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Infrared spectroscopy analysis on charcoal generated by the pyrolysis of *Corymbia citriodora* wood

Análise da espectroscopia de infravermelho em carvão vegetal produzido pela pirólise da madeira de *Corymbia citriodora*

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ABSTRACT

Wood pyrolysis has been use for centuries to obtain charcoal. Nonetheless, the study of wood components altering by the pyrolysis temperature is crucial to determine the charcoal's properties. The present research aims to evaluate by FTIR the chemical altering of wood submitted to various pyrolysis temperatures. Samples of *Corymbia citriodora* species were submitted to temperatures of 240 °C, 280 °C, 320 °C and 400 °C in a fixed bed reactor filled with N_2. The FTIR analysis was performed in the wood residues after pyrolysis. The results showed that cellulose and hemicelluloses presented more susceptibility to thermal degradation than other wood components. It could be observed chemical altering in the wood residue obtained between 240 °C and 280 °C. In addition, the wood residue obtained for treatments over 280 °C presented characteristics similar to vegetal charcoal. There are a continuous change of the wood due to the temperature of the pyrolysis by the change of bands intensity and by the bands shift. The FTIR analysis allowed the evaluation of the wood's pyrolysis process and its chemical variations with the temperatures applicate.

Keywords: thermal degradation, wood, FTIR.

1. INTRODUCTION

Wood has been used as a primary source of energy and of chemicals for centuries. Nonetheless, wood has been replaced by vegetal charcoal since the beginning of the 19th century and after that, oil and its derivatives were also used as an energy source. In the 70's, due to the first glimpses of oil depletion and of energy crises, wood thermal processes regain the Energy industry's interest, specially pyrolysis and carbonization.

The pyrolysis process intends to eliminate part of the wood components by thermal degradation, concentrating carbon in the residue. The pyrolysis process results in formation of bonds between carbons, where cyclic and/or aromatic structures are formed with the temperature rise [1, 2]. These carbon structures are characterized by different degrees of aromaticity and they are the main carbon chains of vegetal charcoal. According to the environment in which the charcoal is placed, these chains can remain intact for centuries and they act as carbon dissipater, absorbing/binding the CO_2 emitted to the atmosphere [3, 4].

Charcoal is used in several applications, but it does not present a set composition, which difficult its application. Studies related to vegetal charcoal's composition, structures and properties are sparse [4]. There are various properties related to vegetal charcoal that remain not completely explained due to the difficulties to set its composition, e.g. charcoal's adsorption and hygroscopic ability [5, 6], direct combustion property [7], aromatic elements emission due to combustion [8, 9]. Charcoal groups different carbon components, presenting a variety of degrees of complexity, which characterization demands time and high cost. Its characterization can be partially done by quick methods which require none or few samples' preparation, but these are insufficient to the complete understand the structure and characteristics of the vegetal charcoal [4].

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Methodologies based on vibrational spectroscopy are alternative methods to traditional physic-chemical techniques [4, 10]. The Fourier Transformed Infrared Spectroscopy – FTIR uses infrared radiation, which is located in the wavelength region between visible light and microwaves. The infrared radiation is characterized by three regions: near infrared (from 4000 cm^{-1} to visible light wavenumber); medium infrared (between 400cm^{-1} and 4000 cm^{-1}), which is the wavelength where the vibration of the bonds related to organic compounds occur; and distant infrared (from 400 cm^{-1} to microwave) [11]. Complementary information regarding functional groups can be provided by FTIR technique, while Raman Spectroscopy can detail information regarding aliphatic and aromatic groups. FTIR analysis has been used to characterize the *biochar* structure, which is used in soils. FTIR and Raman techniques are complementary; both provide functional groups information, since aromatic bonds presenting different degrees of substitution respond directly to FTIR [10, 12].

The organic part of charcoal is composed mainly by two groups of compounds: aromatic and hydroaromatic compounds and alkyl bridges, ether or thioether linkages that connect the aromatic compounds. The "drag" phases involved in the process of obtaining charcoal would be hydrocarbons and aliphatic and aromatic compounds. The charcoal composition varies according to the charcoal's origin and biogeochemical processes [13].

Cademartori *et al.* [14] investigated the changes of *Eucalyptus* wood submitted to thermal treatment (180-240 °C) for 4h and they observed the degradation of hemicelluloses and a decrease of wood's hygroscopicity and mechanical strength. Esteves *et al*. [15] evaluated the changes in *Eucalyptus* and *Pinus* wood species submitted to thermal treatment between 170 °C and 210 °C for 2h and they concluded that the thermal treatment degraded the hemicelluloses and it altered mainly the structure of wood's lignin and amorphous cellulose. In addition, the authors highlight that it is difficult to monitor the wood changes due thermal treatment by FTIR, since various chemical reactions occur simultaneously [15]. The wood of *Pinus sylvestris*, *Fagus orientalis* and *Picea orientalis* heat treated between 190 °C and 212 °C by FTIR and they observed the degradation of hemicelluloses and of amorphous cellulose and altering in the carbohydrate and lignin compounds depending on the wood species [16]. The objective of the present research is to evaluate by medium infrared spectroscopy the *Corymbia citriodora* wood's chemical compounds altering due to thermal treatment of pyrolysis, according to the FTIR absorption bands after thermal treatment under different temperatures.

2. MATERIAL AND METHODS

The wood used in this work was obtained from a plantation of *Corymbia citriodora*, age of 6.5 years, from São Paulo, Southwest of Brazil. Measurement of basic density was performed according to standard NBR 11941[17]. The TAPPI standard [18] and the TAPPI standard [19], respectively, were used to determine the total extractive and lignin Klason contents. Holocellulose content was obtained indirectly by subtracting the sum of total extractive contents and lignin content of 100%. The ash content were determined according to ASTM D-1764 [20].

Wood samples were prepared initially by cutting the wood into cubes of 27 cm^3. The samples were dried in an oven at 103 °C ± 2 °C, and the drying was finished when the samples reached constant mass. Then, the cubes (samples) were submitted to pyrolysis in a fixed bed reactor saturated of N_2. The mass of the samples used in each pyrolysis test was 300 g, where the samples were heated at a rate of 4 °C min^{-1}. The pyrolysis analysis occurred at different temperatures, and after stabilization, the samples remained at the final temperature for 60 min. The final temperatures were 240 °C, 280 °C, 320 °C and 400 °C. The process' yield of a solid material was determined according to Equation 1, where 'SMY' is the solid material yield; 'Mc' is the mass of charcoal (g); 'Mw' is the mass of dry wood (g).

$$SMY\ (\%) = \frac{\mathrm{Mc}}{\mathrm{Mw}}\ \mathrm{x}\ 100 \tag{1}$$

The analysis of the chemical compounds' bonds vibration of the *in nature* wood and of the wood submitted to the pyrolysis processes was performed by FTIR, Perkin Elmer equipment, diffuse reflectance mode, resolution of 4 cm^{-1}, 128 scans per samples, wavenumber range of (4000-400 cm^{-1}). In order to do so, the samples were lyophilized and 2 mg of the samples were mixed with KBr and pressed into pallets, which were analyzed by FTIR.

3. RESULTS AND DISCUSSION

The *Corymbia citriodora* wood presented the following characteristics: density of 0.630 g cm^{-3}; total extractive content of 19%; Klason lignin content of 19%; holocellulose content of 74%; ash content of 1,10%. The total ash content is approximately the same of the Brazilian *Eucalyptus* species studied by Poletto *et al*. [21], (1.1 ± 3) %, although these authors found lower amounts of holocellulose and extractives and higher amounts of lignin in their *Eucalyptus* species [21]. The basic density, which indicates the quality of the wood, where the denser the wood, higher the charcoal yield, presented a high value for an eucalyptus species [22].

The charcoal yield as solid material can be observed in Figure 1, where the charcoal yield diminishes with rise of the pyrolysis' temperature. The pyrolysis yield of wood for heat treatment at 240, 280, 320 and 400 ºC was 78, 59, 47 and 34%, respectively. High temperatures degrade the wood effectively, nonetheless there is also a high evolution of mobile phases, condensable or non-condensable gases [23].

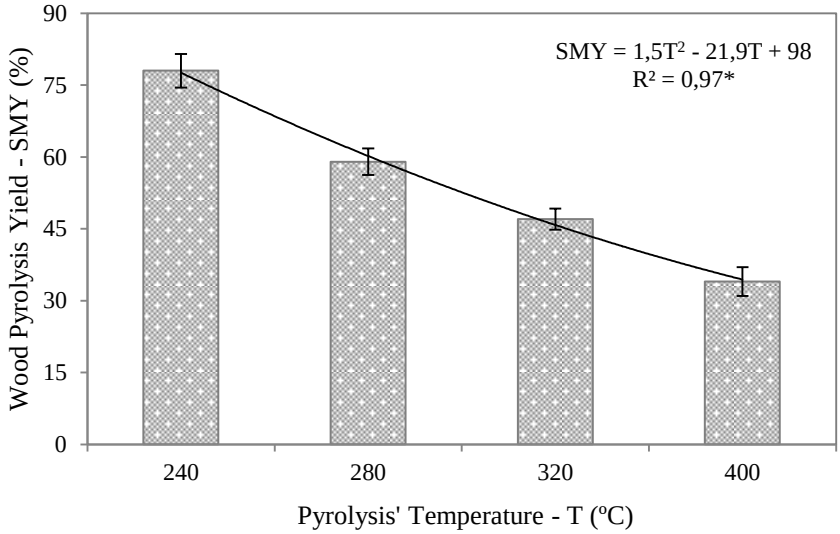

Figure 1: Yield of wood pyrolysis. Significant at 95% probability (p < 0,05).

The thermal degradation of wood begins at low temperatures, approximately 200 °C. In controlled environment, free of oxygen, there is the beginning of the charcoal formation. The wood's complete conversion into charcoal also depends on remaining time inside of the reactor, heating rate, pyrolysis process' methodology, raw material [23, 24, 25].

The FTIR analysis was performed to determine the bands related to the solid material (charcoal) after the pyrolysis treatment, to identify the chemical groups remaining in charcoal or formed after the thermal treatment. The FTIR spectra of *in nature* wood and charcoal after the four thermal treatments are displayed in Figure 2 and Table 1, and it is worth noticing that FTIR spectra of charcoal usually present broad bands [4]. The charcoal obtained from at 240 °C presented spectrum similar to the original wood, where changes were observed for samples treated at 280 °C or higher temperatures.

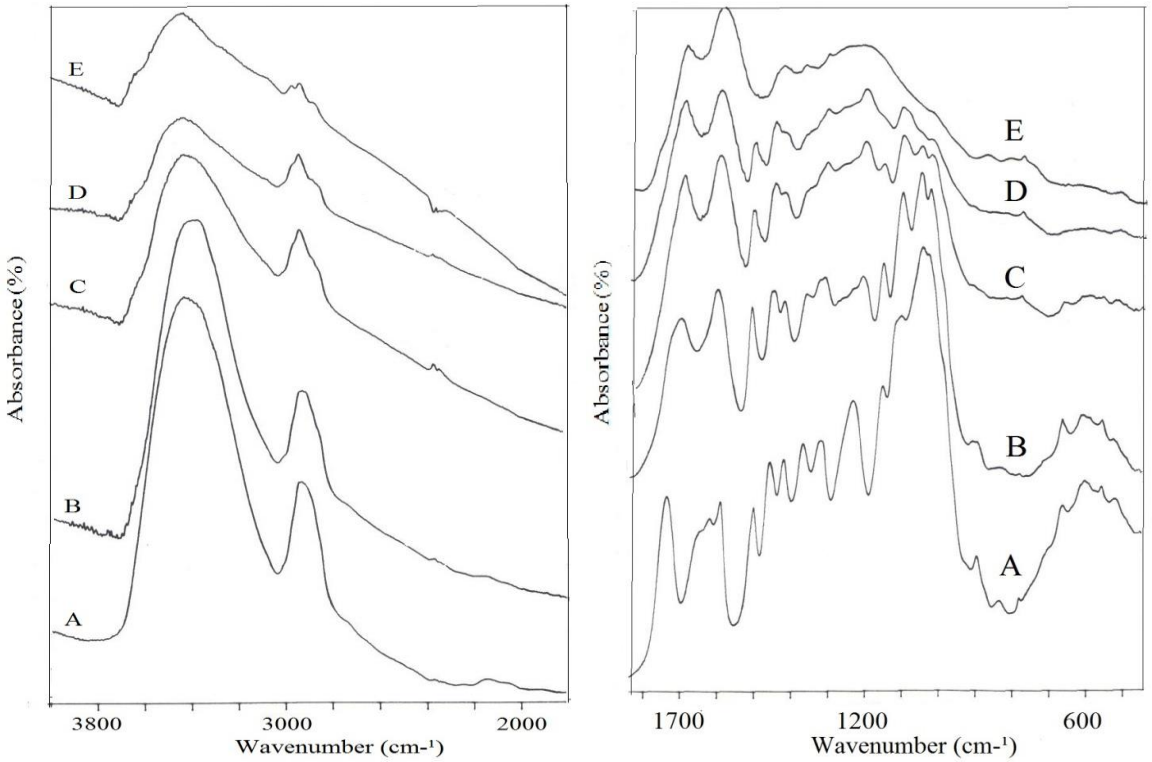

Figure 2: Infrared spectra of the bands 4000 a 450 cm^{-1}, where A is related to the *in nature* wood; and B, C, D and E spectra are related to the thermal treated wood at 240 °C, 280 °C, 320 °C and 400 °C, respectively.

The intensity of the bands at 3420 cm^{-1} and at 2930 cm^{-1} diminished with the increase of the temperature of the pyrolysis (Figure 2). These bands are mainly related to OH, CH_3, CH_2 and CH groups and the diminish of the bands can be related to the degradation of hemicelluloses [26]. These bands broadening and low intensity with the increase of the pyrolysis temperature can be attributed to the loss of water impregnated in the cell wall of wood and to the oxidation or hydrolysis of OH groups of hemicelluloses, that contributes to the increase of carboxylic acids [15, 27]. At high pyrolysis temperature, different absorption bands can be distinguished around 3000 cm^{-1}, related to aromatic carbons, which can be due to chemical reactions that generate aromatic byproducts, which is also related to the amount of lignin in the wood [28, 29]. In addition, the diminished intensity of the band at ~2900 cm^{-1} can be attributed to cellulose's crystallinity altering, which influence the ν (C–H) and ν (O–H) bands intensity [30].

The *in natura* wood presented a band at 2865 cm^{-1}, which is associated to the stretching CH_3 of the lignin methoxyl groups [31, 32, 33]. This band can still be observed in the charcoal and, depending on the temperature of the pyrolysis, this band is more intense in the charcoal than in the wood itself. Regarding this band, Esteves *et al*. [15] observed this band was shifted towards low wavenumber after thermal treatment. Nonetheless, the results of the present study regarding this band indicates that cellulose and hemicelluloses degrade preferably when the wood is submitted to pyrolysis. According to the pyrolysis temperature, there is an angular deviation of the base line between 4000 cm^{-1} and 1900 cm^{-1}. Usually, it occurs due to the presence of charcoal's organic or mineral byproducts [28, 29].

The band at 1740 cm^{-1} (Figure 2), is shifted towards low wavenumber and, with the increase of pyrolysis temperature, this band is less intense than in the wood and it gets broader, indicating that the C=O groups are consumed during the wood pyrolysis and low amounts remain in the charcoal submitted to pyrolysis at high temperatures. The loss of intensity would be due to the cleavage of acetyl/acetoxy groups in xylan [15, 30].

The wood spectrum present one band around 1600 cm^{-1}, where the vibration of the C=O bonds of carboxyl acids and the vibration of ketones of lignin and hemicelluloses (bands at 1600 cm^{-1} and 1620 cm^{-1}) are conjugated [14, 31, 32, 34, 35, 36, 37]. The difference of the bands of wood and the derived charcoal can be due to the degradation of bonds like C=C or COO^- [28, 29] and also due to the degradation of lignin [27]. The charcoal spectra present a high intense band at 1600 cm^{-1}. It is attributed to the vibration of C=C groups of aromatic rings, usually related to the presence of lignin and also to the formation of aromatic compounds originated by the elimination of hydrogen and oxygen of aliphatic compounds during the pyrolysis, where 250 °C is sufficient temperature to it [38].

The presence of a band at 1510 cm^{-1} (C=C) also indicates the presence of an aromatic rings and this band occurs in the wood and charcoal obtained at temperatures between 240 °C and 380 °C, but the charcoal obtained from a pyrolysis at 400 °C this band is not present, ensuring the degradation of lignin [27]. The bands at 1460 cm^{-1} and at 1425 cm^{-1} presented diminished intensity in charcoal and the last band was shifted towards 1450 cm^{-1}. The low intensity of these bands in charcoal could be attributed to the loss of methoxyl groups (monomers) of lignin [30, 39]. Since the bands at 1375 cm^{-1} and at 1325 cm^{-1} are associated to C-H vibration, which occurs in several compounds of the wood, e.g. polysaccharides, hemicelluloses and lignin components, their intensity diminishes in charcoal due to the degradation of the wood components [15, 40].

The pyrolysis reduced the intensity of the bands at 1240 cm^{-1} and at 1110 cm^{-1}. It occurs due to the loss of oxygenated groups and to the thermal degradation of these groups in hemicelluloses [28, 29, 41]. The first band could be associated to the guaiacyl lignin and to the syringyl lignin which is more susceptible to temperature and it can be eliminated during pyrolysis, reducing the band intensity in charcoal [16].

Mainly, all bands at wavenumbers lower than 1000 cm^{-1} are eliminated in charcoal with the increase of pyrolysis temperature. These bands would be related to cellulose and lignin and their decrease indicates the degradation of the wood components [10, 27].

4. CONCLUSIONS

The increase in pyrolysis temperature significantly decreased the yield of solid material from *Corymbia citriodora* wood.

It could be observed the continuous change of the wood due to the temperature of the pyrolysis by the change of bands intensity and by the bands shift.

Because bands of the FTIR analysis the charcoal pyrolyzed at 240 °C was similar to the original wood and for thermal treatments at higher temperatures the samples were closer to charcoal

5. ACKNOWLEDGEMNT

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