Elemental Composition of Biochar Obtained from Agricultural Waste for Soil Amendment and Carbon Sequestration

Saowanee Wijitkosum 1, * and Preamsuda Jiwok 2

1 Environmental Research Institute, Chulalongkorn University, Phayathai Road, Pathumwan, Bangkok 10330, Thailand
2 Chula Unisearch, Chulalongkorn University, Phayathai Road, Pathumwan, Bangkok 10330, Thailand; preamsuda456@gmail.com
* Correspondence: w.m.saowanee@gmail.com or saowanee.w@chula.ac.th; Tel.: +66-0218-8137

Received: 3 September 2019; Accepted: 16 September 2019; Published: 23 September 2019

Abstract: For an agricultural country such as Thailand, converting agricultural waste into biochar offers a potential solution to manage massive quantities of crop residues following harvest. This research studied the structure and chemical composition of biochar obtained from cassava rhizomes, cassava stems and corncobs, produced using a patented locally-manufactured biochar kiln using low-cost appropriate technology designed to be fabricated locally by farmers. The research found that cassava stems yielded the highest number of Brunauer-Emmett-Teller (BET) surface area in the biochar product, while chemical analysis indicated that corncobs yielded the highest amount of C (81.35%). The amount of H in the corncob biochar was also the highest (2.42%). The study also showed biochar produced by slow pyrolysis was of a high quality, with stable C and low H/C ratio. Biochar’s high BET surface area and total pore volume makes it suitable for soil amendment, contributing to reduced soil density, higher soil moisture and aeration and reduced leaching of plant nutrients from the rhizosphere. Biochar also provides a conducive habitat for beneficial soil microorganisms. The findings indicate that soil incorporation of biochar produced from agricultural crop residues can enhance food security and mitigate the contribution of the agricultural sector to climate change impacts.

Keywords: biochar; pyrolysis; thermochemical; biorefinery; biomass; soil amendment; carbon sequestration; climate change; agriculture

1. Introduction

Biorefining is the term given to the sustainable processing of biomass into a spectrum of marketable products and energy [1]. A wide range of technologies are available to separate biomass such as agricultural residues into their respective components (e.g., carbohydrates, proteins, triglycerides, etc.). These components can then be further converted to value-added products such as biofuels and fine chemicals. Biorefineries use a range of methods to convert biomass to value-added products and/or energy. Products typically take the form of chemical intermediates such as biohydrogen, bioethanol, biomethane, biodiesel, pellets, lignin, charcoal [2–4] that may then serve as feedstocks for other industrial processes.

Biorefineries can be categorized by feedstock, type and status of technology (e.g., first- or second-generation biorefinery and intermediate, e.g., syngas platform, sugar platform) [5,6]. At global level, biorefineries generally focus on three main products: biochemical [7], bioenergy (e.g., [8–11]), biofuels (e.g., [12–16]), and applications in the food and polymer industries (e.g., [17–21]). However,
biorefineries can also produce biochar, a high-value marketable product with benefits for the environment and sustainable agriculture [22,23]. Biorefineries use thermochemical processes (pyrolysis and carbonization) to convert biomass into biofuels and other bio-energy products [24,25]. Major thermochemical technologies for biochar production include slow and fast pyrolysis, gasification, torrefaction and hydrothermal carbonization [24].

Slow pyrolysis of biomass can be used to produce biochar, whose properties depend on feedstock properties as well as the reaction temperature and duration [22–26]. The chemical and physical properties of biochar (and thus its value) can be fine-tuned by modification of these reaction conditions [25]. The utility of biochar has been demonstrated in reducing the need for agrochemicals, increases in productivity, long-term improvement in soil conditions and reduction in greenhouse gas emissions through soil sequestration as well as indirectly through increasing the efficiency of fertilizer use [22–26].

Asia’s agricultural sector generates large volumes of agricultural residues every year [26]. Crop residues contribute to 80% of the global production of biomass dry matter (8201 Tg/year) of which 3137 Tg/year are potentially available after pyrolysis [27]. The use of agricultural residues as a feedstock for biochar production is therefore of interest for use as a soil amendment, with potentially significant environmental, production and economic benefits. Thailand’s economy relies on agricultural products. The country’s agricultural sector generates a large volume of crop residues including paddy husks, sawdust, corn cobs, cassava stems and cassava rhizomes. Production data collected by the Department of Agricultural Extension between 2006–2007 indicated that Thailand produced 4.40 million tons of corn and 17.6 million tons of cassava of which 0.84 million tons were corn cobs, 2.11 million tons were cassava stems and 1.76 million tons were cassava rhizomes [28]. Normally, agricultural wastes are simply left in the field to decompose or burned. Burning crop residues adds to GHG emissions, resulting in severe impacts on air quality, biodiversity and human health. Although burning is convenient, quick and cost-effective, and allows fast preparation of the field for the next rotation, some farmers nevertheless choose to incorporate crop residues into the soil to maintain long-term soil fertility. Soil incorporation of biochar from crop residues offers an attractive alternative to open field burning. Instead of burning, farmers can deal with their large volumes of crop residues by converting it into biochar using slow pyrolysis. The biomass is heated at 500–600 °C in a reduced oxygen or fully anoxic atmosphere [29,30]. Compared with other methods, pyrolysis has proved effective in converting residues into biochar as a highly stable solid [31]. Moreover, several studies confirm that biochar is effective as a soil ameliorant and can even increase crop yields [32–34].

Biochar is highly stable, comprising more than 65% carbon. Chemical composition is highly dependent on feedstock and pyrolysis conditions [35–38]. Biomass subjected to pyrolysis is converted to biochar with high fixed carbon content and high stability. Biochar’s stability in soil is crucial to its long-term environmental benefits. Because of its long-term stability, biochar can be used for carbon sequestration, mitigating climate change by locking carbon in the soil. The stability of biochar ensures longevity of expected benefits for soil, crops, water resources and climate change mitigation [39]. Biochar also regulates and increases availability of cationic plant nutrients such as P, K, Na, and Mg [27]. In addition to its direct agronomic benefits (enhanced fertilizer use efficiency, higher yields and improvement in soil fertility), biochar delivers three primary environmental benefits: sequestrating carbon in soils, reducing greenhouse gas emissions [39,40] and reducing pollution via runoff of fertilizers and pesticides into waterways and groundwater.

This research studied the composition, structural characteristics and morphology of biochar obtained via slow pyrolysis from three different types of biomass. The three biochar products were analyzed and compared to identify the most suitable biochar for soil amendment. This pilot study focused on using locally-produced crop residues wastes as feedstock. The biomass was heated in a controlled temperature biochar retort, manufactured locally using low-cost appropriate technology and designed to be fabricated by farmers themselves.
2. Materials and Methods

2.1. Biochar Production

The three sources of crop residues used as feedstock were corncobs, cassava rhizomes and cassava stems. Before heating the biomass, the materials were prepared to similar size distributions and moisture content. The cassava stems and corncobs were cut to less than 15 cm in length, while the cassava rhizomes were cut into lengths shorter than 10 cm. The materials were subjected to slow pyrolysis for 12–24 h in the Controlled Temperature Biochar Retort for Slow Pyrolysis Process (Patent Number 110100118, registered by Thavivongse Sriburi) (Figure 1). The retort was designed to comply with the respective FAO guidelines [41]. In order to control temperature, temperature data were collected from inside the biochar retort and the end of the chimney at different times throughout the heating process [22]. During the pyrolysis process, the materials were heated to a maximum 500–600 °C for 30 min. The ratio of biomass volume to fuel volume was 1.0:0.6, i.e., the mass of fuel should represent 60% of the total biomass weight in order to achieve optimal conditions for pyrolysis [34,41].

The Controlled Temperature Biochar Retort for Slow Pyrolysis Process is cost-efficient and can be built easily by farmers themselves for less than $US 50 using locally available materials and- most importantly- can use locally available biomass as feedstock [22,34,42,43]. The patented design allows control over pyrolysis conditions under limited oxygen availability inside the retort, including air intakes and exhaust holes. The design is critical to produce high-quality biochar—the outer furnace with eight drilled holes and the inner steel biochar retort with four drilled holes, all with a diameter of 2.5 cm—showed a highest yield of biochar and used the least amount of fuel. Moreover, the diameter of the holes must be exactly proportioned as incorrect hole diameter could lead to excessively high temperatures, which may adversely affect the quality of the biochar produced.

![Figure 1. The Controlled Temperature Biochar Retort for Slow Pyrolysis Process.](image)

The retort was designed for farmers in rural areas. It is simple to build and easy to use. The retorts were introduced to local farming communities via projects initiated by organizations under the Royal Project Foundation, including the Huay Sai Royal Development Study Center and Padeng-Biochar Research Center (Pd-BRC).

Pyrolysis temperature in the biochar retort can be controlled in the range of 500–600 °C. Slow for pyrolysis at a moderate temperature (350–550 °C) in the absence of O₂ and a longer residence time resulted in approximately 30% higher biochar yields than fast pyrolysis or gasification [24]. Higher yields of biochar are obtained, (up to 58–60 wt% of feedstock) as compared with similar oven designs. Intagun et al. (2018) [44] found the yield of corncob biochar produced in a “Kon Tiki” flame reached only 34.2 wt%. Cornelissen et al. (2016) [45] found similar low biochar yields of 22 ± 5 wt% from Eupatorium, wood and rice husk feedstocks using Kon Tiki kilns at Farmer Scale. These yield levels were consistent with those found by Pandi et al. (2017) [46] who reported an average biochar yield
of only 19.5 ± 0.5% from Eupatorium feedstock in a Kon Tiki flame curtain and four subtypes of kilns (deep-cone metal kiln; steel shielded soil pit; conical soil pit and steel small cone). O’Toole et al. (2013) [47] produced biochar from wheat-straw with a yield of around 24 ± 4.7%. Beis et al. (2000) [48] studied biochar yield from walnut shell using a Heinze retort with controlled temperature between 400–700 °C. The optimal temperature for their study was 500 °C and the highest biochar yield achieved was 28.9%. The controlled temperature biochar retort used in the current study can achieve yields of approximately double those achieved using other kiln designs.

The biochar produced from the controlled temperature biochar retort for slow pyrolysis process is equivalent in quality to that produced under controlled laboratory conditions and was found in on-farm trials to contribute to soil improvement and boost yields in rice [34], soybean [49] and vegetable farms [23].

2.2. Analysis Methodology

The composition of the biomass samples was analyzed before and after pyrolysis to characterize their texture and morphology. Major parameters for the study were surface area and total pore volume. These parameters were influenced by both type of biomass material and pyrolysis operating conditions. The surface area was analyzed by the Brunauer-Emmett-Teller (BET) method [50–52] and total pore volume and average pore diameter were analyzed by the Barrett-Joyner-Halenda (BJH) method [51]. An Autosorb-1 Surface area and pore size analyzer was employed to measure the surface areas, total pore volume and average pore diameter. The morphology characterization was conducted using a Scanning Electron Microscope (SEM) [50,52] on the JEOL JEM-5410LV SEM machine to determine the surface morphology and surface characteristics.

Analysis of elemental composition of the final material (C, H, N and O) was undertaken to establish the weight fractions of these elements. C, H and N were analyzed using the Elemental Analyzer (CHN), Leo TruSpec CHN model. O was calculated from the difference between percentages of biochar composition (100%) and percentages of other nutrients: C%, H% and N% [53]. The H/C, O/C, C/N molar ratios were also calculated [54]. These ratios provided an indication of the properties of biochar and the transformation efficiency during the slow pyrolysis process.

2.3. Statistical Analysis

Data were displayed as the mean ± SE, derived from four replicates. Turkey’s multiple comparison test was used to analyze the mean variance and compare the significance of the difference between means using the Statistical Package of the Social Science (SPSS) software.

3. Results and Discussion

The aim of this study was to analyze the elemental composition and structural characteristics of high quality biochar derived from different feedstock types as a means of improving soil quality, enhancing crop productivity and sequestering carbon in the soil. The raw materials for biochar production were made of agricultural wastes such as corncobs, cassava rhizome, waste fruits peeling and weeds and also wood branches such as Albizia myriophylla Berith, Cornbretum punetatum Blume, Leucaena leucocephala (Lamk), Samantha saman (Jacq) or even hard wood as Streblus ilicifolius.

The Controlled Temperature Biochar Retort for Slow Pyrolysis Process is cost-efficient and can be built easily using locally available materials and—most importantly—can use locally available biomass as feedstock [22,34,42,43]. The biochar invented oven was low cost and used raw materials from the local area. It is about 50 US dollars [22]. The biochar was produced from the controlled temperature biochar retort for slow pyrolysis process could have a good product and successfully to soil improvement and higher products in rice [34], soybean [49] and vegetables farm [23]. The controlled temperature biochar retort for slow pyrolysis process can control the temperature between 500–600 °C. The invented oven can control air that passes through inside by pyrolysis condition depending on the size and position of pores around it. Biochar yield depends greatly on thermochemical technology.
pyrolysis was most effective; a longer residence time and moderate temperature (350–550 °C) in the absence of O2 resulted in higher biochar yield (+30%) than the fast pyrolysis (12%) or gasification (10%) [24]. The process of the Controlled Temperature Biochar Retort for Slow Pyrolysis Process can produce high Biochar yields of around 58–60% from raw materials when compared to other similar ovens. Intagun et al. (2018) [44] studied the yield of biochar kiln which was produced from corncob in “Kon Tiki” flame curtain and found the yield to be only 34.2 wt%. So, in this study the invented oven can give a 1.76-fold higher yield than their experiment. Cornelissen et al. (2016) [45] studied biochar from Eupatorium, wood and rice husk using Kon Tiki kilns on Farmer-Scale and found that the average biochar yield was only 22 ± 5%. Pandi et al. (2017) [46] found an average biochar yield from Eupatorium feed stock of only 19.5 ± 05% by using “Kon Tiki” flame curtain (four subtypes of flame curtain klinis: deep-cone metal klin; steel shielded soil pit; conical soil pit and steel small cone). O’toole et al. (2013) [47] produced biochar from wheat-straw; the yield is around 24 ± 4.7%. Beis et al. (2000) [48] studied biochar yield from walnut shell using Heinze retort with the controlled temperature between 400–700 °C. The best temperature for their study was 500 °C and the highest biochar yield from walnut shell was 28.9%. All experiments’ biochar yields were still up to two times less than the yield from the invented oven with the controlled temperature biochar retort for slow pyrolysis process in this study. Therefore, the oven and the process for produce biochar from cornco ks, cassava rhizomes and cassava steams can show the high quality of the biochar by measuring element of C, H, N, and O contents between 62.95–81.35, 2.24–2.73, 1.22–1.65 and 15.23–33.44% by dry weight, respectively. Moreover, surface area and total pore volume of the biochar were higher than raw materials. Total pore volume of cornco ks, cassava rhizomes and cassava steams of biochar increased 1091.18, 560.47 and 2001.72%, respectively.

Comparing the chemical composition of each type of feedstock with its biochar product, the analyses of all three samples confirmed an increase in the proportion of C in biochar compared with the original biomass. The amount of C in cornco ks increased by the highest percentage (39.69%),

**Table 1. Properties of biomass feedstocks.**

|                  | Corncob   | Cassava Rhizome | Cassava Stem |
|------------------|-----------|-----------------|--------------|
| C (wt%)          | 41.66 ± 1.12 | 37.60 ± 2.22 | 41.55 ± 0.92 |
| H (wt%)          | 6.84 ± 0.36  | 6.15 ± 0.58  | 6.04 ± 0.13  |
| N (wt%)          | 0.74 ± 0.02  | 0.88 ± 0.04  | 1.27 ± 0.14  |
| O (wt%)          | 50.76 ± 0.89 | 55.37 ± 1.64 | 51.14 ± 1.18 |
| H:C ratio        | 1.97 ± 0.17  | 1.96 ± 0.27  | 1.74 ± 0.06  |
| O:C ratio        | 0.91 ± 0.05  | 1.10 ± 0.09  | 0.92 ± 0.05  |
| C:N ratio        | 65.63 ± 1.89 | 50.16 ± 3.86 | 39.30 ± 3.53 |
| Molecular formula| CH<sub>1.95</sub>O<sub>0.91</sub> | CH<sub>1.96</sub>O<sub>1.10</sub> | CH<sub>1.74</sub>O<sub>0.92</sub> |
| Surface area (m<sup>2</sup>/g) | 2.54 ± 0.41  | 2.78 ± 0.23  | 2.51 ± 0.03  |
| Total pore volume (cm<sup>3</sup>/g) | 0.0034 ± 0.0007 | 0.0043 ± 0.0004 | 0.0058 ± 0.0006 |
| Average pore diameter (Å)  | 31.05 ± 0.75  | 69.57 ± 5.58 | 83.34 ± 1.79 |

Note: Data are shown as the Mean ± SE. a, b, c, Means followed by different letter are significantly different at the 0.05 level (p < 0.05).
followed by cassava rhizomes (26.65%) and cassava stems (21.40%). For H and O the opposite trend was observed.

The distinct chemical composition of biochar resulted from a slow pyrolytic conversion of the biomass feedstock. Biomass is made up of three main components: hemicellulose, cellulose and lignin. In general, these components are represented at levels of 20–40%, 40–60% and 10–25%, respectively, as lignin wt% of the lignocellulosic biomass [55,56]. The slow pyrolysis process dissociates bonds between C and functional groups on the surface area of the biomass, including -OH, aliphatic C-O and aliphatic C-H groups [57–59]. The high temperature drives off volatile compounds and gases including CO$_2$, CO, H$_2$O, and volatile hydrocarbons [31,59–61]. Higher temperatures lead to increased amount of volatile matter which in turn boost the content of aromatic structures, especially when the temperature exceeded 400 °C [58,62,63]. Elevated levels of aromatic compounds contribute to enhanced stability of the biochar structure. The H/C molar ratio indicated formation of aromatic compounds. The O/C molar ratio decreased during carbonization, leading to dehydration reactions which reduced the hydrophilicity of the surface of the biochar material [63–65]. These characteristics give biochar long-term stability, allowing it to endure in soil for hundreds of years [66–68].

Table 2. Properties of biochar product.

|                | Corncob | Cassava Rhizome | Cassava Stem |
|----------------|---------|----------------|-------------|
| C (wt%)        | 81.35 $^\text{a}$ ± 1.42 | 64.25 $^\text{b}$ ± 1.53 | 62.95 $^\text{b}$ ± 3.71 |
| H (wt%)        | 2.42 $^\text{a}$ ± 0.17 | 2.73 $^\text{a}$ ± 0.17 | 2.24 $^\text{a}$ ± 0.12 |
| N (wt%)        | 1.22 $^\text{b}$ ± 0.14 | 1.65 $^\text{a}$ ± 0.08 | 1.37 $^\text{ab}$ ± 0.06 |
| O (wt%)        | 15.23 $^\text{b}$ ± 1.27 | 31.80 $^\text{a}$ ± 1.27 | 33.44 $^\text{a}$ ± 3.81 |
| H/C ratio      | 0.36 $^\text{a}$ ± 0.02 | 0.43 $^\text{a}$ ± 0.12 | 0.42 $^\text{a}$ ± 0.01 |
| O/C ratio      | 0.14 $^\text{b}$ ± 0.015 | 0.37 $^\text{a}$ ± 0.02 | 0.39 $^\text{a}$ ± 0.08 |
| C/N ratio      | 80.60 $^\text{a}$ ± 8.41 | 45.72 $^\text{b}$ ± 2.34 | 54.08 $^\text{b}$ ± 4.51 |
| Molecular formula | CH$_{0.36}$O$_{0.14}$ | CH$_{0.51}$O$_{0.37}$ | CH$_{0.43}$O$_{0.40}$ |
| Surface area (m$^2$/g) | 56.35 $^\text{b}$ ± 0.79 | 18.38 $^\text{b}$ ± 2.21 | 200.46 $^\text{a}$ ± 26.18 |
| Total pore volume (cm$^3$/g) | 0.0405 $^\text{b}$ ± 0.0041 | 0.0284 $^\text{b}$ ± 0.0029 | 0.1219 $^\text{a}$ ± 0.01 |
| Average pore diameter (Å) | 28.72 $^\text{b}$ ± 2.29 | 61.69 $^\text{a}$ ± 1.64 | 24.35 $^\text{b}$ ± 1.82 |

Note: Data are shown as the Mean ± SE. $^\text{a,b}$, Means followed by a different letter are significantly different at the 0.05 level ($p < 0.05$).

Table 2 summarizes the analyses of the structure and morphology of biochar made using different feedstocks. The results revealed that surface area and total pore volume of cassava stem biochar were the highest at 200.46 m$^2$/g and 0.1219 cm$^3$/g, respectively, followed by corncob biochar (56.35 m$^2$/g and 0.0405 cm$^3$/g) and cassava rhizome biochar (18.38 m$^2$/g and 0.0284 cm$^3$/g). As for average pore diameter, cassava rhizome biochar had the widest pore diameter at 61.69 Å, followed by corncob biochar (28.72 Å) and cassava stem biochar (24.35 Å), respectively.

Using scanning electron microscopy (Figure 2), analysis of morphology of the three biochar products revealed that biomass type influenced morphology under identical pyrolysis conditions in the same retort. Moreover, biochar obtained from different parts of the same plants also demonstrated different morphological characteristics and structures. Biochar produced from cassava rhizomes and cassava stems have a higher pore density than corncob biochar, while corncob biochar has a high pore size distribution than biochar produced from cassava rhizomes and stems. These results are consistent with measurements of their respective surface areas and total pore volumes.
These results highlight the importance of biomass type as one of the most important determinants of the C in biochar, appearing mostly in the form of amorphous C in which C atoms are connected in pyrolysis conditions [69–71]. After pyrolysis, the easily decomposed C in the original biomass can be stored “permanently” (>100 years) as biochar [72,73]. The high pyrolysis temperatures lead to dissociation of organic aromatic C bonds, resulting in production of amorphous C [37,58,62,63,74]. The C in biochar appears mostly in the form of amorphous C in which C atoms are connected in aromatic rings [75–77]. Slow pyrolysis results in the release of volatile organic matter, hemicellulose, and lignin, and was associated with overall shrinkage, melting, and cracking, resulting in the highly heterogeneous and complex structure of biochar, with many pores of different diameters [78–81]. These results highlight the importance of biomass type as one of the most important determinants of final biochar properties.

The physical structure of biochar was dependent on the types of biomass feedstock as well as pyrolysis conditions [69–71]. After pyrolysis, the easily decomposed C in the original biomass can be stored “permanently” (>100 years) as biochar [72,73]. The high pyrolysis temperatures lead to dissociation of organic aromatic C bonds, resulting in production of amorphous C [37,58,62,63,74]. The C in biochar appears mostly in the form of amorphous C in which C atoms are connected in aromatic rings [75–77]. Slow pyrolysis results in the release of volatile organic matter, hemicellulose, and lignin, and was associated with overall shrinkage, melting, and cracking, resulting in the highly heterogeneous and complex structure of biochar, with many pores of different diameters [78–81]. These results highlight the importance of biomass type as one of the most important determinants of final biochar properties.

The analysis shows that surface area is directly related to total pore volume, which gives biochar an elevated capacity to adsorb cations across its surface [62,82–84]. A higher matrix surface area increases ion exchange with nutrients at the surface. Therefore, mixing biochar into the soil can increase the soil’s cation exchange capacity [84–86]. Moreover, surface area and total pore volume both influence

**Figure 2.** Scanning Electron Microscopy (SEM) images showing differences in morphology of biochar produced from different biomass feedstocks.
biochar’s ability to retain nutrients and water within the pore matrix, thus stabilizing their availability within the soil to support crop growth [58,87].

The results indicated that biochar with high average pore diameter influenced the volume of water and nutrients retained in the pore matrix; biochar with larger pores is able to retain larger amounts of solution and nutrients and subsequently release them for root uptake.

This study revealed that chemical composition of biochar (C, H, O and N), H/C ratio, O/C ratio, the chemical structure (aliphatic and aromatic structures) as well as the product’s physical characteristics (surface area, total pore volume and pore size) are associated with biochar’s higher cation ion exchange capacity [58,88,89]. Pyrolysis temperature is an important determinant of physical and chemical properties of biochar, since it governs the extent of cleavage of chemical bonds within key components of the biomass (lignin, cellulose, hemicellulose). At 200–300 °C volatile fractions are transformed into low molecular weight liquids and gases instead of biochar [90,91]. Meanwhile, the dehydration of hydroxyl groups and thermal degradation of cellulose and lignin become increasingly significant at higher temperatures [91,92]. During pyrolysis, hemicelluloses decompose first at temperatures ranging from 200 to 260 °C; cellulose breakdown begins at 240–350 °C, and decomposition of lignin begins from 280–500 °C [93]. A dramatically increased surface area in the biomass char is observed to begin at 400–500 °C [94]. When the temperature is increased to 500–600 °C, aromatic organic compounds (mainly amorphous carbon, the main component of biochar) begin to break down [37,74]. The amorphous carbons are structured as aromatic rings, giving biochar its characteristic stability [75–77]. Pyrolysis temperature is therefore a key determinant of biochar yield as well as pore size and volume [80,81].

The bonds between aromatic compounds define the structure and properties of biochar. The main surface functional groups are hydroxyl, methyl, carboxylic and alkene groups [91]. However, Kim et al. (2012) [74] found that carboxyl and carbonyl group originating from carbohydrates appeared with the highest intensity at 300 °C and then decreased at higher temperatures. In contrast, other functional groups were concentrated or formed during decomposition. Aromatic skeletal vibration and aromatic C-H deformation increased until the temperature reached 500 °C [94–96]. As temperature increased, the char became progressively more aromatic and carbonaceous. The hydroxy, aliphatic C-H, carbonyl and olefinic CC groups were lost at higher temperatures. The aromatization process begins at ~350 °C and continues to higher temperatures [97]. Many chemical interactions between biochar and the environment are directly related to its surface chemistry. The presence of surface functional groups such as carboxyl influences cation exchange capacity and the efficacy of biochar as an adsorbent of nutrients [98].

These functional groups facilitate ion exchange and nutrient adsorption over the surface of the biochar [23,34,99,100]. The combined high surface area of biochar and its high CEC leads to higher ion exchange between nutrients in the soil solution [23,101]. The findings provide further evidence to support the utility of biochar as a nutrient source [58,77,102–105], as a soil enhancement to increase soil water holding capacity [58,66,77], supply the plant available silicon pool [106,107], for water retention [58,77] and as a habitat and refugia for soil microorganisms [66,77,105].

Biochar’s value as a soil amendment has been widely reported; soil incorporation can increase and enhance crop yields in terms of quality as well as quantity [32,33,105,108–112]. These findings have been documented in a variety of crops such as corn [108–111,113,114], soybeans [22], sorghum [105], cowpeas and peanuts [111]. In vegetables, benefits have been shown in lettuce (Lactuca sativa), cabbage (Brassica chinensis) [115], Chinese kale [23], tomato [116] and rice [32,34,87,88,105]. Growing crops in soil incorporated with biochar resulted in higher crop yields and improved quality [49,105,110,114,115]. Moreover, the stability of biochar allows it to remain in the soil for a long period. Biochar absorbs and retains plant nutrients from both organic and chemical fertilizers, reducing the leaching of nutrients and potentially reducing the total amount of fertilizers needed, thus reducing production cost [22,87,105,114]. Ultimately, increased productivity and quality of produce will contribute to higher net farm income [43].
Biochar is also an effective soil amendment that can increase soil quality in terms of its physical and chemical composition. Biochar incorporation improves soil aeration and increases the porosity of clay and shale soils [34,88,105,108,117]. Biochar also enhances soil aggregation. Incorporation of biochar into sandy loam soils also improves pH [34,58,66,88,104,115], water holding capacity [88,110,117], cation exchange capacity [89,105,110,111,115] and populations of beneficial soil microorganisms [112]. Moreover, biochar contributes to carbon sequestration [32,39,85,108,118–120], both directly by mixing the biomass into the soil [29,58,104] and indirect sequestration by retaining carbon stocks within the biomass [23,49,55,76]. Biochar can thus contribute to reducing carbon emissions from agriculture [32,90,108,113,117,121].

4. Conclusions

This research aimed to study chemical composition and morphology of biochar produced from three different biomass types: corncobs, cassava rhizomes and cassava stems. These feedstocks underwent slow pyrolysis, reaching maximum temperatures ranging from 500–600 °C. The results show that biochar obtained from these three sources of biomass differed significantly in their elemental composition and morphological structures, with corncobs having the highest amounts of carbon compared to other biomass feedstocks. Analysis of surface area, total pore volume and pore size confirmed prior findings that increased surface area and total pore volume are associated with higher ion exchange capacity and ability to retain water and nutrients. Larger pore diameter may also contribute to more conductive habitats for soil microorganisms. Cassava stem biochar had the highest surface area and total pore volume. Biochar’s chemical composition, morphology and texture indicated that biochar obtained from biomass feedstocks through slow pyrolysis yielded a biochar product with chemical composition and morphology suitable for soil amendment and carbon sequestration, both directly and indirectly.

Author Contributions: Conceptualization: S.W.; methodology, S.W. and P.J.; validation; S.W.; formal analysis, S.W. and P.J.; investigation, S.W.; data curation, S.W.; writing—original draft preparation, P.J.; writing—review and editing, S.W.; supervision, S.W.; project administration, S.W.

Funding: This research was financially supported by the “Innovation in Increasing the Organic Carbon in Soil for Sustainable Agricultural Purpose in Saline Soil Areas: First Year Pilot Project at the Lam Takong Watershed of Chulalongkorn University Fund”, Ratchadaphisek Somphot Endowment Fund (2014), Chulalongkorn University (CU-57-090-CC).

Acknowledgments: The Controlled Temperature Biochar Retort for Slow Pyrolysis Process was supported by Pa-deng Biochar Research Center.

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

References

1. Hingsamer, M.; Jungmeier, G. Chapter 5 Biorefinery. In The Role of Bioenergy in the Emerging Bioeconomy: Resources, Technology, Sustainability and Policy, 1st ed.; Lago, C., Caldés, N., Lechón, Y., Eds.; Academic Press: London, UK, 2019; pp. 179–222.
2. Cherubini, F.; Jungmeier, G. LCA of a biorefinery concept producing bioethanol, bioenergy, and chemicals from switchgrass. Int. J. Life Cycle Assess. 2010, 15, 53–66. [CrossRef]
3. Aguilar-Reynosa, A.; Romani, A.; Rodríguez-Jasso, R.M.; Aguilar, C.N.; Garrote, G.; Ruiz, H.A. Microwave heating processing as alternative of pretreatment in secondgeneration biorefinery: An overview. Energy Convers. Manag. 2017, 136, 50–65. [CrossRef]
4. Lara-Flores, A.A.; Araújo, R.G.; Rodríguez-Jasso, R.M.; Aguedo, M.; Aguilar, C.N.; Trajano, H.L.; Ruiz, H.A. Chapter 8 Bioeconomy and Biorefinery: Valorization of Hemicellulose from Lignocellulosic Biomass and Potential Use of Avocado Residues as a Promising Resource of Bioproducts. In Waste to Wealth, Energy, Environment, and Sustainability, 1st ed.; Singhania, R.R., Agarwal, R.A., Kumar, R.P., Sukumaran, R.K., Eds.; Springer: Singapore, Singapore, 2018; pp. 141–170.
5. Diep, N.Q.; Sakainshi, K.; Nakagoshi, N.; Fujimoto, S.; Minowa, T.; Tran, X.D. Biorefinery: Concepts, current status, and development trends. Int. J. Biomass Renew. 2012, 1, 1–8.
6. Ferreira, A.F. Chapter 1 Biorefinery Concept. In *Biorefineries: Targeting Energy, High Value Products and Waste Valorisation*, 1st ed.; Rabaçal, M., Ferreira, A.F., Silva, C.A.M., Costa, M., Eds.; Springer: Basel, Switzerland, 2017; pp. 1–20.

7. Food and Agriculture Organization of the United Nations. *FAO Statistical Pocketbook 2015*; Food and Agriculture Organization of the United Nations: Rome, Italy, 2015.

8. de Jong, E.; Jungmeier, G. Biorefinery Concepts in Comparison to Petrochemical Refineries. In *Industrial Biorefineries & White Biotechnology*, 1st ed.; Pandey, A., Höfer, R., Taherzadeh, M., Namboothiri, K.M., Larroche, C., Eds.; Elsevier B.V.: Amsterdam, The Netherlands, 2015; pp. 1–31.

9. Sadhukhan, J.; Martinez-Hernandez, E.; Murphy, R.J.; Ng, D.K.S.; Hassim, M.H.; Ng, K.S.; Kin, W.K.; Jaye, I.F.M.; Hang, M.Y.L.H.; Andiappan, V. Role of bioenergy, biorefinery and bioeconomy in sustainable development: Strategic pathways for Malaysia. *Renew. Sustain. Energy Rev.* 2018, 81, 1966–1987. [CrossRef]

10. Amoah, J.; Kahar, P.; Ogino, C.; Kondo, A. Bioenergy and Biorefinery: Feedstock, Biotechnological Conversion, and Products. *Biotechnol. J.* 2019, 1800494. [CrossRef] [PubMed]

11. Chen, Y.; Li, S.; Ho, S.H.; Wang, C.; Lin, Y.C.; Nagarajan, D.; Chang, J.S.; Ren, N. Integration of sludge digestion and microalgae cultivation for enhancing bioenergy and biorefinery. *Renew. Sustain. Energy Rev.* 2018, 96, 76–90. [CrossRef]

12. Taylor, G. Biofuels and the biorefinery concept. *Energy Policy* 2008, 36, 4406–4409. [CrossRef]

13. Valdivia, M.; Galan, J.L.; Laffargue, J.; Ramos, J.L. Biofuels 2020: Biorefineries based on lignocellulosic materials. *Microb. Biotechnol.* 2016, 9, 585–594. [CrossRef]

14. Almeida, J.R.M.; Fávaro, L.C.L.; Quirino, B.F. Biodiesel biorefinery: Opportunities and challenges for microbial production of fuels and chemicals from glycerol waste. *Biotechnol. Biofuels* 2012, 5, 48. [CrossRef]

15. Sarma, S.J.; Ayadi, M.; Brar, S.K. Chapter 2 Biorefinery: General Overview. In *Platform Chemical Biorefinery: Future Green Industry*, 1st ed.; Brar, S.K., Sarma, S.J., Pakshirajan, K., Eds.; Elsevier: Amsterdam, The Netherlands, 2016; pp. 21–32.

16. IEA Bioenergy. Biofuel-driven Biorefineries. 2013. Available online: https://www.nachhaltigwirtschaften.at/resources/iea_pdf/iea_task_42_biofuel_driven_biorefineries_ltr.pdf (accessed on 10 June 2019).

17. Cherubini, F. The biorefinery concept: Using biomass instead of oil for producing energy and chemicals. *Energy Convers. Manag.* 2010, 51, 1412–1421. [CrossRef]

18. Liu, Z.; Liao, W.; Liu, Y. A sustainable biorefinery to convert agricultural residues into value-Added chemicals. *Biotechnol. Biofuels* 2016, 9, 197. [CrossRef] [PubMed]

19. Ghysele, S.; Léon, A.E.; Pala, M.; Schoder, K.A.; Ackerc, J.V.; Ronse, F. Fast pyrolysis of mannan-Rich ivory nut (*Phytelephas aequatorialis*) to valuable biorefinery products. *Chem. Eng. J.* 2019, 373, 446–457. [CrossRef]

20. Dahiya, S.; Kumar, A.N.; Sravan, J.S.; Chatterjee, S.; Sarkar, O.; Mohan, S.V. Food waste biorefinery: Sustainable strategy for circular bioeconomy. *Bioreour. Technol.* 2018, 248, 2–12. [CrossRef] [PubMed]

21. Vaidya, A.A.; Collet, C.; Gaugler, M.; Lloyd-Jones, G. Integrating softwood biorefinery lignin into polyhydroxybutyrate composites and application in 3D printing. *Mater. Today Commun.* 2019, 19, 286–296. [CrossRef]

22. Sriburi, T; Wijitkosum, S. Biochar Amendment Experiments in Thailand: Practical Examples. In *Biochar as Regional Supply Chain Approach in View of Climate Change Mitigation*, 1st ed.; Bruckman, V.J., Varol, E.A., Uzun, B.B., Liu, J., Eds.; Cambridge University Press: Cambridge, UK, 2016; pp. 351–367.

23. Wijitkosum, S.; Jiwonk, P. Effect of biochar on Chinese kale and carbon storage in an agricultural area on a high rise building. *AIMS Agric. Food* 2019, 4, 177–193. [CrossRef]

24. Daful, A.G.; Chandraratne, M. Biochar Production from Biomass Waste-Derived Material. In *Encyclopedia of Renewable and Sustainable Materials*, 1st ed.; Choudhury, I., Hashmi, S., Eds.; Elsevier Science Publishing Co. Inc.: New York, NY, USA, 2018; pp. 1–9. (in press)

25. Masek, O. Chapter 21 Biochar in thermal and thermochemical biorefineries-production of biochar as a coproduct. In *Handbook of Biofuels Production: Process and Technologies*, 2nd ed.; Luque, R., Lin, C.S.K., Wilson, K., Clark, J., Eds.; Woodhead Publishing: Duxford, UK, 2016; pp. 655–671.

26. Wijitkosum, S.; Sriburi, T. Increasing the Amount of Biomass in Field Crops for Carbon Sequestration and Plant Biomass Enhancement Using Biochar. In *Biochar-An Imperative Amendment for Soil and the Environment*; IntechOpen: London, UK, 2018; Available online: http://www.intechopen.com/online-first/increasing-the-amount-of-biomass-in-field-crops-for-carbon-sequestration-and-plant-biomass-enhanceme (accessed on 10 June 2019).
27. Li, Z.; Delvaux, B. Phytolith-Rich biochar: A potential Si fertilizer in desilicated soils. *Geb Bioenergy* 2019. [CrossRef]

28. Department of Alternative Energy Development and Efficiency. *Biomass Energy*, 1st ed.; Energy Research Centre, Department of Alternative Energy Development and Efficiency: Bangkok, Thailand, 2015.

29. Lehmann, J. Bioenergy in the black. *Front. Ecol. Environ.* 2007, 5, 381–387. [CrossRef]

30. Sirijanusorn, S.; Sriprateep, K.; Pattiya, A. Pyrolysis of cassava rhizome in a counter-Rotating twin screw reactor unit. *Bioresour. Technol.* 2013, 139, 343–348. [CrossRef]

31. Kambo, H.S.; Dutta, A. A comparative review of biochar and hydrochar in terms of production physico-Chemical properties and applications. *Renew. Sustain. Energy. Rev.* 2015, 45, 359–378. [CrossRef]

32. Afeng, Z.; Genxing, P.; Jinwei, Z.; Jufeng, Z.; Liqiang, C.; Qaiser, H.; Rongjun, B.; Xiaojun, H.; Xinyan, Y.; et al. Effects of biochar amendment on soil quality, crop yield and greenhouse gas emission in a Chinese rice paddy: A field study of 2 consecutive rice growing cycles. *Field Crop. Res.* 2012, 127, 153–160.

33. de la Rosa, J.M.; Paneque, M.; Miller, A.Z.; Knicker, H. Relating physical and chemical properties of four different biochars and their application rate to biomass production of *Oryza sativa* on a Calcic Cambisol during a pot experiment of 79 days. *Sci. Total Environ.* 2014, 499, 175–184. [CrossRef] [PubMed]

34. Wijitkosum, S.; Kallayasisri, W. The Use of Biochar to Increase Productivity of Indigenous Upland Rice (*)Oryza sativa* L.) and Improve Soil Properties. *Res. J. Pharm. Biol. Chem. Sci.* 2015, 6, 1326–1336.

35. Gaskin, J.; Steiner, C.; Harris, K.; Das, K.; Bibens, B. Effect of low temperature pyrolysis conditions on biochar for agricultural use. *Trans. ASABE* 2008, 51, 2061–2069. [CrossRef]

36. Kim, K.; Kim, T.; Lee, S.; Choi, D.; Yeo, H. Comparison of physicochemical features of biooils and biochars produced from various woody biomass by fast pyrolysis. *Renew. Energy* 2013, 50, 188–195. [CrossRef]

37. Kim, K.H.; Kim, J.; Cho, T.; Choi, J.W. Influence of pyrolysis temperature on physicochemical properties of biochar obtained from the fast pyrolysis of pitch pine (*Pinus rigida*). *Bioresour. Technol.* 2012, 118, 158–162. [CrossRef]

38. Lehmann, J.; Rillig, M.C.; Thies, J.; Masiello, C.A.; Hockaday, W.C.; Crowley, D. Biochar effects on soil biota—A review. *Soil Biol. Biochem.* 2011, 43, 1812–1836. [CrossRef]

39. Lehmann, J.; Gaunt, J.; Rondon, M. Bio-Char sequestration in terrestrial ecosystems—A review. *Mitig. Adapt. Strateg. Glob. Chang.* 2006, 11, 403–427. [CrossRef]

40. Stewart, C.E.; Zheng, J.; Botte, J.; Cotrufo, F. Co-Generated fast pyrolysis biochar mitigates greenhouse gas emission and increases carbon sequestration in temperature soil. *Glob. Change Biol. Bioenergy* 2013, 5, 153–164. [CrossRef]

41. Sriburi, T. Biochar researches for soil amendment at Pa-Deng Biochar Research Center (PdBRG (CC2941)), Thailand. In Proceedings of the International Symposium on Biochar for Climate Change Mitigation and Soil and Environmental Management, Kangwon, Korea, 8–9 December 2011.

42. Sriburi, T.; Wijitkosum, S. Using Biochar for soil Stabilization and Increasing of Yield for Food Security and Sustainable Agriculture Initiatives; National Research Council of Thailand (NRCT): Bangkok, Thailand, 2015.

43. Wijitkosum, S. The use of biochar for food security in maize production. *Res. J. Pharm. Biol. Chem. Sci.* 2015, 6, 463–467. [CrossRef]

44. Intagun, W.; Khamdaeng, T.; Prom-ngarm, P.; Panyoyai, N. Emission and char quality: Effects of core puncture diameter on Bio-Char Kiln efficiency. *World Acad. Sci. Eng. Technol. Int. J. Biotechnol. Bioeng.* 2018, 12, 11. Available online: https://waset.org/publications/10009773/effect-of-core-puncture-diameter-on-bio-char-kiln-efficiency (accessed on 9 August 2019).

45. Cornelissen, G.; Pandit, N.R.; Taylor, P.; Pandit, B.H.; Sparrevik, M.; Schmidt, H.P. Emissions and char quality of flame-Curtain “Kon Tiki” kilns for farmer-scale charcoal/biochar production. *PLoS ONE* 2016, 11, e0154617. [CrossRef]

46. Pandit, N.R.; Mulder, J.; Hale, S.E.; Schmidt, H.P.; Cornelissen, G. Biochar from “Kon Tiki” flame curtain and other kilns: Effects of nutrient enrichment and kiln type on crop yield and soil chemistry. *PLoS ONE* 2017, 12, e0176378. [CrossRef]

47. O’Toole, A.; Knoth de Zarruk, K.; Steffens, M.; Rasse, D.P. Characterization, stability, and plant effects of Kiln-Produced wheat straw biochar. *J. Environ. Qual.* 2013, 42, 429–436. [CrossRef]

48. Beis, S.H.; Onay, O.; Atabay, E.; Kockar, O.M. Pyrolysis of walnut shell in a fixed-Bed reactor. In *World Renewable Energy Congress VI*, 1st ed.; Sayigh, A.A.M., Ed.; Pergamon Press: Oxford, UK, 2000; pp. 1360–1363.
49. Yooyen, J.; Wijitkosum, S.; Sriburi, T. The use of biochar in soybean fields for carbon sequestration. In Proceedings of the International Conference on Solid Wastes 2015: Knowledge Transfer for Sustainable Resource Management (ICSWHK2015), Hong Kong, China, 19–23 May 2015.

50. Ronsse, F.; Van Hecke, S.; Nacenius, R.; Prins, W. Production and characterisation of slow pyrolysis biochar. In Proceedings of the 19th European Biomass Conference and Exhibition, Berlin, Germany, 10–14 June 2011.

51. Wang, T.; Stewart, C.E.; Suna, C.; Wang, Y.; Zheng, J. Effects of biochar addition on evaporation in the five typical Loess Plateau Soils. *Catena* 2018, 162, 29–39. [CrossRef]

52. Liu, W.J.; Jiang, H.; Yu, H.Q. Development of Biochar-Based Functional Materials: Toward a Sustainable Platform Carbon Material. *Chem. Rev.* 2015, 115, 12251–12285. [CrossRef]

53. Lee, Y.; Eum, P.; Ryu, C.; Gang, K.S.; Yang, W.; Park, Y.; Jung, J.; Hyun, S. Comparison of biochar properties from biomass residues produced by slow pyrolysis at 500 °C. *Bioresour. Technol.* 2013, 146, 196–201. [CrossRef]

54. IBI. Standardized Product Definition and Product Testing Guidelines for Biochar That is Use in Soil. Version 2.1. Available online: https://biochar-international.org/wp-content/uploads/2019/01/IBI_Biochar_Standards_V2.1_Final1.pdf (accessed on 1 May 2017).

55. McKendry, P. Energy production from biomass (part 1): Overview of biomass. *Bioresour. Technol.* 2002, 83, 37–46. [CrossRef]

56. Yang, H.; Yan, R.; Chen, H.; Lee, D.H.; Zheng, C. Characteristics of hemicellulose, cellulose and lignin pyrolysis. *Fuel* 2007, 86, 1781–1788. [CrossRef]

57. Chen, Y.; Duan, J.; Luo, Y. Investigation of agricultural residues pyrolysis behavior under inert and oxidative conditions. *J. Anal. Appl. Pyrolysis* 2008, 83, 165–174. [CrossRef]

58. Novak, J.M.; Lima, I.; Xing, B.; Gaskin, J.W.; Steiner, C.; Das, K.C.; Ahmedna, M.; Rehrah, D.; Watts, D.W.; Busscher, W.J.; et al. Characterization of designer biochar produced at different temperatures and their effects on a loamy sand. *Ann. Environ. Sci.* 2009, 3, 195–206.

59. Antal, M.J., Jr.; Gronli, M. The Art, Science, and Technology of Charcoal Production. *Ind. Eng. Chem. Res.* 2003, 42, 1619–1640. [CrossRef]

60. Sun, Y.; Gao, B.; Yao, Y.; Fang, J.; Zhang, M.; Zhou, Y.; Chen, H.; Yang, L. Effects of feedstock type, production method, and pyrolysis temperature on biochar and hydrochar properties. *Chem. Eng. J.* 2014, 240, 574–578. [CrossRef]

61. Brownsort, P.A. Biomass Pyrolysis Processes: Performance Parameters and Their Influence on Biochar System Benefits. Master’s Thesis, The University of Edinburgh, Edinburgh, UK, 2009.

62. Fang, Q.; Chen, B.; Lin, Y.; Guan, Y. Aromatic and Hydrophobic surfaces of wood-derived biochar enhance perchlorate adsorption via hydrogen bonding to oxygen oxygen-containing organic Groups. *Environ. Sci. Technol.* 2013, 48, 279–288. [CrossRef]

63. Doumer, M.E.; Arizaga, G.G.C.; Silva, D.A.; Yamamoto, C.I.; Novotny, E.H.; Santos, J.M.; dos Santos, L.O.; Wisniewski, A., Jr.; de Andrade, J.B.; Mangrich, A.S. Slow pyrolysis of different Brazilian waste biomasses as sources of soil conditioners and energy, and for environmental protection. *J. Anal. Appl. Pyrolysis* 2015, 113, 434–443. [CrossRef]

64. Lee, Y.; Eum, P.; Ryu, C.; Park, Y.; Jung, J. Characteristics of biochar produced from slow pyrolysis of Geodae-Uksae 1. *Bioresour. Technol.* 2013, 130, 345–350. [CrossRef]

65. Al-Wabel, M.I.; Al-Omran, A.; El-Naggar, A.H.; Nadeem, M.; Usman, A.R.A. Pyrolysis temperature induced changes in characteristics and chemical composition of biochar produced from conocarpus wastes. *Bioresour. Technol.* 2013, 131, 374–379. [CrossRef]

66. Gul, S.; Whalen, J.K.; Thomas, B.W.; Sachdeva, V.; Deng, H. Physico-chemical properties and microbial responses in biochar-Amended soil mechanism and future directions. *Agric. Ecosyst. Environ.* 2015, 206, 46–59. [CrossRef]

67. Ennis, C.J.; Evans, A.G.; Islam, M.; Komang, K.; Senior, R. Biochar carbon sequestration, land remediation, and impact on soil microbiology. *Crit. Rev. Environ. Sci. Technol.* 2012, 42, 2311–2364. [CrossRef]

68. Lai, W.Y.; Lai, C.M.; Ke, G.R.; Chung, R.S.; Chen, C.T.; Cheng, C.H.; Pai, C.W.; Chen, S.Y.; Chen, C.C. The effects of woodchip biochar application on crop yield, carbon sequestration and greenhouse gas emission from soils planted with rice or leaf beet. *J. Taiwan Int. Chem. Eng.* 2013, 44, 1039–1044. [CrossRef]

69. Chia, C.H.; Downie, A.; Munroe, P. Characteristics of Biochar: Physical and Structural Properties. In *Biochar for Environmental Management Science, Technology and Implementation*, 2nd ed.; Lehmann, J., Joseph, S., Eds.; Routledge: London, UK, 2015; pp. 89–110.
70. Jin, W.; Singh, K.; Zondlo, J. Pyrolysis Kinetics of Physical Components of Wood and Wood-Polymers Using Isoconversion Method. *Agriculture* 2013, 3, 12–32. [CrossRef]
71. Wei, S.; Zhu, M.; Fan, X.; Song, J.; Peng, P.; Li, K.; Jia, W.; Song, H. Influence of pyrolysis temperature and feedstock on carbon fractions of biochar produced from pyrolysis of rice straw, pine wood, pig manure and sewage sludge. *Chemosphere* 2018, 218, 624–631. [CrossRef]
72. Laird, D.A.; Brown, R.C.; Amonette, J.E.; Lehmann, J. Review of the pyrolysis platform for coproducing bio-oil and biochar. *Biofuel Bioprod. Biorein.* 2009, 3, 547–562. [CrossRef]
73. Leng, L.; Yuan, X.; Zeng, G.; Shao, J.; Chen, X.; Wu, Z.; Wang, H.; Peng, X. Surface characterization of rice husk bio-Char produced by liquefaction and application for cationic dye (malachite green) adsorption. *Fuel* 2015, 155, 77–85. [CrossRef]
74. Batista, E.M.C.C.; Shultz, J.; Matos, T.T.S.; Fornari, M.R.; Ferreira, T.M.; Szpoganicz, B.; de Freitas, R.A.; Hassler, J.W. Agricultural bio-Char production, renewable energy generation and farm carbon sequestration in Western Australia: Certainty, uncertainty and risk. *Agric. Ecosyst. Environ.* 2014, 129, 1–7. [CrossRef]
75. Manya, J.J. Pyrolysis for biochar purposes: A review to establish current knowledge gaps and research needs. *Environ. Sci. Technol.* 2012, 46, 7939–7994. [CrossRef]
76. Downie, A.; Crosky, A.; Munroe, P. Physical properties of biochar. In *Biochar for Environmental Management: Science and Technology*, 1st ed.; Lehmann, J., Joseph, S., Eds.; Earthscan: London, UK, 2009; pp. 13–32.
77. Lehmann, J.; Joseph, S. Biochar for Environmental Management: An Introduction. 2009. Available online: http://www.biochar-international.org/images/Biochar_book_Chapter_1.pdf (accessed on 5 January 2016).
78. Laird, D.A.; Brown, R.C.; Amonette, J.E.; Lehmann, J. Review of the pyrolysis platform for coproducing bio-oil and biochar. *Biofuel Bioprod. Biorein.* 2009, 3, 547–562. [CrossRef]
79. Batista, E.M.C.C.; Shultz, J.; Matos, T.T.S.; Fornari, M.R.; Ferreira, T.M.; Szpoganicz, B.; de Freitas, R.A.; Mangrich, A.S. Effect of surface and porosity of biochar on water holding capacity aiming indirectly at preservation of the Amazon biome. *Sci. Rep.* 2018, 8, 10677. [CrossRef]
80. Pituello, C.; Francisco, O.; Simonetti, G.; Pisi, A.; Torreggiani, A.; Berti, A.; Morari, F. Characterization of chemical—Physical, structural and morphological properties of biochars from biowastes produced at different temperatures. *J. Soils Sediments* 2015, 15, 792–804. [CrossRef]
81. Sohi, S.P.; Lopez-Capel, E.; Krull, E.; Bol, R. Biochar, climate change and soil: A review to guide future research. *CSIRO Land Water Sci. Rep.* 2009, 5, 17–31.
82. Hmid, A.; Mondelli, D.; Fiore, S.; Fanizzi, F.P.; Al Chami, Z.; Dumontet, S. Production and characterization of slow pyrolysis biochar: Influence of feedstock type and pyrolysis conditions. *Bioresour. Technol.* 2014, 155, 3488–3497. [CrossRef]
83. Yuan, J.; Xu, R.; Zhang, H. The forms of alkalis in the biochar produced from crop residues at different temperatures. *Bioresour. Technol.* 2011, 102, 3488–3497. [CrossRef]
84. Downie, A.; Crosky, A.; Munroe, P. Physical properties of biochar. In *Biochar for Environmental Management: Science and Technology*, 1st ed.; Lehmann, J., Joseph, S., Eds.; Earthscan: London, UK, 2009; pp. 13–32.
85. Lehmann, J.; Joseph, S. Biochar for Environmental Management: An Introduction. 2009. Available online: http://www.biochar-international.org/images/Biochar_book_Chapter_1.pdf (accessed on 5 January 2016).
86. Wei, S.; Zhu, M.; Fan, X.; Song, J.; Peng, P.; Li, K.; Jia, W.; Song, H. Influence of pyrolysis temperature and feedstock on carbon fractions of biochar produced from pyrolysis of rice straw, pine wood, pig manure and sewage sludge. *Chemosphere* 2018, 218, 624–631. [CrossRef]
87. Sohi, S.P.; Lopez-Capel, E.; Krull, E.; Bol, R. Biochar, climate change and soil: A review to guide future research. *CSIRO Land Water Sci. Rep.* 2009, 5, 17–31.
88. Ayhan, D. Effects of Temperature and Particle Size on Bio-Char Yield from Pyrolysis of Agricultural Residues. *J. Anal. Appl. Pyrolysis* 2004, 72, 243–248.
89. Downie, A.; Crosky, A.; Munroe, P. Physical properties of biochar. In *Biochar for Environmental Management: Science and Technology*, 1st ed.; Lehmann, J., Joseph, S., Eds.; Earthscan: London, UK, 2009; pp. 13–32.
90. Sohi, S.P.; Lopez-Capel, E.; Krull, E.; Bol, R. Biochar, climate change and soil: A review to guide future research. *CSIRO Land Water Sci. Rep.* 2009, 5, 17–31.
91. Masulili, A.; Utomo, W.H. Rice husk biochar for rice based cropping system in acid soil I. The Characteristics of rice husk biochar and Its Influence on the Properties of Acid Sulfate Soils and Rice Growth in West Kalimantan, Indonesia. *J. Agric. Sci. Technol.* 2010, 2, 39–47. [CrossRef]
92. Zhang, J.; Liu, J.; Liu, R. Effects of pyrolysis temperature and heating time on biochar obtained from the pyrolysis of straw and lignosulfonate. *Bioresour. Technol.* 2015, 176, 288–291. [CrossRef]

93. Babu, B.V. Biomass pyrolysis: A state-of-the-Art review. *Biofuels Bioprod. Biorefin.* 2008, 2, 393–414. [CrossRef]

94. Chen, Y.; Zhang, X.; Chen, W.; Yang, H.; Chen, H. The structure evolution of biochar from biomass pyrolysis and its correlation with gas pollutant adsorption performance. *Bioresour. Technol.* 2017, 246, 101–109. [CrossRef]

95. Chen, Y.; Yang, H.; Wang, X.; Zhang, S.; Chen, H. Biomass-Based pyrolytic polygeneration system on cotton stalk pyrolysis: Influence of temperature. *Bioresour. Technol.* 2012, 107, 411–418. [CrossRef]

96. Xiao, R.R.; Yang, W. Influence of temperature on organic structure of biomass pyrolysis products. *Renew. Energy* 2013, 50, 136–141. [CrossRef]

97. Zhao, Y.J.; Feng, D.D.; Zhang, Y.; Huang, Y.D.; Sun, S.Z. Effect of pyrolysis temperature on char structure and chemical speciation of alkali and alkaline earth metallic species in biochar. *Fuel Process. Technol.* 2016, 141, 54–60. [CrossRef]

98. Oh, T.K.; Choi, B.S.; Shinogi, Y.; Chikushi, J. Characterization of biochar derived from three types of biomass. *J. Fac. Agric. Kyushu. Univ.* 2012, 57, 61–66.

99. Gul, S.; Whalen, J.K. Biochemical cycling of nitrogen and phosphorus in biochar-amended soils. *Soil Biol. Biochem.* 2016, 103, 1–15. [CrossRef]

100. Liang, B.; Lehmann, J.; Sohi, S.P.; Thies, J.E.; O’Neill, B.; Trujillo, L.; Gaunt, J.; Solomon, D.; Grossman, J.; Neves, E.G.; et al. Black carbon affects the cycling of non-black carbon in soil. *Org. Geochem.* 2010, 41, 206–213. [CrossRef]

101. Amonette, J.; Joseph, S. Characteristics of Biochar: Micro Chemical Properties. In *Biochar for Environmental Management: Science and Technology*; Lehmann, J., Joseph, S., Eds.; Earthscan: London, UK, 2009; pp. 33–52.

102. Glaser, B.; Lehmann, J.; Zech, W. Ameliorating physical and chemical properties of highly weathered soils in the tropics with charcoal—A review. *Biol. Fertil. Soils* 2002, 35, 219–230. [CrossRef]

103. Lehmann, J.; da Silva, J.; Steiner, C.; Nehls, T.; Zech, W.; Glaser, B. Nutrient availability and leaching in an archaeological Anthrosol and a Ferralsol of the Central Amazon basin: Fertilizer, manure and charcoal amendments. *Plant Soil* 2003, 249, 343–357. [CrossRef]

104. Laird, D.A.; Fleming, P.; Wang, B.Q.; Horton, R.; Karlen, D. Biochar impact on nutrient leaching from a Midwestern agricultural soil. *Geoderma* 2010, 158, 436–442. [CrossRef]

105. Steiner, C.; Teixeira, W.G.; Lehmann, J.; Nehls, T.; de Macêdo, J.L.; Blum, W.E.; Zech, W. Long term effects of manure, charcoal, and mineral fertilization on crop production and fertility on a highly weathered central Amazonian upland soil. *Plant Soil* 2007, 291, 275–290. [CrossRef]

106. Li, Z.; Unzué-Belmonte, D.; Cornelis, J.T.; Linden, C.V.; Struyf, E.; Ronse, F.; Delvaux, B. Effects of phytolithic rice-straw biochar, soil buffering capacity and pH on silicon bioavailability. *Plant Soil* 2019, 438, 187–203. [CrossRef]

107. Nwajaku, I.M.; Sato, K.; Tokunari, T.; Kitano, S.; Masunaga, T. Improvement of rice husk residue silicon availability for replenishing available silicon in paddy soil. *Int. J. Plant Sci. Soil* 2018, 24, 1–11. [CrossRef]

108. Zhang, A.; Liu, Y.; Pan, G.; Hussain, Q.; Li, L.Q.; Zheng, J.; Zhang, X. Effect of biochar amendment on maize yield and greenhouse gas emissions from a soil organic carbon poor calcarceous loamy soil from Central China Plain. *Plant Soil* 2012, 351, 263–272. [CrossRef]

109. Major, J.; Rondon, M.; Molina, D.; Riha, S.J.; Lehmann, J. Maize yield and nutrition during 4 years after biochar application to a Colombian savanna oxisol. *Plant Soil* 2010, 333, 117–128. [CrossRef]

110. Zheng, W.; Sharma, B.K.; Rajagopal, N. Using Biochar as a Soil Amendment for Sustainable Agriculture; Illinois Department of Agriculture: Champaign, IL, USA, 2010; pp. 1–36.

111. Yamato, M.; Okimori, Y.; Wibowo, I.F.; Anshori, S.; Ogawa, M. Effects of the application of charred bark of Acacia mangium on the yield of maize, cowpea and peanut, and soil chemical properties in South Sumatra, Indonesia. *J. Soil Sci. Plant Nutr.* 2006, 52, 489–495. [CrossRef]

112. Asai, H.; Saito, K.; Samson, B.; Songyikhangsauthorn, K.; Homma, K.; Shiraiwa, T.; Kiyono, Y.; Inoue, Y.; Horie, T. Yield response of indica and tropical japonica genotypes to soil fertility conditions under rainfed uplands in northern Laos. *Field Crops Res.* 2009, 112, 141–148. [CrossRef]

113. Knowles, O.A.; Robinson, B.H.; Contangelo, A.; Clucas, L. Biochar for the mitigation of nitrate leaching from soil amended with biosolids. *Sci. Total Environ.* 2011, 409, 3206–3210. [CrossRef]
114. Doan, T.T.; Henry-des-Tureaux, T.; Rumpel, C.; Janeu, J.; Jouquet, P. Impact of compost, vermicompost and biochar on soil fertility, maize yield and soil erosion in Northern Vietnam: A three year mesocosm experiment. Sci. Total Environ. 2015, 514, 147–154. [CrossRef]

115. Carter, S.; Shackley, S.; Sohi, S.; Suy, T.B.; Haefele, S. The Impact of biochar application on soil properties and plant growth of pot grown Lettuce (Lactuca sativa) and Cabbage (Brassica chinensis). Agronomy 2013, 3, 404–418. [CrossRef]

116. Wijitkosum, S.; Mattayom, B.; Sriburi, T. The effects of biochar on increasing the yield of seeda tomatoes. In Proceedings of the International Conference on Solid Wastes 2015: Knowledge Transfer for Sustainable Resource Management (ICSWHK2015), Hong Kong, China, 19–23 May 2015.

117. Liang, F.; Li, G.T.; Lin, Q.M.; Zhao, X.R. Crop yield and soil properties in the first 3 years after biochar application to a calcareous Soil. J. Integr. Agric. 2014, 13, 525–532. [CrossRef]

118. Sohi, S.P.; Krull, E.; Lopez-Capel, E.; Bol, R. A review of biochar and its use and function in soil. Adv. Agron. 2010, 105, 47–82.

119. Spokas, K.A.; Reicosky, D.C. Impacts of sixteen different biochars on soil greenhouse gas production. Ann. Environ. Sci. 2009, 3, 179–193.

120. Windeatt, J.H.; Ross, A.B.; Williams, P.T.; Forster, P.M.; Nahl, M.A.; Singh, S. Characteristics of biochars from crop residues: Potential for carbon sequestration and soil amendment. J. Environ. Manag. 2014, 146, 189–197. [CrossRef]

121. Thomazini, A.; Spokas, K.; Hall, K.; Ippolito, J.; Lentz, R.; Novak, J. GHG impacts of biochar: Predictability for the same biochar. Agric. Ecosyst. Environ. 2015, 207, 183–191. [CrossRef]