

Article

Thermal Properties of Biochars Derived from Waste Biomass Generated by Agricultural and Forestry Sectors

Xing Yang ^{1,2}, Hailong Wang ^{2,3,*}, Peter James Strong ⁴, Song Xu ^{1,*}, Shujuan Liu ¹, Kouping Lu ², Kuichuan Sheng ^{5,*}, Jia Guo ⁶, Lei Che ⁷, Lizhi He ², Yong Sik Ok ⁸, Guodong Yuan ^{9,10}, Ying Shen ² and Xin Chen ¹

¹ School of Environment and Chemical Engineering, Foshan University, Foshan 528000, China; yx20080907@163.com (X.Y.); liujuan_407@163.com (S.L.); chenxin20170331@163.com (X.C.)

² Key Laboratory of Soil Contamination Bioremediation of Zhejiang Province, School of Environmental and Resource Sciences, Zhejiang Agricultural and Forestry University, Lin'an, Hangzhou 311300, China; kkp111@163.com (K.L.); helizhiyongyuan@163.com (L.H.); shenyings@zafu.edu.cn (Y.S.)

³ Department of Environmental Engineering, Foshan University, Foshan 528000, China

⁴ Centre for Solid Waste Bioprocessing, School of Civil Engineering, School of Chemical Engineering, The University of Queensland, St Lucia, QLD 4072, Australia; j.strong2@uq.edu.au

⁵ College of Biosystems Engineering and Food Science, Zhejiang University, Hangzhou 310058, China

⁶ Zhejiang Chengbang Landscape Co. Ltd., Hangzhou 310008, China; guojiafuture@foxmail.com

⁷ School of Engineering, Huzhou University, Huzhou 313000, China; three_stone_cn@163.com

⁸ School of Natural Resources and Environmental Science & Korea Biochar Research Center, Kangwon National University, Chuncheon 24341, Korea; soilok@kangwon.ac.kr

⁹ Yantai Institute of Coastal Zone Research, Chinese Academy of Sciences, Yantai 264003, China; gdyuan@yic.ac.cn

¹⁰ Guangdong Dazhong Agriculture Science Co. Ltd., Dongguan 523169, China

* Correspondence: nzhailongwang@163.com (H.W.); xuson@yeah.net (S.X.); kcsheng@zju.edu.cn (K.S.)

Academic Editor: S. Kent Hoekman

Received: 18 December 2016; Accepted: 24 March 2017; Published: 2 April 2017

Abstract: Waste residues produced by agricultural and forestry industries can generate energy and are regarded as a promising source of sustainable fuels. Pyrolysis, where waste biomass is heated under low-oxygen conditions, has recently attracted attention as a means to add value to these residues. The material is carbonized and yields a solid product known as biochar. In this study, eight types of biomass were evaluated for their suitability as raw material to produce biochar. Material was pyrolyzed at either 350 °C or 500 °C and changes in ash content, volatile solids, fixed carbon, higher heating value (HHV) and yield were assessed. For pyrolysis at 350 °C, significant correlations ($p < 0.01$) between the biochars' ash and fixed carbon content and their HHVs were observed. Masson pine wood and Chinese fir wood biochars pyrolyzed at 350 °C and the bamboo sawdust biochar pyrolyzed at 500 °C were suitable for direct use in fuel applications, as reflected by their higher HHVs, higher energy density, greater fixed carbon and lower ash contents. Rice straw was a poor substrate as the resultant biochar contained less than 60% fixed carbon and a relatively low HHV. Of the suitable residues, carbonization via pyrolysis is a promising technology to add value to pecan shells and Miscanthus.

Keywords: biochar; biomass; higher heating value (HHV); proximate analysis; renewable energy

1. Introduction

By 2020, the use of petroleum and other liquid fuels is estimated to reach nearly 100 million bpd globally, and this is anticipated to increase a further 10% by 2035 [1]. This increase in energy

demand, coupled to the depletion of petroleum resources, has intensified renewable energy research [2]. Biofuel derived from lignocellulosic biomass is one potential source of renewable energy. Biomass energy currently provides almost 14% of the world's primary energy. It is regarded as the renewable fuel with the highest potential for sustainable development in the future, and its adoption can significantly lower fossil fuel use and CO₂ emissions [3]. In addition, a providing sustainable energy solution is urgently required in developing countries.

In China, the use of biomass residues as a renewable energy source has increased in importance. Approximately 70% of the Chinese population live in rural areas, where a large amount of agricultural biomass residue is generated. It is a challenge to utilize these residues as a fuel in their original form due to their low bulk density, low heating value and the volume of smoke they generate [4]. Lignocellulosic biomass is an abundant organic material that, in addition to its use as a fuel, can be upgraded to generate biochar [5]. Biochar is a general term for a solid product derived from the pyrolysis of agricultural or forestry biomass [6,7]. Pyrolysis is a process where a substrate is heated in the absence of oxygen [3], and this conversion is a new strategy to potentially add value to biomass residues [8].

Depending on its physical and chemical properties, biochar can range from a high-quality fuel [6] to a soil amendment [9]. It may also be used to remediate contaminated soil [10–12] or sequester carbon [13,14]. The processing method and pyrolysis temperature are the decisive elements affecting biochar yield, but chemical and physical properties of the feedstock cannot be ignored [15,16]. There has been considerable research regarding the use of biochar as a soil amendment, including the effect of pyrolysis conditions and substrate type on biochar quality [8]. Moreover, numerous studies focus on biomass as a substrate for the carbonization of biochar and its application as a fuel [17–19]. The resulting biomass-derived biochar can be further processed into fuel briquettes after carbonization and can partially address the challenges of waste biomass management related to air pollution and improving transport efficiency [20]. For this reason, it is important to examine the thermal characteristics of biochars generated from different biomass types and identify those most suited to biochar production.

In this study, biochars were generated using laboratory-scale pyrolytic carbonization of eight types of waste biomass feedstocks commonly available in subtropical China. These feedstocks were pine wood, Chinese fir wood, Chinese fir bark, bamboo leaves, bamboo sawdust, Miscanthus, pecan shells and rice straw. To date, there is little research evaluating the thermal characteristics of biochar generated from these biomass sources. The aims of this research were to:

- (1) evaluate the influence of biomass types and pyrolysis temperatures on the thermal properties of biochars;
- (2) correlate biochar properties such as ash, volatile solid and fixed carbon contents to the higher heating values (HHVs); and
- (3) identify which waste biomass is best suited for fuel biochar production.

In brief, the outcome of this work would determine which substrates were suitable as fuel biochar and provide technical guidance for using agricultural and forestry residues for biochar production.

2. Materials and Methods

2.1. Biomass Feedstock Preparation

Eight types of biomass from the agricultural and forestry sectors in subtropical China were assessed. These were Masson pine wood, Chinese fir wood, Chinese fir bark, bamboo leaves, bamboo sawdust, Miscanthus, pecan shells and rice straw. The biomass was obtained from Lin'an City, northwest of Hangzhou, Zhejiang Province, China. The biomass feedstocks were air-dried, chopped using a pulverizer, and finally ground to a size able to pass through 40-mesh sieves for laboratory analyses.

2.2. Biochar Production

Biochars were produced using a slow pyrolysis procedure, which was performed under an inert nitrogen (purity $\geq 99.99\%$, flow rate: 200 mL min^{-1}) atmosphere in a laboratory-scale (5 L) fixed-bed tubular reactor made of stainless steel. The reactor was heated by an electrical furnace that had the maximum temperature of 800°C . The reactor was filled to 75% of its capacity and heated to either 350°C or 500°C at a heating rate of 5°C min^{-1} . When peak temperature was reached, it was held for 2 h. The pyrolyzed material was then cooled to room temperature under an inert atmosphere. Sixteen biochar samples were generated from the eight kinds of feedstock pyrolyzed at two temperatures. Biochar samples were ground to a size able to pass through 80-mesh sieves for laboratory analyses.

2.3. Laboratory Analyses

The moisture, ash, fixed carbon content, volatile solids and the HHV were determined for each feedstock and corresponding biochar samples. Moisture, ash and volatile solids content were determined according to the NY/T1881-2010 Standard (China) [21]. For the moisture content, ground samples were placed in an oven at 105°C and dried until constant weight. Dried samples were cooled in a desiccator for 1 h prior to weighing. For the ash content, samples were placed in an uncovered crucible in a muffle furnace and the temperature was raised to approximately 275°C in air with a heating rate lower than $10^\circ\text{C min}^{-1}$ (i.e., ambient to 275°C in less than 30 min). This was held for 30 min and then raised to 750°C and held for 3 h. Samples were cooled in a desiccator for 20 min prior to weighing. For the volatile solids content, the muffle furnace was preheated to 920°C , samples were placed inside and processed under an inert atmosphere (nitrogen) and kept at $900 \pm 10^\circ\text{C}$ for 7 min. Samples were cooled in a desiccator for 20 min prior to weighing. The HHV was determined according to the GB/T 213-2008 Standard (China) [22] with a Bomb Calorimeter. The fixed carbon content was calculated from the moisture, ash and volatile solids contents. All analyses were performed in duplicate.

2.4. The Calculations of Biochar Yield, Energy Yield and Energy Density

The biochar (mass) yield (G_m) was calculated as the ratio of the mass of dry biochar (M_2) to the mass of dry biomass (M_1) (Equation (1)). The energy yield (G_e) represented the energy contained in biomass that was retained in the biochar. It was calculated using G_m and the HHVs of biochar (Q_2) and raw biomass (Q_1) (Equation (2)). The energy density (ED) indicated the ratio of energy yield and biochar yield, as presented below (Equation (3)) [23].

$$G_m = \frac{M_2}{M_1} \times 100\% \quad (1)$$

$$G_e = G_m \times \frac{Q_2}{Q_1} \quad (2)$$

$$ED = \frac{G_e}{G_m} \quad (3)$$

2.5. Statistical Analyses

Statistical analyses were performed using the SPSS 17.0 statistical package program. The sample means ($n = 2$) for proximate analyses and HHV were subjected to one-way analysis of variance (ANOVA) and Duncan's multiple range tests. Variability in the data was expressed as the standard error, and the level of significance was set at p value < 0.05 . The correlations between raw biomass and the biochars, as well as that between ash, volatile and fixed carbon content and HHV were based on Pearson's correlation coefficients ($p < 0.01$ and $p < 0.05$).

3. Results and Discussion

3.1. Yield Analyses

The biochar and energy yields for the various substrates are displayed in Figure 1. In this study, slow pyrolysis was used as this generally favors biochar production. Slow pyrolysis, which incorporates longer residence times at slow heating rates at lower temperatures, produces primarily charcoal, while at high temperatures it produces primarily gaseous products [24]. For example, Nam et al. [25] obtained much higher mass yields of rice straw biochars using slow pyrolysis (45–48%) compared to fast pyrolysis (27%). Fast pyrolysis, which incorporates short residence times, fast heating rates, and moderate temperatures, favors the production of bio-oil [24].

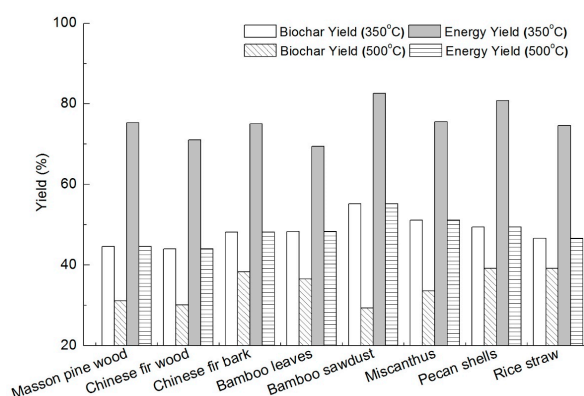


Figure 1. Biochar and energy yield of various substrates pyrolyzed at 350 or 500 °C.

The biochar yields from bamboo sawdust (55%) and Miscanthus (51%) were relatively high at 350 °C. All biochar yields decreased at the higher pyrolysis temperature [26], most notably for bamboo sawdust, which decreased from 55% at 350 °C to 29% at 500 °C. However, at 500 °C the biochar yields from pecan shells and rice straw remained relatively high—both at 39%. Yields are known to vary due to the differences in the relative abundance of cellulose, hemicellulose and lignin within different biomass, which have different thermal degradation kinetics [13]. Xiong et al. [27] also observed biochar yields decreased at higher carbonization temperatures. The differences between the resultant biochars were most likely attributable to the thermal resilience of lignin, as opposed to hemicellulose and cellulose that decompose at temperatures lower than 400 °C (220 to 315 °C and 315 to 400 °C, respectively).

The energy yields displayed a similar trend to the biochar yields. For pyrolysis at 350 °C, the biochar energy yields in decreasing order were: bamboo sawdust > pecan shells > Miscanthus > Masson pine wood > Chinese fir bark > rice straw > Chinese fir wood > bamboo leaves. Energy yields were lower after pyrolysis at 500 °C; the biochar energy yields in decreasing order were: bamboo sawdust > Miscanthus > pecan shells > bamboo leaves > Chinese fir bark > rice straw > Masson pine wood > Chinese fir wood. In the current study, the energy density of biochars pyrolyzed at 350 °C ranged from 1.44 to 1.69, with Masson pine wood, Chinese fir wood and pecan shell biochars above 1.60. Although the energy density of bamboo sawdust biochar obtained at 500 °C (1.88) was greatly improved compared that pyrolyzed at 350 °C (1.49), all other biochars generated at the higher temperature had lower energy densities (ranging from 1.19 to 1.52). Masson pine wood, Chinese fir wood and bamboo sawdust biomass are theoretically excellent biofuels because of their low ash content, but environmental factors and transport costs limit their application [28].

Biochars contain less volatile solids and, to a certain point, have an increased energy density. Harsono et al. [29] obtained 0.2 tons of biochar, 0.3 tons of biogas and 0.025 tons of bio-oil from one ton of palm oil residues after slow pyrolysis. The biogas consisted mainly of CO₂ (40–75%) and CH₄ (15–60%) [30], and trace amounts of water vapor, hydrogen sulfide, siloxanes, hydrocarbons, ammonia,

oxygen, carbon monoxide and nitrogen [31]. Biochar is lighter than the original material, making it easier to transport. Biochar is also moisture resistant and resistant to microbial degradation, which can lessen the impact of seasonal variations as they can be stored for much longer periods than raw biomass [5]. Reza et al. [32] also reported that the biochar was about 41–90% of the original mass, but contained 80–95% of the fuel value of the raw feedstock, i.e., biochar had higher energy density than the raw biomass due to the mass lost to volatilization. In China, families used to collect agricultural and forestry biomass such as crop residuals, weeds, branches and leaves for cooking and heating [33], and lots of biomass residues were burnt in the field, which caused serious air pollution [34]. Wang et al. [35] reported that $PM_{2.5}$ concentrations increased because of biomass burning to an average of $134 \mu g m^{-3}$, which was three times worse than clear days in Shanghai (from 2011 to 2013). Therefore, carbonization by pyrolysis represents a better approach to utilize these residues.

3.2. Proximate Analyses

Proximate analysis is a measure of total biomass components in terms of moisture content, ash content, volatile solids and fixed carbon of the solid fuel [36]. It is a relatively simple, cheap, robust method that is widely used to describe the properties of biomass fuels [37]. In the current study, ash and volatile solid contents varied significantly for the raw biomass as well as the biochars. In addition to the pyrolysis conditions (peak temperature, heating rate and residence time), structural components of the raw biomass also affected resultant biochars [38].

The ash content varied significantly ($p < 0.05$) among different feedstocks (Figure 2). The ash content of pecan shells, bamboo leaves and rice straw were relatively high, while Chinese fir wood, bamboo sawdust, Chinese fir bark and Masson pine wood had very low ash contents (all below 0.5%). The rice straw had the largest ash content (14%), while the Chinese fir wood had the lowest (0.08%). These results were consistent with Obernberger et al. [39], who found that wood generally had a lower ash content than bark, straw or cereal. Variation in ash content is attributable to the different concentrations of ash-forming elements, such as calcium carbonate, potassium silicates, iron and other metals [40]. The ash content of different feedstocks in this study were consistent with data from Liu et al. [41]. As ash is non-combustible, it negatively impacts a material's calorific value [4]. In addition, processing combustible material with a high ash content requires more frequent residue removal, as well as increased boiler maintenance due to higher dust emissions [42]. This results in unnecessary down time and lowers process efficiency, which is why a biomass with a low ash content is preferred as a fuel source.

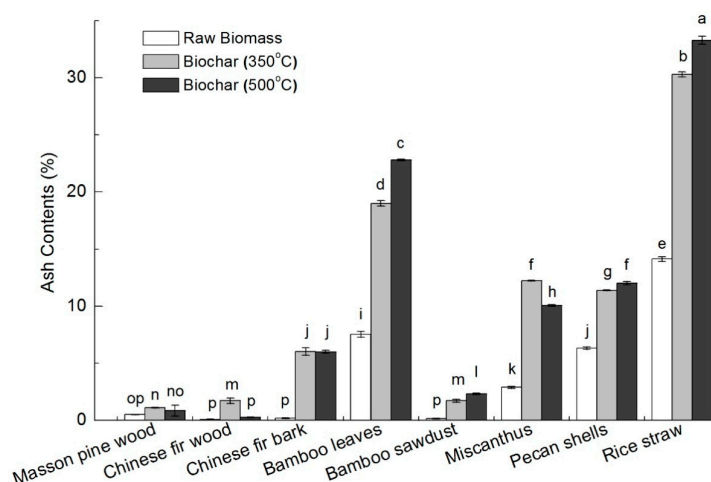


Figure 2. Ash contents of biomass and biochars pyrolyzed at 350 or 500 °C. Different letters above the columns indicate a significant difference ($p < 0.05$) between treatments. Error bars represent standard error of the means ($n = 2$).

In general, the pyrolysis (at 350 or 500 °C) increased the relative ash contents of the biochar, but values varied greatly and ranged from 0.3% (Chinese fir wood at 500 °C) to 33.3% (rice straw biochar at 500 °C). There were significant ($p < 0.05$) differences between the raw biomass and their biochars (Figure 2). The majority of mass loss occurred below 350 °C and the ash content increased dramatically at 350 °C (range: 0.6–16.2%), and generally increased (albeit less markedly) at 500 °C (range: 0.3–19.1%). Ash contents were relatively higher for biochars from pecan shells, rice straw, Miscanthus, Chinese fir bark and bamboo leaves (>10%), whereas the biochars made from Masson pine wood, Chinese fir wood and bamboo sawdust were low (<3%). There was a significant ($p < 0.01$) positive correlation between raw biomass and their biochars in terms of the ash content (Table 1). The results indicate that a raw material with a high ash content generates a biochar with a high ash content. Biomass from Masson pine wood, Chinese fir wood and bamboo sawdust had low starting ash contents, which was reflected in their biochars.

Table 1. Correlation coefficients between properties of raw biomass and biochars pyrolyzed at 350 or 500 °C ($n = 8$).

Properties	Samples	Raw Biomass	Biochar (350 °C)	Biochar (500 °C)
Ash content	Raw biomass	1	0.966 **	0.969 **
	Biochar (350 °C)	0.966 **	1	0.991 **
	Biochar (500 °C)	0.969 **	0.991 **	1
Volatile solid	Raw biomass	1	0.794 **	0.216
	Biochar (350 °C)	0.794 **	1	−0.059
	Biochar (500 °C)	0.216	−0.059	1
Fixed carbon	Raw biomass	1	0.518 *	0.096
	Biochar (350 °C)	0.518 *	1	0.405
	Biochar (500 °C)	0.096	0.405	1
Higher heating value	Raw biomass	1	0.733 **	0.743 **
	Biochar (350 °C)	0.733 **	1	0.708 **
	Biochar (500 °C)	0.743 **	0.708 **	1

Notes: * Correlation is significant at 0.05 level; ** Correlation is significant at 0.01 level.

The volatile solids of biomass and biochars are presented in Figure 3. In contrast to ash content, volatile solids (VS) retention was primarily affected by the pyrolysis temperature. The VS contents of the raw biomass were all greater than 50% (Chinese fir wood had the greatest content at 78%) and an increase in pyrolysis temperature from 350 to 500 °C increased VS release. This is in agreement with Sadaka et al. [43], who reported that VS decreased with increasing carbonization temperature for switchgrass (*Panicum virgatum* L.). Bamboo sawdust had the greatest VS loss with increasing temperature: the VS content decreased to 52% at 350 °C and 11% at 500 °C. The Chinese fir bark biochars had the lowest VS content at the tested pyrolysis temperatures, which decreased from 71% in the feedstock to 30% at 350 °C and dropped to 23% at 500 °C. Biomass typically consists of three components: hemicellulose, cellulose and lignin [37]. The differences may be due to thermal stability variances between hemicellulose, cellulose and lignin, and the relative abundance of these three components in each biomass. Generally, hemicellulose is the most volatile, cellulose is less volatile, while lignin is the most difficult to volatilize [37]. Bark is primarily composed of hemicelluloses and cellulose, while the woody biomass may contain more lignin than bark. At 350 °C, almost all hemicellulose and cellulose were pyrolyzed, while the lignin was more stable and continued to be pyrolyzed at 500 °C. The VS for the full set of biochars generated at 500 °C had the smallest variation, ranging from 11% to 23%, with the majority of the values between 14% and 20%. According to Chaney [44], low-grade fuels with low volatile solid may result in smouldering, which can generate a large amount of smoke and even toxic gases. A high VS content indicated easy ignition and that most of the fuel will volatilize during combustion [4]. In the present study, although the volatile solids content of biochar mainly depended on pyrolysis temperature, a significant ($p < 0.01$) positive correlation was

observed between raw biomass and their biochars from pyrolysis at 350 °C. However, there was no significant correlation between raw biomass and the 500 °C biochar (Table 1).

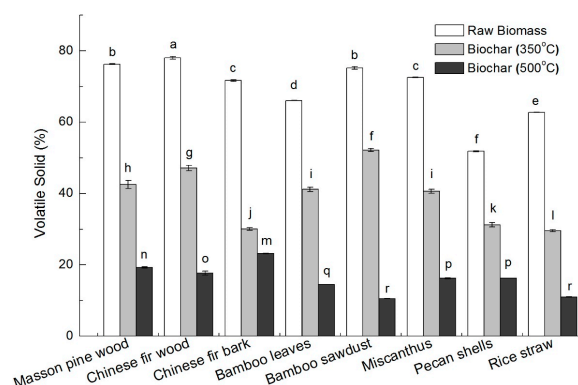


Figure 3. Volatile solids contents of biomass and biochars pyrolyzed at 350 or 500 °C. Letters above the columns indicate the significant difference ($p < 0.05$) between treatments. Error bars represent standard error of the means ($n = 2$).

The fixed carbon content of biochar increased significantly ($p < 0.05$) with increasing pyrolysis temperature due to the increased loss of volatile solids. Thus, the fixed carbon negatively correlated to the VS (Figures 3 and 4), which was consistent with a previous study [43]. The fixed carbon content followed the reverse pattern to the VS with all feedstocks. In addition, fixed carbon provided a rough estimate of the heating value of a fuel and was the primary source of heat generated during combustion [4]. In our study, the fixed carbon content ranged from 10% to 26% for the feedstocks, 38% to 62% after pyrolysis at 350 °C, and 52% to 84% for biochars after pyrolysis at 500 °C. The fixed carbon content increased two to four times after pyrolysis at 350 °C. The bamboo sawdust and Chinese fir bark pyrolyzed at 500 °C displayed the largest and smallest changes to fixed carbon content (increasing by 97% and 6%, respectively) in comparison to the pyrolysis products generated at 350 °C. Rice straw had the lowest fixed carbon contents after pyrolysis at 350 °C (38%) and 500 °C (52%), while Chinese fir wood had the highest fixed carbon content at 350 °C (62%) and bamboo sawdust the highest at 500 °C (84%). The Pearson's correlation test confirmed that the fixed carbon content of the 350 °C biochar correlated negatively ($p < 0.05$) with that of the raw material (Table 1). However, there was no significant correlation between 500 °C biochars and the raw biomass. As with volatile solids, pyrolysis temperature was the dominant factor affecting the fixed carbon content of biochar.

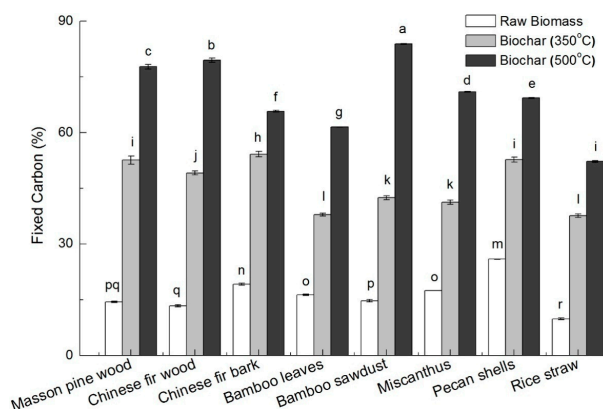


Figure 4. Fixed carbon contents of biomass and biochars pyrolyzed at 350 or 500 °C. Letters above the columns indicate the significant difference ($p < 0.05$) between treatments. Error bars represent standard error of the means ($n = 2$).

3.3. Higher Heating Value

The HHV is one of the most important parameters related to energy analyses. It is defined as the energy released per unit mass or per unit volume of fuel after complete combustion, including the energy contained in the water vapor in the exhaust gases [45]. The HHV indicates the best use for biomass fuel, as it describes the energy content [36]. As is evident in Figure 5, the HHVs of biomass feedstocks were generally similar (ranging from 18.44 to 20.10 MJ kg⁻¹), but the HHVs were lower for pecan shells (16.95 MJ kg⁻¹) and rice straw (15.85 MJ kg⁻¹). However, the HHVs of the eight feedstocks differed after pyrolysis. The HHVs of bamboo sawdust and Miscanthus biochars pyrolyzed at 500 °C were higher than those at 350 °C, while the opposite trend was observed for bamboo leaves and rice straw biochars. This change was due to variations in structural components, and their ratios, which were volatilized or carbonized to different extents at the two temperatures. During the low-temperature carbonization period, the heating value of the biochar initially increased, and decreased as the carbonized components that contributed to the HHV were most likely volatilized to CH₄ and H₂ at higher temperatures [46]. This was also observed by Xiong et al. [27], who found peak heating values of cotton stalk and bamboo sawdust biochar peaked after pyrolysis at 550 or 600 °C, respectively. For the 350 °C biochars the HHVs of Masson pine wood, Chinese fir wood and Chinese fir bark were >30 MJ kg⁻¹—comparable with the HHVs for coals ranging from brown coal to bituminous coal [47]. According to Qian et al. [36], these HHVs were comparable to high quality coal, which typically has a HHV of 25–35 MJ kg⁻¹. Anderson et al. [48] also reported that biochars derived from woody plants had higher HHVs. The Douglas-fir (*Pseudotsuga menziesii*) and Lodgepole pine (*Pinus contorta*) biochars were higher in energy than charcoal, but these were lower in energy compared to medium or high quality coal. In the current study, the bamboo sawdust biochar pyrolysis at 500 °C had the highest HHV at 32.4 MJ kg⁻¹, which was comparable with the HHV of bituminous coal [47].

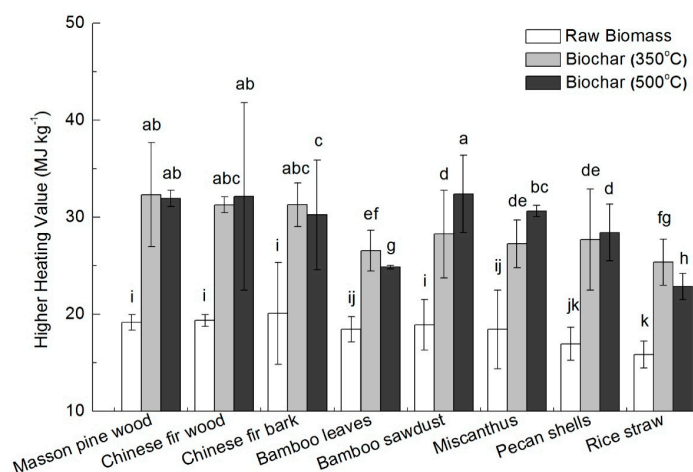


Figure 5. Higher heating values of the raw biomass and biochars pyrolyzed at 350 or 500 °C. Letters above the columns indicate the significant difference ($p < 0.05$) between treatments. Error bars represent standard error of the means ($n = 2$).

3.4. The Correlation between Proximate Analyses and HHV

There was no significant correlation between volatile solids content and HHV (Figure 6), whereas HHV had significant correlations ($p < 0.01$) with ash and fixed carbon contents. Accordingly, biochar samples with a low ash content or a high fixed carbon content display high HHVs. Therefore, suitable substrates for fuel biochar production need to be selected according to their ash and fixed carbon contents. In addition, there was a strong positive correlation ($p < 0.01$) between the HHVs of raw biomass and their corresponding biochars (Table 1).

The lower ash content (1.1%), higher fixed carbon (52.6%), energy density (1.69) and HHV (32.3 MJ kg⁻¹), as well as the higher energy yield (75.3%) indicate that Masson pine wood biochar produced at 350 °C was the most efficient biofuel of the eight substrates tested. In addition, Chinese fir wood biochar pyrolyzed at 350 °C was also a suitable fuel that displayed good thermal properties. After pyrolysis at 500 °C, the thermal properties of bamboo sawdust biochar were enhanced, and the higher HHV (32.4 MJ kg⁻¹), energy density (1.88) and fixed carbon content (83.9%) made it a higher quality fuel than that obtained at 350 °C (28.3 MJ kg⁻¹ HHV; 1.49 energy density; 42.5% fixed carbon content). The rice straw biomass was a poor energy source after pyrolysis, but it has potential remediation applications as it is an effective adsorbent for soil pollutants [14,49] and a good nutrient source due to its high concentration of inorganic elements [50]. Pecan shells and Miscanthus biochars were well suited as energy sources due to their high energy yield when converted to biochar. In Europe, Miscanthus is widely planted to produce liquid biofuels and chemical precursors, as well as improve soil fertility and land aesthetics [51]. In the current study, carbonization via pyrolysis is an innovative and promising method for the utilization of Miscanthus residues. The conversion efficiency for energy and weight of the pecan shells was considerable, and combined with other data, we considered this the best substrate for biochar production.

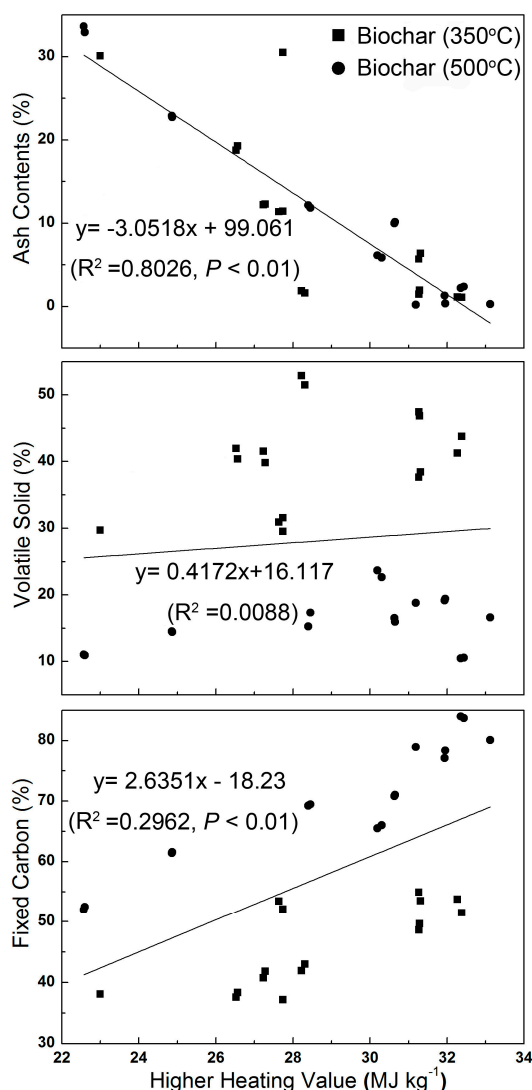


Figure 6. Correlation between the higher heating value and the contents of ash, fixed carbon and volatile solids in biochars ($n = 16$).

4. Conclusions

The results of this study demonstrate that the thermal properties and yields of biochars differ vastly for different biomass feedstocks. The thermal properties of the biochars were dependent on raw material characteristics and the temperature of carbonization during pyrolysis. Similarly, the effects on volatile solid and fixed carbon content were more dependent on pyrolysis temperature, while the ash contents of biochar were dependent on feedstock composition more than pyrolysis temperature. The HHV of the biochars increased after the initial pyrolysis at 350 °C, but the increase tapered or decreased with pyrolysis at 500 °C. Masson pine wood and Chinese fir wood biochars pyrolyzed at 350 °C and bamboo sawdust biochar pyrolyzed at 500 °C were suitable for direct use in fuel applications, as reflected by their higher HHVs, greater fixed carbon contents and lower ash contents. Of the substrates, carbonization via pyrolysis is a promising technology to add value to pecan shells and Miscanthus due to the higher energy and mass retention of the resultant biochars.

Acknowledgments: This study was funded by the National Natural Science Foundation of China (21577131, 41401338), the Natural Science Foundation of Zhejiang Province, China (LZ15D010001), Zhejiang Chengbang Landscape Co. Ltd., Hangzhou, China, and the Special Funding for the Introduced Innovative R&D Team of Dongguan (2014607101003), China. We thank Baoqi Chen and Yanhui Lin for their technical assistance.

Author Contributions: Xing Yang conceived and wrote this paper, Hailong Wang, Song Xu and Kuichuan Sheng conceived and designed the research, Kouping Lu and Lizhi He analyzed the data, Jia Guo and Ying Shen provided and prepared some of the biomass feedstocks and assisted the experiments, Peter James Strong, Shujuan Liu, Yong Sik Ok, Lei Che, Jia Guo and Xin Chen revised the paper and provided some valuable suggestions.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. *International Energy Outlook 2011*; U.S. Energy Information Administration: Washington, DC, USA, 2011.
2. Kunkes, E.L.; Simonetti, D.A.; West, R.M.; Serrano-Ruiz, J.C.; Gärtner, C.A.; Dumesic, J.A. Catalytic conversion of biomass to monofunctional hydrocarbons and targeted liquid-fuel classes. *Science* **2008**, *322*, 417–421. [[CrossRef](#)] [[PubMed](#)]
3. Qin, L.; Li, Q.; Meng, A.; Zhang, Y. Pyrolysis properties of potential biomass fuels in southwestern China. In *Cleaner Combustion and Sustainable World*; Qi, H., Zhao, B., Eds.; Tsinghua University Press: Beijing, China, 2013; pp. 457–464.
4. Akowuah, J.O.; Kemausuor, F.; Mitchual, S. Physico-chemical characteristics and market potential of sawdust charcoal briquette. *Int. J. Energy Environ. Eng.* **2012**, *3*, 1–6. [[CrossRef](#)]
5. Liu, Z.; Quek, A.; Hoekman, S.K.; Balasubramanian, R. Production of solid biochar fuel from waste biomass by hydrothermal carbonization. *Fuel* **2013**, *103*, 943–949. [[CrossRef](#)]
6. Galgani, P.; Voet, E.V.; Korevaar, G. Composting, anaerobic digestion and biochar production in Ghana. Environmental-economic assessment in the context of voluntary carbon markets. *Waste Manag.* **2014**, *34*, 2454–2465. [[CrossRef](#)] [[PubMed](#)]
7. Kung, C.; Chang, M. Effect of agricultural feedstock to energy conversion rate on bioenergy and GHG emissions. *Sustainability* **2015**, *7*, 5981–5995. [[CrossRef](#)]
8. Qian, K.; Kumar, A.; Zhang, H.; Bellmer, D.; Huhnke, R. Recent advances in utilization of biochar. *Renew. Sustain. Energy Rev.* **2015**, *42*, 1055–1064. [[CrossRef](#)]
9. Mao, X.; Xu, X.; Lu, K.; Gielen, G.; Luo, J.; He, L.; Donnison, A.; Xu, Z.; Xu, J.; Yang, W.; et al. Effect of 17 years of organic and inorganic fertilizer applications on soil phosphorus dynamics in a rice–wheat rotation cropping system in eastern China. *J. Soils Sediments* **2015**, *15*, 1889–1899. [[CrossRef](#)]
10. Zhang, X.; Wang, H.; He, L.; Lu, K.; Sarmah, A.; Li, J.; Bolan, N.S.; Pei, J.; Huang, H. Using biochar for remediation of soils contaminated with heavy metals and organic pollutants. *Environ. Sci. Pollut. Res.* **2013**, *20*, 8472–8483. [[CrossRef](#)] [[PubMed](#)]
11. He, L.; Gielen, G.; Bolan, N.S.; Zhang, X.; Qin, H.; Huang, H.; Wang, H. Contamination and remediation of phthalic acid esters in agricultural soils in China. *Agron. Sustain. Dev.* **2015**, *35*, 519–534. [[CrossRef](#)]
12. Zhang, X.; He, L.; Sarmah, A.; Lin, K.; Liu, Y.; Li, J.; Wang, H. Retention and release of diethyl phthalate in biochar-amended vegetable garden soils. *J. Soils Sediments* **2014**, *14*, 1790–1799. [[CrossRef](#)]

13. Novak, J.M.; Lima, I.; Xing, B.; Gaskin, J.W.; Steiner, C.; Das, K.; Ahmedna, M.; Rehrah, D.; Watts, D.W.; Busscher, W.J. Characterization of designer biochar produced at different temperatures and their effects on a loamy sand. *Ann. Environ. Sci.* **2009**, *3*, 195–206.
14. Yang, X.; Liu, J.; McGrouther, K.; Huang, H.; Lu, K.; Guo, X.; He, L.; Lin, X.; Che, L.; Ye, Z.; et al. Effect of biochar on the extractability of heavy metals (Cd, Cu, Pb and Zn) and enzyme activity in soil. *Environ. Sci. Pollut. Res.* **2016**, *23*, 974–984. [[CrossRef](#)] [[PubMed](#)]
15. Yargicoglu, E.N.; Sadasivam, B.Y.; Reddy, K.R.; Spokas, K. Physical and chemical characterization of waste wood derived biochars. *Waste Manag.* **2015**, *36*, 256–268. [[CrossRef](#)] [[PubMed](#)]
16. Yang, X.; Lu, K.; McGrouther, K.; Che, L.; Hu, G.; Wang, Q.; Liu, X.; Shen, L.; Huang, H.; Ye, Z.; et al. Bioavailability of Cd and Zn in soils treated with biochars derived from tobacco stalk and dead pigs. *J. Soils Sediments* **2017**, *17*, 751–762. [[CrossRef](#)]
17. Zulu, L.C. The forbidden fuel: Charcoal, urban woodfuel demand and supply dynamics, community forest management and woodfuel policy in Malawi. *Energy Policy* **2010**, *38*, 3717–3730. [[CrossRef](#)]
18. Mwampamba, T.H.; Owen, M.; Pigaht, M. Opportunities, challenges and way forward for the charcoal briquette industry in Sub-Saharan Africa. *Energy Sustain. Dev.* **2013**, *17*, 158–170. [[CrossRef](#)]
19. Liu, L.; Liu, Y.; Xing, Z. Char trace analysis of composite wood floor under different heating conditions. *Procedia Eng.* **2016**, *135*, 217–220. [[CrossRef](#)]
20. Lohri, C.R.; Rajabu, H.M.; Sweeney, D.J.; Zurbrugg, C. Char fuel production in developing countries—A review of urban biowaste carbonization. *Renew. Sust. Energy Rev.* **2016**, *59*, 1514–1530. [[CrossRef](#)]
21. Ministry of Agriculture of PRC. *Densified Biofuel—Test Methods*; NY/T1881-2010 Standard; China Standards Press: Beijing, China, 2010.
22. *Determination of Calorific Value of Coal*, GB/T 213-2008; General Administration of Quality Supervision, Inspection and Quarantine, Standardization Administration of China: Beijing, China, 2008.
23. Nam, H.; Capareda, S. Experimental investigation of torrefaction of two agricultural wastes of different composition using RSM (response surface methodology). *Energy* **2015**, *91*, 507–516. [[CrossRef](#)]
24. Huber, G.W.; Iborra, S.; Corma, A. Synthesis of transportation fuels from biomass: Chemistry, catalysts, and engineering. *Chem. Rev.* **2006**, *106*, 4044–4098. [[CrossRef](#)] [[PubMed](#)]
25. Nam, H.; Capareda, S.C.; Ashwath, N.; Kongkasawan, J. Experimental investigation of pyrolysis of rice straw using bench-scale auger, batch and fluidized bed reactors. *Energy* **2015**, *93*, 2384–2394. [[CrossRef](#)]
26. Mašek, O.; Brownsort, P.; Cross, A.; Sohi, S. Influence of production conditions on the yield and environmental stability of biochar. *Fuel* **2013**, *103*, 151–155. [[CrossRef](#)]
27. Xiong, S.; Zhang, S.; Wu, Q.; Guo, X.; Dong, A.; Chen, C. Investigation on cotton stalk and bamboo sawdust carbonization for barbecue charcoal preparation. *Bioresour. Technol.* **2014**, *152*, 86–92. [[CrossRef](#)] [[PubMed](#)]
28. Roberts, K.G.; Gloy, B.A.; Joseph, S.; Scott, N.R.; Lehmann, J. Life cycle assessment of biochar systems: Estimating the energetic, economic, and climate change potential. *Environ. Sci. Technol.* **2010**, *44*, 827–833. [[CrossRef](#)] [[PubMed](#)]
29. Harsono, S.S.; Grundmann, P.; Siahaan, D. Role of biogas and biochar palm oil residues for reduction of greenhouse gas emissions in the biodiesel production. *Energy Procedia* **2015**, *65*, 344–351. [[CrossRef](#)]
30. Yan, N.; Ren, B.; Wu, B.; Bao, D.; Zhang, X.; Wang, J. Multi-objective optimization of biomass to biomethane system. *Green Energy Environ.* **2016**, *1*, 156–165. [[CrossRef](#)]
31. Ryckebosch, E.; Drouillon, M.; Vervaeren, H. Techniques for transformation of biogas to biomethane. *Biomass Bioenergy* **2011**, *35*, 1633–1645. [[CrossRef](#)]
32. Reza, M.T.; Lynam, J.G.; Uddin, M.H.; Coronella, C.J. Hydrothermal carbonization: Fate of inorganics. *Biomass Bioenergy* **2013**, *49*, 86–94. [[CrossRef](#)]
33. Chen, J.; Li, C.; Ristovski, Z.; Milic, A.; Gu, Y.; Islam, M.S.; Wang, S.; Hao, J.; Zhang, H.; He, C.; et al. A review of biomass burning: Emissions and impacts on air quality, health and climate in China. *Sci. Total Environ.* **2017**, *579*, 1000–1034.
34. Cheng, Z.; Wang, S.; Fu, X.; Watson, J.G.; Jiang, J.; Fu, Q.; Chen, C. Impact of biomass burning on haze pollution in the Yangtze River delta, China: A case study in summer 2011. *Atmos. Chem. Phys.* **2014**, *14*, 4573–4585. [[CrossRef](#)]
35. Wang, H.; Qiao, L.; Lou, S.; Zhou, M.; Chen, J.M.; Wang, Q.; Tao, S.K.; Chen, C.H.; Huang, H.Y.; Li, L.; et al. PM_{2.5} pollution episode and its contributors from 2011 to 2013 in urban Shanghai, China. *Atmos. Environ.* **2015**, *123*, 298–305. [[CrossRef](#)]

36. Qian, K.; Kumar, A.; Patil, K.; Bellmer, D.; Wang, D.; Yuan, W.; Huhnke, R.L. Effects of biomass feedstocks and gasification conditions on the physiochemical properties of char. *Energies* **2013**, *6*, 3972–3986. [[CrossRef](#)]
37. Yang, H.; Yan, R.; Chen, H.; Zheng, C.; Lee, D.H.; Liang, D.T. In-depth investigation of biomass pyrolysis based on three major components: Hemicellulose, cellulose and lignin. *Energy Fuels* **2006**, *20*, 388–393. [[CrossRef](#)]
38. Kim, D.; Yoshikawa, K.; Park, K.Y. Characteristics of biochar obtained by hydrothermal carbonization of cellulose for renewable energy. *Energies* **2015**, *8*, 14040–14048. [[CrossRef](#)]
39. Obernberger, I.; Biedermann, F.; Widmann, W.; Riedl, R. Concentrations of inorganic elements in biomass fuels and recovery in the different ash fractions. *Biomass Bioenergy* **1997**, *12*, 211–224. [[CrossRef](#)]
40. Lewandowski, I.; Kicherer, A. Combustion quality of biomass: Practical relevance and experiments to modify the biomass quality of *Miscanthus × giganteus*. *Eur. J. Agron.* **1997**, *6*, 163–177. [[CrossRef](#)]
41. Liu, L.; Guo, J.; Lu, F. Chemical composition and ash characteristics of several straw stalks and residues. *J. Zhejiang For. Coll.* **2006**, *23*, 388–392. (In Chinese)
42. Hytönen, J.; Nurmi, J. Heating value and ash content of intensively managed stands. *Wood Res-Slovak.* **2015**, *60*, 71–82.
43. Sadaka, S.; Sharara, M.A.; Ashworth, A.; Keyser, P.; Allen, F.; Wright, A. Characterization of biochar from switchgrass carbonization. *Energies* **2014**, *7*, 548–567. [[CrossRef](#)]
44. Chaney, J.O. Combustion Characteristics of Biomass Briquettes. Ph.D. Thesis, University of Nottingham, Nottingham, UK, 2010.
45. Ghugare, S.B.; Tiwary, S.; Elangovan, V.; Tambe, S.S. Prediction of higher heating value of solid biomass fuels using artificial intelligence formalisms. *Bioenergy Res.* **2013**, *7*, 681–692. [[CrossRef](#)]
46. Imam, T.; Capareda, S. Characterization of bio-oil, syn-gas and bio-char from switchgrass pyrolysis at various temperatures. *J. Anal. Appl. Pyrolysis* **2012**, *93*, 170–177. [[CrossRef](#)]
47. Raveendran, K.; Ganesh, A. Heating value of biomass and biomass pyrolysis products. *Fuel* **1996**, *75*, 1715–1720. [[CrossRef](#)]
48. Anderson, N.; Jones, J.G.; Page-Dumroese, D.; McCollum, D.; Baker, S.; Loeffler, D.; Chung, W. A comparison of producer gas, biochar, and activated carbon from two distributed scale thermochemical conversion systems used to process forest biomass. *Energies* **2013**, *6*, 164–183. [[CrossRef](#)]
49. Wu, W.; Li, J.; Lan, T.; Müller, K.; Niazi, N.K.; Chen, X.; Xu, S.; Zheng, L.; Chu, Y.; Li, J.; et al. Unraveling sorption of lead in aqueous solutions by chemically modified biochar derived from coconut fiber: A microscopic and spectroscopic investigation. *Sci. Total Environ.* **2017**, *576*, 766–774. [[CrossRef](#)] [[PubMed](#)]
50. Dong, D.; Feng, Q.; McGrouther, K.; Yang, M.; Wang, H.; Wu, W. Effects of biochar amendment on rice growth and nitrogen retention in a waterlogged paddy field. *J. Soils Sediments* **2015**, *15*, 153–162. [[CrossRef](#)]
51. Brosse, N.; Dufour, A.; Meng, X.; Sun, Q.; Ragauskas, A. *Miscanthus*: A fast-growing crop for biofuels and chemicals production. *Biofuels Bioprod. Biorefining* **2012**, *6*, 580–598. [[CrossRef](#)]

