Properties of Biochar Produced from *Miscanthus* x *giganteus* and its Influence the Growth of Maize (*Zea mays* L.)

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1. Introduction

In technical terms, biochar, a carbon-rich product, is produced when biomass (e.g. wood, organic manures, and bio-waste materials) is heated (pyrolysed) at temperatures below 700 °C in a limited air supply [1,2]. Pyrolytical-oil (bio-oil), combustible gases, and biochar are formed during pyrolysis. Our investigations focus on the upgrading of bio-oil (not discussed in this communication), and on the production and characterisation of biochar, and its influences on plant growth when used as a soil amender.

Slow, intermediate and fast pyrolysis processes are relevant for the production of biochar [2]. In the slow process (450–650 °C) vapour slowly evacuates from the porous structures of biomass, and the yields of the three products are relatively similar.

2. Materials and Methods

Biochar, from *Miscanthus x giganteus* chips (max. size 1 cm) was prepared in a lab-scale pyrolyser (1 dm^3) at: (a) 400°C for 10 min; (b) 500°C for 30 min; and (c) 600°C for 60 min. A shallow calcareous brown earth loam soil (20% clay, pH 7.5) from the Kinvara series in the Burren area (N. Clare, S. Galway, Ireland) was amended with biochar (3% w/w), and 10 maize (*Zea mays* L.) seeds were planted per pot (13 cm). The system was incubated in a growth chamber for 21 days and artificial light was provided for 13 h/day. The pots were watered (50 cm^3) every fourth day. After 10 days the weakest five plants were removed from each pot. At the end of the growing period all plants were cut at the soil level, weighed, and oven dried at 60°C until a constant weight was reached.

Surface area measurements (BET), using a Gemini Micromeritics apparatus, high heating values (HHV), using a Paar calorimeter, and C, H and N contents (Elementar) were determined for each biochar sample. Scanning electron microscopy (SEM) was used to observe the morphologies of the biochars. Volatile material associated with the biochar was determined from weight loss on heating for 7 min at 900^{o}C, according to the standard procedure CEN/TS 15148:2005.

3. Results and Discussion

Results of growth experiments. Table 1 indicates that favourable plant responses were not obtained for all of the biochar samples. Best results were obtained for the biochar heated at 600°C for 60 min. Biochar heated for 10 min at 400°C suppressed plant growth.

Table 1: Mass of maize seedlings (as a percentage of the controls, where biochar was not added) from soils amended with biochars (3% w/w)

Preparation method	400 °C, 10 minutes	500 °C, 30 minutes	600 °C, 60 minutes
Yield of dry matter (as wg.% of control)	76.6	135	165

Biochar prepared at 400 °C for 10 minutes had a significant lower surface area than that prepared at 600 °C for 60 minutes (Table 2). This could be important for microbial associations that could influence plant growth.

Table 2: Analytical data for biochars prepared under different conditions

Preparation method	400°C, 10 minutes	500°C, 30 minutes	600°C, 60 minutes
Surface area, m^2/g	1.40 – 1.73	3.87 – 7.87	50.9 – 51.1
HHV, MJ/kg	29.4 – 30.3	30.9 – 30.9	31.5 – 32.5
C	74.76	79.67	85.10
H	4.33	3.16	2.40
N	0.39	0.50	0.55

Calorimetry investigations (Table 2) show that the HHV of biochar produced at 600°C for 60 min had the highest heating value; that is confirmed by the carbon and hydrogen contents.

The ^{13}C NMR spectrum of untreated *Miscanthus* (not presented in this communication) showed significant resonances attributable to cellulose and hemicelluloses. There was clear evidence for carbohydrate structures in the 65 to 110 ppm range of resonances. C-4 carbons of amorphous cellulose and hemicelluloses gave resonances at 83 ppm; shoulders at 65 and 89 ppm corresponded to the C-6 and C-4 carbons of crystalline cellulose, respectively; and peaks at 73 and 75 ppm represented overlapping signals for the C-2, C-3, and C-5 carbons of polysaccharides. The anomeric carbon (C-1) carbohydrate resonance was clearly evident (sharp peak at 105 ppm). Signals at 56 ppm, at 130-155 ppm, and at 168-178 ppm could be associated, respectively, with the methoxyl, aromatic, and the carbonyl groups of carboxylic acids and ester functionalities of hemicelluloses and lignin. The peak at 20 ppm could be attributable to the acetyl groups of hemicelluloses [3].

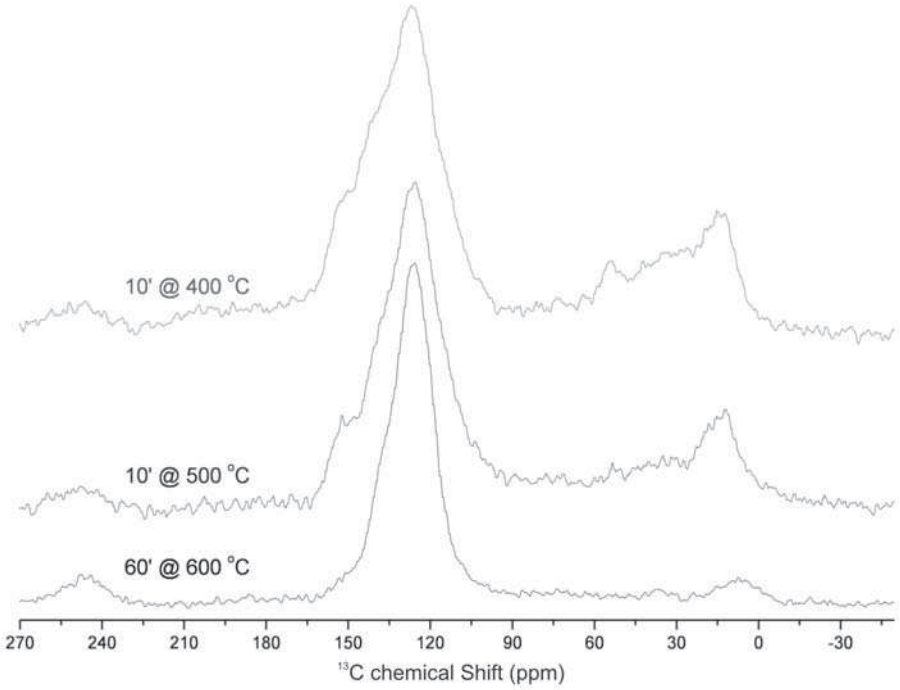

Figure 1: ^{13}C NMR spectra of pyrolysed *Miscanthus*

The spectra for the biochars (Fig. 1) are vastly different from that of the Miscanthus starting material. The ^{13}C NMR patterns emphasize how the structural compositions of the biochars change during pyrolysis. Pyrolysis at 400 ºC and 500 ºC caused biochars to retain their volatile materials, mostly aliphatic-C structures. In particular Miscanthus pyrolysed at 400ºC shows significant peaks in the aliphatic regions 25 to 35 ppm. The resonance at ~15 ppm is from terminal methyl groups. Raising the pyrolysis temperature to greater than 400 ºC, and lengthening the pyrolysis time caused losses of aliphatic-C moieties and an accumulation of largely poly-condensed aromatic-C type compounds dominated by the 130 ppm resonance [4]. The spectrum of the biochar from the 400 ºC reaction has some evidence for lignin contributions, as indicated by the peak at 56 ppm for methoxyl, and the shoulder at ~150 ppm typical of O-aromatic carbons. As the temperature is raised from 400 ºC, through 500 ºC to 600ºC, these lignin signals diminish. Increased heating also resulted in a significant peak shift in the aryl region from 131 to 127 ppm, considered to be indicative of the formation of fused aromatic structures [5, 6]. That signifies the transformation of labile compounds into environmentally recalcitrant forms with important biochemical implications with regard to greater resistance to microbial transformations.

Because the chars produced at 400ºC and 500ºC and at short reaction times (10 min and 30 min) contained recognisable fragments of feedstock biopolymers (lignin signals) it can be concluded that the reaction time was insufficient for complete conversion to char. On the

other hand, the char produced at 600ºC for 60 min contained no recognisable feedstock components, indicating complete conversion to char.

The SEM analysis showed that that the plant cellular morphology was preserved after the biomass was pyrolysed. However, the SEM device does not allow observation of difference in surface area or structure between the samples made under the different conditions.

It is plausible to consider the effectiveness that biochar will have for carbon sequestration leading to the reduction of atmospheric CO_2. The volatile residue after outgassing at 900 ^oC amounted to maximum 40% of the mass of the biochar.

4. Conclusions

In order to obtain the optimum value for soil applications of biochar it is important to establish the preparation criteria that will give rise to properties that will have desired effects. This study shows that at the higher temperature a porous biochar was obtained which can be used to store air and water, and provide a refuge against predators for soil microorganisms. It also has value as a high energy biofuel because of its high carbon content and high HHV.

Pyrolysis and biochar production provides an attractive process for carbon sequestration in soil because of its long term stability in soil.

There is, however, a need to establish a classification system that will define the values of biochar for different applications. NMR, BET, mineral matter (ash) and volatile content determinations would seem appropriate for the provision of data for standardisations.

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Preplanting Application of a Humic Substance and Study on Chlorophyll Content of Wheat Genotypes after Environmental Freezing

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1. Introduction

Freezing tolerances is the result of physiological, chemical, and physical reactions, and of changes in plant cell structure that take place at appropriate developmental stages, under suitable environmental conditions (8). Winter wheat goes through a complex process of cold hardening during the fall that increases its resistance to cold during winter. Its cold hardiness is quickly lost when growth resumes during the spring. Little resistance to freezing is present at that time (10).

Humic substances are the result of organic decomposition and the natural organic compounds comprising 50 to 90 % of the organic matter of peat, lignites, sapropels, as well as of the no-living organic matter of soil and water ecosystems (4). The concentration of HS varies from place to place. Their size, molecular weight, elemental composition, structure, and the number and position of functional groups vary, depending on the origin and age of the material (7). The biological activity of HS encompasses all the activities of HS in regulating plant biochemical and physiological processes, irrespective of their stimulatory or inhibitory roles. Mitigating activity of HS is observed under various stress conditions including both biotic and abiotic ones (6). Potassium humate causes increase in crop quality and tolerance of plant to drought, saline, cold, diseases and pests stresses (3). Research has confirmed that humic substances can indirectly and directly affect the physiological processes of plant growth (11).

The amount of chlorophyll in a leaf is normally expressed in terms of either concentration or content; preference for one over the other may depend on the researcher's objectives. Sometimes, Chl concentration or content is expressed in terms of moles per amount of leaf mass or area, since photon flux and carbon assimilation rates are usually expressed in similar units, and this permits better understanding of physiological processes. The molecular weights of Chl a and Chl b are 892 and 906, respectively. More recently, nondestructive optical methods, based on the absorbance and/ or reflectance of light by the intact leaf, have been developed. Optical methods generally yield a 'chlorophyll index' value that expresses relative chlorophyll content but not absolute Chl content per unit leaf area, or concentration per gram