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# PRODUCTION AND CHARACTERISATION OF SLOW PYROLYSIS BIOCHAR

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ABSTRACT: Biochar is charred material produced from biomass, i.e. by means of pyrolysis, with the intention to be used as a soil amendment and as a method to permanently store $CO_2$ in the soil. In this study, the effect of slow pyrolysis process conditions and biomass feedstock type on key characteristics of the produced biochar was studied. Feedstocks included pine wood, wheat straw, green waste and dried algae while process conditions investigated during batch, slow pyrolysis included treatment temperature and residence time. In proximate analysis of the produced biochars, it was found that the fixed C-content strongly depended on the intensity of the thermal treatment, while the actual yield in fixed carbon was practically insensitive to the treatment temperature or residence time. The pH in solution, higher heating value and BET surface positively correlated with pyrolysis temperature. Finally, in soil incubation tests, it was found that the addition of biochar to the soil initially reduced the C-mineralization rate, indicating that the soil microculture needs to adapt to the new conditions, which was more pronounced when adding chars with high fixed C-content, as chars with low C-content had a larger amount of volatile, easier biodegradable, C-compounds.

KEYWORDS: Biochar, Pyrolysis, Characterisation

## 1 INTRODUCTION

The rising energy cost and concerns over greenhouse gas emissions associated with the use of fossil fuels have prompted significant research interest into the conversion of biomass into biofuels and other value-added renewable products [1].

Among the wide array of biomass conversion technologies, pyrolysis is unique because it not only converts a large fraction of the biomass into a condensable liquid crude biofuel, called bio-oil [2], but additionally produces a solid fraction known as biochar. Although the char fraction obtained from biomass pyrolysis was often considered a waste product and consequently combusted to provide the necessary heat for the pyrolysis process, char can also be used as a soil amendment to increase soil fertility [3].

Up to date, the mechanisms by which the use of biochar increases soil productivity are not yet fully understood. However, it already has been demonstrated that the application of biochar to soils increases water retention capacity and soil aeration, improves cation exchange capacity and thereby providing higher nutrient retention, increases soil organic carbon, neutralizes the pH of acidic soils and improves the soil microbial ecology [4].

In addition to these purported benefits to the soil, biochar consists for a large fraction out of fixed carbon (50 – 85 *w*%) which has been demonstrated to be very stable, with a half-life of over 1000 years in the soil [5, 6]. Consequently, the production of biochar through pyrolysis of biomass, effectively removes carbon from the atmospheric carbon cycle for storage in the soil. Due to this characteristic, biochar could also help in the global challenge of carbon dioxide ($CO_2$) mitigation, as it can result in a net removal of carbon from the atmosphere (**Figure 1**).

Biochar can be produced from various types of processes including slow and fast pyrolysis, and gasification. Each type of process is characterised by different ranges of pyrolysis temperatures, heating rates, biomass and vapour residence times. Given this variety in pyrolysis processes and their accompanying process conditions, in combination with a wide range of available biomass feedstocks for biochar production (including wood, energy crops, agricultural waste residues, sewage sludge, digestate,…), large variability is to be expected in the physicochemical properties of the biochars, and ultimately, in their performance as a soil amendment and/or in their ability to store carbon permanently in the soil.

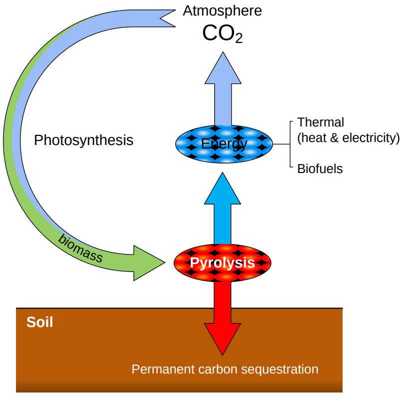

**Figure 1:** The principle of atmospheric carbon sequestration using biochar.

The purpose of this study is an experimental investigation into production of biochar by slow pyrolysis and to relate the various feed and process parameters to the yield, chemical and physical properties of the biochar produced, thereby allowing conclusions to be drawn regarding the selection of biomass feed material and the necessary process conditions that would result in a biochar product that would be optimised with respect to its behaviour within the soil in terms of soil fertility improvement and enlarging the size of the stable carbon sink within the soil.

## 2 MATERIALS AND METHODS

### 2.1. Feedstock materials

The biomass feed materials that were used in the batch pyrolysis experiments (approximately 100 g biomass feed) included wood (pine), green municipal waste, wheat straw and spray-dried algae. Pine wood (Stelmet, Poland) and straw (Strovan, Belgium) were acquired in pelletised form with a diameter of 6 mm.

Green waste was obtained from a local garden contractor and consisted of shredded leaves, twigs and branches of mainly coniferous trees and shrubs. Green waste feedstock material was ground in a cutting mill and passed over a 2 mm screen and finally cold pelletised in a laboratory pellet press (6 mm diameter). The produced pellets were air dried with forced convection for an hour, and then stored at -18°C due to their sensitivity to microbial decay.

Spray dried algae were acquired commercially (SBAE Industries, Belgium) and manually pelletised to a diameter of 15 mm.

### 2.2. Slow pyrolysis set-up

The slow pyrolysis reactions were carried out in a vertical, tubular, stainless steel reactor ($d \times L$ = 3.8 cm × 30 cm) which was heated by an electric furnace, as shown in **Figure 2**. The temperature ramp rate was approximately 17°C/min and the reactor was continuously swept with nitrogen (800 ml/min) to remove the produced gases and tars produced during pyrolysis.

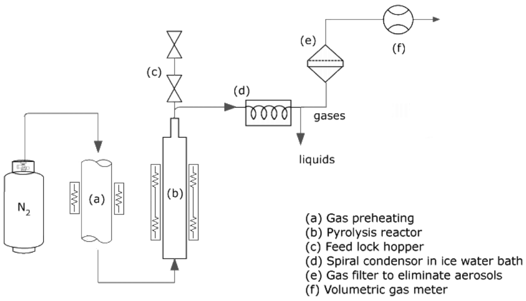

**Figure 2:** Slow pyrolysis set-up for the batch production of biochar.

The process variables that were varied included the highest treatment temperature (HTT) at which the pyrolysis reactions took place. Two different residence times were investigated (10 minutes and 60 minutes) where the residence time is defined as the period during which the temperature is held at the specified HTT.

### 2.3. Biochar characterisation

Next to biochar yield after biomass slow pyrolysis, the following physicochemical characterisations were performed:

- Proximate analysis according to ASTM D1762-84 to determine moisture content, ash, fixed carbon and volatile matter.
- Elemental analysis (C, H, N) was performed using a Flash 2000 Elemental Analyser (Thermo Fisher Scientic, Waltham, MA). Oxygen content was not determined due to interference of inorganic oxides in the ash.
- The HHV (higher heating value) of chars and input materials was determined using an oxygen bomb model 6200 calorimeter with a model 1108 oxygen bomb (Parr Instrument Company, Moline, IL).
- pH of the biochar in suspension was measured using a Model 420 Thermo Orion (Thermo Fisher Scientic, Waltham, MA) after dispersing biochar into a 0.1 N KCl solution in a 1:10 ratio (*w*/*v*).
- BET surface area was measured using nitrogen gas adsorption according to the DIN 66132 norm.

Besides physicochemical testing, two simple short-term biological degradation tests were performed. The first test consisted of a BOD (biological oxygen demand) determination in a 2.6 g/l dispersion of biochar in a buffered solution containing microbial inoculum. This dispersion was incubated at 20°C for 14 days while head-space oxygen consumption was registered.

A second biological degradation test consisted of a soil degradation test. A sandy loam soil sample, retrieved from the area of Lendelede (Belgium) – already containing 7.1 g organic C/kg and having a pH of 5.33 – was used. A total of 3.5 g of biochar was mixed per 0.25 kg of dry soil sample. Afterwards, water was added to the soil sample to reach 50 % water filled pore space and the samples were incubated for 42 days at 25°C. During this incubation period, $CO_2$ production was recorded by absorption into NaOH solution, followed by automatic titration (702 SM Titrino, Metrohm, Herisau, Switzerland).

## 3 RESULTS

### 3.1. Biochar yield

Biochar yields were seen to be negatively correlated with increasing pyrolysis severity (increased HTT and longer residence times). For example, the yield versus HTT for a residence time of 60 min. is illustrated in **Figure 3**. Of the various feedstocks tested, algae had the worst biochar yield and this could be due to its increased ash content (algae sample: 38.4 *w*% ash content) which could promote the catalytic production of gases and tars. Increases in the initial moisture content can also improve the biochar yield and this effect was seen in the conversion of the green municipal waste.

Generally, the yields were lower than results predicted in literature which can be attributed to the high nitrogen sweeping rate used in the biochar production experiments. The nitrogen sweep gas reduces the vapour residence times and thus partially inhibits secondary char forming reactions.

### 3.2. Proximate analysis

The fixed carbon content within the biochar increases with increasing pyrolysis severity (i.e. residence time and highest treatment temperature). However, the fixed carbon yield – being fixed carbon expressed as *w*% of original biomass feedstock – was seen to be relatively independent of both process variations, as demonstrated on **Figure 4**. This can be attributed to the fact that the pyrolysis reactions remove volatile carbon rather than fixed carbon. The increase in the fixed carbon content is a result of the reduction in the overall biochar mass rather than carbon-fixing reactions.

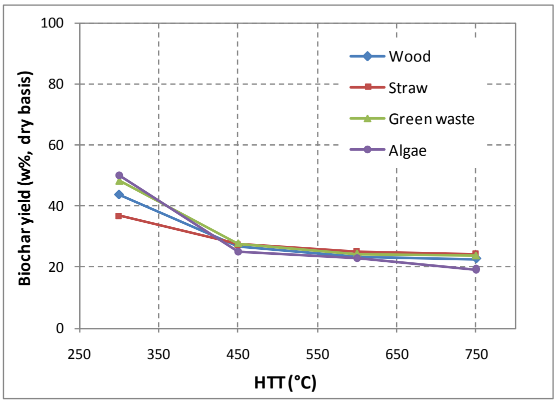

**Figure 3:** Biochar yield as a function of feedstock and HTT, produced at a residence time of 60 min.

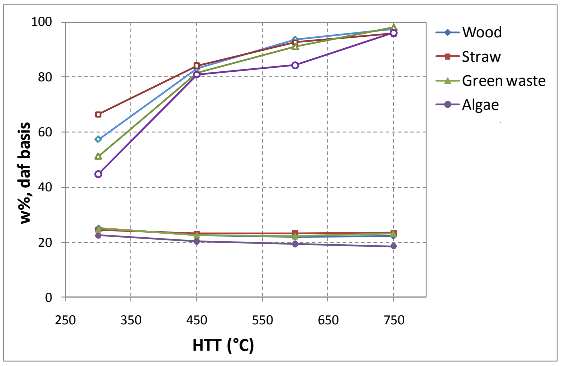

**Figure 4:** Biochar fixed carbon content (open symbols) and fixed carbon yield (closed symbols) as a function of feedstock and HTT, produced at a residence time of 60 min.

## 3.3. Elemental analysis

For the elemental analysis, a gradual increase from the original biomass composition towards high-carbon, low-hydrogen composition was observed with increasing HTT. Although significant differences in elemental composition were observed between the biochars produced from the different feedstocks at lower HTT's, there was a convergence of the H/C ratio to 0.18 for all biomass types at the highest HTT.

The H/C ratios resulting from this research, as demonstrated in **Figure 5**, are very similar to the values published by Brown *et al.* [7]. This value also indicates how many carbon atoms on average are connected to a hydrogen atom, thereby estimating the average size of the polyaromatic condensed graphene sheets, which is also a measure of the biochar stability. The linear correlation that was obtained for the H/C versus the fixed C content shows that the volatile matter that is volatilised during the pyrolysis process will show a higher H/C than the remaining biochar (fixed carbon), and will remove most of the H from the biochar as the reaction takes place.

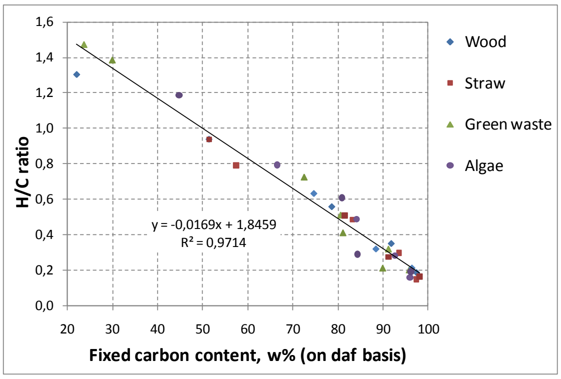

**Figure 5:** The H/C ratios from all produced biochars versus fixed carbon content.

## 3.5. Higher heating value

The higher heating values (HHV) increased with increasing pyrolysis severities (i.e. residence time, HTT) with the exception of algae and this is due to the extremely high ash content within the algae (38.2 *w*%, dry basis). HHV's are favoured by increases in the fixed carbon content of the biochar and this is essentially the transformation that takes place during pyrolysis. The HHV of wood biochar was increased up to almost 35 MJ/kg. The results are displayed in **Figure 6** below.

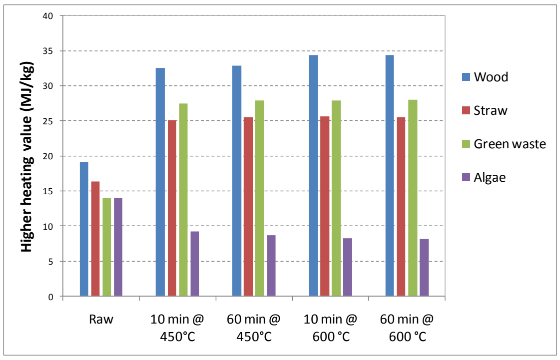

**Figure 6:** The biochar higher heating value (MJ/kg) of the different feedstocks tested, with varying intensity of the slow pyrolysis process (residence time, HTT).

## 3.6. Biochar pH in solution

The results of this analysis, as shown in **Figure 7**, displayed an obvious trend of the pH to increase as the thermochemical treatment is intensified, i.e. longer pyrolysis processes with higher HTT's. Differences can be observed for the biomass types: especially wood has an average pH in solution that is in general two pH units lower than the values for the three other types.

## 3.7. BET surface area

The highest Brunauer-Emmet-Teller (BET) surface area (196 $m^2$/g) was observed at an HTT of 600 °C and at the shorter residence times of 10 minutes when wood was pyrolysed. At low temperatures (300 and 450°C), surface area is generally low, yet it increases with higher residence times. At 600°C more accessible surface is created, but an inverse relationship between surface area and residence time was observed. When the temperature is increased further, the BET surface area reduces again, which is likely due to restructuring taking place in the biochar or due to the onset of ash melting at higher temperatures.

Wood biochar clearly offers the highest potential when it comes to surface area as all other biochar types had a BET surface area below 50 m²/g. Strikingly, the wood feedstock had the lowest ash content area of all feedstocks used (0.2, 7.9, 3.5 and 38.4 *w*% for wood, straw, green waste and algae, respectively). From these results, the higher the amount of inorganics (i.e. ash content) in the biomass feedstock correlate with extra surface area creation in the biochar production process.

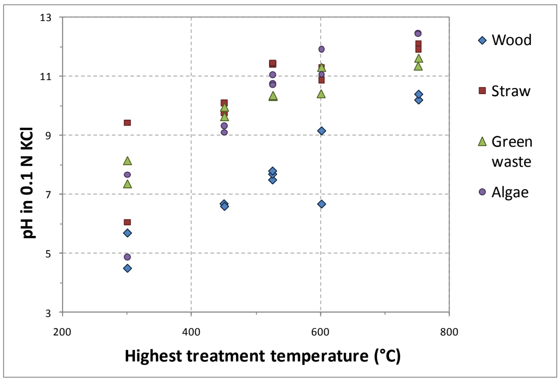

**Figure 7:** The pH of biochar in solution versus HTT of the different biomass feedstock tested.

### 3.8. Biological degradation

In **Figure 8**, the results are given for the cumulative BOD (biological oxygen demand) for biochars produced from wood under different pyrolysis intensities (residence time, HTT). The data showed that the rate of oxygen demand during the two week incubation period decreased progressively. The results show that the BOD is directly proportional to the volatile matter content within the biochar and therefore, increased BOD is favoured by low severity pyrolysis as indicated in **Figure 8**. Over the two-week period, wood biochar showed the lowest BOD as a percentage of theoretical chemical oxygen demand (COD) and was only 0.38% when the biochar is produced at 600 °C with a residence time of 60 minutes.

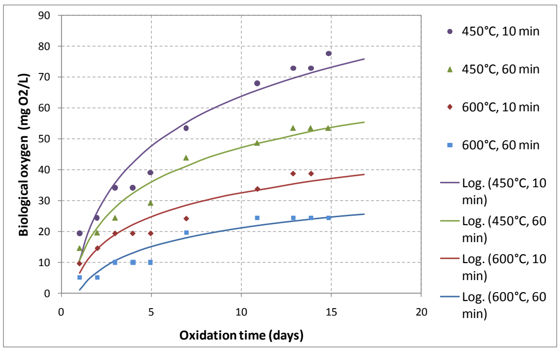

**Figure 8:** Biological oxygen demand (cumulative) over a 14-day incubation period for biochars produced from pine wood, under different pyrolysis severity.

In a second test, biochar was mixed with an actual soil sample and the results show that the initial carbon mineralisation rates are suppressed by the addition of biochar during a "lag phase" before increasing to rates above that of the control (untreated) soil sample – as shown in **Figure 9**. Also, the depression of carbon mineralisation during this lag phase is proportional to the intensity of thermal treatment during pyrolysis, i.e. chars produced at higher HTT tend to have lower initial carbon mineralisation rates. This lag phase could be attributed to the time needed for the soil microculture to adapt to the new conditions. Longer soil incubation tests are needed to yield further insights and to draw conclusions.

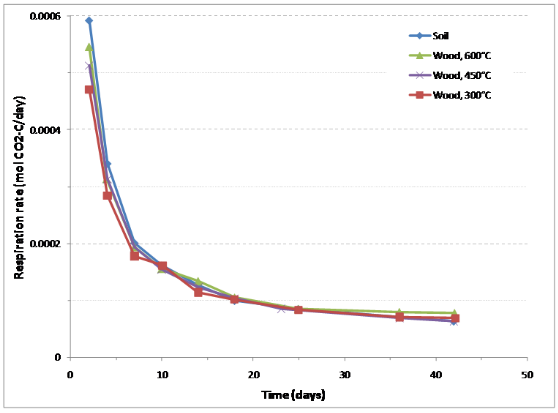

**Figure 8:** Carbon mineralisation in a selected soil sample with the addition of wood biochar, produced at different HTT's, versus incubation time.

## 4 CONCLUSIONS

When studying the physicochemical properties of biochar produced from different types of feedstocks and under different slow pyrolysis conditions, it was found that the biochar yield was negatively correlated with the ash content of the feedstock. When considering the fixed carbon yield of the different biochars, it was found that although the fixed C-content strongly depended on the intensity of the thermal treatment, the actual yield in fixed carbon was practically insensitive to the treatment temperature or residence time. The higher heating value is correlated with the fixed C-content and consequently, higher HVV's were found in chars that were produced during more intense thermal treatments.

Finally, in soil incubation tests, it was found that the addition of biochar to the soil initially reduced the C-mineralization rate, indicating that the soil microculture needs to adapt to the new conditions. This effect was more pronounced when adding chars with high fixed C-content, as chars with low C-content had a larger amount of volatile, easier biodegradable, C-compounds.

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