3rd International Biochar Conference
IBI 2010
Progressing from Terra Preta de Índios to the Whole World

C-13 and P-31 NMR Analyses of swine bones biochar

Novotny, EH[a]*; Auccaise, R[a]; Velloso, MHR[a]; Corrêa, JC[b]; Higarashi, MM[b]; Abreu, VMN[b]; Rocha, JD[c]

[a]Embrapa Solos, Rua Jardim Botânico 1024, 22460-000 Rio de Janeiro-RJ, Brazil; [b]Embrapa Swine and Poultry, Concórdia-SC, Brazil; [c]Embrapa Agroenergy, Brasília-DF, Brazil
E-mail: etelvino@cnps.embrapa.br

Key words: *Pyrolysis, biochar, ^{31}P Solid state NMR*

Introduction

The intensive livestock production results in massive amounts of residues, such as bones. Nowadays, due to sanitary questions, e.g. Bovine Spongiform Encephalopathy, these residues are banned as feed for animals. In this way, a potential destination for this material is pyrolysis, seeking biofuels and biochar production. Due to the chemical composition of the feedstock the obtained biochar will be rich in phosphorus and calcium, important plant nutrients. Additionally, the thermal treatment of the bones will result in a sterile agricultural input.

Despite the fact that the major mineral phase of bone was found, by X-ray diffraction, to be similar to hydroxyapatite, the exact chemical and structural nature of the solid phase(s) of calcium phosphate in bone is still unclear, but the contribution of brushite-like (monoacid orthophosphate) to the bone composition is important and depends on of the animal species and age [1]. The bone composition is an important parameter since the solubility of brushite-like orthophosphate is 1 to 3 order of magnitude greater than of hydroxyapatite in the pH range of 5-6.5.

The X-ray diffraction technique failures to uniquely identify the mineral phase(s) of bone, and probably it will fail to characterise bones biochar, in part from the fact that the mineral crystallites are very small and the resulting X-ray diffraction patterns are too poorly defined to permit a unique solution to the structural analysis. On the other hand, the solid state ^{31}P NMR technique is prone to characterise this kind of material [2], especially when associated with chemiometric tools.

Experimental procedures

In this communication we present the NMR characterisation of three swine bones biochars, labelled as Bones 1, Bones 2 and Bones 3. The bones biochars were obtained at different carbonisation temperature and time. The pyrolysis parameters are displayed in Table 1.

Table 1. Pyrolisys parameters of swine bones biochars samples.

Bones	Physical conditions
1	930 °C 10 min
2	300 °C 45 min 500 °C 7 min
3	300 °C 25 min 500 °C 10 min

The NMR spectra were acquired using a 500 MHz VARIAN spectrometer. The T3NB HXY of 4-mm probe was used to implement the solid state NMR experiments as CP-MAS, DP-MAS and others (not presented in this communication), to detect ^{13}C and ^{31}P nuclei from the pyrolysed samples. The rotors were spun using dry air at 15 kHz for ^{13}C and 10 kHz for ^{31}P. All experiments were carried out at room temperature.

Results and Discussions

The measurements of CP-MAS NMR solid state experiments detecting ^{13}C nuclei and ^{31}P are detailed in Figure 1 and Figure 2, respectively.

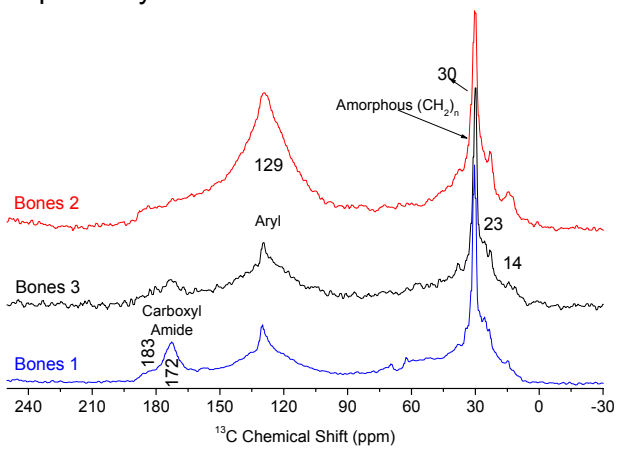

Figure 1. ^{13}C NMR spectra of swine bones biochars, using the CP-MAS NMR solid state.

From Figure 1 is possible to infer that swine bones biochars produced at higher temperature or residence time results in a decrease of carboxyl/amide functionalities and also an increase and broadness of the aromatic signal in the ^{13}C NMR spectra, indicating greater carbonisation. Also in the spinning side band intensity analysis (Figure 2), it is possible to infer that there could be two crystallographic structures with different symmetry. The sample bones 1, submitted to shorter carbonisation time, presents the highest contribution of the ^{31}P compounds with lower symmetry (higher intensity of the spinning side band – Figure 2). This sample also showed itself more efficient at the ^{1}H-^{31}P cross polarisation (data not showed), indicating a stronger ^{1}H-^{31}P dipolar coupling, probably due to a shorter ^{1}H-^{31}P distance.

Solid state ^{31}P NMR spectroscopy joint to the Principal Component and Multivariate Curve Resolution analyses (Figure 3) indicated that the studied biochars were a binary mixture, and had a component that cross-polarises easer and showed a that presents a lower symmetry, probably associated with brushite-like crystallites. The content of brushite-like orthophosphate decreased with the carbonisation degree. Its estimated proportion varied from 100% until 20% (Insert in Figure 3).

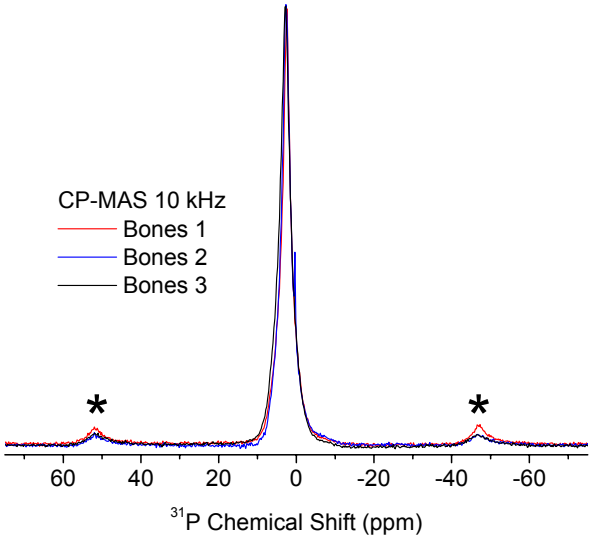

Figure 2. ^{31}P NMR spectra of swine bones biochars using the CP-MAS NMR solid state
* Spinning side bands

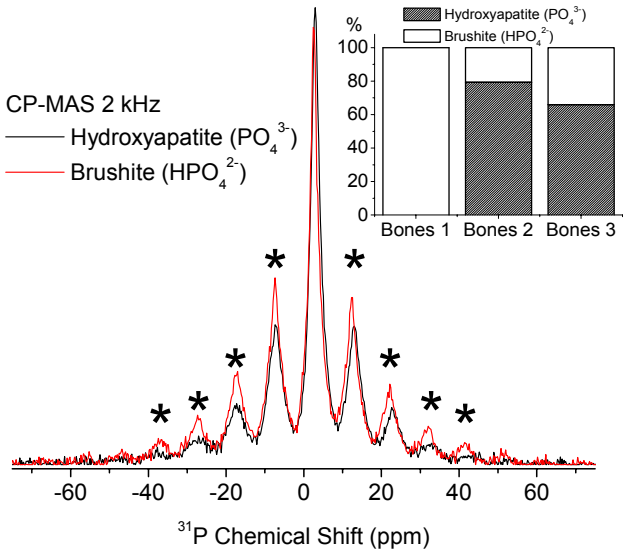

Figure 3. Multivariate Curve Resolution analysis about ^{31}P nuclei from the CP-MAS experimental data
* Spinning side bands

Conclusions

The analysis shows that swine bones could be converted in a promising phosphorus fertiliser by its carbonisation. The adjustment of the pyrolysis temperature or of the residence time could produce fertilisers with different solubility and P release rates.

Acknowledgements

The authors acknowledge the financial support of the Brazilian Science Foundations FAPERJ, CAPES, CNPq.

[1]Wu, Y.; Ackerman, J. L.; Strawich, E. S.; Rey, C.; Kim, H.-M.; Glimcher, M. J., 2003. *Calcif. Tissue Int.*, *72*, 610-626.
[2]Kaflak-Hachulska, A.; Samoson, A.; Kolodziejski, W., 2003. *Calcif. Tissue Int.*, *73*, 476-486.
[3]Curtis, M. D.; Shiu, K.; Butler, W. M.; Huffmann, J. C. 2001. *In: The Rhizosphere: Biochemistry and Organic Substances at the Soil-Plant Interface,* R. Pinton et al. (Eds.), Marcel Dekker, New York, pp. 141-157.