

PYROLYSIS FINAL TEMPERATURE EFFECTS ON BIOCHAR STABILITY

<u>Alho, Carlos Francisco Brazão Vieira¹</u>; Cross, Andrew²; Sohi, Saran Paul²; Maia, Claudia Maria Branco de Freitas³; Novotny, Etelvino Henrique⁴; Lelis, Roberto Carlos da Costa¹

Keywords: biochar, oxidation, stability

Abstract

Pyrolysis technology can be used for producing biochar and bio-oil simultaneously, as an effective and sustainable mean to produce renewable bioenergy and a carbon rich soil amendment that can be used for carbon sequestration and agronomic benefits. However, pyrolysis products yields and biochar stability are strongly affected by the feedstock and pyrolysis variables, especially the final temperature. This study was carried out to evaluate the effect of pyrolysis final temperature on biochar stability after thermochemical oxidation. For this experiment, two species of hardwood and two species of softwood with particle size between 0.5 and 2.0 mm were pyrolized at five different final temperatures (350, 400, 450, 500 and 550°C) for 60 min at an muffle furnace with limited supply of O_2 . Thermochemical oxidation was performed for the solid products (biochar). As pyrolysis final temperature increased, biochar stability increased as well, indicating that these materials would be more resistant to degradation when applied into soil.

Introduction

Biochar is highly resistant to thermal, chemical and photo-oxidation,¹ and because of this recalcitrance, its incorporation into soil is an important mechanism for carbon (C) sequestration.^{2, 3} High-temperature aerobic oxidation^{4, 5} reactions with strong chemical oxidants,⁶ have shown that biochar can be abiotically oxidized over short periods of time. As biochar is present in soil as particles of very small size of mostly below <53 μ m,¹ oxidation may first begin on particle surfaces.⁷ Oxidation of such particles may lead not only to mineralization of this highly stable form of organic C in soil, but may create negatively-charged surfaces, consequently leading to greater cation exchange capacity (CEC) and nutrient retention in soil^{8, 9} that contribute to a higher fertility after biochar application. Additionally, biochar recalcitrant aromatic structure ensures the sustainability of this fertility.¹⁰ However, the functionality of biochar in soil and the response of

www.ixebsh.com.br

¹ Universidade Federal Rural do Rio de Janeiro, * alhojunior@gmail.com

² United Kingdom Biochar Research Centre/University of Edinburgh

³ Embrapa Florestas

⁴ Embrapa Solos



soils to biochar inputs are poorly understood. The need for methods to characterise and quantify functional attributes of biochar in soil is clear and, given the range of products potentially created, these must also be rapid and repeatable, whilst in some way reflective of processes occurring in field soil.¹¹ The aim of this study was to perform thermochemical oxidation of biochar produced from hardwoods and softwoods at different pyrolysis final temperatures in order to predict their stability when applied into soils.

Material and Methods

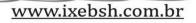
For this experiment, two species of hardwood (*Eucalyptus dunnii* and *Eucalyptus urophylla*) and two species of softwood (*Pinus caribaea* and *Pinus taeda*) with particle size between 0.5 and 2.0 mm were pyrolized with a heating rate of 10 °C.min⁻¹ at five different final temperatures (350, 400, 450, 500 and 550 °C) for 60 minutes at an muffle furnace with limited supply of O_2 adapted with Liebig condensers to collect the condensable gases in order to obtain the bio-oil. Thermochemical oxidation was performed at the University of Edinburgh as part of the Toolkit that has been developed by the United Kingdom Biochar Research Centre to enable a rapid and systematic screening of biochar properties. This process consists in milling the samples in order to enhance physical exposure, put them in test tubes, apply chemical oxidant and keep them in an oven under periodic agitation. Elemental analysis is performed in biochar before and after (residue) thermochemical oxidation in order to calculate the stable fraction, as the percentage of C remaining in the residue.

Results and Discussion

In this study, as pyrolysis final temperature increased, the percentage of C remaining after thermochemical oxidation (Stable C) showed by the elemental analysis, increased as well, for both hardwoods (*Eucalyptus dunnii* and *Eucalyptus urophylla*) and softwoods (*Pinus caribaea* and *Pinus taeda*) as shown in Figure 1 and 2. Although, the stable C percentage for both softwoods was always higher when compared to both hardwoods. This might be due to the higher content of lignin that is usually reported for softwoods when compared to hardwoods.¹² Compared to cellulose, lignin has a higher carbon content and therefore should lead to a higher carbon yield, combined with lower mass loss, as lignin is more stable to degradation.^{13, 14, 15} Cheng et al. (2006) studying oxidation of black carbon by biotic and abiotic processes showed that abiotic oxidation was found to be more important for the creation of negative surface charge and CEC than biotic oxidation.¹⁶ It is now important to perform an accurate analysis of biochar chemical structure (for example NMR ¹³C) in order to evaluate the changes that occur during thermochemical oxidation for each species used in this study for a better understanding of the level of oxidation.

Conclusions

As pyrolysis final temperature increased, biochar stability (considering the percentage of C





remaining in biochar after thermochemical oxidation) increased as well, indicating that these materials would be more resistant to degradation when applied into soil.

Acknowledgements

The authors are grateful to the International Humic Substances Society (IHSS) and the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (Capes) for the financial support.

References

¹Skjemstad, J.O., Clarke, P., Taylor, J.A., Oades, J.M., McClure, S.G. The chemistry and nature of protected carbon in soil. Australian Journal of Soil Research 34, 251–276. 1996.

²Glaser, B., Haumaier, L., Guggenberger, G., Zech, W. The 'Terra Preta' phenomenon: a model for sustainable agriculture in the humid tropics. Naturwissenschaften 88, 37–41. 2001.

³Masiello, C.A. New directions in black carbon organic geochemistry. Mar. Chem., 92, 201-213. 2004.

⁴Morterra, C., Low, M.J.D., Severdia, A.G. IR studies of carbon. 3. The oxidation of cellulose chars. Carbon 22, 5–12. 1984.

⁵Toles, C.A., Marshall, W.E., Johns, M.M. Surface functional groups on acid-activated nutshell carbon. Carbon 38, 1207–1214. 1999.

⁶Moreno-Castilla, C., Lopez-Ramon, M.V., Carrasco-Marin, F. Changes in surface chemistry of activated carbons by wet oxidation. Carbon 38, 1995–2001. 2000.

⁷Lehmann, J., Liang, B., Solomon, D., Lerotic, M., Luizao, F., Kinyangi, J., Schäfer, T., Wirick, S., Jacobsen, C. Near-edge X-ray absorption fine structure (NEXAFS) spectroscopy for mapping nanoscale distribution of organic carbon forms in soil: Application to black carbon particles. Global Biogeochemical Cycles 19, GB1013. 2005.

⁸Glaser, B., Lehmann, J., Zech, W. Ameliorating physical and chemical properties of highly weathered soils in the tropics with charcoal – a review. Biology and Fertility of Soils 35, 219–230. 2002.

⁹Liang, B., Lehmann, J., Solomon, D., Kinyangi, J., Grossman, J., O'Neill, B., Skjemstad, J.O., Thies, J., Luizão, F.J., Petersen, J., Neves, E.G. Black carbon increases cation exchange capacity in soils. Soil Science Society of America Journal, in press. 2006.

¹⁰Novotny, E.H., de Azevedo, E.R., Bonagamba, T.J., Cunha, T.J.F., Madari, B.E., Benites, V.M., Hayes, M.H.B. Studies of the Compositions of Humic Acids from Amazonian Dark Earth Soils. Environ. Sci. Tech., 41, 400-405. 2007.

¹¹Cross, A., Sohi, S.P., The priming potential of biochar products in relation to labile carbon contents and soil organic matter status, Soil Biology & Biochemistry. in press.

¹²Saka, S. Chemical composition and Distribution. Dekker, New York, pp. 3-58. 1991.

¹³Beramendi-Orosco L.E.; Castro-Díaz, M.; Snape, C.E.; Vane, C.H.; Large, D.J. Application of catalytic hydropyrolysis for the rapid preparation of lignin concentrates from wood. Org. Geochem. 35:61–72. 2004.



¹⁴Myung, S.Y.; Eom, Y.J.; Dong, J.I.; Park, Y.K.; Kang, B.S.; Jeon, J.K. Characteristics of thermal decomposition of major components of biomass isolated from wood. J. Korean Ind. Eng. Chem. 15(8):896–900. 2004.

¹⁵Yang, H.; Yan, R; Chen, H.; Lee, H. D.; Zheng, C. Characteristics of hemicellulose, cellulose and lignin pyrolysis. Fuel 86 1781–1788. 2007.

¹⁶Cheng, C.H.; Lehmann, J.; Thies, J. E.; Burton, S. D.; Engelhard, M.H. Oxidation of black carbon by biotic and abiotic processes. Organic Geochemistry 37 1477–1488. 2006.

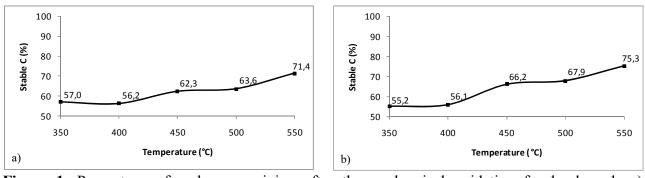


Figure 1. Percentage of carbon remaining after thermochemical oxidation for hardwoods a) *Eucalyptus dunnii* and b) *Eucalyptus urophylla*.

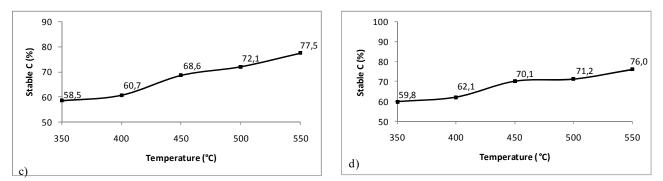


Figure 2. Percentage of carbon remaining after thermochemical oxidation for softwoods c) *Pinus caribaea* and d) *Pinus taeda*.