

## Effect of pyrolysis temperature on P speciation of biochars produced from the solid fraction of manure digestate



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Bekiaris, G.<sup>a</sup>, Jensen, L.S.<sup>a</sup>, Peltre, C.<sup>a</sup>, Bruun, S.<sup>a</sup>

Thermal treatment of animal manure (such as gasification, combustion or pyrolysis) has recently gained attention as a way to produce odorless bio-fertilizers. Pyrolysis produces a more stable product, whilst recent studies have been shown an increase in the P availability of the product in comparison with combustion. In order to gain information in relation to the P availability of biochars, it is important to identify P-species that exists in them.

Traditional, reflectance or transmittance mid-infrared spectroscopy faces some difficulties when it comes to very dark and opaque samples, which have featureless spectra that convey less information about P speciation. Fourier transform infrared-photoacoustic spectroscopy (FTIR-PAS) (described in research brief 1, Bekiaris et al.) allows a directly proportional measurement of the absorption by the sample of IR radiation, which makes it suitable for the recording of the IR spectra of very dark samples. This is because it is not affected by the redistribution of light due to scattering effects or diffraction processes (which is the main limitation in reflectance and transmittance FTIR). In this study, FTIR-PAS was used for the detection of changes in P speciation occurring during charring of manure.

Biochars from the solid fraction of manure digestates where produced in a laboratory oven at a wide range of temperatures (300 to 1050 °C). The IR spectra of various phosphate standards were recorded by FTIR-PAS in order to detect characteristic peaks that could be used later on the identification of the P species that exist in the biochars. The recording of the FTIR-PAS of the biochars was done with a resolution of 4 cm<sup>-1</sup>, while each spectrum was an average of 100 scans in the mid-infrared region between 4000 and 600 cm<sup>-1</sup>.

It was observed that most of the easily degradable organic matter is removed at a pyrolysis temperature up to 450 °C, whilst carbonates (at 1430 and 875 cm<sup>-1</sup>) were removed at temperatures over 600 °C (Figure 1). Based on the correlation with the spectra obtained from the phosphate standards (Figure 1, region 1200-500 cm<sup>-1</sup>), P seems to exist mostly in the form of

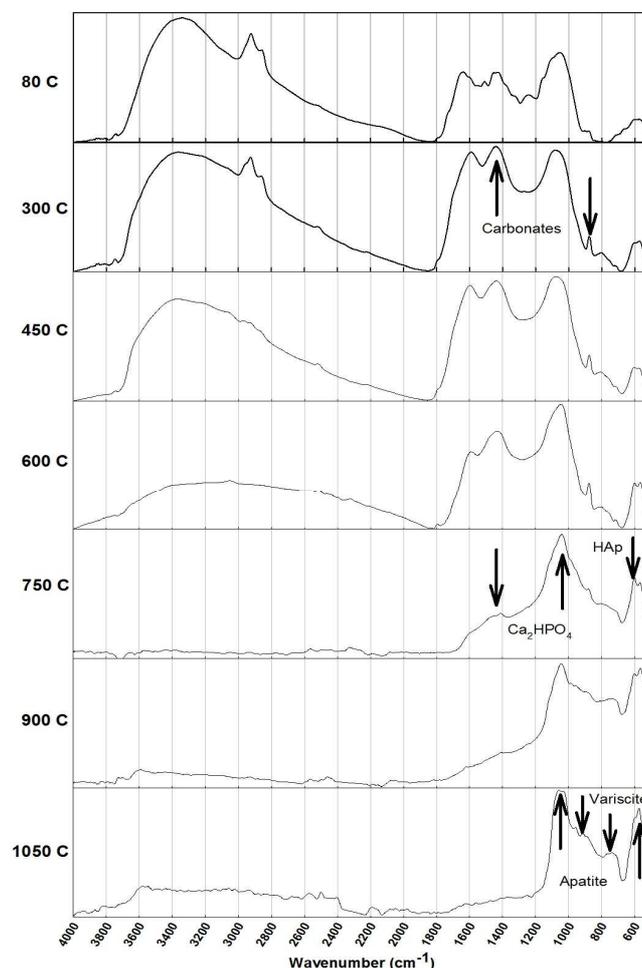


Figure 1. FTIR-PAS spectra of biochars produced from digestate solids in temperatures from 300 to 1050 °C

dicalcium phosphate (Ca<sub>2</sub>HPO<sub>4</sub>) and Hydroxyapatite (HAp) in lower temperatures with a little indication for Variscite, while with the increase of the temperature they are transformed gradually to apatite, pyrophosphates and Variscite.

This was the first attempt to use mid-infrared spectroscopy in the identification of phosphorus species in biochars and gain information in regards to the phosphorus plant availability. These results render FTIR-PAS as a reliable, very fast and inexpensive alternative to other techniques that were used until now for this purpose.

Contact George: [gbe@plen.ku.dk](mailto:gbe@plen.ku.dk)

<sup>a</sup> Department of Plant and Environmental Sciences, Faculty of Science, University of Copenhagen

