



Article

Characterization of the Residue (Endocarp) of *Acrocomia aculeata* and Its Biochars as a Potential Source for Soilless Growing Media

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Abstract: Endocarp residues remaining after coconut oil extraction from *Acrocomia aculeata* are traditionally used for combustion as fuel. As an alternative, we propose its conversion into biochar to substitute peat in planting substrates. To test the feasibility of this approach, untreated endocarp residues (particle size approx. 10 mm) and materials shredded into particles of 4 and 1 mm were pyrolyzed at 200 °C, 325 °C and 450 °C and were subsequently characterized. The pyrolysis-induced loss of organic matter increased the ash contents and pH. Nuclear magnetic resonance (NMR) spectroscopy confirmed the aromatization and a loss of carboxyl C with an increasing pyrolysis temperature. This is commonly associated with an enhanced biochemical recalcitrance. The particle size of the feedstock had no significant effect on the chemical composition or microporosity (BET-adsorption with CO₂) of the biochars, but affected their water holding capacity. With respect to macro- and micronutrients, only the potassium and Olsen P levels occurred in concentrations that are optimal for tomato seed growth. The low nitrogen level of the products may be advantageous for hydroponic culturing since it allows for a higher flexibility for the adaptation of nutrient contents based on the needs of the used culture.

Keywords: coconut palm; macuaba; peat substitution; water holding capacity; solid-state ¹³C NMR; biochar-based substrate



Citation: León-Ovelar, R.; Fernández-Boy, M.E.; Knicker, H. Characterization of the Residue (Endocarp) of *Acrocomia aculeata* and Its Biochars as a Potential Source for Soilless Growing Media. *Horticulturae* **2022**, *8*, 739. <https://doi.org/10.3390/horticulturae8080739>

Academic Editor: Miguel Guzmán

Received: 18 July 2022

Accepted: 12 August 2022

Published: 17 August 2022

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1. Introduction

Acrocomia aculeata (macuaba or coconut palm) belongs to the family of palm trees (Arecaceae). Although it is found all over Central and South America [1], it occurs mainly in Paraguay and Brazil. The *Acrocomia* tree can reach a height of 16 m and, under natural conditions, it produces fruits with a diameter of 2.5 to 6 cm, growing in clusters which can weigh more than 25 kg. In particular, in Paraguay, there is a long traditional industry of extracting and exporting the oil of the seeds of these fruits [2]. It is extracted from its soft meat (kernel or endosperm) and serves as a feedstock for food, pharmaceuticals or cosmetics, but also for animal feed or organic fertilizers. Worldwide, palm oil production has grown rapidly during the last 50 years due to the large demand for vegetable oil. It increased approx. 35 times, from 2 million tons per year in the 1970s to 75 million tons in 2019 [3]. On average, 25% of the mass of fresh ripe fruits corresponds to the endocarp (shell) surrounding the seed, and approximately 58% of the fruit consists of the smooth epicarp and fibrous mesocarp enveloping the endocarp [4]. As a consequence, the production of palm kernel oil is related to a considerable accumulation of organic waste.

Duarte et al. (2016) stated that in predominantly agricultural countries, agro-industrial waste is considered as the main source of biowaste. In Paraguay, for example, between

7 and 10 t·ha⁻¹·year⁻¹ of coconut seeds and husks are generated as agro-industrial by-products. Focusing on four areas in Brazil, Ciconini et al. [2] reported that in these regions between 836 and 1240 kg·ha⁻¹ of endocarp residues are generated. Currently, this material is mostly used in boilers for the production of heat. However, this traditional method is very inefficient because a considerable part of the energy is lost by the escape of hot gases and unburned remains due to incomplete combustion caused by the moisture in the fuel.

A more environmentally sustainable use may be its conversion into so-called biochar, which is the product after thermal treatment under oxygen-free or oxygen-limited conditions (pyrolysis). This material has recently gained considerable interest as a strategy to recycle agro-industrial waste by its conversion into a soil amendment with a high potential for atmospheric carbon sequestration [5]. Aside from improving soil fertility, biochar is expected to increase the organic matter content in the amended soil on a long-term scale which is of essential importance in the fight against soil degradation [5–7].

Sun et al. [8] showed that woody feedstock results in biochars with high porosity which can increase soil aeration and the capacity to retain water and nutrients [9]. However, the intense research in the field of biochar during the last decades has shown that biochar cannot be seen as a one-fits-all approach [10] and that the final impact of a biochar addition on soil productivity and health depends not only on the properties of the biochars, but also on those of the amended soils and the respective climatic conditions. Even the properties of the biochars can vary depending on the production conditions or the kind of feedstock [11].

Recognizing the recycling potential of the biochar approach, most studies on biochar properties are related to residues of wood [12], garden pruning, straw of cereals or rice husks [13]. Other organic residues, such as manure [14] or sewage sludge [15], have been suggested as feedstock for the production of biochars with a slow-release fertilization capacity due to their high contents of nitrogen (N) and phosphorous (P). On the other hand, studies indicate that a soil amendment with biochar with high P levels can increase P leaching [16,17]. However, if leaching is controlled either by specially designed biochars or by the controlled application of N- and P-rich biochars to soils, their amendment may be beneficial for reducing the need for mineral fertilizers in agriculture [18]. Biochars derived from woody feedstocks contain low amounts of N, but their physical porosity suggests that they are appropriate for applications where a (bio)chemically recalcitrant and thus highly inert product with high porosity is needed. Such applications may be the filtering of residual waters or growing of substrate for container-grown plants and hydroponic horticulture. Indeed, its use as an additive in plant growing media is presently of paramount interest since it could reduce the high demand and consumption of peat for private gardening and commercial vegetable production. Here, peat is preferentially used due to its high water holding capacity (WHC) and the fact that it is almost depleted from plant nutrients. The latter allows an individual adaption of nutrient supply according to the needs of the crop by the plant growers. Note, that currently 77–80% of the annually used growing media in the European horticultural industry is derived from peat [19]. This does not only endanger important ecosystems but reduces one of the most important terrestrial carbon sinks.

Facing this challenge and considering the high biochemical recalcitrance of biochar, there has been an increasing interest in using biochar as a peat replacement or as a component of growing media since about 2014 [20–22]. Publication in this area has seen an exponential growth, especially in the last two or three years [22–24]; at least five review articles have been published [24–28].

The woody nature of the shells of *Acrocomia* turns this material into a promising candidate to be recycled as biochar that may be suitable for peat substitution in plant growing media. Aside from reducing the ecological threat of peat excavation, this approach may have the potential to create an income creating waste management strategy and thus a valid alternative to the common inefficient use of such residues as fuel for energy purposes, in particular in low-income regions.

On the other hand, following this line, one has to bear in mind that not all characteristics of biochar are favorable for improving plant growth. Among those are high pH values of the pyrolysis product and in some cases its high concentrations of Na, K, Ca or P which occur due to the selective enrichment of these elements resulting from the organic matter loss during pyrolysis [27,29].

Therefore, to obtain a first idea of the suitability of the biochar from the endocarp of *A. aculeata* for hydroponic and soilless horticulture, the objective of the present research was an in depth chemical and physical characterization of the chemical and physical changes occurring in this material with an increasing process temperature. In addition to classic parameters, such as elemental composition, pH, electrical conductivity and water holding capacity, the contents of Olsen P as well as of common macro- and micronutrients were determined. Physical changes were approached by a scanning electron microscopy (SEM) and we measured the specific surface area and pore volume according to the Brunauer–Emmett–Teller (BET) theory using CO₂ as adsorption gas. Chemical alterations of the organic fraction were detected by solid-state ¹³C nuclear magnetic resonance (NMR) spectroscopy. Analyzing biochars derived from endocarps with different particle size, we intended to investigate to which extent this parameter affects the nature of the final product. This is of particular interest since the necessity of grinding the feedstock prior to pyrolysis can considerably increase production costs. From a commercial perspective, it would be certainly advantageous if this step can be avoided.

With our approach, we intended to prove the hypothesis that low-temperature pyrolysis of the endocarp of *A. aculeata* results in products with properties needed for being suitable as peat replacement in plant growing media. We further tested our assumption that although pyrolysis conditions affect the physical properties of the biochar, the particle size of the feedstock has no major impact on its chemistry.

2. Materials and Methods

2.1. Biochar Production

The feedstocks for the biochars were collected in the Department of Paraguari, located in the eastern region of Paraguay. The residue (endocarp) of *A. aculeata* in its natural or raw state has a size of approximately 10 mm. The material was used without previous chemical treatment or cleaning.

In order to obtain feedstocks with different sizes, aliquots were ground either to fine (<1 mm) or medium (≥4 mm) particles and pyrolyzed in addition to the unground and thus coarse feedstock (~10 mm) (Table 1). The coding for the samples is AC_{f,m,c}, where AC means *Acrocomia aculeata* and the sub-index represents its particle size (fine: f, medium: m, coarse: c).

Table 1. Nomenclature of the used biochars, their production temperatures and retention times.

Biochar	Average Particle Size (mm)	Pyrolysis Temperature (°C)	Duration of Pyrolysis (min)
AC _f	<1 mm	200	120
AC _m	≥4 mm		
AC _c	~10 mm		
AC _f	<1 mm	325	120
AC _m	≥4 mm		
AC _c	~10 mm		
AC _f	<1 mm	450	15
AC _m	≥4 mm		
AC _c	~10 mm		

The biochars have been produced under oxygen-reduced conditions. Approximately 100 g of feedstock was given into a covered aluminum tray which was subsequently placed into a muffle oven [30,31], preheated at temperatures of 200, 325 and 450 °C. When introducing the trays into the oven, a slight drop in the temperature (~3 °C) occurred,

which was quickly recovered after closing the oven. Whereas at temperatures 200 °C and 325 °C a residence time of 120 min was used, the pyrolysis time was reduced to 15 min at 450 °C. After the muffle time, the samples were allowed to cool for 4 h in a desiccator for a second weight record.

2.2. Physical and Chemical Parameters

The pH values were measured in duplicates from the fine and coarse samples of the biochars and the feedstock in a suspension prepared by mixing the sample with water in a ratio of 1:10 (g mL⁻¹) [6] with a Crison Basic 20 pH-Meter, after 60 min of agitation and 60 min of settling. Subsequently, the supernatant solution was separated by filtration (Whatman N° 2 filter) to obtain the electrical conductivity in the filtered solution using a Crison EC-meter Basic 30+.

The water holding capacity (WHC) was determined in duplicates after placing approximately 6 g of the sample on a mesh or thin gauze located at the end of a plastic tube of 12 cm in height. The sample was immersed in distilled water until saturation and kept submerged for 40 min. Then, it was removed from the water and allowed to drain for 2 hours. The weight difference between the saturated and the drained samples was determined by calculating the WHC. The latter is the amount of water which is retained against gravitation and is given as the percentage of the total dry weight of the sample (modified from [6]). The bulk density was measured by weighing 100 mL of sample material.

Olsen P was extracted from the fine samples of the feedstock and its biochars with 0.5 M NaHCO₃ using a soil–solution ratio of 2.5 g:50 mL at pH = 8.5, which was shaken for 30 min. Afterwards, the suspension was filtered and the P concentration in the extract was determined colorimetrically (880 nm) using the procedure of [32]. In brief, an aliquot of the extract was taken, neutralized with 5 N H₂SO₄ and shaken to eliminate CO₂. A reagent containing ammonium molybdate and ascorbic acid reductant was added to form blue phosphomolybdic complexes. All samples were analyzed in triplicate.

The carbon (C), nitrogen (N) and hydrogen (H) contents were obtained via dry combustion with a LECO TRUSPEC CHNS MICRO elemental analyzer and the oxygen content was calculated by difference after determination of the ash content. The ash contents were measured for the uncharred material and the biochars in duplicates from the weight loss of approximately 0.5 g sample after combustion for 8 h in a muffle furnace at 700 °C [6].

The total contents of the elements B, S, P, K, Ca, Mg, Cu, Fe, Mn and Zn were measured for the samples with fine granulometry (<1 mm, AC_f). First, an acid digestion of the samples was performed by microwave with ultrapure HNO₃. The composition of the resulting solutions was analyzed by inductively coupled plasma emission spectrometry (ICP-OES) in an ICP Horiba Jobin Yvon, Ultima 2 Kit (Edison, NJ, USA). This extraction and determination methodology has been adapted from Bachmann et al. [33].

For measuring the content of exchangeable Na, 5 g of sample were given into a centrifuge tube and mixed with 100 mL of a 1 N ammonium acetate solution and shaken for 5 min in a shaker. Subsequently, the tubes were centrifuged and the supernatant was collected. This treatment was repeated three times and the supernatants were united to determine the Na⁺ concentration via atomic absorption spectrometry [17].

The specific surface area was assessed by measuring the adsorption isotherm according to the theory of Brunauer–Emmett–Teller (BET) using an Micromeritics ASAP 2420 (Norcross, GA, USA) with 6 ports for degassed samples with CO₂ as adsorption gas and a sample amount of 0.5 g. Therefore, prior to analysis, the samples were degassed at 180 °C for 6 h, and in a vacuum of 5 mm Hg s⁻¹. The analysis was carried out at 0 °C with equilibrium intervals of 25, and the porosity study was carried out using the classic model (slit pore geometry) of Horvath–Kawazoe.

2.3. Solid-State ¹³C Nuclear Magnetic Resonance (NMR) Spectroscopy

All spectra were acquired with a Bruker Avance III HD 400 MHz (Rheinstetten, Germany) at a frequency of 100.63 MHz using zirconium rotors with a 4 mm outside diameter.

The technique of magic angle spinning (MAS)–cross polarization (CP) was applied with a spinning frequency of 14 kHz. A ramped ^1H pulse reaching from 100 to 50% of the power was applied during a contact time of 1 ms in order to bypass the rotation modulation during the Hartmann–Hahn contact. The ^{13}C chemical shifts were given relative to tetramethylsilane (=0 ppm) and were calibrated with glycine (176.04 ppm). The relative intensities of the signals were obtained by integration of the specific chemical shift ranges assigned to specific C groups, as described by Knicker [34] using MESTRE NOVA 11.03.

In the spectra of the feedstock and the low-temperature biochar, the chemical shift region between 110 and 90 ppm derives mostly from the anomeric C of carbohydrates. Accordingly, the spectra were integrated as follows: 185 to 225 ppm (carbonyl C), 185 to 160 ppm (carboxyl C), 160 to 140 ppm (O-aryl C), 140 to 110 ppm (aryl C), 110 to 60 ppm (O-alkyl C), 60 to 45 ppm (methoxyl C) and 45 to 0 ppm (alkyl C) [34]. With increasing pyrolysis temperature, the contribution of anomeric C in the chemical shift region between 110 and 90 ppm decreased to negligible values while that of aryl C increased. Therefore, in those spectra, the aryl C region was expanded 140 to 90 ppm. Spinning side bands (ssbs) derived from insufficient averaging of the chemical shift anisotropy were mainly visible for the aryl C region. They appeared as an echo at both sides of the main signal at a distance from the rotation frequency and contained signal intensity of the parent resonance line. With a spinning speed of 14 kHz, they appeared between 285 and 245 ppm and 0 and –50 ppm. The intensities of these regions were added to that determined for the chemical shift region between 90 and 160 ppm [35].

2.4. Scanning Electron Microscopy

Field Emission Scanning Electron Microscopy (FESEM) was carried out with all biochars and the uncharred feedstock using a conventional scanning electron microscope (JEOL 6460LV) working in high vacuum, barrel type, thermionic emission and Tungsten filament. FESEM examinations were performed in secondary electron (SE) detection mode with an acceleration voltage of 15 kV and a working distance of 10 mm. Biochar samples sputter-coated with gold were also observed in a FEI Teneo microscope (Hillsboro, OR, USA) using the SE detector and an acceleration voltage of 5 kV.

2.5. Statistical Analysis

The Shapiro–Wilk test and Levene test were used for testing normality and homoscedasticity of data. The effects of pyrolysis temperature and particle size of the feedstock on the properties of the biochar were analyzed by one-way analysis of variance (ANOVA) followed by Tukey's Honestly Significant Difference test. Subsequently, a two-factor ANOVA was performed to obtain F values and significance on each studied variable. Statistical analyses were carried out using SPSS Statistical Software.

3. Results and Discussion

3.1. Mass Loss and Changes of the Elemental Composition during Pyrolysis

Increasing the pyrolysis temperature to 450 °C decreased the biochar yields to 33–35% of the starting weight of the *Acrocomia* nutshells (Table 2), which is in the range reported for the same material by Boas Vilas et al. [36]. A clear impact of the particle size of the feedstock on the weight loss cannot be discerned. Most of the loss occurred during the increase in the temperature from 200 °C to 325 °C, which is related to the fact that the degradation of hemicellulose and cellulose starts around 200 °C to 300 °C and around 250 °C to 350 °C, respectively [8]. However, note that although a slight increase in the ash content was observed with an increasing pyrolysis temperature, they were smaller than 5% of the dry weight of the biochars. Comparable low values were obtained for other nutshell biochars [37] and were explained with the low ash content of such biomass [38].

Table 2. Mass loss (%) and elemental composition of *Acrocomia* nutshells and its biochars as a function of pyrolysis temperature and particle size of the feedstock and of the produced biochars. Values in the columns are means $\pm$ standard deviation ($n = 3$). For Tukey's post hoc tests, the samples were grouped into two groups. The first group comprised the uncharred and biochars produced at 200 °C, whereas the second was composed of the biochars pyrolyzed at 325 °C and 450 °C. Numbers followed by the same letter indicate no significant differences at the $p < 0.05$ level. The O contents were calculated by difference. The elemental composition was used to calculate the C/N (w/w) ($C/N_{w/w}$), atomic H/C and O/C values (H/C_{atm} ; O/C_{atm}).

	Mass Loss (%)	C (%)	N (%)	H (%)	O (%)	Ash (%)	C/N _{w/w}	H/C _{atm}	O/C _{atm}
AC _f	0	47.2 $\pm$ 0.5a	0.4 $\pm$ 0.0a	5.7 $\pm$ 0.2a	44.5	2.2 $\pm$ 0.2	127	1.44	0.71
AC _m	0	45.6 $\pm$ 3.7a	0.3 $\pm$ 0.0a	5.5 $\pm$ 0.6a	47.8	0.8 $\pm$ 0.1	131	1.44	0.79
AC _c	0	47.2 $\pm$ 0.1a	0.3 $\pm$ 0.0a	5.8 $\pm$ 0.0a	44.9	1.8 $\pm$ 0.3	146	1.48	0.71
AC _f 200	17	48.6 $\pm$ 0.5a	0.3 $\pm$ 0.1a	5.8 $\pm$ 0.1a	43.0	2.3 $\pm$ 0.1	142	1.44	0.66
AC _m 200	11	48.6 $\pm$ 0.3a	0.3 $\pm$ 0.0a	5.7 $\pm$ 0.1a	44.5	0.9 $\pm$ 0.1	145	1.40	0.69
AC _c 200	12	49.1 $\pm$ 0.7a	0.3 $\pm$ 0.0a	5.9 $\pm$ 0.2a	42.4	2.3 $\pm$ 0.6	167	1.44	0.65
AC _f 325	58	65.8 $\pm$ 0.2b	0.5 $\pm$ 0.0a	3.9 $\pm$ 0.0b	25.9	3.9 $\pm$ 0.2	136	0.72	0.30
AC _m 325	59	68.4 $\pm$ 0.8c	0.4 $\pm$ 0.1a	3.7 $\pm$ 0.1b	25.1	2.4 $\pm$ 0.0	164	0.65	0.28
AC _c 325	62	71.0 $\pm$ 0.8de	0.4 $\pm$ 0.0a	2.9 $\pm$ 0.0c	21.8	3.8 $\pm$ 0.1	163	0.50	0.23
AC _f 450	65	69.1 $\pm$ 0.7de	0.5 $\pm$ 0.0a	3.2 $\pm$ 0.1c	22.6	4.7 $\pm$ 0.1	145	0.55	0.25
AC _m 450	67	73.4 $\pm$ 0.8e	0.3 $\pm$ 0.0a	3.0 $\pm$ 0.1c	20.6	2.6 $\pm$ 0.1	217	0.49	0.21
AC _c 450	65	72.7 $\pm$ 1.6de	0.3 $\pm$ 0.0a	3.1 $\pm$ 0.1c	20.4	3.5 $\pm$ 0.3	218	0.51	0.21

For the samples AC and AC200, the homogeneity of variances was asserted using Levene's Test which showed that equal variances could be assumed (C: $p = 0.133$, N: $p = 0.200$, H: $p = 0.582$). Tukey's post hoc analysis revealed that heating the feedstock until 200 °C did not lead to significant differences in the elemental composition. However, pyrolysis temperatures of 325 °C and higher caused the volatilization of organic compounds and with that, considerable changes of the elemental composition of the solid products.

Although all elements show losses, they are bigger for O, H and N compared to C, which leads to a relative enrichment of C in the chars. Correspondingly, the C/N ratio (w/w) decreases and the H/C_{atm} and O/C_{atm} ratios increase. Plotting those ratios into a van Krevelen plot (Figure 1) shows the biochars produced up to a temperature of 200 °C in the region typical for lignocellulosic material. Increasing the temperature led to values that plot along the line indicative for dehydration caused by the breakdown of bonds and formation of double bonds. Pyrolysis at 450 °C resulted in a material with an elemental composition that plots in the regions typical for biochars. According to the requirements of the International Biochar Initiative (IBI) and the European Biochar Certificate (EBC) [39], both the biochars produced at 325 and 450 °C can be considered as biochars ($H/C_{atm} < 0.7$, $O/C_{atm} < 0.4$) (Table 2).

Tukey's post hoc HSD analysis of the alteration of the elemental composition in the samples resulting from the increase in the pyrolysis temperature from 325 °C to 450 °C confirmed a heat-induced increase in the C concentration, which goes along with a decrease in the H content; no clear tendency is revealed for N. Prior use of Levene's test showed that equal variances could be assumed for C and H contents ($p = 0.053$; $p = 0.067$), but not for N ($p = 0.001$). Although the one-factor ANOVA provided no clear evidence for the impact of the particle size on the elemental composition of the biochars, a two-factor ANOVA for the linear model was applied for a better evaluation of this interaction. According to the F-test, the C and H contents of the charred material are up to 100 times more affected by temperature than by size. For N, this pattern is less expressed although the effect of temperature is still more significant than the impact of particle size. Since, with respect to the elemental composition, no major impact of the particle size of the feedstock can be identified (Figure 2), we conclude that the final pyrolysis temperature rather than particle size determined the efficiency of the carbonization process.

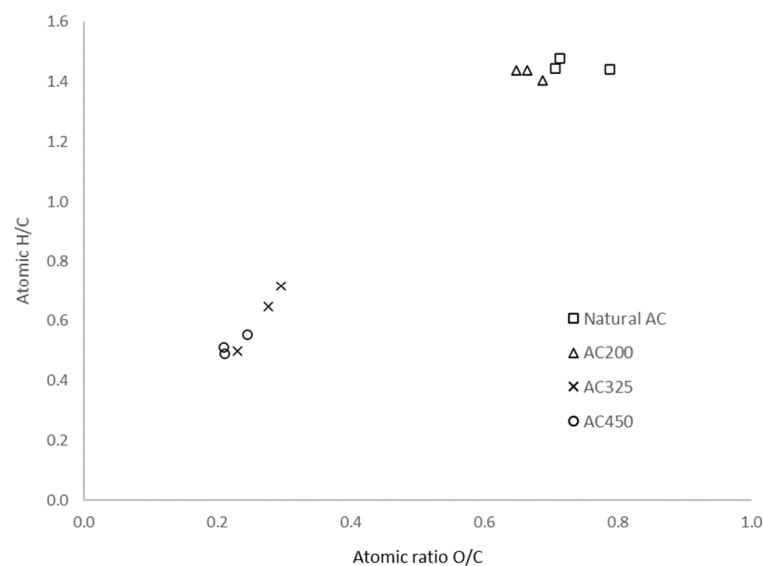


Figure 1. Van Krevelen diagram of uncharred endocarps of different particle sizes and derived from *Acrocomia*, as well as the respective material pyrolyzed at 200 °C, 325 °C and 450 °C.

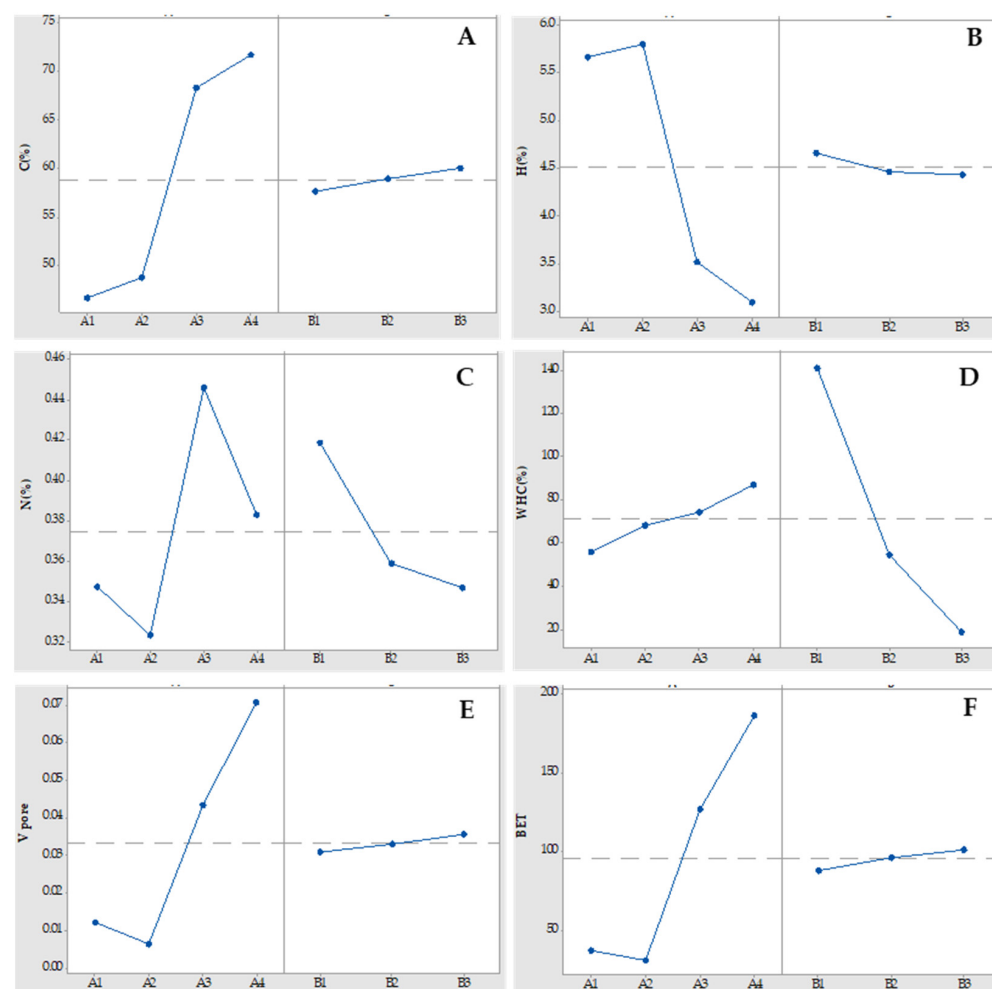


Figure 2. Effects of pyrolysis temperature (A1 = 25 °C, A2 = 200 °C, A3 = 325 °C, A4 = 450 °C) and particle size (B1 = fine, B2 = middle, B3 = coarse) on the elemental composition (A–C), the WHC (%) (D), the maximum pore volume ($\text{cm}^3 \text{g}^{-1}$) (E) and the specific surface area (BET ($\text{m}^2 \text{g}^{-1}$)) (F).

3.2. Solid-State ^{13}C NMR Spectroscopy

The solid-state ^{13}C NMR spectra of the feedstock with different particle sizes show comparable intensity distribution (Figure 3, Table 3), which are typical for woody materials [34]. The signal at 75 ppm can be assigned to C2/C3/C5 in cellulose, whereas those at 83 ppm and 89 ppm are indicative for its C4 in amorphous and crystalline domains, respectively. The C1 is typically found at 104 ppm and C6 at 65 ppm. However, hemicellulose units are also contributing to the chemical shift region of O-alkyl C from 110 to 60 ppm. In total, these C groups contribute 63 to 66% to the total organic C of the feedstock.

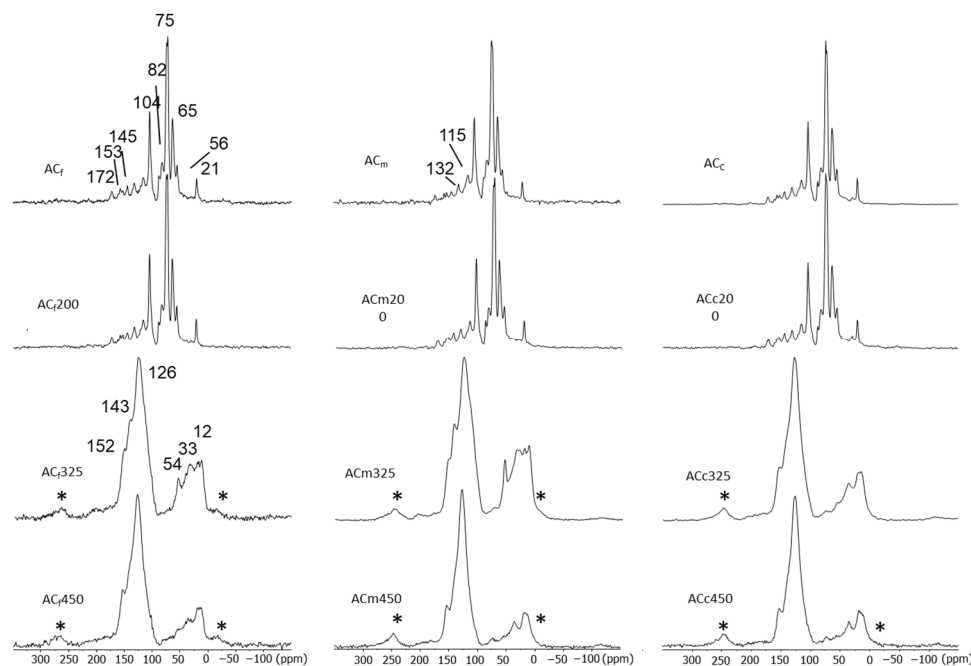


Figure 3. Solid-state ^{13}C NMR spectra of the uncharred endocarp of *Acrocomia* (AC) at different particle sizes (f: fine; m: middle; c: coarse) and its biochars produced at 200 °C (AC200), 325 °C (AC325) and 450 °C (AC450). Asterisks indicate spinning side bands.

Table 3. Intensity distribution (%) in the ^{13}C NMR spectra of the endocarp of *Acrocomia* at different particle sizes (f: fine; m: middle; c: coarse) and its biochars produced at 200 °C (AC200), 325 °C (AC325) and 450 °C (AC450).

	Carboxyl C	O-Aryl C	Aryl C	O-Alkyl C	Methoxyl C	Alkyl C
AC _f	3	5	13	63	9	6
AC _m	3	4	14	66	7	6
AC _c	3	5	15	63	8	7
AC _f 200	5	5	15	59	8	7
AC _m 200	3	5	14	60	8	9
AC _c 200	3	5	14	60	9	9
AC _f 325	7	15	50	3	5	21
AC _m 325	4	12	49	3	6	25
AC _c 325	4	15	55	3	3	20
AC _f 450	7	15	57	2	3	16
AC _m 450	6	12	61	3	3	16
AC _c 450	4	12	62	3	3	17

Resonance lines of aryl C occur between 160 and 110 ppm and comprise 18 to 20% of the total ^{13}C intensity. In woody samples, they derive mostly from lignin giving signals at 153 ppm (C3/C5 in syringyl), 145 ppm (C3/C4 in guaiacyl, C3 in syringyl), 132 ppm (C1) and 115 ppm (C3/C5 in *p* hydroxyphenyl). The respective resonance of methoxyl C

appears at 56 ppm and explains 6 to 7% of the total C of the sample. The signal at 173 ppm and 21 ppm are indicative for the carboxyl C and acetyl C of uronic acids. Increasing the pyrolysis temperature to 200 °C slightly decreases the intensity in the O-alkyl C region, but only a temperature of 325 °C causes a major alteration of the chemical composition.

Calculating the recovery of C for each chemical shift region (Table 4) confirms an almost complete loss of O-alkyl C. Since the amount of C recovered as aryl C increases during pyrolysis to 40% of the total initial C (C_{ti}), some of the cellulose units must have been transformed into new aromatic structures which have their main signal at 126 ppm and contain phenol C, resulting in signals at 152 ppm and 143 ppm. Aside from aryl C, alkyl C, possibly derived from dehydroxylated and only partially degraded carbohydrate residues, accumulates. Increasing the pyrolysis temperature to 450 °C, however, leads to their preferential combustion. In addition, a considerable loss of methoxyl C (54, 56 ppm) and C giving rise to the signal at 143 ppm is evidenced. Bearing in mind that between 325 °C and 450 °C no major loss of oxygen (Table 2) or phenol C is indicated, one may conclude that demethylation, rather than demethoxylation, of the aromatic units occurred.

Table 4. Remaining total C (C_{tr}) and remaining C (C_r) of each C group of the initial total C (C_{ti} in % of C_{ti}) of the *Acrocomia endocarp* after pyrolysis at different temperatures.

	Carboxyl C_r	O-Aryl C_r	Aryl C_r	O-Alkyl C_r	Methoxyl C_r	Alkyl C_r	C_{tr} of C_{ti}
AC _f	3	5	13	63	9	6	100
AC _m	3	4	14	66	7	6	100
AC _c	3	5	15	63	8	7	100
AC _f 200	4	5	13	51	7	6	86
AC _m 200	3	5	14	57	8	9	95
AC _c 200	3	4	13	55	8	9	92
AC _f 325	4	9	30	2	3	12	59
AC _m 325	2	8	31	2	4	16	62
AC _c 325	3	8	31	2	2	11	57
AC _f 450	4	7	29	1	2	8	51
AC _m 450	3	6	33	2	1	9	54
AC _c 450	2	6	33	2	1	9	54

Comparing the relative intensity distributions of the spectra obtained from samples with different particle sizes that were produced at the same pyrolysis temperature reveals no major differences, confirming that a relatively homogenous temperature within the sample material was achieved.

3.3. Physical Properties of the Uncharred Particles of the *Acrocomia endocarp* and Their Biochars

The bulk density of the biochars (Table 5) are in the range commonly reported for biochars [40], but are greater than the value between 0.1 and 0.3 g cm^{−3} reported for well-humified peat [41] or moss substrate [42]. Pyrolysis at 450 °C resulted in a slight decrease in this parameter.

The WHC_{maxw} of the feedstock increases considerably from 13 ± 1% to 127 ± 1% of the sample dry weight with a decreasing particle size (Table 5), most likely because the greater surface of the smaller particles provided more water adsorbing surfaces. This converts to 84% and 8% if a volume-based WHC_{maxv} is used. With the exception of the biochars composed of fine particles, enhancing the pyrolysis temperature had no clear impact on the weight-based WHC_{max} ($p = 0.08$ and F-test for Temp:size is 3.7:121.5). For AC_f, pyrolysis at 450 °C slightly increased the WHC_{maxw} to 169 ± 5% (WHC_{maxv}: 108%). This range was observed for wood biochars produced at the same temperature [6] and is still six times higher than that of the course biochar (28 ± 2%; WHC_{maxv}: 15%). For comparison, the WHC_{maxv} of the humified peat substrate are in the range of 70 to 75% [43].

Table 5. Maximal water holding capacity, WHC_{maxw} (% of dry sample weight), specific surface area, A_{spec} ($m^2 g^{-1}$), maximal pore volume, V ($cm^3 g^{-1}$) and bulk density ($g cm^{-3}$) of *Acrocomia endocarp* and its biochars as a function of pyrolysis temperature and particle size of the feedstock and of the produced biochars. The maximal pore volume was calculated according to the model (slit pore geometry) of Horvath–Kawazoe.

	Bulk Density ($g cm^{-3}$)	WHC_{maxw} (%)	A_{spec} ($m^2 g^{-1}$)	V_{pore} ($cm^3 g^{-1}$)
AC _f	0.65 ± 0.01	127 ± 1	42.2 ± 1	0.01
AC _m	0.76 ± 0.01	28 ± 15	48.0 ± 1	0.02
AC _c	0.60 ± 0.00	13 ± 1	22.6 ± 2	0.01
AC _f 200	0.65 ± 0.04	126 ± 3	30.5 ± 0	0.01
AC _m 200	0.79 ± 0.01	62 ± 5	28.2 ± 9	0.01
AC _c 200	0.61	14 ± 0	35.4 ± 9	0.01
AC _f 325	n.d. *	140 ± 15	105.3 ± 3	0.03
AC _m 325	0.76 ± 0.02	63 ± 5	105.2 ± 1	0.03
AC _c 325	n.d.	18 ± 3	170.5 ± 1	0.06
AC _f 450	0.53	169 ± 5	176.0 ± 0	0.07
AC _m 450	n.d. *	63 ± 2	204.1 ± 1	0.08
AC _c 450	0.52 ± 0.00	28 ± 2	178.7 ± 1	0.07

n = 3 for BET surface area, n = 2 for WHC and bulk density; * not determined.

The application of the BET method using CO₂ (Table 5) could not confirm a clear impact of particle size of the feedstock or the biochar on the specific surface area or the maximum pore volume, indicating that grinding did not lead to major alterations at the levels of meso- and microporosity grinding. This observation indicates that porosity alone cannot be directly related to the WHC of a biochar. In addition, no relationship between BET surface area and WHC_{max} was detectable ($R^2 = 0.040$). Accordingly, it may be concluded that the determination of the BET porosity of biochar may be insufficient for a good prediction of the impact of the biochar addition on the water retention capacity of amended soil.

On the other hand, irrespective of the particle size, enhancing pyrolysis temperatures yielded a higher BET-specific surface area. They increased from 42 to 176 $m^2 g^{-1}$ and from 23 to 179 $m^2 g^{-1}$ for the biochars with fine and coarse particle sizes, respectively. The maximal pore volume showed the same tendency. However, this increase affected only the biochars produced at temperatures of 325 °C and 450 °C, which is the temperature range in which a noticeable weight loss was observed. This suggests that heat-induced degradation and volatilization of organic matter lead to physical alterations that increase the specific surface area. A comparable observation is reported by Wang et al. [44], suggesting that the loss of volatile or aliphatic compounds at higher temperatures increases the surface area, pore formation and pore volume. The specific surface areas determined in the present study are considerably higher than those reported by [45] who found values between 0.4 and 5.8 $m^2 g^{-1}$ for the endocarp of *A. aculeata* after pyrolysis at 250 °C and 450 °C by using N₂ as adsorption gas. In order to explain this difference, one has to bear in mind that with their method only pores ≥ 2 nm were probed which omits the important contribution of the micropores [46]. Their contribution commonly increases with increasing pyrolysis temperature due to the morphological changes caused by chemical alterations. In line with this, Mukherjee et al. [47] studying the surface area of pine, grass and oak biochars at different temperatures using N₂, detected nanopores only in biochars produced at 650 °C. However, with CO₂, they found micropores (<1.5 nm) in the biochars produced at all pyrolysis temperatures (250 °C, 400 °C and 650 °C). Comparable results are reported by Mao et al. [48].

Compared to biochars derived from other wood residues pyrolyzed at 500 °C [47,49], the specific surface area determined with CO₂ adsorption of our biochars is approximately

a factor of 0.5 lower, but are in the range of values ($130 \text{ m}^2 \text{ g}^{-1}$) published by Mao et al. [48] for wood waste (pine and sawdust) pyrolyzed at 500°C .

3.4. Physical Properties of the Uncharred Particles of the *Acrocomia endocarp* and Their Biochars

The FESEM images of AC_f and AC_m show a comparable distribution of pores with a size of approximately $1 \mu\text{m}$ as they naturally occur in cell walls (Figure 4A,B).

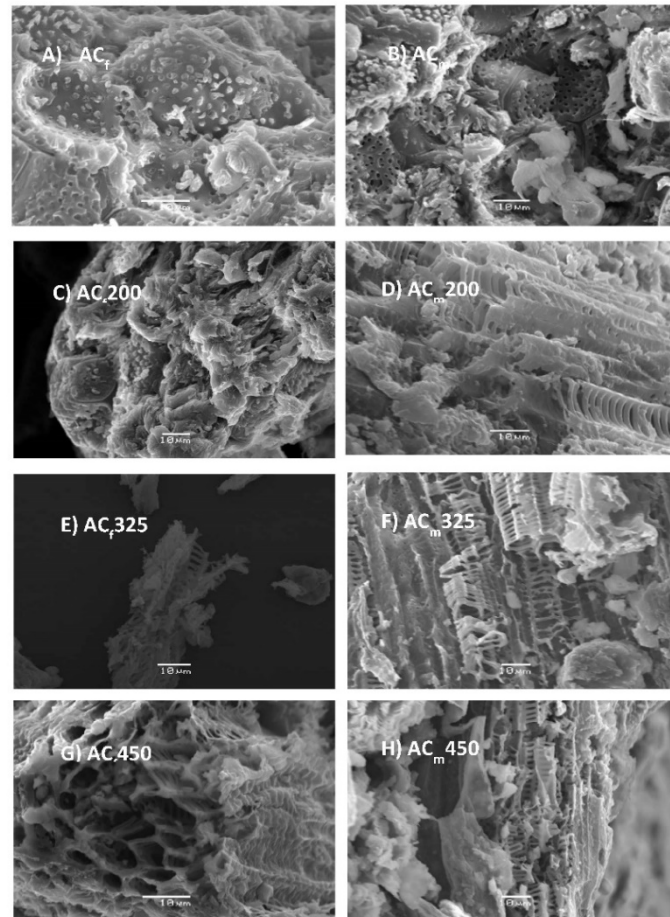


Figure 4. SEM of the *A. aculeata* and its biochars. (A,B) show the natural endocarp, (C,D) correspond to biochar at 200°C , (E,F) to biochar at 325°C and (G,H) to biochar at 450°C . The left column corresponds to the fine samples and the right column to the medium granulometry.

This is in line with the results of BET data showing that on a microscopic level no changes of the porosity are induced by the milling. Figure 4C,D reflect morphological disintegration after pyrolysis at 200°C .

The respective biochar surface shows more crevices and cracks, however, mass loss and chemical characterization did not reveal major chemical alterations. Enhancing the pyrolysis temperature to 325°C and 450°C seems to increase the porosity of the *Acrocomia* biochars and the importance of longitudinal pores with diameters ranging around $10 \mu\text{m}$. The respective images show the xylem vessels with scalariform pores, and the fibers of the parenchyma structures are maintained in both the 1 mm and 4 mm samples. Such characteristics are typical in wood-derived biochars [6].

Since this is the temperature at which cellulose thermally degrades, this change may be interpreted by the loss of carbohydrates leaving perforated, lignified cell walls behind, as it is also indicated by the solid-state ^{13}C NMR spectra. Note that pores in the range of $10 \mu\text{m}$ and bigger will not only play an important role for the adsorption of water but also present a habitat for microorganisms. Both may be an advantage for a potting substrate.

The EDS spectra in Figure 5 confirm that C is the major element in all the samples (fine and medium) and to a lesser extent, Si, Ca, K, P and O.

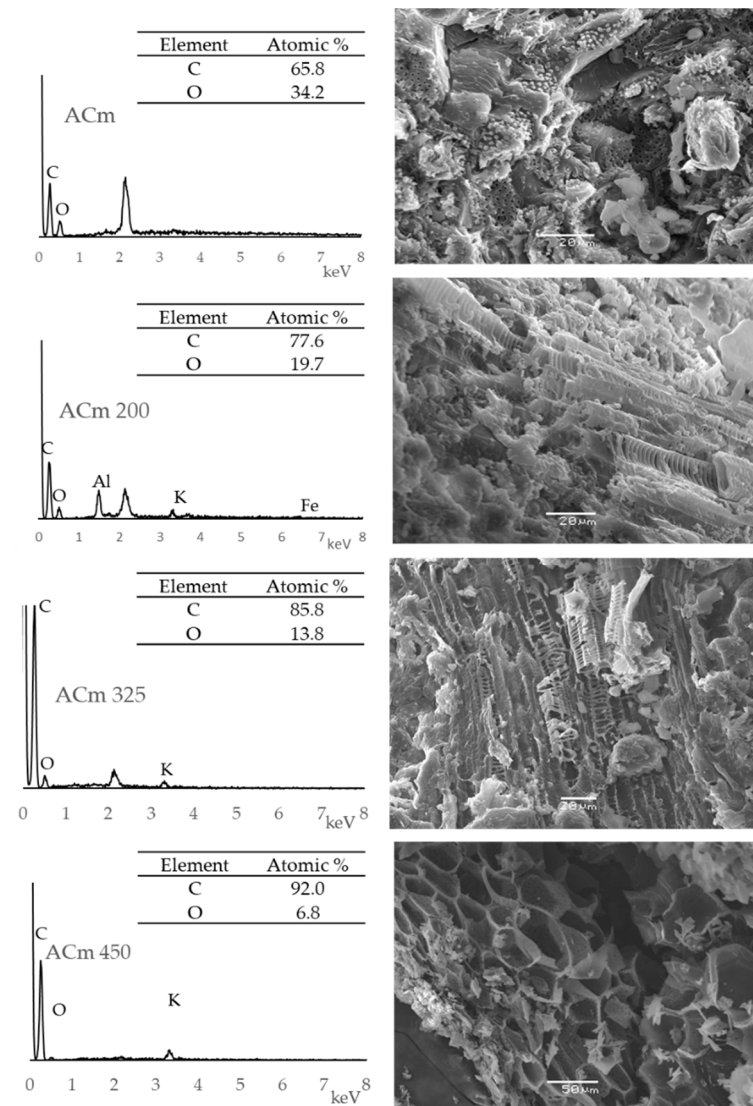


Figure 5. SEM images and their EDS of *A. aculeate* in medium size (4 mm) in its natural form and the three pyrolysis temperatures.

3.5. pH, Electrical Conductivity and Nutrient Contents of the Biochars

Concomitantly to the accumulation of ash due to the loss of organic matter, the pH value measured for the fine biochar increases with the severity of the pyrolysis conditions (Table 6) from 5.9, in the finely grained feedstock, to 8.4. For the coarse biochars, slightly higher values with the same trend are observed with an increasing pyrolysis temperature. Compared to biochar from wood residues, rice husks or tomato plant residues [11,21], the pH of the biochars obtained at 450 °C show lower pH values. This behavior may be advantageous with respect to the potential use of such biochars in soilless substrates. Whereas for acid soils, the addition of biochars with a high pH may be beneficial as liming substrate, in soilless cultures, a higher concentration of such amendments are likely to have a negative impact on nutrient availability and thus on plant growth.

Table 6. pH values and electrical conductivity ($\mu\text{S cm}^{-1}$) of the fine and coarse feed-stock from *Acrocomia aculeata* and the respective biochars pyrolyzed at 200, 325 and 450 °C (mean $\pm$ standard error; n = 3 for finely grained material; n = 2 for coarse material).

	pH		EC ($\mu\text{S cm}^{-1}$)	
	Fine	Coarse	Fine	Coarse
AC	5.9 $\pm$ 0.1	6.5 $\pm$ 0.3	620 $\pm$ 39	53 $\pm$ 5
AC200	5.4 $\pm$ 0.1	5.6 $\pm$ 0.0	526 $\pm$ 13	81 $\pm$ 3
AC325	7.3 $\pm$ 0.1	7.9 $\pm$ 0.4	130 $\pm$ 3	54 $\pm$ 1
AC450	8.4 $\pm$ 0.2	8.6 $\pm$ 0.3	131 $\pm$ 4	96 $\pm$ 17

A high pH of biochar and the implied high contents of cations may be of less importance if the biochar is used as an amendment for soils since it will be buffered and the cation concentration diluted. For potting substrates on the other hand, it may be a major concern since there is a low potential for compensation. Here, the removal of a surplus of cations from biochar may be essential if this material is intended to be used as a substitute for peat in growing substrates.

For a better prediction of the impact of biochars with a high pH amended to planting substrates on soilless cultures, a better understanding of the reasons for the rise in pH during wood pyrolysis is needed. Performing Boehm titration, Mukherjee et al. [47] related the increase in alkalinity to a progressive loss of the acidic surface functional groups, mainly the aliphatic carboxylic acids. Indeed, our biochars show a good and negative correlation between their oxygen (O) concentrations (Table 2) and pH values ($R^2 = 0.912$) (Figure 6) which could support a loss of acid O-containing groups, such as carboxylic C.

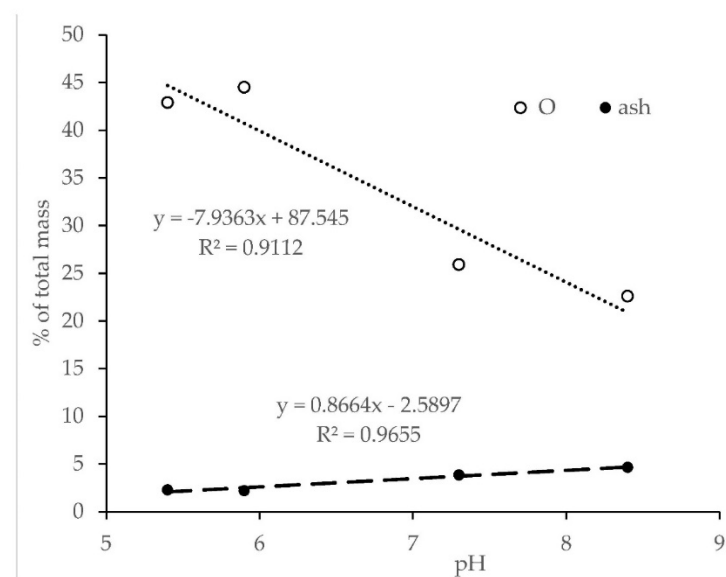


Figure 6. Relationship between oxygen loss and ash content with pH during pyrolysis of *Acrocomia* endocarp.

This interpretation is in line with observations of Narzari et al. [50] that show an increment of soluble salts and Ca with an increasing biochar pH. As a consequence, we conclude that for our samples, the increase in the pH is best explained by the accumulation of cations induced by the loss of organic matter. Thus, the lower pH of our biochars relative to other woody biochars is best explained by the low ash content of the feedstock (Table 2). Having a closer look at the contribution of the single cations, the low Ca content suggests that other cations must be more important for the pH increase as it was also reported elsewhere [27]. In the case of the present biochars, potassium represents, with 2.6 g kg⁻¹ dry mass of AC₄₅₀, a potential candidate. Note that this is approximately three to four times higher than the

concentration recommended for optimal tomato growth in a soil environment [51]. This needs some consideration with respect to plant nutrition. Whereas potassium does not become a part of the chemical structure of plants, it plays many important regulatory roles in plant development. It is involved in enzymatic activities, determines stomatal activity, thus water use efficiency, photosynthetic and transportation processes, as well as the synthesis of proteins and starch [52]. As an antagonist to Mg, excessive levels of K can drop the Mg in plant leaves [19,53]. A further primary risk of too much potassium is a nitrogen deficiency which will stunt the growth of the plant and lead to chlorosis. It also can reduce C assimilation [54].

For the finely grained feedstock and its biochar produced at 200 °C, EC values of 620 ± 39 and $526 \pm 13 \mu\text{S cm}^{-1}$ were measured (Table 6). In contrast to common reports on biochar EC, this parameter decreases considerably to a value of $130 \pm 4 \mu\text{S m}^{-1}$ with an increasing pyrolysis temperature. Compared to other biochars, this can be considered as low but can be related to the small contribution of ash to all samples. On the other hand, the low ash contents cannot explain the behavior of the fine feedstock. Here, one has to bear in mind that organic acid or organic material that dissolves in water can dissociate to form ions. In the finely grained feedstock and its respective biochar produced at 200 °C, soluble organic components are likely to have been released from the feedstock powder into the aqueous solution during sample preparation for the measurement of pH and EC. However, heating the sample above 200 °C seems to destroy those labile compounds and as a consequence, they can no longer contribute to the EC of the charred material. Such a scenario can also explain the big difference in the EC of the finely and coarsely grained feedstock, since the almost undestroyed physical structure of the endocarps prevents an efficient release of such soluble organic matter. As a consequence, the measured EC of those samples is representative of the concentration of the salts that could be dissolved in the water solution used for the determination of EC. Note that only a small concentration of exchangeable sodium (Na_{ex}) was revealed for all samples derived from the finely grained feedstock (Table 7). This allows for the assumption that the Na surplus will not be a problem in growing media to which this material has been added.

Table 7. Contents (mg kg^{-1}) of total K, Ca, Mg, Mn, Zn, B, S and P as well as Olsen P and exchangeable Na (Na_{ex}) of the fine feedstock from *Acrocomia aculeata* and the respective biochars pyrolyzed at 200, 325 and 450 °C (mean $\pm$ standard error, $n = 3$). Contents of Cu and Mn were below detection level. Zn concentration was $<2.4 \text{ mg kg}^{-1}$ dry weight.

	K	Ca	Mg	Fe	B	S	P _t	Olsen P	Na _{ex}
	(mg kg ⁻¹ Dry Weight)								
Optimum for Tomato Seeds [50]	600–700	1000	400–700					60–70	
AC _f	1750 $\pm$ 163	218 $\pm$ 5	148 $\pm$ 1	805 $\pm$ 2	193 $\pm$ 2	233 $\pm$ 1	163 $\pm$ 2	39 $\pm$ 2 (24% ³)	59 $\pm$ 17
AC _f 200	1676 $\pm$ 159	387 $\pm$ 17	153 $\pm$ 1	939 $\pm$ 3	321 $\pm$ 5	281 $\pm$ 3	163 $\pm$ 2	54 $\pm$ 1 (33% ³)	40 ¹
AC _f 325	2567 $\pm$ 179	523 $\pm$ 22	248 $\pm$ 2	1077 $\pm$ 4	110 $\pm$ 2	173 $\pm$ 3	208 $\pm$ 2	68 $\pm$ 7 (32% ³)	n.d. ²
AC _f 450	2610 $\pm$ 223	533 $\pm$ 22	279 $\pm$ 2	1316 $\pm$ 6	257 $\pm$ 5	166 $\pm$ 3	239 $\pm$ 1	81 $\pm$ 6 (34% ³)	52 ¹

¹ $n = 1$, ² not determined, ³ percentage of P_t.

A further major factor which affects plant growth is the availability of nitrogen and phosphate. As our biochars derive from a woody feedstock with a very low N content, the addition of *Acrocomia* biochar to planting substrates will not provide sufficient N for healthy plant growth. On the other hand, Olsen P increased to $81 \pm 6 \text{ mg kg}^{-1}$ and is in the range of optimal values for growing tomato plants outdoors in mineral soils (60 to 70 mg kg^{-1}) [50]. For growing tomato in peat substrates, optimal Olsen P concentrations of 2 ppm are reported [55].

The content of total P (P_t) in the final biochar depends on the content of P_t in the feedstock and on the content of the metals that could stabilize it by forming complexes [56]. Uchimiya and Hiradate [57] found correlations between the total inorganic P and K, Fe, Ca and Mg. Note that calcium can hinder the release of P since they form hydroapatite, whereas P complexed with iron and aluminum can be easily released [56].

For our samples, P_t shows a relative enrichment after pyrolysis which is in line with previous publications [9,19,27]. This can be related to the concomitant losses of carbon (C), nitrogen (N) and hydrogen (H) observed during the heat treatment (Table 2) and by heat-induced immobilization reactions leading to its relative accumulation. However, at temperatures $> 600\text{ }^{\circ}\text{C}$, P can be gasified. The underlying mechanisms explaining this immobilization of P during pyrolysis, however, are not yet completely understood. Complexation of P with Al, Ca and Fe has been observed and suggested to play a key role [13,20,30]. Note that the solubility of P in soils or plant growing substrates depends on the pH and has its maximum in the near neutral pH region which coincide with the lowest degree of P fixation by Ca, Al and Fe minerals [58]. However, in our experiment the relative contribution of Olsen P to P_t in the biochars increased with an increasing pyrolysis temperature. Possibly, their low Ca contents lowered the efficiency of P fixation.

In this context, it is also worth mentioning that in recent pot experiments with biochar-amended soils, it was demonstrated that P immobilized during pyrolysis is partially remobilized during plant growth [59].

Having a closer look at the contents of micronutrients, the biochar from the endocarp of *A. aculeata* is below the optimum values identified for growing tomatoes [50] and values commonly recommended for nutrient solution for hydroponic cultures. As a consequence, they have to be added if the biochars are used as a planting substrate or provided with the nutrient solution if they are applied in hydroponic soilless horticulture.

4. Conclusions

Our studies confirm the potential of biochars produced at a pyrolysis temperature of $450\text{ }^{\circ}\text{C}$ from the endocarp of *A. aculeata* as peat replacement in planting substrates. This may be an attractive approach to combine sustainable biowaste recycling with the protection of natural but not unlimited resources. In contrast to many other wood-derived biochars, the low ash content of the feedstock leads to pH and EC of the biochars which are still in the range that can be tolerated if used for plant growing substrates. The concentration of exchangeable sodium is small enough to avoid negative impacts for plant growth. Whereas phosphate contents of the biochars are high enough to assume that there is no need for the major addition of this nutrient to the final product, nitrogen and other micronutrients have to be supplied.

Our study has also shown that the particle size of the feedstock had no major impact on the chemical properties and microporosity of the pyrolysis product, confirming that degradation reactions are governed by temperature and that a changing surface area did not affect the temperature homogeneity of the sample. This may be an important issue since it can reduce production costs by avoiding the need for an extra step of the grinding and homogenization of the feedstock prior to pyrolysis. This may also give more flexibility with respect to the physical properties of the final product since it allows a post-pyrolysis adaption of its particle size to the needs of the consumer. Comparably, the low contents of nitrogen, calcium and some micronutrients may facilitate the use of the biochar in particular in hydroponic hydroculture, in which nutrient application depends on the specific requirements of the plants.

Author Contributions: Conceptualization, H.K., M.E.F.-B. and R.L.-O.; methodology, H.K., M.E.F.-B. and R.L.-O.; validation, R.L.-O., M.E.F.-B. and H.K.; formal analysis, R.L.-O.; investigation, R.L.-O., M.E.F.-B. and H.K.; resources, M.E.F.-B. and H.K.; data curation, R.L.-O., M.E.F.-B. and H.K.; writing—original draft preparation, R.L.-O.; writing—review and editing, H.K., M.E.F.-B. and R.L.-O.; visualization, R.L.-O., H.K. and M.E.F.-B.; supervision, M.E.F.-B. and H.K.; project administration, H.K.; funding acquisition, H.K. All authors have read and agreed to the published version of the manuscript.

Funding: The former Spanish Ministry of Economy, Industry and Competitiveness (MINECO) and AEI/FEDER are thanked for funding the project CGL2015-64811-P. The solid-state NMR spectroscopic analysis was provided and financed by the service unit “Solid-State NMR Spectroscopy (400 MHz) for Organic Matter Characterization” of the IRNAS-CSIC. Elemental, macro- and micro-elemental analysis, SEM and BET were performed at the Center for Research, Technology and Innovation (CITIUS) of the University of Seville.

Data Availability Statement: The data presented in this study are available on request from the corresponding author.

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses or interpretation of data; in the writing of the manuscript; in the decision to publish the results.

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