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Mild pyrolysis of fast-growing wood species (Caribbean pine and Rose gum): Dimensional changes predicted by the global mass loss

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ABSTRACT

Dimensional changes of Caribbean pine and Rose gum (eucalyptus) were continuously measured during mild pyrolysis (heat treatment) with a dynamic mechanical analyzer (DMA) in creep mode with a negligible force. Mass loss was measured on matched samples by thermo-gravimetric analysis (TGA). All experiments were carried out at 220 °C (air and nitrogen), 250 and 280 °C (nitrogen) with a residence time up to 10 h. Eucalyptus exhibits a greater shrinkage and mass loss than pine. By normalizing the shrinkage (heat treatment shrinkage divided by total hygroscopic shrinkage), one single master curve is obtained per species, whatever the heat treatment conditions (temperature, nature of gas) and material direction. For each species, a unique expression is proposed to predict the dimensional changes due to mild pyrolysis as a function of mass loss and total hygroscopic shrinkage. The ability to predict heat treatment shrinkage is useful from industrial perspective (density prediction, change in bed thickness, modeling tools).

1. Introduction

Mild pyrolysis, also called "heat treatment" or "torrefaction", allows several physico-mechanical properties of lignocellulosic materials to be modified. During this process, the product is exposed to temperature levels in the range of 200 °C–300 °C under inert atmosphere. The final product is intermediate between wood and charcoal, and exhibits certain technological advantages when compared to the original material such as reduced hygroscopicity, dimensional stabilization, increased durability [1–4]. These changes are due to irreversible modifications in the macromolecular organization. Thermal degradation of hemicelluloses and amorphous cellulose together with condensation of lignins are the most remarkable chemical changes [5–7]. The application of mild pyrolysis is also recommended as a pre-treatment of biomass prior to gasification, as it increases the energy density and the grindability of the treated material [8–13].

Eucalyptus and pine are the most representative species in planted forest areas in Brazil, with over 15,000 and 50,000 km^2 of planted area, respectively [14]. Both are fast-growing species and are intensively used in several industrial domains, such as sawmills, fiberboard production, charcoal for "green" iron, pulp and paper [14]. Also, these planted forests produces a large amount of residues, which can be a widely source of

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biomass. Several works demonstrate the benefits of applying heat treatment to improve technological properties of fast-growing species [15,10,16].

Technological modifications of wood caused by heat treatment have been investigated since the beginning of the 20th century [17,18]. Among other alterations, it is well known that this process induces dimensional changes (shrinkage), but the majority of studies just measured sample dimensions before and after the heat process. Indeed, works that monitored dimensional changes during the process were focused on charcoal production, thus applying temperature levels higher than 300 °C. For example, Davidsson and Pettersson [19] monitored through a video camera the size changes of birch wood during rapid pyrolysis (350–900 °C, time < 1400 s). Yet, due to the magnitude (up to several times the hygroscopic shrinkage) these dimensional changes have significant impacts, either during the process itself (stress field in large particles, change in thick bed height, change in bed porosity, change in characteristic diffusion time) or to the final product (density, checks, mechanical resistance).

The main purpose of the present study is i) to evaluate the dimensional changes of fast-growing wood species during heat treatment (temperature < 300 °C) using a reliable experimental protocol, and ii) to propose simple mathematical expressions able to predict heat treatment shrinkage as a function of mass loss and hygroscopic shrinkage. This synthetic information will be useful for all questions where the density or the mechanical quality of the final product matters. For example, these expressions can be useful either to assess the complete transformation chain to optimize the heat treatment process to address practical problems or more likely to be implanted in predictive models including ones at industrial scale [20].

2. Materials and methods

2.1. Material selection and preparation

2.1.1. Sampling of vegetal material

Samples were selected from an eleven-year-old Caribbean pine (*Pinus caribaea* var *hondurensis*) and a seven-year-old Rose gum (*Eucalyptus grandis*) commercial plantation located at Lençóis Paulista, São Paulo, Brazil (Lat. 22°35′ S, Long. 48°48′ W). This study was focused to the valorization of forest residues. Therefore, for both species, only the top portion of the trees, mainly composed of juvenile wood, was selected. The dimensions of the collected pieces were 6 cm (diameter) and 40 cm (length). Pieces were gently dried at room temperature until samples preparation. The bark was removed just before samples preparation. The average basic wood density (oven-dry mass to green volume) was 430 kg m^{-3} (coefficient of variation of 4.9%) for Caribbean pine and 390 kg m^{-3} (coefficient of variation of 6.2%) for Rose gum.

2.1.2. Choice of samples dimensions based on moisture and thermal diffusion

To obtain relevant results, the sample temperature has to be as uniform as possible and should follow the furnace temperature as closely as possible. Both constraints can be fulfilled by reducing the sample size, yet keeping a sample long enough to ensure the accuracy of the shrinkage measurement. This is why the smallest dimension, the sample thickness, was always along the longitudinal dimension. In addition, to obtain the same time constant, a thickness of 2 mm was chosen for both dimensional (DMA) and mass loss (TGA) measurements. Based on classical results for transient diffusion inside the sample, the thermal time constant τ reads as [21]:

$$\tau = \frac{h^2 \rho c_p}{\lambda} (s) \quad (1)$$

where h is the half-thickness of the sample (m), ρ is the wood density (kg m^3), c_p is the specific heat capacity of wood (J kg^{-1} K^{-1}) and λ is the thermal conductivity of wood (J s^{-1} m^{-1} K^{-1}).

Using typical values for dry wood (ρ = 500 kg m^3, c_p = 1250 J kg^{-1} K^{-1} and λ = 0.15 W m^{-1} K^{-1}) and with a total thickness of 2 mm, the time constant τ is less than 5 s. This value is very small compared to the treatment duration ensuring a uniform treatment throughout the section.

As the initial stage of our protocol is devoted to the determination of the hygroscopic shrinkage, the moisture content gradient rather than the temperature gradient matters during this phase. In principle, an order of magnitude of the hydric time constant could be determined by the analog of equation (1) for transient mass diffusion. Keeping in mind that, in wood, kinetics of moisture diffusion is much longer than thermal diffusion, it becomes obvious that the moisture gradient is likely to be important in the sample during the drying phase. A rigorous analysis of this period is however complex, as many phenomena are involved during this period: coupled heat and mass transfer via the latent heat of evaporation, thermal activation of mass diffusion due to the temperature level, competition between internal and external transfers (boundary layer), both in terms of heat and mass transfer.

To address this difficulty, the comprehensive computational model of coupled heat and mass transfer known as *TransPore* [22,23] was used to quantify these coupling phenomena. We perform a simulation in the case of pine, the less favorable species in terms of permeability, using the actual size of the sample, the temperature schedule defined by our protocol and an external heat transfer coefficient of 25 W m^{-2} K^{-1}. As expected, we have obtained negligible temperature differences during the heat treatment regime: in spite of the exothermic and endothermic reactions, all temperatures, gas, sample surface and sample core, are within 0.1 °C throughout the treatment plateau. During the rapid temperature increase, the surface temperature is one degree below the gas temperature and we have obtained a temperature difference between surface and core of less than 0.4 °C. Unfortunately, as expected due to the hydric time constant, the situation is not as good during the drying phase. Due to evaporation, the sample temperature remains significantly lower than the gas temperature. For example, at 15 min, 5 min after the beginning of the 100 °C-plateau, the sample temperatures are equal to 70 °C and 54 °C, respectively, for surface and core. This temperature gradient corresponds to a time delay between surface and core in terms of moisture content: