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EFFECT OF EXTRACTIVE CONTENT ON THE THERMAL STABILITY OF TWO WOOD SPECIES FROM BRAZIL

Matheus Poletto^{1,*}

ABSTRACT

The influence of extractive content on the thermal stability and kinetic degradation of two wood species has been investigated using chemical analysis and thermogravimetry. Two wood species were studied: *Pinus taeda* and *Eucalyptus grandis*. Thermogravimetric results showed that higher extractive contents in the wood accelerate the degradation process and promote an increase in the conversion values at lower temperatures reducing the wood thermal stability. After removing the extractives from wood the thermal stability for both wood species increased. The results also demonstrated that prior information about the wood composition can be helpful to increase the range of industrial applications of wood.

Keywords: Activation energy, *Eucalyptus grandis*, *Pinus taeda*, thermal degradation, thermogravimetric analysis.

INTRODUCTION

Wood is a complex material composed not only of cellulose, hemicellulose and lignin but also contains minor organic components, such as lipids and extractives (Popescu *et al.* 2011, Coloma *et al.* 2015). Wood extractives are non-structural lipophilic constituents of wood consisting mainly of triglycerides, resin acids, free long chain fatty acids, sterols, waxes and steryl esters (Dorado *et al.* 2000, Ishida *et al.* 2007, He *et al.* 2013). Although extractives are a minor component in wood, generally their content varies between 2% and 5% (Shebani *et al.* 2008) and they can cause several problems in industrial applications.

In the pulp and paper manufacture the extractives can accumulate in the paper machines and may promote the breakage of the paper sheet (Dorado *et al.* 2000, Silvério *et al.* 2008, He *et al.* 2013). Pitch can also become entrained in the pulp causing quality defects in the finished product (Dorado *et al.* 2000, Silvério *et al.* 2008, Coloma *et al.* 2015).

Wood and other natural fibers are used as renewable sources of energy. Adequate models to forecast pyrolysis products are necessary for power plant optimization and to better understand the behavior of engines fueled by pyrolysis products (Slopiecka *et al.* 2012). The pyrolysis process is influenced by many factors, such as heating rate, temperature, pressure residence time, moisture, but is also influenced by the composition of biomass material (Slopiecka *et al.* 2012). So it is important to distinguish the behavior of biomass components for a better understanding of the biomass pyrolysis

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process (Zhang *et al.* 2014).

Wood is also used as reinforcement in wood plastic composites used in various applications such as building and automotive industries. Large quantities of extractives in wood can lead to undesirable composite properties (Poletto *et al.* 2012a), such as browning and decreasing of the mechanical strength, as a result of wood thermal degradation during extrusion process. In addition, extractives are mainly hydrophobic substances with low molecular weights (Sheshmani 2013). During the preparation of a composite material wood is mixed with the polymer matrix at high temperatures, e.g. 170-200 °C. At such high temperatures, extractives may tend to migrate to the wood flour surface (Sheshmani 2013) reducing the interactions between wood, polymer matrix and the coupling agent used, which may reduce the composite mechanical strength.

The determination of the wood composition is vital in many industrial applications. In this context, this work aims to evaluate how the main wood components and extractives compounds influence in wood thermal stability. Two wood species from Brazil were investigated using chemical analysis and thermogravimetry.

MATERIALS AND METHODS

Materials

The wood flour samples used in this study were obtained from wastes of the lumber industry located in the northeast of the state of Rio Grande do Sul, Brazil. The wood samples were collected according a Brazilian standard (NBR 10.0007). The species investigated were *Pinus taeda* (PIT) and *Eucalyptus grandis* (EUG). Wood samples having particle size between 500 and 600 µm were used. The samples were dried at 105 °C for 24 h in a vacuum oven before the tests.

Determination of wood components

Benzene and absolute ethanol, purchased from Vetec Chemical, were used to determine the amount of organic extractives in the wood samples. Sulphuric acid, purchased from Vetec Chemical, was used for insoluble lignin determination. The wood extractives were eliminated from the samples via Soxhlet extraction in triplicate using: ethanol/benzene, ethanol and hot water, according to the Tappi T204 cm-97 standard. The Klason lignin content was determined according to the Tappi T222 om-02 standard. The ash content was determined by calcination in a muffle furnace at 600 °C for 2 h. The holocellulose content (cellulose + hemicellulose) was determined according to equation (1) (Poletto *et al.* 2012b):

$$\%Holocellulose = 100 - (\%Lignin + \%Extractives + \%Ash) \quad (1)$$

Thermogravimetric analysis (TGA)

The thermogravimetric analysis (TGA50 - Shimadzu) was carried out under constant nitrogen flow (50 ml/min), from 25 to 600 °C, at a heating rate of 10 °C/min. Approximately 10 mg of each sample was used.

RESULTS AND DISCUSSIONS

Wood components

The chemical composition of the wood species studied is presented in Table 1. EUG presents higher quantities of holocellulose and lignin than PIT. However, PIT contains two times more extractives than EUG. The inorganic content of wood species is usually referred to as its ash content, which is an approximate measure of its mineral salts and other inorganic matters content (Shebani *et al.* 2008, Poletto *et al.* 2012a). It normally varies between 0,2% and 0,5% in wood (Popescu *et al.* 2011, Poletto *et al.* 2012a). However, the ash content for both wood species studied is approximately 4%, which indicate higher quantities of inorganic matter, probably associated with silicon from the sawblades, since the samples were obtained from wastes of the lumber industry.

Table 1. Chemical composition of the wood species investigated.

Wood species	Holocellulose (%)	Lignin (%)	Extractives (%)	Ash (%)
<i>Eucalyptus grandis</i> (EUG)	64,4 ± 0,3	27,6 ± 0,7	4,2 ± 0,2	3,7 ± 0,2
<i>Pinus taeda</i> (PIT)	61,2 ± 0,2	25,6 ± 0,1	9,3 ± 0,7	3,9 ± 0,3

The initial wood degradation temperature is expected to be related to the heat stability of the individual wood components and differences in thermal stability among wood species can be attributed to the variation in chemical composition and structure of wood components (Shebani *et al.* 2008, Poletto *et al.* 2010). Extractives are compounds with low molecular weight and may promote the wood degradation at relative low temperatures (Guo *et al.* 2010, Kilulya *et al.* 2014), reducing wood thermal stability. As there are distinguishable differences in the extractive content of both wood species, a different thermal degradation behavior can probably be expected.

Thermogravimetric analysis

Thermogravimetric analysis (TGA) has been widely used to evaluate the thermal decomposition process of solid state materials such as lignocellulosic materials (Tenorio *et al.* 2013, Pétrissans *et al.* 2014, Toscano *et al.* 2015). The thermal decomposition of wood and other natural fibers involved many competitive and consecutive reactions because of the chemical complexity of lignocellulosic materials. To explore the effects of the removal of wood extractives on the wood thermal decomposition TGA analyses were carried out. Figure 1 gives the percentage of weight loss as a function of temperature, while the inset presents the derivative thermogravimetric (DTG) curves.

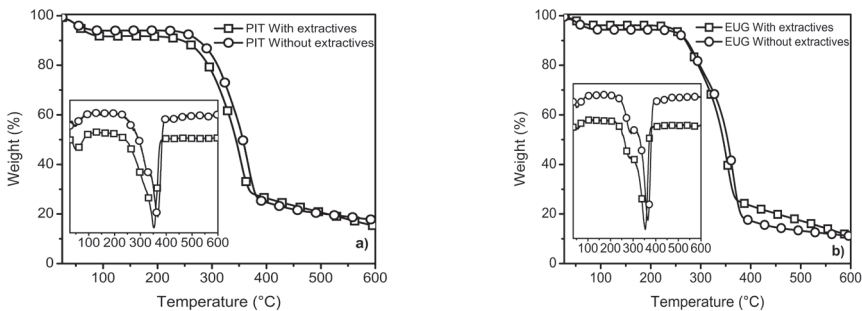


Figure 1. Thermogravimetric curves of PIT (a) and EUG (b) with and without extractives.

The water loss is observed around 100°C for both wood species, and further the thermal degradation occurs as a two step process. In the first process the degradation of hemicellulose takes place at around 300°C, and a shoulder can be seen in the inset of Figure 1. The main degradation of cellulose occurs at around 350°C for both species, as presented in Table 2 and also in the inset of Figure 1.

As can be seen in Figure 1(a) at temperatures around 210°C PIT wood shows a more significant weight loss, while for EUG it occurs at approximately 220°C, as observed in Figure 1(b). This behavior might be associated with the highest content of extractives in this wood. PIT contains at about 9% of extractives, while EUG presents only 4%, as presented in Table 1. Extractives are compounds with low molecular mass as compared to cellulose, and may promote ignitability of the wood at lower temperatures as a result of their higher volatility and thus accelerate the degradation process (Shebani *et al.* 2008, Poletto *et al.* 2012b). So, the degradation of one wood component may accelerate the degradation of the others wood components, as hemicellulose and cellulose reducing the wood thermal stability (Poletto *et al.* 2012b). Shebani *et al.* (2008) observed that wood degradation at low temperatures is usually associated with the extractives present in wood.

Table 2. DTG peaks and residue at 600°C for both wood species studied.

Wood species	Hemicellulose (°C)	Cellulose (°C)	Residue at 600°C (%)
<i>Eucalyptus grandis</i> (EUG) With extractives	284,2	351,0	11,1
<i>Eucalyptus grandis</i> (EUG) Without extractives	290,7	367,4	11,0
<i>Pinus taeda</i> (PIT) With extractives	324,6	351,8	15,1
<i>Pinus taeda</i> (PIT) Without extractives	326,3	363,0	17,6

After remove the extractives the initial degradation temperature increase for both wood species, as can be seen in Figure 1. A more prominent weight loss occurs at around 230°C for both species. The changes in thermogravimetric curve are more evident for PIT than for EUG, with may be associated with the highest content of extractives in this wood, as explained earlier. For PIT without extractives a more significant weight loss occurs at about 20°C higher than when the extractives are present in wood, while for the EUG a more pronounced degradation process occurs only at about 10°C higher when the extractives are present in wood. However, this increase in the thermal stability for both species is important when wood is used as reinforcement in composite materials. The temperatures used during extrusion process are at around 200°C and this increase in the temperature associated with a more pronounced degradation process can lead to thermoplastic polymer composites with higher mechanical and thermal properties by increasing the processing temperature range (Saputra *et al.* 2004, Shebani *et al.* 2009, Poletto *et al.* 2012a).

The temperatures associated with hemicellulose degradation and the main degradation temperature of cellulose also increases after removal of extractives from wood. The changes in the temperature of hemicellulose degradation slightly increase for both wood species as a result of the reduction in the ignitability of wood at lower temperatures. However, the shoulder associated with the hemicellulose degradation was sharply increased. The main degradation temperature of cellulose for EUG increased 16°C while for PIT the main degradation temperature of cellulose increased 11°C. As the extractives were removed from both species, the higher quantities of holocellulose and lignin in EUG might be responsible for the higher increase in the main degradation temperature of cellulose when compared with PIT.

Degradation kinetics

The kinetic study of a degradation process consists in determining the degree of conversion of decomposed fractions. In this study the conversion rate α (alpha) is defined as (Wongsiriamnuay *et al.* 2010, Sanchez-Silva *et al.* 2012, Islam *et al.* 2015):

$$\alpha = \frac{m_0 - m_t}{m_0 - m_f} \tag{2}$$

where m_0 is the initial weight of the sample, m_f is the final weight and m_t is the sample's weight at time (t).

Figure 2 shows the conversion values obtained from equation (2) as a function of time. All curves have a sigmoid shape; however, the behavior of the two wood species varies with and without extractives.

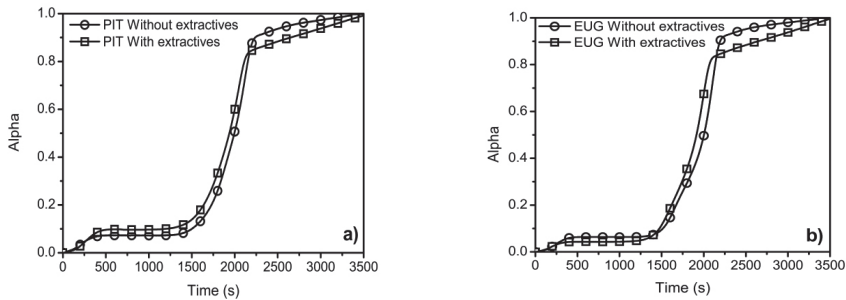


Figure 2. Conversion values as a function of time for wood species studied.

When the extractives were removed from both wood species the time for the same conversion increased, which indicated that the degradation rate was reduced for both wood species without extractives. This result corroborates the behavior observed in Figure 1. The wood species without extractives are more thermal stable and more energy is necessary to promote wood degradation.

Several methods can be used to calculate non-isothermal decomposition kinetic parameters in solid samples (Wongsiriamnuay *et al.* 2010, Sanchez-Silva *et al.* 2012, Islam *et al.* 2015). In this work the method proposed by Horowitz-Metzger (1963) was adopted. The activation energy, E_a , for the wood thermal degradation was determined from the thermograms showed in Figure 1 by using the Horowitz and Metzger method was assumed that wood thermal degradation follows a degradation process based on three-dimensional diffusion (Bianchi *et al.* 2010, Poletto *et al.* 2012c) according to the following equation:

$$\ln \left[1 - (1 - \alpha)^{1/3} \right]^2 = \frac{E_a \theta}{RT_{\max}^2} \tag{3}$$

where α is the conversion value, θ is obtained by $T - T_{\max}$ and T_{\max} is the temperature of maximum rate of weight loss, and R is the ideal gas constant.

According to equation 3, a linear relationship is observed by plotting $\ln[1 - (1 - \alpha)^{1/3}]^2$ versus θ , and the E_a is obtained from the slope of the straight line. The results obtained for conversion values between 0,2-0,8 are shown in Figure 3.

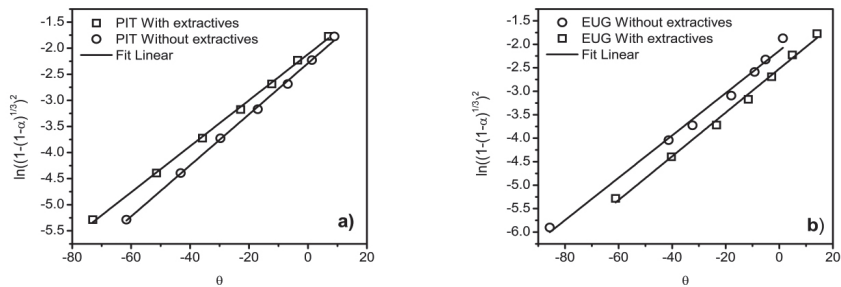


Figure 3. Plot of Horowitz-Metzger method for wood species investigated.

The E_a values for both wood species studied are presented in Table 3. The correlation coefficient (R values) for all samples studied are close to unity, which indicates good adjustment from the experimental values adopting a degradation process based on three-dimensional diffusion.

Table 3. Activation energy and correlation coefficient for wood species with and without extractives.

Wood species	Activation energy (kJ/mol)	R values
<i>Eucalyptus grandis</i> (EUG) With extractives	151,0	0,9975
<i>Eucalyptus grandis</i> (EUG) Without extractives	153,9	0,9957
<i>Pinus taeda</i> (PIT) With extractives	147,4	0,9995
<i>Pinus taeda</i> (PIT) Without extractives	164,7	0,9993

The E_a value for PIT with extractives is lower than the value obtained for EUG with extractives, which indicate that less energy is necessary for initiate a degradation process in PIT than in EUG. As the extractive content in PIT is two times higher than in EUG wood, they may initiate a degradation process at lower temperatures and probably cause the reduction in thermal stability of PIT. When the extractives were removed from wood species studied the activation energy for EUG slightly increases, but for PIT the increase in activation energy is 17 kJ/mol. For PIT wood free of extractives more energy is necessary to initiate a degradation process compared with EUG, which expands the use of PIT wood in different industrial applications as consequence of the higher thermal stability of PIT after removal of extractives.

CONCLUSIONS

The thermal degradation of wood is influenced by its composition. Higher extractive contents accelerate the wood degradation process promoting an increase of conversion values at low temperatures, which reduce the wood thermal stability. When the extractives were removed from wood the thermal stability of both wood species increased and more energy is necessary to initiate a degradation process. The results also indicated that removal of extractives from wood increased the range of industrial applications of wood.

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