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Progressing from Terra Preta de Índios to the Whole World

Biochar from Biorefinery Residuals

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Introduction

The Carbolea Centre at UL is developing biorefinery processes for the production of levulinic acid, furfural, and formic acid from the acid hydrolysis of biomass (*Miscanthus*, sugarcane bagasse, etc.) in a medium pressure and temperature lab-unit reactor system. A bench scale (6 kg/h biomass throughput) fully-integrated continuous reactor was designed and assembled at UL. *Miscanthus* x *giganteus* was subjected to biorefining hydrolysis processes in 3% H_2SO_4. Solid biorefinery residual materials (ca 50% of the biomass) were recovered by filtration of the biorefining digest and subjected to pyrolytic processing at different reactor temperatures and at different hot vapour and solids residence times in order to determine the optimum processing conditions for the production of the biochar, bio-oil, and syngas pyrolysis products. A detailed characterization of the biochars and bio-oils was carried out and the efficacies of the biochars were tested for the promotion of plant growth and for uses as soil amenders. Biochars from *Miscanthus* x *giganteus*, pine, and willow were compared with those of the pyrolysed residuals from the biorefining of *Miscanthus*, and maize (*Zea mays* L) seedlings were grown on soil amended with 1% and 3% biochars.

Results and Discussions

The Scanning Electron Micrographs (SEMs, Figure 1) show that the cell structures in the plants are maintained upon pyrolysis at ambient pressure for 60 min at 600 ^oC, and with a surface area > 50 m^2g^{-1} (Table 1). At 20 bar the surface area was 1 m^2g^{-1}, the cell structures had collapsed and were clogged with tary residuals.

The data in Table 1 show that, under the same pyrolysis conditions, the surface area of the biochar materials from pyrolysis of the residuals was significantly greater (>300 m^2g^{-1}), and the data also show that the surface areas also increased as the pyrolysis time was increased. Yields of biochar were significantly greater for the pyrolysed residuals than for the original biomass, and the yields were not significantly influenced by the time of pyrolysis. The pyrolysed residuals had slightly increased C contents and lower N contents compared to the *Miscanthus* biochar.

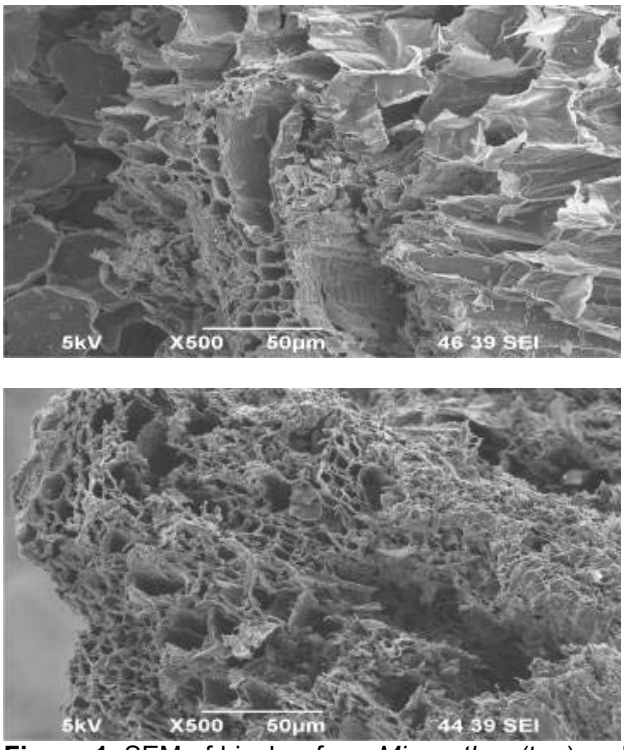

Figure 1. SEM of biochar from *Miscanthus* (top) and willow (botton).

Yields of maize seedlings, after 21 days, were enhanced by 50% when a shallow calcareous soil was amended with 3% of biochar from *Miscanthus*. However, yields from the biochar from the pyrolysed residuals were not significantly influenced by the products from pyrolysis for 10 and 60 min, but were depressed by the product from pyrolysis for 30 min (Figure 2).

Table 1. Yields and properties of biochars from different substrates and reaction conditions

Biochar Source	*Miscanthus*	Hydrolysis residue	Hydrolysis residue	Hydrolysis residue
Pyrolysis time, min	60	60	45	30
Temp (°C)	600	600	600	600
Yield of char (wg%)	19.8 – 20.2	52.41	53.041	53.35
Surface area, m^2g^{-1}	50.9-51.1	310.19	260.89	205.89
HHV, MJ kg^{-1}	31.5-32.5	27.72	27.86	27.88
C, wt.%	85.1	88.39	87.67	87.48
H wt.%	2.40	1.99	2.12	2.15
N wt.%	0.55	0.323	0.379	0.34

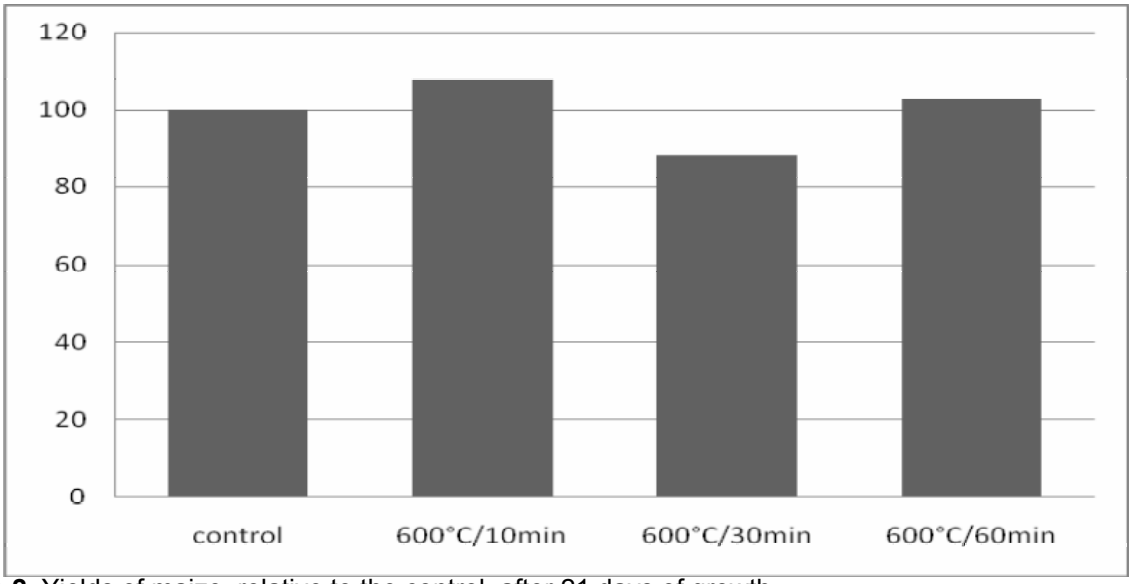

Figure 2. Yields of maize, relative to the control, after 21 days of growth

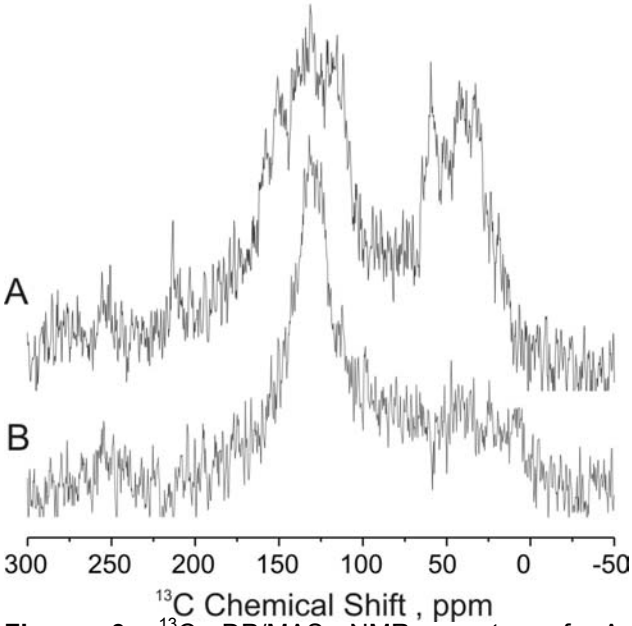

Figure 3. ^{13}C DP/MAS NMR spectra of, A, *Miscanthus* residuals, and B, pyrolysed residuals.

NMR spectrum (Figure 3A) shows that the carbohydrate in the residuals has been degraded/transformed, but the residuals still contain significant lignin and aliphatic hydrocarbon signals.

Conclusions

About 50% of the *Miscanthus* mass is recovered as residual materials in biorefining processes. On pyrolysis, over 50% of the mass of the residuals is retained as biochar. Yields of biochar from pyrolysis of the residuals from the biorefining of *Miscanthus* are significantly greater than those from the parent product, and have higher surface areas and C contents, but slightly lower high heating values (HHV) and N contents. The NMR evidence shows that the residuals from the biorefining process have lost their carbohydrate components (the objective of biorefining is to transform the cellulose and hemicelluloses of plants into platform chemicals).The NMR evidence also indicates that transformed lignin residues, and aliphatic hydrocarbon materials are major components of the residuals, and these are transformed into biochar products (fused aromatic structures)in the pyrolysis process.

Acknowledgements

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