Wood Ash as an Additive in Biomass Pyrolysis: Effects on Biochar Yield, Properties, and Agricultural Performance

Jannis Grafmüller, Alexandra Böhm, Yiling Zhuang, Stephanie Spahr, Pascale Müller, Thomas N. Otto, Thomas D. Bucheli, Jens Leifeld, Robin Giger, Michael Tobler, Hans-Peter Schmidt, Nicolaus Dahmen, and Nikolas Hagemann*

Cite This: *ACS Sustainable Chem. Eng.* 2022, 10, 2720−2729

Read Online

ACCESS | Metrics & More | Article Recommendations | SI Supporting Information

ABSTRACT: The use of wood ash as an additive in biochar production was shown to increase biochar yields and was suggested to improve the recycling of ash-derived nutrients. However, there is limited knowledge on the interaction of ash addition with pyrolysis conditions and their effects on biochar yield and properties. Here, we performed experimental pyrolysis in an auger reactor applying different ash concentrations, temperatures, and residence times. Biochar yield (dry and ash-free) increased by 26% and carbon-conversion efficiency of pyrolysis by 36% when 9 wt % ash was added to softwood. Up to this concentration, yield increase was correlated linearly, while higher ash concentrations did not further increase yield significantly. The ash-induced yield increase was lower at 400 °C than for 425−500 °C. Biochar's content of polycyclic aromatic hydrocarbons was not affected by ash addition. The content of polychlorinated organic pollutants increased with ash amendment but remained well below applicable thresholds. The electron exchange capacity of biochars was increased while the micropore specific surface area and thermal stability decreased with ash addition. The elevated potassium content of ash-amended biochars promoted sunflower growth. Biochar derived from ash-amended biomass is safe to be applied in soil and may be a promising approach for enhanced nutrient recycling and carbon sequestration.

KEYWORDS: *pyrogenic carbon capture and storage, PyCCS, co-pyrolysis, biochar-based fertilization, PAH, PCDD/F, PCB*
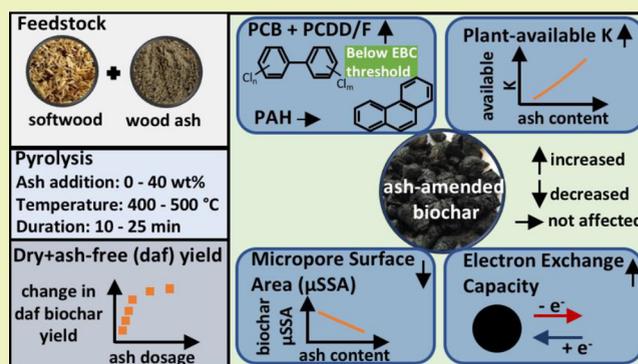
INTRODUCTION

Pyrogenic carbon capture and storage (PyCCS) is a promising approach to mitigate climate change by thermochemically converting biomass-derived carbon (C) into a long-term C-sink via slow pyrolysis, which results in biochar, pyro-oil, and pyro-gas.[1,2] Because pyro-oil and -gas are, at present, mostly burned, only biochar creates C-sinks when used, for example, as agricultural soil conditioners,[3] resulting in C-conversion efficiencies (i.e., the ratio of biomass C retained as a long-term C-sink after pyrolysis) of less than 50%.[2] Because biomass presents a limited resource, C-conversion efficiencies higher than 70% were identified to make PyCCS a relevant negative emission technology.[2,4] Thus, increasing the C-conversion efficiency of biochar production is of prior interest to establish PyCCS.

Recently, the use of wood ash as an additive in slow pyrolysis of biomass has been proposed to increase mass and stable C yields in biochar production.[5,6] Addition of 10 wt % combined bottom and fly ash to spruce wood prior to pyrolysis at 450 °C increased dry and ash-free (daf) biochar yield (i.e., biochar mass yield excluding ash and water content) and fixed C yield by 25% compared to the nonamended control.[5] This effect is attributed to the presence of alkali and alkaline earth metals (AAEMs) in the wood ash, mainly potassium (K), sodium (Na), and calcium (Ca).[7,8] These elements catalyze biochar formation by influencing primary and secondary pyrolysis reaction pathways which is accompanied by a lower yield of condensed pyrolytic gases (i.e., pyro-oil).[7,9−13] It was proposed that additives, such as AAEM metals, can hinder the diffusion of pyro-gases inside the biomass particle and thus increase their transformation into condensed char.[14,15]

Adding pure AAEM salts to woody biomass (i.e., 1−2% K or Na) prior to pyrolysis at varying highest treatment temperatures (HTTs) resulted in a constant yield increase in the range of 350−750 °C.[8] However, to the best of our knowledge, the temperature dependency of yield increase has not yet been
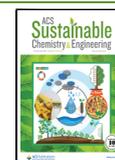
explored for complex and more readily available mixtures of AAEM, such as wood ash.

The ash amendment was shown to increase the pH and electric conductivity (EC) in the biochar suspension and increased the amount of extractable K from the biochars.[5] Furthermore, incubation studies in distilled water revealed a slow-release characteristic of K from ash-amended biochars which was attributed to the formation of K-Al-O-Si species during the pyrolysis process.[17] However, plant growth promotion by augmentation of available K in soils via ash-amended biochar addition has not been demonstrated before. Furthermore, the effect of ash dosage on important biochar properties such as its electron exchange capacity (EEC), specific surface area (SSA), and content of organic pollutants has, to the best of our knowledge, not been studied so far. Biomass pyrolysis always bears the risk of producing biochar that contains polycyclic aromatic hydrocarbons (PAHs), which are formed in the gas phase and may condense on the solid product during pyrolysis.[18] The increased ash-induced occurrence of secondary tar cracking reactions[12] might not only alter the product yield of pyrolysis but could also have an effect on PAH formation. Because chlorine is present in wood ash,[16] the formation of polychlorinated dibenzo-p-dioxins- and -furans (PCDD/F) as well as polychlorinated biphenyls (PCBs) during pyrolysis[18] might be promoted by the ash amendment.

In this study, we focused on investigating the impact of (bottom) wood ash addition to softwood on daf biochar yield, C-conversion efficiency, and selected biochar properties using a pilot-scale auger reactor (PYREKA[19]). We applied different ash dosages (0−40 wt %) and varied the pyrolysis parameters HTT (400−500 °C) and residence time (RT) (10−25 min). The PAH and PCDD/F + PCB content in the biochars was analyzed to evaluate whether ash-amended biochars are safe to be applied in soil. The SSA of the biochars was quantified as a proxy for the sorption capacity of the biochars and the EEC was quantified as it is considered an important property, for example, for the use of biochars in bioremediation processes.[20] Additionally, we evaluated the thermal stability of the biochars to gain insights whether the ash amendment affects biochar persistence.

■ MATERIALS AND METHODS

Feedstock Preparation. Bottom ash (in the following referred to as wood ash) was sampled in a forest wood incineration plant in Sissach (Switzerland) and sieved to <2 mm to remove stones and other artifacts (17% of initial mass). Softwood sawdust (<15 mm, Allspan Spanverarbeitung GmbH, Karlsruhe, Germany) was mixed with 0, 2.0, 4.8, 7.3, 8.9, 16.4, 32.5, and 42.6 wt % wood ash (dry matter (dm) basis). A mixture of sawdust and wood ash, including the treatment without wood ash, was blended with 10 wt % sunflower oil as a binding agent and then pelletized using a pellet mill (6 mm pellet diameter, WK230, EverTec, Groß-Zimmern, Germany). As the oil was added to all different pellets at the same ratio, possible impacts on biochar yields and properties were expected to be the same in all treatments. Dry matter content of biomass pellets was determined in duplicates at 105 °C.

Pyrolysis. Thermal conversion of biomass feedstocks was performed in a PYREKA research pyrolysis unit (Pyreg GmbH, Dörth, Germany), a continuously operated auger reactor purged with N₂, which was described in detail by Hagemann et al.[19] The pyro-gas and the N₂ passed the reactor (8 cm diameter) in the same direction as the solids. If not mentioned otherwise, thermal conversion was performed at 500 °C with 10 min RT. To enable biochar yield calculations, the mass flow of the different biomass pellets (mass of

feedstock passing the reactor per unit of time) was measured in the unheated reactor with five repetitions. Mass flow of biochars was recorded either with two or three replicates and a sampling interval of 15 min or a one-time sampling interval of 30 min. Biomass throughput was set to 0.8 kg h⁻¹ to achieve similar reactor loads for all experiments.

Analysis of Wood Ash, Biomass Feedstock, and Biochars. Biochars were ground with a mortar and pestle and sieved to <500 μm particle size for the greenhouse trials and the quantification of K-availability. For further analysis, biochars were milled to <200 μm using an impact mill (Kinematica AG, Lucerne, Switzerland).

Elemental Analysis, Ash Content, Main and Trace Elements, PAHs, PCDD/F, and PCBs. Elemental analysis of biochars and the wood ash (total C, H, N, and S) was performed in triplicate in a vario EL-cube (Elementar Analysensysteme GmbH, Langenselbold, Germany). Ash contents of biochars, softwood sawdust, and wood ash were determined according to DIN EN ISO 18122 at 550 °C in a muffle furnace (B180, Nabertherm, Lilienthal, Germany). The content of main and trace elements, PAHs, PCDD/F, PCBs, and organic carbon (C_org) in selected biochars was quantified by Eurofins Umwelt Ost GmbH (Bobritzsch-Hilbersdorf, Germany) according to the guidelines of the European Biochar Certificate (EBC).[21] Main and trace elements were also analyzed in the softwood and wood ash by Eurofins.

Differential Scanning Calorimetry (DSC). Thermal stability of biochars was evaluated by recording DSC curves (STA 449 F3 Jupiter, NETZSCH, Selb, Germany). Biochars were diluted with Al₂O₃ to a C-content of 10 wt % to avoid inaccurate recording of exothermic peaks.[22] Samples (20 mg) were heated in synthetic air (50 mL min⁻¹, 20 °C min⁻¹) from room temperature to 700 °C. Thermal stability was evaluated by the temperature at which the exothermic peak during combustion of the biochars was registered.[23]

Electron Exchange Capacity. The EEC of biochars was determined by mediated electrochemical reduction and oxidation using an adapted method from Klüpfel et al.[20] Further information on the measurement procedure is given in Section 1.1 of the Supporting Information (SI).

Potassium Availability. Biochars and wood ash were extracted in a ratio of 1:10 (w/v) with 0.01 M CaCl₂ on an orbital shaker (150 rpm) for 2 h, as recommended in previous work.[5,24] Samples were filtered through a syringe filter (0.45 μm, CHROMAFIL A45/25, HUBERLAB AG, Aesch, Switzerland). The concentration of K in the filtrates was measured with a spectrophotometer and a corresponding cuvette test (Photometer DR3900, Test LCK 328, Hach Lange GmbH, Düsseldorf, Germany).

Specific Surface Area. To calculate the micropore SSA (μSSA) of selected biochars, CO₂-adsorption isotherms were recorded on a NOVA 2000e (Quantachrome Instruments, Anton Paar GmbH, Graz, Austria). The measurement cell was tempered to 273 K, and physisorption experiments were performed in a range of relative pressure from 8×10^{-5} to 3×10^{-2}. The SSA in micropores was calculated applying the Dubinin−Radushkevich (DR) method.[25] Biochars were degassed for 20 h at 130 °C under vacuum before measurements, as recommended in other work.[26]

Greenhouse Trial. Sunflower was grown in a south−north-oriented greenhouse located at Zurich Affoltern (Switzerland) with a constant temperature of 22 ± 2 °C and automatic lighting system (16 h per day). Sunflower was chosen as an experimental plant because of its high K-demand to build up the stem and leaf mass.[27] In each pot with biochar amendment, a mass of 5 g (treatments 5−9, Table S7) or 25 g (treatments 10 and 11) of biochar containing different amounts of ash was applied in the root zone,[28,29] which resulted in a biochar content of 0.14 and 0.7 wt % in the substrate, respectively. The biochar mass per pot with one sunflower plant equaled an application rate of 0.3 and 1.5 t ha⁻¹, respectively, assuming a sowing density of 60.000 plants ha⁻¹. Plants were grown in combination with NS, NPS, and NPKS fertilization (Table S7). The amount of mineral K-fertilization was reduced by the amount of plant-available potassium in the biochar treatments 7−11 to test whether mineral K can be replaced by the ash-amended biochars. Fourteen different treatments

Table 1. Pyrolysis Results, Ash Contents, and Molar H/C Ratios of Ash-Amended Biochars[a,b]

ID	feedstock	HTT[c]	RT[d]	daf[e] biochar yield	carbon conversion efficiency	change in carbon-conversion efficiency[f]	ash content	H/C molar ratio
		°C	min	wt % daf	wt % daf	%	wt % (dry matter)	
Set A: variation of ash amendment to the feedstock								
1	0.0% ash	500	10	20.5 ± 0.5 d	34.5 ± 0.8 b	0.0 ± 0.0 b	2.3	0.47
2	2.0% ash	500	10	21.1 ± 0.6 d	35.3 ± 0.7 b	2.3 ± 3.2 b	10.3	0.44
3	4.8% ash	500	10	22.5 ± 0.5 c,d	37.9 ± 0.8 b	10.0 ± 3.4 b	16.2	0.43
4	7.3% ash	500	10	24.8 ± 0.8 b,c	44.3 ± 1.4 a	28.3 ± 5.0 a	22.1	0.26
5	8.9% ash	500	10	25.8 ± 0.8 a,b	46.9 ± 1.5 a	36.1 ± 5.3 a	24.4	0.25
6	16.4% ash	500	10	25.3 ± 0.4 b,c	38.9 ± 0.7 b	12.7 ± 3.2 b	41.1	0.46
7	32.5% ash	500	10	26.7 ± 0.6 a,b	47.9 ± 1.0 a	38.9 ± 4.3 a	57.9	0.35
8	42.6% ash	500	10	27.6 ± 0.4 a	39.0 ± 0.6 b	13.0 ± 3.1 b	69.0	0.43
Set B: variation of HTT of pyrolysis								
9	0.0% ash	400	10	28.8 ± 0.7 a,b	44.1 ± 1.1 b,c	n.a.[g]	1.5	0.57
10	0.0% ash	425	10	24.3 ± 0.9 c,d	38.8 ± 1.4 c,d	n.a.[g]	1.9	0.27
11	0.0% ash	450	10	22.2 ± 0.5 d,e	36.7 ± 0.9 d	n.a.[g]	1.6	0.27
12	0.0% ash	475	10	20.9 ± 0.5 d,e	35.7 ± 0.8 d	n.a.[g]	2.1	0.29
13	8.9% ash	400	10	30.8 ± 0.7 a	50.5 ± 1.1 a	14.5 ± 3.7 b	24.9	0.62
14	8.9% ash	425	10	29.4 ± 1.3 a,b	48.3 ± 2.1 a,b	24.7 ± 7.0 a,b	21.7	0.29
15	8.9% ash	450	10	28.3 ± 0.8 a,b	49.5 ± 1.4 a,b	35.0 ± 5.1 a	23.3	0.26
16	8.9% ash	475	10	26.2 ± 0.5 b,c	46.1 ± 0.9 a,b	29.0 ± 3.9 a,b	24.2	0.27
Set C: variation of RT of pyrolysis								
17	0.0% ash	500	15	19.7 ± 0.5	27.0 ± 0.6	n.a.[g]	2.9	0.27
18	0.0% ash	500	20	17.8 ± 0.4	31.1 ± 0.8	n.a.[g]	2.9	0.32
19	0.0% ash	500	25	16.8 ± 0.4	30.0 ± 0.7	n.a.[g]	6.7	0.30
20	8.9% ash	500	15	22.4 ± 0.4	41.1 ± 0.8	52.0 ± 4.6	24.7	0.35
21	8.9% ash	500	20	22.1 ± 0.4	40.4 ± 0.8	30.0 ± 4.0	24.9	0.36
22	8.9% ash	500	25	22.5 ± 0.4	42.0 ± 0.7	40.1 ± 4.0	23.0	0.32

[a]Presented uncertainties of replicated pyrolysis experiments ($n = 2$, except for ID 4, 5, 10, 11, 14, 16 where $n = 3$ applies and $n = 1$ for ID 19 and 22) were calculated according to the error propagation law. [b]Different letters within a column of a set indicate a statistically significant difference ($p < 0.05$, Gabriel post hoc test). [c]HTT, highest treatment temperature. [d]RT, residence time of biomass in heated reactor zone. [e]daf, dry and ash-free. [f]Change in carbon efficiency: relative to nonamended control pyrolyzed with the same HTT and RT. [g]n.a., not applicable.

(Table S7) with five replicates each were arranged in a complete randomized block design. The position of the pots within a block was weekly changed at random. Soil from excavation work in the Emmen region (CH) was used (soil analysis in Table S8). A detailed description of the procedure of pot preparation, sowing, and fertilization is provided in Section 10.1 of the Supporting Information.

After 2 months, aboveground biomass was harvested and weighed to determine fresh biomass yields. Dry biomass yields were determined after drying for 24 h at 105 °C. Further evaluated parameters and the visual investigation of the plants for K-related deficiency symptoms are described in Table S9 and Figure S9 in the Supporting Information.

Data Analysis. The yield of daf biochar was calculated according to eq 1. The mass flows of biochar and biomass ($\dot{m}_{BC}$ and $\dot{m}_{BM}$) were corrected for the respective ash fraction a and moisture w. The natural ash content of the softwood (0.4 wt %) was neglected and not subtracted from the feedstock basis.

$$\text{daf biochar yield} = \frac{\dot{m}_{BC} \cdot (1 - a_{BC} - w_{BC})}{\dot{m}_{BM} \cdot (1 - a_{BM} - w_{BM})} \times 100\% \qquad (1)$$

Throughout this study, the term daf biochar is a calculated quantity that results from subtracting the quantified ash and water contents of the respective biochar.

Carbon-conversion efficiency of biomass pyrolysis was calculated as the ratio of total C (TC) contained in the biochars to the TC contained in the pelletized feedstock used to produce this specific amount of biochar according to eq 2

carbon conversion efficiency (%)

$$= y_{BC} \cdot \frac{C_{C,BC}}{a_{feed} \cdot C_{C,ash} + C_{SW,feed} \cdot C_{C,SW} + C_{oil,feed} * C_{C,oil}} \qquad (2)$$

where y_{BC} is the yield of biochar based on fresh feedstock (in wt %), and $c_{C,BC}$, $c_{C,ash}$, $c_{C,SW}$, and $c_{C,oil}$ are the TC contents (wt %) of the biochar, the wood ash additive, the softwood, and the sunflower oil, respectively. For the softwood, wood ash, and sunflower oil, a TC content of 50.3, 1.1, and 75.1 wt %, respectively, was quantified. The content of the wood ash additive in the fresh feedstock is described as a_{feed}, the ratio of softwood correspondingly $c_{SW,feed}$ and the oil as $c_{oil,feed}$. Analysis of variance followed by the Gabriel post hoc-test (for daf biochar yield and C-conversion efficiency) and Ryan-Einot-Gabriel-Welsch Q (REGW-Q) post hoc-test (for the greenhouse trial) was conducted using SPSS Statistics 27 (IBM Corporation, USA). The Gabriel test is suggested to be used for data sets where similar variance can be expected, but the number of replicates is varying.[30] The REGW-Q test is used for data with the same variance and the same number of replicates.[30]

RESULTS AND DISCUSSION

Optimizing Carbon-Conversion Efficiency of Biochar Production. *Influence of Ash Amendment on daf Biochar Yield.* For all 22 biochars produced, the wood ash amendment to biomass feedstocks resulted in higher daf biochar yields and C-conversion efficiencies across different pyrolysis conditions compared to the nonamended controls (Table 1). For ash dosages of up to 8.9 wt %, the yield of daf biochar increased

significantly from 20.5% (no ash amendment) to 25.8% (Table 1, ID 1−5). The change in daf biochar yield increased linearly with ash dosages up to 8.9 wt % ash (R^2 = 0.97, Figure 1A) and thus also correlated with both the molar K to C ratio (Figures 1A, S1) and the ratio of the sum of K, Na, Ca, and Mg to C (AAEM/C, Figure S1) in the feedstock. Adding wood ash up to 8.9 wt % to achieve a K/C ratio of 0.47 mol % or AAEM/C ratio of 2.34 mol % was most efficient to increase daf biochar
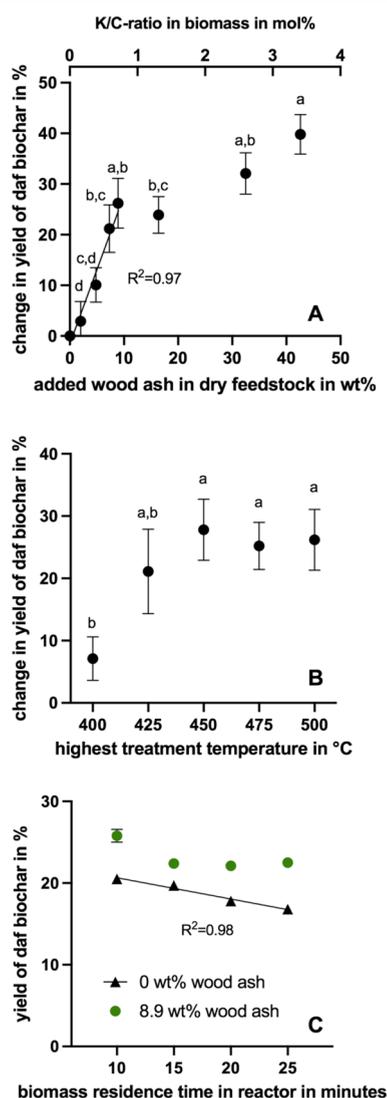
Figure 1. (A) Effect of ash admixture to softwood on daf biochar yield compared to nonamended control (500 °C for 10 min). Error bars represent the uncertainty calculated according to the error propagation law of replicated pyrolysis experiments (n = 2, except for 7.3 and 8.9 wt % ash concentration, where n = 3). Different letters above error bars indicate a significant difference between the data points ($p < 0.05$, Gabriel post hoc-test). (B) Change in daf biochar yield by adding 8.9 wt % wood ash compared to the nonamended control at different pyrolysis temperatures (10 min RT). Error bars represent the uncertainty calculated as specified in panel A (n = 3 for 425, 475, and 500 °C and n = 2 for 400 and 450 °C). (C) daf biochar yield of nonamended control and biomass feedstock with 8.9 wt % added wood ash at different RTs and 500 °C. Error bars represent the uncertainty calculated according to the error propagation law of replicated pyrolysis experiments (n = 2 for 10 and 20 min and the 8.9 wt % biomass with 15 min, otherwise n = 1). When no error bar is displayed, the uncertainty is smaller than the data point symbol.

yields (Figure S1). When increasing the ash dosage to 42.6 wt % (K/C = 3.3 mol %, AAEM/C = 16.7 mol %), no significant further increases in daf yields were observed (Figures 1A and S1). A declining effect of the catalytic elements on increasing daf biochar yields with high ash dosages may indicate an insufficient contact and ratio between the pyrolytic gases and available mineral phases (e.g., catalytic components in the ash could be covered/shielded by others). Consequently, we assume that less ash needs to be added to achieve optimized biochar yields when already mineral-rich biomass is used as a pyrolysis feedstock, such as wood bark which shows a native molar K/C ratio of 0.1−0.3 mol %[31,32] and is known to yield higher daf biochar yields than, for example, stem wood.[33] Confirming our findings, ash addition to already ash-rich feedstocks (maize silage with K/C = 0.5 mol %, and biogas residues with K/C = 0.6 mol %) did not lead to increased daf biochar yields in a pyrolysis process at 500 °C.[17]

Influence of Ash Amendment on C-Conversion Efficiency of Biochar Production. The ash amendment had a similar effect on the C-conversion efficiency (i.e., the conversion rate of biomass C to storable, solid C during pyrolysis) as on daf biochar yields. Carbon-conversion efficiency increased significantly from 35% for the nonamended biochar (ID 1) to 47 and 48% for the 8.9 and 32.5 wt % ash-amended feedstocks ($p < 0.05$, ID 5 and 7, Table 1), which is an increase by 36 and 39%, respectively. Changes in C-conversion efficiency increased linearly (R^2 = 0.95, Table 1) in the range of lower ash dosages (ID 1−5) of up to 8.9 wt %, respectively. These results show that a moderate ash amendment in the feedstock material of <10 wt % can significantly boost the C-conversion efficiency of biochar production. Considering the scanning electron microscopy (SEM) images and energy-dispersive X-ray spectroscopy mappings (Chapter 9 of the Supporting Information), it appears that the ash-derived minerals are attached to the carbon surface and are barely covered by a carbon layer (Figure S6). This suggests that ash-induced char formation occurs mainly within the ash-coated biomass particle rather than on its surface.

Influence of HTT on daf Yields and C-Conversion Efficiency of Ash-Amended Biochars. Yields of daf biochar of nonamended (ID 9−12 and 1) and ash-amended feedstock (ID 13−16 and 5) decreased with increasing HTT in the range of 400 to 500 °C (Table 1). This was expected because volatile biomass components are released to a higher extent during pyrolysis with increased HTT.[34] Pyrolysis with HTTs above 450 °C significantly elevated the ash-induced increases in daf biochar yields compared to pyrolysis at 400 °C (i.e., 6.9% yield increase at 400 °C versus 27.5% yield increase at 450 °C, Figure 1B). This is in contrast to the data obtained after the addition of pure of K- and Na-salts to biochar feedstocks, where the extent of yield increase remained within a narrow range across the HTT range of 350−750 °C.[8] The daf biochar yield (28.3%) obtained for the ash-amended biochar (ID 15, 8.9 wt % ash amendment) at 450 °C in our study is comparable to the yield (29.5%) determined in a previous study for a 10 wt % ash-amended spruce-pellet at 450 °C in an auger reactor.[5]

For nonamended biochars (ID 9−12 and 1), C-conversion efficiencies significantly decreased with increasing HTT (Table 1, $p < 0.05$) despite increasing C contents of the biochars (Table S1). In contrast, no significant decline in C-conversion efficiency was found for the ash-amended biochars (ID 13−16 and 5). Pyrolysis without ash addition at 400 °C (ID 9)
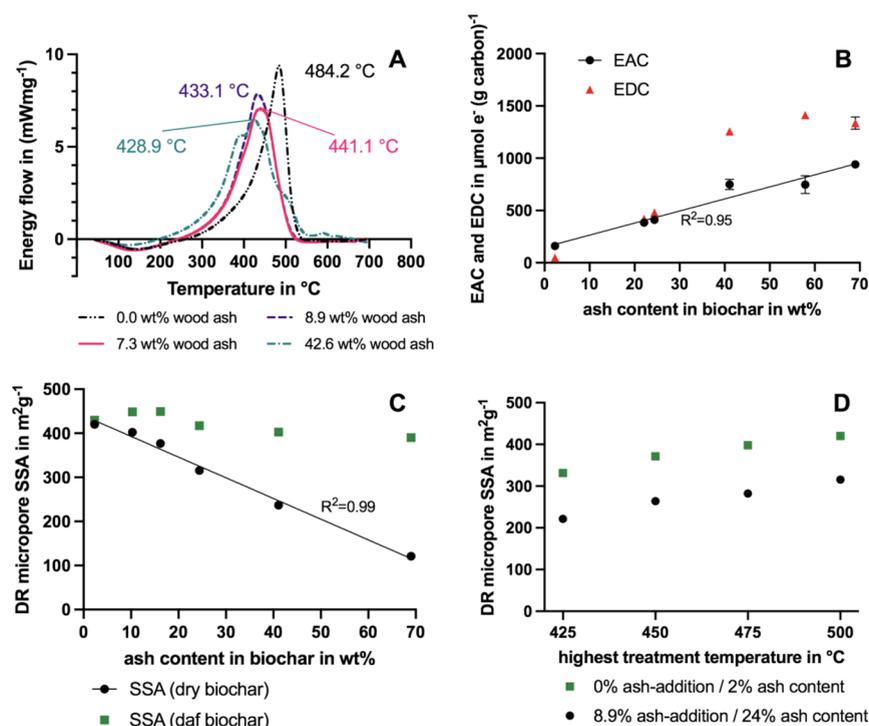
Figure 2. Properties of ash-amended biochars. (A) DSC curves of biochars without and with ash amendment. Samples were diluted to a carbon content of 10 wt % using Al_2O_3. (B) Electron-accepting and -donating capacity (EAC and EDC) of biochars with different ash contents normalized to 1 g of carbon (pyrolysis at 500 °C for 10 min). The error bars represent two standard deviations of replicated measurements ($n = 3$, $n = 2$ only for EAC for biochars with 2 and 41 wt % ash content). When no error bar is displayed, the uncertainty is smaller than the data point symbol. (C) μSSA evaluated by CO_2-physisorption experiments and the DR method of biochars with different ash contents (on dry as well as dry and ash-free (daf) basis) pyrolyzed at 500 °C for 10 min. (D) μSSA of biochars with 0 and 8.9 wt % added wood ash amendment pyrolyzed at different HTTs with 10 min RT.

resulted in similar C-conversion efficiency to the pyrolysis of ash-amended biomass at 500 °C (ID 5). However, the carbon speciation and the molecular structure of the two biochars probably differed both because of the difference in temperature[35,36] and the ash amendment (i.e., higher H/C molar ratio of ID9 compared to ID5, Table 1). Impact of ash addition on biochar carbon speciation needs further investigation, for example, with ^{13}C nuclear magnetic resonance, synchrotron-based near-edge X-ray absorption fine structure, or Fourier transform infrared spectroscopy.

Influence of RT on daf Yields and C-Conversion Efficiency of Ash-Amended Biochars. Longer RT within the range from 10 to 25 min led to a decrease in daf yield and C-conversion efficiency for all biochars produced (Figure 1C, Table 1). For nonamended biomass feedstocks (ID 1 and 17−19), daf biochar yields decreased almost linearly from 20.5 to 16.8% (R^2 = 0.98, Figure 1C). For the 8.9 wt % ash-amended biomass, yields were reduced from 25.8 to 22.5% (ID 5 and 20−22) with stable yield in the RT range of 15−25 min. When biomass is exposed to pyrolysis conditions for a longer period of time, volatilization of labile compounds is increased. The constant yields of ash-amended biochars at RTs higher than 15 min (Figure 1C) indicate that the release of volatiles ceased earlier in the presence of wood ash compared to the nonamended biochars, which is in line with the assumption that AAEMs reduce the activation energy of the pyrolysis reaction and thus speed up the conversion process.[5,37] There is no observable correlation between the ash-induced increase of daf biochar yield or C-conversion efficiency and the RT of solids in the pyrolysis reactor (Table 1).

Properties of Ash-Amended Biochars. *Content of Main and Trace Elements.* For the HTT applied in this study, volatilization of ash components was not expected (98.5% ash content at 550 °C in the muffle furnace), and thus the content of main and trace elements in the biochars increased according to the extent of wood ash addition. The wood ash consisted of 28.7 wt % Ca, 7.8 wt % K, 1.4 wt % P, and 2.0 wt % Mg, which represents a typical composition.[16] Potassium contents in the biochars varied between 1600 mg kg^{-1} (no ash amendment) and 47000 mg kg^{-1} (42.6 wt % ash amendment, Tables S2). Detailed elemental compositions of the biochars (CHNS) are provided in Table S1.

The content of trace elements in ash-amended biochars is of special interest, because wood ashes can contain considerable amounts of, for example, Pb, Cd, Cu, Cr, or As. The ash-amended biochars were found to comply with the EBC guidelines[21] for trace elements up to an ash dosage of approximately 15 wt % of dry biomass feedstock (Table S3). For higher ash amendments (ID 6 and 8, Table S3), limit values of Cu and Pb for biochar application in organic farming were exceeded.[21] The wood ash contained Pb above the limit value for wood ashes approved as compost or soil amendment in Germany[38] was enriched in Cu (below the limit value) and showed low concentrations of other trace elements (Table S3). In an earlier study, the use of combined bottom and fly ash as a pyrolysis additive led to an exceedance of several EBC limits already at ash dosages of 5 wt %, especially for Cr and Cd.[5] Our results indicate that the use of pure bottom ash as a pyrolysis additive should be preferred over the use of mixtures

with fly ashes, because fly ash can be higher concentrated in trace elements.[39,40]

Stability of Ash-Amended Biochars. The biochar's H/C molar ratio, besides other methods such as incubation studies, nuclear magnetic resonance analysis, and thermal analysis (proximate analysis, DSC and others), allows estimation of the resistance of biochars against mineralization when used as a soil amendment.[41−43] H/C ratios ranged from 0.57 to 0.27 for nonamended and from 0.63 to 0.26 (Table 1) for ash-amended biochars and are well below the EBC threshold of 0.7.[21] This limit ratio is based on a conservative estimation which ensures that at least 50% of carbon remains in soil 100 years after biochar amendment.[44] The ash amendment did not influence H/C ratios systematically (Table 1). Differences between H/C and H/C$_{org}$ ratios were negligible, especially for the low ash-amended biochars (Table S4). Biochars amended to soils with molar H/C$_{org}$ ratios lower than 0.4 are associated with mean residence times of over 1000 years,[41] which applies to most of the biochars produced (Table 1). Based on the H/C ratios, there is no indication that ash addition will reduce biochar stability when amended to soils.

DSC curves revealed that ash-amended biochars had lower resistance against thermal oxidation, which was reflected by a shift of the exothermic peak toward lower temperatures (Figure 2A). Because the shift of the exothermic peak could be the result of catalytic effects of AAEM on thermal oxidation in the ash-amended biochars,[15] surrogate chars were prepared as mixtures of biochar produced without ash amendment (ID 1) and wood ash to obtain the same ash content in the surrogate char as in the respective ash-amended biochar. Analyzing these surrogate chars with the same method in the DSC and comparing the location of the exothermic peak with those of the ash-amended biochars allowed evaluating to which extent the shift toward lower temperatures is solely due to the catalytic action of the ash in the DSC. All ash-amended biochars analyzed showed a lower thermal stability than the respective surrogate char (Figures S10−S14), which indicates that prepyrolysis ash amendment to biomass may have negative implications on biochar stability beyond the effect of a higher reactivity because of the incorporated AAEM. For biochar, a positive relationship between its thermal stability and the size of its labile pool was reported. Therefore, thermal stability was proposed as a measure for the C sequestration potential of biochars, besides other methods.[42,45] Also for soil organic matter, a correlation of thermal stability and its biogeochemical stability was found.[22,46,47] Long-term incubation studies should be performed to evaluate the effect of higher C-conversion efficiency of pyrolysis and stability of ash-amended biochars in soil.

EEC of Biochars. Biochar is a reversible electron acceptor and donor and can, therefore, facilitate abiotic and microbial redox processes such as (bio)transformation of contaminants.[20,48,49] The EEC, that is, the sum of electron-accepting and -donating capacity (EAC and EDC) obtained from mediated electrochemical analysis was suggested to quantify environmentally relevant redox properties of biochars.[20] The EAC and EDC of nonamended softwood biochars (500 °C), normalized to the carbon content, were 157 and 48 μmol e$^-$(g carbon)$^{-1}$, respectively, which is comparable to other studies (Figure 2B).[20,50] Both EAC and EDC increased with ash dosage (Figure 2B), resulting in a maximum EAC of 854 μmol e$^-$(g carbon)$^{-1}$ and EDC of 1396 μmol e$^-$(g carbon)$^{-1}$ for 42.6 and 32.5 wt % ash amendment, respectively. This indicates that wood ash amendment in biomass pyrolysis can be a tool to achieve desired electrochemical properties, that is, a high EEC of biochars. The enhancement in absolute EEC (EEC per gram of biochar, Figure S3) is comparable to the increase achieved by a postpyrolysis treatment of biochars, for example, with a modified Hummer's method.[50]

The untreated wood ash itself showed a low EDC and EAC (53 and 12 μmol e$^-$ g^{-1}, respectively), suggesting that the ash itself did not cause the higher EEC (Figure S4). Redox functionality of biochar is assigned to pyrogenic compounds created at HTT > 350 °C.[20,51] Char formed in the presence of a higher amount of ash may contain more redox-active functional groups (i.e., C=O functional groups) and, thus, may cause the increase in the EEC of the ash-amended biochars.[17] Grass-derived biochar systematically showed higher EEC than wood-derived biochar produced under the same pyrolysis conditions—grass has a naturally higher ash content than wood.[20] Chacón and colleagues[50] found a nearly linear increase of EEC with increasing ash content using different biomass (woody biomass, reed, and rice husk) with ash concentrations of 3−9%. Tomato plant biomass (19% ash), however, resulted in a biochar with EEC similar to that obtained from biomass with 7−9% ash (orange tree pruning, reed).[50] Thus, EEC alteration by ash amendment might also be influenced by the type of biomass used as a pyrolysis feedstock.

Micropore Specific Surface Area. The SSA in micropores (pore size <2 nm) of biochars pyrolyzed at 500 °C with 10 min RT decreased linearly (R^2 = 0.99) with the ash content in the biochar from 420 m^2 g^{-1} (ID 1) to 121 m^2 g^{-1} (ID 8, Figure 2C). However, the strong correlation of μSSA with ash contents in the biochars implies that the wood ash itself was not microporous. The micropore SSA calculated on the basis of daf biochar was in a much narrower range (390−450 m^2 g^{-1}, Figure 2C) across the different biochars. Thus, the formation of the porosity in the pyrogenic carbonaceous structure is only marginally altered by ash addition. Pore blockage by the ash-induced formation of char that might decrease the μSSA,[15] if at all, played a minor role. In good agreement with the literature,[26,52] SSAs of all biochars increased with increasing HTT within 400 and 500 °C (Figure 2D). Again, the daf-related SSA of ash-amended biochars was in the range of nonamended biochars (Figure S5).

Organic Pollutants in Ash-Amended Biochar. To assess the environmental risk of using wood ash as an additive in biomass pyrolysis, selected biochars (ID 1, 3, 5, 6, 8, 10, 14, 18, and 21) were analyzed for PAHs, PCDD/Fs, and PCBs. The analyzed biochars contained 5.2−9.3 mg kg^{-1} PAHs, expressed as the sum of the 16 PAHs prioritized by the U.S. Environmental Protection Agency (Table S5). Thereby, no systematic correlation between the presence of PAHs and ash amendment, HTT, or RT was identified (Table S5). Thus, ash amendment did not promote PAH contamination of biochar. In each case, naphthalene accounted for most of the PAHs followed by phenanthrene, pyrene, and fluoranthene. These low-molecular-weight PAHs are well known to be dominant in biochar.[18,53] Furthermore, the relative content of the eight carcinogenic[54] PAHs was not changed by the ash amendment. In general, PAH content is strongly related to the biochar production process and can be limited by minimizing the tendency of pyro-gases to condensate on the pyrogenic solids through process engineering measures.[18,55] Thus, the absolute PAH content of biochars obtained from the laboratory pyrolysis unit is not representative for practice. Still, our data

confirmed that ash amendment does not elevate the PAH content of biochar.

The sum of PCBs (mass concentration expressed as toxicological equivalent, TEQ) increased from 0.41×10^{-3} ng kg^{-1} (0 wt % ash amendment, ID 1, Table S5) to 2.77×10^{-3} ng kg^{-1} (16.4 wt % ash amendment, ID 6). A higher ash amendment in the feedstock (42.6 wt %, ID 8) did not result in a further increase of PCB concentration (2.10×10^{-3} ng kg^{-1}) but resulted in the only biochar with a detectable content of PCDD/F (6.87×10^{-3} ng kg^{-1} TEQ, Table S5). In essence, concentrations of PCDD/F and PCBs were several orders of magnitude below the EBC thresholds.[21]

PCDD/F and PCBs can form during pyrolysis if precursors are present in the feedstock.[18] The wood ash used in this study did not contain PCDD/F or PCBs above the LOD, but 77 mg kg^{-1} extractable chlorine. As chlorine is a constituent of PCDD/F and PCBs, the increase of chlorine content in the feedstocks with ash amendment most likely enhanced the formation of polychlorinated contaminants (Table S5). However, less than 0.06% of ash-derived, extractable chlorine (Table S6) in the feedstock with, for example, 42.6 wt % ash amendment was incorporated into PCB and PCDD/F in the resulting biochar. Because these analytes were below the LOD in the biochar without ash amendment, this ratio could not be calculated for this biochar.

K-Availability in Ash-Amended Biochars and Agricultural Performance. The ash amendment strongly increased the amount of available K in the biochars (increase from 112 to 4758 mg kg^{-1} for 42.6 wt % ash amendment, Figure S2 and Table S2). The ratio of available K to total K was 5.9 to 6.9%, in the biochars with lower ash dosages (ID 1, 2, 3, and 6, Table S2). In the highest ash-enriched biochar, this ratio increased to 10.1%, which can be explained by a saturation of the biochar surface at these high contents of K.

To confirm the plant availability of K from ash-amended biochars, a pot trial with sunflower was conducted comparing different fertilization schemes. In the N- and S-fertilized treatments, that is, without addition of mineral K and P fertilizer, the ash-amended biochar (42.6 wt % ash amendment) leads to a 119% increase in dm aboveground biomass production compared to the control without biochar amendment (Figure 3A, gray columns, Table S9). When mineral P was provided additionally and only K-fertilization had to be compensated by the ash-amended biochar (NPS fertilized treatment), dm biomass production increased by 43% compared to the treatment without ash-amended biochar (Figure 3A, green columns).

In experiments with full mineral fertilization (NPKS), ash-amended biochar could partially replace mineral K-fertilization without decreases in biomass production (same total K-levels (mineral + biochar) in all treatments, Figure 3B). This was tested at two different biochar levels where K-deficiency-related symptoms showed a low incidence (Figure S9) also for the higher biochar dosage (supplying 8% of calculated K-demand, Treatment NPKS + 5 × BC-42.6%).

It is remarkable that the NPS + BC-42.6% ash-amended biochar treatment (Figure 3A, no mineral K-fertilization), supplying only 1.6% of calculated K-demand in plant-available form, yielded a dry biomass weight in the range of the fully fertilized treatments (Figure 3B, reduced mineral K-fertilization in presence of ash-amended biochars). This indicates that the extraction protocol (1 h in 0.01 M $CaCl_2$) proposed by Shepherd et al.[24] underestimated the plant-available K from
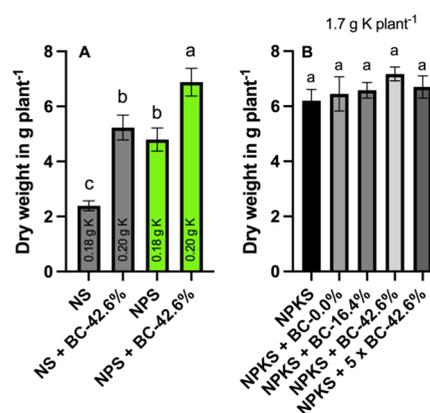
Figure 3. Yields of aboveground dry sunflower biomass for treatments fertilized with (A) nitrogen (N), phosphate (P), and sulfur (S) or N and S only with and without biochar amendment (biochar ID 8, 42.6 wt % ash amendment) and (B) fertilized with N, P, potassium (K), and S with and without biochar amendment (ID 1, 6, and 8). Error bars indicate two standard errors of the mean (standard deviation/$\sqrt{n}$) of replicated ($n = 5$) planting experiments. Different letters above error bars indicate a significant difference among the treatments (REGW-Q post hoc-test, $p < 0.05$). Treatments in panel A only included exchangeable K from the soil (0.18 g K pot^{-1}) and extractable K from the ash-amended biochar (0.02 g K pot^{-1}). In panel B, all treatments were fertilized to a total K content of 1.7 g pot^{-1}.

the biochars in our experiments. To determine the amount of plant-available K from ash-amended biochars, Wu et al.[17] applied an extraction procedure using NH_4OAc and HNO_3 extraction, which was in good accordance with long-term K-release in distilled water[17] and should be preferred over the $CaCl_2$-extraction method. Still, we clearly showed that K from ash-amended biochars is available for plant growth.

■ CONCLUSIONS

Using wood ash as an additive in biochar production provided an added value regarding the yield and C-conversion efficiency especially in the range of low ash dosages up to 10 wt %. Further studies using pure AAEM salt amendments to feedstocks with contrasting native AAEM content are required to achieve a mechanistic understanding and to define precise dosage recommendations to optimize biochar production. Future research should clarify our hypothesis that ash addition is less effective to promote biochar yield and C-conversion-efficiency when mineral-rich biomass is used. Incubation studies should be performed to quantify degradation rates of ash-amended biochars in soil to accurately calculate their C sequestration potential. Based on our results, including the toxicological assessment, the use of wood ash as a pyrolysis additive can be recommended to boost C-conversion efficiency of biomass conversion for PyCCS and to improve mineral nutrient cycling.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssuschemeng.1c07694.

Additional information on methods, further experimental data of biochars produced (SEM images, elemental composition, surface area, EEC, and DSC data), and detailed results from the greenhouse trial (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Nikolas Hagemann — *Ithaka Institute gGmbH, Freiburg 79106, Germany; Environmental Analytics, Agroscope, Zurich 8046, Switzerland; Ithaka Institute, Arbaz 1974, Switzerland*; Email: hagemann@ithaka-institut.org

Authors

Jannis Grafmüller — *Institute for Catalysis Research and Technology, Karlsruhe Institute of Technology, Eggenstein-Leopoldshafen 76344, Germany; Ithaka Institute gGmbH, Freiburg 79106, Germany; Institute of Sustainable Energy Systems and Institute of Process Engineering, Offenburg University of Applied Sciences, Offenburg 77652, Germany;* ⓘ orcid.org/0000-0001-8912-9537

Alexandra Böhm — *Institute for Catalysis Research and Technology, Karlsruhe Institute of Technology, Eggenstein-Leopoldshafen 76344, Germany*

Yiling Zhuang — *Center for Applied Geoscience, Environmental Mineralogy and Chemistry, Eberhard Karls University Tübingen, Tübingen 72076, Germany*

Stephanie Spahr — *Center for Applied Geoscience, Environmental Mineralogy and Chemistry, Eberhard Karls University Tübingen, Tübingen 72076, Germany; Leibniz Institute of Freshwater Ecology and Inland Fisheries (IGB), Berlin 12587, Germany;* ⓘ orcid.org/0000-0002-3004-3162

Pascale Müller — *Institute of Process Engineering, Offenburg University of Applied Sciences, Offenburg 77652, Germany*

Thomas N. Otto — *Institute for Catalysis Research and Technology, Karlsruhe Institute of Technology, Eggenstein-Leopoldshafen 76344, Germany;* ⓘ orcid.org/0000-0003-3137-7399

Thomas D. Bucheli — *Environmental Analytics, Agroscope, Zurich 8046, Switzerland;* ⓘ orcid.org/0000-0001-9971-3104

Jens Leifeld — *Climate and Agriculture Group, Agroscope, Zurich 8046, Switzerland*

Robin Giger — *Climate and Agriculture Group, Agroscope, Zurich 8046, Switzerland*

Michael Tobler — *Holz & Forst Consulting GmbH, Binningen 4102, Switzerland*

Hans-Peter Schmidt — *Ithaka Institute, Arbaz 1974, Switzerland*

Nicolaus Dahmen — *Institute for Catalysis Research and Technology, Karlsruhe Institute of Technology, Eggenstein-Leopoldshafen 76344, Germany*

Complete contact information is available at:
https://pubs.acs.org/10.1021/acssuschemeng.1c07694

■ REFERENCES

(1) Hagemann, N.; Spokas, K.; Schmidt, H.-P.; Kägi, R.; Böhler, M.; Bucheli, T. Activated Carbon, Biochar and Charcoal: Linkages and Synergies across Pyrogenic Carbon's ABCs. *Water* **2018**, *10*, 182.

(2) Schmidt, H.-P.; Anca-Couce, A.; Hagemann, N.; Werner, C.; Gerten, D.; Lucht, W.; Kammann, C. Pyrogenic Carbon Capture and Storage. *GCB Bioenergy* **2019**, *11*, 573−591.

(3) Ye, L.; Camps-Arbestain, M.; Shen, Q.; Lehmann, J.; Singh, B.; Sabir, M. Biochar Effects on Crop Yields with and without Fertilizer: A Meta-analysis of Field Studies Using Separate Controls. *Soil Use Manag.* **2020**, *36*, 2−18.

(4) Werner, C.; Schmidt, H.-P.; Gerten, D.; Lucht, W.; Kammann, C. Biogeochemical Potential of Biomass Pyrolysis Systems for Limiting Global Warming to 1.5 °C. *Environ. Res. Lett.* **2018**, *13*, No. 044036.

(5) Buss, W.; Jansson, S.; Mašek, O. Unexplored Potential of Novel Biochar-Ash Composites for Use as Organo-Mineral Fertilizers. *J. Cleaner Prod.* **2019**, *208*, 960−967.

(6) Buss, W.; Jansson, S.; Wurzer, C.; Mašek, O. Synergies between BECCS and Biochar—Maximizing Carbon Sequestration Potential by Recycling Wood Ash. *ACS Sustainable Chem. Eng.* **2019**, *7*, 4204−4209.

(7) Di Blasi, C. Modeling Chemical and Physical Processes of Wood and Biomass Pyrolysis. *Prog. Energy Combust. Sci.* **2008**, *34*, 47−90.

(8) Mašek, O.; Buss, W.; Brownsort, P.; Rovere, M.; Tagliaferro, A.; Zhao, L.; Cao, X.; Xu, G. Potassium Doping Increases Biochar Carbon Sequestration Potential by 45%, Facilitating Decoupling of Carbon Sequestration from Soil Improvement. *Sci. Rep.* **2019**, *9*, 5514.

(9) Di Blasi, C.; Galgano, A.; Branca, C. Influences of the Chemical State of Alkaline Compounds and the Nature of Alkali Metal on Wood Pyrolysis. *Ind. Eng. Chem. Res.* **2009**, *48*, 3359−3369.

(10) Patwardhan, P. R.; Satrio, J. A.; Brown, R. C.; Shanks, B. H. Influence of Inorganic Salts on the Primary Pyrolysis Products of Cellulose. *Bioresour. Technol.* **2010**, *101*, 4646−4655.

(11) Zhao, L.; Cao, X.; Zheng, W.; Kan, Y. Phosphorus-Assisted Biomass Thermal Conversion: Reducing Carbon Loss and Improving Biochar Stability. *PLoS One* **2014**, *9*, No. e115373.

(12) Anca-Couce, A. Reaction Mechanisms and Multi-Scale Modelling of Lignocellulosic Biomass Pyrolysis. *Prog. Energy Combust. Sci.* **2016**, *53*, 41−79.

(13) Anca-Couce, A.; Mehrabian, R.; Scharler, R.; Obernberger, I. Kinetic Scheme of Biomass Pyrolysis Considering Secondary Charring Reactions. *Energy Convers. Manage.* **2014**, *87*, 687−696.

(14) Jalalabadi, T.; Glenn, M.; Tremain, P.; Moghtaderi, B.; Donne, S.; Allen, J. Modification of Biochar Formation during Slow Pyrolysis in the Presence of Alkali Metal Carbonate Additives. *Energy Fuels* **2019**, *33*, 11235−11245.

(15) Anca-Couce, A.; Dieguez-Alonso, A.; Zobel, N.; Berger, A.; Kienzl, N.; Behrendt, F. Influence of Heterogeneous Secondary Reactions during Slow Pyrolysis on Char Oxidation Reactivity of Woody Biomass. *Energy Fuels* **2017**, *31*, 2335−2344.

(16) Vassilev, S. V.; Baxter, D.; Andersen, L. K.; Vassileva, C. G. An Overview of the Composition and Application of Biomass Ash. Part 1.

Phase—Mineral and Chemical Composition and Classification. *Fuel* **2013**, *105*, 40−76.

(17) Wu, W.; Yan, B.; Zhong, L.; Zhang, R.; Guo, X.; Cui, X.; Lu, W.; Chen, G. Combustion Ash Addition Promotes the Production of K-Enriched Biochar and K Release Characteristics. *J. Cleaner Prod.* **2021**, *311*, No. 127557.

(18) Bucheli, T.D.; Hilber, I.; Schmidt, H.-P. Polycyclic Aromatic Hydrocarbons and Polychlorinated Aromatic Compounds in Biochar. In *Biochar for Environmental Management*; Lehmann, J., Joseph, S., Eds.; Routledge, 2015, 627−656.

(19) Hagemann, N.; Schmidt, H.-P.; Kägi, R.; Böhler, M.; Sigmund, G.; Maccagnan, A.; McArdell, C. S.; Bucheli, T. D. Wood-Based Activated Biochar to Eliminate Organic Micropollutants from Biologically Treated Wastewater. *Sci. Total Environ.* **2020**, *730*, No. 138417.

(20) Klüpfel, L.; Keiluweit, M.; Kleber, M.; Sander, M. Redox Properties of Plant Biomass-Derived Black Carbon (Biochar). *Environ. Sci. Technol.* **2014**, *48*, 5601−5611.

(21) EBC. "*European Biochar Certificate -Guidelines for a Sustainable Production of Biochar*." European Biochar Foundation (EBC), Arbaz, Switzerland. (Http:European-Biochar.Org). Version 9.2E of 2nd December 2020. 2012.

(22) Leifeld, J.; von Lützow, M. Chemical and Microbial Activation Energies of Soil Organic Matter Decomposition. *Biol. Fertil. Soils* **2014**, *50*, 147−153.

(23) Leifeld, J. Thermal Stability of Black Carbon Characterised by Oxidative Differential Scanning Calorimetry. *Org. Geochem.* **2007**, *38*, 112−127.

(24) Shepherd, J. G.; Buss, W.; Sohi, S. P.; Heal, K. V. Bioavailability of Phosphorus, Other Nutrients and Potentially Toxic Elements from Marginal Biomass-Derived Biochar Assessed in Barley (Hordeum Vulgare) Growth Experiments. *Sci. Total Environ.* **2017**, *584-585*, 448−457.

(25) Dubinin, M. M. A Study of the Porous Structure of Active Carbons Using a Variety of Methods. *Q. Rev., Chem. Soc.* **1955**, *9*, 101−114.

(26) Sigmund, G.; Hüffer, T.; Hofmann, T.; Kah, M. Biochar Total Surface Area and Total Pore Volume Determined by N2 and CO2 Physisorption Are Strongly Influenced by Degassing Temperature. *Sci. Total Environ.* **2017**, *580*, 770−775.

(27) LTZ. *Grunddüngung im Ackerbau - Merkblätter für die umweltgerechte Landbewirtschaftung* Accessed on 18.07.2021. https://ltz.landwirtschaft-bw.de/pb/Lde/Startseite/Service/Merkblatt+fuer+die+umweltgerechte+Landbewirtschaftung.

(28) Cornelissen, G.; Martinsen, V.; Shitumbanuma, V.; Alling, V.; Breedveld, G.; Rutherford, D.; Sparrevik, M.; Hale, S.; Obia, A.; Mulder, J. Biochar Effect on Maize Yield and Soil Characteristics in Five Conservation Farming Sites in Zambia. *Agronomy* **2013**, *3*, 256−274.

(29) Schmidt, H.; Pandit, B.; Martinsen, V.; Cornelissen, G.; Conte, P.; Kammann, C. Fourfold Increase in Pumpkin Yield in Response to Low-Dosage Root Zone Application of Urine-Enhanced Biochar to a Fertile Tropical Soil. *Agriculture* **2015**, *5*, 723−741.

(30) Field, A. P. *Discovering Statistics Using IBM SPSS Statistics: And Sex and Drugs and Rock "n" Roll*, 4th edition.; Sage: Los Angeles, 2013.

(31) Neiva, D. M.; Araújo, S.; Gominho, J.; Carneiro, A. C.; Pereira, H. An Integrated Characterization of Picea Abies Industrial Bark Regarding Chemical Composition, Thermal Properties and Polar Extracts Activity. *PLoS One* **2018**, *13*, No. e0208270.

(32) Ruiz-Aquino, F.; González-Peña, M. M.; Valdez-Hernández, J. I.; Revilla, U. S.; Romero-Manzanares, A. Chemical Characterization and Fuel Properties of Wood and Bark of Two Oaks from Oaxaca, Mexico. *Ind. Crops Prod.* **2015**, *65*, 90−95.

(33) Lee, Y.; Park, J.; Ryu, C.; Gang, K. S.; Yang, W.; Park, Y.-K.; Jung, J.; Hyun, S. Comparison of Biochar Properties from Biomass Residues Produced by Slow Pyrolysis at 500°C. *Bioresour. Technol.* **2013**, *148*, 196−201.

(34) Brown, R. C.; del Campo, B.; Boateng, A. A.; Garci-perez, M. Fundamentals of Biochar Production. In *Biochar for environmental management: science, technology and implementation*; Lehmann, J., Joseph, S., Eds.; Routledge, Taylor & Francis Group: London; New York, 2015.

(35) Chia, C. H.; Downie, A.; Munroe, P. Characteristics of Biochar: Physical and Structural Properties. In *Biochar for environmental management: science, technology and implementation*; Lehmann, J., Joseph, S., Eds.; Routledge, Taylor & Francis Group: London; New York, 2015. DOI: 10.4324/9780203762264-12.

(36) Keiluweit, M.; Nico, P. S.; Johnson, M. G.; Kleber, M. Dynamic Molecular Structure of Plant Biomass-Derived Black Carbon (Biochar). *Environ. Sci. Technol.* **2010**, *44*, 1247−1253.

(37) Nowakowski, D.; Jones, J.; Brydson, R.; Ross, A. Potassium Catalysis in the Pyrolysis Behaviour of Short Rotation Willow Coppice. *Fuel* **2007**, *86*, 2389−2402.

(38) BGH. *Bundesgütegemeinschaft Holzasche: Verwertung von Holzaschen URL* Accessed on 18.07.2021. https://www.kompost.de/fileadmin/docs/Archiv/Thema_Position/5.3.2_Thema_Verwertung_von_Holzaschen_2013-final.pdf (accessed 2021 -02 -08).

(39) Hakilla, P. *Utilization of Residual Forest Biomass*; Springer Berlin Heidelberg: Berlin, Heidelberg, 1989.

(40) Pitman, R. M. Wood Ash Use in Forestry - a Review of the Environmental Impacts. *Forestry* **2006**, *79*, 563−588.

(41) Lehmann, J.; Abiven, S.; Kleber, M.; Pan, G.-X. Persistence of Biochar in Soil. In *Biochar for environmental management: science, technology and implementation*; Lehmann, J., Joseph, S., Eds.; Routledge, Taylor & Francis Group: London; New York, 2015; 48.

(42) Leng, L.; Huang, H.; Li, H.; Li, J.; Zhou, W. Biochar Stability Assessment Methods: A Review. *Sci. Total Environ.* **2019**, *647*, 210−222.

(43) Wang, H.; Nan, Q.; Waqas, M.; Wu, W. Stability of Biochar in Mineral Soils: Assessment Methods, Influencing Factors and Potential Problems. *Sci. Total Environ.* **2022**, *806*, No. 150789.

(44) Budai, A.; Zimmerman, A. R.; Cowie, A. L.; Webber, J. B. W.; Singh, B. P.; Glaser, B.; Masiello, C. A.; Shields, F.; Lehmann, J.; Arbestain, M. C.; Williams, M.; Sohi, S.; Joseph, S. *Biochar Carbon Stability Test Method: An Assessment of Methods to Determine Biochar Carbon Stability*. Int. Biochar Initiat. 2013, 30.

(45) Harvey, O. R.; Kuo, L.-J.; Zimmerman, A. R.; Louchouarn, P.; Amonette, J. E.; Herbert, B. E. An Index-Based Approach to Assessing Recalcitrance and Soil Carbon Sequestration Potential of Engineered Black Carbons (Biochars). *Environ. Sci. Technol.* **2012**, *46*, 1415−1421.

(46) Plante, A. F.; Fernández, J. M.; Haddix, M. L.; Steinweg, J. M.; Conant, R. T. Biological, Chemical and Thermal Indices of Soil Organic Matter Stability in Four Grassland Soils. *Soil Biol. Biochem.* **2011**, *43*, 1051−1058.

(47) Sanderman, J.; Grandy, A. S. Ramped Thermal Analysis for Isolating Biologically Meaningful Soil Organic Matter Fractions with Distinct Residence Times. *Soil* **2020**, *6*, 131−144.

(48) Saquing, J. M.; Yu, Y.-H.; Chiu, P. C. Wood-Derived Black Carbon (Biochar) as a Microbial Electron Donor and Acceptor. *Environ. Sci. Technol. Lett.* **2016**, *3*, 62−66.

(49) Sun, T.; Levin, B. D. A.; Guzman, J. J. L.; Enders, A.; Muller, D. A.; Angenent, L. T.; Lehmann, J. Rapid Electron Transfer by the Carbon Matrix in Natural Pyrogenic Carbon. *Nat. Commun.* **2017**, *8*, 14873.

(50) Chacón, F. J.; Sánchez-Monedero, M. A.; Lezama, L.; Cayuela, M. L. Enhancing Biochar Redox Properties through Feedstock Selection, Metal Preloading and Post-Pyrolysis Treatments. *Chem. Eng. J.* **2020**, *395*, No. 125100.

(51) Xin, D.; Saha, N.; Reza, M. T.; Hudson, J.; Chiu, P. C. Pyrolysis Creates Electron Storage Capacity of Black Carbon (Biochar) from Lignocellulosic Biomass. *ACS Sustainable Chem. Eng.* **2021**, *9*, 6821−6831.

(52) Ippolito, J. A.; Cui, L.; Kammann, C.; Wrage-Mönnig, N.; Estavillo, J. M.; Fuertes-Mendizabal, T.; Cayuela, M. L.; Sigua, G.;

Novak, J.; Spokas, K.; Borchard, N. Feedstock Choice, Pyrolysis Temperature and Type Influence Biochar Characteristics: A Comprehensive Meta-Data Analysis Review. *Biochar* **2020**, *2*, 421−438.

(53) Hilber, I.; Mayer, P.; Gouliarmou, V.; Hale, S. E.; Cornelissen, G.; Schmidt, H.-P.; Bucheli, T. D. Bioavailability and Bioaccessibility of Polycyclic Aromatic Hydrocarbons from (Post-Pyrolytically Treated) Biochars. *Chemosphere* **2017**, *174*, 700−707.

(54) Andersson, J. T.; Achten, C. Time to Say Goodbye to the 16 EPA PAHs? Toward an Up-to-Date Use of PACs for Environmental Purposes. *Polycyclic Aromat. Compd.* **2015**, *35*, 330−354.

(55) Odinga, E. S.; Gudda, F. O.; Waigi, M. G.; Wang, J.; Gao, Y. Occurrence, Formation and Environmental Fate of Polycyclic Aromatic Hydrocarbons in Biochars. *Fundam. Res.* **2021**, *1*, 296−305.

■ NOTE ADDED AFTER ASAP PUBLICATION

This paper was published ASAP on February 8, 2022 with a production error in Equation 2. The corrected version was reposted on February 15, 2022.