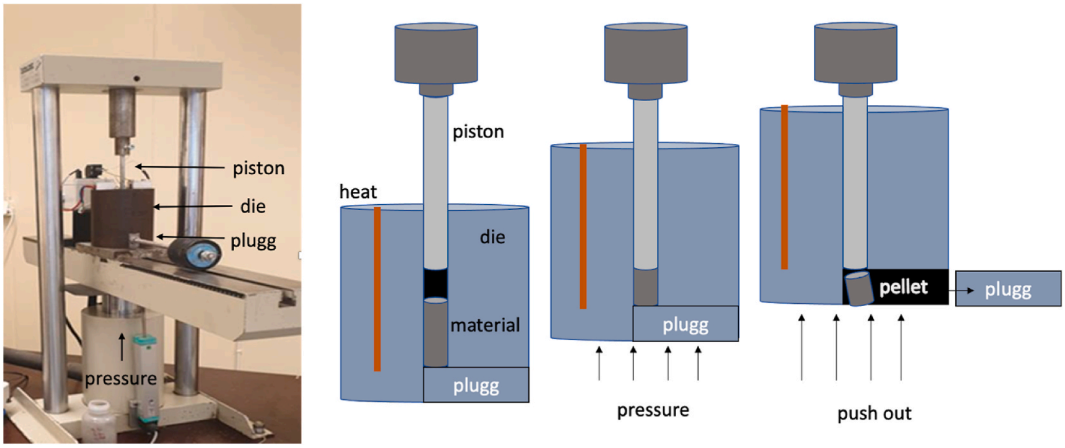

Fig. 1. A schematic representation of the three sub-processes involved in the pelleting of hydrochar powder.

environmental contaminants and soil acidification.

In order to continue sustainable forestry, soil acidification and mal nutrition must be mitigated. Today, ash rich in alkali ions and phosphorus are spread in Swedish forests. However, the ash lacks nitrogen due to the high temperature conditions under which the ash is generated; the nitrogen is often emitted as NO_x gas. Boreal forest soils often lack nitrogen more than phosphorous. Due to relative low carbonization temperature in the HTC process, both nitrogen and phosphorous remains in the HC. Therefore, HC can act as a valuable source of nutrients to degraded soils, as high P content of biochar favours soil nutrient retention [10]. Phosphorus is an element that cannot be substituted by any other element and remains a major plant nutrient that is only available for plant uptake in its inorganic form as $H_2PO_4^-$, HPO_4^{2-} and H_3PO_4 [11,12]. A mix of ash and HC have both liming and fertilizing properties [13]. The downside is that both ash and HC contain heavy metals that originate from the tree concentrated through the industrial processes into the residues.

Although HC has been a subject of many investigations, most prior studies [14–21] largely focus on HC powder and pellets that are derived from woody biomass, agricultural residues and sewage sludge. Not much has been undertaken on the characteristics of HC pellets produced from pulp and paper mill sludge in relation to energy applications where it can offer environmental benefits relative to conventional sludge disposal options [22]. When considering using HC pellets as soil amendment, additives such as wood ash may be needed to improve their potential effects as a soil amendment [13,23]. However, for energy application, adding wood ash to HC pellets is often not recommended as ash may create significant technical issues [24].

HC is fine-texture by nature, which constitutes an issue of concern when HC is used for energy as well as soil amendment. When HC and ash (or a combination of these as one material) is used for soil applications, some quantities may be lost due to wind and rainfall erosion. In view of this, pelleting of HC may be necessary as this will not only address the issues mentioned but will also facilitate handling, transportation, distribution and storage. Pelleting can also enhance gravity feeding where the HC pellets are used as feedstock in combined heat and power (CHP) plants to recover energy [25,26]. The traditional pelleting process is not suitable for ash. However, by pelleting a mixture of both materials (HC and ash) at different ratios, a new blended product with ingredients that corresponds to soil specific needs can be produced.

The purpose of this study therefore was to investigate the physicochemical and morphological characteristics of pure and wood-ash blended HC pellets that are derived from pulp and paper mill biosludge and determine the relevance of the pellets as soil amendment and as a source of energy based on their characteristics. Nonetheless, the only material considered for both soil and energy applications was the pure HC pellet, while the properties of the wood ash-blended HC pellets were assessed in relation to their use as soil nutritional and liming agents only, and not as a source of energy.

2. Materials and methods

2.1. Raw material selection and preparation

Pulp and paper mill biosludge was chosen for this study because of its availability in excess of its usage. Biosludge is a sticky and highly moist organic residue with little or no known value, hence it was considered as the raw material for this work. The biosludge was collected from a local pulp and paper mill and was air-dried to lower its moisture content (MC) to an acceptable level required for further use. Thereafter, the biosludge was oven-dried at 103 °C for 24 h before milling to the desired size.

2.2. Biosludge conversion to hydrochar

A HTC process at pilot-plant scale in Innventia's Parr reactor [12] was employed for the conversion of biosludge into hydrochar (HC). The process was conducted at a temperature of 200 °C, and pressure of 20 bar at a residence time of 2 h with a HC yield of 68% and 60 kg exhaust gas, which was released to the air [27,28]. The biosludge-derived HC powder was later collected from the site, sealed in different airtight vials and stored at room temperature until further use in the current study.

2.3. Hydrochar enrichment with wood ash and compression process

The biosludge-derived HC powder was enriched with wood ash in the proportion 10, 20, 30, 40 and 50% (w/w), with the addition of water in the range of 3–30% (w/w) as plasticizer to improve particle bonding during the pelleting process. The wood ash was collected from biofuel furnaces in Skoghall mill (a pulp and paper unit) located in the Värmland Province of Sweden. Pellets were made using a single pellet press (available at the Division of Environmental and Energy Systems, Karlstad University) using pressure of 1, 2, 4, 6 or 8 kN (Fig. 1). This resulted in 146 pellets which were analyzed for hardness, pH, density and length. The results of this screening study were modelled with MLR (see also section *2.5.3*). Selected for more thorough study were the chemical properties and surface analysis of the pellets with MC of 20% and wood ash proportions of 0, 20 and 50%, under applied pressures of 4 and 8 kN, which are typical compression forces required for the formation of durable pellets [29].

The temperature of the steel cylinder (die temperature) was set at 100 °C. During the compression process, the piston compressed the powder material at a constant speed of 30 mm/min. When the desired pressure was attained, the compression was maintained for 10s, after which the pellets were ejected from the die. At least three pellets were made for each sample. The pellet press and its mode of operation are detailed in Ref. [30].

Further details on the procedure for HC enrichment with wood ash as well as on pelleting of the mixtures are available in Supplementary Information (SI) – see sections S1 and S2.

2.4. Analysis of the biosludge-derived hydrochar pellets

The biosludge-derived hydrochar pellets including the wood ash used for enrichment of the pellets were analyzed using cutting-edge analytical tools to understand quintessential properties of relevance to the application of the hydrochar pellets as soil nutritional and liming agents, and as sources of energy. Specific information about the analytical techniques and their experimental procedures are described in the following subsections. All the experiments were carried out in three replicates and average values reported.

2.4.1. Determination of physical properties

The solid density of the pellet samples was measured in g/cm^3 by measuring the volume and weight of the pellets, the hardness of the pellets was determined in kg using a KAHL motor-driven hardness tester (K3175-0011, Reinbek, Germany), with a spring (3.5 mm diameter) installed for the 0–100 kg range. The results of these tests are presented as average values of ten pellets for solid density, and six pellets for hardness [30]. For the determination of moisture uptake, the pellets were dried at 50 °C for 24 h and their weights determined. Shortly after, the pellets were stored in a climate test chamber at 30 °C and 90% relative humidity until equilibrium was reached. The weight of pellets were measured three times for the first 3 h in the climate test chamber, and then measured occasionally afterwards to determine when the equilibrium was attained [30].

2.4.2. Determination of chemical properties

Elemental composition is an important parameter to consider when assessing the properties of hydrochar for any application. The chemical properties of pure and wood ash-blended hydrochar pellets were determined in terms of their elemental constituents involving both inorganic/heavy metals and trace elemental constituents. Other chemical properties also considered include pH, electrical conductivity (EC), and cation exchange capacity (CEC), which were all considered important properties that are relevant to the use of the HC pellets as soil nutritional and liming agents. The analytical methods employed and their experimental procedures are presented thus:

A CHN-analyzer, an Elementar Vario EL with TCD detector was used for the determination of the weight percentages of carbon (C), hydrogen (H) and nitrogen (N). A 5–50 mg of each sample was weighed into a tin foil boat. This was placed in the instrument where it was combusted at an oven temperature of around 950 °C. The resulting gases from the combustion process of the samples were reduced on a copper column. While nitrogen was directly measured, carbon was absorbed in the absorption columns of the instrument and measured shortly after desorption.

For the determination of the weight concentrations of heavy metals present in the samples, an inductively coupled plasma–optical emission spectrometry (ICP–OES) was used. Prior to analysis, samples were digested at 240 °C in concentrated nitric acid as required by the instrument. Nitric acid was preferred for digestion because it converts metal ions into their nitrate salts, which are highly soluble in water.

A pH meter and an electrical conductivity (EC) meter were respectively used to measure the intensity of acidity or alkalinity and quantity of electrical current of the HC-ash pellets. A 0.5 g of each sample was added into 50 mL ultrapure water and placed in a centrifuge tube for 48 h until there was stability in the pH of the slurry [31]. The same procedure was followed during EC determination.

Cation exchange capacity (CEC) is a measure of a material's negative charges that allows the material to retain positively charged exchangeable cations (like NH^{4+} Ca^{2+}, and K^{+}), and is therefore a desirable quality in soils [32]. In order to measure CEC, first, the dried (105 $^{\circ}C$ overnight), ground samples (<2 mm) were acid digested with ultra-wave digestion technique (Milestone© with unique Single Reaction Chamber (SRC)). Then CEC was determined using inductively coupled plasma optical emission spectroscopy (ICP- OES). The CEC, often expressed as centimoles of charge per kilogram (cmol$^+$/kg) of tested material, of the HC-ash pellets were calculated based on the sum total of the exchangeable cations (Ca^{2+}, Mg^{2+}, K^+ and Na^+) that the material can absorb at a specific pH.

2.4.3. Multi linear regression analysis relevant to physical properties

A multi linear regression (MLR) analysis was undertaken on the physical properties of the HC-ash pellets in order to understand the impact of each variable in predicting the outcome of the response variable. Factors such as ash, moisture content and pressure were assigned as quantitative or multilevel. Responses including hardness, pH, density and length of pellets were defined and not limited to min or max. Data were inserted and the model was chosen as D-Optimal interaction model fitted with MLR MODDE (13.01). The model achieved a R^2 of 0.62 for hardness, 0.89 for pH, 0.65 for length, and a reproducibility of 0.98 for hardness, 0.97 for pH, 0.88 for density and 0.88 for length. More information on the MLR model is provided in SI (section S3).

2.4.4. Higher heating value determination

The quality of any material intended for use as an energy source is usually evaluated on the basis of its higher heating value (HHV). This property refers to the heat released upon the complete combustion of the material, assuming that the moisture originally present in the material and any generated moisture are present in the condensed state [33]. The HHV of the pellets were each calculated based on the weight proportions of major organic elemental constituents of the HC-ash pellets. The HHV of the samples were calculated according to equation (1) [33] and presented in MJ/kg:

$$HHV\ (MJ\,/\,kg) = -1.3675 + 0.3137C + 0.7009H + 0.0318O \tag{1}$$

Where C and H represent the carbon and hydrogen contents of the samples, and O is the sum of the contents of oxygen and other elements (including S, N, Cl, etc.) in the organic matter, i.e., O = 100 - (C + H + ash).

The energy yield of pure HC samples were calculated by the following equation [18]:

$$Energy\ yield = Hydrochar\ yield \times Energy\ densification \tag{2}$$

Where the energy densification = HHV of the hydrochar/HHV of the feedstock.

2.4.5. Fourier transform infrared spectroscopic analysis

Surface functionality analysis was determined to understand the effect of wood ash on the structural composition of the pellets. This was done in accordance with identification of key functional groups using Fourier transform infrared–Attenuated total reflectance spectroscopy (FTIR–ATR) (Perkin Elmer Spectrum Two spectrometer) in an attenuated total reflectance mode. Spectra were scanned in the range 4000–600 cm^{-1} at a resolution of 4 cm^{-1} and were analyzed using the principal component analysis (PCA) in such a way that the samples were classified by their spectral characteristics [34].

2.4.6. Scanning electron microscopic analysis

Scanning electron microscopic (SEM) analysis was performed to observe the effects of ash on the morphological properties and surface structures of the pellets. This was also intended to determine structural changes of relevance to soil and energy production applications of the HC-ash pellets. Morphological characterization was performed with JEOL (JSM-6390LV) coupled with an EDX analyzer and operated at 15

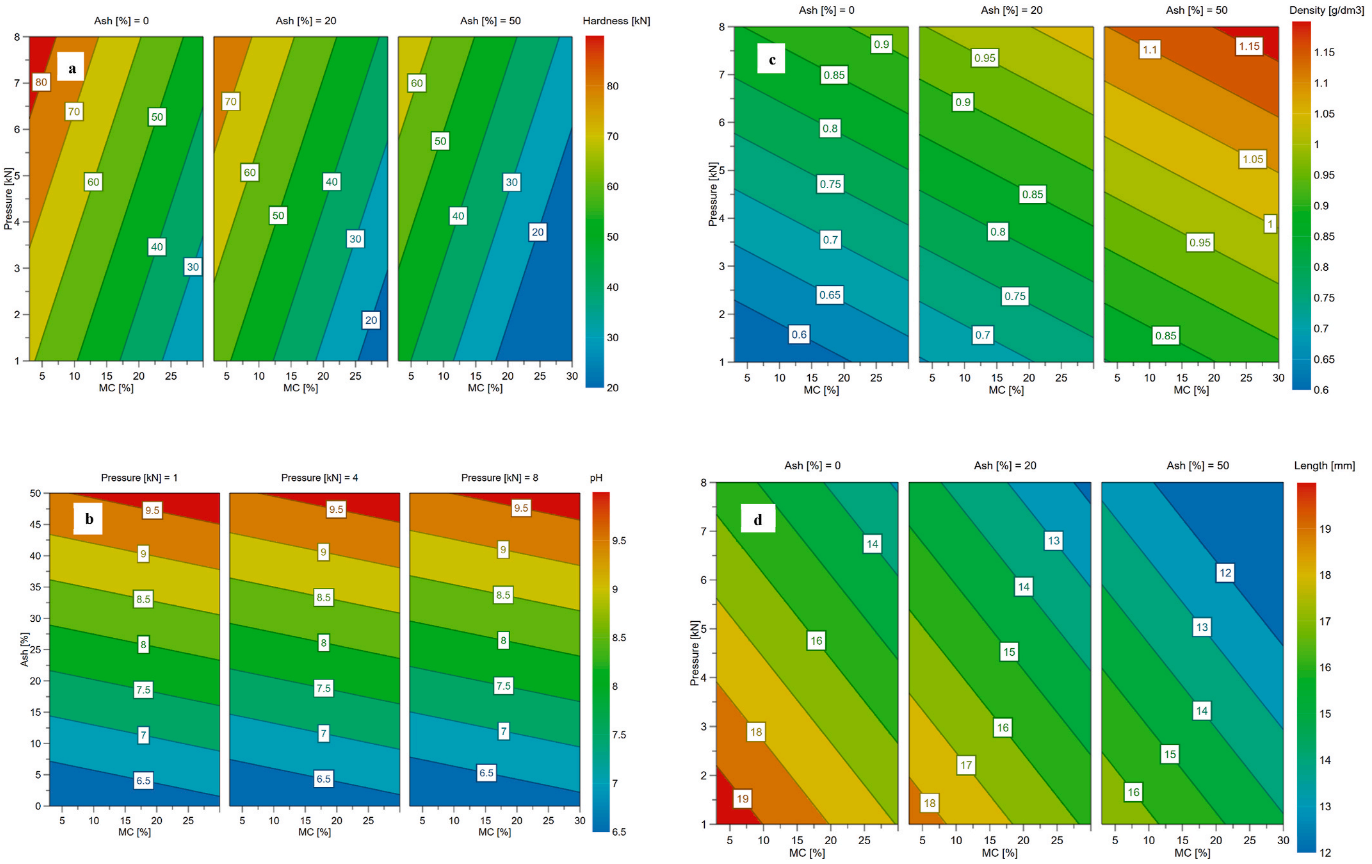

Fig. 2. Modelled effects of MC, ash content and pellet production pressure on the physical properties of HC-ash pellets: a) pellet hardness; b) pH; c) pellet density; d) pellet length.

kV. Before observation, the samples were gold-sputtered by JEOL JFC-1100E ion sputter equipment under argon atmosphere, with an ion current of 10 mA for 7 min. Thus, samples were painted with conductive gold cement to improve conductivity and to make viewing under the SEM less complicated.

2.4.7. *Statistical analysis*

In order to examine the significance of differences among treatments, measured data of physical and chemical characteristics subjected to an analysis of variance (ANOVA) based on the General Linear Model (GLM). The Tukey's HSD test was used to evaluate the differences among the means (n = 3) of the individual treatments and interactions. Data management and analysis were performed using IBM SPSS Statistics for Windows, Version 27.0 (Released 2020. Armonk, NY: IBM Corp). All the statistical testing was performed based on $P < 0.05$ as the critical level for significance.

3. Results and discussion

3.1. *Physical properties*

3.1.1. *Screening study - model predictions*

A response contour plot is useful in determining settings that will maximize or minimize a selected response variable, or to manage to reach a target value. Fig. 2a–d shows response contour plots for all responses tested in this study.

As shown in Fig. 2a–d, the physical properties of HC-ash pellets (hardness, pH, density and length) were plotted as a function of the percentage of ash and moisture content under varying pellet production pressures of 1, 2, 4, 6 and 8 kN. The numbers inscribed in the plots represent the values obtained for the HC properties under the varying proportions of ash and moisture contents. The results show that as the concentration of ash increased, the hardness of the pellet decreased (Fig. 2a), pH increases (Fig. 2b), pellet density increases (Fig. 2c), and the length of the pellets decreases (Fig. 2d). The results confirm that there is a relatively strong correlation between the properties of HC (such as hardness, pH, density and length) and ash concentration, suggesting that the model applied is appropriate for estimating the impact of ash on the properties of HC where time-consuming and experimental determinations of these properties are not available.

Table 1
The measured physical properties of biosludge-derived hydrochar pellets with varying proportions of wood ash (mean value ± standard error, n = 3). Within the row, values with letters in superscript are significantly different ($P < 0.05$) based on an ANOVA and Tukey's HSD mean comparison tests.

Pellets	Pressure - 4 kN			Pressure - 8 kN		
	HC-ash 0%	HC-ash 20%	HC-ash 50%	HC-ash 0%	HC-ash 20%	HC-ash 50%
Density (mg/cm^3)	0.78 ± 0.01^{c}	0.87 ± 0.01^{b}	1.06 ± 0.02^{a}	0.88 ± 0.01^{b}	0.89 ± 0.01^{b}	1.12 ± 0.02^{a}
Hardness (kg/pellet)	29.3 ± 1.8^{c}	23 ± 2.7^{d}	20.0 ± 1.6^{d}	61.3 ± 2.3^{a}	52 ± 2.9^{b}	22.0 ± 1.5^{d}
Length (mm)	15.9 ± 0.2^{a}	13.8 ± 0.1^{b}	11.4 ± 1.0^{c}	14.2 ± 0.2^{b}	13.5 ± 0.2^{b}	10.0 ± 0.1^{c}

The 20% MC was chosen as higher MC causes low hardness and lower MC requires more of energy intensive drying. MC 20% has also been chosen in other biochar pelleting studies [19,35]. Pellets with 0%, 20% and 50% of wood ash (marked as HC-ash 0%, HC-ash 20% and HC-ash 50%) are good representative of all data collected for this current study.

Table 2

Compositions of the elemental constituents of pure and wood ash blended biosludge-derived hydrochar pellets (mean value ± standard error. $n = 3$), and recommendations[a] by the Swedish forestry agency. Within the row, values with superscript letters are significantly different ($P < 0.05$) based on an ANOVA and Tukey's HSD mean comparison tests.

	HC-ash 0%	HC-ash 20%	HC-ash 50%	Wood ash	Recommendation[a]
C (g/kg)	492.05 ± 15.1^{a}	399.95 ± 13.8^{b}	261.80 ± 12.0^{c}	$31.55 \pm 08.9\ ^{d}$	–
H (g/kg)	55.53 ± 0.6^{a}	44.42 ± 0.5^{b}	27.75 ± 0.3^{c}	–	–
N (g/kg)	22.56 ± 0.3^{b}	18.15 ± 0.2^{c}	$11.52 \pm 0.2\ ^{d}$	0.48 ± 0.1^{a}	–
O (g/kg)	415.18 ± 13.2^{d}	$521.\ 6 \pm 16.1^{c}$	681.34 ± 20.3^{b}	947.55 ± 27.4^{a}	–
S (g/kg)	14.759 ± 0.31^{c}	15.890 ± 0.289^{c}	17.586 ± 0.26^{b}	20.414 ± 0.22^{a}	–
P (g/kg)	2.779 ± 0.664^{c}	3.960 ± 0.548^{bc}	5.732 ± 0.375^{b}	8.685 ± 0.08^{a}	>7
Ca (g/kg)	2.724 ± 0.035^{d}	45.512 ± 0.879^{c}	109.694 ± 2.145^{b}	216.664 ± 4.256^{a}	>12.5
K (g/kg)	1.345 ± 0.024^{d}	4.941 ± 0.043^{c}	10.336 ± 0.073^{b}	19.328 ± 0.122^{a}	>30
Mg (g/kg)	1.339 ± 0.018^{d}	2.981 ± 0.041^{c}	5.444 ± 0.076^{b}	9.549 ± 0.134^{a}	>15
As (mg/kg)	0.7 ± 0^{d}	$1{,}00 \pm 0^{c}$	1.44 ± 0.01^{b}	2.19 ± 0.02^{a}	<30
Pb (mg/kg)	23.7 ± 0.1^{d}	24.1 ± 0.1^{c}	24.6 ± 0.1^{b}	25.5 ± 0.1^{a}	<300
Cd (mg/kg)	9.6 ± 0.1^{a}	9.3 ± 0.1^{ab}	9 ± 0.1^{b}	8.3 ± 0.1^{c}	<30
Cu (mg/kg)	71.4 ± 0.1^{a}	70.4 ± 0.2^{a}	69 ± 0.3^{b}	66.5 ± 0.5^{c}	<400
Cr (mg/kg)	38.5 ± 0.4^{d}	42.5 ± 0.4^{c}	48.6 ± 0.5^{b}	58.6 ± 0.6^{a}	<200
Ni (mg/kg)	19.1 ± 0.2^{a}	18.1 ± 0.2^{b}	16.7 ± 0.1^{c}	14.3 ± 0.1^{d}	<70
V (mg/kg)	15.5 ± 0^{d}	21.3 ± 0.1^{c}	30.1 ± 0.2^{b}	44.6 ± 0.4^{a}	<70
Zn (mg/kg)	433 ± 0.9^{d}	584.5 ± 0.8^{c}	811.7 ± 0.7^{b}	1190.4 ± 0.5^{a}	500–7000
C/N molar ratio	21.85 ± 3.59^{b}	22.08 ± 3.73^{b}	22.78 ± 3.79^{b}	$74{,}91 \pm 0.31^{a}$	–
H/C molar ratio	0.11 ± 0.02^{a}	0.11 ± 1.02^{a}	0.10 ± 0.02^{a}	–	–
O/C molar ratio	0.84 ± 0.21^{b}	1.31 ± 0.34^{b}	2.60 ± 0.71^{b}	34.41 ± 6.92^{a}	–

[a] The recommendations for ash to be added in forest soils.

3.1.2. *Enlarged study of selected pellets*

Table 1 presents the measured physical properties of HC-ash pellets with varying percentages of wood ash tested under 4 kN and 8 kN of pressure. The terms in the table are defined as follows: HC-ash 0% represents pure hydrochar pellets; HC-ash 20% depicts hydrochar blended with 20% (w/w) wood ash; HC-ash 50% means hydrochar mixed with 50% (w/w) wood ash.

The density of the HC-ash pellets increased slightly with the percentage of wood ash added at increasing pressure of 4 kN–8 kN (Table 1). This is an indication that wood ash and applied pressure affects pellet density. This agrees with the report from Brewer et al. [36] who alluded that increases in biochar pellet density are mostly due to increases in ash concentration and the gradual condensation of carbon into aromatics. High pellet density favours both applications considered in this study (soil amendment for ash-containing HC pellets and energy production for the HC pellet without ash) because mass loss by strong wind upon soil applications of the HC pellets can be prevented; high pellet density also allows for gravity feeding when the HC pellets are considered for use as a source of energy and ensures feedstock optimum conversion efficiency [21,37]. However, the opposite is the case with regards to the hardness of the HC-ash pellets, which increases significantly with decreasing percentage of wood ash (50%–0%) and with increasing pressure (4 kN–8 kN). Although, pellet hardness may enhance with applied pressure during pelleting, the pressure needed to make a good quality pellet in terms of hardness is largely dependent upon the nature of the material; nonetheless, pellet hardness is a function of the strength of the attraction forces holding particles together [38]. Therefore, a higher pellet hardness value is usually construed to mean greater forces of attraction between combining particles. The strength of the forces of attraction decreases with increasing proportions of wood ash in the pellets. This finding is supported by Kaliyan and Morey [39] who also concluded that pellet hardness is dependent upon raw material composition and the forces holding particles together. Moreover, a higher hardness value could also be an indication that more compressive load is required to break the HC-ash 0% pellet in comparison to the HC-ash 20% and HC-ash 50% pellets respectively. In other words, the HC-ash 0% pellet may be able to withstand deformation under the application of a given load due to much higher forces of attraction between its particles relative to the HC-ash 20% and HC-ash 50% pellets. Hence, the disparity in ash percentage is the likely reason for the differences in the hardness values of the pellets.

With regards to the length of the HC-ash pellets, in terms of percentage difference, there is approximately 5–30% reduction in length between the pellets. This variation in length could be explained by differences in the way the materials responded to process conditions (such as temperature and pressure) of the pellet press during pelleting due to their varying percentages of wood ash. The most logical rule of thumb here could be that as temperature rose during pelleting, hydrolysis reactions reached equilibrium conditions, creating smaller particles in such a way that contact areas between the particles increased, and the internal porosity of the HC reduced to create a more compact pellet; as a consequence, density slowly increased. This could also explain why the HC-ash 50% pellet gave a higher density value in comparison to the HC-ash 20% pellet.

3.2. *Chemical properties*

The chemical properties of the pellet samples were analyzed in terms of their elemental compositions and are shown in Table 2 (full list of elemental composition is available in SI, Table S1). As previously stated, wood ash was not considered for any application and will not be discussed further; its properties were presented as references to the features of the HC pellet samples. Molar ratio was also considered one of the important chemical properties of materials intended for soil and energy purposes hence the molar ratios of the pellets were also shown (Table 2). This is because the degree of carbonization, which is often determined by the molar ratio of the elemental constituents of a material, is beneficial to the two applications of the HC pellets considered in this study. According to Kuhlbusch [40] and Chun et al. [41], the degree of carbonization is often, among other factors, determined by the molar ratio of the elemental constituents of a material, particularly the H/C molar ratio because these two elements (H and C) are mainly associated with organic matter.

The pellets are well suited for soil application purposes on the basis of their contents of C and H. They will serve as carbon sinks, a process referred to as carbon sequestration [23,42], and the weight fractions of H are within limits suitable to enhance soil water retention capacity through the formation of polar H bonds [43].

The amount of N in the HC pellets without ash (HC-ash 0%) is within limits that do not pose significant threats of NO_x emission, should the pellet be used as feedstocks for thermal energy production.

The high C/N molar ratios for all samples correspond to high

Table 3
Extended chemical properties of biosludge-derived hydrochar pellets (mean value ± standard error, n = 3). The values with letters in superscript are significantly different ($P < 0.05$) based on an ANOVA and Tukey's HSD mean comparison tests.

	HC-ash 0%	HC-ash 20%	HC-ash 50%	Wood ash
pH	5.54 ± 0.06^{d}	8.59 ± 0.09^{c}	9.49 ± 0.08^{b}	11.95 ± 0.12^{a}
EC (μs/m)	224.1 ± 20.06^{c}	1119.6 ± 75.82^{d}	1398.5 ± 93.44^{b}	3490.1 ± 176.29^{a}
Moisture uptake (%)	0.2 ± 0.0^{c}	0.4 ± 0.0^{b}	1.1 ± 0.0^{a}	Nd

Nd-Not determined.

Table 4
The CEC of pure and wood ash blended biosludge-derived hydrochar pellets (mean value ± standard error, n = 3).

Sample	CEC (cmol^{+}/kg)
HC-ash 0%	31.76 ± 0.23^{d}
HC-ash 20%	273.93 ± 4.54^{c}
HC-ash 50%	637.16 ± 10.99^{b}
Wood ash	1242.57 ± 21.74^{a}

The mean values with letters in superscript are significantly different at $P < 0.05$ according to ANOVA and Tukey's HSD mean comparison tests.

production temperatures that explains the amounts of N measured for the samples. High temperature conditions result in the volatilization of N [32]. The H/C and O/C molar ratios of all the samples are also quite low and indicate the extent of dehydration and oxidation that the samples underwent during their HTC processes. Although the stability of HC depends on HTC process conditions and the biomass used as feedstock, low O/C results in a more stable HC material, which is desirable for soil applications [44].

As shown in Table 2 (see also SI), the HC-ash pellets are characterized by considerable amounts of heavy metals and trace elements. The contents of heavy metals are well within the threshold accepted by the Swedish Forest Agency for soil application. However, according to Beesley et al. [10], the range of the maximum allowable limits (in mg/kg) of heavy metals in HC are as follows: 1.4–39 for Cd, 64–1 200 for Cr, 63–1 500 for Cu, 70–500 for Pb, and 200–7 000 for Zn [10]. Of the three HC pellets investigated in this study, the HC-ash 20% and HC-ash 50%, due to their increased percentages of wood ash, showed higher concentrations of trace elements like Sc, Se and Y. They also displayed higher amounts of alkali metals like Al, Ca, Cr, K, Mg, Mn, Na, and Zn. However, the leaching potential of trace metals mainly depends on their specific chemical compositions rather than the total content [45]. The HTC process can transform the specific chemical forms of heavy metals in biomass feedstock leading to immobilization of heavy metals in the produced hydrochar [31], and this reduces terrestrial ecotoxicity impacts when hydrochars are incorporated into soils [23]. Eskandari et al. [13] concluded that heavy metal uptake by pine seedlings treated with 20% HC powder or pellet with 50% fertilizer resulted in same quality pine seedlings with similar heavy metal (Cu, Ni, Pb, Zn and Cr) contents as untreated seedlings supplied with 100% fertilizer. Therefore, the results of this analysis demonstrates that the HC pellets mixed with 20% and 50% ash are suited for application as soil nutritional and liming agents on the basis of their chemical properties, since ash contains nutrients that can help improve soil fertility.

However, in addition to the content of heavy metals of the HC pellets and their HTC conditions of production, there is a potential for increased concentrations of PAHs in the pellets. PAHs are a group of pervasive carcinogenic, teratogenic, and mutagenic pollutants that can create a host of adverse health problems [46]. The incomplete combustion of solid fuels (such as coal, petroleum, and biomass) generates substantial amounts of PAHs [47]. Nonetheless, the concern is more on the free PAHs that emanates from the direct release of PAHs emitted from macromolecular structures [48]. These free PAHs exhibit potential threat to the environment due to their easy release to the environment. Notwithstanding, because the Swedish Forestry Agency has not recommended PAH-limits on soil additives, the possibilities of the release of free PAHs from the HC pellets were not evaluated in this study.

3.2.1. The pH, electrical conductivity and moisture uptake

The samples show comparable pH values that are both acidic and alkaline based on the valued presented in Table 3. It is obvious that the pH of the HC pellets increase with the percentage of wood ash and can be attributed to the concentration of alkali and alkaline earth metals (Ba, Be, Ca, and Mg in Table S1) contained in wood ash. The oxygen-containing functional groups within the structures of the materials also played a role in the increases in pH values because oxygen-containing functional groups have affinity for certain compounds including inorganic compounds and water [49–51]. The HTC and pellet press process conditions such as temperature, heating rate and holding time can also raise a material's content of mineral matter [52–54]. The HC pellet without ash (0%) is acidic with low nutrient level (Table 3); therefore, applying this pellet to the soil may not considerably affect soil pH, soil fertility, and acid neutralisation capacity (ANC), as well as cation exchange capacity (CEC). In contrast, the HC-ash 20% and 50% pellets could have significant opposite impacts judging by their higher pH values, which are generally considered alkaline. This substantiates previous findings in the literature, particularly those by Qi et al. [55] who alluded that an acidic biochar have no apparent effects on soil properties, whereas a neutral biochar enhances major soluble nutrients in the soil. Because of the positive relationship between CEC and pH, the solubility of cationic metals like Cu, Pb and Zn, which are bound to the negatively charged surfaces of soils (like clay minerals) increases with decreasing pH; furthermore, the soil application of alkaline biochars often boost soil liming effects of the biochar because the liming effect potential of biochar is determined by its pH [10,56]. Hence, the HC pellets with varying percentages of wood ash (20% and 50%) are recommended for soil application on account of their pH values.

The EC of the pellets also increased with the percentage of wood ash and agrees with literature reporting that differences in EC of biochar are attributed to the disparity in their contents of ash [57,58]. Moreover, since EC is the most broadly used salinity test for soils, materials with higher contents of soluble salts will have greater ability to conduct electrical current and greater tendency to increase soil salinity [57,58]. The results showed that, the HC-ash 50% pellet may have greater tendency to increase soil salinity as the materials with higher contents of soluble salts have higher ability to conduct electrical current and greater tendency to increase soil salinity [57,58]. However, this may adversely affect salt-sensitive crops, therefore knowledge of the amount of soluble salts contained in HC is vital [59].

The HC-ash pellets almost did not show any moisture uptake except the HC-ash 50% pellet, which showed 1% moisture uptake, although the difference in the values are insignificant.

3.2.2. Exchangeable cations analysis

Cation exchange capacity (CEC) analysis is often undertaken when HC is considered for use as a soil remediating agent. This is because the agro-economic value of HC application to soil is determined by the improvements in the soil's CEC [60].

The CEC results of HC-ash pellets show significant differences in their values (Table 4), with the HC-ash 0% exhibiting the lowest amount in comparison to other pellets containing varying percentages of wood ash. This supports the fact that CEC of HC is highly variable as reported by Munera-Echeverri et al. [61]. Nonetheless, the HC-ash 50% pellet demonstrated the highest CEC value and corresponds to its higher O/C molar ratio previously reported in Table 2. According to Lee et al. [62], the CEC of biochar is usually attributed to the presence of highly oxygenated functional groups that are rich in negative charges, such as

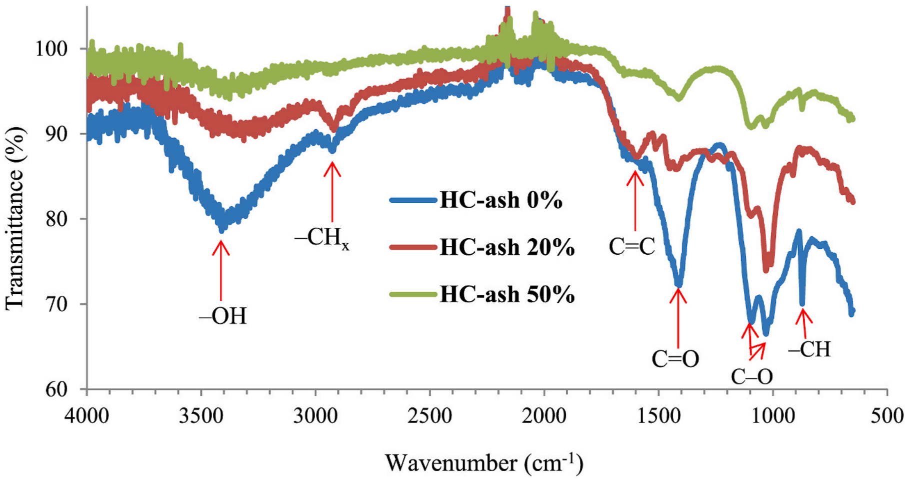

Fig. 4. The FTIR spectra of pure and wood ash-blended biosludge-derived hydrochar pellets.

the hydroxyl (–OH) and carbonyl (C═O) groups. This is corroborated by the FTIR-ATR data presented in Fig. 4 (which identified key functional groups) and indicates that a higher O/C molar ratio is associated with a greater CEC value. Under soil application conditions, therefore, biochar with higher CEC value may lead to introduction of fairly large amounts of carbon and exchangeable cations in the soil [32]. Just like the EC, the CEC is usually not considered when HC is to be used as a source of energy.

3.3. Higher heating value

Since only the pure HC pellet (HC-ash 0%) was considered for energy production application, it remains the only sample whose higher heating value (HHV) was determined. This analysis (HHV) was necessary to understand how much energy was available for conversion when HC-ash 0% is considered for combustion in firing units. A heating value of 19.4 MJ/kg and energy yield of 70% was obtained for the pure HC pellet. The heating value of the HC pellet was found to be around 4% higher that the heating value of the original feedstock. This result indicates that HC produced from biosludge have the potential to be used as a biofuel source. These findings are in line with the reports from other researchers where in comparison with the biomass feedstock, HC pellets showed a higher mass and energy density as a result of an increase in the content of carbon [20,21,63]. Zhu et al. [19]calculated an energy yield of over 60% for HC pellets derived from cotton stalk under a HTC temperature in the range 180–200 °C. They alluded that the energy yield of HC decreases with increasing temperature from 180 °C to 300 °C. Liu et al. [20] also reported that HC pellets from woody biomass and agricultural residues have elevated heating values and enhanced mass densities relative to the raw biomass materials. A heating value of 19 MJ/kg and a HC energy yield of 93% were estimated for HC produced from anaerobic granular sludge. According to Mittapalli et al. [61], a HC yield of 80% results in high energy yield.

3.4. Surface functionality analysis

Hydrochar is a porous carbonaceous material with high specific surface area and a number of polar and non-polar functional groups with great affinity for inorganic ions like the heavy metal ions, phosphates, and nitrates [50,64]. As part of the determination of chemical properties, the surface functionality of pure and wood ash-blended biosludge-derived HC pellets used in this study was undertaken to identify key functional groups and to determine structural changes caused by blending with wood ash. The pure sample was used as the reference material in this case and results interpreted in relation to the use of the pellets as a soil amendment and as a source of energy. The FTIR–ATR was used for this analysis and the results are presented in the form of infrared spectra (Fig. 4). To avoid ambiguity, spectra interpretation has been limited to regions where changes are most prominent.

The FTIR spectra of the pure and wood ash-blended biosludge-derived HC pellets appear similar in shape with complex transmittance bands that depicts intensity at a particular wavenumber. However, the similarities in spectra cannot necessarily be construed to mean same characteristics. The surface functional groups believed to be associated with the three HC pellet samples (HC-ash 0%, HC-ash 20%, and HC-ash 50%) have been identified using arrows that are pointing in the direction of the peaks. The symbols written beneath the arrows are the key chemical organic functional groups.

The transmittance peaks associated with the identified functional groups appear stronger in HC-ash 0% than in HC-ash 20% and HC-ash 50%, which displayed weaker peaks across the entire region of the IR spectra. This condition is obviously attributed to the concentration effect of wood ash. Notwithstanding, the weaker peak intensities of the wood ash-containing samples are most prominent around 3 350 cm^{-1} (assigned mostly to the hydroxyl, –OH groups), 1 566 cm^{-1} (due to C═C stretching) and 1 399 cm^{-1} (mainly attributed to the asymmetric stretching of the carbonyl, C═O groups) [63]. Furthermore, the spectrum of the HC-ash 50% pellet barely displayed any peaks that could be linked to any functional groups, which means that the pellet may have lost its organic nature to high ash percentage. However, the new peak formed around 1 571 cm^{-1} in the spectrum of the HC-ash 20% pellet is associated with the C═C group. Within this region, the C═C group is almost non-existent in the reference HC pellet (HC-ash 0%), as well as in the sample with the highest proportion of wood ash (HC-ash 50%). This indicates that the two pellet samples (HC-ash 0% and HC-ash 50%) probably underwent decarbonylation (loss of carbonyl groups) during their HTC and pelleting processes. In relation to soil application however, the functional groups identified generally can enhance soil organic carbon and can influence soil nutrient availability, particularly via CEC [65,66]. In terms of energy production, the functional groups can facilitate dehydration, decarboxylation and depolymerisation reactions under thermal conditions required for energy production via thermochemical means for optimum production efficiency [34]. However, it is important to mention once again that the HC pellet sample considered for use as a source of energy remains the HC pellet without wood ash (HC-ash 0%).

3.5. Morphological and microstructural analysis

The characteristics of a material change upon the addition of other materials (such as additives or binders) to the material or even upon thermal or hydrothermal treatment [67]. Under such circumstances, the

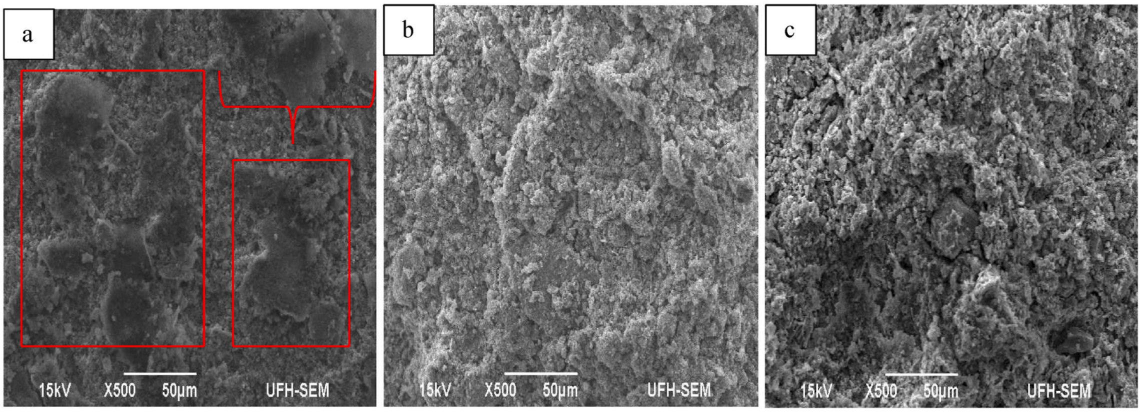

Fig. 5. The SEM images of pure and wood ash-blended biosludge-derived hydrochar pellets; a) HC-ash 0% showing coagulated carbon particles in the areas that are highlighted in red; b) HC-ash 20%; c) HC-ash 50%.

morphological examination of the material is required to ascertain the specific effects of the additives or pre-treatments. The cross-sections of the SEM images of the pure and wood ash-blended HC pellets are presented in Fig. 5. The images were obtained under the same conditions of measurement as those inscribed in them.

The SEM images are similar in appearance and are, therefore, consistent with the FTIR spectral similarities of the samples presented in a previous section. The images demonstrate compact structures with surface morphologies that show no obvious cracks or micropores (Fig. 5a–c). The absence of cracks and compact features of the pellets were facilitated by process conditions of the pellet press used during pelleting. The compact morphology is an indication of increased bulk density and promotes rapid heat transfer during thermal conversion of the pellets into energy because lower air/fuel ratios are achieved under this condition [68]. The lack of cracks and compact morphology features are evidence of active inter-particle bonding that are typical of pellets with great structural strength [69]. The image of the HC-ash 0% (Fig. 5a) reveals coagulated carbon structures that may have occurred due to temperature conditions and the presence of oxygen-containing functional groups with great affinity for water, which enables gelatinization of major components [51]. During compression into pellets, water was added to the HC material prior to pelleting to increase particle bonding. Nevertheless, due to the brighter colour of the SEM images of HC-ash 20% and HC-ash 50% pellets, ash particles can be easily spotted in the images (Fig. 5b and c). The bright colour images are associated with the presence of alkali silicates in ash, such as calcium silicate (Ca_2SiO_4), a compound which enhances soil chemical properties including soil pH and CEC [70,71]. This observation corroborates the heavy metal analysis data presented in Table S1, which showed calcium as the dominant metallic element of the wood ash blended with the HC pellets. The images are also characterized by rough, irregular and complex surface structures with protrusions that tend to increase particle surface area. However, the extent of roughness, irregularity and complexity in the surface morphologies of the pellets vary in accordance with their percentages of wood ash. For instance, the surface morphology of HC-ash 0% pellet (Fig. 5a) appears smoother and darker in colour as compared to the HC-ash 20% and HC-ash 50% pellets (Fig. 5b and c). Thus, the morphological features described favour the use of the pellets as soil amendment because the features are compatible with soil characteristics and will positively alter soil quality [72]. That said, for use as a source of energy, the HC-ash 0% pellet is definitely the pellet of choice on account of its zero ash proportion and morphological characteristics.

4. Conclusions and recommendations

The effect of wood ash on the physicochemical and morphological properties of biosludge-derived hydrochar (HC) pellets was investigated in this study and results interpreted in relation to the use of the pellets as soil improving and liming agents and as a source of energy. Therefore, it can be generally concluded that when produced HC from biosludge is blended with up to 20%–50% of wood ash and mechanically compressed into pellets, in accordance with the percentage of wood ash, will have greater density, pH and EC as well as higher CEC values and surface functionality in comparison to HC pellets without wood ash. In addition to the percentage compositions of other elemental constituents, which were all within limits required for both applications considered in this study, it was also found that the three HC pellets studied (HC-ash 0%, HC-ash 20%, and HC-ash 50%) contain varying proportions of structural carbon with double bonds and aromatic rings that appear non-degradable and difficult to break down. However, the two wood ash-blended HC pellets (HC-ash 20% and HC-ash 50%) showed higher levels of alkali and alkaline earth metals hence their higher pH, EC and CEC values. These properties make the wood ash-blended HC pellets more suited for application as soil nutritional and liming agents. In fact, the ash fraction of the pellets can provide considerable alkalinity and confer liming properties that can allow the use of the pellets as liming agents in acidic soils. This is because pH and soil nutrient retention capacity can both be improved via the liming process. Although, the pellets may have shown good hydrophilic and hydrophobic properties, their moisture uptake ability need further investigation and determination of additional characteristics, such as porosity and surface area. Additionally, since the HC pellets were generally considered for use as a soil conditioner, more studies are required to evaluate the leaching and contents of free PAHs in the pellets when used as a soil amendment.

Lastly, the pellet without ash (HC-ash 0%) revealed potential to be used as a source of energy on the basis of its physical, chemical and morphological features, as well as on account of its heating value, however, its combustion characteristics need to be investigated to conclusively establish its suitability as a feedstock for energy production in CHP plants.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.biombioe.2022.106531.

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