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Effects of average molar weight, crystallinity, and hemicelluloses content on the enzymatic hydrolysis of sisal pulp, filter paper, and microcrystalline cellulose

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ABSTRACT

Properties of cellulosic materials, such as average molar mass (MMvis), crystallinity index and hemicelluloses content may influence the efficiency of the enzymatic conversion of cellulose to glucose. Studies on the simultaneous influence of these parameters have been scarcely found in the literature. In the present study, the conversion of cellulose to glucose was investigated using cellulosic materials with different MMvis, crystallinity, and hemicelluloses content: microcrystalline cellulose (MCC, MMvis = 22104 g mol^{-1}, CI = 79%, no hemicelluloses detected), sisal pulp (SP, MMvis = 94618 g mol^{-1}, CI = 66%, hemicelluloses content = 2.6%) and filter paper (FP, MMvis = 98530 g mol^{-1}, CI = 63%, hemicelluloses content = 19.2%). During the reactions, aliquots were withdrawn and, in addition to the liquors, the unreacted cellulosic materials were evaluated by MMvis, CI, SEM, length and thickness, which can help further understand the reaction as a whole. The liquors were characterized by high-performance liquid chromatography (HPLC) and Miller's method (or DNS). The highest yield for the conversion of cellulose to glucose was observed for SP (88%), followed by MCC (64%) and FP (52%). The results indicated that the presence of high hemicelluloses content (FP) had a more significant interference effect than high crystallinity (MCC).

1. Introduction

A potential feedstock for biofuel production is lignocellulosic biomass, which is abundant and cheap (Haldar et al., 2016; Nguyen et al., 2017a,b; García-Torreiro et al., 2016). Lignocellulosic biomass is composed mainly of lignin, cellulose, and hemicelluloses. Lignin is strongly linked to cellulose and hemicelluloses (Rocha et al., 2015; Moodley and Kana, 2017) and is one of the interferents of enzymatic hydrolysis (Jiang et al., 2017; Brienzo et al., 2016; Avanthi and Banerjee, 2016; Hashmi et al., 2017). Hemicelluloses are compounded by different pentoses and hexoses sugar monomers (xylose, arabinose, mannose, and galactose) (Mussatto and Dragone, 2016). Cellulose is a linear polymer of glucose monomers linked by β-(1→4)-glycosidic bonds.

The conversion of cellulosic biomass into fermentable sugars can occur through acid or enzyme catalysis. In the present study, enzymatic hydrolysis was performed using *cellulases* consisting of three components: *(1) endo-b1-4-glucanases (endo-b1- 4-D-glucan 4-glucanohydrolase, EC 3.2.1.4); (2) exo-b1-4-glucanase or cellobiohydrolase (exo-b1-4-D-glucan 4-cellobiohydrolase, EC 3.2.1.91); and (3) b-glucosidase (EC 3.2.1.21)* (Shuddhodana et al., 2016). The action of *cellulases* is simultaneous, wherein endoglucanases randomly attack β-linked bonds in cellulose, releasing short chains and increasing the numbers of reducing and nonreducing terminals, while exoglucanases produce cellobiose and glucose from the ends of the cellulose chains, and β-glucosidases convert cellobiose and cello-oligosaccharides to glucose (Xue et al., 2017).

When the cellulosic material has a high crystallinity index (CI) and/or a high average molar mass, the conversion efficiency of the material to reducing sugars may decrease (Daza Serna et al., 2016; Karimi and Taherzadeh, 2016a, 2016b).

A high CI indicates that the cellulosic material presents chains with a high degree of ordination, which hinders the access of the cellulases to the chains, affecting the conversion to glucose (Alvira et al., 2010). A high average molar mass indicates a considerable amount of long chains, which can result in a network formed by numerous hydrogen bonds and render access of the cellulases to the chains difficult (Karimi and Taherzadeh, 2016b). In addition, the presence of hemicelluloses can hinder the contact of the enzymes with the cellulose chains, diminishing the effectiveness of the reaction (Sun et al., 2016).

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This study aimed to investigate how the combination of CI, average viscometric molar mass (MMvis), and hemicelluloses content would affect the efficiency of the cellulose enzymatic hydrolysis. Studies on the simultaneous influence of these parameters have been scarcely found in the literature. Thus, the enzymatic conversion of cellulose into glucose was evaluated for three different cellulosic materials, filter paper (FP), microcrystalline cellulose (MCC) and sisal pulp (SP), with different hemicellulose contents, as well as different MMvis and CI values.

FP was selected due its high hemicelluloses content, intermediate MMvis, and low CI when compared to the other selected cellulosic materials.

MCC is obtained by hydrolysis of cellulose chains under strong mineral acid catalysis (Deng et al., 2016), wherein the noncrystalline regions of cellulose and hemicelluloses (if present) are hydrolyzed, and the cellulose chains become shorter (lower degree of polymerization) and highly crystalline (Trache et al., 2016). In an industrial scenario, wood and cotton are the main sources of MCC (Trache et al., 2016).

SP was obtained from sisal (*Agave sisalana*) lignocellulosic fiber subjected to the Kraft and elemental chlorine-free processes (Supplier Company). As a result, the content of lignin and hemicelluloses extensively decreased. Prior to enzymatic hydrolysis, the pulp was submitted to alkali solution pretreatment, namely, mercerization (de Paula et al., 2012; Kaschuk et al., 2017; Lacerda et al., 2015, 2013, 2012), aiming to change the physicochemical properties of the sisal pulp. The mercerization decreased the hemicelluloses content from 15% ± 2 to 2.6% ± 0.2, which increased the cellulose content from 85% ± 2 to 97.4% ± 2, while the CI decreased from 74% to 66% and the MMvis decreased from 119357 $g mol^{-1}$ ± 590 to 94618 $g mol^{-1}$ ± 300 (Kaschuk et al., 2017). When compared to the other selected cellulosic materials (FP and MCC), SP was selected due to its low hemicelluloses content and its intermediate values of MMvis and CI.

In the present study, aliquots were withdrawn from the medium during the enzymatic hydrolysis reactions, and the unreacted cellulosic material was filtered off from the obtained liquor. Unreacted cellulosic materials were evaluated according to CI and MMvis, by scanning electron microscopy (SEM) and determination of length and thickness (MorFI). The evaluations of these properties during the reaction can yield important information on the changes in cellulosic material during enzymatic hydrolysis reactions, which in turn can help further understand the reaction as a whole. Despite the relevance of investigating properties of the unreacted biomasses during their enzymatic hydrolysis, this approach is seldom found in the literature.

The content of the liquors generated by the hydrolysis of FP, MCC and SP was analyzed by high-performance liquid chromatography (HPLC) and Miller's method (or dinitrosalicylic acid [DNS] method).

2. Methodology

The results concerning SP are related to a prior study (Kaschuk et al., 2017) and were used for comparison purposes in the present paper.

The starting cellulosic material and the steps performed for the characterization are shown in Fig. 1.

The sisal pulp (Fig. 1, SP) used (ISO whiteness of 86%, length and thickness of 2.9 mm and 18.4 μm respectively, according to the provider's information) was obtained from the leaves of *Agave sisalana* cultivated in the state of Bahia, a semi-arid region of Northeast Brazil

The SP and the FP were ground in a Marconi mill (MA048), and all cellulosic materials were dried by circulating air at 105 °C for 4 h before the characterizations and enzymatic hydrolysis reactions.

Fig. 2 shows the methodology for the enzymatic hydrolysis performed with SP, FP, and MCC.

The enzyme complex also contains high levels of β-glucosidases and hemicellulases (supplier data), which act in the conversion of cellulose and hemicelluloses (Kaschuk et al., 2017).

2.1. Characterizations

2.1.1. α-Cellulose and hemicellulose contents

A total of 10 mL of a solution of 17.5% of NaOH (Synth) was added to 1 g of cellulosic material. After 2 min, the sample was macerated for 8 min and 10 mL of 17.5% NaOH was further added. After 20 min, the final mass corresponded to α-cellulose content and the difference of mass (initial and final) to the hemicellulose content. The analysis was performed in triplicate.

2.1.2. Average molar mass (MMvis)

The viscometry was used to obtain the average molar mass (MMvis), following the standard TAPPI T230 om-2008 (TAPPI PRESS, 2008). The flow time of solutions of cellulosic materials in ethylenediamine cupric solvent 2% (Qeel):water (1:1(v/v)) was measured in a glass capillary viscometer (Ubbelohde, f = 0.63 mm, AVS-350 Schott-Geräte). The measurements were performed in triplicate.

2.1.3. Crystallinity index (CI)

Cellulose has two characteristic X-ray diffraction peaks, which refer to the crystallographic planes (Bragg angles, 2θ). The first peak ($\mathbf{I_1}$) relates to the noncrystalline part of cellulose (18° for cellulose I and 16° for cellulose II), and the second ($\mathbf{I_2}$) peak corresponds to the crystalline part (22° ≤ 2θ ≤ 23° for cellulose I and 18° ≤ 2θ ≤ 22° for cellulose II). Using the intensity values of those peaks and the equation (Eq. (01)) described by Buschle-Dillere Zeronian (Buschle-Diller and Zeronian, 1992), the crystallinity index was calculated.

$$\mathbf{Ic} = 1 - \frac{\mathbf{I1}}{\mathbf{I2}} \quad (01)$$

Eq. (01) is based on the Segal method (Segal et al., 1959), which was chosen in this study because of the ease of implementing it from powder diffractometer data.

The X-ray diffraction was obtained by X-ray diffractometer URD-6 model, CARL ZEISS JENA, the power of 40 kV/20 mA, and λ(Cukα) = 1.5406 Å. The CI analyses were performed in duplicate only for some randomly selected samples due to equipment facilities. The errors were approximately ± 3.0%.

2.1.4. Length and thickness

The MorFi Compact (Techpap) measures the length and thickness of fibers in a water suspension. In this paper, the variation in the length and thickness of fibers during enzymatic hydrolysis was observed to evaluate the changes caused by the enzyme complex on different pulp (Lacerda et al., 2013).

2.1.5. Scanning electron microscopy (SEM)

The surface of cellulosic materials was observed using scanning electron microscopy (SEM). The LEO-440 equipment with tungsten filament for generation of electrons was used. Cellulosic materials are not conductor materials, and for this reason, the samples were coated with gold (conductive material).

2.1.6. High-performance liquid chromatography (HPLC)

The equipment used was Shimadzu with index detector (RID-A Shimadzu) and column Aminex HPX9287H (300 × 7.8 mm BIO-RAD). The standards used were D-glucose (Sigma-Aldrich), D-xylose (Sigma-Aldrich), L-arabinose (Sigma-Aldrich) formic acid (49–51%, Sigma-Aldrich), acetic acid (49–51%, Sigma-Aldrich), and the eluent mixture of 0.005 mol L^{-1} sulfuric acid (Merck Chemicals) with a 0.6 mL min^{-1} flow rate at 45 °C.

2.1.7. Method DNS (Miller's method)

Two solutions were prepared from 10 g of 3,5-dinitrosalicylic acid (Vetec) dissolved in 200 mL of 2 molL^{-1} NaOH (Synth) aqueous solution, and 300 g of tartrate of sodium and potassium (Vetec) dissolved in

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