Thermal decomposition of wood: Kinetics and degradation mechanisms

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Highlights
- Higher extractives content accelerate the wood degradation process.
- Higher organized cellulose regions prevent wood thermal degradation.
- Wood degradation mechanism is mainly governed by diffusion process.

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Abstract
The influence of wood components and cellulose crystallinity on the kinetic degradation of different wood species has been investigated using thermogravimetry. Four wood species were studied: Pinus elliottii (PIE), Eucalyptus grandis (EUG), Mezilaurus itauba (ITA) and Dipteryx odorata (DIP). Thermogravimetric results showed that higher extractive contents in the wood accelerate the degradation process and promote an increase in the conversion values at low temperatures. Alternatively, the results indicated that the cellulose crystallinity inhibits wood degradation; organized cellulose regions slow the degradation process because the well-packed cellulose chains impede heat diffusion, which improves the wood’s thermal stability. The wood degradation mechanism occurs by diffusion processes when the conversion values are below 0.4. When the conversion values are above 0.5, the degradation is a result of random nucleation with one nucleus in each particle.

1. Introduction
Sustainable heat and power generation from biomass are at the center of scientific and industrial interests, owing to the increasing awareness of the diminution of fossil fuels and the higher sensibility toward environmental preservation from pollutants generated by energetic systems (Di Blasi, 2008). Biomass is a source of short-cycle carbon, which is of utmost importance for future energy needs (Wongsiriamnuay and Tippayawong, 2010a). Wood is the main source of biomass (Di Blasi, 2008). Thus, wood remains one of the most important biomass materials for several applications because of its renewability, high-yield applications and appropriate characteristics (Wongsiriamnuay and Tippayawong, 2010a). Additionally, the growth of wood reduces the CO2 in the atmosphere through photosynthesis (Wongsiriamnuay and Tippayawong, 2010a; Shuping et al., 2010).

From the chemical point of view, wood is a composite material comprised of cellulose, hemicellulose and lignin, along with smaller quantities of extractives and inorganic matter. From the physical point of view, wood is a complex structure with anisotropic properties (Di Blasi, 2008; Popescu et al., 2011). The chemical and physical properties of wood such as moisture content, chemical composition, density and crystallinity are factors that affect the characteristics of thermal decomposition and degradation kinetics (Di Blasi, 2008; Orfão et al., 1999; Popescu et al., 2011).

Pyrolysis can be described as the biomass conversion by heat in absence of oxygen in a relatively low range of temperatures (300–600°C) which results in the production fuel gasses, charcoal and...
bio-oil (Sanchez-Silva et al., 2012; Orfão et al., 1999). Also, pyrolysis is of special interest since it is a prior step in combustion and gasification processes (Sanchez-Silva et al., 2012). So, it seems essential to obtain a deep knowledge of biomass pyrolysis in order to gain further understanding of the combustion and gasification processes (Sanchez-Silva et al., 2012). Kinetic analyses are useful for understanding the thermal degradation process and providing information for a pyrolysis process design using wood (Kim et al., 2010; Wongsriamnuay and Tippayawong, 2010b). Therefore, this work focuses on determining if these are actually representative of the studied process (Sanchez-Silva et al., 2012). Kinetic analyses are useful for understanding biomass pyrolysis. The authors proposed two steps of degradation of cellulose, hemicellulose and lignin separately to fast pyrolysis process of wood. Yang et al. (2006) investigated the processes (Sanchez-Silva et al., 2012). So, it seems necessary to obtain a deep knowledge of biomass pyrolysis in order to gain further understanding of the combustion and gasification processes (Sanchez-Silva et al., 2012). Kinetic analyses are useful for understanding the thermal degradation process and providing information for a pyrolysis process design using wood. 1.1. Theoretical background In the lumber industry. This understanding of the process will enable an evaluation of the kinetic degradation mechanism that describes the decomposition of a sample's weight at time (t). The rate constant k is generally given by the Arrhenius equation:

\[ k(T) = Ae^{\frac{E_a}{RT}} \]  

where \( E_a \) is the apparent activation energy (kJ mol\(^{-1}\)), \( R \) is the gas constant (8.314 kJ mol\(^{-1}\)), \( A \) is the pre-exponential factor (min\(^{-1}\)) and, \( T \) is the absolute temperature (K). The combination of Eqs. (1) and (3) gives the following relationship:

\[ \frac{dx}{dt} = Ae^{-E_a/RT}f(x) \]  

For a dynamic thermogravimetric analysis (TGA) in a non-isothermal experiment, introducing the heating rate \( \beta = dt/dT \) into Eq. 4, Eq. 5 is obtained as:

\[ \frac{dx}{dt} = \left( \frac{A}{\beta} \right) e^{-E_a/RT}f(x) \]  

Eqs (4) and (5) are the fundamental expressions of analytical methods used to calculate kinetic parameters on the basis of the TGA data (Sanchez-Jimenez et al., 2010; Poletto et al., 2010; Shuping et al., 2010; Sanchez-Silva et al., 2012).

1.1. Flynn–Wall–Ozawa method

The activation energy values for the degradation process were determined by the isoviscous Flynn–Wall–Ozawa (FWO) method. This method can be used for determination of the \( E_a \) values without any knowledge of the reaction mechanisms. This is defined by Eq. 6 (Flynn and Wall, 1966; Ozawa, 1965):

\[ \log \beta = \log \left[ \frac{AE_a}{g(\alpha)R} \right] - 2.315 - 0.4567 \frac{E_a}{RT} \]  

where \( \beta \) is the heating rate, \( A \) is the pre-exponential factor, \( g(\alpha) \) is a function of the conversion, \( E_a \) is the activation energy and \( R \) is the gas constant. Therefore, for different heating rates (\( \beta \)) and a given degree of conversion (\( \alpha \)), a linear relationship is observed by plotting \( \log \beta \) vs. \( 1/T \), and the \( E_a \) is obtained from the slope of the straight line (Flynn and Wall, 1966; Ozawa, 1965; Pistor et al., 2010).

<table>
<thead>
<tr>
<th>Mechanism – Solid state process</th>
<th>( g(\alpha) )</th>
<th>( f(x) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1 – Nucleation and growth (Anamari Eq. 1)</td>
<td>([-\ln(1 - \alpha)]^{1/2})</td>
<td>(2(1 - \alpha))</td>
</tr>
<tr>
<td>A2 – Nucleation and growth (Anamari Eq. 2)</td>
<td>([-\ln(1 - \alpha)]^{1/3})</td>
<td>(3(1 - \alpha))</td>
</tr>
<tr>
<td>A3 – Nucleation and growth (Anamari Eq. 3)</td>
<td>([-\ln(1 - \alpha)]^{1/4})</td>
<td>(4(1 - \alpha))</td>
</tr>
<tr>
<td>R1 – Phase boundary controlled reaction (one-dimensional movement)</td>
<td>(1 - (1 - \alpha)^{1/2})</td>
<td>(2(1 - \alpha)^{1/2})</td>
</tr>
<tr>
<td>R2 – Phase boundary controlled reaction (contracting area)</td>
<td>(1 - (1 - \alpha)^{1/3})</td>
<td>(3(1 - \alpha)^{1/3})</td>
</tr>
<tr>
<td>D1 – One-dimensional diffusion</td>
<td>(1 - (1 - \alpha)^{1/2})</td>
<td>(3(1 - \alpha)^{1/3})</td>
</tr>
<tr>
<td>D2 – Three-dimensional diffusion (Valenti equation)</td>
<td>(1 - (1 - \alpha)^{1/2})</td>
<td>(3(1 - \alpha)^{1/3})</td>
</tr>
<tr>
<td>D3 – Three-dimensional diffusion (Jander equation)</td>
<td>(1 - (1 - \alpha)^{1/2})</td>
<td>(3(1 - \alpha)^{1/3})</td>
</tr>
<tr>
<td>F1 – Random nucleation with one nucleus on the individual particle</td>
<td>(-\ln(1 - \alpha))</td>
<td>(1)</td>
</tr>
<tr>
<td>F2 – Random nucleation with two nuclei on the individual particle</td>
<td>(1/(1 - \alpha))</td>
<td>(1)</td>
</tr>
<tr>
<td>F3 – Random nucleation with three nuclei on the individual particle</td>
<td>(1/(1 - \alpha)^{1/2})</td>
<td>(1)</td>
</tr>
</tbody>
</table>
1.1.2. Criado method

The degradation reaction mechanism can be determined using the Criado method (Criado et al., 1989; Núñez et al., 2000), which can accurately determine the reaction mechanism in a solid reaction process. This is defined by a $Z(\alpha)$ type function:

$$Z(\alpha) = \frac{dx/dt}{b} \pi(x)T$$

where $x = E_a/Rt$ and $\pi(x)$ is an approximation of the temperature integral that cannot be expressed in a simple analytical form. In this study, were used the fourth rational expression of Senum and Yang (Pérez-Maqueda and Criado, 2000), which gives errors of lower than 5% when $x > 20$. The master curves as a function of the conversion degree corresponding to the different models listed in Table 1 (Bianchi et al., 2011; Shuping et al., 2010) were obtained according to Eq. 8:

$$Z(\alpha) = f(\alpha)g(\alpha)$$

From Eqs. (5) and (8), the following relationship can be derived:

$$Z(\alpha) = \frac{dx}{dt} E_a e^{E_a/R}P(\alpha)$$

Eq. (9) is used to represent the experimental curve. By comparing these two curves, the type of mechanism involved in the thermal degradation can be identified.

2. Methods

2.1. Materials

The wood flour samples used in this study were obtained from wastes of the Brazil lumber industry. The wood species investigated were *Pinus elliottii* (PIE), *Eucalyptus grandis* (EUG), *Mezilaurus itauba* (ITA) and *Dipteryx odorata* (DIP). Samples having a particle size of 200–300 μm were dried in a vacuum oven at 105 °C for 24 h before the TGA. The wood moisture content before dried ranges between 4 and 6 wt.% (Poletto et al., 2011a). Wood composition and crystalline index (Cr.I.) are shown in Table 2 (Poletto et al., 2012).

2.2. Thermogravimetric analysis (TGA)

The thermogravimetric analysis (TGA50 – Shimadzu) was carried out under N$_2$ atmosphere with a purge gas flow of 50 cm$^3$-min$^{-1}$ from 25 to 600 °C. Approximately 10 mg of each sample was used. The analysis was carried out at four different heating rates (5, 10, 20 and 40 °C min$^{-1}$). The results obtained were used to calculate the kinetics parameters.

3. Results and discussions

3.1. Thermogravimetric analysis

The ITA wood shows a more significant weight loss than others wood species. For this wood the degradation process starts at around 180 °C, according to a previous work (Poletto et al., 2012). This behavior might be associated with the content of extractives in this wood, approximately 14% as presented in Table 2, which is higher than the other wood samples. This results in degradation at lower temperatures (Shebani et al., 2008; Poletto et al., 2012). PIE and EUG begin the degradation process between 180 and 200 °C; they have more thermal stability than ITA probably because they contain a higher amount of cellulose and lignin and a lower quantity of extractives. However, the DIP wood that contains approximately 11% extractives showed the highest thermal stability in this range of temperature. DIP has the highest cellulose crystalline index, which probably slows the thermal decomposition of the wood.

When the $\alpha$ values are between 0.1 and 0.2, the ITA sample has higher conversion values at lower temperatures, followed by EUG, DIP and PIE. The higher quantities of extractives in ITA may accelerate the degradation process and promote an increase in the conversion values at relatively low temperature. Extractives are compounds with low molecular mass (Guitiérrez et al., 1998; Mészáros et al., 2007) when compared with cellulose; they are formed by lipids, phenolic compounds, terpenoids, fatty acids, resin acids and waxes (Mészáros et al., 2007; Shebani et al., 2008) that promote the degradation of wood at relative lower temperatures as a result of their high volatility (Mészáros et al., 2007). The EUG sample has the second largest conversion in the low temperature range. EUG possesses higher quantities of adsorbed water and has prominent hemicellulose degradation at 250–300 °C that can lead to a higher conversion value at a lower temperature. In addition, the structure of lignin can help to interpret this result. The syringyl, as well as the guaiacyl units are built into the lignin macromolecule mainly by ether bonds, and the ether bonds between syringyl units are easier to split than those between guaiacyl units (Wang et al., 2009). This fact result in a higher thermal stability of softwood lignin mainly composed by guaiacyl units when compared with hardwood lignin composed by a mix of guaiacyl and syringyl units (Wang et al., 2009). So, the lowest thermal stability for EUG, a hardwood, and the highest thermal stability for PIE, a softwood, may also help to explain the higher thermal stability of this two wood samples when the conversion values are between 0.1 and 0.2, since according Table 2 PIE had the highest lignin content, followed by EUG. In contrast, the DIP and PIE species retain their lower conversion values as the temperature increases. Because DIP contains 11% extractives, the degradation process occurs slower than for the ITA sample that contains approximately 14% extractives; this is probably because the higher crystallinity of cellulose in DIP and a slower degradation of hemicelluloses. The PIE species, which contains less absorbed water than EUG, has the lowest conversion rate when temperature increases; PIE has a low content of extractives, the highest lignin content and a slower degradation of hemicellulose. To summarize, at low conversion values, the degradation process in wood seems to be mainly dominated by the following parameters, or some interrelationships between these parameters: the volatilization of water, the degradation of extractives, the degradation of lignin, the break-down of hemicelluloses, and the degradation of amorphous domains of cellulose.

When the conversion values are between 0.4 and 0.6, mainly the degradation of cellulose occurs. The wood species studied show a different thermal degradation behavior than when compared

<table>
<thead>
<tr>
<th>Wood species</th>
<th>Holocellulose (%)</th>
<th>Lignin (%)</th>
<th>Extractives (%)</th>
<th>Ash (%)</th>
<th>Cr. I. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Eucalyptus grandis</em> (EUG)</td>
<td>62.7 ± 1.4</td>
<td>32.1 ± 1.0</td>
<td>4.1 ± 0.2</td>
<td>1.1 ± 0.3</td>
<td>34.4</td>
</tr>
<tr>
<td><em>Pinus elliottii</em> (PIE)</td>
<td>61.2 ± 1.1</td>
<td>33.8 ± 1.0</td>
<td>4.5 ± 0.1</td>
<td>0.8 ± 0.1</td>
<td>34.1</td>
</tr>
<tr>
<td><em>Dipteryx odorata</em> (DIP)</td>
<td>57.1 ± 0.6</td>
<td>30.4 ± 0.4</td>
<td>11.1 ± 0.1</td>
<td>1.5 ± 0.2</td>
<td>43.0</td>
</tr>
<tr>
<td><em>Mezilaurus itauba</em> (ITA)</td>
<td>57.8 ± 1.0</td>
<td>28.0 ± 0.3</td>
<td>13.6 ± 0.7</td>
<td>0.7 ± 0.1</td>
<td>37.8</td>
</tr>
</tbody>
</table>
with low conversion values. Once again, ITA has the highest conversion values at low temperatures but is followed by PIE, EUG and DIP. In this range of conversion, the fast degradation process in ITA is probably influenced by the lower thermal stability of hemicellulose and the lower contents of holocellulose and lignin than other species studied. These factors lead to an acceleration of the degradation of cellulose because the degradation of one component may accelerate the degradation of the other wood components (Poletto et al., 2012). PIE and EUG possess comparable degradation profiles in this range of conversion, which may be associated with their similar chemical compositions and crystal-line indices presented in Table 2. However, PIE has a slightly lower degradation value than EUG when the temperature increases. This slower cellulose degradation might be associated with the lower reactivity of hemicelluloses in PIE, which is a softwood species, than in EUG, which is a hardwood species. Grønli et al. (2002) observed that hemicellulose degradation is slower in softwoods than in hardwoods by studying softwoods from pine species and several hardwood species. The authors verified that hemicelluloses from softwood have a lower reactivity than hemicelluloses from hardwood, which is associated with the differences in chemical composition of the two species' hemicelluloses.

The DIP sample demonstrates the highest thermal stability throughout the second range of conversion evaluated. The organized cellulose chains in this wood may prevent the wood degradation given that the well-packed cellulose chains impede heat diffusion through the sample. The lower degradation of hemicellulose improves the thermal stability of DIP, even with substantial amounts of extractives. In summary, when the degradation occurs at low conversion values, the heat from heating source diffuses quickly in non-ordered regions and causes fast degradation of compounds with a low molecular mass. Alternatively, highly ordered cellulose regions may act as barriers to heat diffusion and impede the degradation of cellulose, increasing the wood's thermal stability. The rate of wood decomposition tends to increase when the heating rate also increases, because higher thermal energy was provide to the sample which causes better heat transfer between the surrounding and inside the samples (Wongsiriamnuay and Tippayawong, 2010a). However, external diffusion effects or heat or mass transfer limitations for the samples may also occurs.

3.2. Kinetics results

The plots of the FWO method, which was used for the determination of the $E_a$ values for all species studied, show a general trend. Because the kinetic behavior is similar for all of the wood species studied, only ITA was chosen as a representative model for the presentation of the $E_a$ results. Therefore, Fig. 1 shows the results of the application of the FWO method with $x$ values from 0.1 to 0.8. The linear fits obtained from the plot of $\log b$ vs. $1/T$ are also shown in Fig. 2. The $E_a$ values were calculated from the angular coefficient obtained from the straight line fit. Table 3 summarizes the $E_a$ values for all of the wood samples studied.

As seen in Table 3, when $x = 0.1$, the $E_a$ values are approximately 185 kJ mol$^{-1}$ for the EUG and PIE species that contain lower quantities of extractives. They are approximately 175 kJ mol$^{-1}$ for the ITA and DIP species that contain higher extractive contents. These results confirm the fact that the extractives promote the degradation of wood at relatively low temperatures, reducing the thermal stability of wood. When the conversion is 0.2, all wood species studied have an $E_a$ of nearly 200 kJ mol$^{-1}$. The slight increase in the $E_a$ values of the wood samples when $x > 0.2$ implies the possible occurrence of a decomposition process of the main components (Yao et al., 2008). When $x > 0.2$ the temperature lies at around 300 °C, which is an indicative that the degradation process begins to occur in the hemicelluloses and in the amorphous domains of the cellulose leading to an increase of the $E_a$ values. According to Mamleev et al. (2006) the depolymerization of cellulose by transglycosylation during pyrolysis involves an activation energy close to 200 kJ mol$^{-1}$. ITA and PIE have $E_a$ values close to 200 kJ mol$^{-1}$ only at conversion values of 0.2–0.3. This indicates that they have a lower thermal stability than EUG and DIP probably because they contain lower quantities of cellulose and a lower crystallinity index, respectively. However, the $E_a$ values for EUG and DIP were approximately 200 kJ mol$^{-1}$ during all conversion values evaluated. EUG has the highest quantities of holocellulose and lignin, which leads to higher $E_a$ values. DIP has ordered cellulose regions that retard the degradation process, leading to a higher $E_a$ as the temperature increases.

The $E_a$ values obtained using the FWO method were used to determine the thermal degradation mechanisms proposed by Criado et al. (1989), since according to FWO method the activation energy can be determined without any knowledge of the reaction mechanisms and then these values were used in Criado method. This method uses reference theoretical curves obtained from Eq. 8 that are derivatives of the $f(x)$ and $g(x)$ functions represented in Table 1; called master curves, they are compared to experimental data to determine the mechanism of the solid-state degradation process (Criado et al., 1989; Sánchez-Jiménez et al., 2009). As seen in Table 1, the algebraic expressions that represent the theoretical mechanisms are separated into four groups: $A_n$, $R_n$, $D_n$ and $F_n$. Respectively, these mechanisms describe: nuclei formation processes for the propagation of thermal degradation; diffusion processes that are related to the heat transfer capacity along the material structure; reaction mechanisms controlled by the surface of the sample; and the random degradation of nuclei. The determination of the $Z(x)$ values was carried out using a heating rate ($\beta$) of 10 °C min$^{-1}$, and the calculated $Z(x)$ values were determined by applying the $E_a$ values obtained with the FWO method to Eq. 9. Fig. 2 presents the master curves as well as the results of the experimental data obtained.

The experimental data in Fig. 2 shows that for all wood species studied in the range of $x = 0.2–0.4$, they overlap the D1, D2 and D3 curves. According to literature, these degradation mechanisms refer to a diffusion process in one, two and three dimensions, respectively (Criado et al., 1989). Similar results were described by Wu and Dollimore (1998), Blanchi et al. (2010) and Poletto et al. (2011b) for other cellulosic fibers. Based on this result, at lower conversion values, the heating transfer occurs by diffusion throughout the sample. However, the higher thermal stability of DIP may be related to a difficulty in the heat transfer process because of the higher-ordered cellulose regions. When the conver-
When conversion values are higher than 0.5, the degradation mechanism for PIE, EUG and DIP species tends towards F1, which corresponds to random nucleation with one nucleus in the individual particle (Criado et al., 1989). In this type of mechanism, the degradation is initiated from random points that act as growth center for the development of the degradation reaction. Based on this, at conversion values above 0.5, the higher temperatures involved in the degradation process at approximately 350°C may promote the rupture of some ordered cellulose chains. These low molecular mass chains can possible act as centers for random nucleation and growth for the degradation reaction. The amorphous cellulose domains also can probably act as a center for degradation and stimulate the degradation process. Its degradation occurs in lower conversion ranges when the heat is propagated throughout the sample, as discussed above.

The shape of the experimental curve for ITA is similar to the curves for the other species. However, the Z values overlap the D3 mechanism, associated with the diffusion process in three dimensions. This behavior may be associated with the highest degradation of the extractives and the hemicellulose content that can lead to a higher volatility of the main wood components at relatively low temperatures. This can probably promote an acceleration of the cellulose degradation by diffusion, not only by the diffusion of the heat from heating source but also by diffusion of the hot gasses formed throughout the sample. The same mechanism for wood was observed by Wang et al. (2006).

### 4. Conclusions

The thermal degradation of wood is influenced by its composition and crystallinity. Higher extractive contents accelerate the degradation process, promoting an increase of conversion values at low temperatures. Higher reactivity of hemicelluloses and lignin...
can accelerate the degradation reaction and cause cellulose degradation at low temperatures. Organized cellulose regions may prevent wood degradation; well-packed cellulose chains impede the heat diffusion, promoting a slower degradation process. Wood degradation is governed by diffusion when the conversion values are below 0.4 and tends to random nucleation, a F1 mechanism, when the conversion values are above 0.5.

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