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An experimental comparison of lignin yield from the Klason and Willstatter extraction methods

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ABSTRACT

This work compares the performance of two lignin extraction methods applied to several crops grown in Brazil and contributes to identify the biomass with more potential for generation of thermal energy from the point of view of its lignin content and properties. A full factorial (2^2) design involving two particle size distribution (105 to 500 μm and 1000 to 2000 μm) and two extraction methods (Klason and Wilstatter) were chosen as controlled factors for the tests, including the determination of granulometry, extractives and holocelluloses, higher heating values, and the proximate and ultimate analysis. Results showed that lignins obtained utilizing both methods have elevated higher heating values, suggesting they could generate thermal energy from thermochemical processes, mainly those lignins extracted from the Klason method. Even though the tendency for obtaining more lignin yield by using the Klason extraction method and fine particles was observed for almost all raw material tested, the statistical analysis suggested that for the experimental range studied the extraction method and the particle size distribution do not affect the lignin yields at 95% of confidence level (p-value <0.05), except the lignin yield obtained from sugarcane bagasse. For this biomass, the extraction method chosen led to relevant differences in the lignin yield (22.6% by using Willstatter to 24.9% by using Klason), suggesting that the lower pH level used by the Klason method promotes a more efficient lignin extraction.

Introduction

Lignin is of specialist's interest in several areas of science and industrial sectors, which are studying it for new practical applications (Hatfield and Fukushima, 2005; Mansouri and Salvadó, 2007; and Wang et al., 2009). In fact, lignin is expected to play an important role in the near future, once it can be used to produce thermal energy and byproducts (Hage et al., 2009; Matsushita et al., 2013; Sena–Martins et al., 2008). If industries of ethanol of second generation based on biomass grow, enormous amounts of lignins will be discharged as phenol wastes (Kim et al., 2009). Lignin can affect the transformation process of biomass into fermentable sugars in two ways: it can irreversibly absorb hydrolytic enzymes by blocking their action on cellulose, and due being hydrophobic it can also prevent the bloat of cellulose, decreasing the surface area accessible to the enzymes (Palonen et al., 2004). Chang and Holtzapple (2000) found that removing lignin is a dominant factor to enhance the enzymatic digestibility of biomass. Indeed, Draude et al. (2001) proved that removing 67% of lignin from wood pulp was sufficient to increase up to twice the rate of the cellulosic hydrolysis, increasing by almost three times the sugars resulting from this process of conversion. Similar results were also obtained from corn crops (Yang and Wyman, 2004).

Several works have been carried out aiming to study the lignin yields and its properties by using analytical methods such as pyrolysis, spectrometry, high performance liquid chromatography, fractionations and separations, among other techniques, which have been previously presented by Lalvani et al. (2000), Celeghini and Lanças (2001), Demirbas (2003, 2005, 2009), Yanhua et al. (2004), Huan et al. (2010), and Bikovens et al. (2010). Data about lignin contained in straws, husks and leafs of various crops are still scattered and scarce. Most of information is generally focused in characterizing lignin from wood (Beis et al, 2010; Buranov and Mazza, 2008; Domínguez et al., 2008).

Previous studies suggest the size and shape of particles affecting the properties of diverse materials during treatment processes, due to changes in the contact surface area (Bridgeman et al., 2007; Luo et al., 2009; and Shen et al., 2009). In addition, studying lignins and black liquor, Zhu and Theliander (2011) and Agarwal et al. (2011) evidenced the presence of more lignin by changing the pH and the temperature of the hydrolysis treatment. More studies aiming to verify if such variables substantially influence on lignin yields and their properties become necessary.

This work quantifies the lignin content of several crops, generating information about their characteristics and indicating these materials

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as potential sources for thermal energy generation. Two particle size distributions and two different methods of lignin hydrolysis extraction (Klason and Willstatter) were evaluated. For data treatment, a full factorial (2^2) analysis was used in order to know the effects between the particle size distribution and methods on lignin yields.

Materials and methods

The biomass samples analyzed in this study were obtained in farms and food processing plants located in both Santa Catarina and Paraná States, at South of Brazil. The specimens evaluated were: wheat straw (*Triticum aestivium*), corn straw (*Zea mays*), rice husks (*Oryza sativa*), sugarcane bagasse (*Saccharum officinarum*), wood chips (*Cedrelinga catenaeformis*) and elephant grass (*Pennisetum purpureum Schumach*). Fig. 1 shows the biomass samples analyzed in this study.

Four samples of each biomass were chosen for tests. The analysis was performed in duplicate utilizing biomass *in natura* and its respective lignin fractions. The measurements included the determination of the particle size distribution, extractives and holocelluloses, higher heating values, the proximate and ultimate analysis. The preparation of samples was based on the Technical Association of the Pulp and Paper Industry (TAPPI) T-264 (2007); T-257 (2012) and the American Society of Agricultural and Biological Engineers (ASABE) S593.1 (2011).

Feedstock properties

Samples of biomass were crushed using a knife mill (SOLAB), and the particle size distribution was performed using a set of standard sieves (Tyler mesh). The sieves had openings among 105–500 μm (150 and 32 mesh), 1000–2000 μm (16 and 09 mesh) and 4000 μm (5 mesh). Particles larger than 4000 μm and lower than 105 μm were not considered for tests. The procedure was based on the Brazilian Association of Technical Standards (ABNT) NBR-7402 (1982). Table 1 shows the particle size distribution of the six samples of biomass and the respective Sauter mean diameter (d_m) of particles, which was calculated according Eq. (1) (Howard, 1989):

$$d_m = \left(\sum \frac{x_i}{d_i}\right)^{-1} \quad (1)$$

Table 1
Mass fraction distribution and particle mean diameter of the biomass samples.

Sieve openings (mm)	d_i (mm)	Mass fraction, x_i (%)					
		Sugarcane bagasse	Corn straw	Wood chips	Rice husk	Elephant–grass	Wheat straw
2.000–4.000	3.000	0.503	0.411	0.402	0.441	0.433	0.453
1.000–2.000	1.500	0.312	0.397	0.395	0.279	0.381	0.396
0.500–1.000	0.750	0.125	0.162	0.119	0.178	0.131	0.112
0.105–0.500	0.3025	0.060	0.030	0.084	0.102	0.055	0.039
$\sum x_i/d_i$		0.740	0.617	0.832	0.907	0.753	0.692
d_m (mm)		1.35	1.62	1.20	1.10	1.33	1.45

The Sauter mean diameter represents the diameter of a sphere that has the same volume/surface area ratio as a particle of interest, and it is widely used in applications involving thermochemical processes, such as combustion and gasification of biomass. In Eq. (1), x_i is the fraction of mass of the sample retained by a particular aperture size and d_i, the arithmetic mean of two adjacent sieve aperture sizes.

In the proximate analysis the moisture content was determined using an oven maintained at 110 °C during 6 h until no further changes of weight occurred. In the determination of volatiles individual samples were placed inside porcelain crucibles with a lid and heated at 850 °C during 60 min using a vertical muffle furnace (QUIMIS) with heating capacity of up to 1100 °C. The determination of ashes was performed based on the American Society for Testing and Materials (ASTM) E-830 (2004) and D-1102 (2007). During tests samples were kept inside a muffle furnace and heated at 750 °C during 1 h until completly carbonized, the content of fixed carbon was determined by weight difference.

The ultimate analysis was performed utilizing an automated chemical analyzer (TRUSPEC-LECO, CHONS). In tests, 10 mg of an individual sample was evaluated, and the resolutions of the instrument for the basic elements were: carbon: 0.3 ppm or 0.5% R.S.D. (relative standard deviation), Hydrogen: 100 ppm or 1.0% R.S.D., nitrogen/oxygen: 40 p.p.m. or 0.5% R.S.D., and sulfur 5 p.p.m. or 1% R.S.D.

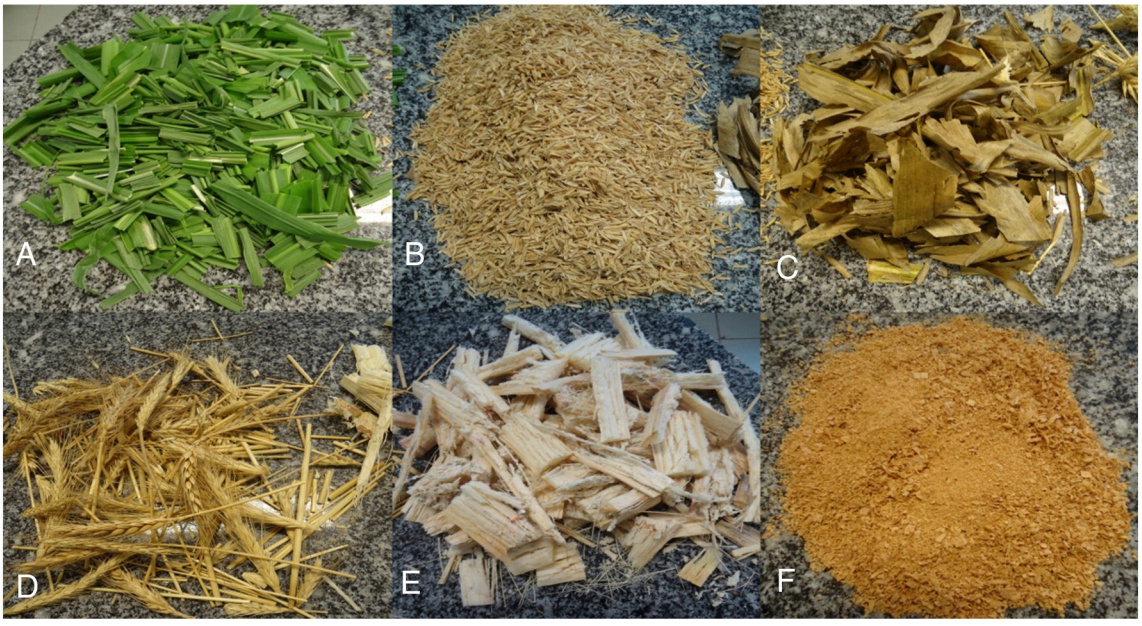

Fig. 1. Samples of the biomass analyzed in this work. a) Elephant grass, b) rice husks, c) corn straw, d) wheat straw, e) sugarcane bagasse, and f) wood chips.