0717-3644 0718-221X

# POTENTIAL USE OF NIR AND VISIBLE SPECTROSCOPY TO ANALYZE CHEMICAL PROPERTIES OF THERMALLY TREATED WOOD

Elaine Cristina Lengowski<sup>1,\*</sup>, Graciela Inês Bolzon de Muñiz<sup>2</sup>, Umberto Klock<sup>2</sup>, Silvana Nisgoski<sup>2</sup>

# ABSTRACT

The modification of wood by thermal treatments produces characteristic changes in its chemical composition and surface color and can improve the structural and esthetic quality. The objective of this paper is to evaluate the potential of near infrared and visible spectroscopy to predict the modifications in chemical composition of *Eucalyptys grandis* and *Pinus taeda* after thermal treatment. Near infrared and visible spectra were collected directly on the longitudinal surface of wood samples. The thermally modified wood of both species showed higher content of lignin and extractives than the untreated wood. There was darkening of thermally modified wood, as a result of chemical modification caused by heat. The Near infrared/visible technique identified the groups that were modified by treatment. NIR and visible spectroscopy can be used to predict chemical composition of natural or thermally treated *Eucalyptus grandis* and *Pinus taeda*.

Keywords: Chemical analysis, *Eucalyptus grandis*, *Pinus taeda*, thermal modification, wood color, wood composition.

### **INTRODUCTION**

The application of thermal treatment in the wood industry has been growing in recent years. Studies have reported that heat process can modify some properties of wood as natural durability, dimensional stability, hygroscopicity (Olarescu *et al.* 2014, Militz and Altgen 2016, Pertuzzatti *et al.* 2016, Huang *et al.* 2018) and mechanical properties (Kuzman *et al.* 2015, Militz and Altgen 2016). Differences have also been verified in the equilibrium moisture content, volumetric swelling and chemical composition of juvenile and mature wood (Gonzáles-Peña *et al.* 2009, Esteves *et al.* 2011, Severo *et al.* 2012). The review of Esteves and Pereira (2009) reported changes in mass loss, chemical composition, anatomical structures, equilibrium moisture, dimensional stability, durability, mechanical properties, wettability, weathering, finishing, gluing, color and quality control. These results were confirmed in *Pinus elliottii* (Conte *et al.* 2014, Pertuzzatti *et al.* 2016), in eucalyptus species (Garcia *et al.* 2014, Zanuncio *et al.* 2014a, Zanuncio *et al.* 2014b, Zanuncio *et al.* 2014c), and other commercial wood as *Lecythis pisonis* (De Paula *et al.* 2016), *Simarouba amara* (Freitas *et al.* 2016) and *Tectona grandis* (Méndez-Mejías and Moya 2016).

One important change in heat-treated wood is its generally darker appearance, which can be explained by the combination of several factors: (a) the dissolution, oxidation and decomposition of the extractives and other chemical components; (b) formation of oxidative products, such as quinones and products of degradation of hemicelluloses and lignin, which migrate to the wood surfaces; (c) the

<sup>&</sup>lt;sup>1</sup>Federal University of Mato Grosso, Department of Forest Engineering, Cuiabá, Brazil.

<sup>&</sup>lt;sup>2</sup>Federal University of Paraná, Laboratory of Wood Chemistry, Department of Forest Engineering and Technology, Federal University of Parana, Av. Lothario Meissner, Jardim Botânico, Curitiba-PR, Brazil.

<sup>\*</sup>Corresponding author: elainelengowski@yahoo.com.br

Received: 10.05.2017 Accepted: 07.05.2018

removal or migration of extractives and nutritive compounds such as low molecular weight sugars and amino acids towards the wood surfaces; and (d) the relative increase in the lignin content after the treatment, mainly due to the degradation of the hemicelluloses (Torres *et al.* 2012, Cademartori *et al.* 2013, Stangerlin *et al.* 2013, Bekhta *et al.* 2014). The wood with large quantities of extractives soluble in water present more intense changes of color after the treatment (Varga and Van Der Zee 2008). Some literature report that in hardwoods, color modification is less pronounced than in softwoods in function of different lignin content because this component is responsible for 80-95% of light absorbance in wood (Mitsui 2004, Moura and Brito 2011). Higher extractive contents and higher reactivity of hemicelluloses and lignin can accelerate the degradation process at low temperature; on the other hand, organized cellulose regions may promote a slow degradation process (Poletto *et al.* 2012).

The natural pine wood color (pale yellow) is not stable to light exposure, becoming grayish after exposure to sunlight, and when exposed in air it becomes whitish. Thermal treatment confers a reddish brown color, which is appreciated by most consumers (Esteves *et al.* 2008, Zanuncio *et al.* 2014b). Thermal modification has potential to improve the structural and esthetic quality of wood, in particular that from *Pinus* spp. and *Eucalyptus* spp. species with good properties, fast growing, but sometimes with unattractive coloration. In addition, the use of cultivated species to replace native wood species is necessary to preserve and reduce the pressure on the native forest.

Application of near-infrared spectroscopy to study thermally treated wood has revealed a close relationship between the chemical changes of thermally modified *Fagus sylvatica* samples and the corresponding NIR spectra (Schwanninger *et al.* 2004), alterations on phenolic, carbonyl, carboxyl, acetyl and hydroxyl groups (Mitsui *et al.* 2008, Chen *et al.* 2014, Li *et al.* 2015, Méndez-Mejías and Moya 2016), and changes in pine and eucalyptus properties (Esteves and Pereira 2008). It has potential for use in quality control of thermally modified wood, because it allows evaluation of several wood properties by obtaining a single spectrum (Bächle *et al.* 2010, Méndez-Mejías and Moya 2016).

Therefore, the objective of this paper is to evaluate the modifications in chemical composition of *Eucalyptus grandis* and *Pinus taeda* based on near infrared and visible spectroscopy of solid samples. This paper is the first to evaluate the spectral analyses from visible spectroscopy to predict changes on chemical composition after the thermal treatment of wood. The consolidate technical to analyze this is NIR spectroscopy, however, if we can use the visible spectroscopy we can evaluate two properties in one equipment, color parameters and quality of treatment applied on the wood, and also the colorimeter is more cheaper.

# MATERIALS AND METHODS

# Materials

Trees of *Eucalyptus grandis* W. Hill and *Pinus taeda* L. came from plantations with age of 18 years. Boards with dimensions of 110 x 20 x 3 cm respectively in length, width and thickness were thermally treated. Wood untreated and thermally modified (Figure 1), came from the company TWBrazil, located in Ponta Grossa, Parana state, Brazil. The thermal modification was performed by the VAP HolzSysteme® process, applying heat of 160 °C in a saturated steam atmosphere with efficient elimination of oxygen. The treatment was done in five stages: an initial heating ramp of 0,76 °C ·min<sup>-1</sup> until constant temperature (110 °C), 25 minutes at this temperature; a second ramp of 0,20 °C ·min<sup>-1</sup> until the final temperature (160 °C); 45 minutes at maximum temperature; and natural cooling. The total time of the process was about 16 hours, carried out in two 8-hour heating-cooling cycles. Four boards per treatment were analyzed. One sample of each board, with dimensions of 20 cm (length) x 8 cm (width) and 3 cm (thickness), were extracted on the middle of board and applied for color and spectroscopy analysis.



Figure 1: Boards of *Eucalyptus grandis*: (a) natural and (b) thermally modified; and *Pinus taeda*: (c) natural and (d) thermally modified.

# Methods

## Near Infrared spectroscopy

In each sample, eight spectra were collected directly on the longitudinal surface, four in radial section and four in tangential section, in a room with temperature of  $23 \pm 2$  °C and relative humidity of 60%. A total of 128 spectra were obtained, 32 by treatment. The infrared analyses were performed with a Bruker Tensor 37 spectrometer (Bruker Optics, Ettlingen, Germany) equipped with an integrating sphere and operating in reflectance mode. Spectra were obtained at 64 scans with resolution of 4 cm<sup>-1</sup> and a spectral range of 10000–4000 cm<sup>-1</sup> transformed to nm in Opus version 6.5 program (Bruker Optics). For analysis, the spectra were averaged for each surface, i.e., 2 in each radial and 2 in each tangential section in one sample, and 16 were evaluated for each treatment.

#### **Color measurements**

Wood color was measured with a Konica Minolta CM-5 spectrophotometer coupled to a computer, with adjustment to a D65 light source and  $10^{\circ}$  observation angle (CIE-Lab standard). The reflectance data were obtained with a spectral range from 400 - 750 nm. Eight spectra were collected per sample directly on the longitudinal surface (4 in radial and 4 in tangential section). A total of 128 spectra were obtained, 32 for each species and treatment, and analysis was performed with all spectra.

The following color parameters were measured according to the CIELAB: color space: lightness  $(L^*)$ , green-red coordinate  $(a^*)$ , blue-yellow coordinate  $(b^*)$ , color saturation  $(C^*)$ , and hue angle (h). A colorimetric scan of the surface of these samples was performed randomly, with a total of 10 readings per sample (radial/tangential section). The values of color saturation (C) and hue angle (h) were calculated by Equation 1 and Equation 2:

$$C^* = \sqrt{a^{*2} + b^{*2}} \quad (1)$$
$$h = \arctan\left(\frac{b^*}{a^*}\right) \quad (2)$$

The changes between natural and thermally modified wood were analyzed based on DE (total color variation), calculated by Equation 3:

$$\Delta E = \sqrt{\Delta L^{*^2} + \Delta a^{*^2} + \Delta b^{*^2}} \qquad (3)$$

#### **Spectral analysis**

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 natural and thermally modified wood. PCA was based on algorithm NIPALS and cross validation with centered data. PCA is widely applied for analysis of spectroscopy data as a preliminary step to observe variance structure of data and visualization of its natural clustering, followed by multivariate methods (Acquah *et al.* 2016).

Partial least squares (PLS) with cross validation were applied to build models for chemical property prediction. The adequate number of factors was evaluated based on lowest error of prediction and highest correlation coefficient, without eliminating samples in building the models. The main aim of PLS is analysis of numerous X-variables (spectra data) to predict response variables (chemical composition). The most important information is the number of principal components (PCs) selected, which will be included in regression models to result in a lower prediction error, that is, to present the lowest difference between references and estimated values (Kumar *et al.* 2014).

In spectral analysis, pretreatment of data is important to eliminate noise and remove physical phenomena in order to improve the subsequent analysis. Multiplicative scatter correction (MSC) pretreatment was applied to the data, and in this case, the mean of the calibration set was used as the reference for the test set. MSC is a scatter-corrective pretreatment technique applied to reduce the variability between samples due to scattering and also to adjust for baseline shifts (Fearn *et al.* 2009).

Samples were randomly divided into 96 for calibration (75% of spectra) and 32 for external prediction (25% of spectra). Spectral analysis was based on ASTM E1655-05-2012 (ASTM 2012). Although number of samples is few, the objective of the manuscript is to test the potential of technique to predict chemical changes. For NIR, literature report good results, but for reflectance spectra of visible light available data are related to physical properties.

#### **Chemical analysis**

Samples of natural and thermally modified wood were ground in a Wiley mill (De Leo, Porto Alegre, Brazil) and classified. The material between 40-60 mesh was analyzed. Chemical characterization was done in triplicate in accordance with TAPPI methods (TAPPI T204-om97-2004 for total extractives; TAPPI T222-om02-2004 for lignin content; TAPPI T211-om02-2004 for ash content. Holocellulose content was calculated by difference from total extractives, insoluble lignin and ash content.

#### **Statistical analysis**

Statistical analysis was applied to identify differences in chemical composition and color between natural and thermally modified wood. Comparisons of means were performed by the Tukey test at 5% significance level.

#### **RESULTS AND DISCUSSION**

#### **Chemical composition**

Thermal treatment resulted in an increase in extractives (44,61% and 27,56%) and lignin content (36,18% and 9,08%), but reduced holocellulose content (15,68% and 4,41%), respectively for

*Eucalyptus grandis* and *Pinus taeda* (Table 1). Heat treatment causes degradation of hemicelluloses (Brito *et al.* 2008), while solubilization of water extractives can contribute to increase these compound's content (Esteves *et al.* 2011, Tong and Zhang 2016). Lignin condensation reactions with other cell wall components results in crosslinking and contributes to an apparent increase in its content. On the other hand, extractives can be degraded or leave the wood and new compounds can be formed (Esteves and Pereira 2009, Tong and Zhang 2016).

Material	Extractives	Lignin	Holocellulose
	(%)	(%)	(%)
<i>Eucalyptus grandis</i> – natural	6,77 a	22,06 a	71,17 a
	(0,90)	(5,05)	(1,54)
Eucalyptus grandis – 160 °C	9,79 b	30,07 b	60,15 b
	(0,66)	(3,46)	(1,66)
<i>Pinus taeda</i> – natural	2,54 c	27,97 b	69,49 a
	(0,99)	(3,94)	(1,61)
Pinus taeda - 160 °C	3,24 d	30,50 b	66,26 c
	(1,08)	(2,68)	(1,29)

 Table 1: Mean (standard deviation) of wood chemical composition.

\*Equal letters in a column indicate no statistical difference by the Tukey test at 5% probability.

The increase in lignin content has also been observed in *Eucalyptus citriodora* (Silva 2012), *Eucalytpus saligna* and *Pinus caribaea* var. *hondurensis* (Brito *et al.* 2008), *Pinus taeda* (Silva 2012), *Pinus elliottii* (Severo *et al.* 2012) and *Pinus* spp. (Tong and Zhang 2016), while it remained equal for *Pinus caribaea* with treatment of 200 °C (Poubel *et al.* 2013). For extractives, reduction in *Eucalyptus saligna* (Brito *et al.* 2008), *Eucalyptus citriodora* (Silva 2012) and *Eucalyptus grandis* (Zanuncio *et al.* 2014b), and increase in *Pinus caribaea* var. *hondurensis* (Brito *et al.* 2008), *Pinus caribaea* (Poubel *et al.* 2012) and *Pinus spp.* (Tong and Zhang 2016) have been reported. 2013), *Pinus elliottii* (Severo *et al.* 2012) and *Pinus spp.* (Tong and Zhang 2016) have been reported. Esteves *et al.* (2008) studied extractives content in *Eucalyptus globulus* and observed an increase at the start of treatment. Reduction in holocellulose content has also been observed in *Eucalyptus grandis* (Zanuncio *et al.* 2014b), *Pinus caribaea* (Poubel *et al.* 2013), *Pinus elliottii* (Severo *et al.* 2016). Also differences between juvenile and mature wood were reported (Severo *et al.* 2012). Negative correlation between Klason lignin and luminosity was found for *Eucalyptus grandis* and *Pinus caribaea* var. *hondurensis* (Moura and Brito 2011).

# Colorimetry

The results of color measurements as well as multiple comparisons between means by the Tukey test are reported in Table 2.

	mounouron.				
Material	L*	a*	b*	C*	h
Eucalyptus grandis – natural	65,75a	13,03a	20,46a	24,27a	57,62a
<i>Eucalyptus grandis</i> – 160 °C	36,43b	8,64b	13,07b	15,68b	56,40b
Pinus taeda – natural	77,32c	6,71c	30,05c	30,81c	77,53c
<i>Pinus taeda</i> – 160 °C	52,64d	9,51d	23,71d	25,56a	68,18d

 Table 2: Colorimetric parameters of *Eucalyptus grandis* and *Pinus taeda* with and without thermal modification.

Lightness (L\*), green-red coordinate (a\*), blue-yellow coordinate (b\*), saturation (C\*) and hue angle (h). Equal letters in a column indicate no statistical difference by the Tukey test at 5% probability.

The results indicate a significant reduction in lightness (L\*) in both species after thermal treatment. In *Eucalyptus grandis*, the decrease was more pronounced (44,6%) than in *Pinus taeda* (31,9%), probably in function of chemical groups of extractives and its volatilization. The same behavior has been observed in other studies with *Eucalyptus grandis* (Moura and Brito 2011, Griebeler, 2013,

Cademartori *et al.* 2013), *Eucalyptus saligna* (Pincelli *et al.* 2012), *Eucalyptus globulus* (Esteves *et al.* 2008), *Pinus caribaea* (Pincelli *et al.* 2012), *Pinus caribaea* var. *hondurensis* (Moura and Brito 2011) and *Pinus pinaster* (Esteves *et al.* 2008).

According to Varga and Van Den Zee (2008), dissolution, oxidization and decomposition of extractives are the main reasons for color changes and modification of surface chemistry. Components that absorb visible light are formed during heat treatment. Examples are the formation of condensation products, low molecular-weight phenolic substances and oxidation products such as quinine like substances from lignin. Splitting of aliphatic side chains in lignin and condensation reactions (Chen *et al.* 2012a), percentage decline of hydroxyl groups and percentage increase of acid groups and esterified structure were found after heat treatment and caused darker color (Chen *et al.* 2012b, Yildiz *et al.* 2013).

For the chromatic coordinate a\*, positive values are related to high levels of red color. In eucalyptus wood, a reduction of this parameter was observed, but in pinus wood an increase was observed. Pincelli *et al.* (2012) observed the same behavior in *Eucalyptus saligna* and *Pinus caribaea* wood, at different temperatures (120-180 °C). This change depends on the species and final temperature. This is related to volatilization of some chemical compounds that give a red color (Moura and Brito 2011, Zanuncio *et al.* 2014b) and is strongly correlated with the concentration of phenolic extractives (Gierlinger *et al.* 2004, Zanuncio *et al.* 2014b). The presence of polar extractives is reported to influence color variations during thermal modification (Fan *et al.* 2010).

For the chromatic coordinate b\*, positive values are related to high levels of yellow color. In both species, a decrease in these values was observed. The behavior found for pinus wood is not in agreement with the findings of Pincelli *et al.* (2012), who observed a maximum gain in yellow color with heating to 160 °C. Griebeler (2013) did not observed variation in b\* in *Eucalyptus grandis* thermally modification at 160 °C.

Color saturation (C) was greater in pinus than eucalyptus. Treated pinus wood had similar saturation as natural eucalyptus wood. C is calculated as a function of chromatic coordinates a\* and b\*, and is dependent on the pattern of their variation. In both species, color saturation decreased after modification. An increase in this parameter was observed in *Pinus caribaea* (Pincelli *et al.* 2012) and in *Eucalyptus grandis* (Griebeler 2013) until 160 °C. Fan *et al.* (2010) found that decreases are mainly influenced by b\* values, while changes in a\* values have less effect on color saturation.

For hue angle (h\*), both species had the same behavior, a decrease in the parameter. Other studies have obtained the same results (Pincelli *et al.* 2012, Griebeler 2013). The reduction of tonality differences between species by heat treatment is reportedly a tool for homogenizing wood tonality and adding value to non-traditional species (Esteves *et al.* 2008).

The colorimetric parameters of the species studied, based on the classification table reported by Camargos and Gonçalez (2001), show the difference in wood color: natural eucalyptus was classified as rose and thermally modified as dark brown; natural pine was classified as light yellow and thermally modified as brown olive.

Color variation between natural and thermal treated wood (Table 3) shows reduction of luminosity (negative DL) for both species; reduction of parameters a\* and b\* for *Eucalyptus grandis*, and reduction of parameter b\* and increase of parameter a\* for *Pinus taeda*, resulting in an appreciable change in total color (DE). Values higher than 12 in (DE) are classified as very appreciable by Hikita *et al.* (2001).

 Table 3: Variation in colorimetric parameters in samples of *Eucalyptus grandis* and *Pinus taeda* after thermal modification, in relation to natural wood.

Treatment	ΔL*	Δa*	Δb*	ΔΕ
<i>E. grandis</i> x <i>E. grandis</i> 160 °C	-29,32	-4,39	-7,39	30,77
<i>P. taeda</i> x <i>P. taeda</i> 160 °C	-24,68	3,04	-14,08	28,93

Changes in wood color after heating are the result of several reactions (dehydration, hydrolysis, oxidation), principally involving extractives, and contribute to formation of double bonds, carbonyl functionalities and quinoid structures, but lignin and hemicellulose can also play important roles in formation of color substances during heat treatment (Chen *et al.* 2014). The extractives can form new color substances during heat treatment. The possible condensation of tannins and the oxidation of the hydroxyl groups in flavone molecules can be a reason for formation of new color substances (Fan *et al.* 2010).

Heat modification has a negative effect on light reflection (Figure 2). Low reflection rate of violet, blue and green light, between 400-520 nm, contribute to a dark brown color (Fan *et al.* 2010). The reflectance of thermally treated wood increased with, a maximum in the red region (620-740 nm). Esteves *et al.* (2008) observed that in pine wood, reflectance increased more in radial planes, and in eucalyptus wood in tangential sections, and that the relationship between chemical composition and lightness decrease for pine with a strong correlation ( $R^2 = 0.96$ ).



Figure 2: Reflectance curves of visible spectra of studied species.

The better photostability of thermally treated wood is partially explained by the increase of lignin stability by condensation and increase in phenol content during the heat treatment. Persze and Tolvaj (2012) presented results about photodegradation of wood and summarized the primary changes in the decomposition of lignin, with the liberation of free phenoxyl radicals. These radicals react with oxygen to produce carbonyl chromophoric groups, which are responsible for discoloration.

### Near Infrared spectroscopy

The mean spectral patterns of natural and thermally modified wood (Figure 3) show the same main lignocellulosic composition (Schwanninger *et al.* 2011, Tsuchikawa and Schwanninger 2013) and some baseline influence. According to Schwanninger *et al.* (2011), the region near 2334, 227, 1471-1473 nm is related to cellulose and hemicelluloses; wavelengths near 2134, 1440, 1447-1448 nm are related to lignin and extractives; bands at 1927 nm and region from 1435 to 1438 nm are attributed to water content. Changes in these regions after thermal treatment are attributed to changes on OH groups (Mitsui *et al.* 2008).



Figure 3: Mean NIR spectra of studied species.

Wavenumbers between 1500-1900 nm are related to first combinations of harmonics from CH,  $CH_2$ ,  $CH_3$ , and ArCH, forming the first harmonic region of  $RCO_2H$  and  $RCO_2-R$  and  $H_2O$  and the second harmonic of C=O (hemicelluloses). These regions, present in hemicellulose and amorphous cellulose, are more sensitive to temperature, resulting in changes after thermal treatment. Changes in the 1705-1724 nm region show degradation of carbohydrates and in acetylating reactions in hemicelluloses, while at 1674 nm, alterations are related to lignin (Michell and Schimleck 1996, Fackler and Schwanninger 2010).

The behavior of wood components due to thermal degradation are different in function of polymer composition and whether they are isolated or combined in the wood cell matrix (Popescu *et al.* 2011). Also evaluated species and final temperature and heating rate present influence in final spectra (Mehrotra *et al.* 2010).

#### **Spectral analysis**

Principal component analysis (PCA) of near-infrared (Figure 4a) and visible spectra (Figure 4b) shows a better distinction of species and treatment in the visible range. In NIR analysis, MSC pretreatment was applied and natural wood (*E. grandis* and *P. taeda*) were grouped and distinct from the treated wood. Also, the influence of surface color is evident in distinguishing samples after thermal treatment. In the visible range, all samples are distinct (natural and treated wood and both species). Bächle *et al.* (2012) also reported the possibility of distinguishing thermally treated beech, spruce and ash, and recommended the application of PCA in quality control.

In NIR spectra (Figure 5a), wavelength at 1316, 1406, 1921, 2120, 2175 and 2269 nm present more influence in discrimination of species and treatments. This bands are related to cell wall components, cellulose, hemicelluloses and lignin, also extractives present in species. Some influence of moisture content is visible in region near 1921 nm, showing that degradation process of wood components is influenced by species in the same heat conditions. In visible spectra (Figure 5b), almost all wavelengths present influence in samples distinction, because natural reflectance of species is based on color pigments of each one: i) region from 495-589 nm are related to green and yellow color and region from 670-700 nm is attributed to red color. *Eucalyptus* wood and samples treated are red to brown, and pinus wood is pale yellow.



Figure 4: Principal component analysis of (a) NIR spectra and (b) visible spectra (B).



Figure 5: X-loadings of NIR spectra (a) pretreated with MSC and (b)visible spectra

Prediction of chemical composition of samples was done based on spectra pretreated with MSC. Different species (*Eucalyptus* and *Pinus*) and treatment (natural and thermally treated) were evaluated from visible and near spectra by partial least square (PLS) analysis. Error of prediction and correlation coefficients of models based on natural and thermally treated wood (Table 4) showed the potential application of NIR and visible spectra to predict lignin, holocellulose and total extractives of *Eucalyptus grandis* and *Pinus taeda* wood, both natural and thermally modified at 160 °C.

	Calibration			External prediction		
	PC Numbe	er R <sup>2</sup>	RMSEC	R <sup>2</sup>	RMSEP	
NIR spectra	1					
Lignin	3	0,92	0,96	0,87	1,23	
Holocellulose	3	0,92	1,18	0,93	1,08	
Total Extractives	3	0,89	0,94	0,86	1,08	
Visible spectra						
Lignin	2	0,92	0,93	0,92	0,93	
Holocellulose	2	0,93	1,10	0,88	1,50	
Total Extractives	2	0,90	0,90	0,76	1,43	

 Table 4: PLS model for chemical composition prediction studied species.

Literature report prediction of chemical properties based on near infrared spectra (Karlinasari *et al.* 2014, Via *et al.* 2014) and the influence of sample preparation (Hein *et al.* 2009), but analyses of visible spectra are scarce (Prades *et al.* 2014).

These results indicate the possibility of applying VIS/NIR on production lines in industries making solid wood products and where the final quality depends on chemical composition of raw material. The possibility of using color measurements in industry to predict chemical properties can be an innovation for quality control in the furniture and flooring industry, because the components can influence external aspects by reacting with varnish and paints, for example. Our results shows the potential of color parameters, for its application in industry, other analysis with more samples, species and thermal treatments must be done.

### CONCLUSIONS

Thermal treatment changed chemical composition and color of wood treated at 160 °C in a saturated steam atmosphere with efficient elimination of oxygen. Extractives and lignin content increased and holocellulose content decreased in *Eucalyptus grandis* and *Pinus taeda*.

An appreciable change in total color between natural and thermal treated wood was observed, with reduction in luminosity for both species. A decrease in a\* and b\* chromatic coordinate was verified for *Eucalyptus grandis* and reduction of parameter b\* and increase of parameter a\* for *Pinus taeda*. Visible spectra were able to distinguish all samples and treatments.

NIR spectra showed changes in chemical composition of cell wall after thermal treatment and the influence of species on wood degradation process. Data were efficient in distinction of natural and treated wood.

NIR and visible spectra were used to predict chemical composition of *Eucalyptus grandis* and *Pinus taeda* in natural condition and after thermal treatment with R<sup>2</sup> from 0,76 to 0,92 showing its potential, and must be tested on line in industry.

### REFERENCES

Acquah, G.E.; Via. B.K.; Billor, N.; Fasina, O.O.; Eckhardt, L.G. 2016. Identifying plant part composition of forest logging residue using infrared spectral data and linear discriminant analysis. *Sensors* 16(9): 1375.

**ASTM. 2012**. Standard practices for infrared multivariate, quantitative analysis. ASTM. E1655-05. 2012.

**Bächle, H.; Zimmer, B.; Wegener, G. 2012.** Classification of thermally modified wood by FT-NIR spectroscopy and SIMCA. *Wood Science and Technology* 46 (6):1181–1192.

**Bächle, H.; Zimmer, B.; Windeisen. E.; Wegener, G. 2010.** Evaluation of thermally modified beech and spruce wood and their properties by FT-NIR spectroscopy. *Wood Science and Technology* 44 (3):421–433.

Bekhta, P.; Proszyk, S.; Lis, B.; Krystofiak, T. 2014. Gloss of thermally densified alder (*Alnus glutinosa* Goertn.), beech (*Fagus sylvatica* L.), birch (*Betula verrucosa* Ehrh.), and pine (*Pinus sylvestris* L.) wood veneers. *European Journal of Wood and Wood Products* 72 (6):799–808.

Brito, J.O.; Silva, F.G.; Leão, M.M.; Almeida, G. 2008. Chemical composition changes in eucalyptus and pinus woods submitted to heat treatment. *Bioresource Technology* 99 (18): 8545–8548.

Cademartori, P.H.G.; Schneid, E.; Gatto, D.A.; Stangerlin, D.M.; Beltrame, R. 2013. Thermal modification of *Eucalyptus grandis* wood: variation of colorimetric parameters. *Maderas-Cienc Tecnol* 15(1): 57-64.

**Camargos, J.A.A.; Gonçalez, J.C. 2001.** A colorimetria aplicada como instrumento na elaboração de uma tabela de cores de madeira. *Brasil Florestal* 71: 30-41.

**Chen, Y.; Fan, Y.; Gao, J.; Li, H. 2012a.** Coloring characteristics of in situ lignin during heat treatment. *Wood Science and Technology* 46(1): 33-40.

Chen, Y.; Fan, Y.; Gao, J.; Li, H. 2012b. The effect of heat treatment on the chemical and color change of black locus (*Robinia pseudoacacia*) wood flour. *BioResources* 7(1): 1157-1170.

Chen, Y.; Tshabalala, M.A.; Gao, J, Stark, N.M.; Fan, Y. 2014. Color and surface chemistry changes of extracted wood flour after heating at 120 °C. *Wood Science and Technology* 48 (1):137-150.

Conte, B.; Missio, A.L.; Pertuzzatti, A.; Cademartori, P.H.G.; Gatto, D.A. 2014. Physical and colorimetric properties of *Pinus elliottii* var. *elliottii* thermally treated wood. *Scientia Forestalis* 42(104): 555-563.

**De Paula, M.H.; Gonçalez, J.C.; De Mesquita, R.R.S.; Lima, C.M.; Rodrigues, T.O. 2016**. Heat treatment effect on the color of the heartwood and sapwood in a Sapucaia tree (*Lecythis pisonis* Cambess). *Australian Journal Basic and Applied Science* 10(13): 108-115.

**Esteves, B.; Pereira, H. 2008.** Quality assessment of heat-treated wood by NIR spectroscopy. *Holz als Roh- und Werkstoff* 66 (5):323–332.

**Esteves, B.; Videira, R.; Pereira, H. 2008**. Heat-induced colour changes of pine (*Pinus pinaster*) and eucalypt (*Eucalyptus globulus*) wood. *Wood Science and Technology* 42(5): 369-384.

**Esteves, B.; Videira, R.; Pereira, H. 2011**. Chemistry and ecotoxicity of heat-treated pine wood extractives. *Wood Science and Technology* 45 (4):661–676.

**Esteves, B.M.; Pereira, H.M. 2009.** Wood modification by heat treatment: a review. *BioResources* 4(1): 370-404.

**Fackler, K.; Schwanninger, M. 2010**. Polysaccharide degradation and lignin modification during brown rot of spruce wood: a polarised Fourier transform near infrared study. *Journal of Near Infrared Spectroscopy* 18(6):403–416.

Fan, Y.; Gao, J.; Chen, Y. 2010. Colour response of black locust (*Robinia pseudoacacia* L.) to solvent extraction and heat treatment. *Wood Science and Technology* 44 (4): 667-678.

Fearn, T.; Riccioli, C.; Garrido-Varo, A.; Guerrero-Ginel, J.E. 2009. On the geometry of SNV and MSC. *Chemometrics and Intelligent Laboratory Systems* 96(1): 22–26.

Freitas, A. S.; Gonçalez, J.C.; Del Menezzi, C.H. 2016. Thermomechanical treatment and the effects on the properties of *Simarouba amara (Aubl.). Floresta e Ambiente* 23(4): 565-572.

Garcia, R.A.; Oliveira, N.S.; Nascimento, A.M.; Souza, N.D. 2014. Colorimetry of woods from *Eucalyptus* and *Corymbia* genus and its correlation with density. *Cerne* 20(4): 509-517.

Gierlinger, N.; Jacques, D.; Grabner, M.; Wimmer, R.; Schwanninge, M.; Rozenberg, P.; Pâques L.E. 2004. Colour of larch heartwood and relationships to extractives and brown-rot decay resistance. *Trees* 18 (1):102-108.

**Gonzáles-Peña, M.M.; Curling, S.F.; Hale, M.D.C. 2009**. On the effect of heat on the chemical composition and dimensions of thermally-modified wood. *Polymer Degradation and Stability* 94(12): 2184–2193.

**Griebeler, C.G.O. 2013.** Colorimetria da madeira de *Eucalyptus grandis* W.Hill ex Maiden modificada termicamente. Master thesis of the Federal University of Parana.

Hein, P.R.G.; Lima, J.T.; Chaix, G. 2009. Effects of sample preparation on NIR spectroscopic estimation of chemical properties of *Eucalyptus urophylla* S.T. Blake wood. *Holzforschung* 64(1): 45–54.

**Hikita, Y.; Toyoda, T.; Azuma, M. 2001.** Weathering testing of timber – discoloration. In: Inamura Y. High performance utilization of wood for outdoor uses. Kyoto, Japão, Press-Net.

Huang, X.; Kocaefe, D.; Kocaefe, Y.; Pichette, A. 2018. Combined effect of acetylation and heat treatment on the physical, mechanical and biological behavior of jack pine (*Pinus banksiana*) wood. *European Journal of Wood and Wood Products* 76: 525–540.

Karlinasari, L.; Sabed, M.; Wistara, I.N.J.; Purwanto, Y.A. 2014. Near infrared (NIR) spectroscopy for estimating the chemical composition of (*Acacia mangium* Willd.) wood. *Journal of Indian Academic Wood Science* 11(2): 162-167.

Kumar, N.; Bansal, A.; Sarma, G.S.; Rawal, R.K. 2014. Chemometrics tools used in analytical chemistry: An overview. *Talanta* 123:186–199.

Kuzman, M.K.; Kutnar, A.; Ayrilmis, N.; Kariz, M. 2015. Effect of heat treatment on mechanical properties of selected wood joints. *European Journal of Wood Products* 73: 689–691.

Li, M. Y.; Cheng, S. C.; Li, D.; Wang, S.N.; Huang, A. M.; Sun, S.Q. 2015. Structural characterization of steam heat treated *Tectona grandis* wood analyzed by FT-IR and 2D-IR correlation spectroscopy. *Chinese Chemical Letters* 26(2) 221-225.

Mehrotra, R.; Singh, P.; Kandpal, H. 2010. Near infrared spectroscopic investigation of the thermal degradation of Wood. *Thermochimica Acta* 507–508: 60–65.

Méndez-Mejías, L.D.; Moya, R. 2016. Effects on density, shrinking, color changing and chemical surface analysis through FTIR of *Tectona grandis* thermo-treated. *Scientia Forestalis* 44(122): 811-820.

Michell, A.J.; Schimleck, L.R. 1996. NIR spectroscopy of woods from *Eucalyptus globulus*. *Appita Journal* 49:23–26.

**Militz, H.; Altgen, M. 2016.** Processes and properties of thermally modified wood manufactured in Europe. In: Deterioration and protection of sustainable biomaterials. *ACS Symposium Series* 1158(16): 269–285.

**Mitsui, K. 2004.** Changes in the properties of light-irradiation wood with heat-treatment. Part 2. Effect of light-irradiation time and wavelength. *Holz als Roh-und Werkstoff* 62(1): 23-30.

Mitsui, K.; Inagaki, T.; Tsuchikawa, S. 2008. Monitoring of hydroxyl groups in wood during heat treatment using NIR spectroscopy. *Biomacromolecules* 9(1): 286–288.

Moura, L.F.; Brito, J.O. 2011. Effect of thermal rectification on colorimetric properties of *Eucalyptus grandis* and *Pinus caribaea* var *hondurensis* woods. *Scientia Forestalis* 39(89):69-76.

**Olarescu, M.C.; Campean, M.; Ispas, M.; Cosereanu, C. 2014.** Effect of thermal treatment on some properties of lime wood. *European Journal of Wood Products* 72(4): 559–562.

**Persze, L.; Tolvaj, L. 2012.** Photodegradation of wood at elevated temperature: colour change. *Journal of Photochemistry and Photobiology B: Biology* 108: 44-47.

**Pertuzzatti, A. 2016**. Physical properties of *Pinus elliottii* var. elliottii thermally treated wood under two different atmospheres. *Ciência da Madeira* 7(15): 7-15, 2016.

Pincelli, A.L.P.S.M.; Moura, L.F.; Brito, J.O. 2012. Effect of thermal retification on colors of *Eucalyptus saligna* and *Pinus caribaea* woods. *Maderas-Cienc Tecnol* 14(2): 239-248.

Poletto, M.; Zattera, A.J.; Santana, R.M.C. 2012. Thermal decomposition of wood: Kinetics and degradation mechanisms. *Bioresource Technology* 126: 7–12.

**Popescu, M.C.; Popescu, C.M.; Lisa, G.; Sakata, Y. 2011**. Evaluation of morphological and chemical aspects of different wood species by spectroscopy and thermal methods. *Journal of Molecular Structure* 988: 65-72.

**Poubel, D.S.; Garcia, R.A.; Santos, W.A.; Oliveira, G.L.; Abreu, H.S. 2013.** Efeito da termorretificação nas propriedades físicas e químicas da madeira de *Pinus caribaea. Cerne* 19 (3): 391-98.

Prades, C.; Gomes-Sanchez, I.; Garcia-Olmo, G.; Gonzales-Hernadez, F.; Gonzales-Adrados J.R. 2014. Application of VIS/NIR spectroscopy for estimating chemical, physical and mechanical properties of cork stoppers. *Wood Science and Technology* 48 (4):811–830.

Schwanninger, M.; Hinterstoisser, B.; Gierlinger, N.; Wimmer, R.; Hanger, J. 2004. Application of fourier transform near infrared spectroscopy (FT-NIR) to thermally modified wood. *Holz als Rohund Werkstoff* 62 (6):483–485.

Schwanninger, M.; Rodrigues, J.C. Fackler, K. 2011. A review of band assignments in near infrared spectra of wood and wood components. *Journal of Near Infrared Spectroscopy* 19: 287-308.

Severo, E.T.; Calonego, F.W.; Sansígolo, C.A. 2012. Physical and chemical changes in juvenile and mature woods of *Pinus elliottii var. elliottii* by thermal modification. *European Journal of Wood and Wood Products* 70(5): 741–747.

Silva, M.R. 2012. Efeito do tratamento térmico nas propriedades químicas, físicas e mecânicas em elementos estruturais de *Eucalyptus citriodora* e *Pinus taeda*. PhD Thesis of the University of São Paulo.

Stangerlin, D.M.; Costa, A.F.; Gonçalez, J.C.; Pastore, T.C.M.; Garlet, A. 2013. Monitoring of biodeterioration of three Amazonian wood species by the colorimetry technique. *Acta Amazonica* 43: 429–438.

**TAPPI. 2004.** Solvent extractives of wood and pulp. T204 – om 97. 2004. In: Tappi Test Methods. TAPPI Press: Norcross, GA.

**TAPPI. 2004.** Ash in wood, pulp, paper and paperboard: combustion at 525°C. T211 – om 02. 2004. In: Tappi Test Methods. TAPPI Press: Norcross, GA

**TAPPI. 2004.** Acid-insoluble lignin in wood and pulp. T222 – om 02. 2004. In: Tappi Test Methods. TAPPI Press: Norcross, GA.

Tong, I.; Zhang, W. 2016. Using Fourier transform near-infrared spectroscopy to predict the mechanical properties of thermally modified southern pine wood. *Applied Spectroscopy* 70(10): 1–9.

**Torres, S.S.; Jomaa, W.; Marc, F. Puiggali, J.R. 2012.** Colour alteration and chemistry changes in oak wood (*Quercus pedunculata* Ehrh.) during plain vacuum drying. *Wood Science Technology* 46: 177–191.

Tsuchikawa, S.; Schwanninger, M. 2013. A review of recent near-infrared research for wood and paper (Part 2). *Applied Spectroscopy Review* 48:560-587.

**Varga, D.; Van Der Zee, M.E. 2008.** Influence of steaming on selected wood properties of four hardwood species. *Holz als Roh-und Werkstoff* 66(1): 11-18.

Via, B.K.; Zhou, C.; Acquah, G.; Jiang, W.; Eckhardt, L. 2014. Near infrared spectroscopy calibration for wood chemistry: which chemometric technique is best for prediction and interpretation? *Sensors* 14: 13532-13547.

Yildiz, S.; Tomak, E. D.; Yildiz, U. C.; Ustaomer, D. 2013. Effect of artificial weathering on the properties of heat treated wood. *Polymer Degradation and Stability* 98(8): 1419-1427.

Zanuncio, A.J.V.; Motta, J.P.; Da Silveira, T.A.; Farias, E.S.; Trugilho, P.F. 2014a. Pysical and colorimetric changes in *Eucalyptus grandis* wood after heat treatment. *Bioresources* 9(1): 293-302.

Zanuncio, A.J.V.; Nobre, J.R.C.; Motta, J.P.; Trugilho, P.F. 2014b. Química e colorimetria da madeira de *Eucalyptus grandis* w. Mill ex Maiden termorretificada. *Revista Árvore*38(4): 765-770.

Zanuncio, A.J.V.; Nobre, J.R.C.; Motta, J.P.; Trugilho, P.F. 2014c. Heat treatment and color of *Eucalyptus grandis* wood. *Floresta e Ambiente* 21(1): 85-90.