Carbohydrate Polymers 92 (2013) 334–344

Contents lists available at SciVerse ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Sugar yields from dilute oxalic acid pretreatment of maple wood compared to those with other dilute acids and hot water

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ARTICLE INFO

Article history:
Received 19 June 2012
Received in revised form
23 September 2012
Accepted 25 September 2012
Available online 2 October 2012

Keywords:
Enzymatic hydrolysis
Maple wood
Oxalic acid
Pretreatment
Xylooligomers

ABSTRACT

Dilute oxalic acid pretreatment was applied to maple wood to improve compatibility with downstream operations, and its performance in pretreatment and subsequent enzymatic hydrolysis was compared to results for hydrothermal and dilute hydrochloric and sulfuric acid pretreatments. The highest total xylose yield of ~84% of the theoretical maximum was for both 0.5% oxalic and sulfuric acid pretreatment at 160 °C, compared to ~81% yield for hydrothermal pretreatment at 200 °C and for 0.5% hydrochloric acid pretreatment at 140 °C. The xylooligomer fraction from dilute oxalic acid pretreatment was only 6.3% of the total xylose in solution, similar to results with dilute hydrochloric and sulfuric acids but much lower than the ~70% value for hydrothermal pretreatment. Combining any of the four pretreatments with enzymatic hydrolysis with 60 FPU cellulase/g of glucan plus xylan in the pretreated maple wood resulted in virtually the same total glucose plus xylose yields of ~85% of the maximum possible.

1. Introduction

Ever increasing energy demands and pressing environmental challenges underline the importance of developing sustainable energy sources, and cellulosic biomass provides the only large-scale, low-cost resource from which we could produce enough liquid fuels to replace substantial fossil sources that dominate current energy use and we rely on so heavily for transportation (Brandt, 2010; Kerr, 2011). According to a joint study by the U.S. Department of Energy and U.S. Department of Agriculture, the quantities of cellulosic biomass available annually for conversion into renewable fuels in the US increases from about 119 million dry tons currently to about 129 million dry tons in 2030, at a price of less than $80 per dry ton for forestry biomass and less than $60 per dry ton for agricultural biomass ("U.S. Billion-Ton Update: Biomass Supply for a Bioenergy and Bioproducts Industry," 2011). Consistent with the 2005 billion ton study, one billion dry tons of cellulosic biomass could be converted into enough fuels to displace about 30% of current U.S. petroleum consumption ("U.S. Billion-Ton Update: Biomass Supply for a Bioenergy and Bioproducts Industry," 2011).

Red maple (*Acer rubrum*), also known as scarlet maple, swamp maple, soft maple, Carolina red maple, Drummond red maple, and water maple, is one of the most desirable woody materials among cellulosic feedstocks because it grows fast with good form and quality (Korkut & Guller, 2008; Mian & Timell, 1960). Due to its ecological flexibility and adaptability to a wide range of microhabitats, red maple is one of the most abundant trees in eastern North America (Hutnick & Yawney, 1961; Little, 1979; Mian & Timell, 1960; Mittal, Chatterjee, Scott, & Amidon, 2009a). Similar to other hardwoods and grasses, red maple is comprised of hemicellulose, cellulose, and lignin. Hemicellulose is a heterogeneous polysaccharide whose building blocks include xylan, uronic (in methylated form in hardwoods) and acetic acid substitutes, arabinan, arabinoxylan, arabinogalactan, glucomannan, galactoglucomannan, and xyloglucan (Heredia, Jimenez, & Guillen, 1995; Mitchell & Ritter, 1940; Scheller & Ulvskov, 2010; Wedig, Jaster, & Moore, 1987). Furthermore, xylan typically comprises the largest fraction of many hardwoods, grasses, and agricultural residues. Xylan chains in hemicellulose can be broken down by hydrolysis to oligosaccharides and xylose, with subsequent xylose dehydration to furfural and formic acid (Lavarack, Griffin, & Rodman, 2002; Mamman et al., 2008; Mosier, Wyman, et al., 2005; Roberto, Mussatto, & Rodrigues, 2003). Since hemicelluloses can make up about 20–30% of cellulosic biomass in such plants, its utilization is very important

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http://dx.doi.org/10.1016/j.carbpol.2012.09.070

to achieving the high yields vital to commercial success (Foust, Aden, Dutta, & Phillips, 2009; Hamelinck, Hooijdonk, & Faaij, 2005). Many studies have focused on sugar production from hemicellulose for fermentation to ethanol, with pretreating biomass at temperatures of about 140–210 °C releasing most of the xylan into the aqueous phase as monomers and oligosaccharides; most of the carbohydrates left in the solids can be converted into monomers in a subsequent enzymatic hydrolysis step (Humbird et al., 2011). Adding dilute acid generally improves overall sugar yields and substantially reduces the oligomeric fraction, improving compatibility with state-of-the-art fermentations (Humbird et al., 2011; Wyman et al., 2011). However, in addition to hemicellulose sugars for fermentation to ethanol, other products such as furfural and xylitol can be made from these constituents by thermochemical reactions to provide reactive intermediates for catalytic conversion to hydrocarbon fuels and chemicals (Huber, Cortright, & Dumesic, 2004; Huber, Chheda, Barrett, & Dumesic, 2005).

Dilute sulfuric acid has achieved good yields of monomeric sugars from hemicellulose in maple wood as well as many other cellulosic materials (Wyman et al., 2011). Hydrochloric acid has also been shown to improve furfural yields from biomass (Hu, Lin, Liu, & Liu, 2010; Mittal, Chatterjee, Scott, & Amidon, 2009b). However, such inorganic acids require neutralization and removal to avoid negative effects on downstream processing and can be particularly problematic for catalytic processing of sugars from pretreatment into hydrocarbon fuels (Foust et al., 2009). Thus, in this study, an organic acid was applied to breakdown hemicellulose into sugars to improve compatibility with downstream catalytic reactions.

Because oxalic acid has been shown to offer significant energy savings in pulping operations and its high pK_a value makes oxalic acid much more acidic than formic (Xu, Thomsen, & Thomsen, 2009b), acetic (Xu, Thomsen, & Thomsen, 2009a), and maleic acids (Kootstra, Beeftink, Scott, & Sanders, 2009), which have been used for biomass pretreatment (Kenealy, Horn, & Houtman, 2007), this study applied oxalic acid to breakdown the hemicellulose in maple wood into sugars, and the sugar yields were compared to those with dilute sulfuric and hydrochloric acids with the same material. Although hydrothermal pretreatment generally realizes somewhat lower yields, it has been successfully applied to many types of biomass in reactors ranging in size from bench top to pilot scale (Kim, Mosier, & Ladisch, 2009; Mosier, Hendrickson, et al., 2005; Overend & Chornet, 1987) and offers advantageous features that include low chemical inputs and good compatibility with downstream catalytic processing. In this paper, glucose and xylose yields from pretreatment and subsequent enzymatic hydrolysis of red maple by each of these four options were compared.

2. Materials and methods

2.1. Substrate and reagents

Red maple wood from Auburn, NY was provided by Mascoma Corporation, Lebanon, NH and shipped as fresh sawdust with ~35% moisture content. Upon receipt, the fresh wet maple wood was air dried for 30 days to a 7–10% moisture content, sealed in heavy duty zipped bags, and stored in a laboratory freezer at −18 °C until use. Before pretreatment or analysis, the air-dried wood was milled to pass through a 1/2 mm interior sieve (Mesh no. 35) using a laboratory mill (Model 4, Arthur H. Thomas Company, Philadelphia, PA).

All sugars, 5-hydroxymethyl-2-furaldehyde (purity 99%, catalog no. W501808-1G-K; lot no. 67196EJ), and oxalic acid (purity 98%, catalog no. 194131, lot no.: 0001434315) were purchased from Sigma–Aldrich (St. Louis, MO). Reagent grade furfural (purity >99%, catalog no. F-94-500, lot no. 33796TJ) and acetic acid (glacial, catalog no. A38-500, lot no. 063552) were purchased from Fisher Scientific (Pittsburgh, PA). Spezyme® CP cellulase (62 FPU/ml, protein content 116.0 mg/ml) and information on its activity and protein content were graciously provided by Genencor® (Genencor, Rochester, NY). Novozyme 188 β-glucosidase (activity 665.0 CBU/ml, protein content 125.0 mg/ml, lot no. 066K0676) was purchased from Sigma (St. Louis, MO), with the activity and protein content of Novozyme 188 based on that reported by Dien et al. (2008).

2.2. Compositional analysis

The moisture contents of untreated and pretreated maple wood solids were determined with a UV moisture analyzer (Model: HB43-S Halogen Moisture Analyzer, Mettler Toledo, Columbus, OH). Ash content was determined according to NREL Laboratory Analytical Procedures (Sluiter, Hames, et al., 2005) by ashing samples in a muffle furnace at 575 ± 25 °C for at least 4 h. Extractives determination was as specified in NREL Laboratory Analytical Procedures (Sluiter, Ruiz, Scarlata, Sluiter, & Templeton, 2005). The maple wood sample and extraction paper thimble (Whatman no. 2800-258, Fisher Scientific, Pittsburgh, PA) were dried in a vacuum oven (model 281A, Fisher Scientific, Pittsburgh, PA) at 45 °C for 2 days prior to extraction experiments. About 2 g of maple wood was extracted in a tarred thimble for 4 h with 170 ml water (double distilled) followed by soaking in 170 ml of 200 proof ethanol for 24 h in a glass Soxhlet apparatus (250 ml Pyrex® extractor system, model 3840M, Corning, Lowell, MA). After extraction, the samples with the thimble were dried in a vacuum oven at 45 °C to estimate extractives content.

Acid soluble and insoluble (Klason) lignin, glucan, xylan, acetate, and sugar polymers were measured by a modified NREL Laboratory Analytical Procedure (Sluiter et al., 2008). The procedure employed the following two-step acid hydrolysis approach: (1) about 300 mg of substrate was placed into a shell vial and hydrolyzed with 3 ml of concentrated (72%, w/w) sulfuric acid at 30 °C for 1 h and (2) the hydrolyzed substrate was diluted to 4% (w/w) sulfuric acid for further secondary hydrolysis for 1 h at 121 °C.

2.3. Determination of oligomers and total xylose

Total sugars in the liquid, which included monomers and oligomers, were measured by post-hydrolysis with 4 wt% sulfuric acid at 121 °C for 1 h. The total oligomer amount was determined as the difference between the amount of monomers measured after post-hydrolysis after correcting for losses in post-hydrolysis and the amount measured before post-hydrolysis (Sluiter et al., 2006):

$$\text{Oligomers (g)} = \text{total xylose (g) in the hydrolysate corrected for degradation after post hydrolysis} - \text{monomers (g) in the hydrolysate liquid before post hydrolysis} \quad (1)$$

2.4. Product analysis

Sugar monomers in the liquid portion were analyzed quantitatively using a Waters Alliance HPLC system (model 2695) equipped with a 2414 refractive detector and a Waters 2695 auto sampler using Empower 2 software (Waters Co., Milford, MA). Both Bio-Rad Aminex HPX-87P and HPX-87H columns (Bio-Rad Laboratories, Hercules, CA) were used to analyze sugars and other products. The mobile phase was 0.005 mol/l sulfuric acid in water for the