

BIOCHAR STABLE FRACTION QUANTIFICATION BY THERMO-CHEMICAL OXIDATION AND ASSESSEMENT BY ^{13}C NMR SPECTROSCOPY

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ABSTRACT: Although biochar is often regarded as inert, it can be oxidized, and finally mineralized into carbon dioxide. However, it is unclear how much of this material is rapidly oxidized, that is, how much remain in the soil for longer periods. Efforts have been undertaken to develop methodologies to quantify the stable fraction present in biochar, quickly, easily reproducible, and that somehow represents real field conditions. Therefore, the aim of this study was to evaluate the effect of different pyrolysis final temperatures on the stability of biochar produced from *Eucalyptus dunnii* wood by analyzing biochar samples before and after a thermo-chemical oxidation using ^{13}C NMR spectroscopy. Stable-C fraction increased as higher pyrolysis final temperature was. Thermo-chemical oxidation was responsible for removing labile structures still present as well as aromatic structures less resistant to degradation. Thermo-chemical oxidation was also responsible for the functionalization of biochars, being this effect milder as higher pyrolysis final temperature was. The balance between C storage (Stable-C fraction) and agronomic benefits (functionalization) of biochar should be carefully evaluated, as its characteristics can vary depending on the conditions by which it was produced.

KEYWORDS: biochar, carbon sequestration, stability, thermo-chemical oxidation, functionalization

INTRODUCTION: The term biochar was recently proposed after studies with regard to the quality of Terra Preta de Índio's (TPI) soil organic matter as a model for sustainable use of soils in agreement with climate changes and carbon (C) sequestration issues (LEHMANN & JOSEPH, 2009). The term is used for lingo-cellulosic materials undergoing pyrolysis (environments with little or no oxygen supply), similar to the process for charcoal production. However, biochar distinguishes from charcoal and other similar

materials, since it is produced to be applied to soils in order to improve their chemical, physical and biological characteristics. Its distinct use presents some requirements and challenges (MAŠEK et al, 2011). Although biochar is often regarded as inert, it can be oxidized, and finally mineralized into carbon dioxide (GOLDBERG, 1985). However, it is unclear how much of this material is rapidly oxidized, that is, how much remain in the soil for longer periods. Some authors have proposed methods using high temperatures aerobic oxidation (TOLES et al., 1999), reaction with strong oxidizing chemicals (MORENO-CASTILLA et al, 2000), or ozone oxidation (SERGIDES et al, 1987; KAWAMOTO et al, 2005), which demonstrates that biochar can be abiotically oxidized in the short term. Other authors suggested that abiotic oxidation can occur through chemical adsorption of oxygen by aging processes (PURI, 1963, PURI, 1970; BILLINGE & EVANS, 1984; ADAMS et al, 1988). However, the short term oxidation under ambient temperature and atmosphere has not been recognized and/or sufficiently quantified, and the extent of both effects (biotic and abiotic) oxidation is still not sufficiently clear (CHENG et al, 2006). Therefore, efforts have been undertaken to develop methodologies to quantify the stable fraction present in biochar, quickly, easily reproducible, and that somehow represents real field conditions. Therefore, the aim of this study was to evaluate the effect of different pyrolysis final temperatures on the stability of biochar produced from *Eucalyptus dunnii* wood by analyzing biochar samples before and after a thermo-chemical oxidation using ^{13}C Nuclear Magnetic Resonance (NMR) spectroscopy.

MATERIAL AND METHODS: *Eucalyptus dunnii* (DUN) wood samples were obtained from experimental plantations in Embrapa Florestas (Colombo, Brazil). Wood samples were ground-

ed in a knife mill and then sorted for greater uniformity of particle size. The fraction retained between sieves of 0.5 and 2.00 mm was used. Initially, wood samples were dried at 103 °C for 48 h for moisture removal before pyrolysis. Approximately 10 g of wood samples were weighed and placed in commercial aluminum foil then placed in metal tubes. Pyrolysis was performed in triplicate in a muffle furnace (Quimis, model 319) with limited oxygen supply, equipped with heat indicator (Incon, model CNT 110) at a heating rate of 10 °C.min⁻¹ (slow pyrolysis) to three final temperature (350, 450, and 550 °C) maintained for 60 min. After this time the muffle furnace was turned off for gradual cooling of samples.

Thermo-chemical oxidation was performed according to CROSS & SOHI (2012), as a proposed accelerated aging of biochar aiming to oxidize unstable fraction (labile) and to evaluate biochar stability by quantifying the remaining (stable) C content after oxidation. Initially biochar samples were pulverized in a ball mill to increase particles physical exposure and then dried at 80 °C for 24 h. Approximately 0.2 g sample were weighed in a test tube, then 7 mL of 5% hydrogen peroxide (H₂O₂) solution was added under stirring. Samples were then kept in an oven at 80 °C for 48 h under periodical stirring (approximately every 2 h). After this period, samples were dried at 105 °C for 24h. Samples were then placed in a desiccator for approximately 60 min before weighing to obtain Stable-C yield gravimetrically. Elemental analysis was performed (C content) before and after thermo-chemical oxidation.

Solid-state ¹³C NMR spectra were obtained in a 500 MHz spectrometer (Varian), using a 4 mm triple resonance probe (T3 NB HXY) to implement VACP-MAS (Variable Amplitude Cross Polarization - Magic Angle Spinning) experiment to detect the ¹³C nuclei of biochar samples before and after oxidation. The speed of rotors was 15 kHz under compressed dry air at room temperature. The time of π/2 pulses calibration for H nuclei was 3.4 μs, C signal acquisition time was 16 ms, and repetition time was 500 ms. Initially, equipment calibration was proceeded using glycine sample as a reference, C methyl at 43.7 ppm, and the speed of rotors of 5 kHz, under compressed dry air at room temperature. Subsequently, the data were processed in software VNMRJ[®] version 3.1 (Agilent).

RESULTS AND DISCUSSION: It is observed that as higher pyrolysis final temperature was, higher was the Stable-C content, ranging from 73.86, 80.79 and 86.67% for 350, 450 and 550°C, respectively. For the lowest pyrolysis final temperature (350 °C), it is observed that thermo-chemical oxidation was responsible for removing part of the labile structures still present in biochars as well as remove aromatic structures less resistant to degradation, which may be evidenced by a decrease in the frequency and narrowing of the region corresponding to aromatic structures, which explains the higher mass loss of these samples after oxidation, which also result in lower levels of Stable-C fraction. Thus, there was no selective oxidation observed as both labile and non-labile (in this case, aromatic) underwent oxidation. For biochars produced at 450 and 550°C, there was a predominance of aromatic structures therefore thermo-chemical oxidation acted mainly on these structures. However, in a much milder way, occurring only slight decrease in the frequency of aromatic structures, being this effect even lower when comparing biochars produced at 550°C to 450°C. Thermo-chemical oxidation was responsible for the functionalization of biochars, which can be evidenced by signal at 172 ppm, related to the carboxylic groups, giving the similar structure of TPI's humic acids as reported by NOVOTNY et al. (2007), as being structures that ensure the high fertility of TPI's as well as its sustainability, since these functional groups are bonded directly to the aromatic structure of these materials. However, this effect is much less evident at temperatures of 450 to 550°C (Figure 1). Similar effect is expected to occur in natural environments through biotic (microorganisms) and abiotic (weathering) oxidation acting on biochars once applied to soil. However, these results suggest that, although more stable, biochars produced at higher temperatures (above 400-450 °C), oxidation of peripheral aromatic structures and appearance of carboxylic groups linked to aromatic matrix may take longer. In this sense, when thinking about producing biochar, and especially the effects of pyrolysis final temperature on the properties of biochar, the balance between C storage and agronomic benefits must be well understood. It is possible that biochars are produced with different functions (or C sequestration or agronomic benefits) and, biochars combining the two characteristics, which is preferable.

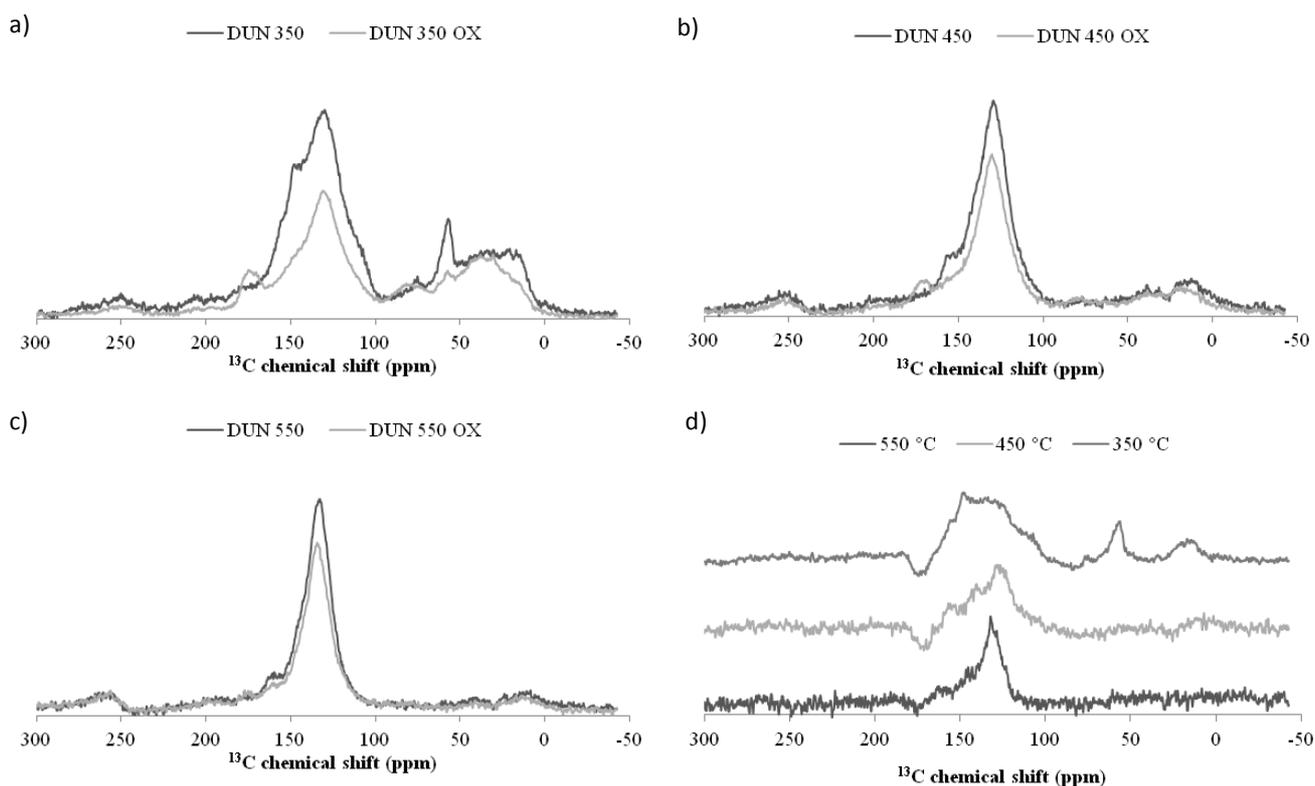


Figure 1. Solid state ^{13}C NMR spectra for the different temperatures (a to c) and the spectra of the differences (d).

CONCLUSIONS: Thermo-chemical oxidation was responsible for removing labile structures still present as well as aromatic structures less resistant to degradation. Thermo-chemical oxidation was also responsible for the functionalization of biochars, being this effect milder as higher pyrolysis final temperature was. The balance between C storage (Stable-C fraction) and agronomic benefits (functionalization) of biochar should be carefully evaluated, as its characteristics can vary depending on the conditions by it was produced.

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