



Research paper

Effect of acidic pretreatment on the chemistry and distribution of lignin in aspen wood and wheat straw substrates

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ABSTRACT

In this work, aspen and wheat straw substrates were pretreated using aqueous dilute acid (DA) and chemimechanical (CM) pretreatment, and the impact of these pretreatments on biomass lignin was investigated. Here DA pretreatment refers to the acidic treatment of biomass powders and CM pretreatment refers to the acidic treatments of chips or stalks followed by disc refining. The resulting substrates were observed using advanced microscopy techniques to determine changes in lignin distribution throughout the fiber cell wall due to the acid treatments. Following acid treatment, lignin within the cell wall was divided into spherical or elongated bundles. The surface of DA and CM pretreated substrates were shown to differ, with CM pretreated aspen exhibited a more cellulose-rich surface. X-ray Photoelectron Spectroscopy data indicated reduced surface lignin on CM pretreated aspen and increased surface lignin on CM pretreated wheat straw. Fourier transform infrared spectroscopy (FT-IR) spectra illustrated changes in bands related to hemicellulose lignin, and surface hydroxyl content suggesting possible differences in lignin chemistry. It was hypothesized that differences in lignin distribution based on biomass type and pretreatment method were due to interactions between the chemical treatment and the mechanical size reductions steps. Particle size prior to chemical treatment could impact the movement of lignin onto sample surface, and chemical treatment prior to size reduction could impact the fracture plane during the downsizing process. It is expected that both these effects could impact lignin distribution within the sample and on the sample surface.

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1. Introduction

The native structure of lignocellulose is highly resistant to the breakdown of component cellulose by cellulase enzymes. This resistance, termed recalcitrance, results in low yields of glucose from the enzyme hydrolysis process, and is a major barrier to the efficient biochemical conversion of renewable biomass into ethanol and other fuels [1]. To counteract this recalcitrance, biomass generally undergoes a pretreatment step, using chemical and mechanical treatments to produce an altered lignocellulose substrate that is easily digested by enzymes. In the production of cellulosic ethanol, the pretreatment and enzyme hydrolysis steps are disproportionately expensive, accounting for about 40% of the production costs [2]. To lower the cost of both the enzyme hydrolysis and pretreatment steps, there needs to be better understanding of how specific components of lignocellulose impact

biomass recalcitrance and how pretreatment technology affects these components.

Lignin, one of the main structural polymers constituting lignocellulose, is an amorphous, cross-linked polyphenolic polymer formed from three aromatic alcohol precursors, viz. p-coumaryl, coniferyl and sinapyl alcohol [3,4]. Within the lignin structure, the respective aromatic parts of these alcohols are termed p-hydroxyphenyl (H), guaiacyl (G) and syringyl (S) units. These units are linked by either carbon–carbon (C–C) bonds, such as β -5, β -1, 5-5 and β - β linkages, or ether bonds (C–O–C), such as β -O-4, α -O-4, and 4-O-5 linkages [5]. Lignin also forms covalent bonds with hemicellulose at the α -carbon site and the C-4 in the benzene ring [6]. Unlike cellulose or hemicellulose, there is little or no pattern in unit ordering and bond type; and lignin chemistry is generally described based on the ratio of aromatic units, functional groups or bond types. Between different biomass types, there are notable differences in the amount of lignin and its specific chemistry. Softwood has the highest lignin composition, followed by hardwood and herbaceous biomass [3]. The lignin structure of softwood

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is primarily guaiacyl (G) type lignin, named due to being over 90% derived from coniferyl alcohol, while hardwood, straws and grasses contain guaiacyl-syringyl (G-S) type lignin. Typically, hardwood lignin is generally 50% derived from coniferyl and 50% from syringyl alcohols, while grasses have 40% coniferyl, 40% syringyl and 20% derived from coumaryl alcohol and other aromatic derivatives [4,6].

Lignin is understood to impact enzyme hydrolysis via physically blocking cellulose surface area, and by and by immobilizing cellulase enzymes through non-productive binding [7,8]. As a physical barrier, lignin surrounds the outer surface of the cell wall in the form of middle lamella, and also occupies the pore space between cellulose microfibrils within the cell wall [9,10]. Lignin is also closely associated with cell wall carbohydrates in the form of the lignin-carbohydrate complex, wherein lignin forms covalent bonds with xylose and other hemicellulose sugars [11]. This reduces the cellulose surface available for enzyme adsorption. Non-productive binding occurs when cellulase enzymes are brought and bound to the lignin surface by adhesive forces. Once the cellulase and lignin are irreversibly bound, the former is no longer available to hydrolyze cellulose, thus reducing overall enzymatic activity during the hydrolysis reaction. Previous studies have indicated that hydrophobic interactions between lignin and cellulase contribute to the phenomena of non-productive binding [12,13]. Separate work by Berlin et al. [8] and [14] has also suggested that –OH, and partially charged interactions may also contribute to the forces involved in enzyme adsorption, though the specific importance of each interaction is not known.

The effect of pretreatment on lignin varies significantly depending on the method used. Methods utilizing organic solvents, alkaline chemicals or bisulfite can either partially or completely remove component lignin, producing lignin byproducts with altered chemical structure, e.g. lignosulfonate [15,16]. While the removal of lignin is ideal for producing a substrate that is easily digested by cellulase enzymes, applicable methods will typically be more expensive, e.g. organosolv, or require more chemicals, e.g. sulfite pretreatment. In comparison, hydrothermal pretreatments utilize high-temperature aqueous or steam treatment to remove hemicellulose rather than lignin [17]. These methods are generally acidic, either from the addition of acid catalyst, e.g. aqueous dilute acid, or from the release of acetyl groups at high temperature, e.g. autohydrolysis or steam explosion. These pretreatments remove very little lignin, but are still effective at increasing substrate digestibility by cellulase enzymes [18,19].

Aqueous dilute acid pretreatment is a type of hydrothermal pretreatment wherein ground biomass is treated in dilute sulfuric acid liquor at 140–210 °C, resulting in cellulose swelling and the removal of hemicellulose. This method has been used for both woody and herbaceous biomass, though it is less common for wood [20–22]. The effect of dilute acid pretreatment on lignin is understood to be relatively complex, with alterations to both the physical distribution of lignin within the cell wall and to lignin chemistry. Donohoe et al. [23] examined the phenomenon of lignin redeposition for corn stover which had undergone dilute acid pretreatment. Following acid treatment, they found depositions of lignin spheres located on the particle surface, while within the cell wall lignin had coalesced into discrete bundles. It was suggested that during acid pretreatment, lignin coalesces and is extruded out of the cell wall, with a portion redepositing on the surface in the form of spheres. Further work by Li et al. [24] has indicated that redeposition of lignin can significantly reduce hydrolysis yields. Alterations to lignin chemistry following dilute acid pretreatment have also been noted. Samuel et al. [25] examined the structure of ball-milled switchgrass lignin before and after acid treatment, and found that there was a 36% decrease in the predominant β -O-4 bond, and a decrease in the ratio of syringyl to guaiacyl units (S/G).

Analysis of redeposited lignin following dilute acid pretreatment of poplar showed that the lignin droplets had higher S/G ratios than the original lignin [24].

In our previous studies [26,27], a method termed chemimechanical pretreatment was developed based on aqueous dilute acid pretreatment methodology. During chemimechanical pretreatment, wood chips undergo dilute acid treatment followed by a disc-refining step to produce a fibrous substrate. This configuration was able to decrease net specific energy usage up to 95% during the mechanical downsizing step and increase substrate digestibility when compared to aqueous dilute acid. It is hypothesized that one reason for this increased digestibility is differences in lignin structure or distribution between dilute acid and chemimechanical pretreated substrates. As the mechanical downsizing step occurs after chemical treatment, the chemimechanical substrates will most likely not have the same pattern of lignin redeposition as seen in dilute acid substrates. Furthermore, the acid treatment could alter the fracture point or pattern of deconstruction during the subsequent disc-refining step, which results in the formation of different substrate surface.

The present work investigates changes to lignin structure following acidic hydrothermal pretreatment, including lignin morphology and distribution within the cell wall and on the substrate surface. Differences in lignin and cellulose chemistry were also investigated using Fourier Transform Infrared (FT-IR) and X-ray photoelectron (XPS) spectroscopy. By better qualifying these changes, current pretreatment technology can be optimized by targeting process characteristics that minimize unwanted changes to substrate lignin. As a further investigation of process effects on lignin, both chemimechanical and dilute acid pretreated biomass were compared to native (mechanically-refined) biomass. A comparison of these two technologies will better qualify how the interaction between the chemical and mechanical treatment impacts the structure of lignin in the pretreated substrate.

2. Materials and methods

2.1. Materials

Aspen wood chips were graciously donated by AV Nackawic, located in Nackawic, NB, Canada. The chips were prepared from *Populus balsamifera* harvested in New Brunswick, and were sampled from wood chip storage at the Nackawic plant during the winter of 2012. Time of harvest and chain of custody prior to delivery at AV Nackawic are unknown, and it is possible that this information could be relevant to the substrate factors investigated in this paper. After delivery, oversized and undersized aspen wood chips were removed using a wood chip classifier, and the remaining chip size was less than 8 mm in thickness, and between 13 mm and 32 mm in length and width, respectively. Aspen wood chips were sealed and stored at 4 °C before pretreatment and analysis. *Triticum aestivum* (wheat-straw) was received from College of Agriculture and Bioresources at the University of Saskatchewan in Saskatoon, SK, Canada. This feedstock was originally procured from a local Saskatchewan farm during the summer of 2011. During harvest, the wheat-straw was in the ripening stage, particularly the “kernel hard” phase. Wheat straw was dried to 10–20% water mass fraction, cut into 2 inch segments, then sealed and stored at 4 °C before pretreatment and analysis. The chemical reagents were purchased from Sigma–Aldrich (St. Louis, MO, USA) and used as received.

2.2. Sample preparation

Wheat straw (WS) and aspen wood (AP) underwent either a chemimechanical pretreatment method, dilute acid pretreatment

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