Characterization of 60 types of Chinese biomass waste and resultant biochars in terms of their candidacy for soil application

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Comparison of biochars from 60 types of biomass

Xiaoyin Sun*1, Ruifeng Shan1, Xuhui Li2, Jihua Pan1, Xing Liu1, Ruonan Deng1, Junyao Song1

1. Key Laboratory of Nansi Lake Westland Ecological Conservation & Environmental Protection (Shandong Province), College of Geography and Tourism, Qufu Normal University, Rizhao 276826, China;

2. College of Environment and Planning, Henan University, Kaifeng 475004, China.

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Abstract: The composition and pyrolysis characteristics of 60 types of biomass waste from the following six source categories were compared: agricultural residues, woody pruning waste from gardens and lawns, aquatic plant material from eutrophic water bodies, nutshells and fruit peels, livestock manure and residual sludge from municipal wastewater treatment. The yield and physico-chemical characteristics of the biochar produced from these feedstocks at 350 °C, 500 °C and 650 °C were also examined. Results of correlation and canonical correspondence analysis between feedstock composition and biochar properties showed that feedstock type played an important role in controlling yield and properties of biochars. The yields of biochar dry ash free (daf.) basis were positively correlated to cellulosic, lignin and lignin/cellulosic content of feedstock, as well as ash content hampered the biochar production. Furthermore, the intensity of correlation between biochar yield and its feedstock composition was improved with pyrolysis temperature and degree of feedstock decomposition. The fixed carbon content in biochar was also negatively influenced by ash content of feedstock, and it increased with increasing pyrolysis temperature when the ash content was below 34.57 % in...
feedstock and decreased when the ash content exceeded. The fixed carbon production in biochar per unit ash free mass (af.) positively related to cellulous, lignin and lignin/cellulous content in feedstock, which were same with the yield of biochar (daf.). But on the contrary, the volatiles content in biochar (af.) had negative correlation with these organic constituents. For most feedstocks, the differences in the biochar characteristics among the biomass categories were greater than within any individual category. C/N, H/C and O/C atomic ratio and bulk density of biochar from different type of biomass were also compared. The results will provide guidance for the reutilization of biomass wastes and production of biochar with specified properties for soil amendment applications.

Introduction

Biochar is the carbon-rich product made from the pyrolysis of biomass under oxygen-limited conditions and relatively low temperatures (Lehmann & Joseph, 2015). As a soil amendment, biochar has received increasing attention due to its potential for soil carbon sequestration and the remediation of contaminated soil (Tripathi et al., 2016). Therefore, waste biomass material pyrolysis for biochar is considered to offer an attractive alternative to solid waste recovery and utilization. A wide range of biomass waste is available for producing biochar, including woody, agricultural, aquatic, human and animal, and industrial waste biomass (Vassilev et al., 2012). As an agricultural country, China produces approximately 800 million tons of agricultural straw residue (Jiang et al., 2012) and 223.5 million tons of livestock manure annually (Geng et al., 2013), though approximately 20 % of the agricultural straw is
burned in the field. In addition, there are about 14.4 million tons of garden waste biomass production annually in China (Shi et al., 2013), which included woody pruning waste and leaf litter from gardens and lawns. And the production of garden waste biomass is increasing quickly with the expansion of urban and greenspace areas in China, which is higher than the total annual harvest from national forests in the US (Bratkovich et al., 2008). Part of garden waste is being recovered for composting, but a large proportion is simply discarded as municipal solid waste. Therefore, biochar produced from these biomass wastes and applied to the soil could be a win-win approach, which not only reduces pollution and carbon emissions but also contributes to agricultural productivity, resource use efficiency and soil bioremediation goals (Li & Wang, 2013).

In recent years, studies on biomass pyrolysis have revealed that the characteristics of the resulting biochar can vary significantly depending on feedstock types and processing temperatures (Lehmann & Joseph, 2015). The biomass composition and physico-chemical properties vary greatly among different botanical species and even within a species depending upon the plant parts, growing conditions and harvest times (Lehmann & Joseph, 2015, Suliman et al., 2016). The properties of the biochar produced from these biomass materials are correspondingly diverse. Several studies have compared the yields and properties of biochar produced from different biomass feedstock, these studies suggest that higher biochar yields are generally obtained from feedstocks with high lignin and mineral contents (Demirbas, 2004, Demirbas,2006, Lv et al., 2010, Nanda et al., 2013). According to Demirbas, hazelnut shell containing higher lignin as compared to oak wood and wheat straw
has higher biochar yield (Demirbas, 2006). Similar findings were reported by Nanda et al. that pinewood containing most lignin as compared to other biomass has the highest biochar yield and wheat straw with the lowest lignin content produced the lowest biochar (Nanda et al., 2013). Biomass waste can be classified into five categories by the source from where it’s obtained, including woody biomass, agricultural residues, aquatic plant, human and animal waste and industrial waste biomass (Vassilev et al., 2012). Industrial biomass waste is the waste produced from the industry related biomass raw materials, such as sugarcane residue from sugar refinery, waste from food processing factory and others. The constituents of biomass waste from industry are diverse and complex, but they are similar to the raw material which used and some can be classified into the category of raw material based on their constituents. Biochar from feedstocks within the same category of source might show similar properties as those made from parent material of different types. For example, woody and agricultural biomass, which have high carbon and oxygen contents, typically produce more carbon-rich biochar than biochar from sewage sludge (Hossain et al., 2011) and livestock manure (Cao & Harris, 2010, Xu & Chen, 2013).

Many studies have investigated the impact of one or several sources of biomass feedstocks on the physico-chemical properties of the resulting biochar (Demirbas, 2004, Demirbas, 2006, Lv et al., 2010, Nanda et al., 2015), which often fall into one or two biomass categories and the results might seem less systematic. The properties of biochar determine its applications to soil, and a particular biochar may not be adapted to all types of soils. Therefore, optimizing biochar for a specific application may require a purposeful selection of feedstocks and This article is protected by copyright. All rights reserved.
production conditions to manufacture the biochar with desired characteristics. It is thus important to broadly and cohesively analyze the properties of different categories of biomass sources and their resulting biochar products under different production conditions.

To this end, this study collected 60 types of commonly available biomass waste, including 23 types of agricultural residues which covered almost all of crop species in China, 2 types of livestock manure, 14 types of woody pruning waste from gardens and lawns, 12 types of nutshell and fruit peels from human food, 8 types of aquatic plant waste from eutrophic water bodies, and one type of industrial biomass, residual sludge from a municipal wastewater treatment plant. In China, agricultural residues are the most important source of biomass waste, followed by the forest and garden waste biomass, human and animal waste, and industrial waste biomass. Aquatic plants selected in this study have been widely grown in eutrophic water bodies and constructed wetlands for water purification. The biomass of these plants must be properly harvested and disposal to protect the aquatic environment, and previous study demonstrated that these plants are valuable feedstocks for producing biochars (Cui et al.,2016). Therefore, the objectives of this study were to investigate the composition and pyrolysis characteristics of different types of biomass waste in China and to examine how feedstock sources and pyrolysis temperatures affect the yield and properties of biochar. The obtained results will provide guidance for the selection of biomass wastes and pyrolysis temperatures for the production of biochar with specified properties for soil amendment applications.
Materials and methods

Collection and characterization of biomass

Sixty types of biomass waste were collected in Shandong Province, China, from 6 categories: agricultural residues, woody pruning waste from gardens and lawns, nutshells and fruit peels from human food waste, aquatic plants from eutrophic water bodies, livestock manure, and industrial waste (Table S1). The biomass studied covered almost all categories of biomass waste in China. Agricultural straw, stems and husks were collected, which included crop categories such as wheat, corn, peanut, soybean, rice, sorghum, cotton, sunflower, rape, batatas, and other crops. All of the crop residues were obtained from same areas with the same climate and soil type in Shandong Province, China. Pruning waste came from the campus of Qufu Normal University and included branches, leaves, and grass. Nutshells and fruit peels came from campus food waste, and sugarcane waste was obtained from a sugar mill in Rizhao, Shandong province. In this study, the sugarcane bagasse collected from the sugar refinery was classified into the nutshells and fruit peels category because of their similar composition. Aquatic plants included reed, lotus leaf, water hyacinth, Hydrocharis and Enteromorpha, the latter three of which are common plants in eutrophic waters. Reed, lotus leaf, water hyacinth and Hydrocharis came from Nansi Lake in Shandong Province, while Enteromorpha came from the coast of Rizhao. Dairy and chicken manure was obtained from a dairy farm and chicken farm in Rizhao, respectively. Residual sludge came from the 2nd municipal wastewater treatment plant in Rizhao, which mainly treats domestic wastewater.
All of the feedstocks were oven dried at 60 °C to reduce the moisture to less than 10 % (w/w) and then milled to less than 2 mm for biochar production. Furthermore, the samples were passed through a 100 mesh sieve (0.154 mm) prior to feedstock characterization, including thermogravimetric, fabric, elemental and proximate analyses. Thermogravimetric (TG) and derivative thermogravimetric (DTG) experiments were carried out on the powdered samples using a STA 449 thermal analyzer (Netzsch, Selb, Germany) under a nitrogen atmosphere that was heated from room temperature to 850 °C at rate of 10 °C/min. Characteristic pyrolysis temperatures (including onset, midpoint, inflection and end temperatures), maximum rates of mass loss, mass changes and residual mass rates were calculated based on the TG curves using Netzsch Proteus Analysis software version 4.8.5 (Netzsch, Selb, Germany).

The cellulose and lignin contents in the biomass waste were determined using the Van Soest method (Van Soest et al., 1991). Elemental (carbon, nitrogen, hydrogen and sulfur) analyses of the feedstocks were conducted on an elemental analyzer (Vario EL III, Elementar, Hanau, Germany), and the oxygen content was derived by subtraction of the C, N, H, S and ash content from the total mass of the sample. Proximate analysis methods were conducted using CNCA (China National Coal Association) Proximate Analysis Methods for Solid Biomass Fuel (GB/T 28731-2012) (CNCA, 2012). Briefly, the moisture content was determined from the weight loss of the biomass waste processed in a furnace preheated to 105 °C using a crucible with a cover for 2 hours. To determine the volatile matter, a dedicated crucible with
an inner-buckle cover (33 mm in diameter and 40 mm tall) was utilized to maintain the samples in air-free conditions. Each sample was weighed in a crucible and placed in the furnace preheated to 900 °C for 7 minutes; the weight loss of the sample was recorded as the volatile matter content. To determine the ash content, a dedicated crucible with a rectangular cuboid-shape (length×width×height, 45 mm×22 mm×14 mm) was utilized. Samples weighed in a crucible were placed in the furnace, and the temperature was increased to 250 °C for 1 hour and then increased to 550 °C for 2 hours. The samples turned off-white in color after heating, and heating was continued if the color did not change into off-white completely. The weight of the residual was recorded as the ash content. The fixed carbon content was derived by subtracting the ash, volatile matter and moisture values. Elemental analyses were conducted in duplicate, and proximate analyses were conducted triplicate.

Biochar production and physico-chemical properties

Biochars were produced from the above feedstocks at various temperatures under oxygen-limited conditions in a muffle. The inert gas used for pyrolysis was nitrogen with a flow rate of 10 L/min. The selected peak charring temperatures included 350 °C, 500 °C and 650 °C, and the heating rate was approximately 20 °C/min for each sample. The pre-dried biomass was placed in a ceramic crucible, covered with a fitting lid, and pyrolyzed under a N₂ atmosphere in a muffle for 2 hours at a given temperature. After the temperature decreased to room temperature, the biochar products were manually removed and weighed to calculate the biochar product yield. All of the biochar samples were ground with a mortar and pestle and sieved through a 100 mesh for the analyses.
Elemental analyses of the biochars were conducted on an elemental analyzer (Vario EL III, Elementar, Hanau, Germany). Proximate analysis methods were conducted to determine the biomass. These results were then used to calculate the C/N, atomic H/C and O/C ratios, which are indicative of the bonding arrangement and polarity. The bulk densities of the biochar were analyzed according to the apparent density determination method of the granular activated carbon, which was determined by measuring the volume packed by a free fall from a vibrating feeder into an appropriately sized graduated cylinder and determining the mass of the known volume. For measurements of pH values, biochars were weighed to 1±0.01 g and placed in 100 mL conical flasks and then 20 mL of deionized water was added to each flask. The flasks were agitated on an orbital shaker table for 2 hours, and then the pH of each equilibrated solution was determined. The filtered solution was used to determine the electrical conductivity. Elemental analyses were performed in duplicate, and the other analyses were performed in triplicate.

Data analysis

All of the experiments were conducted in duplicate or triplicate, and the average values were reported. The correlation for the biomass characteristics and the resulting biochar was carried out using SPSS for Windows version 20.0 (SPSS Inc., Chicago, IL). Canonical correspondence analysis of the biochar yield and biomass properties was conducted with CANOCO 5.0 (Ter Braak & Šmilauer, 2012).
Results

Chemical composition of the biomass wastes

The results from the proximate, elemental and fiber analyses for the different categories of biomass wastes are presented in Table 1; the different biomass categories exhibited large variations. The data clearly show that the residual sludge and livestock manure have higher ash contents and lower organic constituents compared to the plant biomass. Moreover, the ash content of the aquatic biomass waste was the highest among all of the plant biomass waste types, though the volatile and fixed carbon contents were lower. The volatile and carbon contents of the woody pruning wastes ranked first in the plant biomass type. Aquatic biomass from eutrophic waterbodies possessed the highest amount of hydrogen, nitrogen and sulfur. Sulfur and nitrogen contents were very low in the pruning and agricultural biomass, though they were high in aquatic plants and municipal residual sludge.

Among the category of agricultural residue, sunflower stem, sunflower heads, rice straw and rice husk contained higher ash contents at 11.5 %, 11.2 %, 11.9 % and 10.08 %, respectively, than other agricultural residues. The average content of other 19 agricultural residue samples was only 5.06 %. The tall fescue collected from the lawns, as herbaceous plant, had a high ash content compared with other pruning wastes from the garden.
Different plant parts exhibited different compositions. In the agricultural biomass category, the constituents in straw and shells from the same crop showed many differences. For the same crop, the volatile, fixed carbon, carbon and lignin contents in straw were higher than in the shells mostly; the ash and cellulose contents in straw were also generally lower than those in the shells (Table S2). In the woody biomass category from pruning wastes, the compositions of leaves and branches from the same tree also varied greatly. The volatile, fixed carbon, carbon, lignin and cellulose contents in the branches were higher than in the leaves, while the ash content in the branches was lower than in the leaves (Table S3).

Thermal properties of the biomass wastes

Fig. 1 shows the results of the thermogravimetric analysis (TGA) and differential thermograph (DTG) for the biomass waste samples to predict the pyrolysis behaviors of each biomass waste tested, as well as the pyrolysis characters analyzed from TG curves were listed in Table S4. Pyrolysis characteristics of biomass varied with the biomass waste constituents, and the correlation between pyrolysis characteristic and composition of the biomass were significant (Table S5). As displayed by Table S5, the biomass maximum rate of mass loss and corresponding temperature (Inflection temperature) during pyrolysis correlated positively to the content of volatiles, fixed carbon, oxygen, cellulose and lignin, while the correlations were negative to the content of ash, nitrogen and hydrogen. The characteristic temperatures of pyrolysis, including onset, midpoint, inflection and end temperature, correlated to the cellulose content of biomass significantly, while the lignin content correlated closely only to the first three characteristic temperatures.
Biomass waste samples exhibited different pyrolysis curves, though the overall changes were roughly similar for the same categories of biomass waste according to TG and DTG curves, except for the individual types (Fig. 1). The maximal weight loss peaks and decomposition strength of hemicellulose, cellulose and lignin in different biomasses were sample-dependent.

Following the evaporation of the moisture at between 80 °C and 120 °C, the main mass loss actively occurred in the range from 120 °C to 600 °C due to the progressive hemicellulose, cellulose and lignin pyrolysis, even though the derivative weight loss peaked at different temperatures. Previous studies have assigned the major maximal weight loss peak in DTG curves as per the degradation of hemicellulose (200–300 °C) and the shoulders with the degradation of cellulose (250–350 °C) and lignin (200–500 °C) (Lehmann & Joseph, 2015).

The intensities of peaks and decomposition strength of hemicellulose, cellulose and lignin in different biomasses were depended on the content of these organic components in biomass.

As shown in the DTG curves (Fig. 1), the average value for the maximum weight loss rate for the agriculture residue, pruning waste, aquatic plant, nutshell and fruit peel, livestock manure and municipal residual sludge were 6.9 %, 5.0 %, 4.9 %, 5.6 %, 2.8 %, and 2.1 %/min, respectively (Table S4).

In the agricultural residues category, sunflower heads (sample 21) displayed different pyrolysis characteristics, as revealed by the TG and DTG curves. The DTG curve shape for crop stalk was similar to the corresponding husk curve because of the homogeneous composition. In the pruning wastes category, the maximum weight loss rates for bamboo branch (sample 24) and tall fescue (sample 37) were higher because of the higher cellulose
contents. As green algae, the thermal properties for Enteromorpha (sample 38 and 39) showed significant differences from the aquatic and terrestrial plants. TG and DTG curves of nutshells and fruit peels varied greatly because there was great difference in the composition of these samples (Fig.1(d)). As suggested by Fig. 1(f), the overall changes of DTG curves for livestock manure were similar to those of the food source for livestock (samples 59 and 9 and samples 60 and 3), but the intensities of maximal weight loss peaks were different because of their fiber contents.

Biochar yields

As shown in previous studies (Lehmann & Joseph, 2015), the biochar yield decreased as the pyrolysis temperature increased. Between 500 °C and 650 °C, the biochar yield did not change substantially, indicating that most of the volatile fraction had been removed at the lower temperatures. The biochar product yields from the 60 types of biomass waste are displayed in Fig. 2(a). The municipal residual sludge (sample 58) and dairy manure (sample 59) yielded much higher amounts of biochar than plant biomass. Biochar yields for the green algae Enteromorpha (samples 38 and 39) were second. Yields for other aquatic plants, which included reed leaves (sample 42), water hyacinth (sample 43), lotus leaf (sample 44) and Hydrocharis (sample 45), and rice straw and husk (samples 12 and 13, respectively) were third. The biochar yields from other biomasses, including nutshells and fruit peels, agricultural residues and pruning wastes, were generally lower than those from aquatic plants.
The effects of the feedstock characteristics and biochar yield are illustrated in Table 2 and Fig. 2. On the whole, the biochar yields were negatively correlated with the feedstock organic contents, including cellulose, lignin, volatiles, fixed carbon, carbon and oxygen contents, while the ash and nitrogen contents were positively correlated with the biochar yield. There was no distinct correlation between the hydrogen content and the biochar yield in this study. With respect to the feedstock pyrolysis characteristics, the pyrolysis parameters generated by the TG for feedstock were significantly correlated with the biochar yield, with the exception of the onset temperature (Table S6).

Canonical correspondence analysis (CCA) of the biochar yields and the results from proximate, elemental and fiber analyses of the feedstock was performed. As shown in Fig. 2, arrows point in the direction of the steepest increase in the variable values, while the angle between the arrows indicates the correlation between the individual variables; the correlation increased with a decrease in the angle. The approximated correlation is positive when the angle is sharp and negative when the angle is larger than 90 degrees. The length of an arrow suggests the correlation between the feedstock factors and the biochar yield. The distance between the symbols approximates the dissimilarity of the biochar yield as measured by its Euclidean distance. The CCA results agreed with correlations in the table 2 roughly.

To remove the effects of moisture and ash, the biochar yield is expressed on a dry ash free (daf.) basis. The correlation between the feedstock and biochar yield (daf.) are listed in Table 2, which displays opposite results to that of total mass yield of the biochar. With respect to the different pyrolysis temperatures, the correlations between the feedstock characteristic and
the biochar yield were not significant at 350 °C and the intensities of their correlations were increased with pyrolysis temperature. The ash content of feedstock had a negative correlation of biochar yield (daf.), as well as the cellulose, lignin, volatiles, fixed carbon and oxygen content of feedstock correlated positively to biochar yield in 650 °C. It's worth noting that the content ratio of lignin/cellulosic in feedstock correlated to the biochar yields(daf.) positively.

Biochar bulk density

In this study, the bulk (or apparent) densities of biochars were determined. The correlations for the bulk density between the feedstocks and the resulting biochars at 350 °C, 500 °C and 650 °C were 0.790, 0.832 and 0.885, respectively, which were significant. The results for the bulk density suggested that there were significant variations in the biochars derived from the different feedstock categories (Table 3). Generally, the biochar bulk density results exhibited the following order, from greatest to least: sludge, livestock manure, pruning waste, fruit peels and agricultural residues. The bulk densities of the biochar produced from manure and sludge were higher than that of plant biomass because of the feedstock densities. Among the different types of plant biomass wastes, biochars produced from pruning waste and nutshells possessed the highest bulk density.
Proximate analyses

Proximate analyses of the biochar provide quantitative concentrations of the volatile, fixed carbon and ash contents. As shown in Fig. 3, the ash contents of the biochar increased, while the volatile contents decreased, with the increase in the pyrolysis temperature. However, the changes in the fixed carbon contents with the pyrolysis temperature depended on the feedstock characteristics. The biochar fixed carbon contents increased with increasing feedstock treatment temperatures when the ash content was below 34.57% and the volatile content exceeded 55.16% (Fig. 4). In contrast, the biochar fixed carbon content decreased with the pyrolysis temperature.

Fig. 5 and Table 4 displayed the relation between feedstock composition and the yield of the fixed carbon production per unit ash free mass in biochar (af.). The ash content in feedstock had a negative correlation to the fixed carbon production in biochar (daf.), as well as the content of fixed carbon, volatiles, cellulose, lignin and lignin/cellulose in feedstock related positively. Besides that, the nitrogen content correlated negatively to the fixed carbon production in biochar (af.). In contrast, volatiles content in biochar (af.) had a negative correlation to the content of fixed carbon, volatiles, cellulose, lignin and lignin/cellulose in feedstock (Table 4 and Fig. 5).

Substantial differences were observed in the volatile, fixed carbon and ash contents in the biochar resulting from different biomass types (Fig. 3). As noted above, livestock manure, residual sludge and aquatic plants possessed large proportions of ash, and the biochar yields

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produced by these feedstocks were higher than those of other biomass types, which were inherited from feedstocks. The largest fixed carbon content and lowest volatile content were found in the nutshell biochars (filbert hull, coconut shell, chestnut shell and walnut shell).

Part of the agricultural residues and pruning wastes (peanut shell, bamboo branch, sunflower seed hulls, corncob, pine branch, soybean straw, sorghum stalk, etc.) were second, followed by the other agricultural residues, pruning wastes and fruit peels. The fixed carbon content of the biochar produced by aquatic plant wastes was the lowest among the plant biomass waste types. Sludge and livestock manure biochar had the lowest fixed carbon contents among all of the biomass wastes.

Elemental analysis

The feedstock characteristics influenced the elemental composition of the biochar, and the correlation for the carbon contents between the feedstocks and biochars was significant and reasonable. The carbon content in the biochar at 500 °C ranged from 14.36 % to 85.57 %, and the average recovery of carbon from feedstock was 48.02 %. Among all types of biochar produced by the biomass waste, nutshell biochars, such as coconut shell, walnut shell, filbert hull, and chestnut shell, which had a carbon content exceeding 80 %, contained higher carbon concentrations. In the case of agricultural residue category, the biochars produced from corn stalk and related residues (corncob and corn husk) possessed the highest carbon contents, at 80.04 %, 79.02 % and 77.80 %, respectively. For the biochars from pruning waste, the carbon contents in the bamboo branch biochar were at the top of the list in this category, followed by
pine branch. The biochars from cow manure and municipal residual sludge had the lowest carbon contents; for example, the carbon content of cow manure biochar was only 16.78 % of the coconut shell biochar. The C/N ratios of biochar ranged from 7.03 to 192.38. The biochars from sludge, animal manure and aquatic plant had the lower ratio of C/N which were not above 30 mostly (Table S7). The average ratios of C/N of fruit peel, agricultural residues and pruning waste were 88.75, 52.01 and 40.89, respectively. Previous studied have founded that biochars with a C/N ratio above 30 could contribute to decrease emissions of N₂O from soil (Brassard et al., 2016).

The H/C and O/C atomic ratios of biochars were typically correlated with the degree of aromaticity and the polarity of the biochar; the H/C and O/C ratios are plotted against one another in a Van Krevelen diagram (Fig. 6). The H/C and O/C atomic ratios for the feedstocks ranged from 0.94-2.43 and 0.05-1.00, respectively, while those for the biochar at 500 °C ranged from 0.42-0.81 and 0-0.27, respectively. The average value of H/C atomic ratios for biochar from residual sludge, livestock manure and aquatic plants were 0.67, 0.66 and 0.57, respectively, as well as that of biochar from agricultural residues, pruning waste and fruit peel were 0.49, 0.48 and 0.47, respectively. In contrast, the average value of O/C atomic ratios for biochar decreased in the order: agricultural residues, pruning waste, fruit peel, aquatic plants, residual sludge and manure (Table S8).
EC and pH

Biochar pH and EC values increased with increases in the pyrolysis temperature (Fig.7). Additionally, the correlation between the biochar pH and EC values was significant. The coefficients for the biochar at 350 °C, 500 °C and 650 °C were 0.723, 0.729 and 0.702, respectively. The pH values ranged from 7.14 for chestnut shell at 350 °C to 11.98 for banana peel at 650 °C, while the EC values ranged from 99 us/cm for chestnut shell at 350 °C to 23,500 us/cm for banana peel. Fig. 6 shows that the biochar pH and EC values were impacted by the ash content. The coefficients between the biochar ash contents and pH values at 350 °C, 500 °C and 650 °C were 0.37, 0.38 and 0.60, respectively, while the coefficients between the biochar ash contents and the EC values at 350 °C, 500 °C and 650 °C were 0.42, 0.36 and 0.37, respectively.

The average biochar pH and EC values for the six feedstock categories are listed in Table S9. As shown in Table S9, the biochar pH and EC values from pruning waste from garden and lawn were lowest of all categories. The biochar pH values from residual sludge were higher than those of other feedstock categories, though the biochar EC value, which was 1564 us/cm at 650 °C, was low. On the whole, the biochar EC values from aquatic plant wastes were higher than those of other feedstocks. With respect to the agricultural residues, the rice straw biochar at 650 °C had the highest pH value of 11.49. Among pruning wastes, the biochar pH value for lawn waste (Festuca arundinacea) (pH = 11.16 at 650 °C) was higher than that of garden pruning waste (pH < 10.50).

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Discussion

Biochar yield and characteristics are influenced by biomass feedstock and pyrolysis conditions (e.g. treatment temperature), so it is important to perform biochar manufacture with different feedstock at different pyrolysis conditions, and to determine the properties of the resulting biochar. This work characterized a wide range of biochars from numerous feedstocks in China to identify the suitable biochar for agronomy application. In our study, chemical composition and properties varied with feedstock and treatment temperature. Especially for biochar fixed carbon yield, the key indicator of potential ability of carbon sequestration, it increased with increasing treatment temperatures when the ash content was below 34.57% in feedstock and decreased when the ash content exceeded 34.57%. While expressed by per unit ash free mass in biochar, the fixed carbon production was decreased with increasing biochar manufacture temperatures consistently. The reason was that the feedstock ash content hampered the fixed carbon production in biochar (af.) , supported by their negative correlations (Table 4). Similar findings were reported by Enders et al that the fixed carbon content of biochar increased with increasing treatment temperature for low ash feedstocks and decreased for high ash feedstocks (Enders et al, 2012). The ash content, which were alkali and alkaline earth metallic species mainly, had a strong catalytic effect to pyrolysis and hampered the generation of fixed carbon (Bridgwater et al, 2007). The content of cellulose, lignin and lignin/cellulose content in feedstock related positively to the fixed carbon production in biochar (af.). The correlations suggested that feedstock cellulose and lignin promoted the production of fixed carbon in biochar but fixed carbon generation was higher in the feedstock which had more lignin content as compared to cellulose. The lignin is
more thermally stable than cellulose during pyrolysis, thus the production of fixed carbon in biochar increased with the raise of lignin/cellulose content in biomass. It was noted that nitrogen content hampered the production of fixed carbon in biochar, supported by their negative correlations. The biomass wastes possessed high nitrogen content, such as sludge, manure and aquatic plant from eutrophied waterbody, had less efficiency to fixed carbon production as biochar manufacture.

The biochar product yield is an important factor for realizing economic benefit in biomass waste reutilization. The biochar yield of municipal residual sludge and dairy manure top the list, followed by aquatic plants and then the other biomass wastes. However, when we removed the effects of moisture and ash, the factors that impact biochar yield (daf.) showed contrasting correlations (Table 2), which suggested that the cellulose and lignin contents in feedstock enhanced biochar formation; the ash content of feedstock also had a negative effect on the biochar yield (daf.). Furthermore, the relation between the biochar yield (daf.) and the lignin-cellulose content ratio was positive (Table 2). Some sporadic comparisons have reported similar findings that biomass samples having higher lignin contents produced higher amounts of char (Demirbas, 2004, Lv et al., 2010). The reason for this difference is that the cellulose component in the biomass is liable to produce volatile products, while the lignin content is important for the biochar yield (Tripathi et al., 2016).
To identify suitable temperatures for biochar manufacturing, the effect of treatment temperature on product yield and biochar properties should be examined. The extent of the correlations between the feedstock and biochar varied at different pyrolysis temperatures; the correlation increased with increasing pyrolysis temperatures because the cellulosic and lignin contents of most biomass categories completely decompose at 650 °C and the coefficients of feedstock composition and biochar yield were significant (Fig. 1). At lower pyrolysis temperatures, the degree of decomposition varied with the type of biomass and the intensity of the correlation between the feedstock and biochar decreased.

The characteristics of biochars from different biomass waste categories varied greatly and their performance in soil application also had greatly difference. Brassard et al reported that biochars with a lower N content (C/N ratio >30) were more suitable for mitigation of N₂O emissions from soils. In this sense, biochars from residual sludge, animal manure and aquatic plant from artificial wetland or eutrophic water body were not appropriate for soil amendment, which C/N ratios in biochar produced at 500 °C were under 30 averagely. On the other hand, they could improve soil fertility because of their higher nitrogen content and other mineral elements. In addition, among six categories of biomass feedstock, biochars from sludge and livestock manure had the lowest fixed carbon contents, as well as the fixed carbon content of aquatic plant biochar was the lowest among all plant biomass waste types. Because of high ash content, biochar from sludge, livestock manure and aquatic plant possessed high pH values, which were suitable to acid soil amendment.
Among the plant biomasses, the results suggest that high carbon and oxygen contents are characteristic of woody pruning wastes, agricultural residues, nutshell and fruit peel biomasses, which lead to increased biochar formation. Therefore, these waste categories are the most suitable for biochar production. The ash, volatile and fixed carbon contents of biochar from all of the categories were mapped in a triangle plot, which displayed the private feedstock content and resulting biochar yields and can be useful as a tool for guiding biochar applications and selection for specific soils.

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Supporting Information legends

Table S1 The list of feedstock

Table S2 The composition of crop straw and shells (%)

Table S3 The compositions of leaves and branches

Table S4 The pyrolysis character analyzed from TG curves of different biomass categories
Table S5 Correlation of pyrolysis character and constituents of biomass

Table S6 Correlation of pyrolysis character and bulk density of feedstock and yield of biochar product under different pyrolysis temperature

Table S7 The C/N ratio, H/C and O/C atomic ratios of biochars

Table S8 The pH and electric conductivity value of biochar at different pyrolysis temperature

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Tables

Table 1

Compositions of the 6 categories of biomass waste. The results from the proximate, elemental and fiber analyses for the different categories of biomass wastes exhibited large variations.

| Biomass categories | Fiber analysis (%) | Proximate analysis (%) | Ultimate analysis (%) |
|--------------------|--------------------|------------------------|-----------------------|
|                    | Cellulose | Lignin | Volatiles | Fixed carbon | Ash | Carbon | Hydrogen | Nitrogen | Oxygen a | Sulfur |
| Agricultural residues | 44.16 ± 14.23 | 76.13 ± 16.99±1.91 | 6.26 | 44.39 | 5.49 | 0.80 | 39.48 | - |
|                      | 10.89 ± 3.20 | 3.20 | 44.39 | 0.78 | 0.49 | ± 6.93 | - |
| Pruning waste        | 44.12 ± 14.81 | 79.81 ± 15.63±1.91 | 4.84 | 53.28 | 5.84 | 1.16 | 32.38 | - |
|                      | 11.96 ± 1.87 | 2.44 | 7.07 | 0.42 | 0.51 | ± | - |
| Aquatic waste        | 40.71 ± 13.29 | 67.98 ± 12.91±1.91 | 18.04 | 38.66 | 9.65 | 2.04 | 26.50 | 0.36 |
|                      | 20.76 ± 5.03 | 5.93 | 4.33 | 5.94 | 0.92 | ± 6.88 | - |
|                      | 10.38 | - | - | - | ± | - |
| Nutshell and fruit peel | 41.44 ± 18.80 | 76.87 ± 19.72±1.91 | 3.40 | 45.96 | 6.90 | 0.66 | 39.84 | - |
|                      | 13.43 ± 4.75 | 4.45 | 8.18 | 4.15 | 10.32 | - |
| Livestock manure     | 17.81 ± 9.43 | 49.47 ± 7.61±2.59 | 38.98 | 26.61 | 3.75 | 3.41 | 23.30 | - |
|                      | 16.64 ± 25.72 | 1.67 | 33.88 | 12.38 | 16.18 | - |
| Residual sludge      | - | - | 52.80 ± 3.70±0.26 | 41.19 | 29.49 | 4.62 | 4.19 | 20.43 | 0.08 |
|                      | 0.32 | - | ± 0.35 | 0.26 | 0.31 | ± 0.56 | - |
|                      | 0.18 | - | - | - |

a. O was measured by the difference of C, H, N, S, and ash from 100.

- Not detected.
Table 2: Correlation between the feedstock composition and the biochar product yield under different pyrolysis temperatures. The results of correlation for biochar yield and biochar yield expressed on a dry ash free (daf.) basis had significant difference. On the whole, the biochar yields were negatively correlated with the feedstock organic contents, including cellulose, lignin, volatiles, fixed carbon, carbon and oxygen contents, while the ash and nitrogen contents were positively correlated with the biochar yield. The correlation between the feedstock and biochar yield (daf.) displays opposite results to that of total mass yield of the biochar.

| Biochar product yield | Fiber analysis | Proximate analysis | Ultimate analysis |
|-----------------------|---------------|--------------------|-------------------|
|                       | Cellulose | Lignin | Lignin/Cellulose | Volatiles | Fixed carbon | Ash | Carbon | Nitrogen | Oxygen |
| Biochar mass yield    |          |        |                 |            |            |     |        |          |        |
| 350 °C                | -0.30**  | -      | -                | -0.85**    | 0.85**     | -   | 0.40** | -0.55**  |         |
| 500 °C                | 0.28     | -      | -                | -0.96**    | 0.93**     | -0.49** | 0.40** | -0.38**  |         |
| 650 °C                | 0.25     | 0.28   | 0.24             | -0.95**    | 0.93**     | -0.49** | 0.47** | 0.36**   |         |
| Biochar yield (daf)   |          |        |                 |            |            |     |        |          |        |
| 350 °C                | -        | -      | -                | -          | -          | -   | -      | -        |         |
| 500 °C                | 0.39**   | 0.33   | 0.24             | -0.57**    | -          | -   | -      | -        |         |
| 650 °C                | 0.53**   | 0.47** | 0.37             | 0.30**     | -0.56**    | -0.29 | 0.34   |          |         |

**. Correlation is significant at the 0.01 level (2-tailed).
* . Correlation is significant at the 0.05 level (2-tailed).
-. Correlation is not significant.
Table 3 Bulk density of the biochar and its feedstock. The results for the bulk density suggested that there were significant variations in the biochars derived from the different feedstock categories.

| Biomass categories       | Bulk density of feedstock (g/cm$^3$) | Bulk density of biochar (g/cm$^3$)  |
|--------------------------|--------------------------------------|-------------------------------------|
|                          |                                      | HTT at 350 °C                      | HTT at 500 °C                      | HTT at 650 °C                      |
| Agricultural residues    | 0.230 ± 0.079                        | 0.136 ± 0.051                      | 0.185 ± 0.071                      | 0.137 ± 0.058                      |
| Pruning waste            | 0.354 ± 0.058                        | 0.222 ± 0.035                      | 0.347 ± 0.073                      | 0.257 ± 0.039                      |
| Aquatic waste            | 0.189 ± 0.049                        | 0.185 ± 0.058                      | 0.237 ± 0.082                      | 0.162 ± 0.082                      |
| Nutshell and fruit peel  | 0.387 ± 0.168                        | 0.213 ± 0.132                      | 0.271 ± 0.118                      | 0.248 ± 0.116                      |
| Livestock manure         | 0.658 ± 0.194                        | 0.560 ± 0.313                      | 0.607 ± 0.331                      | 0.570 ± 0.297                      |
| Residual sludge          | 0.690 ± 0.011                        | 0.649 ± 0.012                      | 0.652 ± 0.014                      | 0.539 ± 0.018                      |
Table 4 The relation between feedstock composition and the content of ash, fixed carbon and volatiles in biochar (daf.). The ash content in feedstock had a negative correlation to the fixed carbon production in biochar (daf.), as well as the content of fixed carbon, volatiles, cellulose, lignin and lignin/cellulose in feedstock related positively.

| Biochar (daf.) | Fiber analysis | Proximate analysis | Ultimate analysis |
|---------------|---------------|--------------------|-------------------|
|               | Cellulose     | Lignin             | Ash               | Carbon | Nitrogen | Oxygen | Hydrogen |
|               | Lignin/Cellulose | Volatiles | Fixed carbon |       |         |        |          |
| Ash content   |               |                     |                   |        |          |        |          |
| 350°C         | -0.36         | -0.57"             | -0.36             | -0.91" | -0.57"   | 0.98"  | -0.48"   | 0.62" | -0.52" |
| 500°C         | -0.38         | -0.58"             | -0.37             | -0.90" | -0.56"   | 0.97"  | -0.45"   | 0.66" | -0.55" |
| 650°C         | -0.38         | -0.56"             | -0.35             | -0.89" | -0.53"   | 0.95"  | -0.45"   | 0.62" | -0.57" |
| Fixed carbon  |               |                     |                   |        |          |        |          |
| 350°C         | 0.42"         | 0.58"              | 0.36              | 0.56"  | 0.67"    | -0.71" | -         | -0.52" | 0.67"  |
| 500°C         | 0.28          | 0.48"              | 0.33              | 0.75"  | 0.60"    | -0.80" | -         | -0.50" | 0.60"  |
| 650°C         | 0.29          | 0.52"              | 0.36              | 0.72"  | 0.60"    | -0.76" | -         | -0.58" | 0.57"  |
| Volatiles     |               |                     |                   |        |          |        |          |
| 350°C         | -0.43"        | -0.57"             | -0.36             | -0.57" | -0.68"   | 0.74"  | -         | 0.47"  | -0.61" |
| 500°C         | -0.34         | -0.52"             | -0.34             | -0.77" | -0.62"   | 0.85"  | -0.30"   | 0.42"  | -0.55" |
| 650°C         | -0.44"        | -0.57"             | -0.35             | -0.81" | -0.66"   | 0.90"  | -0.31"   | 0.52"  | -0.55" |

**. Correlation is significant at the 0.01 level (2-tailed).
*. Correlation is significant at the 0.05 level (2-tailed).
-. Correlation is not significant.
Figure captions

Fig. 1 TG-DTG curves to six categories of biomass wastes. The overall changes of TG and DTG profiles were roughly similar for the same categories of biomass waste. And the major maximal weight loss peak in DTG curves suggested the decomposition of fabric contents of biomass.

Fig. 2 Canonical correspondence analysis (CCA) biplot of the biochar yield and feedstock characteristics. The supplementary variables in CCA account for 85.8% and 74.7%, respectively; and adjusted explained variation is 81.3% and 70.9%, respectively. (a) Biochar yield depended on the ash content of feedstock mainly. (b) When the biochar yield is expressed on a dry ash free (daf.) basis, the ash content of feedstock correlated negatively to biochar yield (daf.), as well as the cellulose and lignin content of feedstock correlated positively to biochar yield.

Fig. 3 Proximate analysis ternary diagram for biochars and their feedstocks. With the increase in the pyrolysis temperature, the ash contents of the biochar increased, while the volatile contents decreased. The changes in the fixed carbon contents with the pyrolysis temperature depended on the ash content of feedstock.
Fig. 4 Relationship between the increases in fixed carbon content in biochar and proximate analysis of feedstock. The biochar fixed carbon contents increased with increasing feedstock treatment temperatures when the ash content was below 34.57 % and the volatile content exceeded 55.16 %.

Fig. 5 CCA biplot of feedstock composition and the production of volatiles, fixed carbon and ash content in biochar (af.). The supplementary variables in CCA to volatiles (a), fixed carbon (b) and ash (c) accounted for 78.5 %, 98.5% and 81.0%, respectively, as well as adjusted explained variation was 71.5%, 74.9% and 98.1%, respectively.

Fig. 6 The H/C and O/C atomic ratios for the feedstock and biochar. The H/C and O/C ratios of biochar were decreased to feedstock.

Fig. 7 Relationship between the ash contents, pH and EC values of biochars. Biochar pH values increased with increases in the pyrolysis temperature. The EC value of biochar correlated pH significantly.
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