

## NMR Characterisation of Biofine's by-products Char

Etelvino H. Novotny<sup>1,2</sup>, Michael H.B. Hayes<sup>1</sup>, Eduardo R. de Azevedo<sup>3</sup>, Tito J. Bonagamba<sup>3</sup>, Steve W. Fitzpatrick<sup>4</sup>

1) Chemical and Environmental Sciences, University of Limerick, Ireland;  
2) Embrapa Soils, Brazil; 3) Instituto de Física de São Carlos-USP, Brazil; 4) Biofine, Biometrics, USA

etelvino@cnpis.embrapa.br

Financial Support : Irish Research Council for Science, Engineering and Technology

### INTRODUCTION

>The Biofine Process converts cellulose and hemicellulose components into platform chemicals that can provide a range of chemicals that now are obtained from petroleum.

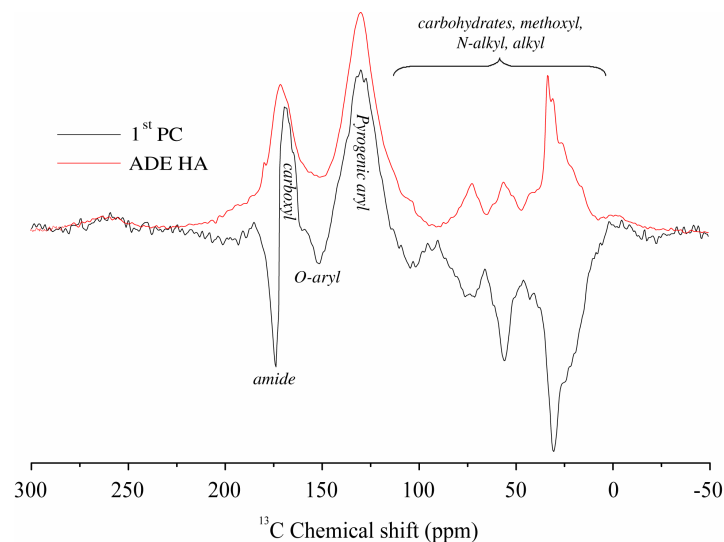
>The residual char can amount to 25-35% of the biomass material introduced. This char has a calorific value similar to that of bituminous coal. On the other hand, the char could be used as a soil conditioner to achieve enhanced and sustainable soil fertility along the lines observed for the "Terra Preta de Índio" or Amazonian Dark Soils (ADE).

>Soils in the Amazon Region: acid, with low CEC, low fertility, and low production potential

>ADE: archeo-anthropogenic horizon of pre-Columbian origin **P** higher fertility and more stable organic matter (OM).

>This high fertility of ADE, and especially its sustainability, is attributed to the high levels of organic matter and to its physical-chemical properties **P** up to 35-45% of the organic C in ADE is in the form of pyrogenic C.

>Pyrogenic C derived from the partial carbonization of ligno-cellulosic materials **P** hydrogen-deficient condensed aromatic structures and high charge density from carboxylic groups linked mainly to the aromatic core (Figure 1).



**Figure 1** - Loading of first PC from solid-state  $^{13}\text{C}$  NMR spectra obtained from HA samples extracted of Amazonian soils (ADE and adjacent non-anthropogenic control soils). Novotny et al. *Environ. Sci. Technol.* 41:400-405 (2007).

### MATERIAL AND METHODS

•Two samples of char-like by-products from the Biofine process were used in this study. The precursors materials were paper and [which plant?] straw.

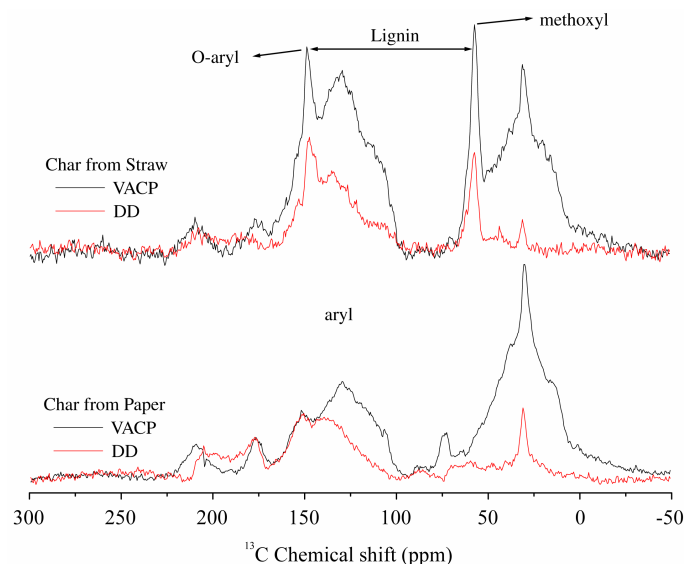
•Variable Amplitude Cross-Polarization (VACP)  $^{13}\text{C}$  NMR experiments were carried out using a VARIAN INOVA spectrometer at  $^{13}\text{C}$  and  $^1\text{H}$  frequencies of 100.5 and 400.0 MHz, respectively. CSA filtered spectra using composite pulse are also obtained.

### RESULTS AND DISCUSSION

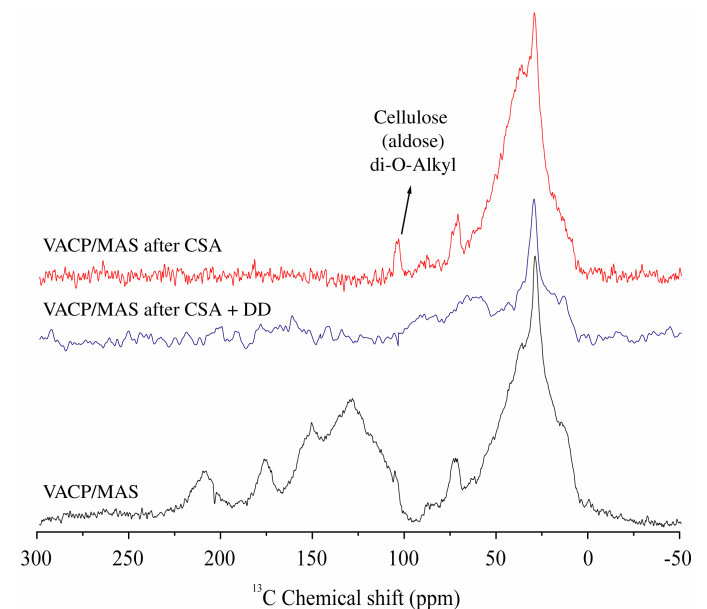
>The char-like by-products from the Biofine process show the symmetrical aromatic resonance characteristic of charcoal materials (Figure 2).

>Additionally these maintain some characteristics of the precursor materials. In the case of the straw substrate signals typical of lignin (e.g.: O-aryl and methoxyl) are evident (Figure 2), and in the case of char from paper, there is evidence for typical cellulose resonances (e.g.: O-alkyl and di-O-alkyl, Figure 3).

>Such characteristics can be important in the transformations of these materials in the soils because the presence of labile compounds would facilitate colonization by microorganisms (primer effect) in the added char and also, after alterations, could produce other reactive functionalities (e.g.: uronic acids).



**Figure 2** – Solid state  $^{13}\text{C}$  NMR spectra of char from straw and from paper.



**Figure 3** – Solid state  $^{13}\text{C}$  NMR spectra of char from paper.

### CONCLUSIONS

•It is possible to pyrolyse the Biofine char to release energy producing gases and to yield residual products with the compositions of conventional chars. Thus the Biofine process has the ability to produce platform chemicals with the potential to replace petrochemicals, and to provide residual materials with considerable potential for soil amendment

•Chemical treatments of char-like materials to provide the functionalization of the aryl groups with carboxylic moieties are being carried out.