CHEMICAL CHARACTERIZATION OF *Handroanthus vellosoi* WOOD[1]

CARACTERIZAÇÃO QUÍMICA DA MADEIRA DE *Handroanthus vellosoi*

Ivanka Rosada de OLIVEIRA[2]; Vagner Roberto BOTARO[3]; Mônica Aparecida de ALMEIDA[4];
Eduardo Luiz LONGUI[5, 6]; Israel Luiz de LIMA[5];
Sandra Monteiro Borges FLORSHEIM[5]; Antonio Carlos Scatena ZANATTO[5]

ABSTRACT – The main chemical components of wood are cellulose, hemicellulose, lignin and extractives. Knowledge of these components content enables to understand how the wood will behave as a raw material in its many uses. The aim of this research was to determine in wood of *Handroanthus vellosoi* (Toledo) Mattos, Bignoniaceae contents of extractives in ethanol/cyclohexane, extractives in water, Klason lignin, holocellulose and ash. Six trees were cut from the "Estação Experimental de Luiz Antônio" after 24 years of growth. From stem of each tree were removed three disks: trunk base, one and two meters in height and was taken a sample near to the bark. We used standard procedures for chemical analysis of wood. We did not observe statistically significant differences in the levels of chemical constituents studied with respect to the axial position, which may be related to low sampling. Only by observing the values obtained from extractive ethanol/cyclohexane, extractives in water, Klason lignin, holocellulose and ash notices that they are close, though they are slightly different from those cited in other studies of *Handroanthus* species. This result may be related to a variation between species within the genus or even between different parts of an individual trunk.

Keywords: axial position; chemical constituents; ipê amarelo; *Handroanthus*; tropical woods.

RESUMO – Os principais constituintes químicos da madeira são: celulose, hemicelulose, lignina e extrativos. O conhecimento dos teores desses constituintes permite compreender como será o comportamento da madeira como matéria-prima nos mais diversos usos. Objetivou-se determinar, na madeira de *Handroanthus vellosoi* (Toledo) Mattos, Bignoniaceae, os teores de extrativos em etanol/cicloexano, extrativos em água, lignina de Klason, holocelulose e cinzas. Para tanto, seis árvores foram cortadas na Estação Experimental de Luiz Antônio após 24 anos de crescimento. Do tronco de cada árvore foram retirados três discos: base do tronco, um e dois metros de altura, sendo retirada uma amostra próxima da casca para as análises químicas. Utilizaram-se os procedimentos padrão para as análises químicas da madeira. Não foram observadas diferenças estatisticamente significativas nos teores dos constituintes químicos estudados em relação à posição axial, o que pode estar relacionado com a baixa amostragem. Apenas observando os valores obtidos a partir dos extrativos em etanol/cicloexano, extrativos em água, lignina de Klason, holocelulose e cinzas, notou-se que eles estão próximos, embora sejam um pouco diferentes daqueles citados em outros estudos para espécies de *Handroanthus*. Este resultado pode estar relacionado à variação entre espécies dentro do gênero, ou mesmo entre diferentes partes do tronco.

Palavras-chave: posição axial; constituintes químicos; ipê amarelo; *Handroanthus*; madeiras tropicais.

[1]Recebido para análise em 10.04.12. Aceito para publicação em 22.11.12.
[2]Acadêmica do curso de Engenharia Florestal, Universidade Federal de São Carlos *campus* Sorocaba.
[3]Laboratório do Departamento de Biologia, Universidade Federal de São Carlos *campus* Sorocaba.
[4]Departamento de Ciências Ambientais, Universidade Federal de São Carlos *campus* Sorocaba.
[5]Instituto Florestal, Rua do Horto, 931, 02377-000 São Paulo, SP, Brasil.
[6]Autor para correspondência: Eduardo Luiz Longui – edulongui@gmail.com

1 INTRODUCTION

Knowledge of the chemical nature of wood allows the understanding of its behavior as a raw material in several applications (Lepage et al., 1986; Mori et al., 2003; Morais et al., 2005; Silva et al., 2005). The main chemical components of wood are cellulose, hemicellulose and lignin, which are polymers form cell walls. The extractives are also of major importance in wood properties (Lepage et al., 1986).

Cellulose is a structural component of all cell walls; about 15-30% of the dry weight of all primary cell walls and an even higher percentage of the secondary cell walls is composed of cellulose (Carpita and McCann, 2000). Hemicellulose is a non-cellulosic polysaccharide and it relates to the cellulose in the cell wall. Hemicellulose is comprised of polyoses are glucosides, mannose, galactose, xylose and arabinose, and these different components can lead to high levels of variation both within and between tree species. In general, harder woods have higher levels of hemicellulose than softer woods (Fengel and Wegener, 1989 apud Perissotto, 2005).

Another component of cell walls, lignin is the main component of some secondary walls, and is formed by a system of aromatic phenylpropanoids. Lignin is incorporated into the cell wall during development and is distributed between the microfibrils, making the wall more rigid and resistant to degradation (Jordão and Andrade, 2000; Carpita and McCann, 2000).

Extractives are substances formed from modified carbohydrates produced in photosynthesis, and may account for more than 20% of the dry weight in tropical timber. They consist of a number of organic compounds such as waxes, alkaloids, phenolic compounds, mucilage, gums, resins, terpenes, saponins and essential oils. The extractives act as reserve material or as part of the defense mechanism of plants against attacks from microorganisms and contribute to the color and odor of the woods (Panshin and Zeeuw, 1964; Pettersen, 1984).

Knowing the different levels of chemical components of wood contribute to the choice of wood for certain uses (Barnett and Jeronimids, 2003). Despite the wide use of *Eucalyptus* in the production of pulp and paper, various native woods awaken interest on its chemical composition, based on indigenous knowledge and recipes. As an example, we quote *Handroanthus* species, Bignoniaceae, because although the wood has no commercial value for the production of pulp and paper (Carvalho, 2003), its extracted compounds, have anticancer, anti-inflammatory, analgesic, antibiotic, antimalarial, antitripanossomal and antiulcerogenic properties, making it of great interest for pharmacological studies (Araújo et al., 2002).

In this study, our objective was to determine contents of extractives in ethanol/cyclohexane, water extractives, Klason lignin, holocellulose and ash of the wood chemical components of *Handroanthus vellosoi* (Toledo) Mattos, Bignoniaceae, a deciduous species, occurring naturally in the Atlantic Rain Forest and Semideciduous Forest (Lorenzi, 2002). Its wood has been used in construction, mainly in the form of parquet floors, as sleepers, posts, beams and provides raw material for carpentry (Carvalho, 2003).

2 MATERIALS AND METHODS

2.1 Collection of Samples

The wood samples were obtained from trees planted in 1986 at the Estação Experimental de Luiz Antonio – EELA, located at coordinates 21º40'S, 47º49'W, altitude 550 m, with a tropical climate (Cwa), a dry winter and an average annual rainfall of 1280 mm (Freitas, 2008). In October 2010, six trees were cut and counted after 24 years of growth. When cutting the trees, from each stem were removed three disks in the axial direction: base, 1 and 2 meters in height, and each of the disks was removed a sample close to the bark to study the more recently formed wood, and by the age of the trees possibly representative of adult wood. We obtained a total of 18 samples.

2.2 Chemical Analysis

2.2.1 Ash content

The ash content was performed according to TAPPI standard T 211 om-93. Samples were added approximately 1.0 g in tared mass crucible and calcined beforehand at 525 ºC for 1 h. The samples were carbonized advance with a Bunsen burner flame until no. The crucibles were taken to muffle isotherm under 600 ± 5 ºC for a period of 3 h. Then the cooling was done in a desiccator with silica gel for subsequent weighing of the samples in semi analytical balance. The ash content of the samples was determined by the ratio between the final and initial mass according to Equation 1:

$$\text{Ash}\% = \frac{m1}{m2} x100 \quad (1)$$

Where,
m1 = mass (g) ash, and
m2 = mass (g) of the sample of the dry fibers (g).

2.2.2 Content of Water Soluble Extractives

The extractive content was performed according to standard TAPPI T 207 om-98. Samples of approximately 3.0 g were added to a beaker containing 500 ml distilled water and subjected to mechanical agitation by means of heater plate-shaker at 70 ± 5 ºC for 1h. After this extraction period, the sample was filtered simple funnel with filter paper and subsequently taken to an oven at 105 ± 5 ºC for a period of 4 h. Then the samples were subjected to cooling in a desiccator with silica gel and weighed on an analytical balance. The masses being subsequently calculated according to Equation 2:

$$\text{Ext H20 } \% = \frac{m1 - m2}{m2} x100 \quad (2)$$

Where,
m1 = mass (g) of the initial dry sample before extraction; and
m2 = mass (g) of the sample after extraction of the dry fibers.

2.2.3 Content of extractives soluble in ethanol/cyclohexane

The content of extractives soluble in ethanol/cyclohexane was determined by standard TAPPI T 204 om-93. About 1.0 g of sample were inserted into cartridge pulp within the Soxhlet process to Soxhlet extraction system. The extraction period was 8 h. Samples were dried at 105 ± 5 ºC for 3 hours. They were then taken to the desiccator with silica gel for cooling. The percentage of extractives was calculated according to Equation 3, after weighing on an analytical balance.

$$\text{Ext } \% = \frac{m1 - m2}{m2} x100 \quad (3)$$

Where,
m1 = mass (g) of the initial dry sample before extraction, and
m2 = mass (g) of the sample after extraction of the dry fibers.

2.2.4 Content of Insoluble Klason Lignin

For insoluble Klason lignin followed standard TAPPI T 222 om-98 About 1.0 g of the dried sample was placed in a mortar with 15 mL of sulfuric acid PA (72%), with the same carefully macerated to promote maximum fiber separation and allowed to rest for a period of one week in an acid medium. The mixture was transferred to a 1 L flask and the volume adjusted to 560 mL with distilled water, and heated under reflux for 4 h. The insoluble lignin was filtered on a sintered glass funnel nº 4. The filtrate was collected for the determination of soluble lignin. The insoluble lignin, retained in a sintered glass funnel, dried in an oven at 105 ± 5 ºC for a period of 4 hours, and then cooled in a desiccator with silica gel and weighed on a semi-analytical balance. The insoluble Klason lignin content was determined according to Equation 4:

$$\text{Lignina Klason } \% = \frac{m1}{m2} x100 \quad (4)$$

Where,
m1 = mass (g) of dry insoluble Klason lignin (sample mass - mass of ashes after calcination at 600 ºC), and
m2 = mass (g) of dry sample.

2.2.5 Holocellulose content

The holocellulose content was calculated by mass difference, once known the amounts of lignin and extractives. According to Equation 5:

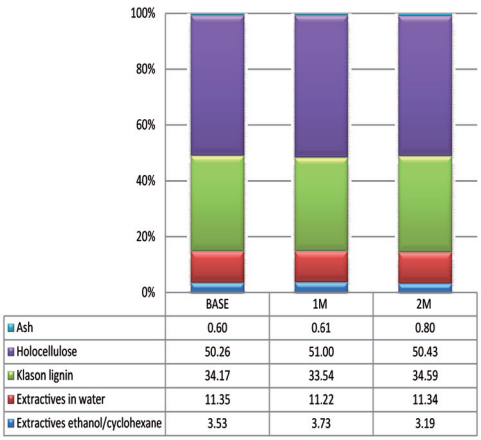
Holocelulose % = [(100% - extractives content soluble in organic solvent) – (content lignin + content ash)] (5)

All analyzes were performed in triplicate.

We carried out analysis of variance (ANOVA) to compare the different positions on the stem.

3 RESULTS AND DISCUSSION

The percentage of extractives ethanol/cyclohexane, extractives in water, Klason lignin, holocellulose and ash are shown in Figure 1. No significant variation was observed in chemical composition between the three heights analyzed. When compared with other studies with *Handroanthus* species or other tropical woods we observed variation in the wood chemical components.



	BASE	1M	2M
Ash	0.60	0.61	0.80
Holocellulose	50.26	51.00	50.43
Klason lignin	34.17	33.54	34.59
Extractives in water	11.35	11.22	11.34
Extractives ethanol/cyclohexane	3.53	3.73	3.19

Figure 1. Average percentage of extractive ethanol/cyclohexane, extractives in water, Klason lignin, holocellulose and ash at three axial stem positions in the six trees of *Handroanthus vellosoi* wood. There were no significant differences between the positions according to the One Way Analysis of Variance ($P < 0.05$).

Figura 1. Porcentagem média de extrativos em etanol/cicloexano, extrativos em água, lignina de Klason, holocelulose e cinzas em três posições axiais na madeira de seis árvores de *Handroanthus vellosoi*. Não foram encontradas diferenças significativas entre as posições de acordo com o teste One Way Analysis of Variance ($P < 0,05$).

Longui et al. (2010a), when studying *Handroanthus* sp., observed a higher percentage in water-soluble extractives content, 14.6% and soluble in ethanol/benzene, 16.6% compared to the average values among the three positions of this study, 11.3% and 3.5 with ethanol/cyclohexane, respectively. However, in another study, Longui et al. (2012) reported that the amount of total extractives was relatively small, 10.4% compared to the 14.8% observed in the present study. Neto et al. (2012) found a lower value for the extractives (water + ethanol/cyclohexane) of *Handroanthus impetiginosus* (6.88%) when compared with those found in this study to *Handroanthus vellosoi* (14.8%).

It is noteworthy that the woods investigated by Longui et al. (2010a) and Longui et al. (2012) were older than those examined in this study, indicating that the variation in the extractive content is not strongly influenced, at least in part by the age of the tree. Also, the samples studied here were removed from the region near the bark, which is lighter than the center of the stem (heartwood) and therefore presumably has lower extract content. It is speculated that the extract content is related to the rate of photosynthesis and the percentage of carbohydrates produced by it and that change originate.

In species from other genera, Leão (2006) has studied tropical species *Myroxylon balsamum* and *Amburana cearensis*, the author found that the extractives content were higher in *A. cearensis* trees, 24.04 % than *Handroanthus vellosoi*, 14.8%, and lowest in the wood of *Myroxylon balsamum* 8.41%. In another study, Lima et al. (2007) in *Gochnatia polymorpha* found similar extractive ethanol/cyclohexane content, 3.82% and lower extractive in hot water, 4.04%, when compared to *H. vellosoi*, 3.5% and 11.3%, respectively.

Extractives can also be considered a parameter of quality wood, because they give color, smell and natural resistance to decay (Pereira et al., 2003). Many species of *Handroanthus* wood are known for their naturally high durability (Carvalho, 2003) and extractives actively participate in this property.

Regarding lignin in others species, Queiroz (2001) in *Astronium graveolens* showed lignin content of 28.16%, Leão (2006) reports lignin content of 24.33% in *A. cearensis* and 24.39% in *M. balsamum*, Lima et al. (2007) in *Gochnatia polymorpha* observed lignin content of 24%; for *Handroanthus* species, Neto et al. (2012) reported 28.4% in *H. impetiginosus*, indicating lower values compared to the present study for *H. vellosoi*, 34.1%, but similar results were reported by Longui et al. (2012) in *Handroanthus* spp., 32.6%.

The lignin is responsible for cell wall stiffening and consequently the wood as a whole (Lepage et al., 1986; Pereira et al., 2003). The lignin also may vary along the stem due to the development of reaction wood. Tomazello Filho et al. (1985) observed that the compression wood in *Pinus oocarpa* differs chemically from normal wood due to the higher lignin and extractives and lower holocellulose contents. According to Mattheck and Kluber (1995), the walls of tracheids in *Pinus* species, are richer in lignin than normal wood of those cells because of the higher risk of buckling. Furthermore, as a hydrophobic component of cell walls, the lignin has the ability to limit access of water to the portion of carbohydrates (cellulose), thereby decreasing the influence of water in the hydrogen bonded structure of the wood (Winandy and Rowell, 2005). Possibly, the high lignin present in wood may explain the low *Handroanthus* shrinkage, is cited as an example Mainieri and Chimelo (1989) for *Handroanthus serratifolius* wood with 6.60% and 8% of radial and tangential shrinkage, respectively.

Holocellulose contents also vary from *Handroanthus* species, Neto et al. (2012) reported 63.85% in *H. impetiginosus*, while Longui et al. (2012) mentioned 56% in *Handroanthus* spp., closest to the value of this study 50.5%. As for other species, holocellulose may be even higher than those observed for *Handroanthus vellosoi,* e.g., Queiroz (2001) in *Astronium graveolens* 65.6% and Lima et al. (2007) in *Gochnatia polymorpha* 73.2%.

The holocellulose and cellulose contents are also related to the properties of wood, Takaaki et al. (2007) and Salmén and Bergström (2009) founded a positive correlation between the wood resistance and cellulose levels. *Handroanthus* species, in general, have high values of mechanical properties and possibly the lignin and holocellulose are related to the wood properties, which in addition to color, provide in agree (Brunelli et al., 1997), raw material suitable for furniture, floors and other uses.

In this study, we did not observe changes in the levels of chemical components at different heights near to the bark, which could indicate an adaptation related to the resistance of the trunk at the base and one and two meters high. This result is interesting because the *Handroanthus* wood is also quite homogeneous, with small variations in their properties along the stem (Longui et al., 2010a; Longui et al., 2010b).

The amount of ash obtained is in the range reported for other tropical species, and may contain up to 5%. In wood, represents the inorganic matter, which consists of minerals. Their content may vary with the species, availability in the soil, individual characteristics and time of year (Cardoso et al., 2001). Neto et al. (2012) found 0.87% for ash content in *Handroanthus impetiginosus*, slightly above the average found in our study of 0.67%, but very close to our value to two meters 0.8%, showing that this difference occurs depending on the samples position in the stem.

4 CONCLUSIONS

No statistically significant differences were observed in the levels of chemical constituents studied with respect to the axial position, which may be related to low sampling. Only by observing the values obtained from extractive ethanol/cyclohexane, extractives in water, Klason lignin, holocellulose and ash notices that they are close, though they are slightly different from those cited in other studies of *Handroanthus* species. This result may be related to a variation between species within the genus or even between different parts of an individual stem.

5 REFERENCES

ARAÚJO, E.L. et al. Lapachol: segurança e eficácia na terapêutica. **Revista Brasileira de Farmacognosia**, v. 12, supl., p. 57-59, 2002.

BRUNELLI, A.A.; LEAL, J.J.; LONGO, F.G. (Coord.). **Madeiras:** material para o design. São Paulo: SCTDE, 1997. 73 p.

CARDOSO, G.V. et al. Sampling procedure development for ash content determination using the woods of *Eucalyptus saligna* and *Eucalyptus globulus*. In: CONGRESSO ANUAL DE CELULOSE E PAPEL, 34., 2001, Santa Maria. **Anais…** Santa Maria: Universidade Federal de Santa Maria, 2001. p. 1-7.

CARPITA, N.; McCANN, M. The cell wall. In: BUCHANAN, B.B.; GRUISSEM, W.; JONES, R.L. (Ed.). **Biochemistry & molecular biology of plants**. Rockville: American Society of Plant Physiologists, 2000. p. 52-109.

CARVALHO, P.E.R. **Espécies arbóreas brasileiras**. Brasília, DF: Embrapa Informação Tecnológica, 2003. v. 1, 547 p.

FREITAS, M.L.M. Variação genética para caracteres quantitativos em população de *Gallesia integrifolia* (Spreng.) Harms, São Paulo. **Rev. Inst. Flor.**, v. 20, n. 2, p. 165-173, 2008.

JORDÃO, B.Q.; ANDRADE, C.G.T.J. Célula vegetal. In: JUNQUEIRA, L.C.; CARNEIRO, J. **Biologia celular e molecular**. 7. ed. Rio de Janeiro: Guanabara Koogan, 2000. 399 p.

LEÃO, M.M. **Influência do termotratamento na composição química da madeira de amburana (*Amburana cearensis*), bálsamo (*Myroxylon balsamum*) e carvalho (*Quercus* sp.) e o impacto de uma solução modelo de cachaça**. 2006. 85 f. Dissertação (Mestrado em Recursos Florestais) – Escola Superior de Agricultura "Luiz de Queiroz", Universidade de São Paulo, Piracicaba.

LEPAGE, E.S. et al. **Manual de preservação de madeiras**. São Paulo: Instituto de Pesquisas Tecnológicas do Estado de São Paulo, Divisão de Madeiras, 1986. v. 1.

LIMA, S.R. et al. Estudo dos constituintes macromoleculares, extrativos voláteis e compostos fenólicos da madeira de candeia – *Moquinia polymorpha* (Less.). **Ciência Florestal**, v. 17, n. 2, p. 145-155, 2007.

LONGUI, E.L. et al. The potential of ipê (*Handroanthus* spp.) and maçaranduba (*Manilkara* spp.) woods in the manufacture of bows for string instruments. **IAWA Journal**, v. 31, n. 2, p. 149-160, 2010a.

_____.; LOMBARDI, D.R.; ALVES, E.S. Potential Brazilian wood species for bows of string instruments. **Holzforschung**, v. 64, p. 511-520, 2010b.

_____. et al. Relationship among extractives, lignin and holocellulose contents with performance index of seven wood species used for bows of stringed instruments. **IAWA Journal**, v. 33, p. 141-149, 2012.

LORENZI, H. **Árvores brasileiras:** manual de identificação e cultivo de plantas arbóreas do Brasil. 4. ed. Nova Odessa: Instituto Plantarum, 2002. v. 1, 394 p.

MAINIERI, C.; CHIMELO, J.P. **Fichas de características das madeiras brasileiras**. 2. ed. São Paulo: Instituto de Pesquisas Tecnológicas do Estado de São Paulo, 1989. 418 p. (Publicação IPT 1791).

MATTHECK, C.; KLUBER, H. **Wood** – the internal optimization of trees. Berlin: Springer Verlag, 1995. 129 p.

MORAIS, S.A.L.; NASCIMENTO, E.A.; MELO, D.C. Análise da madeira do *Pinus oocarpa* parte II – caracterização estrutural da lignina de madeira moída. **Revista Árvore**, v. 29, p. 471-478, 2005.

MORI, C.L.S.O. et al. Caracterização da madeira de angico-vermelho (*Anadenanthera peregrina* (Benth) Speng) para confecção de móveis. **Brasil Florestal**, v. 23, p. 21-27, 2003.

NETO, P.N.M. et al. Características físico-químicas e energéticas de duas espécies de ocorrência no Semiárido Brasileiro. **Ciência Florestal**, v. 22, p. 579-588, 2012.

PANSHIN, A.J.; ZEEUW, C. de. **Textbook of wood technology:** structure, identification, properties and uses of the commercial woods of the United States and Canada. 3rd ed. New York: McGraw-Hill, 1964. 643 p.

PEREIRA, H.; GRAÇA, J.; RODRIGUES, J.C. Wood chemistry in relation to quality. In: BARNETT, J.R.; JERONIMIDIS, G. (Ed). **Wood quality and its biological basis**. Oxford: CRC Press, 2003. cap. 3, p. 53-86.

PERISSOTTO, D.O. **Estudo comparativo das propriedades químicas de polpas Kraft convencionais e MCC de eucalipto**. 2005. 113 f. Tese (Doutorado em Química Orgânica) – Universidade Federal do Paraná, Curitiba.

PETTERSEN, R.C. The chemical composition of wood. In: ROWELL, R.M. (Ed.). **The chemistry of solid wood**. Washington, D.C.: American Chemical Society, 1984. p. 57-123. (Advances in Chemistry Series 207).

QUEIROZ, C.R.A.A. **Análise da lignina e dos polifenóis da aroeira preta (*Astronium urundeuva*)**. 2001. 142 f. Dissertação (Mestrado em Química) – Universidade Federal de Uberlândia, Uberlândia.

SILVA, J.C. et al. Influência da idade e da posição ao longo do tronco na composição química da madeira de *Eucalyptus grandis* Hill ex Maiden. **Revista Árvore**, v. 29, p. 455-460, 2005.

SALMÉN, L.; BERGSTRÖM, E. Cellulose structural arrangement in relation to spectral changes in tensile loading FTIR. **Cellulose**, 2009. Disponível em: <http://www.springerlink.com/content/f8815564w6588543>. Acesso em: 13 jun. 2009.

TAKAAKI, F.; HIROYUKI, Y.; SATORU, T. Estimation of wood stiffness and strength properties of hybrid larch by near-infrared spectroscopy. **Applied Spectroscopy**, v. 61, p. 150-170, 2007.

TECHNICAL ASSOCIATION OF PULP AND PAPER INDUSTRY – TAPPI. **TAPPI test methods, standard methods for pulp and paper**. Atlanta: TAPPI Press, 1992.

TOMAZELLO FILHO, M.; BARRICHELO, L.E.C.; COSTA, J.C. Análise da madeira de compressão em *Pinus oocarpa* e *Pinus strobus* var. *chiapensis*. **IPEF**, v. 31, p. 69-73, 1985.

WINANDY, J.E.; ROWELL R. Chemistry of wood strength. In: ROWELL, R. (Ed.). **Handbook of wood chemistry and wood composites**. Boca Raton: Taylor & Francis, 2005. p. 303-347.