



Comparison of laboratory delignification methods, their selectivity, and impacts on physiochemical characteristics of cellulosic biomass



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HIGHLIGHTS

- ▶ Delignification was performed employing sodium chlorite–acetic acid and peracetic acid.
- ▶ Various raw and pretreated biomass solids and pure cellulose were used.
- ▶ Delignification selectivity and effects on cellulose structure were determined.
- ▶ Peracetic acid was more selective than sodium chlorite–acetic acid.
- ▶ Cellulose MW, reducing ends, and CrI were affected less in delignification with PAA.

ARTICLE INFO

Article history:

Received 7 October 2012

Received in revised form 3 December 2012

Accepted 5 December 2012

Available online 13 December 2012

Keywords:

Delignification
Selectivity
Cellulose
Crystallinity
Reducing ends

ABSTRACT

Two established delignification methods employing sodium chlorite–acetic acid (SC/AA) and peracetic acid (PAA) are often used, and are reportedly highly selective. However, these reports are mostly for highly recalcitrant and unpretreated softwoods and hardwoods species, and information for less recalcitrant lignocellulosic feedstocks and pretreated biomass is scarce. Furthermore, the effects on cellulose structure are not documented. Thus, in this study, delignification kinetics and selectivity were evaluated when SC/AA and PAA were applied to untreated switchgrass, poplar, corn stover, and pine sawdust; poplar subjected to AFEX, controlled pH, lime, and SO₂ pretreatments; and the cellulose model compounds. Both methods proved effective in removing >90% lignin, but selectivity for lignin and carbohydrates removal was substrate and pretreatment dependent. For untreated biomass, PAA was more selective in removing lignin than SC/AA; however, both methods were less selective for pretreated solids. Cellulose characterizations revealed that PAA had less pronounced impacts on cellulose structure.

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1. Introduction

Cellulose, hemicellulose, and lignin are three major components of lignocellulosic biomass, with amounts varying with biomass types (hardwood, softwood, agricultural residues, and energy crops), primary vs. secondary cell walls, ages, and locations (Chundawat et al., 2010; Wyman, 1990). Lignin is believed to surround cellulose and hemicellulose as a complex structure that makes cellulosic biomass highly recalcitrant to enzymes, pathogens and

microorganisms (Lynd et al., 1991; Studer et al., 2011). To understand the complex structure of cellulosic biomass and the impact of biomass features on its enzymatic digestibility, delignification is often performed by two common laboratory methods: acidified sodium chlorite or peracetic acid (Chang and Holtzapple, 2000; Ding et al., 2012; Ishizawa et al., 2009; Naran et al., 2009). The sodium chlorite–acetic acid (SC/AA) method, originally known as the Wise method (Wise et al., 1946), is usually performed at 60–70 °C for 4–8 h with successive addition (every hour or two) of fresh sodium chlorite and acetic acid at loadings of 0.3–0.6 g sodium chlorite/g dry biomass and 0.1–0.6 ml acetic acid/g dry biomass (Ahlgren and Goring, 1971; Hubbell and Ragauskas, 2010; Timell, 1961). Whereas, peracetic acid (PAA) delignification is performed at more moderate conditions: 25 °C with PAA loadings of 4–5.5 g/g dry biomass and times of 24–48 h (Chang and Holtzapple,

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2000; Poljak, 1948; Zhu et al., 2008). The SC/AA method has become an established mostly for softwoods and proven to be highly selective at less harsh conditions (Ahlgren and Goring, 1971; Jungnikl et al., 2008). Similarly, PAA delignification of poplar wood was shown to be highly selective in terms of acetate removal (<14%) (Chang and Holtzapfle, 2000). However, these two methods have not been evaluated for their selectivity and impacts on other biomass features for considerably lesser recalcitrant feedstocks such as agricultural residues and energy crops. Furthermore, delignification by these two methods and others such as alkaline peroxide is often performed on pretreated biomass to evaluate the effects of residual lignin on biomass digestibility (Ishizawa et al., 2009; Kumar et al., 2012; Selig et al., 2009; Yang et al., 2002).

It is well known that most leading thermochemical pretreatments remove, dislocate, and/or change lignin structure during pretreatment, and, therefore, the residual lignin after pretreatment is physicochemically different from that in the untreated starting material (Hu and Ragauskas, 2011; Kumar et al., 2009; Samuel et al., 2010; Sannigrahi et al., 2008). However, highly selective lignin removal is important to pinpoint its effects on biomass digestibility but has rarely been reported for application of PAA or SC/AA to pretreated biomass. Furthermore, the chemical reagents employed to delignify cellulosic biomass are known oxidizing agents and, therefore, can affect cellulose reactivity through oxidation (Xu et al., 2009) and structural changes. For example, Ishizawa et al. showed that following SC/AA delignification, Avicel cellulose reactivity was unchanged but amorphous cellulose suffered a loss in reactivity (Ishizawa et al., 2009), most possibly due to oxidation of reducing ends. Hubbell and Ragauskas (Hubbell and Ragauskas, 2010) consistent with a study by Kumar et al. (Kumar et al., 2009) showed that extensive delignification of pure cellulose via the SC/AA method can affect cellulose degree of polymerization (DP). However, such data is not available for PAA delignification.

In this study, delignification kinetics and lignin selectivity of SC/AA and PAA were evaluated for untreated switchgrass (SWG), poplar, corn stover (CS), and pine sawdust (PSD) and for poplar pretreated by leading pretreatment technologies of ammonia fiber expansion (AFEX), controlled pH (CpH), lime, and sulfur dioxide (SO₂). To determine the effects of delignification on cellulose structure, gel permeation chromatography, NMR, and FT-IR analysis were applied to solids delignified by these two methods. Furthermore, to evaluate the effects of the delignification methods on cellulose reducing ends and crystallinity, cellulose model compounds were also subjected to SC/AA and PAA delignification.

2. Methods

2.1. Substrates and reagents

Switchgrass (*Dacotah*, *P. virgatum*; ¼ inch) was generously provided by Ceres, Inc. (Thousand Oaks, CA), more information on the material can be found elsewhere (Shi et al., 2011). Corn stover (¼ inch) was kindly provided by National Renewable Energy (NREL) in Golden, Colorado. Poplar (¼ inch) was graciously provided by Dr. Venkatesh Balan at Michigan State University, MI. Poplar solids pretreated by some of the leading pretreatments were prepared by the Biomass Refining Consortium for Applied Fundamentals and Innovation (CAFI) partners as follows: ammonia fiber expansion (AFEX) by Dr. Bruce Dale at Michigan State University, controlled pH (CpH) by Dr. Michael Ladisch and Dr. Nathan Mosier at Purdue University, lime by Dr. Mark Holtzapfle at Texas A&M University, and SO₂ by Dr. Jack Saddler at the University of British Columbia. The pretreatment conditions for these technologies are reported elsewhere (Kumar et al., 2009). Pine sawdust (PSD) was obtained from Dr. Joseph Norbeck's laboratory at the

Center for Environmental Research and Technology (CE-CERT), University of California, Riverside. Avicel® PH 101 cellulose (Lot No. BCBD6923V, Fluka), cotton linter (Lot No. 090M0144V), α-cellulose (Lot No. 050M0140V), and peracetic acid (32 wt.%, Batch No. 53796CM) were purchased from Sigma–Aldrich (St. Louis, MO, US). Glacial acetic acid (Acros, Lot No. B0512763) and unstablized sodium chlorite (80% purity, Acros organics, Lot No. B0130435) were from Fisher Scientific (Pittsburgh, PA).

2.2. Delignification

Prior to all experiments, Dacotah SWG was washed several times with hot DI water (80 °C) to remove free non-structural sugars that have been shown to be present in significant amounts (Garlock et al., 2011; Shi et al., 2011). The washed switchgrass was squeezed by hand to remove excess water and then dried in a 45 °C incubator (Model No. 472960, Labline, Melrose Park, IL) for several days. Other substrates were used as received.

2.2.1. Sodium chlorite–acetic acid (SC/AA)

Solids were delignified at 70 ± 2 °C in a water bath (Model 10 I, Cole-Parmer, Vernon Hills, IL) with an initial liquid to solids ratio of 32. Five grams of dry biomass was weighed into 250 ml Erlenmeyer flasks (Fisher Scientific, Pittsburgh, PA) in duplicates, and then 160 ml of deionized (DI) water was added followed by 0.6 g/g dry biomass of sodium chlorite (NaClO₂) and 0.6 ml/g dry biomass of acetic acid. The slurry was thoroughly mixed by shaking the flasks, and then a 50 ml Erlenmeyer flask was inverted in the neck of the reaction flask. The flasks were incubated in a fume hood at 70 °C with intermittent mixing, and fresh charges of sodium chlorite and acetic acid were added to the reaction every 2 h for up to 8 h. Controls with biomass and just water were also run under identical conditions. Similarly, pure cellulose model compounds were subjected to the same delignification conditions at 70 °C for 6 h. After reaction, the slurry was vacuum filtered on a glass fiber filter to separate the liquid from the solids (Cat No. 09-804-110A, Fisher Scientific, Pittsburgh, PA), and the solids were repeatedly washed with room temperature DI water until the pH of the filtrate was nearly neutral. Solids were carefully scraped off the glass fiber filter paper and collected in Ziplock bags. For mass balances, the wet weight of the delignified solids was recorded, and the solids moisture content in triplicates was analyzed using a Halogen moisture analyzer (MX5, Mettler Toledo, Columbus, OH). The amount of biomass recovered (yield) following delignification was calculated as:

Biomass recovery (yield; Y_B), % = 100 * [Amount of wet biomass recovered after reaction (g) * (100-% Avg. moisture content of the recovered solids)]/Initial amount of dry solids (g).

2.2.2. Peracetic acid (PAA)

Following the procedure of Chang and Holtzapfle, peracetic delignification was performed in duplicates at 25 ± 2 °C and 5 wt.% solids loadings for 24–48 h (Chang and Holtzapfle, 2000). The reaction was conducted in 250 ml Erlenmeyer flasks (Fisher Scientific, Pittsburgh, PA) heated in a temperature controlled water bath (Model 10L, Cole-Parmer, Vernon Hills, IL). PAA loadings of 0.75 g/g dry solids, 2.0 g/g dry solids, 3.5 g/g dry solids, and 5.5 g/g dry solids were used. All reactions were conducted for 24 h at all loadings except 5.5 g/g dry solids, which was run for 48 h. For cellulose model compounds, the reaction was only conducted at a PAA loading of 5.5 g/g dry solids at 25 °C for 48 h. After the reaction, the slurry was vacuum filtered, and the solids were washed repeatedly with room temperature DI water until the filtrate pH was close to neutral. Solids were collected, and the moisture content was determined as described in the previous section for SC/AA.

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