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

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Abstract

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

CO₂ abatement; carbon stability; fixed carbon; proximate analysis; combustion

Abbreviations

FC, fixed carbon; BECCS, bioenergy carbon capture and storage
1 Introduction

Bioenergy carbon capture and storage (BECCS) is a technology that generates energy from biomass and subsequently captures and stores the emitted CO$_2$ in geological formations. While the gaseous emissions are captured and used, the solid residue, the ash, which makes up around 1% of the mass of wood, is often landfilled $^{1-3}$. Although, wood ash is not a problematic material from a technical perspective, there is a clear potential for improvement when it comes to handling and resource utilization. With up-scaling and widespread use of BECCS as a carbon-negative technology, the amount of wood ash could increase drastically in coming years which threatens the sustainability of the system $^3$.

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

Although there is still debate about precisely how long biochar remains in soil, many studies have shown that biochar has a much higher stability than its feedstock material $^{4,8-11}$. In the absence of methods to determine the exact residence time of biochar in soil, proximate analysis has been suggested as one of the methods to assess the biochar fraction that is stable for at least 100 years in soil $^{11-14}$, the timeframe that is typically used for climate change simulations $^{15}$. 
During pyrolysis, three co-products (pyrolysis liquids, gases and solid biochar) are formed. The product distribution and properties depend on a number of factors, such as highest treatment temperature (HTT) or feedstock type $^{16,17}$. Increasing the carbon retention in the solids and the stable carbon content within biochar, maximises the carbon sequestration potential of biochar. It is known that alkali and alkaline earth metals in the ash of biomass can catalyse the biochar formation $^{18-20}$ and hence can increase the carbon sequestration potential of biochar $^{21}$. However, to our knowledge no one has investigated the effect of complex mixtures of minerals in waste materials that include alkali and alkaline earth metals, such as biomass ash, on the stable carbon yield in biochar. This can be a very valuable proposition as it would bring benefits for biochar production while simultaneously managing biomass ash, e.g. as a by-product from BECCS.

The aim of this study was to investigate the effect of wood ash amendment on the carbon sequestration potential and costs of biochar. Spruce wood was blended with ash from a wood boiler in different ratios, then pelletised and pyrolysed at 450°C. The resulting biochar was analysed for its carbon stability via proximate analysis and the fixed carbon (FC) yield was determined. Subsequently, the CO$_2$ abatement costs using wood ash-amended biochar were calculated and compared to unamended biochar.
2 Materials and Methods

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

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

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

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

2.3 Thermogravimetric analysis (TGA) – proximate analysis
Following pyrolysis, we performed proximate analysis in the same TGA/DSC instrument to determine the biochar fixed carbon (FC) content. Previous studies have shown that FC is a good predictor for the carbon sequestration potential of biochar and that it approximates the fraction that is stable after around ~100 years of biochar ageing in soil \(^{11-14}\).
After pyrolysis, the biochars (10-30 mg) were finely ground and transferred back into the 150 µL alumina crucibles. The material was heated-up to 900°C in a nitrogen atmosphere (determination of volatile matter content), followed by switching from nitrogen to air flow to oxidize the biochar. The % of the biochar that was oxidized is the FC content used in this study to assess the carbon stability. The remaining fraction is the ash content.

### 2.4 Data processing and statistics

#### 2.4.1 Biochar yield

The following equations were used to calculate the biochar yields:

1. **Biochar yield (% feedstock)**
   \[
   \text{biochar yield (\% feedstock)} = \frac{\text{biochar (g)}}{\text{feedstock (g)}}
   \]

2. **Ash free biochar yield (% feedstock)**
   \[
   \text{ash free biochar yield (\% feedstock)} = \frac{\text{ash free biochar (g)}}{\text{feedstock (g)}}
   \]

3. **Ash free biochar yield (% ash free feedstock)**
   \[
   \text{ash free biochar yield (\% ash free feedstock)} = \frac{\text{ash free biochar (g)}}{\text{ash free feedstock (g)}}
   \]

All values are on dry basis.

#### 2.4.2 Fixed carbon (FC)

4. **FC content (% biochar)**
   \[
   \text{FC content (\% biochar)} = \frac{\text{FC (g)}}{\text{biochar (g)}}
   \]

5. **FC content (% ash free biochar)**
   \[
   \text{FC content (\% ash free biochar)} = \frac{\text{FC (g)}}{\text{ash free biochar (g)}}
   \]

6. **FC yield (% feedstock)**
   \[
   \text{FC yield (% feedstock)} = \frac{\text{biochar (g)}}{\text{feedstock (g)}} \times \text{FC content (\% biochar)}
   \]
   \[
   = \frac{\text{ash free biochar (g)}}{\text{feedstock (g)}} \times \text{FC content (\% ash free biochar)}
   \]
(7) FC yield (% ash free feedstock)

\[ \text{FC yield} = \frac{\text{biochar (g)}}{\text{ash free feedstock (g)}} \times \text{FC content (% biochar)} \]

\[ = \frac{\text{ash free biochar (g)}}{\text{ash free feedstock (g)}} \times \text{FC content (% ash free biochar)} \]

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

2.4.3 CO2 abatement costs

Feedstock, biochar production and application costs in USD were taken from Table 10 in Shackley et al. (2011) based on sawmill residues. Sales for electricity and renewable obligation certificates used in Shackley et al. were not taken into account since the excess energy from the pyrolysis unit would be used to dry the feedstock. The costs of feedstock and biochar production per t of biochar were converted into costs per t of feedstock based on the biochar yield (% feedstock) of 22.4% of the untreated control in our study (SI Table 1).

Wood ash was considered a residue and although negative costs could have been assumed (gate fees), in our scenario the more conservative assumption of zero costs for wood ash was used.

Furthermore, pelleting costs of 7.5 USD t\(^{-1}\) feedstock were, based on Mani et al. (2006) (excluding material costs (already taken into account), personnel costs (assuming the personnel operating the pyrolysis equipment also operates the pelleting machines) and drying costs (excess heat from the pyrolysis unit is used to dry the wood)).

The overall costs were split into three fractions:
(i) Feedstock and feedstock transport costs (50 USD t\(^{-1}\) feedstock) were multiplied by the FC yield (% ash-free feedstock) which corresponds to the amount of ash-free wood needed to produce 1 t of FC.

(ii) Costs for biochar production consisting of pelleting (capital and operation), labour, plant costs and capital costs (31 USD t\(^{-1}\) feedstock) which were multiplied by the FC yield (% feedstock) which is the amount of FC produced per t of feedstock (wood + ash addition).

(iii) Costs for biochar storage and application (22.5 USD t\(^{-1}\) biochar) which were multiplied by the FC content (% biochar) of the biochar which corresponds to the costs for deployment of 1 t of FC in the soil.

The sum of the costs was converted into CO\(_2\) abatement costs in USD, the costs for sequestering 1 t of biochar-CO\(_2\) in soil.
3 Results

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

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

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

The FC yield (% ash-free feedstock) (Figure 2E, F) was significantly higher in the 50% ash-amended treatment compared to the control (Figure 2E). The spruce wood (organic fraction in the feedstock) was converted into FC with a much higher conversion efficiency when wood ash was added compared to unamended spruce.
In a previous study, we pyrolysed pellets with the same ash contents in an auger pyrolysis unit with similar results for biochar yield and FC content confirming the reproducibility of the results in a continuous unit.

Figure 1: Composition of the feedstock and biochar in organic fraction (positive values) and ash fraction (negative values) with increasing wood ash addition. The proportion of biochar and fixed carbon (FC) is shown relative to the feedstock (biochar and FC yield).
Figure 2: Effect of wood ash addition to spruce wood prior to pyrolysis on (A) FC content (% biochar), (C) FC yield (% feedstock) and (E) FC yield (% ash-free feedstock) compared to the unamended control, respectively (n = 5). The letters indicate statistically significant differences (one-way ANOVA and Tukey post-hoc test) with a significance level of 0.05. The right panels (B, D, F) show how the parameters were calculated (ratio of the highlighted bars) based on Figure 1 using the 50% ash-amended material as example.
Figure 3: CO$_2$ abatement costs for sequestering carbon in soil in the form of (wood-ash amended) pine biochar in USD t$^{-1}$ CO$_2$. Costs were separated into costs for feedstock, biochar production and application. Data are based on saw mill residues from Shackley et al. (2011) and costs for pelletising were taken from Mani et al. (2006).
4 Discussion

4.1 Carbon sequestration potential of biochar

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

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

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

Adding wood ash to biochar converts the organic fraction of wood into stable carbon much more efficiently. With increasing competition for biomass resources, decreasing the amount of biomass needed to sequester 1 t of CO$_2$ can be vital for feasibility of large-scale biochar deployment. The carbon sequestration potential of biochar has been reported to be 0.7-1.8 Gt C eq. y$^{-1}$ 6,7,25 and with 50% ash addition using the same amount of available biomass, this would increase to 1.2-2.6 Gt C eq. y$^{-1}$.

4.2 Biochar CO2-abatement costs

Our results also have implications for the CO$_2$-abatement costs, i.e., the costs to sequester 1 t of biochar-carbon in the ground (Figure 3). The feedstock input costs (including feedstock transportation) are drastically reduced with the addition of 50% wood ash, because the conversion efficiency from woody biomass into FC is much higher. However, due to the extra ash content in the material, a longer production time is necessary (in a continuous process).
pyrolysis unit) or more production runs (in a batch unit) to produce the same amount of FC compared to the feedstock without wood ash addition. Therefore, the biochar production costs are higher (Figure 3). Furthermore, the resulting biochar has a lower FC content (%) biochar) compared to the untreated or the 20% wood ash-amended sample and hence, more biochar needs to be applied to sequester the same amount of FC in the ground, contributing additional costs for biochar application.

With 50% wood ash addition, overall, the costs for feedstock, biochar production and application are 6% higher than in the unamended control (Figure 3). With increasing feedstock costs due to competition for land area and biomass materials and decreasing biochar production costs due to economy of scale, the CO₂-abatement costs, however, will become lower compared to pure pine biochar. The 20% ash sample has cost advantages in both, feedstock and biochar production costs, over the unamended control, therefore, will be cheaper irrespective of the feedstock costs. With 20% wood ash addition the overall CO₂-abatement costs are the lowest with 114 USD t⁻¹ CO₂ compared to 134 USD t⁻¹ CO₂ in the control which are cost savings of 15% (Figure 3).

4.3 BECCS and biochar synergies
While other studies showed increases in biochar yield and / or carbon stability using relatively high concentrations of pure chemicals, here we show for the first time that the use of underutilised material, biomass ash (e.g. from BECCS operations), that is still often landfilled can significantly increase the carbon sequestration potential of biochar and decrease the CO₂-abatement costs. Besides sequestering carbon in the ground, incorporating biochar-ash composites recycles nutrients back to the plants. Biochar application will allow for increased plant growth due to improvement of the soil properties by biochar and direct nutrient supply. Although biochar and BECCS operations are in competition for biomass, using biomass ash and some of the woody material designated for BECCS to produce and
apply biochar-ash composites in biomass plantations brings synergies for both processes. Increased plant growth after biochar-ash application will increase the amount of biomass available for BECCS in the next biomass cycle. This approach offers new synergies among different renewable energy and climate change mitigation technologies, such as biochar, bioenergy, and BECCS, making them more economical, productive and environmentally sustainable.

Supporting Information

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

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5 References


