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THERMOGRAVIMETRIC CHARACTERIZATION OF EUCALYPTUS WOOD

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ABSTRACT

Thermogravimetry analysis of eucalyptus wood, performed under oxidative atmosphere, highlights significant differences based on different species and geographical origins. The highest degradation rate can become two times greater for *Eucalyptus globulus* than for *Eucalyptus grandis*. Extractives volatilization occurs in a broad temperature interval, which superposes hemicellulose and cellulose volatilizations. Thermal degradation (pyrolysis and combustion) of eucalyptus wood can be fitted using simplified models based on five pseudo-components: hemicellulose, crystalline and amorphous celluloses, lignin and extractives. From this simulation it is possible to calculate an approximate composition of wood.

INTRODUCCIÓN

Eucalyptus wood is usually used as raw material to obtain cellulosic pulp because of their fast growing, the high yield in pulping process and the high cellulose content. In the kraft pulping process the wood chips are subjected to the action of sodium hydroxide and sodium sulphide at high temperature and pressure. However, not all eucalyptus woods need the same digestion conditions. There are many differences between eucalyptus woods from different species and geographical origins (MIRANDA and PEREIRA, 2002).

In the wood cell wall, cellulose forms microfibrils which have crystalline and amorphous regions. Crystalline cellulose forms crystallites along microfibril, in which cellulose chains form planes that are hydrogen bonded between equatorial hydroxyl groups. On the other hand, amorphous cellulose consists in both the non-crystalline cellulose located between crystallites and the unordered cellulose (paracrystalline) located in the superficial layer of microfibril (O'SULLIVAN, 1997)(IOELOVICH *et al.*, 2010).

Thermogravimetry analysis has been recently used as analytical method on biomasses and pulps (BARNETO *et al.,* 2009, 2010). Their employ is associated to the simulation of the thermal degradation of samples from simplified models based on pseudo-components. Using nucleation kinetics it is possible to monitor the behavior of individual components of samples under inert or oxidative environments. This strategy allows describing the pseudo-components degradations on the basis of a set of kinetic parameters that includes pre-exponential factor, activation energy, reaction order, nucleation order and volatiles mass. In the present work this method is used on samples of eucalyptus wood obtained from ENCE mill at Huelva (Spain).

MATERIAL AND METHODS

Samples

Wood samples were obtained from different eucalyptus species: *Eucalyptus grandis* from Uruguay (EGrU), *Eucalyptus globulus* from Chile (EGlC) and *Eucalyptus globulus* from Spain (EGlS).

Thermogravimetric analysis

Thermogravimetric runs were carried out with a Mettler Toledo analyzer model TGA/SDTA851e/LF1600 – from Metter Toledo International Inc. – USA -, on samples of around 5 mg. Pyrolysis and combustion runs were carried out in nitrogen and synthetic air (N_2:O_2 = 4:1), respectively. Three heating rates (5°C, 10ºC, and 20ºC/min) have been used from 25ºC to 900ºC.

In order to obtain the degradation behavior of individual components of samples, thermogravimetric data were fitted from a wood simplified model based on five pseudo-components, which represent hemicellulose (*H*), crystalline cellulose (C_1), amorphous cellulose (C_2), lignin (*L*) and extractives (*E*) (BARNETO *et al.*, 2010). A pseudo-component is a fraction of sample, not necessarily a pure substance, which thermally degrades in a specific way into a concrete temperature interval. In the present approximation it is accepted that, under inert atmosphere, solid pseudo-components undergo volatilizations that yield light volatiles and char, which remains in thermobalance. Under air environment, this char previously obtained oxidizes, yielding new volatiles. The pseudo-components volatilization has been simulated using a nucleation model based on the Prout-Tompkims equation (BURNHAM *et al.*, 1996). Integration and optimization of

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the kinetic equations were carried out using the Runge-Kutta and Gauss-Newton methods, respectively.

RESULTS AND DISCUSSION

Figure 1 compares the thermal degradation profiles of eucalyptus wood under inert (pyrolysis) and oxidative (combustion) environments. As it can be seen, under pyrolysis conditions the mass loss occurs in one step, being basically the consequence of hemicellulose (shoulder at 299ºC) and cellulose (peak at 363ºC) volatilizations. The tail at high temperatures is caused by lignin and char volatilizations (BARNETO *et al*., 2009, 2010). On the contrary, the eucalyptus wood degradation under air environment shows two mass loss steps. The first is similar to observed under pyrolysis conditions, but it occurs at lower temperature showing a higher mass loss rate. In this case, the hemicellulose and cellulose degradations occur at 294ºC and 328ºC, respectively. The second peak, caused by char oxidation, occurs close to 450ºC. The shape of this peak can drastically change when the heating rate changes too. **Figure 2** shows that both peaks are shifted toward high temperature when heating rate increases. In this case, although the shape of the curve almost not changes, the peaks are sharper in both cellulose volatilization and char oxidation. The same result is obtained under inert atmosphere.

Differences between eucalyptus species

The Eucalyptus genus consists of more than 600 trees and shrubs species. In paper manufacture are usually used the *E. globulus, E. grandis, E. Nitens* and *E. Dunii* species. In the present work we have compared woods from two species (*E. globulus* and *E. grandis*) and three geographical origins (Chile and Spain for *E. globulus* and Uruguay for *E. grandis*).

Figures 3 and 4 depict that the thermal degradations of studied eucalyptus woods show significant differences, being evident that oxygen presence increase it (see figure 3). According to thermogravimetry data, *E. globulus* thermally degrades better than *E. grandis*, and the *E. globulus* from Chile better than *E. globulus* from Spain.

Differences between the highest mass loss rates of *E. globulus* from Chile and *E. grandis* from Uruguay are very important (25.4 min^{-1} versus 13.0 min^{-1}) and they are not explainable from small changes in wood composition. In this case it is necessary to attempt to structural differences which have importance in the wood digestion. According to MIRANDA and PEREIRA (2002), the geographical origin of *E. globulus* have influence on the extractive content, the fiber morphology and the pulping yield.

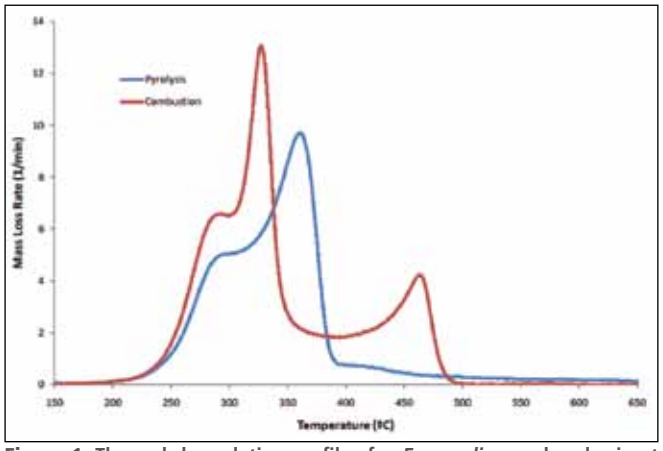

Figure 1. Thermal degradation profiles for *E. grandis* wood under inert and oxidative environments

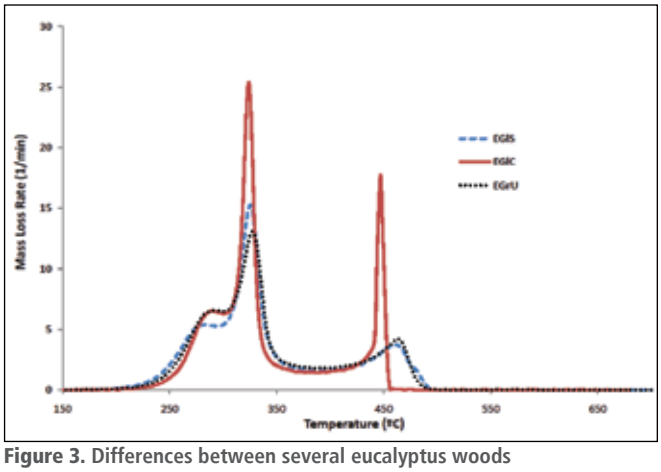

Figure 3. Differences between several eucalyptus woods

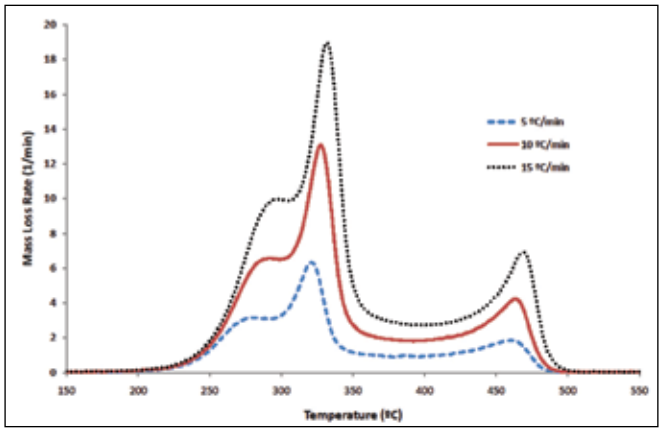

Figure 2. Thermal degradation of wood under oxidative environment (*E. grandis*). Heating rate effect

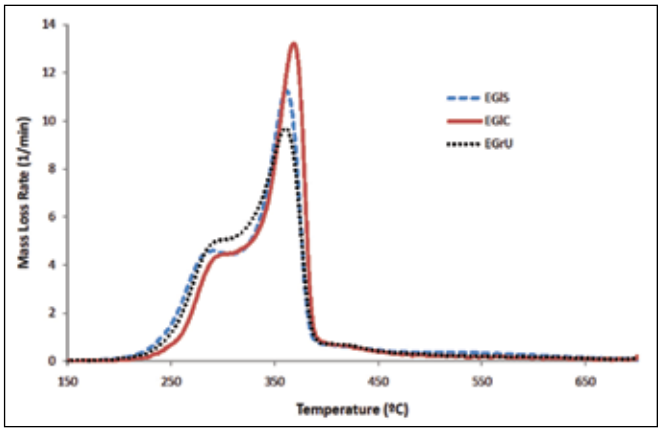

Figure 4. Thermal degradations of three eucalyptus woods under inert environment

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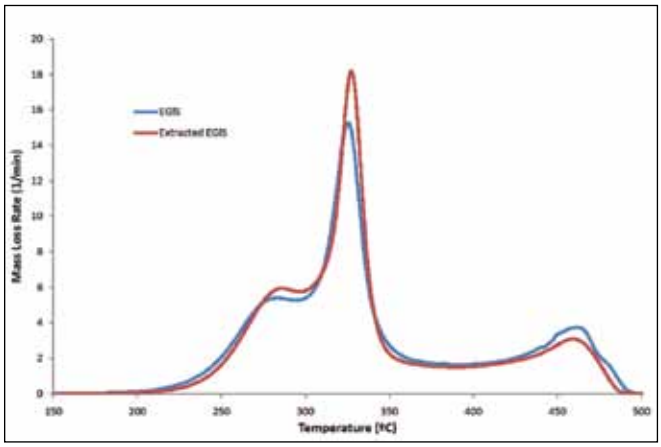

Figure 5. Extractives in eucalyptus wood. Effects on thermogravimetric analysis

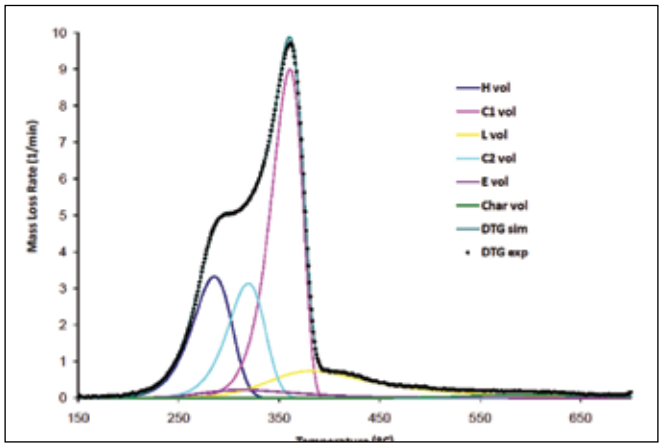

Figure 6. Simulation of the thermal degradation of *E. grandis* wood at 10ºC/min under inert environment

Thermogravimetric analysis of eucalyptus wood - Extractives influence

In eucalyptus wood, the extractives fraction is complex and contains both polar and non-polar substances. Most extractives are removed during pulping process, but some of them remain in pulp, being responsible of pitch. Between polar extractives are phenolic derivatives, which are precursor of lignin, tannins and flavonoids. Between non-polar extractives are included terpenoids, steroids, hydrocarbons, waxes and, mainly, fatty acids and alcohols (SJÖSTROM, 1993) (RENCORET *et al*., 2007).

Figure 5 compares the combustion of two samples of *E. grandis* wood, one of them was previously extracted with ethanol-benzene. As it can be seen, the extractives removal (close 6 %wt) has influence on the thermal degradation of wood. According to Figure 5, the curve of extracted wood is over the non-extracted wood curve in the volatilization zone, but it is under this curve in the char oxidation zone. This behavior can be explained if we accept that extractives volatilization occurs in a broad temperature interval from 200ºC to 350ºC, yielding char in a higher proportion than hemicellulose and cellulose.

E. grandis wood pyrolysis simulation

Eucalyptus wood pyrolysis has been fitted from five pseudo-components, which include two celluloses types that degrade at different temperatures (see **Figure 6**). It is important to point out that fitting process shows that the eucalyptus wood volatilization between 200ºC and 350ºC cannot be explained from two consecutives volatilizations (for example, hemicellulose and cellulose), being necessary to use three pseudo-components to explain experimental data. The first explains the shoulder at low temperature and is compatible with the thermal degradation of xylan (representative hemicellulose): activation energy 86 kJ/mol, reaction order 1, and highest mass loss rate close 288ºC (DI BLASSI and LANZETTA, 1997). The third explains the sharp peak in DTG (Differential Thermogravimetric) curve and is compatible with the thermal degradation of crystalline cellulose: activation energy 204 kJ/mol, reaction order 1, and highest mass lost rate close 363ºC. However, the second volatilization, characterized by kinetic parameters similar to those obtained for cellulose, occurs at lower temperature than crystalline cellulose, but at higher temperature than hemicellulose (close to 323ºC). This fraction represents amorphous cellulose.

On the other hand, lignin volatilization yields a broad peak from 250ºC to 700ºC. In this case, the kinetic parameters are: activation energy 66 kJ/mol and reaction order close 3. Finally, extractives volatilization, which occurs between 200ºC and 350ºC, yields another broad peak that superposes the hemicellulose and cellulose volatilizations. Their characteristics kinetic parameters are: activation energy 100 kJ/mol and reaction order higher than 3.

E. grandis wood combustion simulation

Wood combustion has two mass loss stages: an initial volatilization, which occurs between 200ºC and 350ºC, and a final char oxidation at high temperature close to 450ºC (see **Figure 7**). Although oxygen is present, the initial volatilization stage is similar to observed under pyrolysis conditions, and can be explained from the same pseudo-components volatilizations: hemicellulose, amorphous cellulose, crystalline cellulose, lignin and extractives. However, under this oxidative environ-

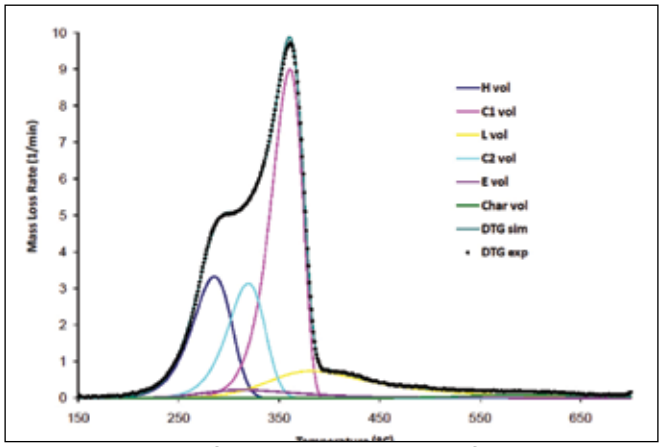

Figure 7. Simulation of the thermal degradation of *E. grandis* wood at 10ºC/min under oxidative environment

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Table 1. Eucalyptus wood composition

	Hemicellulose (% wt)	Cellulose (% wt)	Lignin (% wt)	Extractives (% wt)
Thermogravimetric analysis	19	51	23	6
Garrote and Parajó (2002)	Xylan 16,6 Araban 0,54 Acetyl 3,54	Glucan 46,3	22,9	
Miranda & Pereira (2002)	Xylan 14,1	Glucan 50,7	25,5	3,2
Brito *et al.* (2008)	Xylan 13,1 Araban 0,47 Mannose 1,54 Galactose 1,29	Glucose 51,49	27,1	4,8

ment, peaks are narrower and sharper, reaching higher mass loss rates. That is, oxygen presence favors the wood volatilization.

As expected, under oxidative conditions kinetic parameters, which characterize the pseudo-components volatilizations, are similar to previously obtained during pyrolysis. However, the nucleation order (kinetic parameter which appears in nucleation kinetics like Prout-Tompkims equation) increases. The nucleation kinetics allows explaining the volatilization process as two consecutive processes: the nucleus formation (connected with the nucleation order and the heating rate), and the nucleus growing (connected with the activation energy and reaction order). Oxidative conditions favour the nucleus production and, without changes in other kinetic parameters, the nucleation order increasing. That is, using a nucleation kinetic we can explain changes in the shape of peaks without change in activation energy and reaction order. Under air atmosphere, the nucleation order for hemicellulose and cellulose volatilizations at 10ºC/min reaches values close to 0.6. On the other hand, kinetic parameters which describe char oxidation are similar to those obtained for mineral carbon: activation energy close to 140 kJ/mol and reaction order close to 1. The shape of char oxidation peaks significantly changes when heating rate increases. In this case, the nucleation order can reach high values (higher than 1).

Adding the mass losses caused by volatilization and char oxidation one can calculate the mass of each pseudo-component and, consequently, the wood composition (based on pseudo-components). Obtained results are compatible with those obtained from literature (see **Table 1**) (GARROTE and PARRAJO, 2002) (BRITO *et al.*, 2008).

CONCLUSIONS

- The species and geographical origin influence the thermal degradation of eucalyptus wood. Between analyzed samples, *E. globulus* from Chile is the most degradable and *E. grandis* from Uruguay the least degradable. Wood differences are greater under oxidative environment.

- Wood extractives affect to thermogravimetric analysis. Their volatilization superposes hemicellulose and cellulose volatilizations. Eucalyptus extractives proportionally yield more char than polysaccharides.

- In order to model the pyrolysis and combustion of eucalyptus wood, it is necessary to employ two cellulose fractions that degrade at different temperatures: amorphous and crystalline celluloses. In studied samples, amorphous cellulose represents close the quarter of total cellulose.

- Kinetic parameters which characterize the pseudo-components degradations are similar to those reported for individual components of wood. Moreover, the wood composition calculated from thermogravimetric analysis agrees with the obtained from other analytical methods.

Acknowledges

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