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Assessment of chemical transformations in eucalyptus, sugarcane bagasse and straw during hydrothermal, dilute acid, and alkaline pretreatments

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ABSTRACT

The impact of hydrothermal, dilute acid, and alkaline pretreatments on the chemical structure of eucalyptus, sugarcane bagasse, and straw were compared with a view to their subsequent bioconversion into ethanol. Sugarcane bagasse and straw contain high amounts of extractives (15.0% and 12.2%, respectively), ash (2.3% and 7.9%, respectively), and silica (1.4% and 5.8%, respectively). If not properly corrected, the presence of silica would lead to the overestimation of the lignin, while high amounts of extractives would cause the overestimation of the content of sugars in biomass. Applying a novel approach through the use of complete mass balance, bagasse and straw were proven to contain lower amounts of lignin (18.0 % and 13.9%, respectively) than previously reported for these raw materials, and certainly a much lower amount of lignin than eucalyptus (27.4%). The syringyl to guaiacyl units ratio (*S*/*G*) for lignin in bagasse and straw (1.1 and 0.5, respectively) was lower than that for eucalyptus (2.7), indicating a different reactivity during chemical pretreatments. The xylan content in sugarcane bagasse and straw was much higher than that in eucalyptus, with a significantly lower degree of substitution for uronic acids and acetyl groups. The sugarcane straw showed the highest mass loss during the investigated pretreatments, especially under alkaline conditions, with a total biomass yield of only 37.3%. During the hydrothermal and dilute acid treatments, mostly hemicelluloses were removed, followed by the formation a significant amount of pseudo-lignin structures, while the alkaline pretreatment affected the lignin content. With eucalyptus, the formation of structures similar in their behavior to extractives (i.e., soluble in toluene and ethanol, subsequently referred to as "pseudo-extractives") was observed during all three pretreatments, with 12.4% for hydrothermal, 18.9% for dilute acid, and 8.7% for alkaline pretreatment. This information, combined with actual yields, should be taken into account when assessing the impact of pretreatments on the chemical composition and structure of biomass.

1. Introduction

There is a growing interest worldwide in the development of new methodologies to produce products, chemicals, energy, and fuels from renewable sources (Ragauskas et al., 2006). The forecast for the period 2010–2040 suggests that the global demand for oil consumption will increase by 26.2 %. At least part of these energy requirements could be supplied by renewable sources (Kralova and Sjöblom, 2010).

Sugarcane is one of the Brazil's main agricultural crops. The country's production for 2014/15 is 659 million tons of sugarcane cultivated on 9.1 million ha of land, with an average productivity of 72 tons/ha. Sugarcane is used mainly to produce sugar and ethanol (1st generation) from sucrose (Conab, 2014). Bagasse (sugarcane stalks) and straw (sugarcane tips and leaves) are the main wastes generated by the sugarcane industry. After being processed, sugarcane forms 14 % bagasse and 14 % straw on a dry weight basis (Oliveira et al., 2013). As a result, the generation of 92 million tons of bagasse and 92 million tons of straw is expected during the 2014/15 harvest.

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Sugarcane bagasse and straw are lignocellulosic biomasses that both have a great potential for their bioconversion to 2nd generation biofuels (Santos et al., 2014; Oliveira et al., 2013; Cardona et al., 2010). According to several authors, bagasse consists of 39–45 % cellulose, 23–27 % hemicelluloses, 19–32 % lignin, 1–3 % ashes, and 5–7% extractives (Canilha et al., 2011; Rabelo et al., 2011; Rocha et al., 2011; da Silva et al., 2010), while straw has a typical chemical composition of 33–45 % cellulose, 18–30 % hemicelluloses, 17–41 % lignin, 2–12 % ashes, and 5–17 % extractives (Santos et al., 2014; Costa et al., 2013; da Silva et al., 2010; Saad et al., 2008). Wood biomass is another possible raw material for bioethanol production. Eucalyptus is the most cultivated species in Brazil and is used for different industrial processes (Gonzáles-García et al., 2012). Eucalyptus has relatively low extractives and ash content, and more than 90% of its chemical composition is formed by cellulose, hemicelluloses and lignin. The typical chemical composition of eucalyptus is 46–49 % cellulose, 18–23 % hemicelluloses, 29–33 % lignin, 0.1–0.2% ash, and 2–5% extractives (Pereira et al., 2013; Zanuncio et al., 2013).

The biological conversion of lignocellulosic biomass to biofuels includes the following main steps: pretreatment, enzymatic hydrolysis, fermentation, distillation/dehydration to meet fuel specification and effluent treatment (Rubin, 2008). Pretreatment is one of the key steps for the efficient and cost-competitive conversion of lignocellulosic materials into bioethanol. The main role of pretreatment technologies is to reduce biomass recalcitrance (protection made by the complex characteristics of lignocellulose which avoid carbohydrates degradation by enzymes) and, thereby, to enable higher sugar yield through enzymatic hydrolysis (Pu et al., 2013; Foston and Ragauskas, 2012; Zhao et al., 2012; Chandra et al., 2007). Numerous methods, including dilute acid, hydrothermal, alkaline, organic solvents, ionic liquids (IL's), and ammonia fiber expansion (AFEX), have been developed to overcome biomass recalcitrance. Despite the different mechanism of each pretreatment, the goal for each of them is to increase cellulose accessibility (Meng and Ragauskas, 2014). The impact of these commonly applied pretreatment technologies on lignocellulosic structure has been recently reviewed by Hu and Ragauskas (2012).

Dilute acid pretreatment is considered to be the most promising pretreatment technology for enhancing sugar release by enzymatic hydrolysis (Pu et al., 2013; Yang and Wyman, 2008; Chandra et al., 2007). During the dilute acid pretreatment, biomass is subjected to the combined action of an acid pH, heat and pressure, with a residence times from 1 min to 1 h. Typically, sulfuric acid with a concentration of 0.4–2.0% (w/w) at a temperature of 140–200 °C is used. Hydrothermal pretreatment, also called autohydrolysis or hot water pretreatments just uses water as a reaction medium without additional chemicals and, therefore, has a low recycling and environmental cost. Usually performed in high temperature (140–220 °C) and pressure, the mildly acid condition of this treatment is result from the release of organic acids from biomass (Pu et al., 2013; Garrote et al., 1999). These acid pretreatments, dilute acid and hydrothermal, promote structural changes in lignin and cellulose, as well as solubilization of hemicelluloses (Santos et al., 2014; Lee et al., 2010), resulting in the increased specific surface area of fibres and increased plant cell wall pore size and, thus, reduced biomass recalcitrance. However, increasing dilute acid and hydrothermal pretreatments severity may cause the degradation of xylan to furfural, which is an inhibitor to the formation of ethanol during fermentation.

In the alkaline pretreatment, cellulose accessibility and hydrolysis are increased due the removal of lignin, some acetyl groups, and various uronic acid substitutions on hemicellulose (Chen et al., 2012). Alkaline treatment also results in swelling of cellulose, which leads to an increase in the internal surface area (Alvira et al., 2010). Sodium hydroxide (NaOH) is the alkaline source most often used. For sugarcane bagasse, this pretreatment has been shown to extract most of the lignin and significantly improve cellulose accessibility during the enzymatic hydrolysis (Pandey et al., 2000). Similar results were obtained for sugarcane straw (Hari Krishna et al., 1998).

Despite the existence of a significant amount of data regarding the chemical composition of various biomasses, the methodologies used to obtain these values differ in various studies, resulting in different numbers for the same materials. These discrepancies create a problem when comparing the results of various investigations, and there is an obvious need for the standardization of the methodologies used for the determination and reporting of the chemical composition of the new types of industrial lignocellulosic biomasses such as agricultural wastes (Canilha et al., 2012).

A correct evaluation of the chemical composition and its changes during the various pretreatments for novel types of lignocellulosic material (such as sugarcane bagasse and straw) is necessary for the assessment of the impact of various pretreatments on the chemical composition and structure of biomass.

The objectives of the present work were: (1) to perform a comprehensive chemical characterization of original and pretreated eucalyptus, sugarcane bagasse and sugarcane straw biomasses using a novel approach that takes into consideration each biomass constituent, including extractives and silica contents; and (2) to evaluate three types of pretreatments – hydrothermal, dilute acid, and alkaline – with respect to their impact on the chemical composition and structure of main biomass constituents, such as cellulose, lignin and hemicellulose. It is hoped that such information will contribute to a better understanding of the biomass recalcitrance phenomenon and provide useful guidance for researchers when deciding on the most suitable pretreatment technology for future bioconversion of these biomasses.

2. Experimental

2.1. Materials

A 7-year old clonal hybrid of eucalyptus (*Eucalyptus urophylla* × *Eucalyptus grandis*) was supplied by a pulp company in the form of chips. The 5-month old sugarcane (cultivar RB867515) bagasse and straw (leaves and tips) were supplied by Ridesa Experimental Station (Viçosa, Minas Gerais State, Brazil) in the form of small pieces (10 mm diameter). The sugarcane bagasse was obtained after chipping and pressing the sugarcane stalk. The sugarcane straw was collected in the field and fragmented in a shredder. All materials were stored in airtight plastic bags at room temperature prior to use. The chemicals used were sulfuric acid 95–97% and sodium hydroxide lentils (analytical grade), both purchased from Merck Milipore, Germany.

2.2. Methods

Samples of eucalyptus, bagasse and straw (100 g each) were subjected to various pretreatments: (1) hydrothermal; (2) acid – 4.5% H_2SO_4 w/w; and (3) alkaline – 15% NaOH (on a dry biomass basis). The liquor:biomass ratio used was 2:1 for eucalyptus and 7:1 for bagasse and straw (dry weight basis). All the pretreatments (1, 2, and 3) were performed in a Regmed reactor (2 L capacity) with constant agitation for 90 min to reach the set temperature (175 °C) and an additional 15 min for the pretreatment itself. After the treatment, the reactor was cooled, and the treated biomass was washed with an excess of water and centrifuged at 800 rpm for 4 min. The treated biomass was conditioned for 24 h at 23 ± 1 °C and 50 ± 2% relative humidity and then stored at room temperature in airtight containers.