Developments in structural characterization of lignocellulosic biomass

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Introduction

Lignocellulose is an insoluble solid and, as such, has structure. This means that compositional analysis provide an incomplete description of lignocellulose. The missing structural information refers to spatial organization of the chemical components.

There are three distinct structural levels in lignocellulose (with their corresponding typical dimensions): *i)* cell wall components such as cellulose microfibrils (with ≈3 nm diameter); *ii)* cell walls and lumina (1-50 μm); and *iii)* cell aggregates forming the biomass particles in particulates (100 μm – 10 mm).

This work describes the CTBE effort to establish instrumentation and methods to characterize lignocellulose structural properties in these three levels. X-ray diffraction (XRD) is used to determine cellulosic materials crystallinity with a recently developed quantitative method [1]. Moreover, cellulose crystal sizes are also determined by XRD. Thermoporometry by Differential Scanning Calorimetry (DSC) measures nanometric pores in wet lignocellulose, as well as amounts of non-freezing interface water. Physisorption analysis informs on the specific surface area. Light-scattering particle sizing determines particle size distributions, envelope densities, and envelope surface areas. These analytical techniques were applied to raw and treated sugarcane bagasse as well as to commercial celluloses.

Results and Conclusions

Hydrothermal pretreatment as well as NaOH delignification applied to bagasse leads to an increase in average cellulose crystal sizes, as measured from the 200 XRD line width. This size increment is attributed to aggregation of neighbor cellulose microfibrils. An associated secondary effect is the reduction in crystal distortion, as measured by a decrease in unit cell *a* parameter.

Materials crystallinity was determined by XRD, with crystallinity defined as the ratio of crystal mass to total dry mass. This definition allows direct comparison to chemical compositions determined by chemical methods. Commonly, crystallinities were found to be higher than cellulose content, but never higher than holocellulose (cellulose plus hemicellulose) content. This fact, together with the dependence on crystal sizes, was interpreted as an evidence that hemicellulose adhered to cellulose underlying crystals may count as part of crystalline domains, as resolved by an XRD criterion. Moreover, results indicate very limited contribution of totally amorphous cellulose domains. It is alternatively proposed that most amorphous cellulose (and hemicellulose) is associated to the borders of crystalline domains.

The same novel XRD method was applied to several cellulosic materials, including pulps, filter paper, and microcrystalline celluloses. Crystal sizes and crystallinities determined by XRD were quantitatively related to non-freezing interface water determined from DSC thermoporometry. Our result

indicates that cellulose structural and water interaction parameters can be quantitatively related by sound physical models.

In other part of the work, bagasse particulates were produced by sieving and milling followed by characterization by N_2 physisorption and light-scattering particle sizing. Particle size distribution shifts as well as fibrous character modulation were achieved by controlling, respectively, sieve size and rotor speed in a centrifugal mill. Physisorption surface areas were found to correlate well with envelope surface areas derived from light scattering. Adsorption surface areas were divided in one original contribution (related to wall-lumen surfaces) plus novel areas (created by particle ruptures due to milling).

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Author publications

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[3] Driemeier C, Oliveira M.M, Mendes F.M, and Gomez E.O. (2011) *Characterization of sugarcane bagasse powders* (submitted).