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NIR and anatomy of wood and charcoal from Moraceae and Euphorbiaceae species

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ABSTRACT In Brazil, charcoal has widely use in the iron industry and plays an important row as a domestic fuel for traditional roast. The carbonization of illegal logged native wood simultaneously with planted exotic species demands ways to avoid frauds controlling the transport of charcoal. The aim of this study was to provide information on the anatomical characteristics of carbonized wood for *Brosimum acutifolium, Ficus citrifolia, Hieronyma laxiflora* and *Sapium glandulatum* and test the potential of near infrared in discrimination of species in charcoal based on solid material. Samples from pith to bark were oriented in the three anatomical planes, wrapped in aluminum foil and carbonized in a muffle furnace, with a final temperature of 450 °C and a heating rate of 1.66 °C.min^{-1}. Infrared analyzes were performed in a Bruker Tensor 37 spectrophotometer equipped with an integrating sphere and operating in reflectance mode in a spectral range of 10,000–4,000 cm^{-1}. Qualitative anatomical structure of wood remains in charcoal, and can be used to species discriminations. Near infrared can be applied for wood discrimination of some species from Euphorbiaceae and Moraceae, but in charcoal the distinction of family is more adequate.
Keywords: near infrared, wood structure, species discrimination.

Introduction

Brazil is the world's largest producer of charcoal and almost of the production goes to internal market (MOREIRA, 2011). In 2005, almost 35% of native charcoal was produced from Cerrado's species (DUBOC et al., 2007). Also, the charcoal consumption represents the deforestation of approximately 1.6 million hectares or 16.000 km² of the Cerrado Biome (MMA, 2011). In 2012, 38.7% of Brazilian planted forests were designated to charcoal and firewood production. Charcoal consumption, for iron and steel industries, originated only from planted forests, increased 61.4% between 2009 and 2012 (ABRAF, 2013). Despite this, charcoal supply is still present in illegal cutting of native forests, which represented 30-35% of total output in 2010 (IBGE 2010). In 2015, it was observed a reduction on steel uses and an increase in residential consume of charcoal (BRASIL, 2015).

In addition to preventive measures, the supervision on the use of charcoal fits like a corrective procedure, which seeks to impede the transport of illegal material in Brazil and therefore, avoiding that illegal charcoal to reach its destination. However, the identification of charred wood is hard and requires wood anatomical knowledge. In recent years, studies related to charcoal identification based on anatomical structure showed that the qualitative characteristics of wood remained in charcoal and the comparison of cell dimensions behaviors proofed to be different between species, but even so, it is possible to identify the charcoal (MUÑIZ et al. 2012; NISGOSKI et al. 2012, GONÇALVES et al. 2012, 2014).

Other possibility can be the use of nondestructive techniques such as infrared spectroscopy, with the information collected directly from material surface. Near infrared is being used in research and in monitoring online in different industries for detection of morphological, chemical, physical

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and mechanical properties of lignocellulosic materials (TSUCHIKAWA; SCHWANNINGER, 2013). In charcoal identifications some examples are studies of Davrieux et al. (2010) and Muñiz et al. (2013).

Forest exploitation for wood and charcoal often occurs without consideration for sustainability, and efforts to enforce environmental laws frequently presents a lack of information to identify charcoal according to the species, especially to distinguish between native and planted species. Therefore, the aim of this study was to provide information on the anatomical characteristics of carbonized wood of *Brosimum acutifolium, Ficus citrifolia, Hieronyma laxiflora* and *Sapium glandulatum* to contribute to efforts to differentiate species and control illegal trade. Also test the potential of near infrared in discrimination of species in charcoal based on solid material.

Material and Methods

The wood samples of the species *Brosimum acutifolium* Huber (amapá doce), *Ficus citrifolia* Mill. (figueira) – Moraceae; *Hieronyma laxiflora* (Tul.) Müll. Arg. (vermelhinho) and *Sapium glandulatum* (Vell.) Pax. (leiteiro cascudo) – Euphorbiaceae, came from the city of Nova Maringá, Mato Grosso state (13°1′2″S, 57°4′8″W). The trees were fall in natural forest, and disks were extracted from the diameter at breast height (DBH), with thickness of about 8 cm. Eight samples from pith to bark were obtained of each species, with dimensions of 2 x 2 x 5 cm, oriented in the three anatomical planes for wood and charcoal analysis. Each sample was wrapped in aluminum foil and carbonized in a muffle furnace, in atmosphere with oxygen restriction, with a final temperature of 450 °C and a heating rate of 1.66 °C.min^{-1}. The carbonized material remained at the final temperature for two hours.

The description of the anatomical elements of wood and charcoal samples followed the orientations of the International Association of Wood Anatomists (IAWA 1989), on the basis of 25 readings regarding frequency and tangential diameter of the vessels, and frequency, height and width of the rays in micrometers. The images of the general distribution of the cells in the transversal plane were obtained with a stereomicroscope with digital camera (Zeiss Discovery V12). The details of charcoal structure were obtained by scanning electron microscopy (SEM) with a tabletop microscope (Hitachi TM-1000).

For comparison of cell dimensions of the wood and charcoal an analysis of variance (ANOVA) at an error probability of 5% was performed. When null hypothesis was rejected, a Tukey test was realized.

Infrared analyses were performed in a Bruker Tensor 37 spectrophotometer (Bruker Optics, Ettlingen, Germany) equipped with an integrating sphere and operating in reflectance mode, 64 scans were averaged with resolution of 4 cm^{-1} and a spectral range of 10,000–4,000 cm^{-1}. In a room with temperature of 23 ± 2 °C and relative humidity of 60%, the wood and charcoal samples were placed on top of integrating sphere and one spectra was obtained from each face: transversal, radial and tangential, resulting in a total of 6 separate spectra for each sample, in a total of 8 per species.

The Unscrambler X chemometric program (version 10.1, from CAMO Software AS) was used to analyze the data. Exploratory modeling was done by analyzing the score and loading graphs obtained by principal components analysis (PCA) to verify possible differences in wood and charcoal. Baseline offset and second derivative of Savitzy-Golay (polynomial order = 2, smoothing point = 3) were applied in raw data. Spectral analysis was based on American Society for Testing and Materials - ASTM E1655-05 (ASTM 2012).

Results and Discussion

Wood and charcoal anatomy

Anatomical structure of wood and charcoal are illustrated in Figure 1, and details in scanning electron microscopy (SEM) are presented in Figure 2.

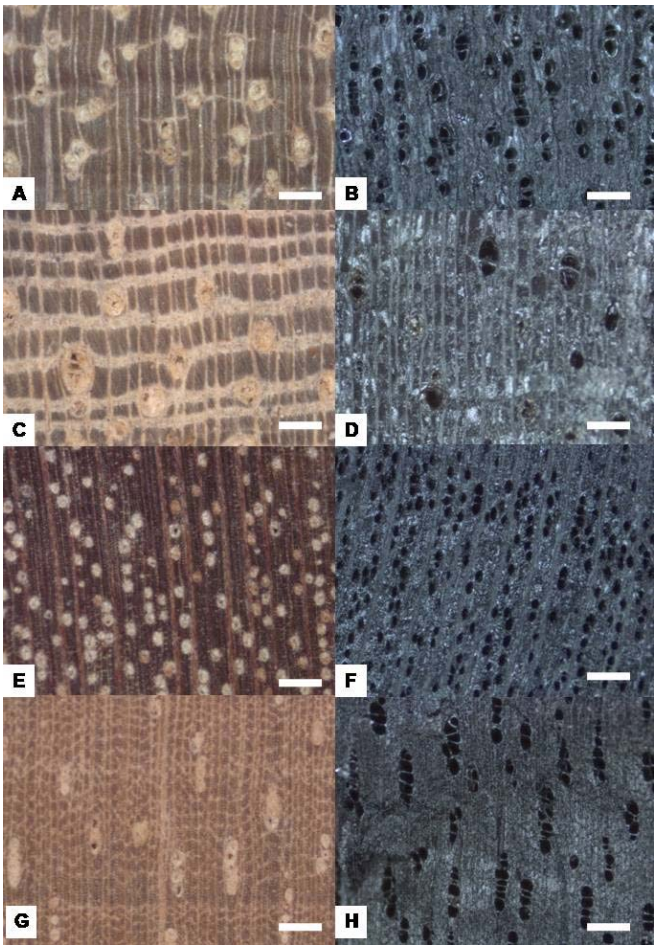

Figure 1. Wood (A,C,E,G) and charcoal (B,D,F,H). *Brosimum acutifolium* (A,B); Ficus citrifolia (C,D); *Hieronyma laxiflora* (E,F); *Sapium glandulatum* (G,H). Scale bar = 500µm.
Figura 1. Madeira (A,C,E,G) e Carvão (B,D,F,H). *Brosimum acutifolium* (A,B); *Ficus citrifolia* (C,D); *Hieronyma laxiflora* (E,F); *Sapium glandulatum* (G,H). Escala = 500µm.

***Brosimum acutifolium*:** in wood (Figure 1A) growth rings are distinct, distinguished by difference in fiber walls; diffuse-porous, vessels solitary and in radial multiples; simple perforation plates; axial parenchyma aliform; heterogeneous rays, uni and multiseriated. In carbonized wood (Figure 1B) the vessels are more distinct, and axial parenchyma and growth rings are not evident.

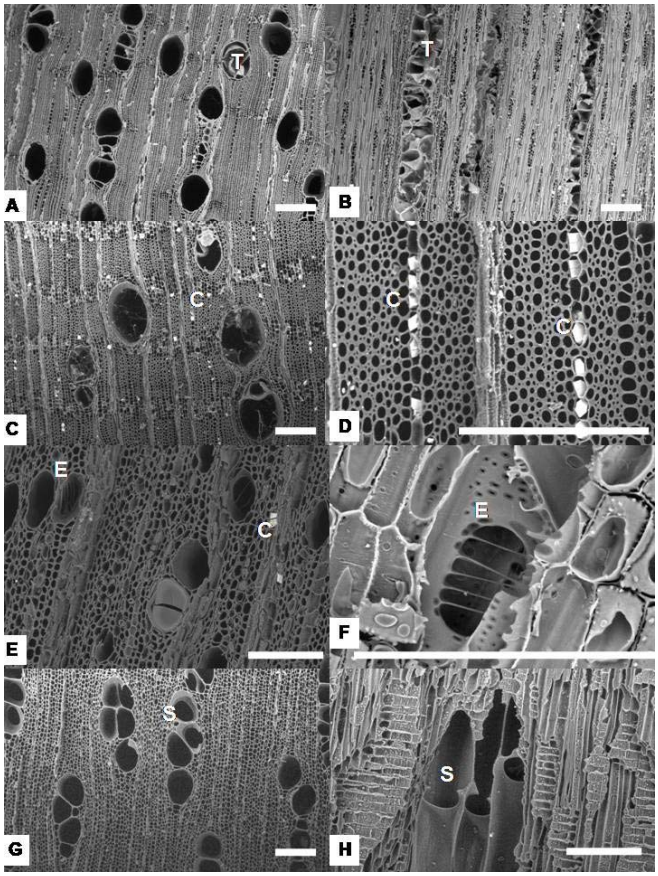

Figure 2. SEM imagens of *Brosimum acutifolium* (A,B); *Ficus citrifolia* (C,D); *Hieronyma laxiflora* (E,F); *Sapium glandulatum* (G,H). Details of tyloses (T), crystals (C), scalariform perforation plate (E), simple perforation plate (S). Scale bar = 200µm.
Figura 2. Imagens em microscopia eletrônica de varredura (MEV) de *Brosimum acutifolium* (A,B); *Ficus citrifolia* (C,D); *Hieronyma laxiflora* (E,F); *Sapium glandulatum* (G,H). Detalhes de tilos (T), cristais (C), placa de perfuração escalariforme (E), placa de perfuração simples (S). Escala = 200µm.

Ficus citrifolia: in wood (Figure 1C) growth rings are indistinct; diffuse-porous, vessels solitary and radial multiples present; simple perforation plate; axial parenchyma in bands; heterogeneous rays, multiseriate. Crystals in axial and radial parenchyma. In charcoal (Figure 1D), vessels are more evident, and crystals (Figure 2C,D) are highlighted.

Hieronyma laxiflora: in wood (Figure 1E) growth rings are indistinct; diffuse-porous, vessels solitary predominant; simple and scalariform perforation plate (Figure 2E,F); axial

parenchyma diffuse-in-aggregates; heterogeneous rays, multiseriate. In charcoal (Figure 1F), vessels are more evident.

Sapium glandulatum: in wood (Figure 1G) growth rings are indistinct; diffuse-porous, vessels in radial multiples predominant; simple perforation plate (Figure 2G,H); axial parenchyma reticulate; heterogeneous rays, uniseriate. In charcoal (Figure 1H), radial arrangement of vessels are more distinct.

The quantitative anatomical characteristics of wood and charcoal samples are summarized in Tables 1-2.

Based on statistical analysis, it is possible to observe a pattern in quantitative changes in vessels dimensions after carbonization (Table 1). Vessel diameter decreased and frequency increased at least 50% (*Hieronyma laxiflora*). The changes were expected in function of material contraction. These alterations were not observed in *Sapium glandulatum.* In *Brosimum acutifolium* it was observed the biggest differences between wood and charcoal, with approximately an increase in vessel frequency of three times and a decrease in vessel diameter of 36%.

In radial dimensions (Table 2), same behavior was observed, all species presented decrease in ray height and an increase in ray frequency. In ray width only *Hieronyma laxiflora* presented an increase of approximately 28%, other species presented decrease in this dimension. Literature report that ray comportment is not standard and is variable in function of species anatomical and chemical composition and also carbonization process (GONÇALVES et al. 2012; MUÑIZ et al. 2012).

Table 1. Mean and (standard deviation) in vessels dimension and frequency in wood and charcoal.
Tabela 1. Média e (desvio padrão) das dimensões e frequência dos vasos na madeira e carvão.

Species	Vessel.mm^{-2}		Vessel diameter (µm)	
	Wood	Charcoal	Wood	Charcoal
Brosimum acutifolium	3,28^{a}	10,00^{b}	162,42^{a}	104,00^{b}
	(1,28)	(2,61)	(21,21)	(17,90)
Ficus citrifolia	1,20^{a}	2,48^{b}	232,92^{a}	194,57^{b}
	(0,82)	(1,50)	(45,00)	(45,68)
Hieronyma laxiflora	12,80^{a}	19,44^{b}	100,47^{a}	80,56^{b}
	(2,86)	(5,77)	(11,78)	(15,64)
Sapium glandulatum	8,28^{a}	13,54^{b}	119,29^{a}	124,39^{a}
	(3,21)	(3,98)	(24,29)	(30,49)

*Same letter in line means no significant difference between wood and charcoal by Tukey test with 5% of probability.

Table 2. Mean and (standard deviation) in rays dimension and frequency in wood and charcoal.
Tabela 2. Média e (desvio padrão) das dimensões e frequência dos raios na madeira e carvão.

Species	Ray height (µm)		Ray width (µm)		Rays/mm	
	Wood	Charcoal	Wood	Charcoal	Wood	Charcoal
Brosimum acutifolium	416,29^{a}	404,07^{a}	41,82^{a}	34,30^{b}	6,20^{a}	5,24^{b}
	(159,49)	(121,27)	(9,82)	(7,46)	(1,22)	(1,71)
Ficus citrifolia	556,86^{a}	174,88^{b}	53,37^{a}	14,65^{b}	4,56^{a}	7,20^{b}
	(254,28)	(73,55)	(18,60)	(3,09)	(1,04)	(1,08)
Hieronyma laxiflora	1465,95^{a}	1145,89^{b}	90,28^{a}	115,22^{b}	2,80^{a}	4,16^{b}
	(400,05)	(486,02)	(18,67)	(13,38)	(0,91)	(0,99)
Sapium glandulatum	302,96^{a}	100,41^{b}	25,33^{a}	6,24^{b}	5,92^{a}	13,32^{b}
	(144,70)	(37,34)	(6,45)	(2,18)	(1,08)	(1,97)

*Same letter in line means no significant difference between wood and charcoal by Tukey test with 5% of probability.

Other studies showed the influence of the fiber walls thickness, axial parenchyma cell quantity and distribution and ray dimension on dimensional cellular changes in carbonization process (GONÇALVES et al. 2012; MUÑIZ et al. 2012; NISGOSKI et al. 2012, 2014).

NIR spectroscopy

NIR spectra of wood and charcoal are similar in studied species (Figure 3). Bands of lignocellulosic material are present in wood, and in charcoal small absorption were verified, following the results in literature (DAVRIEUX et al. 2010; MUÑIZ et al. 2013).

Informative wavenumbers are correlated with the presence of polysaccharides, lipids and protein, which are related to cell structure: region near 8370 cm^{-1} (1) are associated with the CH second overtone and CH_3– groups; bands around 7000 $cm^{-1}$and 6287 cm^{-1} (2) are correlated to the amorphous and crystalline region of cellulose, respectively; the range 6900-6850 cm^{-1} (3) is associated with the C-H combination of aromatics, phenolic OH group of lignin and extractives; wave numbers near 5974 $cm^{-1}$are attributed to the aromatic ring of lignin; region near 5800 cm^{-1}, corresponds to the furanose/pyranose functional group present in hemicellulose; bands in 5816-5814 cm^{-1} are related to all components of wood; bands at 5587 cm^{-1}, 5760 cm^{-1} and 4739 $cm^{-1}$are associated with cellulose; bands in 5200-5050 cm^{-1} refers to water (4) and 4700 cm^{-1} (5) corresponds to CH deformations attributed to water; 4686 cm^{-1} are related with acetyl groups, lignin and extractives; while that at 4198 cm^{-1} corresponds to holocellulose; and that at 4014 cm^{-1} is associated with C-H and C-C stretching and cellulose in wood and wood products (SCHWANNINGER et al. 2011).

PCA was carried out to verify the distribution of samples from wood and charcoal with data preprocessed with second derivative of Savitzy-Golay (Figure 4).

In wood, first principal component is responsible for explaining 82% of variation in spectra characteristics and it is possible to make a distinction of species (Figure 4a). In char-

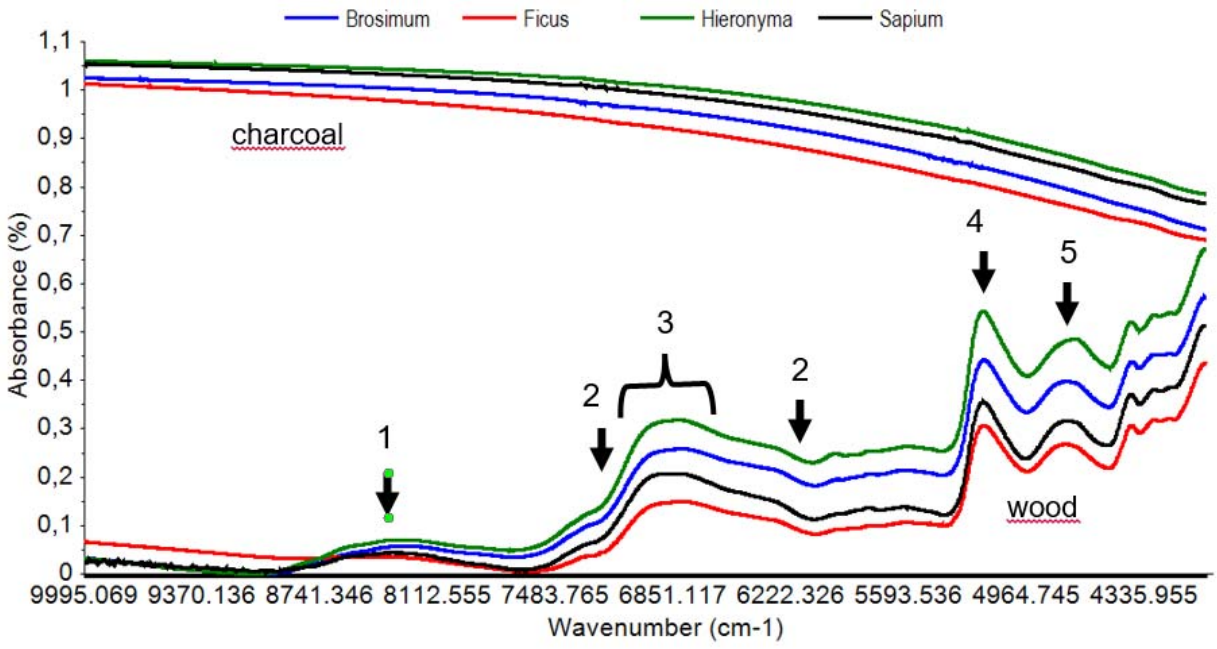

Figure 3. Mean spectra of wood and charcoal.
Figura 3. Espectros médios da madeira e carvão.

coal, first and second principal component can explain 34% of variation between species and family distinction is evident (Figure 4b). Also in charcoal, PCA graphic shows a tendency of separation of species, principally in Moraceae family, from *Brosimum* and *Ficus*, probably in function of anatomical structure that presents, with more evidence, more parenchyma cells and bigger pores in comparison to Euphorbiaceae.

In wood, chemical constituents are responsible for color and other specific characteristics, so the discrimination based on near infrared, which present chemical information, is possible in solid samples (BRAGA et al. 2011), are influenced by sample preparation (HEIN et al. 2010; NISGOSKI et al. 2015) and also origins of timber can be determined (SANDAK et al. 2011). In charcoal, polymers are degraded during carboniza-

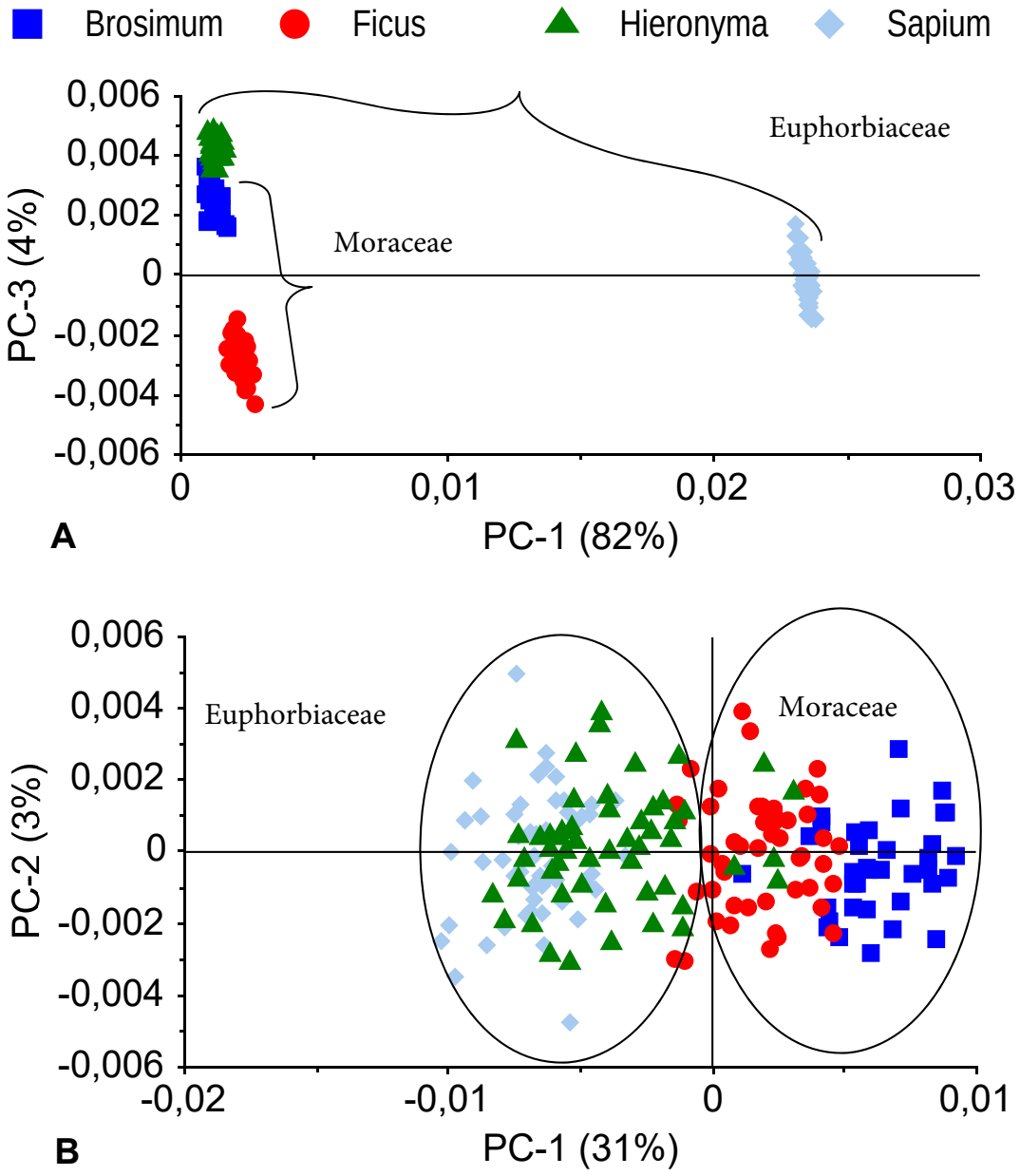

Figure 4.PCA with second derivative of wood (A) and charcoal (B) samples.
Figura 4. PCA com segunda derivada das amostras de madeira (A) e carvão (B).

tion process and this comportment, at the same conditions, is dependent of species (DAVRIEUX et al. 2010; MUÑIZ et al. 2013), so the changes in chemical composition depend on starting material (PASTOR-VILLEGAS et al. 2007).

Literature report that higher extractives contents associated with lower crystallinity and lower crystallite size accelerate the degradation process and reduce wood thermal stability (POLETTO et al. 2012). A detail study on chemical degradation of the four studied species is recommended.

Conclusion

Qualitative anatomical structure of wood remains in charcoal, and can be used to species discriminations. The quantitative changes depend on species characteristics. Near infrared can be applied for wood discrimination of some species from Euphorbiaceae and Moraceae, but in charcoal the distinction of family is more adequate.

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