Using Solid State $^{13}$C NMR to Study Pyrolysis Final Temperature Effects on Biochar Stability

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Abstract: Recent results in biochar research show that it is not only composed of stable carbon, since a portion of these materials is degraded relatively easily once applied to soil, and this condition is most dependent on pyrolysis conditions, especially the final temperature. Thus, the aim of this study was to evaluate pyrolysis final temperature effects on the stability of biochar produced from forest residues using solid-state $^{13}$C NMR. Pyrolysis was performed at a heating rate of 10 °C·min$^{-1}$ up to the final temperature of interest (350, 450 and 550 °C), maintaining this temperature for 60 min. Solid-state $^{13}$C NMR spectra were obtained on a Varian 500MHz spectrometer for fresh wood and biochars produced at 350, 450 and 550 °C for Eucalyptus dunnii (DUN), and Pinus caribaea (CAR). Comparing fresh samples with their respective biochars, regardless of the botanical group, after pyrolysis, carbohydrates are degraded, and there is a change in the structure of the materials, with a predominance of aromatic structures, which are more resistant to degradation, therefore reflecting in the increased stability of these materials. For 350 °C, it is still possible to observe signals related to lignin indicating that up this temperature it has not been completely degraded. The spectra of biochars produced at 450 and 550 °C are very similar, indicating that there is no need to produce biochars at very high final temperatures, since the structure of these materials obtained at 550 °C slightly altered as of 450 °C, keeping the predominance of aromatic structures.

Keywords: Biochar, Pyrogenic carbon, Forest residues, Organic matter stability, NMR

Introduction

Biochar is a term used for the solid product obtained from pyrolysis of lignocellulosic materials with the purpose of concentrating carbon (C) in a stable form, to be applied to soil in a deliberately form, in order to storage carbon and for other agronomic benefits.

In this sense, the forest sector, which produces a large amount of lignocellulosic waste from the industries of mechanical processing of wood, as well as byproducts in the pulp and paper industries and biorefineries, can provide considerable amount of raw material for biochar production.

Although biochar is a relatively new concept, recent progress in research is considerable, and results show that biochar is not only composed of stable carbon, fully resistant to degradation, but a portion of the material is degraded relatively easily once applied to soil, and this condition is not only dependent on the characteristics of the raw material itself, but most of the pyrolysis conditions, especially the final temperature.

However, it is not fully clear how much biochar can storage C and what would be the ideal conditions for biochar production, considering the intrinsic variables of different sources of lignocellulosic materials and pyrolysis conditions.

Therefore, efforts have been taken to develop methodologies to quantify the stable fraction present in biochar, quickly and easily reproduced.

Thus, the aim of this study was to evaluate pyrolysis final temperature effects on the stability of biochar produced from forest residues of softwood (Pinus
caribaea) and hardwood (Eucalyptus dunnii) samples by the use of solid-state $^{13}$C NMR.

Material and Methods

Biochar production: Initially, wood samples were dried at ±105 °C for 48 h to remove and standardize moisture content before pyrolysis starts. Pyrolysis was performed in triplicate, at a heating rate of 10 °C·min$^{-1}$ up to the final temperature of interest (350, 450 and 550 °C), maintaining this temperature for 60 min and after this time, the furnace was turned off to let materials to cool down until room temperature. The equipment used was a Quimis muffle furnace, model 319 with limited oxygen supply, equipped with a controller/thermal indicator INCON model CNT 110 and fitted with Liebig condensers coupled to KitaZatos to collect condensable gases and obtain the bio-oil fraction.

Variable-amplitude cross-polarization (VACP) solid-state $^{13}$C NMR experiments were carried out using a 500 MHz Varian spectrometer at $^{13}$C and $^1$H frequencies of 125 and 500 MHz, respectively. Magic-angle spinning (MAS) at 15 kHz was employed. Typical cross-polarisation times of 1 ms, acquisition times of 16 ms, and recycle delays of 500 ms (5 s for fresh samples) were used. High-power Two-Pulse Phase-Modulation (TPPM) proton decoupling of 70 kHz was applied.

Results and Discussion

Solid state $^{13}$C NMR was used to study the effects of pyrolysis final temperature on the structure of the materials, comparing fresh samples of DUN (Fig. 1) and CAR (Fig. 2), with their biochars produced at 350, 450 and 550 °C.

For fresh samples, it was observed in the region between 50 and 105 ppm, signals related to cellulose. These signals overlap with other signals from aliphatic carbons of lignin and partly with the hemicellulose (Haw et al., 1984; Leary et al., 1986). Signals between 72 and 75 ppm correspond to C-2, 3 and 5 of cellulose. Signals at 89 and 65 ppm respectively, correspond to C-4 and C-6 of the crystalline portion of cellulose, while the signals at 84 and 62 ppm correspond to C-4 and C-6 in amorphous region of cellulose, respectively. (Atalla and VanderHart, 1999; VanderHart and Atalla, 1984). At 105 ppm, referring to C-1 of cellulose, for

CAR (conifer), there was a small shoulder at 102 ppm, attributed to the hemicellulose, which is weakly observed for hardwood species (Wikberg and Maunu, 2004).

Fig. 1 Solid-state VACP $^{13}$C NMR spectra for fresh Eucalyptus dunnii (DUN) and its respective biochars produced at 350, 450 and 550 °C (DUN 350, DUN 450 and DUN 550, respectively)

Fig. 2 Solid-state VACP $^{13}$C NMR spectra for fresh Pinus caribaea (CAR) and its respective biochars produced at 350, 450 and 550 °C (CAR 350, CAR 450 and CAR 550, respectively)

A signal is observed at 21 ppm, related to the acetyl methyl groups present in the hemicellulose as both for DUN and CAR, whereas the signal at 173 ppm, related to the carboxyl of acetyl groups present in the hemicellulose is only observable in DUN. Conifers and hardwoods differ in the content and composition of hemicelluloses, where conifers present abundant mannose and have more of galactose compared to hardwood, which present abundant xylose units and more acetyl groups when compared to conifers.

The signal at 56 ppm is related to the methoxyl groups of lignin, while the region between 125 and 160 ppm, related to aromatic C in lignin. The signals at 153 and 148 ppm are related to C-3 and C-5 of syringyl (S) units. The signal at 153 ppm is related to C-4 etherified, which is most evident in DUN, since
hardwood have both S and guaiacyl (G) units. The signal at 148 ppm is also related to C-3 and C-4 of G units, which can also be observed, although not explicitly, in CAR. Also, the signal 136 ppm is attributed to C-1 and C-4 for the S and G units, where C-4 is etherified (Wikberg and Maunu, 2004).

When comparing fresh samples with their respective biochars produced at different temperatures, regardless of the botanical group, after pyrolysis, carbohydrates (cellulose and hemicellulose) are degraded, and there is a change in the structure of the materials, with a predominance of aromatic structures (around 128 ppm), which are more resistant to degradation, therefore reflecting in the increased stability of these materials.

For the lowest final temperature used (350 °C), it is still possible to observe signals at 56 and 148 ppm, related to lignin, since this is the cell wall component most resistant to thermodegradation and at this temperature it has not been completely degraded. It is worth noting that in the present case, these signals appear shifted to DUN.

The spectra of biochars produced at 450 and 550 °C are very similar, indicating that there is no need to produce biochars at very high final temperatures, since the structure of these materials obtained at 550 °C slightly altered as of 400-450 °C, keeping the predominance of aromatic structures. However, it is possible to observe a narrowed region concerning aromatic structures, indicating a decrease in the diversity of aromatic structures. The same pattern was reported by Pereira et al. (2011) for biochars produced from Salix sp. (hardwood) and Pinus sp. (softwood) at 400 and 550 °C.

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References


