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**Citation for published version:**

Buss, W, Jansson, S, Wurzer, C & Mašek, O 2019, 'Synergies between BECCS and Biochar - Maximizing Carbon Sequestration Potential by Recycling Wood Ash', *ACS Sustainable Chemistry and Engineering*, vol. 7, no. 4, pp. 4204-4209. <https://doi.org/10.1021/acssuschemeng.8b05871>

**Digital Object Identifier (DOI):**

[10.1021/acssuschemeng.8b05871](https://doi.org/10.1021/acssuschemeng.8b05871)

**Link:**

[Link to publication record in Edinburgh Research Explorer](#)

**Document Version:**

Peer reviewed version

**Published In:**

ACS Sustainable Chemistry and Engineering

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# 1 Synergies between BECCS and biochar - maximizing 2 carbon sequestration potential by recycling wood ash

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11 Paper type: Original Research Article

## 12 Abstract

13 Bioenergy carbon capture and storage (BECCS) and biochar are key carbon-negative  
14 technologies. In this study, synergies between these technologies were explored by using ash  
15 from wood combustion, a by-product from BECCS, as an additive (0, 5, 10, 20, 50 wt%) in  
16 biochar production (wood pyrolysis at 450°C). The addition of wood ash catalysed biochar  
17 formation and increased the yield of fixed carbon (FC) (per dry feedstock), i.e. the  
18 sequesterable carbon per wood input. At the highest ash addition (50%), 45% less wood was  
19 needed to yield the same amount of FC. Since the land area available for growing biomass is  
20 becoming scarcer, our approach significantly increases biochar's potential to sequester  
21 carbon. However, increasing the feedstock ash content results in less feedstock carbon  
22 available for conversion into FC. Consequently, the yield of FC per pyrolysis run (based on  
23 ash-free feedstock) in the 50% ash-amended material was lower than in the control. An  
24 economic analysis showed that the 20% ash-amended biochar brings the biggest cost savings  
25 over the control, with a 15% decrease in CO<sub>2</sub>-abatement costs. Biochar-ash composites  
26 increase the carbon sequestration potential of biochar significantly, reduce the CO<sub>2</sub>-  
27 abatement costs and recycle nutrients which can result in increased plant growth in turn,  
28 bringing synergies for BECCS and biochar deployment.

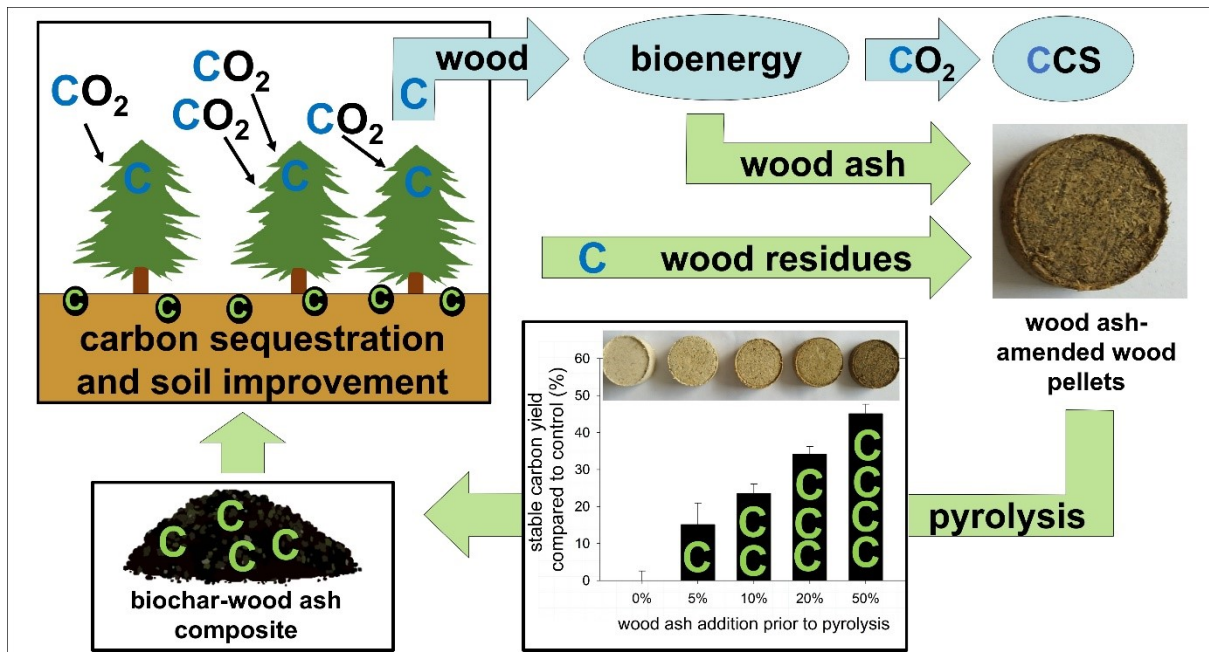
29      **Keywords**

30      CO<sub>2</sub> abatement; carbon stability; fixed carbon; proximate analysis; combustion

31      **Abbreviations**

32      FC, fixed carbon; BECCS, bioenergy carbon capture and storage

## Graphical Abstract



## 36 **1 Introduction**

37 Bioenergy carbon capture and storage (BECCS) is a technology that generates energy from  
38 biomass and subsequently captures and stores the emitted CO<sub>2</sub> in geological formations.

39 While the gaseous emissions are captured and used, the solid residue, the ash, which makes  
40 up around 1% of the mass of wood, is often landfilled <sup>1-3</sup>. Although, wood ash is not a  
41 problematic material from a technical perspective, there is a clear potential for improvement  
42 when it comes to handling and resource utilization. With up-scaling and widespread use of  
43 BECCS as a carbon-negative technology, the amount of wood ash could increase drastically  
44 in coming years which threatens the sustainability of the system <sup>3</sup>.

45 Biochar is the product formed during pyrolysis of biomass, a process using elevated  
46 temperatures (350-750°C) and oxygen limited conditions. The thermochemical conversion  
47 changes the structure of the biomass, increasing its carbon content and the crosslinking of  
48 carbon atoms resulting in a highly stable, aromatic carbon lattice <sup>4,5</sup>. Its chemical and  
49 microbial stability has resulted in biochar being proposed for sequestration of carbon in soil  
50 to mitigate climate change <sup>4,6</sup>. Biochar is considered to have lower negative environmental  
51 impact (land use, water use, nutrient use and albedo), lower costs and energy requirements  
52 compared to other carbon-negative technologies <sup>7</sup>.

53 Although there is still debate about precisely how long biochar remains in soil, many studies  
54 have shown that biochar has a much higher stability than its feedstock material <sup>4,8-11</sup>. In the  
55 absence of methods to determine the exact residence time of biochar in soil, proximate  
56 analysis has been suggested as one of the methods to assess the biochar fraction that is stable  
57 for at least 100 years in soil <sup>11-14</sup>, the timeframe that is typically used for climate change  
58 simulations <sup>15</sup>.

59 During pyrolysis, three co-products (pyrolysis liquids, gases and solid biochar) are formed.  
60 The product distribution and properties depend on a number of factors, such as highest  
61 treatment temperature (HTT) or feedstock type <sup>16,17</sup>. Increasing the carbon retention in the  
62 solids and the stable carbon content within biochar, maximises the carbon sequestration  
63 potential of biochar. It is known that alkali and alkaline earth metals in the ash of biomass can  
64 catalyse the biochar formation <sup>18-20</sup> and hence can increase the carbon sequestration potential  
65 of biochar <sup>21</sup>. However, to our knowledge no one has investigated the effect of complex  
66 mixtures of minerals in waste materials that include alkali and alkaline earth metals, such as  
67 biomass ash, on the stable carbon yield in biochar. This can be a very valuable proposition as  
68 it would bring benefits for biochar production while simultaneously managing biomass ash,  
69 e.g. as a by-product from BECCS.

70 The aim of this study was to investigate the effect of wood ash amendment on the carbon  
71 sequestration potential and costs of biochar. Spruce wood was blended with ash from a wood  
72 boiler in different ratios, then pelletised and pyrolysed at 450°C. The resulting biochar was  
73 analysed for its carbon stability via proximate analysis and the fixed carbon (FC) yield was  
74 determined. Subsequently, the CO<sub>2</sub> abatement costs using wood ash-amended biochar were  
75 calculated and compared to unamended biochar.

## 76 **2 Materials and Methods**

### 77 **2.1 Feedstock preparation**

78 Wood ash was sourced from a district heating plant in the north of Sweden (Bureå) which  
79 uses a blend of spruce and pine as fuel.

80 For producing wood ash-enriched wood pellets, spruce wood was ground to a particle size of  
81 < 2 mm and wood ash was sieved to < 0.5 mm. Blends of 3 g spruce wood with 0, 5, 10, 20  
82 and 50% wood ash (w/w) were prepared in ziplock bags and 2 mL of water was added to  
83 avoid density separation and ensure thorough mixing.

84 A stainless-steel die (internal diameter of 25.4 mm) was used to produce 2 pellets at a time  
85 (divided by a stainless-steel spacer) in an oven at 160°C for 1.5 hours. More details can be  
86 found in Buss et al. (2018).

### 87 **2.2 Thermogravimetric analysis (TGA) – pyrolysis**

88 Around 40 mg pieces were broken off the spruce-wood ash pellets and pyrolysed under  
89 nitrogen (flow of 50 mL min<sup>-1</sup>) in a Mettler-Toledo TGA/DSC1 thermogravimetric analyser  
90 in 150 µL alumina crucibles. The samples were heated from a starting temperature of 25°C  
91 up to HTT of 450°C at a heating rate of 90°C min<sup>-1</sup> and then kept at HTT for 10 min. After  
92 pyrolysis, the crucibles were left in the furnace under a nitrogen atmosphere to cool down to  
93 room temperature. The analysis was performed in 5 replicates for each of the 5 feedstocks.

### 94 **2.3 Thermogravimetric analysis (TGA) – proximate analysis**

95 Following pyrolysis, we performed proximate analysis in the same TGA/DSC instrument to  
96 determine the biochar fixed carbon (FC) content. Previous studies have shown that FC is a  
97 good predictor for the carbon sequestration potential of biochar and that it approximates the  
98 fraction that is stable after around ~100 years of biochar ageing in soil <sup>11–14</sup>.

99 After pyrolysis, the biochars (10-30 mg) were finely ground and transferred back into the 150  
100  $\mu\text{L}$  alumina crucibles. The material was heated-up to  $900^{\circ}\text{C}$  in a nitrogen atmosphere  
101 (determination of volatile matter content), followed by switching from nitrogen to air flow to  
102 oxidize the biochar. The % of the biochar that was oxidized is the FC content used in this  
103 study to assess the carbon stability. The remaining fraction is the ash content.

## 104 **2.4 Data processing and statistics**

### 105 **2.4.1 Biochar yield**

106 The following equations were used to calculate the biochar yields:

$$107 \quad (1) \text{ biochar yield (\% feedstock)} = \frac{\text{biochar (g)}}{\text{feedstock (g)}}$$

$$108 \quad (2) \text{ ash free biochar yield (\% feedstock)} = \frac{\text{ash free biochar (g)}}{\text{feedstock (g)}}$$

$$109 \quad (3) \text{ ash free biochar yield (\% ash free feedstock)} = \frac{\text{ash free biochar (g)}}{\text{ash free feedstock (g)}}$$

110 All values are on dry basis.

### 111 **2.4.2 Fixed carbon (FC)**

$$112 \quad (4) \text{ FC content (\% biochar)} = \frac{\text{FC (g)}}{\text{biochar (g)}}$$

$$113 \quad (5) \text{ FC content (\% ash free biochar)} = \frac{\text{FC (g)}}{\text{ash free biochar (g)}}$$

$$114 \quad (6) \text{ FC yield (\% feedstock)} = \frac{\text{biochar (g)}}{\text{feedstock (g)}} * \text{FC content (\% biochar)}$$

$$115 \quad = \frac{\text{ash free biochar (g)}}{\text{feedstock (g)}} * \text{FC content (\% ash free biochar)}$$



116 (7) *FC yield (% ash free feedstock)*

$$117 = \frac{\text{biochar (g)}}{\text{ash free feedstock (g)}} * \text{FC content (\% biochar)}$$

$$118 = \frac{\text{ash free biochar (g)}}{\text{ash free feedstock (g)}} * \text{FC content (\% ash free biochar)}$$

119 Subsequently, each replicate of the treatments was subtracted from the mean of the  
120 unamended control and given as percentage change compared to the control. One-way  
121 ANOVAs followed by Tukey's post-hoc tests were performed with SigmaPlot 11.0 to  
122 determine significant differences with a significance level of 0.05.

### 123 **2.4.3 CO<sub>2</sub> abatement costs**

124 Feedstock, biochar production and application costs in USD were taken from Table 10 in  
125 Shackley et al. (2011) based on sawmill residues. Sales for electricity and renewable  
126 obligation certificates used in Shackley et al. were not taken into account since the excess  
127 energy from the pyrolysis unit would be used to dry the feedstock. The costs of feedstock and  
128 biochar production per t of biochar were converted into costs per t of feedstock based on the  
129 biochar yield (% feedstock) of 22.4% of the untreated control in our study (SI Table 1).  
130 Wood ash was considered a residue and although negative costs could have been assumed  
131 (gate fees), in our scenario the more conservative assumption of zero costs for wood ash was  
132 used.

133 Furthermore, pelleting costs of 7.5 USD t<sup>-1</sup> feedstock were, based on Mani et al. (2006)  
134 (excluding material costs (already taken into account), personnel costs (assuming the  
135 personnel operating the pyrolysis equipment also operates the pelleting machines) and drying  
136 costs (excess heat from the pyrolysis unit is used to dry the wood)).

137 The overall costs were split into three fractions:

138 (i) Feedstock and feedstock transport costs (50 USD t<sup>-1</sup> feedstock) were multiplied by the FC  
139 yield (% ash-free feedstock) which corresponds to the amount of ash-free wood needed to  
140 produce 1 t of FC.

141 (ii) Costs for biochar production consisting of pelleting (capital and operation), labour, plant  
142 costs and capital costs (31 USD t<sup>-1</sup> feedstock) which were multiplied by the FC yield (%  
143 feedstock) which is the amount of FC produced per t of feedstock (wood + ash addition).

144 (iii) Costs for biochar storage and application (22.5 USD t<sup>-1</sup> biochar) which were multiplied  
145 by the FC content (% biochar) of the biochar which corresponds to the costs for deployment  
146 of 1 t of FC in the soil.

147 The sum of the costs was converted into CO<sub>2</sub> abatement costs in USD, the costs for  
148 sequestering 1 t of biochar-CO<sub>2</sub> in soil.

### 149 **3 Results**

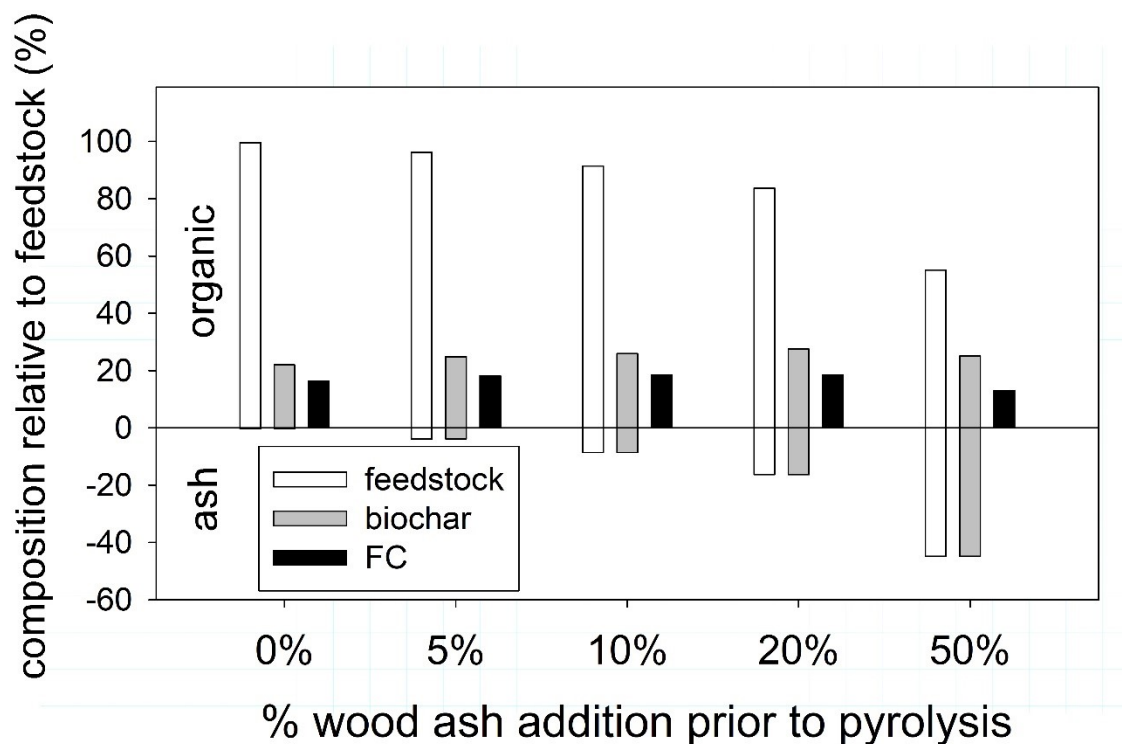
150 In a previous study, we showed that wood ash can catalyse biochar formation by shifting the  
151 exothermic peak during pyrolysis to lower temperatures<sup>22</sup>. Here we show for the first time  
152 that wood ash addition can also increase the FC yield.

153 The amount of ash-free biochar (proportion of “organic” fraction in biochar in Figure 1)  
154 slightly increased with wood ash addition (Figure 1; SI Table 1). Importantly, far less wood  
155 (proportion of “organic” fraction in feedstock in Figure 1) was needed to generate the same  
156 amount of ash-free biochar when extra wood ash was added (= increase in ash-free biochar  
157 yield; SI Table 1) (see section 2.4 for equations). The FC content (% biochar) in the biochar  
158 decreased significantly with wood ash addition because of the extra ash in the feedstock  
159 which decreased the amount of carbon in the feedstock available for conversion into FC  
160 (Figure 2A, B).

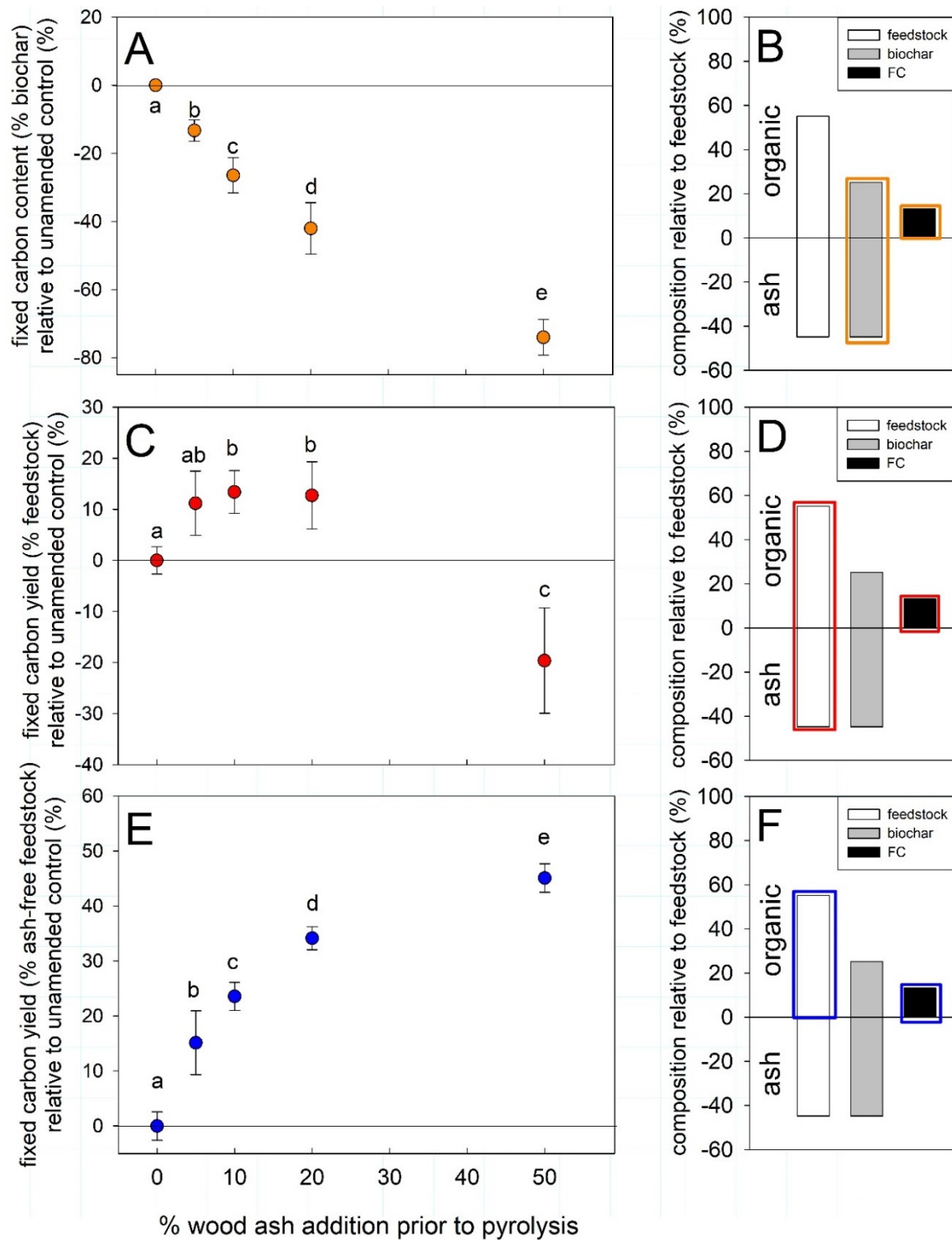
161 The FC yield (% feedstock) (Figure 2C, D), which is the amount of FC produced per dry  
162 feedstock input (consisting of organic fraction and ash), increased significantly with wood  
163 ash addition (Figure 2C) due to the increase in ash-free biochar yield (see section 2.4 for  
164 equations). Yet, the FC yield (% feedstock) in the 50% ash-amended biochar was 19.6%  
165 lower than the control (Figure 2C); less FC was generated per pyrolysis run as 50% of the  
166 feedstock material was organic-free ash which cannot be converted into FC.

167 The FC yield (% ash-free feedstock) (Figure 2E, F) was significantly higher in the 50% ash-  
168 amended treatment compared to the control (Figure 2E). The spruce wood (organic fraction  
169 in the feedstock) was converted into FC with a much higher conversion efficiency when  
170 wood ash was added compared to unamended spruce.

171 In a previous study, we pyrolysed pellets with the same ash contents in an auger pyrolysis  
172 unit with similar results for biochar yield and FC content confirming the reproducibility of  
173 the results in a continuous unit <sup>22</sup>.

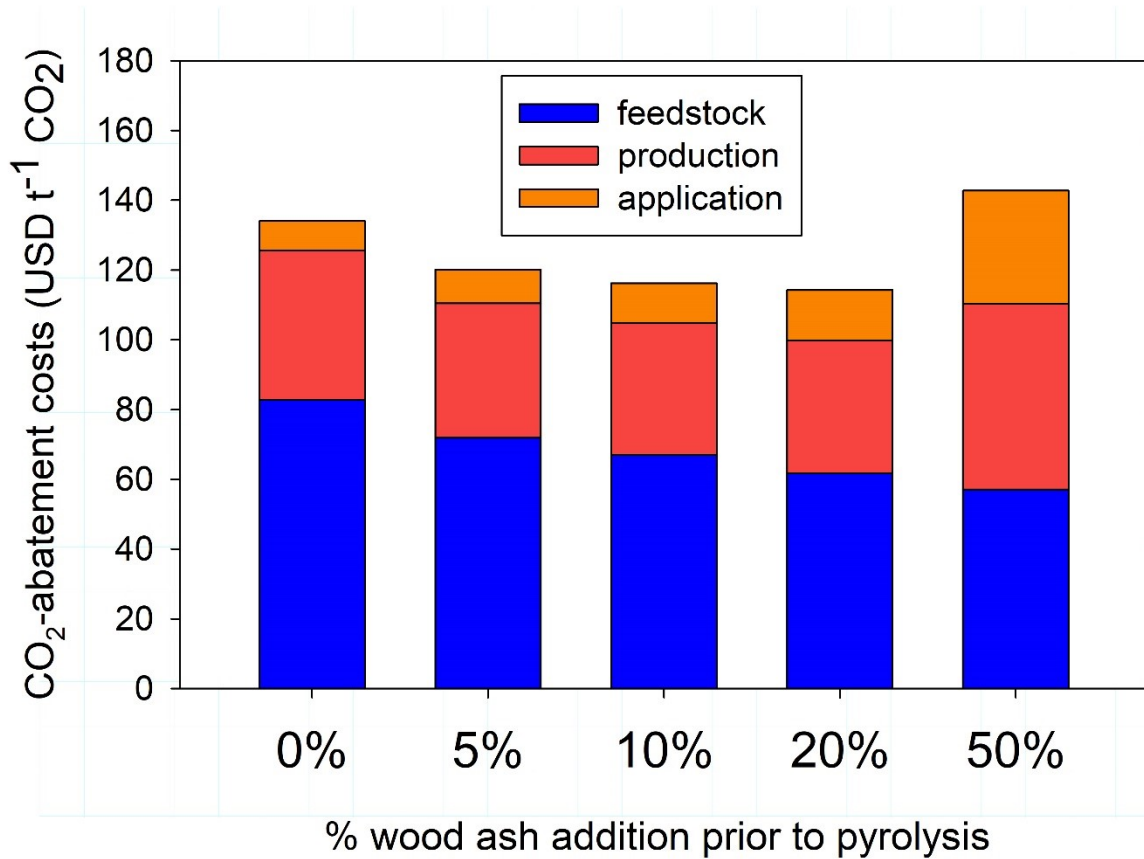


174  
175 Figure 1: Composition of the feedstock and biochar in organic fraction (positive values) and  
176 ash fraction (negative values) with increasing wood ash addition. The proportion of biochar  
177 and fixed carbon (FC) is shown relative to the feedstock (biochar and FC yield).



178

179 Figure 2: Effect of wood ash addition to spruce wood prior to pyrolysis on (A) FC content (%  
 180 biochar), (C) FC yield (% feedstock) and (E) FC yield (% ash-free feedstock) compared to  
 181 the unamended control, respectively (n = 5). The letters indicate statistically significant  
 182 differences (one-way ANOVA and Tukey post-hoc test) with a significance level of 0.05.  
 183 The right panels (B, D, F) show how the parameters were calculated (ratio of the highlighted  
 184 bars) based on Figure 1 using the 50% ash-amended material as example.



185

186 Figure 3: CO<sub>2</sub> abatement costs for sequestering carbon in soil in the form of (wood-ash  
 187 amended) pine biochar in USD t<sup>-1</sup> CO<sub>2</sub>. Costs were separated into costs for feedstock, biochar  
 188 production and application. Data are based on saw mill residues from Shackley et al. (2011)  
 189 and costs for pelletising were taken from Mani et al. (2006).

190

## 191 **4 Discussion**

### 192 **4.1 Carbon sequestration potential of biochar**

193 Our findings have significant implications for the carbon sequestration potential of biochar.  
194 For maximising the amount of FC per pyrolysis run (or per hour for continuous pyrolysis  
195 units), the optimal ash content in the feedstock in our experiment was 5-15% which increased  
196 the FC yield (% feedstock) by ~20% (Figure 2C; SI Figure 1).

197 While the addition of 50% wood ash to spruce reduced the amount of FC produced per  
198 pyrolysis run (Figure 2C), it increased the FC yield (% ash-free feedstock) per wood biomass  
199 input by  $45.8 \pm 2.6\%$  (Figure 2E). Therefore, if the goal is to minimise the amount of biomass  
200 needed to produce 1 t of FC, 50% wood ash addition yielded the best results (Figure 2E).

201 This is a significant finding and highlights the need to consider the ash content when  
202 assessing the carbon sequestration potential of biochar.

203 Adding wood ash to biochar converts the organic fraction of wood into stable carbon much  
204 more efficiently. With increasing competition for biomass resources, decreasing the amount  
205 of biomass needed to sequester 1 t of CO<sub>2</sub> can be vital for feasibility of large-scale biochar  
206 deployment. The carbon sequestration potential of biochar has been reported to be 0.7-1.8 Gt  
207 C<sub>eq.</sub> y<sup>-1</sup> <sup>6,7,25</sup> and with 50% ash addition using the same amount of available biomass, this  
208 would increase to 1.2-2.6 Gt C<sub>eq.</sub> y<sup>-1</sup>.

### 209 **4.2 Biochar CO<sub>2</sub>-abatement costs**

210 Our results also have implications for the CO<sub>2</sub>-abatement costs, i.e., the costs to sequester 1 t  
211 of biochar-carbon in the ground (Figure 3). The feedstock input costs (including feedstock  
212 transportation) are drastically reduced with the addition of 50% wood ash, because the  
213 conversion efficiency from woody biomass into FC is much higher. However, due to the  
214 extra ash content in the material, a longer production time is necessary (in a continuous

215 pyrolysis unit) or more production runs (in a batch unit) to produce the same amount of FC  
216 compared to the feedstock without wood ash addition. Therefore, the biochar production  
217 costs are higher (Figure 3). Furthermore, the resulting biochar has a lower FC content (%  
218 biochar) compared to the untreated or the 20% wood ash-amended sample and hence, more  
219 biochar needs to be applied to sequester the same amount of FC in the ground, contributing  
220 additional costs for biochar application.

221 With 50% wood ash addition, overall, the costs for feedstock, biochar production and  
222 application are 6% higher than in the unamended control (Figure 3). With increasing  
223 feedstock costs due to competition for land area and biomass materials and decreasing  
224 biochar production costs due to economy of scale, the CO<sub>2</sub>-abatement costs, however, will  
225 become lower compared to pure pine biochar.

226 The 20% ash sample has cost advantages in both, feedstock and biochar production costs,  
227 over the unamended control, therefore, will be cheaper irrespective of the feedstock costs.

228 With 20% wood ash addition the overall CO<sub>2</sub>-abatement costs are the lowest with 114 USD t<sup>-1</sup>  
229 CO<sub>2</sub> compared to 134 USD t<sup>-1</sup> CO<sub>2</sub> in the control which are cost savings of 15% (Figure 3).

### 230 **4.3 BECCS and biochar synergies**

231 While other studies showed increases in biochar yield and / or carbon stability using  
232 relatively high concentrations of pure chemicals <sup>21,26-28</sup>, here we show for the first time that  
233 the use of underutilised material, biomass ash (e.g. from BECCS operations), that is still often  
234 landfilled can significantly increase the carbon sequestration potential of biochar and  
235 decrease the CO<sub>2</sub>-abatement costs. Besides sequestering carbon in the ground, incorporating  
236 biochar-ash composites recycles nutrients back to the plants. Biochar application will allow  
237 for increased plant growth due to improvement of the soil properties by biochar and direct  
238 nutrient supply <sup>22,29</sup>. Although biochar and BECCS operations are in competition for biomass,  
239 using biomass ash and some of the woody material designated for BECCS to produce and



240 apply biochar-ash composites in biomass plantations brings synergies for both processes.  
241 Increased plant growth after biochar-ash application will increase the amount of biomass  
242 available for BECCS in the next biomass cycle. This approach offers new synergies among  
243 different renewable energy and climate change mitigation technologies, such as biochar,  
244 bioenergy, and BECCS, making them more economical, productive and environmentally  
245 sustainable.

## 246 **Supporting Information**

247 Supporting Information are available with the manuscript online. The SI contain additional  
248 data on biochar yield and properties.

## 249 **Acknowledgements**

250 The authors would like to acknowledge Bio4Energy ([www.bio4energy.se](http://www.bio4energy.se)), a strategic  
251 research environment created by the Swedish government, for supporting this work. The  
252 authors would also like to acknowledge Dr. Jan Mumme for his groundwork and help on this  
253 project.

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