



# **Report on the Properties of Pyrolysis Residues Produced and their Utility as Biochars**

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## 1. Executive Summary

The biochar produced from Acid Hydrolysis Residues (AHR) was chemically functionalised and the product characterised by  $^{13}\text{C}$ -NMR and Scanning Electron Microscopy (SEM). The obtained product was tested in a leaching experiment to evaluate its capacity to decrease K losses. The raw material (sugarcane bagasse) and its residues (AHR and biochar from AHR) was incubated in soil during 90 days, to evaluate the  $\text{CO}_2$  and  $\text{N}_2\text{O}$  soil emissions and also in pot experiment to evaluate their effects in soybean production and tree seedlings growing. The partial life cycle analysis was performed and compared to the bagasse burning to electric power production, also the economic analysis was performed.

The water soluble (at alkaline pH) fraction of the functionalised biochar presented a structure, as determined by  $^{13}\text{C}$ -NMR, very similar to the peculiar organic matter found in *Terra Preta de Índios* (Linhares et al., 2012) i.e. a very recalcitrant backbone, formed by polycondensed aryl structure, and reactive, due to the massive presence of carboxyl groups attached directly to the aromatic backbone. The X-ray photoelectron spectroscopy (XPS) confirmed the previous hypothesis (Linhares et al., 2012) of aryl chloride production during the functionalisation process, by the other hand, the acid washing of the AHR, before the pyrolysis, removed the Cr in the material. The functionalised biochar was very effective to decrease (31% to 12%) the K losses by leaching in sandy soil, while in clayey soil, where the K leaching was very low in the control treatment, no statistical difference was detected.

The produced biochar presented a very small surface area ( $2.16 \text{ m}^2 \text{ g}^{-1}$ ) and a narrow pore size distribution with the majority of the pores with 3-4 nm, too small to held microorganisms or fungi hyphae.

Concerning the Simultaneous Thermal Analysis (Thermogravimetry - TGA - and Differential Scanning Calorimetry – DSC – analysis), as expected, the Biochar is more thermo resistant than AHR, with lower content of volatiles and thermo labile compounds and higher proportion of recalcitrant organic material, besides, the recalcitrant exothermic event occurs at higher temperature than the AHR. These results corroborate the former structural analyses by  $^{13}\text{C}$ -NMR.

Both residues (AHR and Biochar) decreased significantly the  $\text{CO}_2$  emissions from the soil, compared to crude sugarcane bagasse. The results for  $\text{N}_2\text{O}$  were inconsistent (very high variability among the repetitions) and is not considered in this report. During the observation period (88 days), the Biochar treatment presented the same accumulated emission that the control while the AHR treatment emitted  $4.99 \text{ Mg ha}^{-1}$  of  $\text{CO}_2$ , that is 26% of the crude bagasse emission ( $19.03 \text{ Mg ha}^{-1}$  of  $\text{CO}_2$ ). The  $\delta^{13}\text{C}$  analysis corroborate these results, i.e. the emitted  $\text{CO}_2$  of the biochar treatment were free of C from the C4 sugarcane bagasse (emission from the native organic matter), while the extra  $\text{CO}_2$  emitted from bagasse and AHR were clearly C4 signed.

Compared to the burning of the produced sugarcane bagasse, for electric power generation, the use of the AHR and Biochar, as soil amendments, resulted in decrease of total  $\text{CO}_2$  emissions of 67 and 66%, respectively.

In the pot experiment, biochar increased the soybean grain production by 16% and tree seedling by 66%, the AHR presented a higher performance for soybean (20%) and similar for tree seedling.

The use of Biochar as soil amendment is ever economically advantageous, however for AHR, if the opportunity cost (AHR as fuel) is considered, a lost is expected. For



Biochar, the economic profit ranges from €4.22 to €90.42 Mg<sup>-1</sup> of applied Biochar, according the selected scenario. For AHR this range is (€0.37) (loss) to €18.79 Mg<sup>-1</sup> of applied AHR. Considering a 30% economic return, a price of €19.05 Mg<sup>-1</sup> for Biochar (up to €63.29 Mg<sup>-1</sup> with residual effect) or €13.15 Mg<sup>-1</sup> is acceptable.

**Significant achievements:**

Several laboratory analyses were performed to characterize the AHR and the biochar seeking for their agronomic use. Incubation experiment proved the potential of the biochar to sequester Carbon in the soil; the product obtained after chemical functionalisation of the biochar reduces the K losses by leaching, however a modification of the process is necessary to avoid the production of potentially toxic compounds; agronomic evaluation of the AHR and biochar showed that they increase the soybean productivity and tree seedling biomass production; the economic evaluation indicates the economical viability of both AHR and biochar, specially taking in account the residual effect of the biochar (at least 3 years).

**Objectives:**

To test the capacity of biochar to guarantee the sustainable biomass production, avoiding soil degradation; sequestering C in the soil; and reducing the glasshouse gas emissions.



## 2. INTRODUCTION

Nowadays the study on carbon storage and its stability in agricultural farmland and forest has been emerging all over the world. Many measures to alleviate the impacts of global warming have been applied to date. Biomass and biochar have been used as soil amendments, however, the practical use of biochar and its mechanism in the soils have not been well known yet.

The charcoal presents the condensed aromatic groups, that guarantee its recalcitrance in the soil, being an efficient material for Carbon sequestration (estimates of its half-life vary of centuries to millennia), however it doesn't present the carboxylic groups, important for its reactivity and contribution for soil CEC, like the organic matter found in *Terra Preta de Índios*, archaeological soils enriched by pyrogenic carbon (carbonised biomass) by human activity. The application of charcoal (Biochar) to the soil, and consequent chemical and biological alterations, will end up generating those acid groups, however that process can delay decades. In that context, and seeking the production of a new agricultural input, preliminary studies indicate that is possible the functionalisation of those materials by chemical (acid oxidation), biological (compost) or enzymatic ways and the enrichment of this with nutrients, such like N, P and K turning them slow-release fertilizer, increasing the efficiency and reducing the losses of the applied nutrients.

Additionally, the application of charcoal to the soil propitiates other benefits, such as: increase of the productivity; suppression of the emissions of methane ( $\text{CH}_4$ ); reduction of the emissions of nitrous oxide ( $\text{N}_x\text{O}$ ); reduction of the need of fertilizers and; reduction of the nutrients leaching. Besides the economic benefits, the environmental benefits should also be taken into account, especially in what it concerns to the global climatic changes, in that context those benefits is added by the reduction of the greenhouse gases emission – GGE ( $\text{CO}_2$ ,  $\text{CH}_4$  and  $\text{N}_x\text{O}$ ) and greater energy efficiency of the agriculture due to the largest productivity, smaller use of fertilizers and smaller losses of nutrients.

Brazil is the largest world producer of charcoal, answering for 38.5% of the production. They are produced 8 million tons of charcoal annually from planted forests, of these up to 15% is found in the form of fine charcoal, a by-product frequently not used in the metallurgical industry, larger consumer of the vegetable coal. Additionally Brazil produces, in the sugar and alcohol industry, about 59.5 million tons of sugar-cane bagasse, most of that bagasse is used in the own distilleries for energy generation; however is still a surplus of 12%, what it could produce 2.3 million tons of charcoal. Besides this, other pyrolysis techniques, and in special employing the biorefinery concept, core of DIBANET project, can supply the energy needs of the distilleries and this having as by-product the biochar. There is several other materials that can be feed the biorefineries, mainly industrial and urban residues that present problems of it discards, such as: residues of the wood industry; of the agro-industry (coffee husks, banana residues, coconut fibbers etc) paper and cellulose industry; biofuels; sewage sludge etc.

### 3. RESULTS

#### Chemical functionalisation of biochar and potassium leaching test

The objective of this work was to obtain organic compounds similar to the ones found in the organic matter of anthropogenic dark earth of Amazonia (ADE) using a chemical functionalization procedure on the produced biochar, as well as to determine their capacity to reduce the losses of K by leaching. The biochar was oxidized with sodium hypochlorite. The NMR spectra (Figure 1) indicate that the obtained products were polycondensed aromatic structures with carboxyl groups: a soil amendment that can contribute to soil fertility, reducing the losses of cationic nutrients (e.g. K) and to its sustainable use.

The proposed structure for this amendment, i.e.: the reactive carboxyl groups attached directly to the recalcitrant aromatic structure, was confirmed by direct identification of this structures by X-ray photoelectron spectroscopy (XPS).

Five components are required to fit the C 1s peak (Figure 2). The binding energy of 284.3 eV corresponds essentially to non-functionalized  $sp^2$  carbons (Papirer et al., 1995). Filik et. al (2003) reported the binding energy of 284 eV to a graphite sample with a full-width half-maximum (FWHM) of 0.98. The humic acids like fraction (HA) have more C=C bounds than fulvic acids like fraction – FA (Table 1). More polycondensed aromatic structure of HA provides a more recalcitrant structure in comparison to FA one (Linahres et al., 2012).

The XPS peaks in 287.5 and 288.4 eV correspond to aryl-carbonyl and aryl-carboxyl groups, respectively. The most difference in C 1s peak observed comparing the fractions FA and HA was relative to carboxyl peak (Figure 2b). Fulvic acid-like fraction showed 15% of carboxyl groups while HA presented 4-7% (Figure 2b). The high carboxylic moieties explain the high solubility of FA at any pH, due to reactivity of the compound and low condensation of the aromatic ring (Linhares et al., 2012).

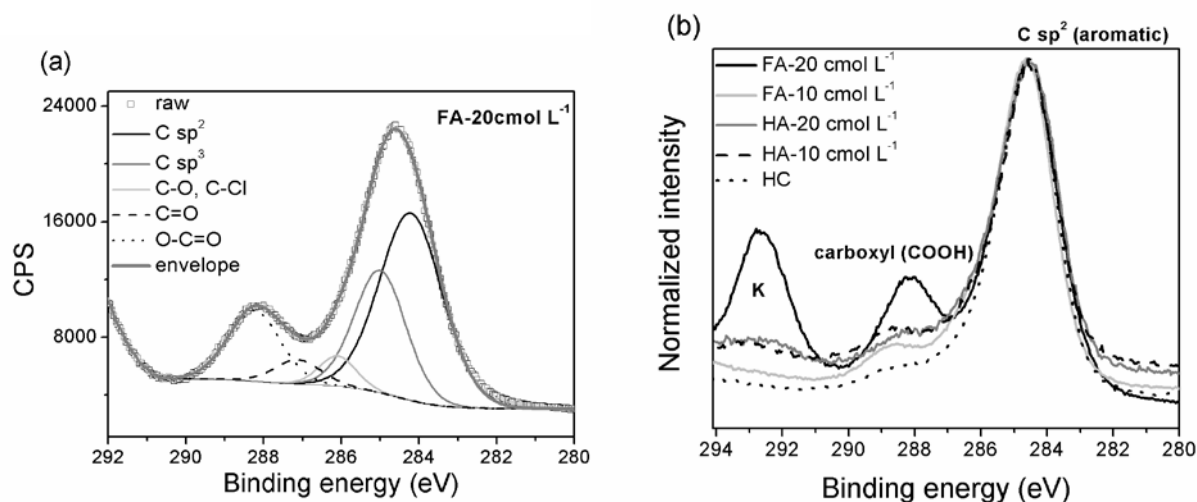
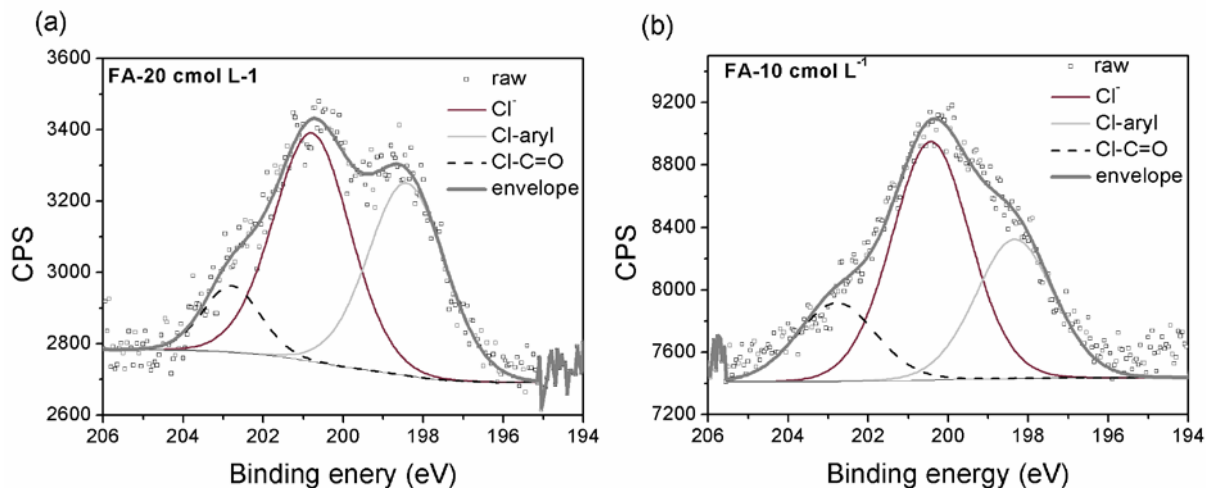


Figure 2 - High resolution XPS spectra in C 1s region where: (a) fulvic acids like fraction showing the curve fitting procedure, (b) C 1s of humic acids like (HA) and fulvic acids like (FA) fractions obtained with NaOCl concentrations of 10 and 20 cmol L<sup>-1</sup>, and Biochar (HC) sample. The peak fit (a) was realized considering the following contributions: C=C ( $sp^2$ ) – peak I, C-C ( $sp^3$ ) and C-Cl ( $sp^2$ ) – peak II, C-O, C-O-C, C-Cl (C  $sp^3$ ) – peak III, C=O – peak IV, and O-C=O – peak V.



However, in the same way that in former study using model biochar (Linhares et al., 2012) aryl chloride was formed during the synthesis of the organic compounds, but now this was confirmed by direct identification by XPS. The peak at binding energies of 285.2 eV (Figure 2a) is essentially attributed to  $sp^2$  carbon atoms linked to one chlorine atom (chlorine substituted  $sp^2$  carbon atoms at the periphery of the polyaromatic structures) (Pérez-Cadenas et al., 2003). Epoxy and phenol groups also contribute near to this binding energy region ( $\sim 285.8$  eV) (Larciprete et al., 2012). Both fractions, FA and HA showed similar amounts of this peak, between 23-28 %, while in biochar (HC) sample, this peak was not detectable. Since the binding energy of C  $sp^2$ -Cl (285.2 eV) overlaps with the oxygen-containing carbon atoms, the final percentage evaluated corresponds to an overall contribution of the two chemical sites, and a examination of a Cl 2p peak is necessary to obtain the Cl-aryl bound percentage in the humic/fulvic fractions.

Chlorine atoms can easily bound to carbon surfaces increasing its Lewis acidity but decreasing its Brönsted acidity due to resonance effect into the aromatic rings (Pérez-Cadenas et al., 2003). The binding energy of  $\sim 200.5$  eV indicate that chlorine atoms were covalently bonded to  $sp^2$  carbon, as reported for organochlorine compounds (Papirer et al., 1995). High resolution Cl 2p peak (Figure 3 a-d) arises from two major components: chlorine in inorganic form (B.E.  $< 199$  eV) where chloride ions are in the salt form bounded with Na, K, Ca or Fe elements, and chlorine atoms in organic form (B.E.  $> 200$  eV) where chlorine atoms are bounded to aromatic C  $sp^2$  atoms or in Cl-C=O bounds (Fiedler and Herzschruc, 1993; Wang et al., 2012).





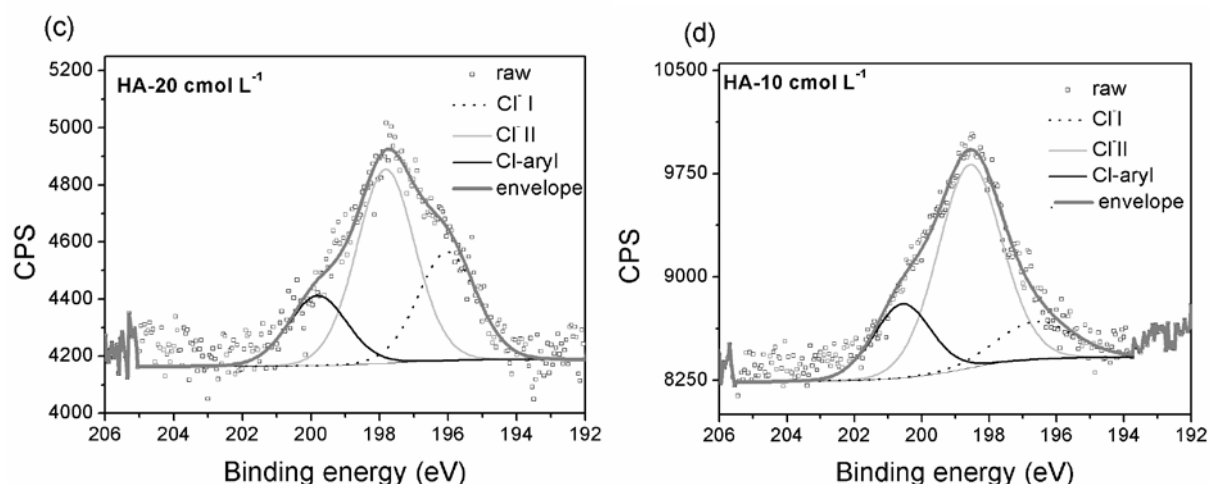


Figure 3 - High resolution XPS spectra in Cl 2p region comparing fulvic acid-like (FA) fractions obtained with NaOCl concentrations of 20 (a) and 10  $\text{cmol L}^{-1}$  (b), humic acid-like (HA) fractions obtained with NaOCl concentrations of 20 (c) and 10  $\text{cmol L}^{-1}$  (d).

Fulvic acids like fractions showed higher content of aryl chloride in their composition, approximately 50% (Figure 3a-b), while the HA fractions showed mainly chloride in salt form, ~80% (Figure 3c-d). This fact corroborates the former results obtained for model biochar (Linhares et al., 2012). Biochar was oxidized with sodium hypochlorite at different concentrations leading to the formation of aryl chloride during the reaction. This byproduct was partially removed through a purification process (Linhares et al., 2012), however, part of this aryl chloride remained in the final products (Figure 2a and 3a-d), that corroborates the infrared and ecotoxicological tests performed in the former study (Linhares et al., 2012). The biochar sample not presented aryl chloride binding energies signals, confirming that its formation is during the functionalisation procedure.

Figure 4 shows Scanning Electron Microscopy (SEM) images of biochar (HC) and its extracts after chemical functionalisation (FA and HA). Comparing the fractions with the HC sample, more similarity can be observed between HC (Figure 4a) and HA (Figure 4b). Compacted microaggregates are found in HA and HC samples, however the size of aggregates in HC are larger than in HA. Chen et al. (2007) reported that the aggregation phenomenon is an important factor in the transport of heavy metal ions in natural environment. Zhang et al. (2009) reported that humic substances form thin thread and net-like structures in dilute solution and grow larger rings and sheets with increasing humic and cation concentration. Humic acid fraction is insoluble at acid medium ( $\text{pH}=1$ ) because the aggregation phenomenon in this pH range.

The soluble FA (Figure 4c) forms distinguishable small particles. This characteristic promotes high metal adsorption capability (Xu et al., 2006). The metals present in this fraction (Fe, K, Na, Ca) can form bridges with carboxyl and other functional groups of humic substances.

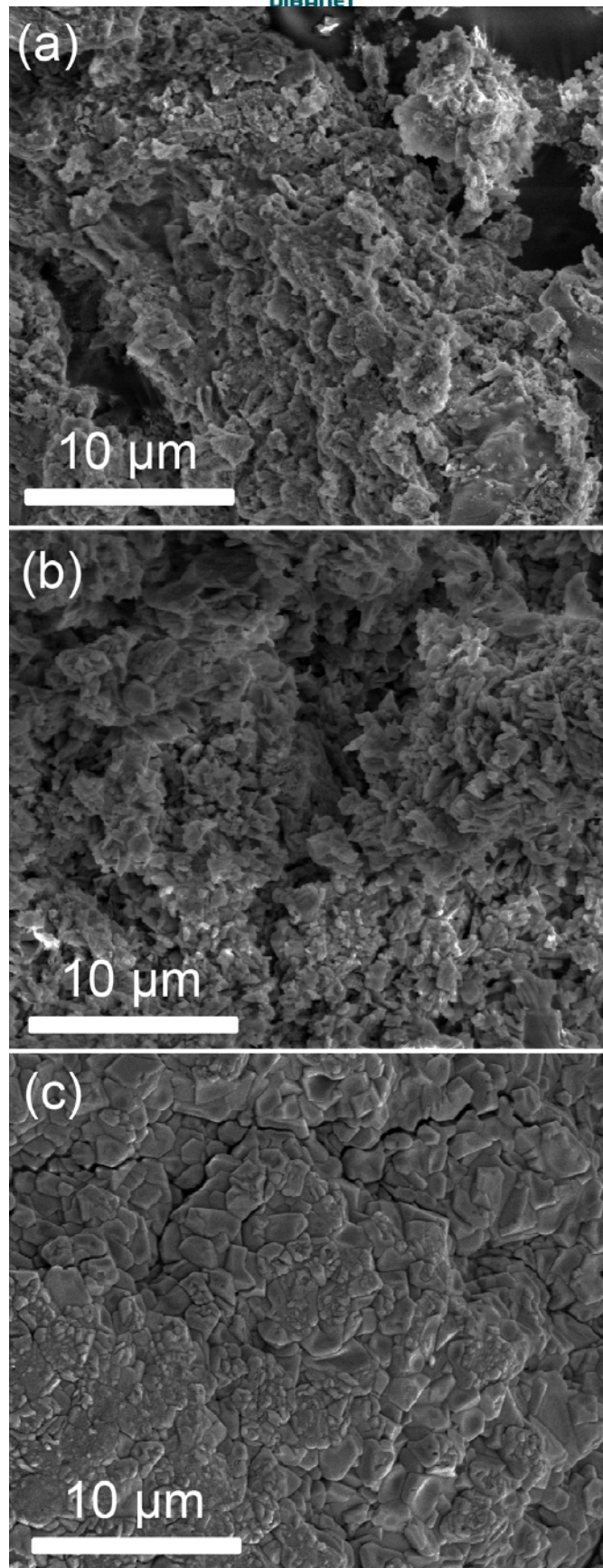


Figure 4 - SEM images of: (a) biochar (HC); (b) humic acid-like fraction and; (c) fulvic acid-like fraction (FA).





The obtained functionalized biochar reduced the K losses by leaching (60 days leaching experiment) in the sandy soil (Figure 5), however no statistical difference was observed in the clayey soil, probably due to the low K losses in the control (without amendment) treatment.

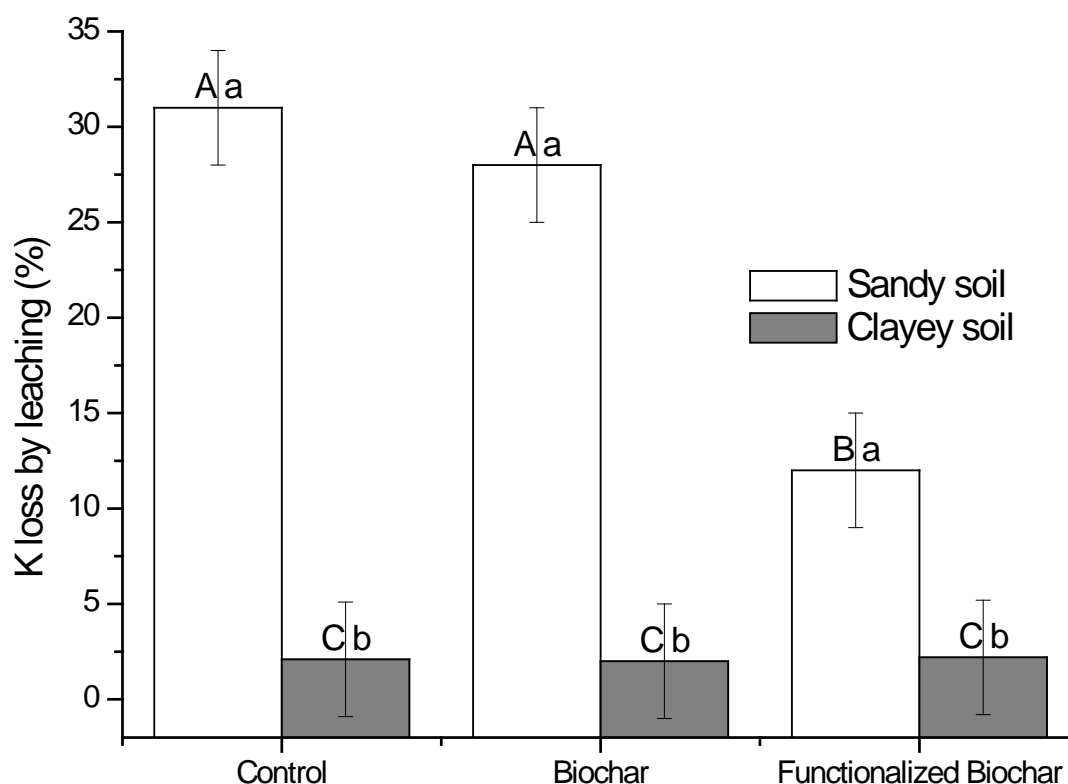


Figure 5 – Potassium losses by leaching (% of the total applied) after 60 days of leaching period. Bars with the same upper case letters do not differ at 5% significant level comparing the biochar treatments. The lower case letters is the comparison between the sandy and clayey soils.

#### **Brunauer–Emmett–Teller (BET) surface area and pore size distribution**

The objective of this work is the characterization of the physical properties (pore size distribution and surface area) of the biochar, these parameters are important for water holding capacity and the role of biochar in protect microorganisms.

N<sub>2</sub> sorption isotherms of biochar from AHR (Figure 6) were of Type II (non porous or macroporous material) and Type IV (mesoporous material).

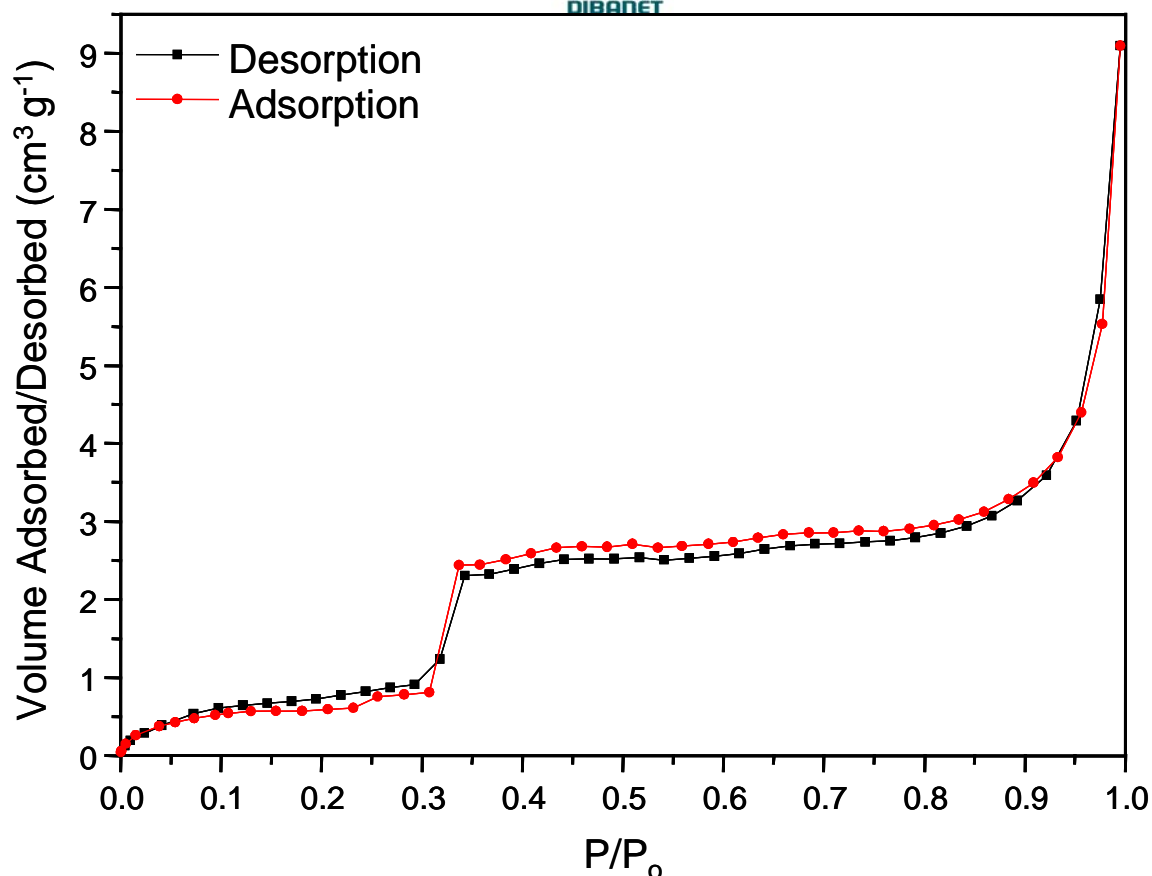


Figure 6 – Liquid N<sub>2</sub> (77 K) sorption isotherms of biochar from AHR.

The surface area, determined by the Brunauer–Emmett–Teller equation (Figure 7a), resulted in a surface area of only 2.16 m<sup>2</sup> g<sup>-1</sup>, a very low value compared to the *Miscanthus* biochar produced at atmospheric pressure (162 m<sup>2</sup> g<sup>-1</sup>) but higher than the one observed in *Miscanthus* biochar produced at high pressure (26 bar = 0.137 m<sup>2</sup> g<sup>-1</sup>), being the pressure determinant to the surface area, probably the employed pyrolysis process occurred at a pressure higher than the atmospheric. The pore size distribution presented a narrow profile (Figure 7b) with the majority of the pores with 3-4 nm, too small to hold fungi hyphae or another microorganisms. The estimated pore volume was 0.007 cm<sup>3</sup> g<sup>-1</sup>.

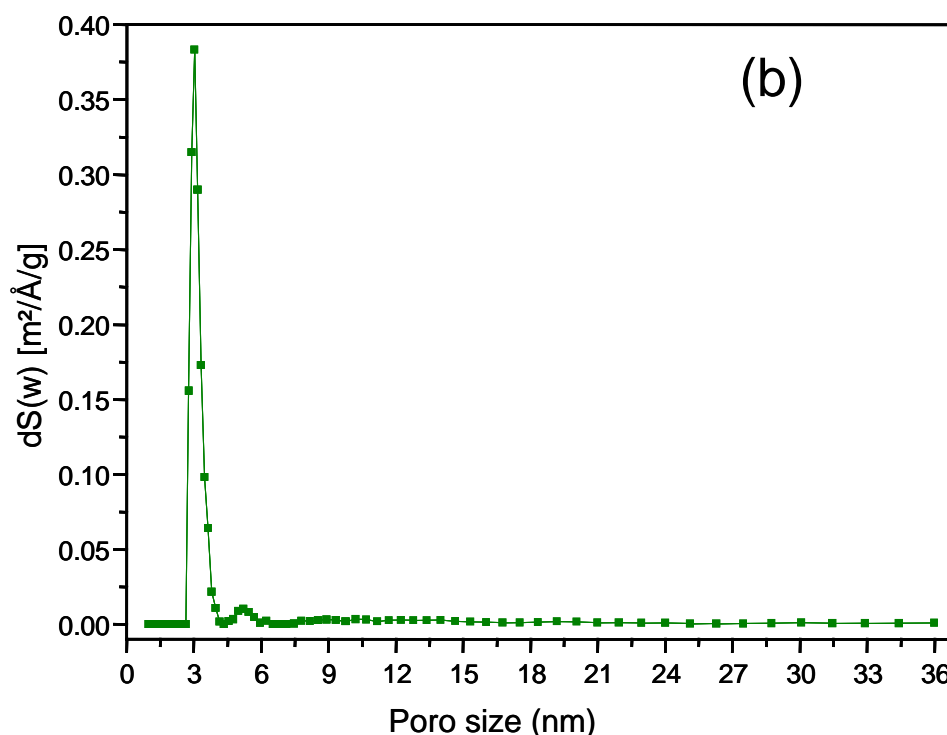
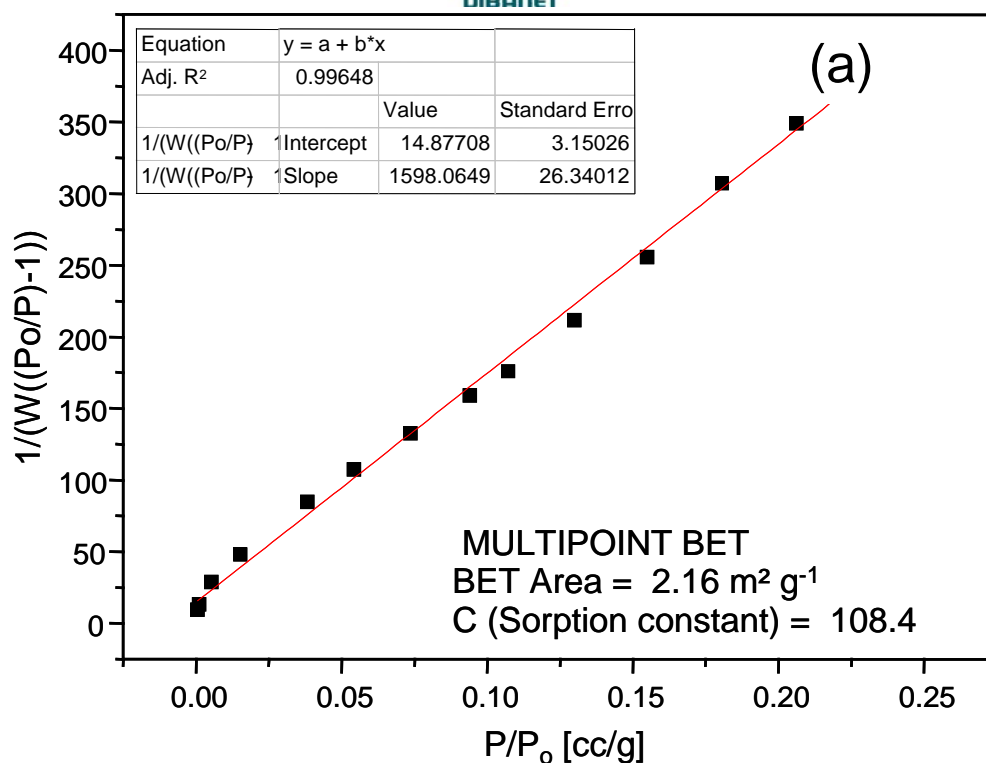


Figure 7 – Multipoint BET adjustment of Biochar from AHR (a) and Pore size distribution determined by the Density Functional Theory (DFT) of the same sample (b).

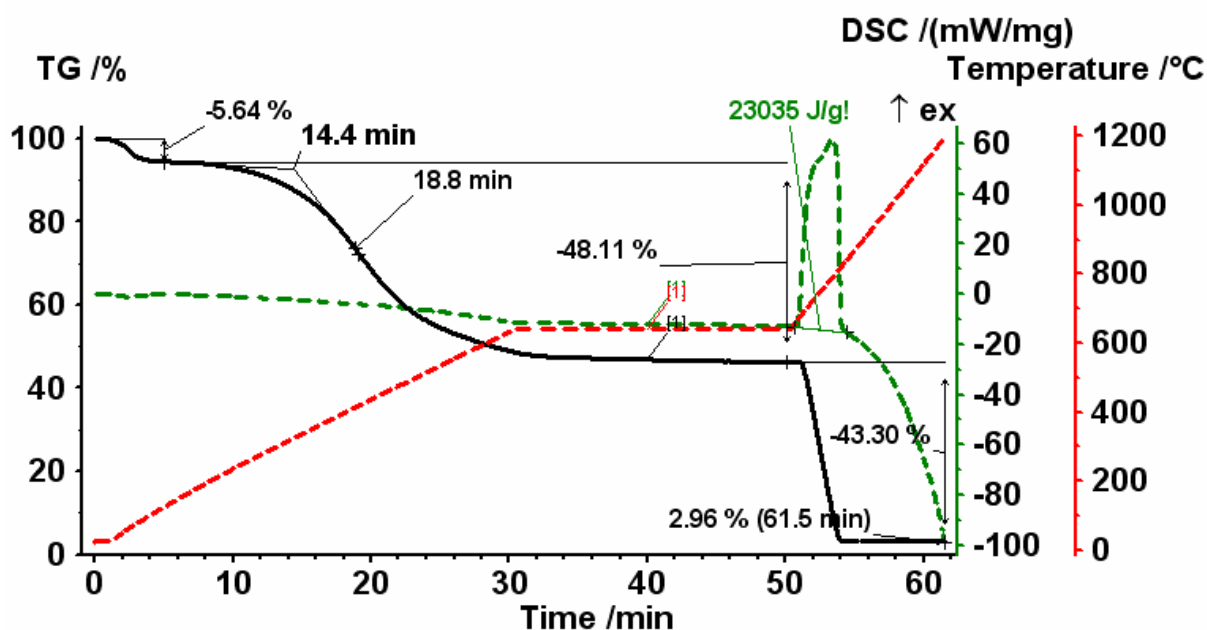
### Simultaneous Thermal Analysis (TGA/DSC)

The objective of this work is to characterize the thermal degradation of AHR and Biochar. The thermo stability of these materials can be used to infer about their



environmental stability and so their potential as C sequester and so to request Certified Emission Reduction (CER), an additional revenue to the farmers.

The AHR showed a 10% mass loss of relative thermo labile (mass loss between 105-350 °C) while the Biochar, in the same region, lost only 1.6% of its mass (Figure 8). For the AHR, probably this lost correspond to the thermal degradation (decarboxilation) of residual fat acids detected in the NMR spectrum and for Biochar probably this lost correspond to light volatiles. This highest content of thermo labile compounds extend to 640 °C, since from 105-640 °C the AHR lost 48.1% of its mass while the Biochar just 12.7%. On the other hand, the thermo stable compounds in Biochar (640-1000 °C) correspond to 73% of the total mass and AHR just 12.7%. Besides, the mass loss of Biochar extend to up 1000 °C while for AHR the lost stop around 840 °C, this mass loss is a exothermic event and it occurs at highest temperature for Biochar. Considering these results, besides the higher content of thermo stable material, this material in Biochar needs higher temperature to degrade than AHR, resulting that the Biochar, as expected, is more thermo stable in the whole than AHR. These results corroborate the former structural analyses by  $^{13}\text{C}$ -NMR. Additionally, the Biochar present a higher Gross Calorific Value (HHV) since the exothermic peak released more energy and the amount of this recalcitrant component is higher in Biochar than in AHR, this is important if biochar is considered to be used as fuel, however it is very important take in account the importance of return C to the soil to avoid the soil degradation. The ash contents were 3 and 7.6% for AHR and Biochar, respectively.



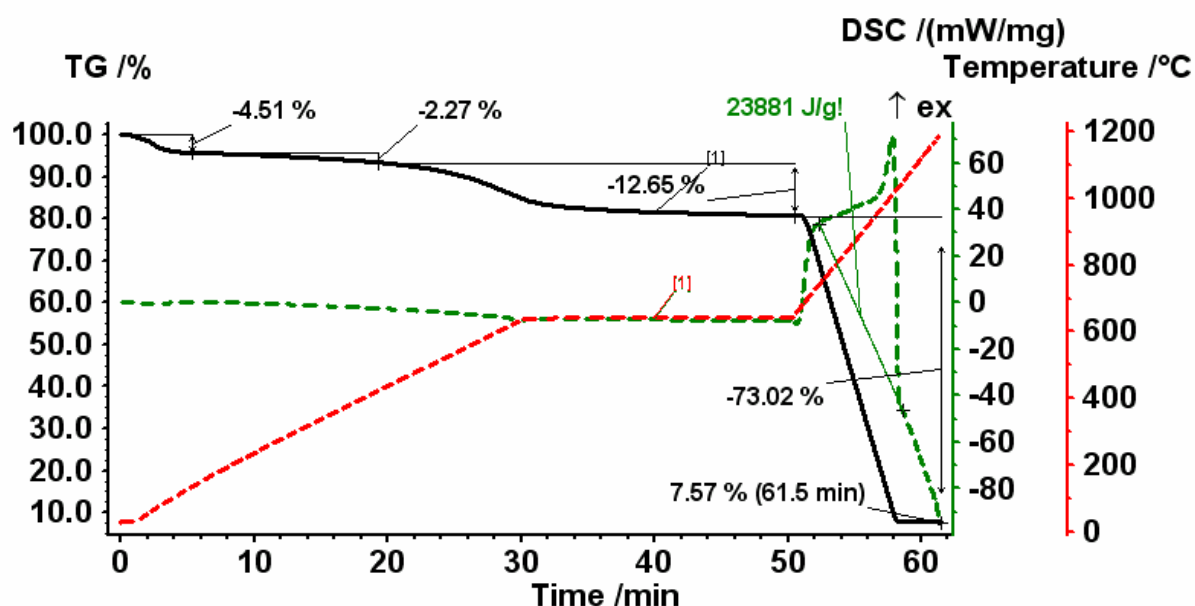


Figure 8 – Simultaneous Thermal Analysis (Thermogravimetry and Differential Scanning Calorimetry) of AHR (top) and of Biochar from AHR (bottom).

### Biochar and soil CO<sub>2</sub> emissions

The objective of this work was to evaluate the effect of AHR and biochar application on soil CO<sub>2</sub> emissions and determinates their capacity to C sequestration and potential to request Certified Emission Reduction (CER). The experiment was carried out in closed chambers under greenhouse conditions in a C3 (under forest) clayey soil. All the comparative trials were made considering the average productivity of sugarcane bagasse (48 Mg ha<sup>-1</sup>, wet basis that represent 24 Mg ha<sup>-1</sup> dried), since the yield of AHR was 35% and of Biochar was 21% from the original bagasse, the tested doses were:

- 24 Mg ha<sup>-1</sup> of dry sugarcane bagasse;
- 8.4 Mg ha<sup>-1</sup> of AHR;
- 5.04 Mg ha<sup>-1</sup> of Biochar.

Seeking to following the origin of the emitted CO<sub>2</sub>, the stable isotopic ratio technique ( $\delta^{13}\text{C}$ ) was employed, for this a soil under forest (C3 carbon fixation plants), that differ significantly from the tested materials (Table 1) was selected.

During the observation period (88 days), the Biochar treatment presented the same accumulated emission (4.06 mg of C, in CO<sub>2</sub> form, per kg of soil per h) that the control (4.07 mg C-CO<sub>2</sub> kg<sup>-1</sup> h<sup>-1</sup>), the AHR treatment emitted 5.25 mg C-CO<sub>2</sub> kg<sup>-1</sup> h<sup>-1</sup> and the crude bagasse treatment 8.58 mg C-CO<sub>2</sub> kg<sup>-1</sup> h<sup>-1</sup> (Figure 9). Considering the surplus emission in relation to the control, and converting in total emission in the whole period per hectare, the AHR treatment emitted 4.99 Mg ha<sup>-1</sup> of CO<sub>2</sub> (Figure 10) that is 26% of the crude bagasse emission (19.03 Mg ha<sup>-1</sup> of CO<sub>2</sub>). These emissions correspond to the mineralization (evolution to CO<sub>2</sub>) of 52 and 26% of the added sugarcane bagasse and AHR, respectively.



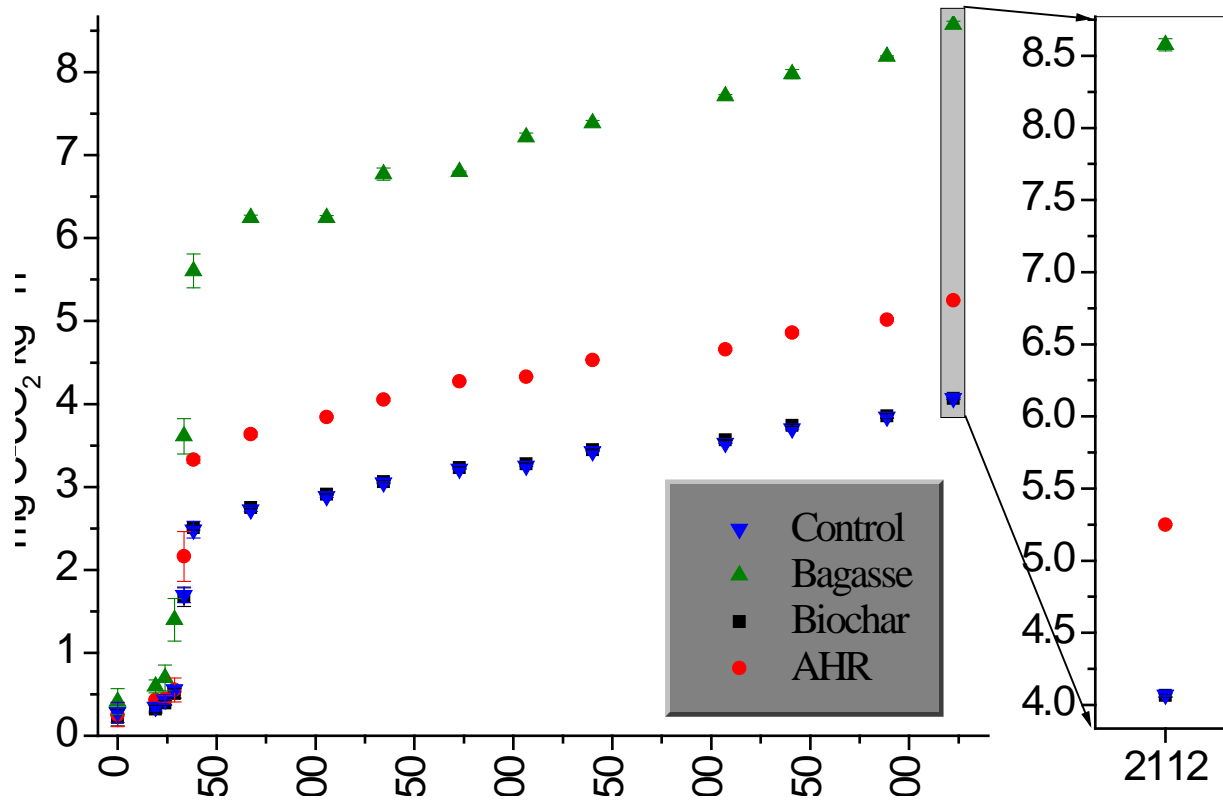


Figure 9 – Accumulated CO<sub>2</sub> emission

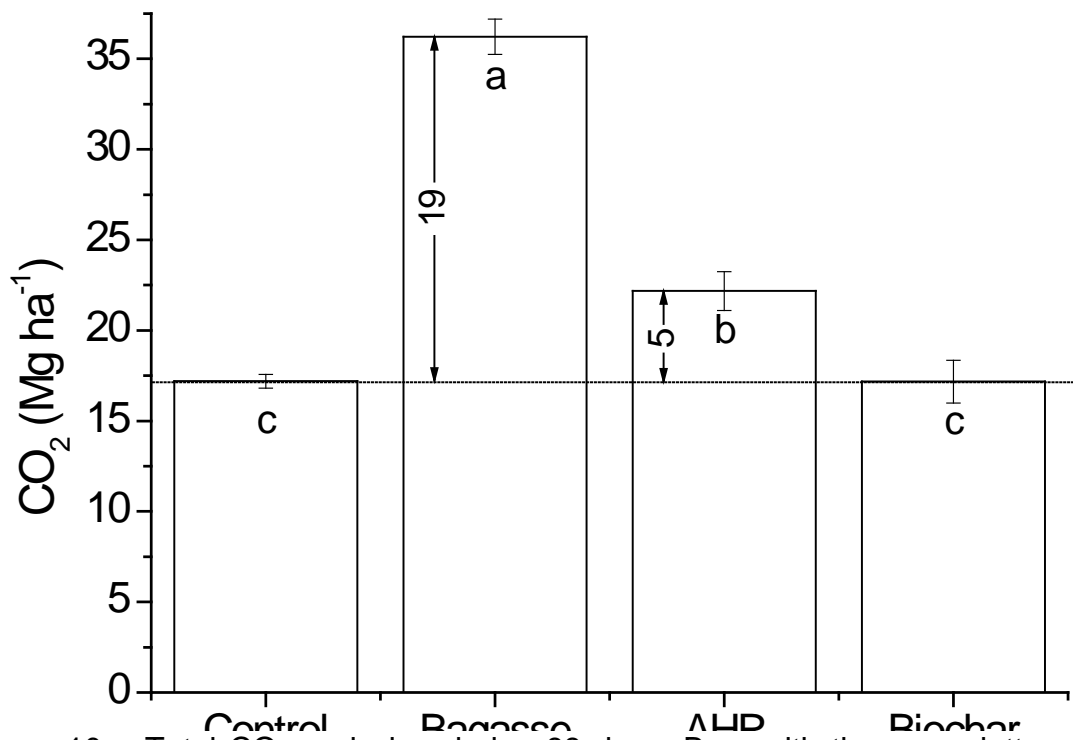


Figure 10 – Total CO<sub>2</sub> emission during 88 days. Bars with the same letters do not differ at 5% significant level. The numbers in the double arrows are the surplus emission compared to the control.



The  $\delta^{13}\text{C}$  analysis corroborates these results, i.e. the emitted  $\text{CO}_2$  of the biochar treatment were free of C from the C4 sugarcane bagasse (emission from the native organic matter), while the extra  $\text{CO}_2$  emitted from bagasse and AHR were clearly C4 signed (Table 1).

Table 1 –  $^{13}\text{C}$  signatures ( $\delta\text{‰ }^{13}\text{C}$  pdb) of studied soil and materials and of the emitted  $\text{CO}_2$ .

Sample/Treatment	Sample $\delta\text{‰ }^{13}\text{C}$ pdb	Emitted $\text{CO}_2$ $\delta\text{‰ }^{13}\text{C}$ pdb
Sugarcane bagasse	-13.48	-18.54
AHR	-13.51	-21.73
Biochar	-13.54	-24.09
Soil (Control)	-24.11	-24.12

Compared to the burning of the produced sugarcane bagasse, for electric power generation, the use of the AHR and Biochar, as soil amendments, resulted in decrease of total  $\text{CO}_2$  emissions to 67 and 66%, respectively, however it is important to stress the shorter half-life of the AHR in the soil than biochar (Figure 9). For these accounts, the total  $\text{CO}_2$  emissions during the AHR and Biochar production were computed (including the full burning of the main acid hydrolysis products: furfural and levulinic acid), as well as the  $\text{CO}_2$  emitted by the biooil produced. On the other hand, the potential Certified Emission Reduction (CER) of these products and of the electric power generation by the bagasse burning were computed as well.

### Agronomic evaluation of AHR and Biochar

The objective of this work is to evaluate the effect of AHR and Biochar in the soybean production (glasshouse trial) and in the growing of tree seedling. For the soybean experiment, 5 kg pots were filled with limed and fertilized clayey soil and the equivalent doses of Biochar ( $5.04 \text{ Mg ha}^{-1}$ ) and AHR ( $8.4 \text{ Mg ha}^{-1}$ ) were incorporated into the soil. A control treatment was included. The experimental design was full randomized with 5 replicates and the experiment was conducted until full cycle of the soybean. For the tree (*Acacia mangium*) seedling trial, seedling trays ( $180 \text{ cm}^3$  each cell) was filled with 50:50 sand:soil mixture and 10% (w/w) of Biochar and AHR were tested in a full randomized trial, the control treatment was included. The experiment was conducted during 90 days.

Biochar increased the soybean grain production by 16% and and AHR by 20% (Figure 11a). For tree seedling both amendments increased the dry mass production by 66% (Figure 11b).

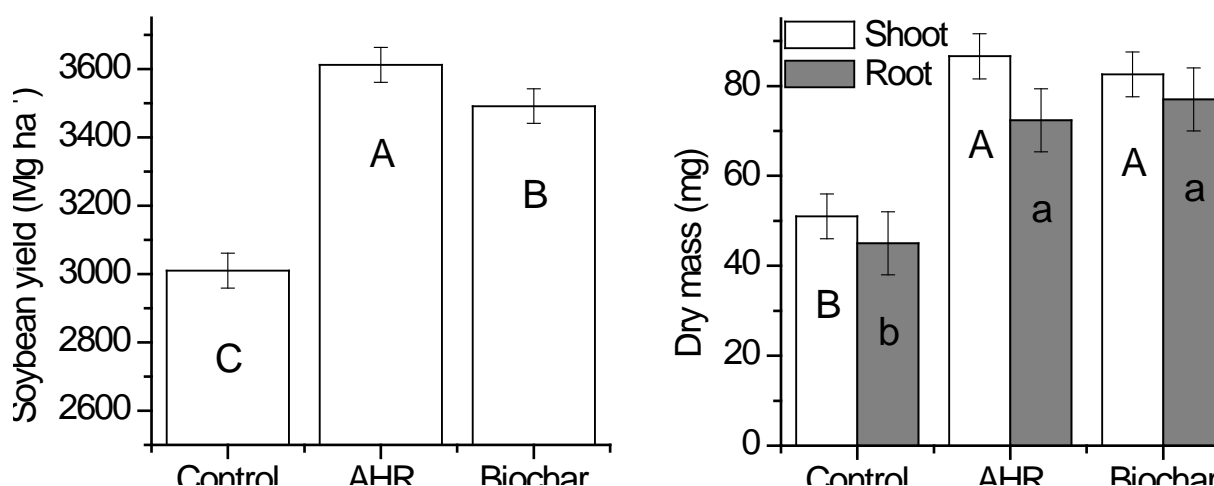


Figure 11 – Soybean yield and tree seedling growing in function of Biochar ( $5.04 \text{ Mg ha}^{-1}$ ) and AHR ( $8.4 \text{ Mg ha}^{-1}$ ) application. Bars with the same upper case letters do not differ at 5% significant level. The lower case letters refer to root yield evaluation.

### Economic evaluation of AHR and Biochar

Taking in account the results of the increase of soybean yield and its current price (March/2013) in Brazil (Table 2), the biooil value as fuel, and also the potential CER revenue (decrease in  $\text{CO}_2$  emissions) due to the use of AHR and Biochar as soil amendment, and the cost involved in this use a brief economic evaluation of AHR or Biochar use is done.

For estimate the application cost it was considered all the costs (fixed and variable costs) such as: transport, application, machine depreciation, money cost, amortization etc, of a similar input - limestone (in application rates and technique sense) in a typical Brazilian agriculture region (Middle West) was considered. Additionally three scenarios were evaluated: Biochar and AHR as residues (cost null); Biochar and AHR as a commercial input and; opportunity cost (Biochar and AHR as fuel). An additional situation was considered, the residual effect of Biochar verified in former studies using model compounds (at least 3 years). The used values are in the Table 2.

Table 2 – Market values considered in the economical evaluation

Item	Value
<b>Costs</b>	
Application (based in limestone application for soybean in Mato Grosso do Sul State)	€4.39 $\text{Mg}^{-1}$ of input
AHR or Biochar commercial value (based in the market value for fines of charcoal in Middle West Brazil)	€5.00 $\text{Mg}^{-1}$
AHR as fuel (considering a value of €6.39 $\text{MJ}^{-1}$ )	€19.16 $\text{Mg}^{-1}$ of AHR
Biochar as fuel (considering a value of €6.39 $\text{MJ}^{-1}$ )	€22.99 $\text{Mg}^{-1}$ of Biochar
<b>Revenue</b>	
Soybean (Brazilian price at March/2013)	€319.28 $\text{Mg}^{-1}$ of



CER (European Climate Exchange value of March/2013 value)	soybean €0.30 CER <sup>-1</sup>
Biooil as fuel (considering a value of €6.39 MJ <sup>-1</sup> )	€12.26 Mg <sup>-1</sup> of Biooil

The Table 3 summarize the results for the different scenarios.

Table 3 – Economic profit (in € Mg<sup>-1</sup> of soil amendment)

Soil amendment	As fuel	Commercial value	Residue
Biochar	4.22	22.21	27.21
Biochar (3 years residual effect)	67.43	85.42	90.42
AHR	-0.37	13.79	18.79

The only situation that the farmer will have loss using Biochar or AHR as a soil amendment is in the case that AHR value is stipulated as a fuel. In all the situations it is more profitable the use of Biochar instead AHR. Besides, it is economically advantageous the use of Biochar as soil amendment that burn it to generate electric power. In a single year harvest (supposing no residual effect), the economic profit ranges from €4.22 to €27.21 Mg<sup>-1</sup> of applied Biochar. In the case that the observed residual effect is considered, a gain up to €90.42 Mg<sup>-1</sup> is possible, depending of the price of the Biochar.

The maximal price (null economic profit) is equal to AHR and Biochar as residue (last column in Table 3), in this way, considering 30% economic return, a price of €19.05 Mg<sup>-1</sup> for Biochar (up to €63.29 Mg<sup>-1</sup> with residual effect) or €13.15 Mg<sup>-1</sup> is acceptable.

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# Properties of Pyrolysis Residues Produced and their Utility as Biochars

## Embrapa Soils – Etelvino Henrique Novotny

### Introduction

Charcoal (Biochar) could contribute to carbon sequestration and work as a soil amendment.

Charcoal presents the condensed aromatic groups, that guarantee its recalcitrance in the soil, being an efficient material for C sequestration.

However it doesn't present the carboxylic groups, important for its reactivity and contribution for soil CEC, like the organic matter found in Terra Preta de Índios, archaeological soils enriched by pyrogenic carbon (carbonised biomass) by human activity.

The application of charcoal (Biochar) to the soil, and consequent chemical and biological alterations, will end up generating those acid groups, however that process can delay decades.

Preliminary studies indicate that is possible the functionalisation of those materials by chemical, biological (compost) or enzymatic ways.

Additionally, the application of charcoal to the soil propitiates other benefits, such as: increase of the productivity; suppression of the emissions of CH<sub>4</sub> and N<sub>x</sub>O; reduction of the need of fertilizers and; reduction of the nutrients leaching.

Brazil produces about 200 million tons of sugar-cane bagasse, most of that bagasse is used in the own distilleries for energy generation, however is still a surplus of 12%, what it could produce 2.3 million tons of charcoal.

Besides this, other pyrolysis techniques, and in special employing the biorefinery concept, core of DIBANET project, can supply the energy needs of the distilleries and this having as by-product the biochar.

There is several other materials that can be feed the biorefineries, such as: residues of the wood and cellulose industry; of the agro-industry (coffee husks, banana residues, coconut fibers etc); biofuels; sewage sludge etc.

### Results and Discussion

The acid hydrolysis was very effective to remove the carbohydrates from the biomass (Figure 1), since the main signal from the NMR were from alkyl and lignin, however the contribution of furanyl structures, product of thermal decomposition of cellulose, cannot be excluded.

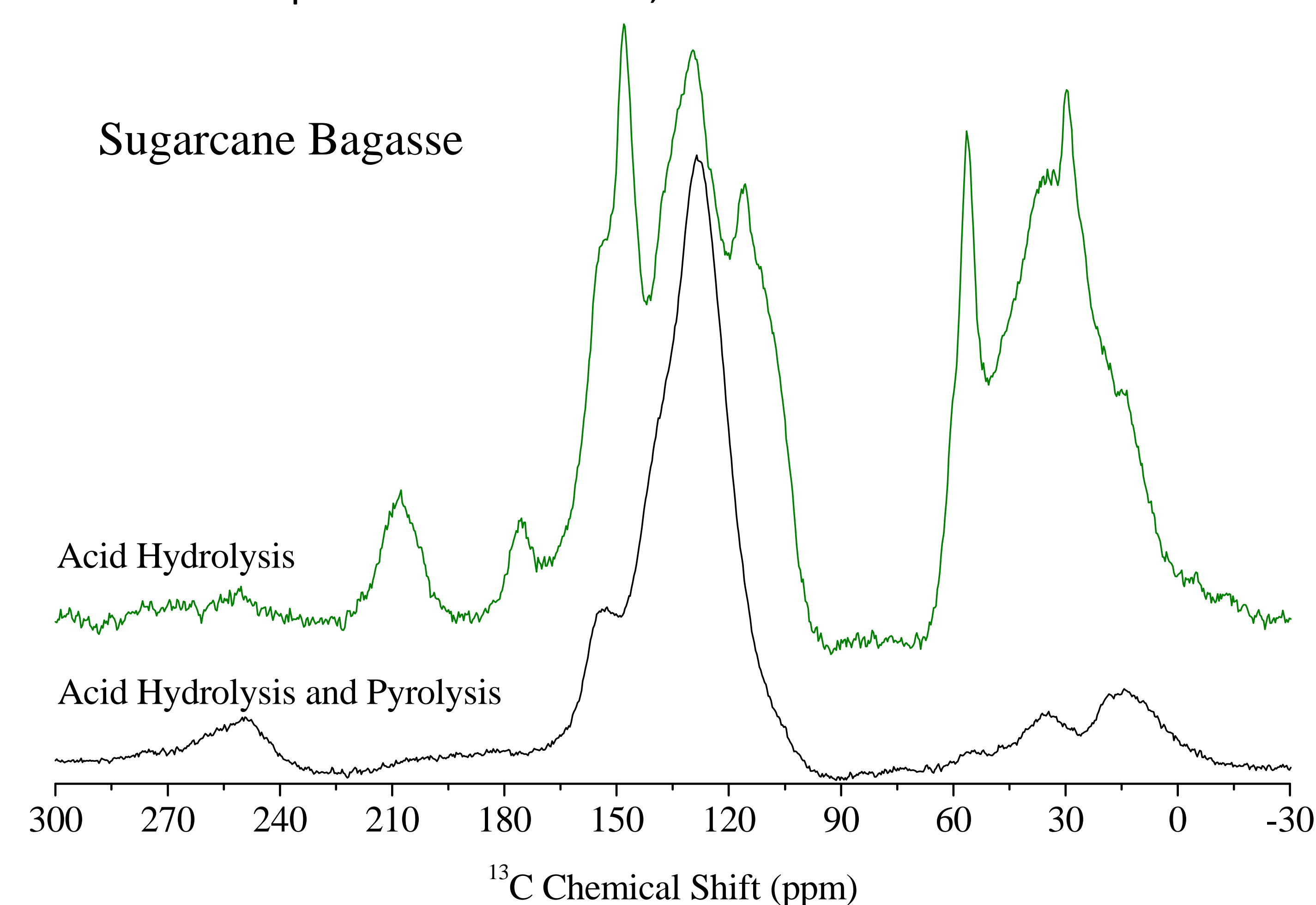


Figure 1 - Solid state <sup>13</sup>C NMR spectra of acid hydrolysis residue from sugarcane bagasse and of the biochar produced from this residue.

On the other hand, the AHRs obtained by Unicamp (Figure 2) presented significative amounts of residual carbohydrates (O-alkyl at 72 ppm and di-O-alkyl at 105 ppm), indicating that the laboratory scale acid hydrolysis is not so effective as the pilot one.

Interesting is the strong signal of O-aryl at 144 ppm in the AHR of coffee husk. Since this signal is not accompanied by one equivalent signal at 56 ppm from methoxyl, probably it is not from lignin. Possible compounds are polyphenols (strong aryl signals at 116 and 130 ppm), another interesting product in the biorefining concept. The banana stem also present important O-aryls signals, however, in this case, the strong methoxyl signal indicates lignin.

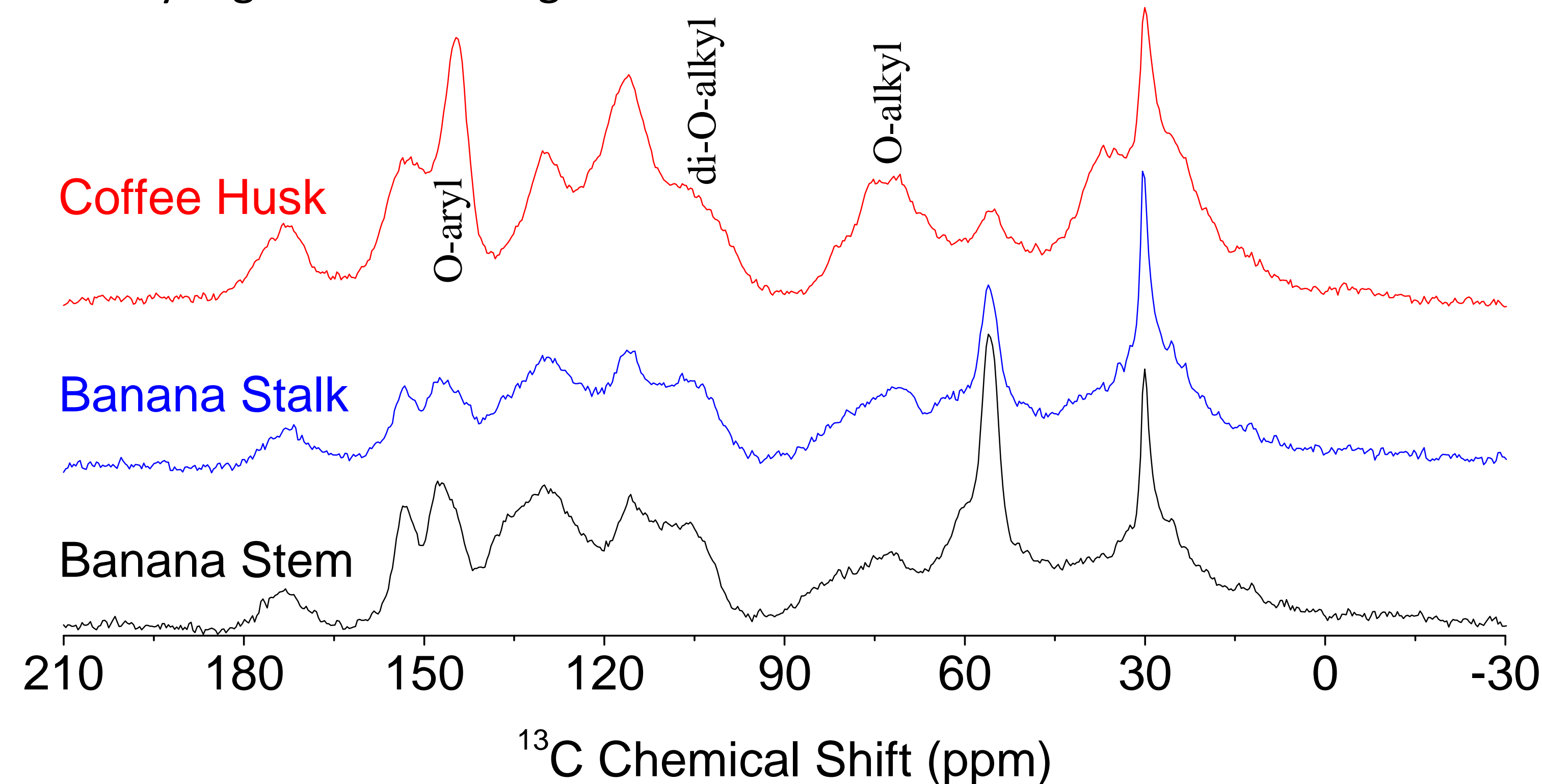


Figure 2 – Solid state <sup>13</sup>C NMR spectra of acid hydrolysis residue from banana and coffee residues, prepared at Unicamp.

The crude biomass (sugarcane bagasse) and the AHR resulted in accumulated soil CO<sub>2</sub> emission of 173% and 123%, respectively, of the soil emission without organic amendment (Figure 3).

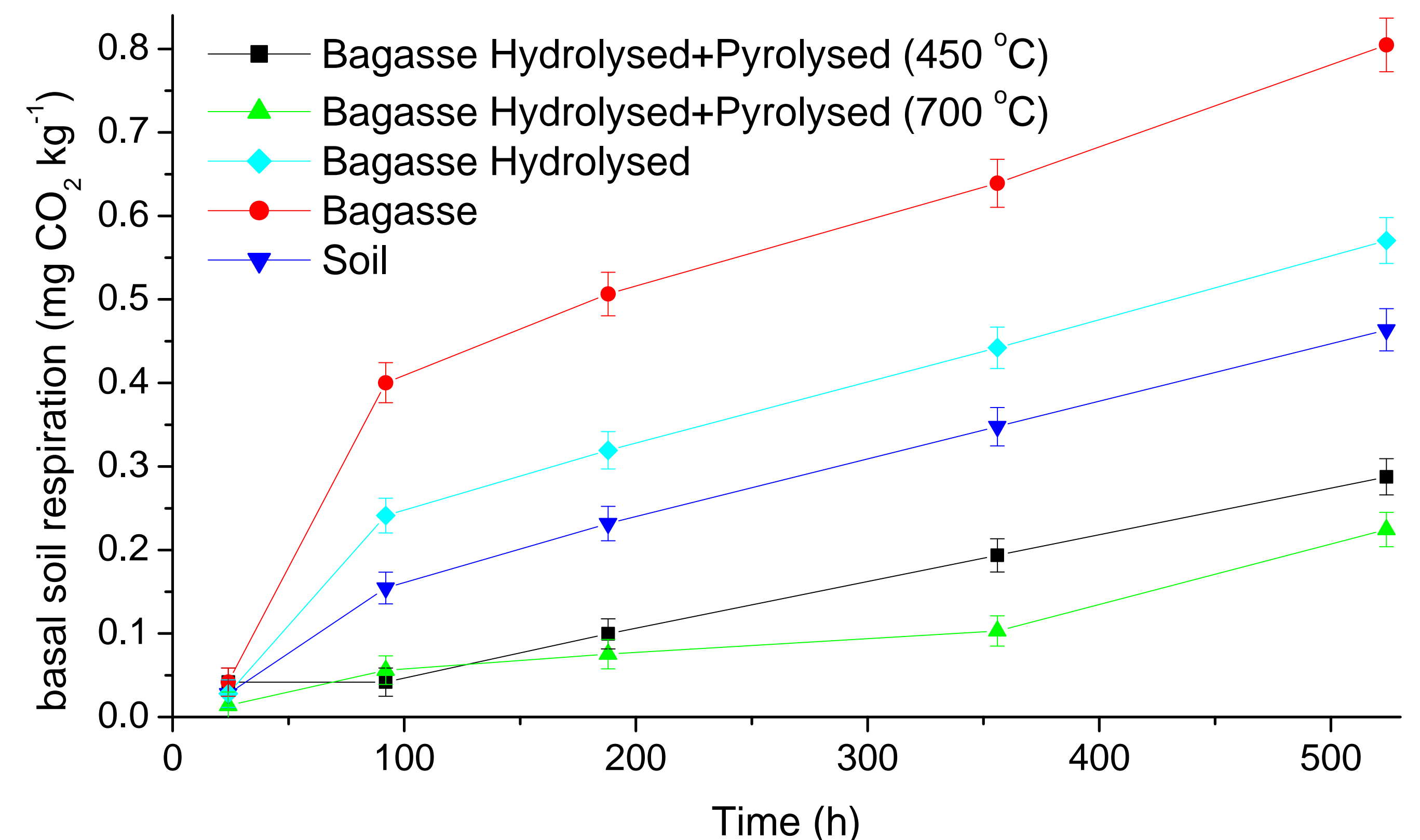


Figure 3 – CO<sub>2</sub> emission from the soil treated with crude sugarcane bagasse; AHR of this sugarcane bagasse; and biochar produced from this AHR.

The pyrolysis of the AHR reduced the accumulated CO<sub>2</sub> emission at 62% (biochar produced at 450 °C) and 48% (700 °C), compared with the soil without organic amendment (Figure 3). The pyrolysed AHR, produced at 450 and 700 °C, emitted 36 and 28% of the CO<sub>2</sub> emitted by the crude biomass, showing the potential of the pyrolysis to stabilize the C in the soil and provide C sequestration, with best results with higher carbonisation.

However, the observed decrease, below the control, could be due to the Cr contamination of the AHR and biochar (Tabel 1) that could inhibit the soil microorganism activity. But it is still unclear if this chromium is in a bioavailable form, further analysis of the plant issue will be confirm this.

Table 1 - Trace metals contents (mg kg<sup>-1</sup>) of the sugarcane bagasse

Sample	Cu	Fe	Mn	Zn	Cr	Ni
AHR sugarcane bagasse	262	347	3	3	465	119
Biochar from AHR	430	582	5	6	730	201