

# Biochar for Carbon Sequestration, Reduction of Greenhouse Gas Emissions and Enhancement of Soil Fertility; A Review of the Materials Science

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## Abstract

When biomass is pyrolysed it produces a syngas, bio-oils and charcoal. When this charcoal (biochar) is applied to soils, research has shown that it can increase soil health, crop yields, reduce leaching of organic and inorganic fertilisers, and some evidence exists that it can reduce soil emissions of N<sub>2</sub>O and CH<sub>4</sub>... Biochars have been found to be very stable in many soil environments, when compared to uncharred organic matter, and have considerable potential to sequester carbon from the atmosphere. Progress has been made in understanding the material properties of these chars that result in their efficacy. In this paper an overview of the literature will be presented along with recent results of research work carried out at the University of NSW and Cornell University. Areas where further work is required will be outlined.

*Keywords: Biochar, Biosequestration, Pyrolysis, Greenhouse gas emissions*

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## 1. Introduction

An intensification of agricultural production on a global scale is necessary in order to secure the food supply for an increasing world population. As a result, more and more organic carbon is being removed from the soil leading to dramatic soil degradation. Many of Australia's agricultural soils are already reaching critically low levels of soil organic carbon. Intensive agriculture and horticulture in Australia have depleted organic carbon levels in soil from an estimated 3% to less than 1% [1]. Organic carbon in the soil enables soil biota to flourish, assisting the processes of nutrient flow, increases cation exchange capacity, water and nutrient retention.

One method of increasing soil health is through the application of carbonized materials (biochars) that have long term stability [2]. These materials, added as pyrolysed organic matter, can be produced from purpose grown biomass (wood and grasses) and biomass waste streams such as paper sludge, manure or greenwaste. Moreover, these chars appear to be able to reduce the emissions of N<sub>2</sub>O and CH<sub>4</sub>.. [3] from soil. Over the past 3 years considerable research has been undertaken to measure the physical and chemical properties of the biochars and relate these to their long term stability, effect on soil health and improved crop yields and reduction in emissions. An overview of the available literature will be undertaken of chars

produced at temperatures between 400°C and 600°C, along with a summary of the research carried out at UNSW. This paper will not review the extensive research carried out on activated carbon.

## 2. Characterisation of Feedstocks

Biochar has been produced from a wide range of biomass feedstocks. For agronomic use these are characterized by the relative proportion of lignin, hemicellulose, cellulose, mineral content, protein, carbohydrate and other extractives and their internal structure. The relative proportion of these constituents will influence the final chemical composition and structure of the char (for a given set of process conditions).

Mineral matter in plants forms different functions and occurs in different forms [4]. Potassium and chlorine ions are highly mobile and will start to vaporize at relatively low temperatures during thermal decomposition. Calcium is mainly located in the cell walls and the ions are bound to organic acids. Silicon is bound in the cell walls as silica or as opal phytoliths. Both are released during pyrolysis at much higher temperatures than potassium. Magnesium is both ionically and covalently bonded with organic molecules and only vaporizes at high temperatures. Phosphorous and sulphur are associated with complex organic compounds within the cell and are relatively stable at low pyrolysis temperatures. Nitrogen is associated with a number of different organic molecules and can be

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released at relatively low pyrolysis temperatures. Other elements such as iron or manganese exist in a number of organic and inorganic forms in the biomass and are largely retained during pyrolysis.

Wood and related plants (e.g. bamboo, coconut shells) are characterized by a very low ash composition (<3%) and a very open porous structure. When wood is pyrolysed it maintains its internal cellular structure (Fig. 1). Animal manures and some other high mineral ash residues are not very porous but increase their porosity when pyrolysed. Husks (e.g. rice) can have both high ash content and high porosity. They will maintain their structure when pyrolysed.

## 2. Effect of Process Conditions on the Properties of Biochars

A range of temperatures, heating rates, time at final reaction temperature, pressures (1 to 10bar gauge) and partial pressures of oxygen/steam are used to produce biochars. The reactions conditions are one of the main determinants of the yield of biochar and its physical and chemical composition. Much research is still required to fully characterize the affect of these parameters but the following is a summary of findings to date.

### 2.1 Properties between 400°C and 600°C

At temperatures near 400°C a cross-linked amorphous aromatic structure is formed from the reaction of volatile gases with the unreacted biomass. This structure is porous and could contain randomly curved sheets [5]. At the surfaces of the biochar there are a range of functional groups that include pyranone, phenolic, carboxylic, lactone and amine groups. Asada [6] noted that the formation of free radicals in biochar that is produced at a temperature below 600°C. These radicals could be associated with aromatic and aliphatic compounds, especially those that contain nitrogen and sulphur.

Metals and non metals can be ionically or covalently bonded with the aromatic compounds. Mobile atoms such as potassium could be intercalated in the carbon aromatic structure [7]. In high ash biochars crystalline and amorphous mineral phases exist between these aromatic structures. The distribution of mineral phases is complex and varied and depends on the structure of the original biomass. As the temperature increases it is probable that the composition and the structure of these metallic phases will change [7]. Further work is required to fully characterize these changes.

As the temperature increases above 450°C microcrystalline graphene sheet formation occurs. Kercher [8] has hypothesized that as the temperature increases the disordered carbon decomposes and

becomes incorporated into the graphene sheets of the turbostratic carbon. The rigid covalent structure of the disordered carbon cannot rearrange during decomposition to allow the non-uniform growth of turbostratic crystallites. Instead, some graphene sheets grow extensively, and other sheets become terminated and pinned by structural defects [8]. The conversion of low-density disordered carbon into high-density graphene sheets causes the volumetric contraction observed during carbonization. Kercher [8] found that the graphene sheets had their maximum thickness around 450°C. It is probable that the micro-crystal structure and the defect structure of the biochars are affected by the type, quantity and structure of the mineral matter. For low ash biochars the electrical conductivity of the biochar increases as the volume of graphene sheets increases [9]. Higher mineral ash biochars probably have higher conductivity especially those that have high potassium ion contents due to the mobility of the potassium ions. Further research is required to determine the affect of mineral content on the internal structure and electrical conductivity.

Final process temperature determines the average pore size, the number of micro pores/unit mass and the total surface area. Sousa [10] found for *pinus elliotti* biochar that maximum concentration of pores and minimum pore diameter occurred around 450°C (around 2µm). The surface area of wood biochar at 400°C is approximately 50-100m<sup>2</sup>/g and at 500°C 300-500m<sup>2</sup>/g [11]. The cation exchange capacity (CEC) and pH of fresh biochar from wood increases as the temperature of pyrolysis rises [12].

There is a wide range of highly oxygenated volatile compounds (e.g. levoglucosan, hydroxyacetaldehyde, furfurals, and methoxyphenols) that are retained on the surface of the pores of the biochar at temperatures below 500°C. Some of these compounds are water soluble. The quantity and composition of the volatile organic compounds on the pore surfaces change. At approximately 500°C phenolic ethers, alkyl phenolics and heterocyclic ethers may be deposited on the biochar surface [13]. As the processing temperature increase the percentage of the different functional groups in the carbon matrix changes with the carboxylic and carboxylic anhydrides, and lactones groups decomposing to CO<sub>2</sub>. In high ash biochars amine functional groups are converted to pyridine groups at higher temperatures [14].

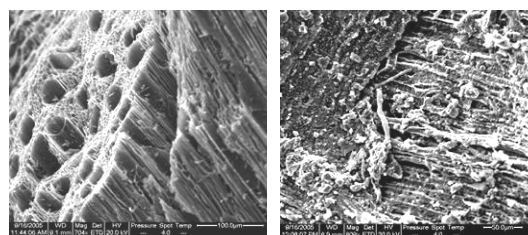


Figure 1: Images of char particles under the SEM a) wood-based char, b) manure-based char.

## 2.2 Effects of Pressure, Particle Size, Time and Atmosphere

There is very little consistent data on the effects of the other process variables on the structure and composition of biochars produced at high heating rates ( $>50^{\circ}\text{C}/\text{minute}$ ) and/or higher pressure ( $>2$  atmospheres). At high pressures (and in the presence of steam) porosity can be high and density low due to the rapid breakdown of the biopolymers [15]. The structure of the amorphous biochar is different to that found in pyrolysis carried out at atmospheric temperatures in that there is less cross linkage and a great proportion of dimers and monomers [15]. Antal [16] notes that the functional groups are similar for wood biochars made at both high and low pressures under slower heating rates. For most particulate wood biochars it appears that high heating rates result in biochars that are amorphous, have lower alkaline metal content [17] and that have low porosity due to the formation of a melt phase [18].

Most biochar has been produced in pit, beehive or vertical shaft kilns that have residence times ranging from 24 hours up to 1 month. More recently reactors have been developed that utilise residues that have a relatively small particle size ( $<15\text{mm}$ ) and have reaction times that vary from seconds (for fast pyrolysis) to 1 hour for slow pyrolysis. Very little systematic research has been undertaken on the effect of time and particle size on the composition and structure of different biochars. Mathematical modeling indicates that, for a given particle size, the shorter the process time the greater is the concentration gradient of carbon and the more volatile minerals across the particle [19]. It is probable that the microcrystalline graphene sheets will grow when the biochar is held for long times at the final reaction temperature [8]. However, this needs to be verified experimentally.

There is some evidence to indicate that the residual bio-oils on char produced from the very slow pyrolysis of logs and branches have a much greater percentage of low molecular weight compounds (this was the conventional method of manufacturing wood alcohol) [20]. Schnitzer [21] has carried out a detailed analysis of the residual bio-oils on biochars derived from the fast pyrolysis of chicken manure. They found that the individual compounds identified were grouped into the following six compound classes: (a) N-heterocyclics; (b) substituted furans; (c) phenol and substituted phenols; (d) benzene and substituted benzenes; (e) carbocyclics; and (f) aliphatics. Prominent N-heterocyclics in bio-oil were methyl- and ethyl-substituted pyrroles, pyridines, pyrimidine, pyrazines, and pteridine. The alkanes and alkenes ranged from  $n\text{-C}_7$  to  $n\text{-C}_{18}$  and  $\text{C}_{7:1}$  to  $\text{C}_{18:1}$ , respectively, and those in the biochar from  $n\text{-C}_7$  to  $n\text{-C}_{19}$  and  $\text{C}_{7:1}$  to  $\text{C}_{19:1}$ , respectively.

The proportion of different functional groups, the surface porosity and the form of mineral matter changes when biochars are reacted with oxygen, and/or steam and/or  $\text{CO}_2$  at their final pyrolysis temperature. The reactions of low mineral ash chars to oxidizing environments should be different to high mineral ash chars. Koutcheiko [22] measured an increase in the pyridinic-N and quaternary-N and a decrease in the amine functional groups and pyrrolic N when chicken manure biochar was reacted with  $\text{CO}_2$ .

## 3. Reaction of Biochars with Soils, Microbes and Plants

There are complex interactions between water within the pores and on the surface of the biochar, the soil, plants, and micro-organisms. Sugimoto [23] suggest that water has an ice like structure in the nanopores of biochar produced above  $400^{\circ}\text{C}$ . Water is probably in the supercooled state when adsorbed into biochars produced above  $450^{\circ}\text{C}$  [24]. Turov [23] noted that the interactions of water with carbon can be considered as interactions of clusters or droplets localized near oxygen containing groups. In those entities water molecules interact with each other stronger than with hydrophobic patches of the carbon surface. Thus the kinetics and the energetics of reactions that take place at the interface between biochar and the water will be influenced by the charring temperature and the distribution of functional groups.

When biochar is applied to wet soil there will be an almost immediate change in the pH of the soil around the biochar, increase in the soil porosity, dissolution of organic and inorganic compounds, an exchange of cations (and possibly anions) between the clay and silt particles and the biochar and an adsorption of gases, metals and other organic compounds on the biochar surface.

Leaching and dissolution experiments ([25,26] indicate that high ash biochars produced at temperatures below  $550^{\circ}\text{C}$  release potassium, sodium, phosphorous, sulphur, sulphates inorganic carbonates and organic compounds into moisture surrounding the biochar particle. This dissolution may take place within the first week of placing the biochar in the soil and there may be an exchange of cations, anions and organic compounds with the surrounding soil, microbes and plants. Over a much longer period of time calcium, magnesium, iron will dissolve out of the biochar. Much lower concentrations of cations and anions are released from low ash biochars (especially wood) than high ash biochar (chicken manure).

Many of the residual bio-oils on the biochar surface are unstable and can react with water, air and with each other to form new compounds [28]. Thus organic acids may react with alcohols to form esters, organic acids with olefins to form esters, aldehydes and water to form

hydrates (referred to as glycols), aldehydes and alcohols to form hemiacetals, aldehydes and proteins to form dimers of the proteins.

Biochar, when placed in soil, can also adsorb heavy metals and other dissolved organic compounds [13]. The adsorption processes appear to be complex and depend on the concentration and distribution of mineral phases, functional groups, radicals and defects on the internal pore and external biochar surfaces. Swiatkowski [14] have postulated that metals can be absorbed on biochar that has been oxidized via a series of acid base reactions.

Micro-organisms can start to grow on the surfaces and in the pores on biochar within the first month of being applied to soils containing composting material [29]. The root hairs also penetrate the macropores of the biochar and take in moisture and nutrients. Biochar is also ingested by worms and are excreted with coatings of organic compounds which provide food for other micro-organisms. Examination of black carbons in soil has shown that there is considerable interaction between the clay minerals and the biochar [30]. This organo-clay layer may reduce weathering of the biochar. It is possible that binding can take place through interaction between the clay minerals and the functional groups on the surface.

#### 4. Conclusions

Biochars produced from biomass are very complex. Very little systematic analysis of the amorphous and microcrystalline structure and chemical composition of biochars produced from different biomass under a range of process conditions have been undertaken. There is only a basic understanding of how biochar structure and composition improve soil fertility, crop yields, GHG emissions and long term stability in soils. Over the next 2 years extensive characterisation of biochars made from high and low mineral ash biomass under different process conditions will be undertaken using a range of analytical techniques at UNSW and Cornell University.

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