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

DRUV-VIS analyses in the biochar preparation process

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Key words: *Biochar, DRUV-VIS, Kubelka-Munk remission function*

Introduction

Diffuse reflectance is an excellent analytical tool for condensed materials in the mid-IR, NIR and UV-VIS spectral ranges. It can be used for analysis of intractable (not soluble) solid samples. The reflectance spectra can be converted to the Kubelka–Munk remission function defined by, $f(KM) = (1-R)^2/2R = k/s$, where R is the reflectance, k is the absorption coefficient, and s is the scattering coefficient. Assuming that the scattering coefficient varies only slightly as a function of wavelength over the range of interest, the shapes of the Kubelka-Munk remission function and the actual absorption spectrum in that wavelength range should be identical. In order to increase the resolution of the spectral curves, we applied the second derivative mode of the Kubelka-Munk function using the OriginPro, version 7.5, software. Towards the development of cheap and more at hand analytical alternatives in the production of "biochar", this work has been carried out to characterize the synthesized biochars by DRUV-VIS. Through the pyrolysis at low temperatures, 300 °C, velocity of heating of 10 °C min^{-1} and period of heating of 60 min, biochar was prepared from the raw products, castor oil cake, *Eucalyptus* saw dust and *Pinus* saw dust. The DRUV-VIS spectra were obtained at room temperature in the region of 190-900 nm, at intervals of 0.5 nm, with a Shimadzu UV-2401PC spectrophotometer equipped with a Model 240-52454-01 integration sphere. The reflectance spectra were converted to the Kubelka–Munk remission function, and to the second derivative mode [1, 2]. For validation of the method the sample were analyzed also by NMR spectroscopy. 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 Hz, respectively. The technique used was variable amplitude cross-polarization (VACP).

Results and Discussions

The ^{13}C NMR spectra of the raw material samples are shown in the top of figure 1, and only the castor oil cake sample presents typical absorption of aliphatic (0 – 48 ppm), aromatic (110 – 150 ppm) and carboxylic structures (160 – 180 ppm).

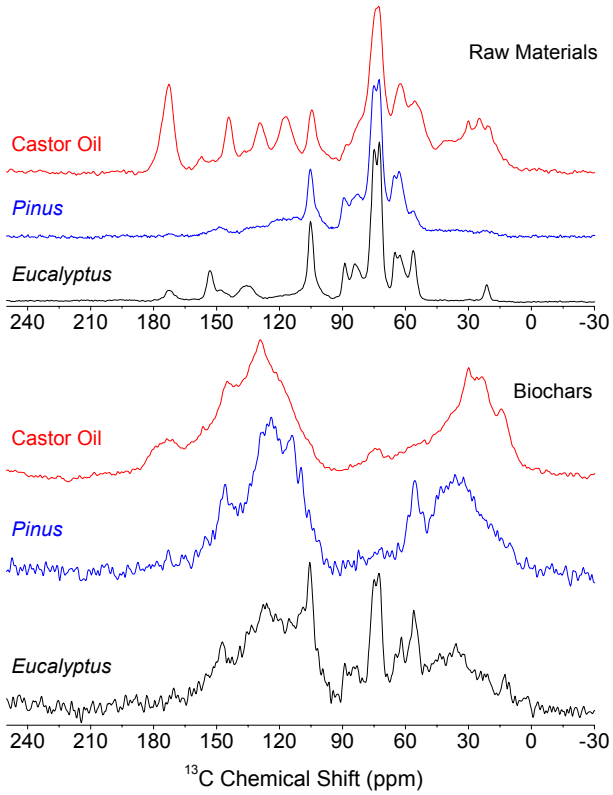

Figure 1. ^{13}C NMR spectra of the raw materials, castor oil cake, *Pinus* and *Eucalyptus* saw dust (top), and of the samples in the same order submitted to treatment of pyrolysis as described in the text (bottom).

The three raw materials present intense absorption between 50 and 100 ppm typical of carbohydrates, methoxyl and N-alkyl structures. When submitted to the pyrolysis treatment the biomass samples develop aromatic and aliphatic structures but only the castor oil cake maintains some carboxylic groups. The saw dusts preserve some of the metoxyl groups (~50 ppm) after the pyrolysis experiments.

Figure 2 shows the reflectance, the absorbance after the K-M treatment and the second derivative K-M mode spectra of the three studied samples after the pyrolysis treatment.

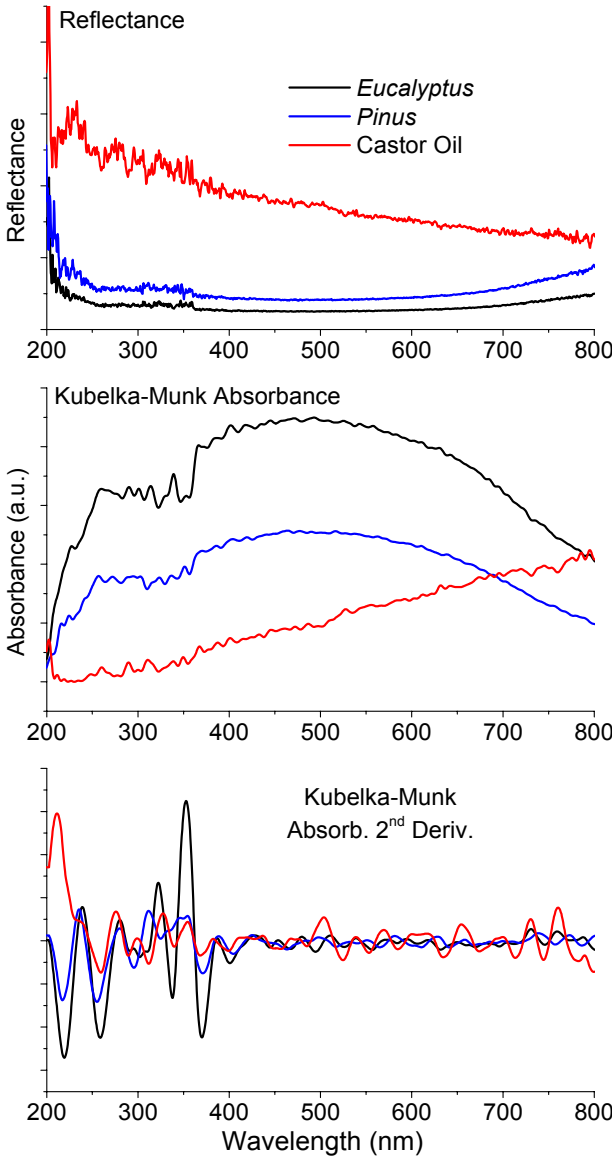

Figure 2. Reflectance spectra of the *Pinus* saw dust, PN4, *Eucalyptus* saw dust, E4, and castor oil cake, P4, after the pyrolysis treatment (top), Kubelka-Munk absorbance (center), and K-M second derivative mode (boton).

Like for the ^{13}C NMR analysis results the two materials coming from *Pinus* and *Eucalyptus* saw dust present similar results that are different from the castor oil cake material. Although one can note the difference among the three samples by reflectance or K-M absorbance, only through the K-M second derivative mode spectra it is possible to see more clear differences among the three samples. The maximum in the absorption spectra corresponds to the minimum in the second-derivative mode spectra. The biochars from the *Eucalyptus* saw dust shows four major peaks at 215, 260, 340, and 370 nm while the *Pinus* biochar shows similar spectrum. The biochar obtained from the castor oil cake presents a very different spectrum with the band at 260 and 370 nm well specific. Like saw by NMR analysis the two biochar from tree biomass are similar and well different from the castor oil cake biochar.

Conclusions

By DRUV-VIS spectroscopy and working with the Kubelka-Munk remission function we characterize the similarities of the biochar obtained by the pyrolysis of *Pinus* and *Eucalyptus* saw dust, and differences from the biochar obtained from castor oil cake.

Acknowledgements

The authors are grateful to CNPq and CAPES for research fellowship, FINEP for the financial support and to the UFPR/CD for the infrastructural work conditions.

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