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WOOD AND CHARCOAL IDENTIFICATION OF FIVE SPECIES FROM THE MISCELLANEOUS GROUP KNOWN IN BRAZIL AS "*Angelim*" BY *NEAR-IR* AND WOOD ANATOMY

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ABSTRACT

Samples of wood sold as "angelim" in Brazil were studied. Disks from the trunks of *Diplotropis purpurea*, *Hymenolobium petraeum*, *Parkia pendula*, *Vatairea guianensis* and *Vatairea paraensis* were obtained from Mato Grosso state. Samples from pith to bark of each species were obtained, oriented in the three anatomical planes. Each sample was 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}. The description of the anatomical elements of wood and charcoal samples followed the orientations of the International Association of Wood Anatomists, on the basis of 25 readings regarding frequency and tangential diameter of the vessels and height and width of the rays in micrometers. Infrared analyses were performed with a Bruker Tensor 37 spectrophotometer equipped with an integrating sphere and operating in reflectance mode, with resolution of 4 cm^{-1} and a spectral range of 10000-4000 cm^{-1}. The wood and charcoal samples were placed on top of integrating sphere and one spectrum was obtained from each surface, resulting in six spectra for each physical sample. The results of anatomical analysis showed that the qualitative characteristics of wood remained in charcoal, so the method can be applied for species discrimination. When comparing cell dimensions, we observed different behavior between species in the same carbonization process in function of cell wall thickness and parenchyma distribution. In infrared analysis, pretreatment influenced adequate discrimination of "angelim" species in wood and charcoal. Linear discriminant analysis based on PCA scores and the region between 4000-6200 cm^{-1} was more efficient. Near infrared analysis can be used for differentiation of wood and charcoal of "angelim" species.

Keywords: Carbonization, NIR spectroscopy, ray cells, species discrimination, wood vessels.

INTRODUCTION

Wood commerce is generally based on species' common names, often determined by external characteristics like color and shape. In Brazil, for example, the name "angelim" is applied to the genera *Andira*, *Dinizia*, *Hymenolobium* and *Vatairea*, which have different anatomical and technological properties (Ferreira *et al.* 2004). In turn, two species of the genus *Bowdichia* and four of *Diplotropis* are popularly called "sucupira" (Soares *et al.* 2014).

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Wood technological properties are species related, so when wood from different species is sold under the same common name, the final product may not have the same quality expected by consumers. The most widely used method for wood identification is based on visual properties and description of anatomical structures, but for many groups of species, this identification is rarely accurate to the species level, and in some cases, only the botanical family can be correctly identified (Gasson 2011).

When the analysis is based on carbonized material, the difficulty of species discrimination increases. Studies of charcoal identification based on anatomical structure have shown that the qualitative characteristics of wood remain in charcoal and the identification is possible when comparing with a wood database, but this requires time and anatomical knowledge of wood (Muñiz *et al.* 2012, Gonçalves *et al.* 2012, 2014). One alternative is the use of nondestructive techniques like infrared spectroscopy, with the information collected directly from material surface.

A review by Tsuchikawa and Schwanninger (2013) showed the application of near infrared for online monitoring in different industries to detect morphological, chemical, physical and mechanical properties of lignocellulosic materials. Studies by Pastore *et al.* (2011) and Braga *et al.* (2011) described the identification and differentiation of species similar to *Swietenia macrophylla* (CITES Appendix II). Near infrared studies for species identification include discrimination of samples of different geographic origins, and influence of sample granulometry and surface features (Sandak *et al.* 2011, Nisgoski *et al.* 2015a, Hwang *et al.* 2016). Additionally, different data pretreatment and classification methods can be employed (Tominaga 1999).

Some studies for wood species identification are based on analysis of increment cores, chips or powder (Adedipe *et al*. 2008, Russ *et al*. 2009, Casale *et al.* 2010, Sandak *et al.* 2011, Pastore *et al*. 2011, Braga *et al*. 2011). For carbonized material, near infrared spectrometry has been used to distinguish species (Davrieux *et al.* 2010, Nisgoski *et al.* 2015b) and carbonization processes (Monteiro *et al.* 2010).

Identification of wood or any other material by spectral data depends on classification and pattern recognition techniques. Principal component analysis (PCA) is an unsupervised pattern recognition technique usually applied as the first step in the detection of clusters in the collected data (Ciosek *et al.* 2005). The results provided by PCA can be further refined by supervised pattern recognition techniques. Soft independent modeling of class analogy (SIMCA) is a method of multivariate classification based on PCA modeling, performed for each class in the calibration set. It is especially suited when high within-class variability is possible (Bylesjo *et al.* 2006, Stumpe *et al*. 2012). NIR spectra analyzed by this technique have shown good results in classifying veneers contaminated by blue stain fungi for plywood production (Carneiro *et al.* 2013) and classifying thermally modified wood (Bächle *et al.* 2012).

Linear discriminant analysis (LDA) focuses on dissimilarity between classes and can be used when data are classified in symmetric structures (Tominaga 1999). PCA associated with linear discriminant analysis (PCA-LDA) is based on PCA scores and allows the discrimination of groups based on spectra. Pre-processing is important to eliminate noise and remove physical phenomena in the spectra in order to improve the subsequent multivariate regression, classification model or exploratory analysis (Rinnan *et al.* 2009). Derivatives can remove additive and multiplicative effects in the spectra, as well as baselines and linear trends. Savitzky-Golay derivation includes a smoothing step (Siesler *et al.* 2002). Multiplicative scatter correction (MSC) is a scatter-corrective pretreatment technique applied to reduce the variability between samples due to scattering and also to adjust for baseline shifts (Martens *et al.* 1983, Geladi *et al.* 1985).

The main objective of this paper is the discrimination of wood and charcoal from different species of “angelim” based on anatomical structure and near infrared analysis. Two other goals are to contribute to control of illegal logging, by providing information on carbonized wood, and to test the potential use of solid charcoal material in near infrared analysis.

MATERIALS AND METHODS

The wood samples of the species *Diplotropis purpurea (*Rich.) Amshoff. - Fabaceae (sucupira), *Hymenolobium petraeum* Ducke - Fabaceae (angelim pedra), *Parkia pendula* (Willd.) Benth. Ex Walp.- Mimosaceae (angelim saia), *Vatairea guianensis* Aubl. - Fabaceae (angelim cascudo) and *Vatairea paraensis* Ducke - Fabaceae (angelim amargo) came from the municipality of Nova Maringá, Mato Grosso state (13°1′2″S, 57°4′8″W). The trees were cut in a natural forest and stem discs with thickness of about 80 mm were taken at breast height (1,3 m). Samples of each species from pith to bark were obtained, with dimensions of 20 x 20 x 50 mm, oriented in the three anatomical planes. In function of disk diameter, the number of samples varied from 8-10 per species. The samples were air dried and remained in a climatic chamber at temperature of 20 ± 3 °C and relative humidity of 65 ± 1%.

For charcoal production, each sample was 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}. The carbonized material remained at the final temperature for two hours. Aluminum foil was removed only for near infrared analysis.

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 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 cell dimensions of the wood and charcoal were compared by the Tukey test at a probability of 5%.

Infrared analyses were performed with 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 10000–4000 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 the integrating sphere and one spectrum was obtained from each face (transversal, radial and tangential), resulting in a total of six separate spectra for each physical sample, for a total of 48-60 per species. Face measurement presented different spectral characteristics, so all spectra were used and named as a sample, without average. For analysis, we used 40 spectra of each species for calibration and the others (8-20) for classification testing.

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 component analysis (PCA) to verify possible differences in wood and charcoal. Individual models were based on the NIPALS algorithm and validated with cross validation. Second derivative of Savitzky-Golay (polynomial order = 2, smoothing point = 3) and multiplicative scatter correction (MSC) were applied to raw data. For MSC, the mean of the calibration set was used as the reference for the test set. SIMCA and PCA-LDA classifications were also performed. In the case of the SIMCA models, a maximum four PCs were used. LDA was calculated based on constant weight, through the quadratic method, assuming equal prior probabilities and using PCA scores projected for four components. Spectral analysis was based on ASTM E1655-05 (ASTM 2000).

RESULTS AND DISCUSSION

Wood and charcoal anatomy

The micrographs of wood and charcoal samples, in transversal section (Figure 1), show the similar anatomical characteristics, such as diffuse pores, arranged in solitary and radial multiples, axial parenchyma lozenge-aliform and confluent, ray fine to medium, distinct. In charcoal, the more evident anatomical alterations caused by thermal degradation were vessel contraction and less distinction of parenchyma cells.

The qualitative characteristics of wood remained in charcoal. When comparing cell dimensions (Table 1), different behavior was observed: in *Diplotropis purpurea*, a decrease was observed in vessel diameter, ray height and ray width, and an increase in ray frequency; in *Hymenolobium petraeum*, frequency of vessels and rays and ray width increased; in *Parkia pendula*, a decrease was verified in vessel diameter and ray width; in *Vatairea guianensis*, a more significant increase in ray frequency (54%) was observed; and in *Vatairea paraensis*, a significant decrease in vessel diameter (41%) and increase in ray width (43%) were present.

Similar differences have been reported in other studies, associated with the presence and distribution of parenchyma cells and fiber wall thickness (Muñiz *et al*. 2012, Gonçalves *et al.* 2012).

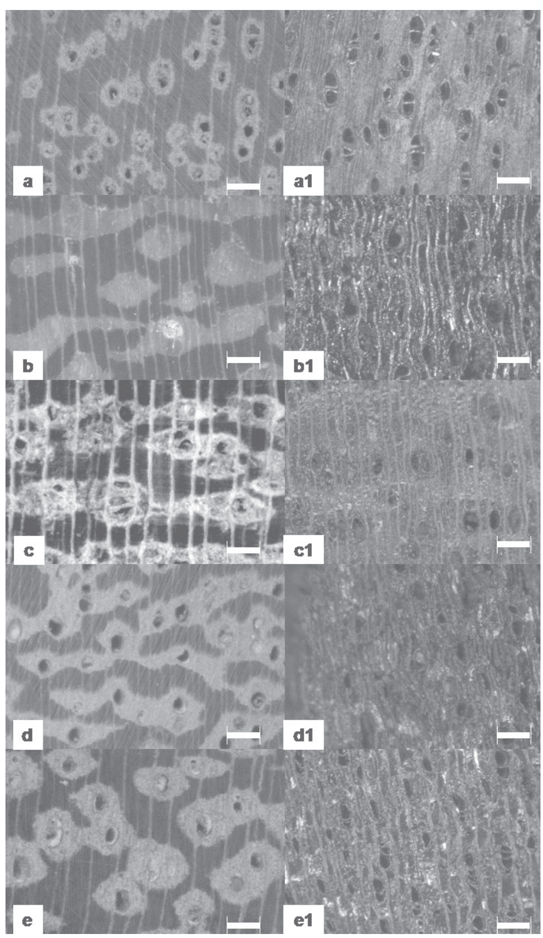

Figure 1. Transversal section of wood and charcoal from *Diplotropis purpurea* (a,a1), *Hymenolobium petraeum* (b,b1), *Parkia pendula* (c,c1), *Vatairea guianensis* (d,d1), *Vatairea paraensis* (e,e1). Scale bar = 500 µm.

Table 1. Summary of changes in anatomical characteristics between wood and charcoal. Data are given as mean and standard deviation.

Species	Vessel diameter (µm)		Vessel/mm²		Ray height(µm)		Ray width (µm)		Rays/mm	
	W	C	W	C	W	C	W	C	W	C
Diplotropis purpurea	240,8a (33,5)	129,6b (39,4)	4,4a (1,6)	5,4a (2,2)	467,6a (128,9)	292,3b (87,6)	42,4a (9,3)	31,3b (7,2)	5,4a (1,1)	7,1b (1,7)
Hymenolobium petraeum	222,4a (29,2)	200,5a (67,5)	3,1a (1,3)	5,0b (1,9)	353,7a (110,4)	361,2a (80,1)	33,0a (9,8)	42,5b (7,7)	4,2a (0,9)	5,4b (1,5)
Parkia pendula	192,2a (41,5)	162,4b (54,1)	2,6a (1,1)	3,4b (1,5)	270,6a (100,4)	300,5a (90,8)	51,4a (12,3)	44,7b (8,84)	4,1a (1,2)	4,0a (1,3)
Vatairea guianensis	187,2a (34,3)	159,3b (44,7)	3,9a (2,1)	3,6a (1,8)	321,4a (102,5)	340,4a (86,1)	28,7a (5,7)	31,5a (6,4)	6,1a (1,0)	9,4b (1,5)
Vatairea paraensis	246,2a (31,1)	144,4b (30,9)	3,2a (1,3)	3,8a (2,0)	509,0a (210,9)	463,4a (150,4)	55,5a (13,4)	79,2b (21,2)	3,6a (0,8)	4,6a (1,1)

W = wood, C = charcoal. *Equal letters in lines indicate no significant difference between wood and charcoal by the Tukey test at 5% probability.

NIR characteristics of wood and charcoal

NIR spectra of "angelim" species are similar and some regions present more distinction between species in wood and in charcoal. In wood (Figure 2a), bands at 8749cm^{-1} and 8547 cm^{-1} are related to aromatics of lignin; bands at 6800 cm^{-1} and 4401 cm^{-1} are attributed to hemicelluloses; regions near 6110-5697 cm^{-1} and 4335-4146 cm^{-1} are related to all cell wall components; the peak at 5200 cm^{-1} is from water, while that at 5995 cm^{-1} is related to extractives content (Tsuchikawa and Siesler 2003, Yonenobu and Tsuchikawa 2003, Schwaninger *et al.* 2011). In charcoal, small absorption was verified (Davrieux *et al.* 2010, Muñiz *et al.* 2013) and some irregularities in spectra were influenced by water OH bands (region near 7073-7181 and 5142 cm^{-1}) and degradation of cell wall components (4335-4146 cm^{-1}).

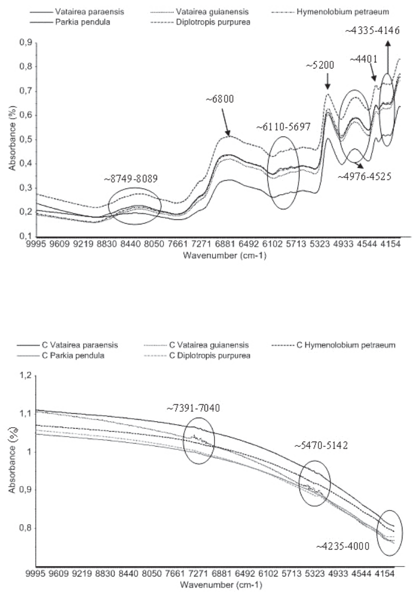

Figure 2. Mean spectra of wood and charcoal (C) samples of "angelim" species.

Second derivative eliminates baseline influence and shows the regions with most difference between wood and charcoal. All spectra by species were averaged and are compared in Figure 3.

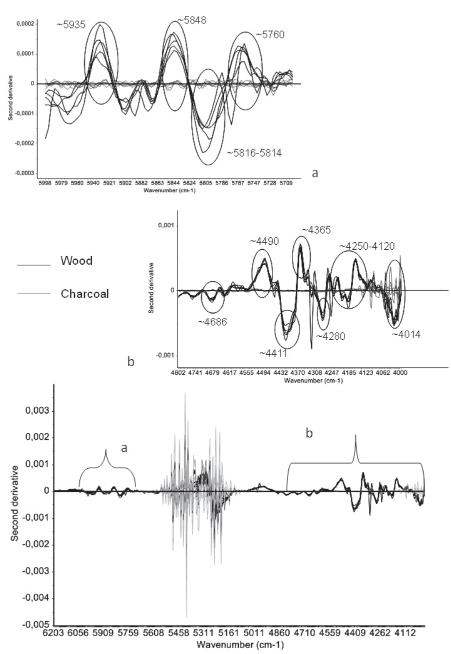

Figure 3. Second derivative of NIR spectra of wood and charcoal samples of "angelim" species.

Chemical and anatomical composition of species results in different NIR absorbance values, and for discrimination some regions can have more influence. A spectral range from 4249-6100 cm^{-1} was efficient in distinguishing wood species similar to mahogany (Pastore *et al*. 2011) and 4000-6200 cm^{-1} showed potential in discriminating six origins of *Criptomeria japonica* planted in southern Brazil (Nisgoski *et al.* 2016). In this study with "angelim" species, regions with influence of water content were eliminated, and comparing wood and charcoal, two regions presented some differences, from 6200 to 5500 cm^{-1} (Figure 3a) and from 5000 to 4000 cm^{-1} (Figure 3b).

In wood samples, *Vatairea guianensis* presented peaks with stronger intensities at 4320 cm^{-1} and 4251 cm^{-1}, which are related to cellulose groups. In the comparison of wood and charcoal spectra, some contrast was observed in bands that represent cell wall components, as expected, revealing the differences in chemical composition and thermal degradation: peaks at ~5935 cm^{-1}, ~4411 cm^{-1}, ~4280 cm^{-1} and 4014 cm^{-1}, related to lignin; peaks at ~5848 cm^{-1}, ~4686 cm^{-1}, related to hemicelluloses; and peaks at ~5760 cm^{-1}, ~4365 cm^{-1}, ~4252 cm^{-1}, related to cellulose, are more distinct in wood samples.

Degrees of degradation based on the same carbonization process are species related (Muñiz *et al.* 2013). Each of the three major components of wood has its own characteristic properties related to thermal degradation, based on polymer composition. Thus, behavior is different if the components are isolated or combined in the wood cell matrix (Popescu *et al.* 2011). Between 30-250 ºC, no large changes were observed in the nanostructure of cellulose microfibrils, while between 250-315 ºC the structure of cellulose fibrils were completely degraded and significant weight loss was observed. Between 315-1200 ºC, nanometer-sized inhomogeneities in the pyrolyzed wood samples appeared (Smith *et al.* 2012).

PCA was carried out to verify the distribution of samples from wood and charcoal with original data, Savitzky-Golay second derivative and MSC (Figure 4). For wood, the PCA graphs by species showed separation of spectra into two groups, in function of anatomical sections: group one from transversal section, group two from longitudinal sections (radial and tangential) for original data and pretreated with MSC. In second derivative, spectra distribution was more homogeneous and non-section separation was observed, resulting in the best discrimination of "angelim" species in total analysis of wood species.

For charcoal, the PCA graphs by species revealed a distinction of groups by section, but after pretreatment by second derivative and MSC, just a tendency remained. Also for charcoal, the best discrimination of "angelim" species was observed with second derivative.

There are variations among species in NIR absorbance values, and for their discrimination, some regions can have more influence based on chemical and anatomical characteristics. Measurements taken at different points of a given sample can produce variations, but still allow distinction from other samples (Brunner *et al.* 1996). In species discrimination, second derivative pre-processing has also been applied in other studies (Sandak *et al.* 2011, Zhang *et al.* 2014).

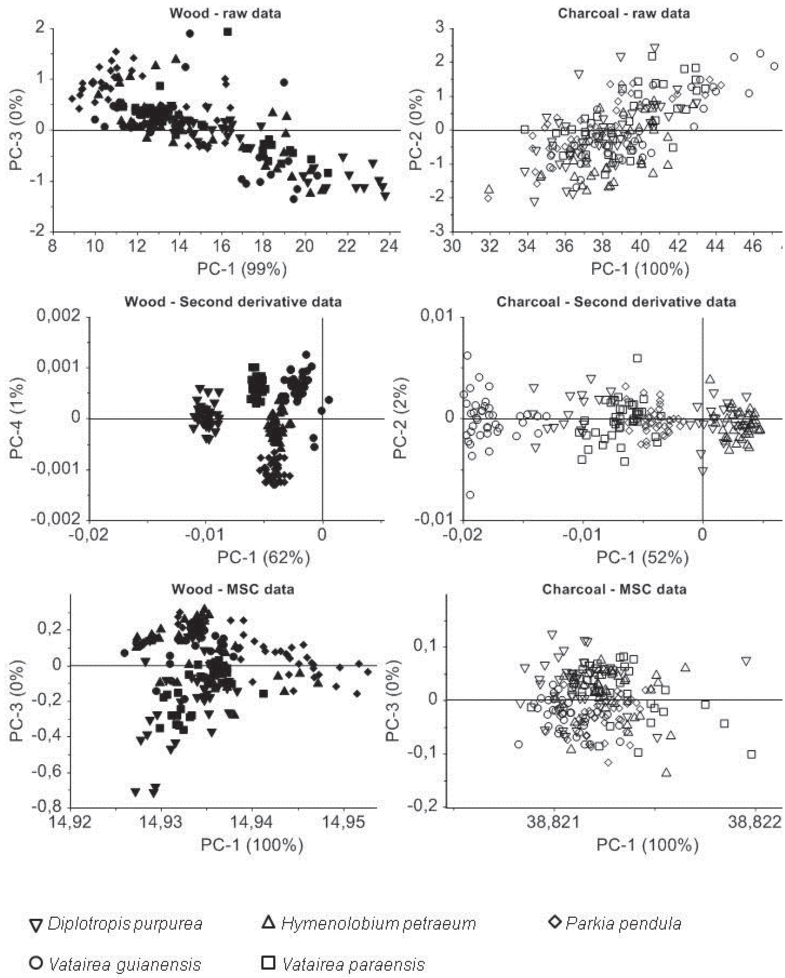

Figure 4. PCA score graph of wood and charcoal of “angelim” species with different pretreatments.

Classification of test samples by SIMCA (Tables 2-3) and PCA-LDA (Tables 4-5) was done based on the original spectra and pretreatments using second derivative and multiplicative scatter correction (MSC). We also compared all spectra and regions between 4000-5000 cm^{-1} plus 5500-6200 cm^{-1}. In SIMCA classification, there was an overlapping classification, resulting in some samples not being uniquely classified, so that some individual samples may have been classified to two or more species. Each species therefore has both its right and wrong number of classified samples presented in the tables.

For SIMCA classification (Table 2), only the second derivatives of data from *Diplotropis purpurea* wood were correctly classified both with all spectra and region from 4000-5000 cm^{-1} plus 5500-6200 cm^{-1}. Misclassifications occurred for all other species, meaning that the analysis returned more than one species for each spectrum. Individual spectra not classified or with wrong response were almost all from transversal sections. This can be the result of the point where the spectra were obtained was performed (in a vessel, parenchyma, fiber or ray cell). In anatomical analysis, transversal sections bring more information about cell type and distribution, but chemical composition can be very similar. Also, surface irregularities might have influenced the results (Brunner *et al.* 1996), since the samples were only sawed.

For charcoal (Table 3), SIMCA classification was only 75% efficient for *Vatairea guianensis* with second derivative pretreatment, for all spectra and the region between 4000-5000 cm^{-1} plus 5500-6200 cm^{-1}. This result is related to different degradation of species.

Table 2. SIMCA classification of wood samples.

SIMCA CLASSIFICATION										
			Unique					**Non unique (+ 1)**	**Not classified**	**Correct Classif (%)**
		n	***Vatairea paraensis***	***Vatairea guianensis***	***Hymenolobium petraeum***	***Parkia pendula***	***Diplotropis purpurea***			
Vatairea paraensis										
Raw data	All spectra	13	0	0	0	0	0	13	0	0
	Region*		0	0	0	0	0	13	0	0
2nd derivative	All spectra		0	0	0	0	1	12	0	0
	Region*		7	0	0	0	2	4	0	53,8
MSC	All spectra		0	0	0	0	0	13	0	0
	Region*		0	0	0	2	0	9	2	0
Vatairea guianensis										
Raw data	All spectra	8	0	0	0	0	0	8	0	0
	Region*		0	0	0	0	0	8	0	0
2nd derivative	All spectra		0	1	0	0	0	6	1	12,5
	Region*		0	2	0	0	0	5	1	25,0
MSC	All spectra		0	0	0	2	0	6	0	0
	Region*		0	0	0	2	0	5	1	0
Hymenolobium petraeum										
Raw data	All spectra	14	0	0	0	0	0	14	0	0
	Region*		0	0	0	0	2	12	0	0
2nd derivative	All spectra		0	0	1	0	0	10	3	7,1
	Region*		0	0	1	0	0	8	5	7,1
MSC	All spectra		0	0	1	0	0	12	1	7,1
	Region*		0	0	0	2	1	9	2	0
Parkia pendula										
Raw data	All spectra	14	0	1	0	0	0	13	0	0
	Region*		0	0	0	0	0	14	0	0
2nd derivative	All spectra		0	0	0	0	0	14	0	0
	Region*		1	0	0	0	0	13	0	0
MSC	All spectra		0	0	0	1	0	10	3	7,1
	Region*		0	0	0	4	0	10	0	28,6
Diplotropis purpurea										
Raw data	All spectra	20	0	0	0	0	0	20	0	0
	Region*		0	0	0	0	3	17	0	15,0
2nd derivative	All spectra		0	0	0	0	20	0	0	100
	Region*		0	0	0	0	19	0	1	95,0
MSC	All spectra		0	0	1	0	0	19	0	0
	Region*		0	0	0	0	1	14	5	5,0

* Region between 4000-5000 cm^{-1} plus 5500-6200 cm^{-1}.

Table 3. SIMCA classification of charcoal samples.

SIMCA CLASSIFICATION										
		Unique						Non unique (+ 1)	Not classified	Correct Classif (%)
		n	*Vatairea paraensis*	*Vatairea guianensis*	*Hymenolobium petraeum*	*Parkia pendula*	*Diplotropis purpurea*			
Vatairea paraensis										
Raw data	All spectra	13	0	0	0	0	0	13	0	0
	Region*		0	0	0	0	0	13	0	0
2nd derivative	All spectra		0	0	0	0	0	13	0	0
	Region*		0	0	0	0	0	13	0	0
MSC	All spectra		0	0	0	0	0	11	2	0
	Region*		0	0	0	0	0	11	2	0
Vatairea guianensis										
Raw data	All spectra	8	0	2	0	0	0	6	0	25,0
	Region*		0	0	0	0	0	8	0	0
2nd derivative	All spectra		0	6	0	0	0	2	0	75,0
	Region*		0	6	0	0	0	2	0	75,0
MSC	All spectra		0	0	0	0	0	7	1	0
	Region*		0	0	0	0	0	7	1	0
Hymenolobium petraeum										
Raw data	All spectra	14	1	0	0	0	0	12	1	0
	Region*		0	0	0	0	0	12	2	0
2nd derivative	All spectra		0	0	0	0	0	14	0	0
	Region*		0	0	0	0	0	14	0	0
MSC	All spectra		0	0	0	0	0	13	1	0
	Region*		0	0	0	0	0	13	1	0
Parkia pendula										
Raw data	All spectra	14	0	0	0	0	0	14	0	0
	Region*		0	0	0	0	0	14	0	0
2nd derivative	All spectra		0	0	0	0	0	14	0	0
	Region*		0	0	0	0	0	14	0	0
MSC	All spectra		0	0	0	0	0	14	0	0
	Region*		0	0	0	0	0	14	0	0
Diplotropis purpurea										
Raw data	All spectra	20	0	0	0	0	0	20	0	0
	Region*		0	0	0	0	0	20	0	0
2nd derivative	All spectra		0	0	0	0	0	20	0	0
	Region*		0	0	0	0	0	20	0	0
MSC	All spectra		0	0	0	0	0	20	0	0
	Region*		0	0	0	0	2	18	0	10,0

* Region between 4000-5000 cm^{-1} plus 5500-6200 cm^{-1}.

The potential of FT-NIR spectra to classify wood was demonstrated with raw data (Brunner *et al.* 1996) and total spectra with Mahalanobis generalized distance (Tsuchikawa *et al.* 2003). In other studies, SIMCA classification was efficient to distinguish thermally modified wood of spruce, beech and ash (Bächle *et al.* 2012) and to separate red oak and white oak wood (Adedipe *et al.* 2008).

PCA-LDA showed better results in "angelim" species discrimination. For wood (Table 4), samples of *Vatairea paraensis, Vatairea guianensis, Parkia pendula* and *Diplotropis purpurea* presented 100% correct classification with second derivative data and all spectra. For *Vatairea paraensis* and *Diplotropis purpurea*, the region between 4000-5000 cm^{-1} plus 5500-6200 cm^{-1} presented the same result. For charcoal (Table 5), PCA-LDA resulted in 100% correct classification for *Vatairea guianensis* (second derivative, all spectra and region between 4000-5000 cm^{-1} plus 5500-6200 cm^{-1}), *Hymenolobium petraeum* (region with raw data and second derivative), *Parkia pendula* (region with raw data and MSC) and *Diplotropis purpurea* (raw data with all spectra; region with raw data, second derivative and MSC). In these results, the region between 4000-5000 cm^{-1} plus 5500-6200 cm^{-1} presented more influence for correct classification and is related to species degradation in the same carbonization process.

The better results for region is because we eliminated the influence of water bands and the chemical differences remained based on cell wall distribution and composition or degradation, in the case of charcoal. PCA-LDA focuses on differences between species, and the natural variation of anatomical structure and chemical composition of "angelim" species, including the sections analyzed, resulted in more complete characterization of each sample, making the method more informative and robust.

Table 4. PCA-LDA classification of wood samples.

PCA-LDA CLASSIFICATION										
		Unique						Non unique (+ 1)	Not classified	Correct Classif (%)
		n	*Vatairea paraensis*	*Vatairea guianensis*	*Hymenolobium petraeum*	*Parkia pendula*	*Diplotropis purpurea*			
Vatairea paraensis										
Raw data	All spectra	13	6	0	1	0	6	0	0	46,1
	Region*		6	0	1	0	6	0	0	46,1
2nd derivative	All spectra		13	0	0	0	0	0	0	100
	Region*		13	0	0	0	0	0	0	100
MSC	All spectra		4	0	1	0	8	0	0	30,8
	Region*		6	0	0	0	7	0	0	46,1
Vatairea guianensis										
Raw data	All spectra	8	2	1	0	2	3	0	0	12,5
	Region*		0	5	0	2	1	0	0	62,5
2nd derivative	All spectra		0	8	0	0	0	0	0	100
	Region*		0	7	1	0	0	0	0	87,5
MSC	All spectra		0	1	4	1	2	0	0	12,5
	Region*		1	2	4	0	1	0	0	25,0
Hymenolobium petraeum										
Raw data	All spectra	14	6	2	0	0	6	0	0	0
	Region*		1	3	5	1	4	0	0	35,7
2nd derivative	All spectra		0	4	10	0	0	0	0	71,4
	Region*		0	3	11	0	0	0	0	78,6
MSC	All spectra		2	2	10	0	0	0	0	71,4
	Region*		1	2	8	2	1	0	0	57,1
Parkia pendula										
Raw data	All spectra	14	4	1	2	7	0	0	0	50,0
	Region*		0	2	1	11	0	0	0	78,6
2nd derivative	All spectra		0	0	0	14	0	0	0	100
	Region*		7	0	0	7	0	0	0	50,0
MSC	All spectra		0	0	4	10	0	0	0	71,4
	Region*		1	0	5	8	0	0	0	57,1
Diplotropis purpurea										
Raw data	All spectra	20	6	1	3	1	9	0	0	45,0
	Region*		3	0	0	0	17	0	0	85,0
2nd derivative	All spectra		0	0	0	0	20	0	0	100
	Region*		0	0	0	0	20	0	0	100
MSC	All spectra		3	0	0	0	17	0	0	85,0
	Region*		2	0	0	0	18	0	0	90,0

* Region between 4000-5000 cm^{-1} plus 5500-6200 cm^{-1}.

Table 5. PCA-LDA classification of charcoal samples.

PCA-LDA CLASSIFICATION										
		Unique						**Non unique (+ 1)**	**Not classified**	**Correct Classif (%)**
		n	***Vatairea paraensis***	***Vatairea guianensis***	***Hymenolobium petraeum***	***Parkia pendula***	***Diplotropis purpurea***			
Vatairea paraensis										
Raw data	All spectra	13	7	0	6	0	0	0	0	53,8
	Region*		11	0	0	0	2	0	0	84,6
2nd derivative	All spectra		9	0	0	0	4	0	0	69,2
	Region*		12	0	0	0	1	0	0	92,3
MSC	All spectra		9	0	0	0	4	0	0	69,2
	Region*		12	0	0	0	1	0	0	92,3
Vatairea guianensis										
Raw data	All spectra	8	1	6	0	0	1	0	0	75,0
	Region*		0	7	0	0	1	0	0	87,5
2nd derivative	All spectra		0	8	0	0	0	0	0	100
	Region*		0	8	0	0	0	0	0	100
MSC	All spectra		0	7	0	0	1	0	0	87,5
	Region*		0	8	0	0	0	0	0	100
Hymenolobium petraeum										
Raw data	All spectra	14	4	0	7	1	2	0	0	50,0
	Region*		0	0	14	0	0	0	0	100
2nd derivative	All spectra		0	0	11	0	3	0	0	78,6
	Region*		0	0	14	0	0	0	0	100
MSC	All spectra		0	0	13	0	1	0	0	92,8
	Region*		0	8	13	0	1	0	0	92,8
Parkia pendula										
Raw data	All spectra	14	1	0	5	8	0	0	0	57,1
	Region*		0	0	0	14	0	0	0	100
2nd derivative	All spectra		5	0	0	9	0	0	0	64,3
	Region*		4	0	0	10	0	0	0	71,4
MSC	All spectra		3	0	0	11	0	0	0	78,6
	Region*		0	0	0	14	0	0	0	100
Diplotropis purpurea										
Raw data	All spectra	20	0	0	0	0	20	0	0	100
	Region*		0	0	0	0	20	0	0	100
2nd derivative	All spectra		1	0	11	6	2	0	0	10,0
	Region*		0	0	0	0	20	0	0	100
MSC	All spectra		2	0	3	0	15	0	0	75,0
	Region*		0	0	0	0	20	0	0	100

* Region between 4000-5000 cm^{-1} plus 5500-6200 cm^{-1}.

Data pre-processing influenced the results, which were different for wood and charcoal samples of “angelim” species (Table 6). For solid wood, the best performance was with second derivative, and for solid charcoal, MSC presented the highest percentage of correct classification. SIMCA was not efficient for “angelim” species discrimination. PCA-LDA presented the best results and the use of the region between 4000-5000 cm^{-1} plus 5500-6200 cm^{-1} was more suitable. These results show the influence of sample characteristics (surface direction and irregularities) and carbonization process.

Table 6. Total correct classification of wood and charcoal samples of five “angelim” species.

Classification method	Pretreatment	Correct classification of wood samples (%)		Correct classification of charcoal samples (%)	
		All spectra	4000-5000 + 5500-6200 cm^{-1}	All spectra	4000-5000 + 5500-6200 cm^{-1}
SIMCA	Raw	0	4	3	0
	2nd derivative	33	42	9	6
	MSC	3	7	0	2
PCA-LDA	Raw	33	64	84	96
	2nd derivative	94	84	56	93
	MSC	61	61	80	97

In studies with solid wood samples, a higher number of samples was found to be better to establish distributions, because wood surface (Braga *et al.* 2011), shape and particle size (Nisgoski *et al.* 2015a) can have a significant influence on species discrimination by NIR. Only based on PCA graphs, Nisgoski *et al.* (2015b) obtained results adequate for wood discrimination of two species of Euphorbiaceae and two species of Moraceae, but for charcoal only the family could be distinguished.

In this study with “angelim” species, the number of test samples was small but the objective was achieved and the potential of near infrared application with solid samples for distinction of wood and charcoal as demonstrated.

CONCLUSIONS

The results of anatomical analysis showed that the qualitative characteristics of wood remained in charcoal and can be applied for species discrimination. In function of natural variation of species characteristics, charcoal must be compared with reference material collections. When comparing cell dimensions, we observed different behavior between species in the same carbonization process in function of cell wall thickness and parenchyma distribution.

In infrared analysis, the results were influenced by the section where the spectra were collected, the pretreatment was applied, classification method and spectrum region analyzed. The distribution of spectra from each species' transversal section was distinct from the spectral distributions of the radial and tangential sections when raw data were analyzed. Second derivative eliminated this distinction and resulted in the best discrimination of "angelim" species.

SIMCA classification was not adequate for these species' discrimination based on wood and charcoal. PCA-LDA was more efficient and reached more than 90% correct classification. Bands with influence of water must be eliminated and the region between 4000-5000 plus 5500-6200 cm^{-1} was more efficient for "angelim" species discrimination.

For rapid analysis for forest control or detection of illegal commerce, spectra collected directly from wood and charcoal can be used to distinguish of species sold as "angelim".

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