Pyrolisis Parameters Evaluation in the Biochar Preparation Process

E. Inayve P. de Rezende[a], A.P. Mangoni[a], I. Messerschmidt[a], A.S. Mangrich[a*],
E.H. Novotny[b], M.H.R. Velloso[b]

[a]Universidade Federal do Paraná, Centro Politécnico, Jardim das Américas, C.P. 19081,
81531-990, Curitiba, PR, Brazil; [b]EMBRAPA Solos, R. Jardim Botânico, 1024, 22460-000,
Rio de Janeiro, RJ, Brazil
E-mail: mangrich@quimica.ufpr.br

1. Introduction

Considerable efforts are being proposed to mitigate the environmental problems caused by the significant increase of CO_2 concentration in the atmosphere. The methodology of using biochar, obtained by pyrolysis of biomass, as a organic soil conditioner to mitigate this problem has gained support of a considerable number of components of the scientific community. The use of biochar in soil to produce positive effects on soil fertility was applied in the Amazon region by pre-Columbian indigenous community[1]. David R. Montgomery in its 2020 visions about care with world soil´s sad: "Over the next few decades, approaches such as low-till and organic methods could restore native soil fertility and store enough soil organic matter to offset global fossil-fuel emissions by 5–15%. Offsets, and soil fertility, could be further increased through adding biochar — charcoal made by heating organic wastes"[2]. Biochar presents as structural features characteristic condensed aromatic compounds, hydrogen-deficient, highly resistant to oxidation, and therefore the action of soil microorganisms, thereby contributing to carbon sequestration. Yet it may be partially oxidized in their peripherals aromatic groups, producing carboxylic and phenolic groups that contribute to soil CEC, buffering the acidity, complexing ions and inorganic structures, retaining water via hydrogen bonds and, consequently, increasing security (stabilization) and fertility of soil [3,4]. In the pyrolysis of biomass study in our laboratory, methods have been developed not only to produce biochar, but also aim to produce bio-fuels. Towards the development of scientific knowledge, technology and innovation in the use of organic by-products, especially derived from the biofuel industries, this work has been carried out to prepare "biochar" from the castor oil cake, through the pyrolysis at low temperatures (300-350 ° C) and deficiency of air.

2. Material and Methods

The castor oil cake, gridding in ball mills to a particle size of 80 meshes was placed in porcelain boats in the inner glass tube furnace EDG FT-40 microprocessor-controlled. The factors assessed by a 2^3 factorial design were: heating rate (V), final temperature (T) and warm-up period (P), at the levels of 5 and 10 ° C min^{-1}, 300 and 350 ° C and 30 and 60 min,

respectively. The solid material obtained was characterized by EPR, FTIR and NMR spectroscopy.

EPR spectroscopy. The EPR spectra were obtained at room temperature (~ 300 K) on a Bruker EMX spectrometer operating at X-band (~ 9.5 GHz) using 100 kHz modulation frequency and 0.05 mT amplitude modulation. The parameters values were obtained by the treatment of experimental spectra with the aid of WinEPR software and weak pitch standard from Bruker Company.

FTIR spectroscopy. The FTIR analyses were performed on a spectrophotometer model FTIR Biorad Excalibur Series (FTS-3500 GX) with the spectra resolution of 4 cm^{-1} in the region from 4000 to 400 cm^{-1}. The sample pellets for analyses were made using approximately 1 mg of the biochar sample and 99 mg of KBr spectroscopic grade and submitting the homogenized mixture to pressure. For each spectrum 32 scans were summed.

NMR spectra. Solid-state ^{13}C NMR experiments were carried out using a Varian VNMRS 500 MHz spectrometer at ^{13}C and ^{1}H frequencies of 125.7 and 500.0 MHz, respectively. The technique used was variable amplitude cross-polarization (VACP).

3. Results and Discussion

EPR spectra. By EPR spectroscopy the g-factor, spin density and power saturation of the signal values were obtained. The values of the g-factor of EPR found are around 2.003, indicating the presence of free radicals in organic structures (OFR). The parameter values of spin density and power saturation of the signal can be seen in Figure 1. For the spin density parameter, the highest values are of those samples with longer periods of heating (P1, P2, P5, P6). For the power saturation of the EPR signal, the sample P2 (V = 30 ^{0}C min^{-1}, T = 350 ^{0}C, P = 60 min and D = 11.81 x 1018 spins g-1) sustained the greatest power of EPR while the sample P4 (V = 30 ^{0}C min^{-1}, T = 350 ^{0}C, P = 30 min and D = 4.60 x 10^{18} spins g^{-1}) showed a lower saturation power. Thus, the sample P2, by EPR spectroscopy, is presented with more integration spin arrangement of aromatic structures (better dissipates the energy resulting from the relaxation of spins), supporting more power, suggesting that the heating time was the most important factor for the formation of stable internal structure of the sample.

FITR spectra. The FTIR spectra of the samples were very similar, all featuring mainly a broad band at 3680-3300 cm^{-1}, associated with the O-H stretching from alcohol carboxylic acids and water. Energy absorption in 1625 cm^{-1} attributed to the structural vibrations of C = C

aromatics, asymmetric stretching of C = OO- and bending of O-H groups. Shoulder at 1706 cm^{-1} is assigned to C = O stretching of ketone, ester and carboxylic acid.
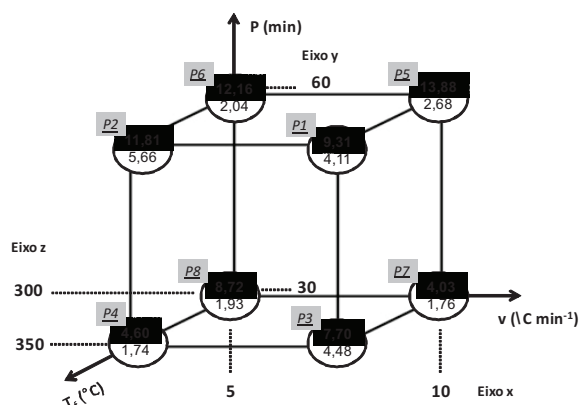
Figure 1: Diagram for the effects in planning 2^3 interpretation (Bold values inside the circles correspond to spin density (x10^{16} spins g^{-1}) and those below without bold are power (x10^{-4} W))

NMR spectra. To aid in the analyses of the results, the Multivariate Curve Resolution (MCR) procedure was carried out using the software 'The Unscrambler® v9.7' (CAMO Software AS). The basic goals of MCR are: the determination of the number of components co-existing in the chemical system; the extraction of the pure spectra of the components (qualitative analysis); and extracting the concentration profiles of the components (quantitative analysis).

The results of this analysis indicate that the set of analysed samples can be modelled by means of a two component mixture – binary, one of a partially carbonised material (Component 1, Fig. 2a), with aromatic groups presenting poor ring condensation (129 ppm) and alkyl groups. The other estimated compound is still less carbonised, presenting features of the precursors, like O-alkyl (72 ppm) and di-O-alkyl (shoulder at ~110 ppm) from cellulose; O-aryl (143 ppm) from lignin and aliphatic carboxyl (173 ppm).
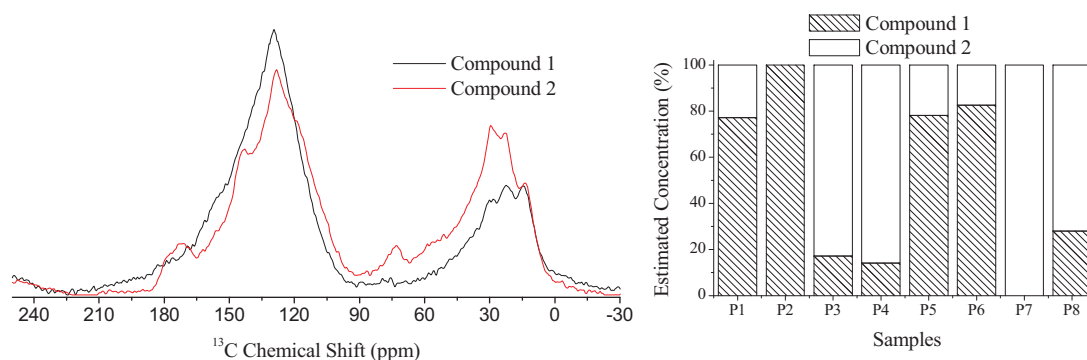
Figura 2 – Results of multivariate curve resolution (MCR) analysis. (a) Estimated spectra; (b) Estimated concentrations

The samples treated at lower temperature (300 °C - P3, P4, P7 and P8) were those that showed signals from the precursor (castor oil cake). In other words, the cited oxygen substituted groups present in the compound 2 are preserved from the castor oil cake due to the low carbonisation temperature employed, since this temperature avoided that these thermolabile compounds were decomposed or altered, unlike the samples treated at 350 °C.

Acknowledgements

References

1. S. Bruun and J. Luxhoi, *Environ. Sci. & Technology*, March 1 (2008);
2. D. R. Montgomery, *Nature*, 463, p. 26-32 (2010);
3. E. H. Novotny at al., *J. Braz. Chem. Soc.*, 20 (6), p. 1003-1010 (2009);
4. T. Whitman and J. Lehmann, Environ. *Sci. & Policy*, p. 1024-1027 (2009).