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Lignin contributions to the nanoscale porosity of raw and treated lignocelluloses as observed by calorimetric thermoporometry

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ABSTRACT

Thermoporometry probes water in nanoscale confinement, the so-called freezing bound water (FBW). Although well established for characterization of delignified cellulosics, application and interpretation of thermoporometry has been elusive for lignin-containing biomass. Here we show that calorimetric thermoporometry discriminates two types of lignin contributions to the nanoscale porosity of a wide set of raw and treated lignocelluloses. First, the well-known role of lignin as pore filler is observed as delignification-promoted gains in FBW, mainly in pores of 10–200 nm. Second, lignocelluloses submitted to acidic aqueous treatments present an additional FBW contribution, mainly in pores <4 nm. This FBW at smaller dimensions is attributed to surface irregularities of the lignin aggregates left by the acidic treatments. Hence, our findings demonstrate that thermoporometry detects a confined water state associated with restructured lignin, thus contributing to the understanding of processes for biomass valorization.

1. Introduction

Lignocellulosic biomass is a vast renewable resource made mainly from structural carbohydrates (cellulose and hemicelluloses) and a complex aromatic macromolecule (lignin). These components are entangled in a hierarchical structure so as to form cell walls, tissues and, ultimately, entire plants. Deconstruction of lignocellulosic biomass into simpler, reactive molecules (*e.g.*, monomeric sugars) is a major goal toward biomass valorization (Lynd et al., 1999). However, biomass reactivity is often impaired by its compact structure that limits the transport of reactants, catalysts, and reaction products through the biomass porous structure. In particular, nanoscale pores within cell walls are thought to be critical for enzymatic catalysis, which requires accessibility for enzymes ~5 nm in size (Arantes and Saddler, 2011; Ding et al., 2012; Grethlein, 1985).

Lignin is usually thought as a pore filler, occupying intercellular spaces (middle lamella) as well as nanoscale voids in-between the fibrillar cellulosic network from secondary cell walls (Ding et al., 2012; Donaldson, 2001). Although this seems to be an appropriate picture for raw biomass, chemical processing can remove, restructure, and relocate the lignin (Pu et al., 2015). A class of processes that include dilute acid, steam explosion, and hydrothermal is here termed *acidic treatments*, where the acidity may result from high-temperature water autoionization, release of biomass acetyl groups (Garrote et al., 1999), or acid addition. Acidic treatments were reported to phase-separate lignin with formation of globular lignin aggregates (Donaldson et al., 1988; Donohoe et al., 2008; Langan et al., 2014; Pingali et al., 2010). How such restructured and relocated lignins contribute to biomass nanoscale porosity is an open question that we want to address.

Nanoscale pores in water-saturated cellulosic samples can be probed by calorimetric thermoporometry. The technique – also named cryoporometry or thermoporosimetry – is based on (1) the temperature depression of ice–water transitions occurring under nanoscale confinement and (2) calorimetric detection of the phase transition (Brun et al., 1977; Landry, 2005; Petrov and Furó, 2009). Most applications of thermoporometry to cellulosics have been based on step-melting programs starting from ≈−30 °C for characterization of delignified samples (Fahlén and Salmén, 2005; Maloney, 1998; Park et al., 2006). Recently, we expanded the potential of the method, decreasing freezing temperature to −70 °C and introducing several corrections in the analysis of step-melting thermograms (Driemeier et al., 2012).

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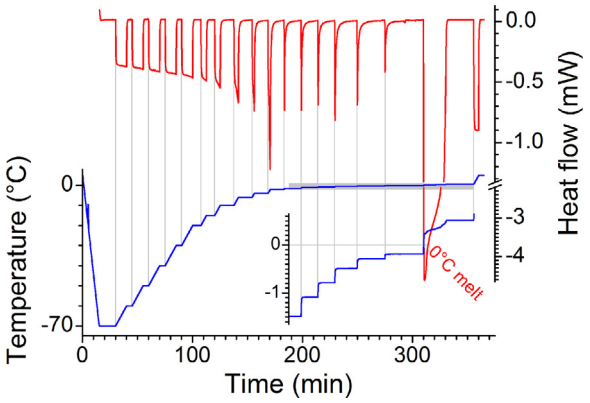

Fig. 1. The thermoporometry temperature program (blue) and an example of measured calorimetric response (from a sample of sugarcane rind hydrothermally treated and delignified). The most intense calorimetric signal results from 0 °C melting of free water. The inset expands the temperature scale of the gray-shaded area. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

After this analytical development (Driemeier et al., 2012), calorimetric thermoporometry was established as routine analysis in CTBE/CNPEM. Since then, wide range of samples has been characterized, including delignified (Driemeier et al., 2012) as well as lignified samples such as raw sugarcane tissues (Maziero et al., 2013). Over a thousand analyses were recorded in the last four years and distinct signatures in thermoporometric profiles have been observed in raw, delignified, and acidic treated lignocelluloses. In this article, these distinct thermoporometric signatures are demonstrated. Beyond lignin as pore filler, our results reveal characteristic pores (~<4 nm) that we attribute to be within the lignin aggregates left by acidic treatments.

2. Materials and methods

2.1. Samples for this study

Six lignocellulosic feedstocks were analyzed specifically for this study: sugarcane rind, sugarcane pith, sisal fiber, coconut fiber, pine sawdust, and eucalyptus sawdust. Sugarcane stalks were provided by Usina Ipiranga de Áçucar e Álcool Ltda. Stalks were cut in disks whose center (pith) was drilled out, separating it from the periphery (rind). Pith was later pressed and washed to remove sugars, while rind was cut in pieces, washed, and extracted (in soxhlet system, 24 h in *n*-hexane plus 24 h in water) for removal of waxes and residual sugars. The sisal fibers were purchased from Sisalsul Fibras Naturais. The milled (4 mm) coconut fibers were kindly provided by Laboratorio de Tecnologia da Biomassa from Embrapa. The eucalyptus and pine sawdusts were gently provided by Laboratório de Madeira e Estruturas de Madeiras (LaMEM) from Universidade de São Paulo.

These feedstocks were submitted to hydrothermal treatments (*i.e.*, pressurized hot water) performed in a 195 mL batch reactor at 180 °C for 1 h in a solid:liquid ratio of 1:10 (Garrote et al., 1999; Driemeier et al., 2015). Reaction products were washed until neutral pH. The hydrothermally treated solids were delignified (bleached) by the chloride method in an initial solution of 1% (m/m) sodium chloride and 0.3% (m/m) acetic acid mechanically stirred at 70 °C for 3 h, with addition of 0,12% of sodium chlorine and 0,04% of acetic acid after the first and second hours (Browning, 1967). Delignification was finished by filtration and washing with cold distilled water and methanol. All samples were air-dried for storage. Although air drying might promote some irreversible pore collapse, significant influence on the thermoporometric signatures was not observed.

Lignin contents in the hydrothermally treated samples were determined by the Klasson method, summing acid-insoluble (determined gravimetrically) and acid-soluble (determined by UV–visible spectroscopy) lignins (Novo et al., 2011).

2.2. Samples from lab record

In addition to the samples analyzed specifically from this study (Section 2.1), selected results from the CTBE/CNPEM records are presented in order to demonstrate the generality of the observed signatures in the thermoporometry profiles. The selected samples submitted to acidic treatments include: poplar wood submitted to steam explosion at either 160 °C or 200 °C, depithed sugarcane bagasse submitted to hydrothermal treatments at 170 °C for either 25 min or 90 min (Driemeier et al., 2015), and sugarcane bagasse submitted to dilute acid treatments in either 1.5% (m/v) H_3PO_4 or 1% (m/v) H_2SO_4 (Silva, 2014). The delignified samples selected from lab records were previously reported (Driemeier et al., 2012). They include a peracetic pulp from sugarcane bagasse, α-cellulose (acquired from Sigma–Aldrich), Celufloc 200 (acquired from Celuflok), two bleached eucalyptus kraft pulps (from Brazilian mills), and an eucalyptus pulp produced in assisted subcritical CO_2–ethanol–water (Pimenta 2005).

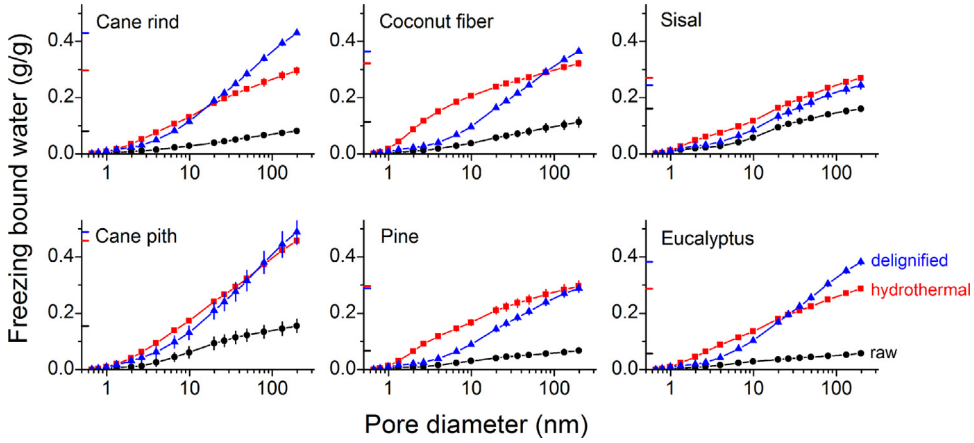

Fig. 2. Thermoporometry profiles for different feedstocks in raw, hydrothermally treated, and delignified states. Each profile is the cumulative distribution of freezing bound water presented as function of pore diameter in log scale. Error bars are standard deviation of duplicates, visible when exceeding symbol size. Ticks at the *y*-axes reproduce the profile maxima.