Preparation and Characterization of Biodiesel Industry Waste Partially Carbonized Material in Order to Produce an Organic Soil Conditioner

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1. INTRODUCTION

This work seeks to determine the best methods of production of partly carbonized waste of biodiesel industry – castor (*Ricinus communis*) meal – aimed at obtaining material comparable to organic matter of soils *Terras Pretas de Índios* to be used as a soil conditioner. The subject *Terras Pretas de Índios* has aroused interest in the international scientific community that in recent years several articles and letters of Nature and Science were devoted to the subject (e.g. 1, 2, 3) and The American Association for the Advancement of Science (AAAS) organized a symposium in their annual meeting in 2006 with the title: Amazonian Dark Earths: New Discoveries.

This work corresponds to chemical studies in the sense of scientific knowledge and technological development and innovation in the use of organic by-products, especially from the biofuels industries, seeking the excellent performance of the so-called *Terras Pretas de Índios* of the Amazon (4). In these work the carbonized materials were obtained by controlled heating of different mixture of biodiesel industry tort with glycerol, starch as industrial Brazilian by-product, and potassium sulfate (K_2SO_4) as a macronutrient addictive. The obtained products were analyzed by EPR, NMR, and DRUV-Vis spectroscopy.

2. MATERIALS AND METHODS

Samples preparation. In a closed furnace the samples were heating from the room temperature (~300 K) to 773 K with the heating velocity of 1 ^{0}C min^{-1}, and lifted at 773 K for two hours. After returned to the room temperature the samples were recovered, milled in a pot mill and sieved in an 80 meshes sieve. Details about the sample composition can be found in the Table 1.

NMR. Solid-state ^{13}C NMR experiments were carried out using a VARIAN INOVA spectrometer at ^{13}C and ^{1}H frequencies of 100.5 and 400.0 MHz, respectively. The techniques used were: Variable Amplitude Cross-Polarisation (VACP) and Recoupled Dipolar Dephasing (DD) experiments, both with Magic Angle Spinning (MAS) at spinning frequencies of 13 kHz. Typical cross-polarisation times of 1 ms, acquisition times of 13 ms, and recycle delays of 500 ms were used. The DD experiments were carried out with a dipolar dephasing time of 67 μs.

EPR. EPR spectra of the powdered samples were registered at room temperature (~300 K) in quartz tubes. A Bruker ESP 300E spectrophotometer (LABEPR/DQ/UFPR) was used, operating at a frequency of 9.7 GHz (X-band), with a 100 kHz modulation frequency, 2.024 G modulation amplitude and ~20 mW microwave power.

DRUV-Vis. The DRUV–Vis analyses were performed on solid samples contained in a 26-mm-diameter sample holder, operating in the range 190 – 900 nm, using a Shimadzu UV-2401 PC spectrophotometer equipped with a Model 240-52454-01 integration sphere.

3. RESULTS AND DISCUSSION

NMR spectra. The VACP ^{13}C NMR spectra (Figure 1) present the typical pyrogenic carbon signal (condensed aromatic signal at 127 ppm retained in the DD spectra), in the aromatic region have also a shoulder in the O-aryl region (152 ppm). This signal can arise from phenolic or aryl-ether, but in this case the aliphatic radical must be greater that methyl, because it don't have the corresponding methoxyl (~56 ppm) signal in DD spectra. Additionally some residual aliphatic signals (60-0 ppm) remain after the carbonization. The differences among the samples are very subtle, but the ones without castor cake present more methyl (18 ppm), methylene (36 ppm) and O-aryl (152 ppm) groups.

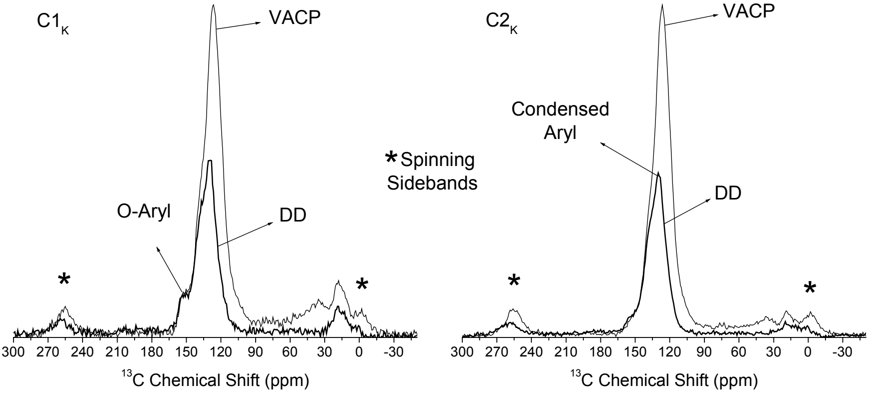

Figure 1. Full VACP and corresponding DD spectra of char samples.

Table 1. EPR parameters obtained of the studied samples

Sample	Spins g^{-1}	g-factor	ΔH (mT)
C1 (starch : glycerol, 7:3)	5.59×10^{18}	2.0040	0.54
C2 (starch : glycerol : castor cake, 7:3:1)	6.17×10^{18}	2.0044	0.43
$C1_K$ (starch : glycerol : K_2SO_4, 7:3:1)	2.95×10^{18}	2.0044	0.53
$C2_K$ (starch : glycerol : castor cake : K_2SO_4, 7:3:1:1)	5.05×10^{18}	2.0042	0.40
Castor cake	6.34×10^{15}	2.0049	0.70

The non charred castor cake sample presents a typical organic free radical signal (Figure 2) and the concentration of these organic free radicals, as determined by EPR analysis, increases sharply (three magnitude orders greater) with the carbonization (Table 1). The values obtained in the charred samples are in the range of those already reported for soil HA with large humification degree. On the other hand, the g-factor and peak-peak linewidth decrease with the carbonization. The greater linewidth of non charred sample is partially due to occurrence of two slightly different organic free radical centers (unsymmetrical signal and second derivative – Figure 2).

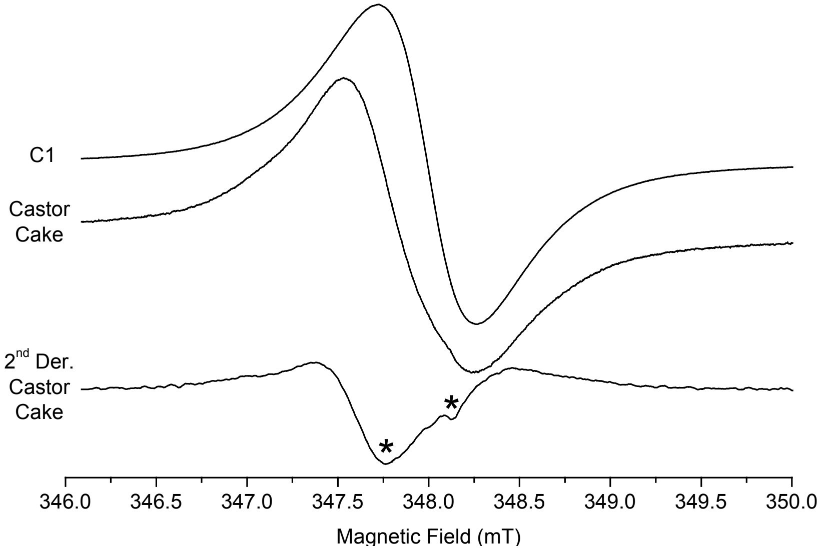

Figure 2. EPR spectra of castor cake and char samples. The two partially overlapped signals in the castor cake sample are star marked in the second derivative spectra.

The samples with K_2SO_4 ($C1_K$ and $C2_K$) presented a smaller organic free radical concentration than the corresponding samples without this salt; this could be explained by their greater ash content causing a diluting effect. On the other hand, the samples with castor cake in the mixture (C2 and $C2_K$) presented a greater organic free radical concentration.

The DRUV-Vis spectrum (data not showed) of the castor cake sample suggests the existence of aryl-hydroxyl pigments, such as anthocyanins (reflectance bands at 219 and 264 nm (5)). The carbonization produces a very black char, with an almost equivalent reflectance in the whole visible spectra. This feature can be attributed to the condensed aromatic structure of pyrogenic carbon, as indicated by the NMR data showed.

4. CONCLUSIONS

The controlled heating of the mixture of industrial Brazilian by-products, biodiesel industry castor cake, with glycerol and starch produced a material with some characteristics of organic soil conditioner. EPR, NMR and DRUV-Vis spectroscopy, as spectroscopic technique to analyze solid state samples, were vital to the obtained product characterization.

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