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EFFECT OF THE BRAZILIAN THERMAL MODIFICATION PROCESS ON THE CHEMICAL COMPOSITION OF *Eucalyptus grandis* JUVENILE WOOD – PART 2: SOLUBILITY AND ASH CONTENTS

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ABSTRACT

This article reports continuation of a study of the influence of the Brazilian process of thermal modification called VAP HolzSysteme® on the chemical composition of eucalyptus wood. Flatsawn boards of *Eucalyptus grandis* juvenile wood were tested for four treatment levels: untreated, and thermally modified at final cycle temperatures of 140 °C, 160 °C or 180 °C. Chemical analyses were carried out according to the standards of the Technical Association of the Pulp and Paper Industry and encompassed 1% NaOH solubility and ash content. The 1% NaOH solubility increased in the wood thermally modified at 140 °C and 160 °C in relation to the untreated wood, but did not increase further 180 °C, indicating that the treatment at 180 °C was not enough to cause more degradation of hemicelluloses. In practice, the thermal modification process had no effect on the ash content of wood. The statistical difference observed between the treatment levels untreated and 160°C (0,04 percentage points) can be attributed to the heterogeneity of wood as a material.

Keywords: VAP HolzSysteme®, 1% NaOH solubility, ash content.

INTRODUCTION

This article reports continuation of study of the influence of the Brazilian process of thermal modification called VAP HolzSysteme® on the chemical composition of *Eucalyptus grandis* juvenile wood, and encompasses 1% NaOH solubility and ash content analyses. These analyses are not commonly carried out for thermally modified wood, as subsequently discussed, but are a complement to the first article which reported the contents of holocellulose, insoluble lignin and total extractives, along with water (hot and cold) and ethanol:toluene (1:2 v.v.) solubilities.

One of the best enhancements that thermal modification processes impart to wood is to increase decay resistance (Esteves and Pereira 2009, Hill 2006, Xie *et al.* 2002). This characteristic is highlighted by the main European companies that produce thermally modified wood in industrial scale (International ThermoWood Association 2016, Perdure 2016, Platowood 2016).

Basically, the changes in the properties of thermally modified wood are caused by alterations in the chemistry of the original material. For example, Ringman *et al.* (2014) carried out an extensive review of the main theories related to brown decay resistance imparted by different wood modification processes, which are mainly based on changes in the chemical composition of wood.

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Chemical analyses are part of a group of previous evaluations (anatomy, physical and mechanical properties) to shed light on potential of use of wood as a raw material and due to it, many studies have been carried out regarding chemical composition of thermally modified wood. However, studies of this kind about *Eucalyptus* wood are still scarce (Brito *et al.* 2008, Esteves *et al*. 2008, Moura *et al*. 2012).

The previous chemical analyses of thermally modified *Eucalyptus* wood have commonly encompassed the determination of the contents of extractives (and also their identification), lignin (Klason and soluble), holocellulose and individual sugars (Brito *et al.* 2008, Esteves *et al*. 2008, Moura *et al*. 2012), but have not included analyses of 1% NaOH solubility and ash content.

For example, 1% NaOH solution extracts low molecular weight carbohydrates, mainly hemicelluloses and degraded cellulose in wood, so this analysis indicates decay and weathering levels. The higher the degradation is of a particular type of wood, the higher is its percentage of 1% NaOH soluble material (Brand *et al*. 2011, Tappi 2002b).

For this study, the following research problem was proposed: what is the effect of increasing thermal modification temperature on the 1% NaOH solubility and ash content of *Eucalyptus grandis* juvenile wood? The initial hypotheses were: 1% NaOH solubility will significantly increase with temperature and the changes in ash content will not be significant.

The aim of the present study was to evaluate the effect of the VAP HolzSysteme® process on the 1% NaOH solubility and the ash content of *Eucalyptus grandis* juvenile wood.

MATERIAL AND METHODS

Wood material and thermal modification

The *Eucalyptus grandis* W. Hill wood used in this study was from an 18-year-old stand (from seeds) planted in the municipality of Telêmaco Borba, Paraná state, southern Brazil. Five trees were felled but, for this study, we sampled only one juvenile corewood flatsawn board (30 x 200 x 3000 mm), without pith, cut from the first log of each tree. The rest of the wood was also brokendown and used to compose the batches.

The five sampled boards were trimmed into four equal parts in length and equally distributed among the four treatment levels investigated: untreated wood (as control) and thermally modified wood at final cycle temperatures of 140, 160 and 180°C. These temperatures are the ones commonly used by the company where the research was carried out and the thermally modified wood produced by the company is intended for indoor use.

After sawing and dividing the lumber for each treatment, the lumber was air dried under shelter until 15% of final moisture content. Thereafter, it was thermally modified according to the VAP HolzSysteme® process, in industrial scale equipment (steel cylinder 6m^3 of capacity), where one batch was processed separately for each final cycle temperature.

The equipment works with steam, generated in a boiler, which is conducted through pipes and injected in the cylinder. The steam works as heat-transfer medium and also limits oxidative processes, classifying the process as hygrothermal (Hill 2006). VAP HolzSysteme® process is typically divided in five phases, which lengths approximately eight hours, with an extra phase of cooling, which also lengths about eight hours. The exact schedule is proprietary information, but a more detailed description of the process was provided by Batista *et al*. (2015).

Chemical analyses

The chemical analyses were performed in the Wood Chemistry Laboratory of Federal University of Paraná, Brazil. First, the trimmed boards were milled in a Wiley mill and sieved to obtain a 40 – 60 mesh fraction, which was used for chemical analyses according to the Tappi T264 cm-97 standard (Tappi 1997). The sieved fractions of each treatment level were separated by board, resulting in five unities of sampling by treatment level.

The sawdust used for the chemical analyses was taken from the sampling unities, resulting in five repetitions by treatment for the different analyses, which encompassed the determination of ash content and 1% NaOH solubility, respectively according to the Tappi T211 om-02 (Tappi 2002a) and T212 om-02 (Tappi 2002b) standards.

Statistical analysis

Statistical analysis was performed according to a completely randomized design, with 95% confidence level for all tests. The effect of the treatments was checked by applying analysis of variance (ANOVA), with Bartlett's test used for its validation, which verifies a basic premise for realization of ANOVA, the homogeneity of variances among treatments (Ribeiro Júnior 2001). In cases of homogeneous variances, ANOVA was applied, while in cases of statistically significant difference between means, the Tukey multiple range test was used to determine which means were different.

RESULTS AND DISCUSSION

1% NaOH solubility

The averages (and coefficients of variation) of 1% NaOH solubility of the control (untreated), 140 °C, 160 °C and 180 °C treatments were, respectively, 12,38% (11%), 18,77% (13%); 33,81% (12%) and 34,48% (13%). The average of the untreated wood was in the range of the results presented in other Brazilian studies of the same species (Maron and Neves 2004, Mocelin *et al*. 2002, Santana 2009, Silvério 2008), expressing the different factors that can influence the chemical composition of a wood sample, such as age and site, for example.

Figure 1 depicts the behavior of the average 1% NaOH solubility for each treatment.

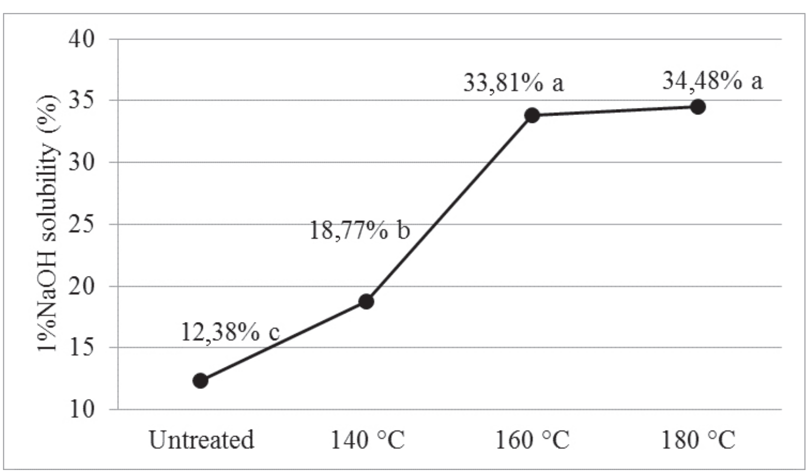

Figure 1. Average of 1% NaOH solubility for each treatment and its respective statistical decision according to the Tukey test.

According to Bartlett's test (test statistic= 1,446; p-value= 0,079); there was no significant difference of the variances of the treatments, and the ANOVA results (F-ratio= 65,33; p-value= 0,000) showed that there was a significant statistical difference between the averages of the treatments. The letters in the graph correspond to the statistical decision according to the Tukey test.

According to the results presented in Figure 1, the 1% NaOH solubility increased constantly from untreated wood until thermally modified wood at 160°C. There was no significant difference between the averages of treatments at 160°C and 180°C, which showed that this temperature increase (20 °C) was not enough to cause further wood degradation. This result also rejected our initial hypothesis about the behavior of the 1% NaOH solubility according to increasing temperature of thermal modification.

Since some properties of thermally modified wood are improved due to hemicelluloses degradation, e.g., dimensional stability and fungal decay resistance, we previously recommend the maximum temperature of 160°C for the VAP HolzSysteme® process. This is because we expect, although it needs further confirmation, there will be no gain either in dimensional stability or fungal decay resistance at 180°C when compared to 160°C, according to the results of 1% NaOH solubility. In addition, the process carried out at 160°C is cheaper than that at 180°C, because the former is shorter and consumes less energy.

Besides the water soluble fraction, the 1% NaOH solution also dissolves higher amounts of low molecular weight carbohydrates, hemicelluloses and degraded cellulose. However, the most important indication of the analysis for this study was the real level of degradation of the evaluated treatments, where higher averages mean more degradation of wood and vice versa.

According to the literature (Esteves *et al*. 2008, Fengel and Wegener 1989, Sundqvist 2004), the temperatures applied were not enough to cause significant cellulose and lignin degradation. Therefore, the dissolved fraction was mainly composed of hemicelluloses and its low molecular weight derivatives.

Ash content

The averages (and coefficients of variation) of ash content of the untreated (control), 140°C, 160°C and 180°C treatments were respectively 0,16% (15%); 0,15% (4%), 0,20% (11%) and 0,19% (9%).

Figure 2 depicts the behavior of the average ash content for each treatment. According to Bartlett's test (test statistic = 1,495; p-value= 0,059); there was no significant difference of the variances of the treatments, and the ANOVA results (F-ratio= 8,64; p-value= 0,0007) showed that there was a significant statistical difference between the averages of the treatments. The letters in the graph correspond to the statistical decision according to the Tukey test.

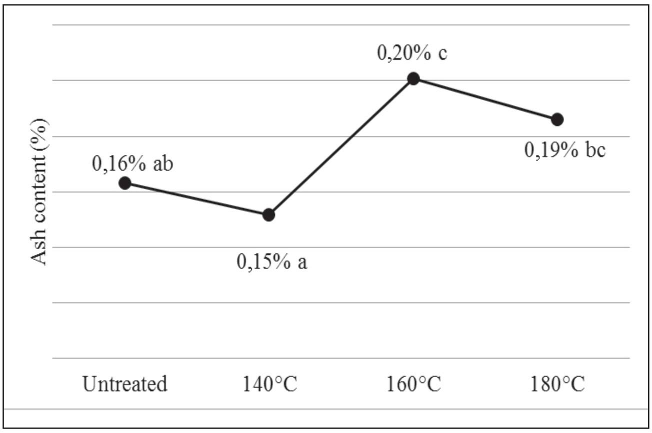

Figure 2. Average ash content for each treatment and its respective statistical decision according to the Tukey test.

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The average ash content of the untreated wood was within the range of 0,03 to 0,44% presented by Mocelin *et al*. (2002) for 24-year-old *Eucalyptus grandis* wood from the same site as the wood examined in the present study. However, the average ash content was smaller than presented by other authors who have also studied *Eucalyptus* spp. wood (Kimo 1986, Santana 2009, Trugilho *et al*. 2007), which indicates the influence of other factors on the ash content of wood, such as genetic material, soil and age, for example.

The averages of the treatments at 140°C and 180°C were not statistically different from the untreated wood, indicating that the effect of the thermal modification process on the ash content was not significant. Only the average of the treatment at 160 °C was higher than that of untreated wood, but only by 0,04 percentage point.

The inorganic fraction of wood, which is determined by Tappi standard as ash content, is basically composed of carbonates of calcium, potassium and magnesium, and also phosphates, silicates and sulphates, also known commonly as salts (Sjöstrom and Westermark 1999).

In general, salts have high melting and boiling points because they are composed of molecules that are united by strong bonds, depending on the rays and charges of the ions and cations that form them (Souza 2012). For example, the melting point of calcium carbonate is 1200°C (Bandeirante Brazmo 2000), which is an extremely high temperature.

According to the results presented and the thermal modification temperatures reported elsewhere in the literature, we can affirm that the thermal modification process had no effect on the ash content of wood. This result confirms the initial hypothesis, and in future studies this analysis can be forgone.

CONCLUSIONS

The 1% NaOH solubility increased between untreated wood and thermally modified wood at 140 °C and 160 °C, but did not increase more at 180 °C, indicating that the treatment at 180°C was not enough to cause more degradation of hemicelluloses.

In practice, the thermal modification process had no effect on the ash content of wood. The statistical difference observed between the treatment levels untreated and 160 °C (0,04 percentage points) can be attributed to the heterogeneity of wood as a material.

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