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Effect of acid concentration and pulp properties on hydrolysis reactions of mercerized sisal

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ABSTRACT

The influence of sulfuric acid concentration (H_2SO_4 5–25%, 100 °C), crystallinity and fibers size on the hydrolysis reaction of sisal pulps were investigated, with the goal of evaluating both the liquor composition, as an important step in the production of bioethanol, and the residual non-hydrolyzed pulp, to determine its potential application as materials. Aliquots were withdrawn from the reaction media, and the liquor composition was analyzed by HPLC. The residual non-hydrolyzed pulps were characterized by SEM, their average molar mass and crystallinity index, and their size distribution was determined using a fiber analyzer. Sulfuric acid 25% led to the highest glucose content (approximately 10 g L^{-1}), and this acid concentration was chosen to evaluate the influence of both the fiber size and crystallinity of the starting pulp on hydrolysis. The results showed that fibers with higher length and lower crystallinity favored glucose production in approximately 12%, with respect to the highly crystalline shorter fibers.

1. Introduction

Energy consumption has increased over the last century as the world population has grown and more countries have become industrialized. Crude oil has been the primary resource for meeting this increased energy demand. Unlike fossil fuels, ethanol produced through the fermentation of sugars is a renewable energy source (Jamal, Alam, Salleh, & Nadzir, 2005) and can be used as either a partial or complete gasoline replacement. Biological feedstocks, such as sugarcane bagasse (a residue of the sugar and alcohol industries), containing appreciable amounts of sugars or other materials that can be converted into sugars can be used as raw materials for the production of so-called *second generation* or *new generation* ethanol (Balat, Balat, & Öz, 2008; Binod et al., 2010; Chen, Pen, Yu, & Hwang, 2011; He & Zhang, 2011; Kataria & Ghosh, 2011; Lee, Chen, Chang, & Yang, 2012; Sarkar, Ghosh, Bannerjee, & Aikat, 2012).

Sisal can be highlighted within the search for raw materials containing polysaccharides that can be converted to glucose. Brazil is the largest producer and exporter both of sisal fibers and of the manufactured products made from sisal in the world; however, the amount of value added to sisal is still low (besides fibers, sisal is primarily exported as twines, pads, rugs and carpets, Sindifibras, 2012). Sisal fibers are lignocellulosic and have a high cellulose content (approximately 70%, according to Megiatto, Hoareau, Gardrat, Frollini, & Castellan, 2007), which makes them a potential alternative to sugarcane bagasse and other sources for the production of second generation ethanol as well as both micro and nano scaled materials for high value-added items.

The production of bioethanol from lignocellulosic biomasses is very challenging because of the heterogeneous nature of this feedstock. Pretreatment using physical, chemical and physico-chemical methods (Chen et al., 2011; Eggeman & Elander, 2005; Galbe & Zacchi, 2007; Lacerda, de Paula, Zambon, & Frollini, 2012; Rocha, Gonçalves, Oliveira, Olivares, & Rossell, 2012; Sanchez & Cardona, 2008) are frequently used to disrupt the cellulose–hemicelluloses–lignin complex and make the cellulose and hemicellulose more accessible for conversion into sugars via hydrolysis, which allows the subsequent fermentation steps to occur (Porzio, Prussi, & Chiaramonti, 2011). The performance of physical pretreatments, such as biomass comminution (e.g., milling), is usually poor while the costs are high (Yang & Wyman, 2008). However, because the process consists of a reaction in heterogeneous media, the size and crystallinity of the suspended fibers are factors that deserve attention. Higher surface areas and lower crystallinity increase the accessibility of the solution that contains protons to the polysaccharides chains, in the case of acid hydrolysis.

Among the different chemical pretreatments, acid pretreatment is known to separate pentoses and hexoses, whereas alkali pretreatment (mercerization) is known to separate lignin from lignocellulosic biomass (Binod et al., 2012). The mercerization process, which was used as a pretreatment for the initial pulp because it had been proven efficient in a previous study (Lacerda et al., 2012), alters the fine structure and morphology of the fiber as well as the conformation of the cellulose chains (changing them

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from cellulose I to II). During this process, the material swells, the polysaccharide chains are rearranged, and the crystalline portion is usually diminished. These changes result in higher adsorption of reagents because mercerization increases the specific surface area of the fiber, which makes the chains more easily accessible (Ass, Belgacem, & Frollini, 2006).

In the present study, which is part of a broader one using both sisal lignocellulosic fibers and pulp (Almeida, Frollini, Castellan, & Coma, 2010; de Paula, Lacerda, & Frollini, 2008; Lacerda et al., 2012; Megiatto, Silva, Ramires, & Frollini, 2009; Megiatto, Ramires, & Frollini, 2010; Ramires, Megiatto, Gardrat, Castellan, & Frollini, 2010), the influence of sulfuric acid concentration, crystallinity and fibers size on the hydrolysis reaction of sisal pulps was investigated.

The stages of the acid hydrolysis of sisal pulp were reported, with the goal of evaluating the liquor composition (sugars and their decomposition products) as an important step in the production of bioethanol. The physicochemical and morphological characteristics of the non-hydrolyzed celluloses were also evaluated during this reaction to determine its potential application as materials. It should be noted that variations in the average length and thickness of the non-hydrolyzed cellulose were monitored from the beginning to the end of the reaction using a fiber analyzer. Such analysis is routinely used in the pulp and paper industries, and in the present study it has been used for monitoring the hydrolysis of pulps. The reactions described here were performed at 100 °C under different sulfuric acid concentrations (5–25% (v/v)) with various average fibers sizes and crystallinity for the initial pulp.

Sulfuric acid was chosen for this initial broad exploration to make the results comparable to those obtained from studies currently under consideration, which use oxalic acid (produced from renewable sources) (Lacerda, Zambon, & Frollini, 2011) and enzymes as catalysts.

2. Materials and methods

2.1. Materials

The sisal pulp used for all stages of this study was kindly provided by the company Lwarcel (Lençóis Paulistas, São Paulo, Brazil). In this company the lignocellulosic fiber was delignified through the *kraft* process (*elementary chlorine-free* bleaching sequence) to produce a pulp with an average length and thickness of 2.9 mm and 18.4 μm, respectively, and 86% ISO Brightness according to the supplier.

The Klason lignin was determined according to TAPPI T222 om-02 for the pulp received from the company. No lignin was detected. All pulp samples were milled by passing them through cutting knives using a vertical mill with feed hopper (MARCONI MA-048, 30 mesh stainless steel), and dried in a vacuum oven at 60 °C for 4 h.

The pulp was mercerized in a sodium hydroxide solution (NaOH pellets, Qhemis) (ASTM1695-07). Sulfuric acid (H_2SO_4, Qhemis) was used for the hydrolysis reaction. A 2% cupriethylenediamine (CED) solution (Qeel) was used for the viscometric analysis. Glucose, xylose, arabinose, formic acid, acetic acid, furfural and hydroxymethylfurfural (Sigma–Aldrich) were used as standards for high-performance liquid chromatography (HPLC).

2.2. Methods

2.2.1. Initial and residual non-hydrolyzed pulp characterization

2.2.1.1. Hemicellulose and α-cellulose content. The cellulose sample was added to a 17.5% NaOH solution (Sun, Lawther, & Banks, 1995), and the α-cellulose content was calculated from the final mass. The difference between the total mass and the α-cellulose mass found in the pulp sample corresponded to the hemicellulose content (Browning, 1967).

2.2.1.2. Scanning electron microscopy (SEM). LEO-440 equipment was used for the SEM analysis with a tungsten filament to generate electrons, as previously described (Ramires et al., 2010). The samples were dried in a vacuum oven for 4 h and covered with gold.

2.2.1.3. Average molar mass (MM_{vis}) by viscometry. Viscometry was used to determine the average molar mass of both the starting and non-hydrolyzed cellulose using aliquots withdrawn from the reaction medium at different times during the reaction. Cellulose was solubilized in a copper (II)-ethylenediamine:water solution (1:1 (v/v)), and the flow time in a glass capillary viscometer (Ubbelohde, f = 0.63 mm, AVS-350 Schott-Geräte) was measured.

The average molar mass of the samples was determined as previously described (Morgado, Frollini, Castellan, Rosa, & Coma, 2011; TAPPI T230 om-2008). All measurements were performed in triplicate.

2.2.1.4. Crystallinity index (CI) by X-ray diffraction. The initial and non-hydrolyzed cellulose obtained from five pulp samples withdrawn at t = 10, 30, 120, 240 and 360 min, which had been previously dried in a vacuum oven (60 °C, 4 h), was analyzed by X-ray diffraction to determine the CI using a universal X-ray diffractometer (URD-6 model, CARL ZEISS JENA, 40 kV/20 mA, λ(Cukα) = 1.5406 Å). As described elsewhere (Ass et al., 2006), the CI was calculated according to equation $CI = 1 - (I_1/I_2)$, where I_1 is the minimum intensity, which is proportional to the amorphous fraction of the cellulose ($18^\circ \leq 2\theta \leq 19^\circ$ for cellulose I and $13^\circ \leq 2\theta \leq 15^\circ$ for cellulose II), and I_2 is the maximum intensity, which corresponds to the signal for the crystalline fraction ($22^\circ \leq 2\theta \leq 23^\circ$ for cellulose I and $18^\circ \leq 2\theta \leq 22^\circ$ for cellulose II) (Buschle-Diller & Zeronian, 1992).

2.2.1.5. Average thickness and length of the fibers. The average thickness and length of the fibers were obtained using MorFi Compact (Techpap) equipment, which obtains results by measuring approximately 5000 fibers suspended in water. The MorFi automatic fiber-analysis system also provides the *fiber-occurrence density* (Millions-per-Gram), which enables the construction of a density map, ie a three-dimensional graph having the following characteristics: the values of average length in the x axis, the values of average thickness in the y axis, and the values of the fiber-occurrence density in the z axis.

2.2.2. Mercerization (ASTM1695-07)

The mercerization process was performed using 20 g of pulp suspended in 1 L of a 20 wt% NaOH solution for 3 h at 50 °C with stirring. The pulp was filtered, washed with deionized water until the initial pH of the washing water was reached, and dried first at room temperature and then in a vacuum oven at 60 °C for 4 h.

2.2.3. Pulp fractionation

The previously mercerized pulp was fractionated in a Retsch AS 200 vibratory sieve shaker (Embrapa Cattle-Southeast, São Carlos-SP, Brazil) with 106-μm, 75-μm, 45-μm and 25-μm pores.

2.2.4. Acid hydrolysis

For the hydrolysis reactions, 30 g of dried, milled and mercerized pulp were added to 900 mL solutions of between 5 and 25% (v/v) H_2SO_4 at 100 °C. All reactions were performed over a 6-h period. An H_2SO_4 concentration of 25% was chosen to perform the reactions in the next step with differing fibers size.