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

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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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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

HPX-87H column and double distilled water for the HPX-87P column at a flow rate of 0.6 ml/min.

2.5. Pretreatment

Tubular batch reactors were made of 0.5 in. O.D. Hastelloy C-276 tubing with a 0.035 in. wall thickness cut to a length of 6 in. to give a total volume of 14.3 ml and a working volume of 10 ml to allow for water expansion when heated to pretreatment temperatures. These reactors were heated to reaction temperature with a 4 kW fluidized sand bath (Model SBL-2D, Techne Co., Princeton, NJ), with the reactor internal temperature monitored with a K type thermocouple probe (Omega KQSS-316G-12, Omega Engineering Co., Stamford, CT). The heat up times were 2 min for 140 °C, 2.5 min for 160 °C, 3.4 min for 180 °C, and 3.8 min for 200 °C. The heat-up times were not included in the stated reaction time. At the end of the desired pretreatment time, the reactors were dropped into a water bath, with about 40 s sufficient to cool the contents to room temperature.

Ground maple wood was presoaked in water or in 0.5 wt% or 2 wt% acid overnight at a solids loading of 10 wt%. Hydrothermal pretreatment at 180 °C and 200 °C and dilute acid pretreatment at 160 °C with both 0.5% and 2% acid concentrations were run over a range of reaction times to allow determination of times that resulted in the highest sugar yields. Due to the strong acidity of hydrochloric acid, pretreatment at 140 °C with 0.5% hydrochloric acid was conducted at comparable combined severities to those employed for sulfuric acid by adjusting for pH differences (Yang & Wyman, 2008). After pretreatment, the reaction tubes were cooled to room temperature in a water bath, the tubes were opened, and then the slurry was immediately filtered to separate liquid from pretreated solids. The pretreated solids were washed with room temperature deionized water to remove acids, free sugars, and degradations products that otherwise could inhibit subsequent enzymatic hydrolysis and occlude the outcomes. Since the mass balances were performed both on liquid and solids part before washing, the washing would not affect the amount of total sugars and biomass recovered. Following washing, the pretreated solids were refrigerated at 4 °C before further analysis.

To facilitate comparison of results from hydrothermal pretreatments at different temperatures, the log of the severity parameter ($\log R_0$) was employed, as shown in Eq. (2), with the pretreatment temperature T in °C and the time t in min (Overend & Chornet, 1987):

$$\log R_0 = \log\left(t \cdot \exp\left(\frac{T-100}{14.75}\right)\right) \quad (2)$$

For dilute acid pretreatments, the effect of pH on severity was accounted for in the combined severity parameter, as calculated by Eq. (3) (Chum, Johnson, Black, & Overend, 1990):

$$\log \mathrm{CS} = \log\ R_0 - \mathrm{pH} \quad (3)$$

The pH values used were measured in the liquid hydrolysate collected after pretreatment.

The yields of glucose, xylose, and the two together from pretreatment (stage 1) were calculated on the basis of glucose and xylose equivalents in raw biomass via Eqs. (4)–(6):

$$\text{glucose yield (\%)} = \frac{\text{glucose concentration (g/l)} \times \text{volume of liquid hydrolysate (l)}}{\text{glucose equivalents in raw biomass (g)}} \times 100 \quad (4)$$

Table 1
Composition of maple wood and comparison to that reported for sugar maple.

Composition	Red maple (this study)	Sugar maple (Mittal et al., 2009a)
Klason lignin	24.9 ± 0.3	22.3
Acid soluble lignin	2.2 ± 0.1	3.8
Glucan	41.8 ± 0.3	41.0 ± 0.6[a]
Xylan	18.4 ± 0.2	13.3 ± 0.4[a]
Galactan	0.3 ± 0.02	1.9 ± 0.8[a]
Arabinan	0.34 ± 0.01	0.5 ± 0.2[a]
Mannan	2.0 ± 0.1	2.2 ± 0.2[a]
Acetate	5.3 ± 0.1	3.8 ± 0.1
Ash	2.33 ± 0.01	N/A
Extractives	3.1 ± 0.3	3.2
Total	98.0	92

[a] Calculated based on the equivalent amount of monomeric sugar for comparison (Mittal et al., 2009a).

$$\text{xylose yield (\%)} = \frac{\text{xylose concentration (g/l)} \times \text{volume of liquid hydrolysate (l)}}{\text{xylose equivalents in raw biomass (g)}} \times 100 \quad (5)$$

$$\text{(glucose + xylose) yield (\%)} = \frac{\text{xylose yield} \times \text{xylose in raw biomass (g)} + \text{glucose yield} \times \text{glucose in raw biomass (g)}}{\text{(glucose + xylose) equivalents in raw biomass (g)}} \quad (6)$$

2.6. Enzymatic hydrolysis

Maple wood solids resulting from two pretreatments at identical conditions were washed and enzymatically hydrolyzed according to NREL LAP (Selig, Weiss, & Ji, 2008) modified to use a 2 wt% solids loadings in a 50 mM citrate buffer (pH 4.9 ± 0.2) at 50 °C and 150 rpm for 72 h in Infors-HT Multitron shakers (Model AJ125; Infors-HT, Laurel, MD). Sodium azide (0.1 wt%) was added to prevent microbial growth on released sugars. A cellulase loading of 60 FPU/g (glucan + xylan) in the pretreated solids was supplemented with beta-glucosidase at a CBU to FPU ratio of 4. Glucose and xylose yields in enzymatic hydrolysis (stage 2) were calculated in the same way as those in pretreatment (stage 1). Hydrolysis samples were collected and analyzed at 72 h, and glucose and xylose yields from the pretreated biomass were calculated similar to those for stage 1 on the basis of glucose and xylose equivalents in the pretreated biomass via Eqs. (7) and (8):

$$\text{glucose yield in stage 2 (\%)} = \frac{\text{glucose concentration (g/l)} \times \text{volume of liquid hydrolysate (l)}}{\text{glucose equivalents in the pretreated biomass (g)}} \times 100 \quad (7)$$

$$\text{xylose yield in stage 2 (\%)} = \frac{\text{xylose concentration (g/l)} \times \text{volume of liquid hydrolysate (l)}}{\text{xylose equivalents in the pretreated biomass (g)}} \times 100 \quad (8)$$

2.7. Definitions

In this paper, pretreament is also referred to as stage 1 while enzymatic hydrolysis is referred to as stage 2 to avoid confusion. In addition, “total” yields of xylose, glucose, or the two together refer to the combination of yields of a sugar and its oligomers from just pretreatment or just enzymatic hydrolysis. On the other hand,

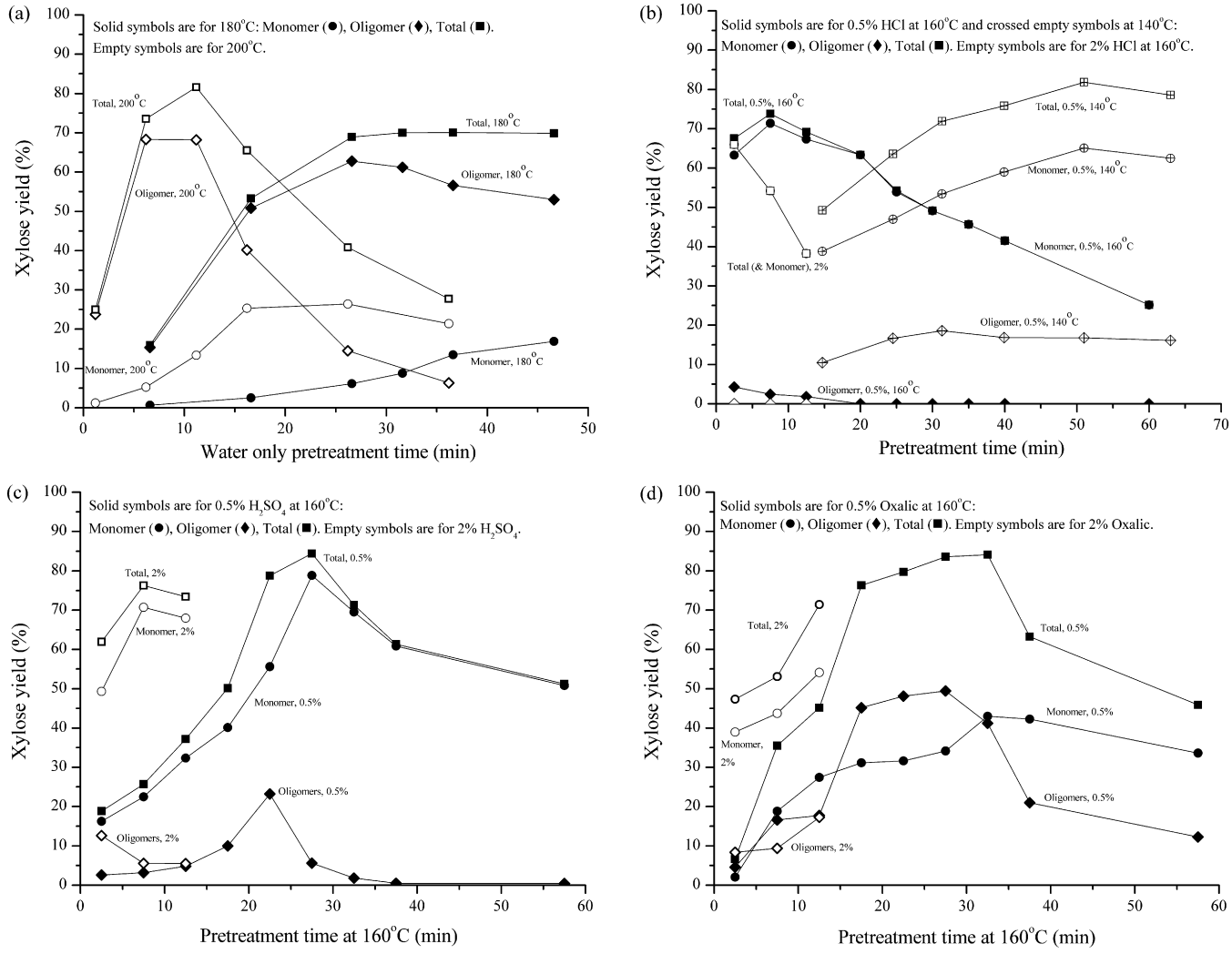

Fig. 1. Stage 1 xylose monomeric, oligomeric, and total xylose yields vs. times for (a) hydrothermal, (b) dilute hydrochloric acid, (c) dilute surfuric acid, and (d) dilute oxalic acid pretreatments.

"combined" yields of a sugar, its oligomers, or the combination of the two refers to yields from pretreatment (stage 1) and enzymatic hydrolysis (stage 2) together.

3. Results and discussion

3.1. Maple wood composition

The moisture content of the red maple employed here after drying for composition analysis was 7.33 ± 0.10%. Table 1 lists the composition of this raw maple wood adjusted to a dry basis along with composition information for sugar maple reported by Mittal et al. for comparison (Mittal et al., 2009a). Thus, the red maple in this study had slightly lower galactan but higher Klason lignin, xylan, and acetate contents than sugar maple (*Acer saccharum*) (Mittal et al., 2009a). However, the two contained similar amounts of other components.

3.2. Xylose monomer and oligomer yields versus time for stage 1 pretreatment

Fig. 1a shows yields of xylose, xylooligomers, and the sum of the two recovered in the liquid hydrolysate following hydrothermal pretreatment of maple wood at 180 °C and 200 °C. Reaction times were chosen to span those reported to be optimal for other biomass in the literature (Mittal et al., 2009b). The yields of xylose and xylooligomers increased, reached peaked values, and then dropped with increasing time, as expected, for pretreatments at 180 °C and 200 °C. However, xylooligomer yields peaked at 26.6 min at 180 °C and 6.2 min at 200 °C, much sooner than for xylose yields (46.6 min at 180 °C and 26.2 min at 200 °C). The total xylose yields peaked at virtually the same time as peak xylooligomer yields because xylooligomers made up most of the total xylose in the liquid hydrolysate from maple wood hydrothermal pretreatment. At 180 °C, the total xylose yield increased with time from ~16% at 6.6 min to ~70% at a pretreatment time of 31.6 min and then remained nearly constant over the time period studied. At 200 °C, a maximum total xylose yield of 81.6% was achieved at a pretreatment time of 11.2 min. Greater than 90% of the total xylose in solution was as xylooligomers for hydrothermal pretreatment at 180 °C for 26.6 min (68% xylooligomers of the 73% total xylose yield) but dropped to about 60% of the total for hydrothermal pretreatment at 200 °C at 11.2 min (40% xylooligomers of the 65% total xylose yield).

Fig. 1b–d shows the time course of xylose yields from stage 1 pretreatments with dilute hydrochloric, sulfuric, and oxalic acids, respectively. The times selected for dilute sulfuric acid pretreatment at 160 °C with 0.5% acid were chosen to span times reported

in the literature to give the highest combined total xylose yields with other biomass materials (Cara, Romero, Oliva, Saez, & Castro, 2007; Perez et al., 2008). However, a sulfuric acid concentration of 2% was also applied to determine its effect on performance. Fig. 1c shows that the total stage 1 xylose yields in the hydrolysate for pretreatment with 0.5% sulfuric acid at 160 °C increased to a peak value of 84.4% at a pretreatment time of 27.5 min and then dropped with longer times. However, the peak stage 1 oligomer yield was reached at 22.5 min, slightly before the total stage 1 xylose yield peaked. Applying 2% sulfuric acid for pretreatment reduced the maximum total stage 1 xylose yield to about 76% for pretreatment for 7.5 min, as also shown in Fig. 1c. Fig. 1b shows that a maximum total stage 1 xylose yield of 73.8% was obtained for 7.5 min of pretreatment at 160 °C with 0.5% hydrochloric acid but dropped to 65.9% for 2.5 min of pretreatment with 2% hydrochloric acid at the same temperature. Most of the xylose from stage 1 was as monomers in both cases.

The highest total xylose yield of 73.8% in the liquid hydrolysate from maple wood pretreated with 0.5% hydrochloric acid at 160 °C was ~10% lower than that with 0.5% sulfuric acid at 160 °C. Furthermore, total xylose yields dropped rapidly from 65.9% to 38.3% as the pretreatment time was increased from 2.5 min to 12.5 min with 2% hydrochloric acid at 160 °C. This outcome suggested that 160 °C is too high a temperature for maple wood pretreatment with 0.5% hydrochloric acid and lower temperatures could improve total xylose yields. Accordingly, pretreatment at 140 °C improved the highest total stage 1 xylose yield to 81.8% in 51 min, consistent with 0.5% hydrochloric acid being stronger than 0.5% sulfuric or oxalic acid.

Fig. 1d shows that the highest total stage 1 xylose yield of 84.2% including 41.2% as oligomers occurred following 32.5 min of pretreatment with 0.5% oxalic acid at 160 °C. Overall, oxalic acid pretreatment resulted in very high ratios of monomeric xylose to oligomers from stage 1, similar to results with sulfuric and hydrochloric acids but in contrast to the high amounts of oligomers from hydrothermal pretreatment. Furthermore, the highest xylose stage 1 monomer yields were realized after the peaks in oligomer yields for each pretreatment, as expected for the series reaction of long chained hemicellulose to shorter chain oligomers and on to sugar monomers and then sugar breakdown products. Although shorter reaction times were required to reach peak stage 1 values at higher acid concentrations for all three acid pretreatments, higher total stage 1 xylose yields were realized at the lower acid concentrations. In addition, 0.5% hydrochloric acid pretreatment of maple wood produced a higher ratio of monomers than pretreatment with 0.5% sulfuric acid, which in turn produced higher ratios of monomers than pretreatment with 0.5 wt% oxalic acid at 160 °C.

3.3. Relationship of yields to severity parameter

The severity parameter or combined severity parameter defined earlier can facilitate comparisons of yields at different temperatures and times for hydrothermal pretreatment or for different combinations of temperatures, times, and/or acid concentrations for dilute acid pretreatments, respectively. On this basis, Fig. 2a plots total monomeric plus oligomeric xylose yields vs. the log of the severity parameter for hydrothermal pretreatments at the two temperatures run. The total xylose yields from hydrothermal pretreatment at 180 °C had a somewhat broad maximum over a log severity range from 3.78 to 4.02, with a peak at about 70%. The maximum total xylose yields for hydrothermal pretreatment at 200 °C occurred at a similar severity value to 180 °C but peaked more sharply at a yield of 81.6% at a log severity of 3.99. However, the highest total xylose yields of 70% at 180 °C and 81.6% at 200 °C occurred in the log severity range of 3.9–4.0. These differences in total xylose yields in the liquid hydrolysate from maple wood suggested that the highest total xylose yield was not only related to severity but also increased with temperature for hydrothermal pretreatment.

Fig. 2b presents total xylose yields vs. the log of the combined severity parameter for the different dilute acid pretreatments. For dilute acid pretreatment with 0.5% of each of the three acids at 160 °C, the highest total xylose yields for oxalic acid, hydrochloric acid, and sulfuric acid occurred at log combined severities of 1.81, 2.00, and 2.05, respectively, as shown in Fig. 2b. For pretreatments with 2 wt% of each acid, the highest yields occurred at higher combined severity values than for pretreatments with 0.5 wt% acid. Furthermore, the spread in combined severities was less for 2.0% acid concentrations, with values of 1.95, 1.84, and 2.00 for oxalic acid, hydrochloric acid, and sulfuric acid, respectively. For 0.5% acid, the pH values of the liquid hydrolysate following pretreatments for 2.5 min to 57.5 min ranged from 0.92 to 0.85 for hydrochloride acid, 1.18–1.06 for sulfuric acid, and from 1.61 to 1.32 for oxalic acid. The corresponding pH values measured prior to pretreatment along with those calculated based on the amount of acid added for dilute hydrochloric, sulfuric, and oxalic acids were 0.85/0.389, 1.09/0.992, and 1.32/1.145, respectively. For 2% acid pretreatments, the pH values of the liquid hydrolysate following pretreatment times of 2.5–12.5 min ranged from 0.34 to 0.29 for hydrochloride acid, 0.64 to 0.61 for sulfuric acid, and from 0.99 to 0.87 for oxalic acid. The corresponding measured and calculated initial pH values for 2% acid pretreatments were 0.29/−0.040, 0.61/0.389, and 0.95/0.623 for dilute hydrochloric, sulfuric, and oxalic acids, respectively. In comparison, the pH values measured for the hydrolysates from hydrothermal pretreatment ranged from 4.48 to 3.24 over the reaction time from 6.6 min to 46.6 min at 180 °C and from 4.48 to 3.24 over the reaction time from 1.2 min to 36.2 min at 200 °C. The pH values for the three acids and with just hot water are consistent with the expected effect of the following dissociation constants: hydrochloric acid $pK_a = -7$ < sulfuric acid $pK_{a1} = -3$ and sulfuric acid $pK_{a2} = 1.99$ < oxalic acid $pK_{a1} = 1.27$ and oxalic acid $pK_{a2} = 4.28$ < water $pK_a = 15.75$.

Although the severity parameter corresponding to the highest stage 1 yields followed pH and pK_a patterns, the highest total stage 1 xylose yields did not follow the same trends in that the log combined severities for the highest total stage 1 xylose yields were 1.81, 1.89, and 2.08 for oxalic, hydrochloric acid, and sulfuric acid, respectively. Furthermore, the combined severity of 1.89 that realized the highest total stage 1 xylose yield of 81.8% with hydrochloric acid was for a concentration of 0.5% at 140 °C, but increasing the temperature to 160 °C reduced the maximum total xylose yield to 73.8% at 160 °C at nearly the same combined severity of 1.87. Thus, these results suggest that temperature affected xylose yields more than time or acidity alone.

Because the pH could not be measured during the reaction, the pH values following post-pretreatment were used to calculate the combined severity parameters by Eq. (3). These pH values were dictated primarily by the initial acid concentration and ionic activity, with the latter influenced by temperature and acid properties. Generally, the pH at a particular acid concentration increases as the temperature increases. For example, the pH for 0.5 wt% H_2SO_4 increases from 1.15 at 25 °C to 1.28 at 140 °C when calculated by the method described by Lloyd (Lloyd & Wyman, 2004; Ulich, 1930). However, pH values of other acids such as oxalic acid could not be calculated due to lack of data. Although pH values measured following pretreatment were used for the combined severity calculations because they were more representative of the pH during pretreatment than initial pH values would be, differences between the actual pH and that after pretreatment could contribute to discrepancies in identifying the optimal pH for maximum xylose yields, as discussed above. The computed values of activity coefficients for SO_4^{2-} and $C_2O_4^{2-}$ were very close but lower than that for Cl^- (Kielland, 1937).

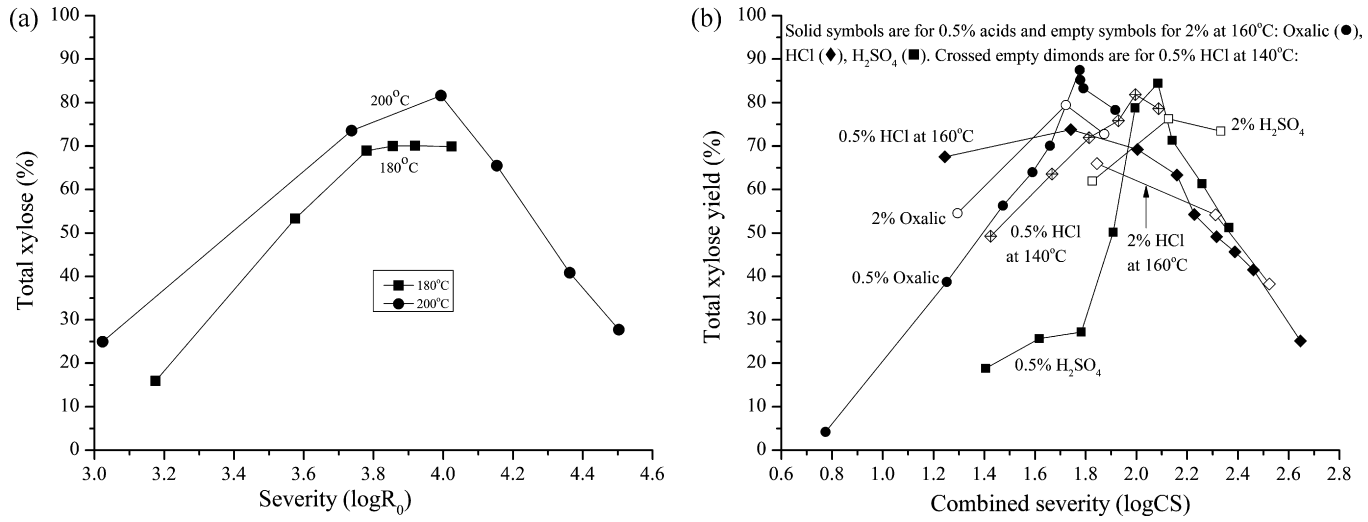

Fig. 2. Total stage 1 xylose (monomers plus oligomers) yields (a) versus log severity for hydrothermal pretreatment and (b) versus combined severity for different dilute acid pretreatments.

Among the three acids applied here, hydrochloric acid, the strongest, stood out for its ability to catalyze xylose decomposition into furfural and other products (Jensen, 2009; Lloyd & Wyman, 2005; Lu, Zhang, Liang, Yang, & Dan, 2008). Thus, although its low pH would aid hydrolysis of hemicellulose to soluble xylose and reduce times to reach maximum yields, it also promoted xylose dehydration and thereby reduced yields compared to a less aggressive acid, as shown in this study. In contrast to hydrochloric acid, sulfuric and particularly oxalic acids are weaker oxidizers that promote less xylose dehydration but are still strong enough to catalyze xylan/xylooligomers hydrolysis.

3.4. Other degradation products and total organic carbon at highest yield conditions

The mass of glucose and xylose and their corresponding dehydration products 5-HMF and furfural in the pretreatment hydrolysates are listed in Table 2 based on 100 g of dry maple wood for conditions that gave the highest total glucose plus xylose yields from coupled stage 1 and 2 operations to facilitate performance comparisons among the different pretreatments. These results show that pretreatments with 0.5% sulfuric acid and 0.5% hydrochloric acid resulted in greater degradation of glucose and xylose. The results also reveal lower xylose yields and significantly higher furfural yields (~9.0%) from stage 1 pretreatment with 0.5% hydrochloric acid than for any of the other methods. Table 2 also shows that pretreatment with 0.5% sulfuric acid produced more glucose and 5-HMF compared to pretreatment with 0.5% hydrochloric acid. Although pretreatment with 0.5% oxalic acid also produced a significant amount of furfural, the amount was less than for the other acid pretreatments and only slightly greater than from hydrothermal pretreatment. The HMF yield was lowest for 0.5 wt% oxalic acid among the different acid pretreatments followed by hydrothermal pretreatment. Since 5-HMF and furfural are major inhibitors to subsequent enzymatic hydrolysis or fermentation, oxalic pretreatment could prove less toxic to downstream biological steps. This finding is consistent with the literature that showed that 5-HMF and furfural yields were higher with hydrochloric acid than other mineral acids despite being used at the same [H^+] concentrations and other reaction conditions (Chheda, Roman-Leshkov, & Dumesic, 2007; Marcotullio, Cardoso, De Jong, & Verkooijen, 2009; Yemis & Mazza, 2011). The total organic carbon recovered in the liquid hydrolysates tabulated in Table 2 provides a measure of the amount of biomass solubilized and potentially available for downstream catalytic conversion or losses to waste treatment. Thus, all three acid pretreatments released more carbon into the liquid than pretreatment with just hot water, with hydrochloric acid producing the most soluble carbon.

In summary, important differences were seen in product yields and distributions from stage 1 for all four pretreatments, with hydrothermal giving the greatest differences. In terms of stage 1 xylose and xylooligomer production, hydrothermal, oxalic acid, and sulfuric acid pretreatment all achieved high yields. Although hydrochloric acid pretreatment did not realize as high total xylose yields, it produced more furfural. Furthermore, differences in the distribution of xylose and oligomers in hydrolysates from the different pretreatments could have important implications for downstream processing such as the need for post-hydrolysis of xylooligomers to monomers for fermentation to ethanol or for conversion to drop-in hydrocarbon fuels. In addition, conditioning methods such as those applied in earlier studies by NREL (Wooley, Ruth, Sheehan, Ibsen, & Majdeski, 1999) may be needed to remove inhibitors from the hydrolysates, with possible consequences including significant loss of sugar and generation of salts that can be problematic to downstream operations. In a follow up study of the fermentation of the liquid hydrolyzates from each of these pretreatments that is to be published, ethanol yields from the oxalic acid pretreatment liquor of were higher than from the other three pretreatments.

3.5. Combined glucose, xylose, and total glucose plus xylose yields from combined pretreatment and enzymatic hydrolysis

For biological conversion of biomass to fuels, high yields of sugars from both hemicellulose and cellulose are required, making high yields of glucose in enzymatic hydrolysis of the cellulose left following pretreatment vital to economic success. Thus, combined glucose, xylose, and total glucose plus xylose yields from stage 1 pretreatment combined with stage 2 enzymatic hydrolysis were compared, as summarized in Figs. 3–5 for the four pretreatments applied here, in which xylose yields, glucose yields, and glucose plus xylose yields are shown in Figs. 3–5, respectively.

Fig. 3a–d presents xylose yields from pretreatment (stage 1) and enzymatic hydrolysis (stage 2) and their combinations for hydrothermal and dilute hydrochloric, sulfuric, and oxalic acid pretreatments, respectively. In all cases, most of the xylose was

Table 2
Product yields in liquid hydrolysate on the basis of 100 g dry maple wood.

Reaction conditions	Product yields in liquid hydrolysate (%)				
	Glucose	5-HMF	Total xylose (monomer)	Furfural	Total organic carbon[a]
Hydrothermal, 200 °C, 11.2 min	1.6	0.8	81.6 (13.4)	3.7	14.1
0.5% sulfuric acid 160 °C, 27.5 min	5.9	1.8	84.4 (78.8)	5.1	18.3
0.5% hydrochloric acid, 160 °C, 7.5 min,	5.6	1.4	73.8 (71.4)	8.7	19.6
0.5% hydrochloric acid, 140 °C, 51 min	4.7	1.0	81.8 (65.0)	7.0	19.4
0.5% Oxalic acid 160 °C, 27.5 min	1.7	0.5	87.5 (73.9)	4.1	17.5

[a] Based on the raw maple 45.48% total carbon content.

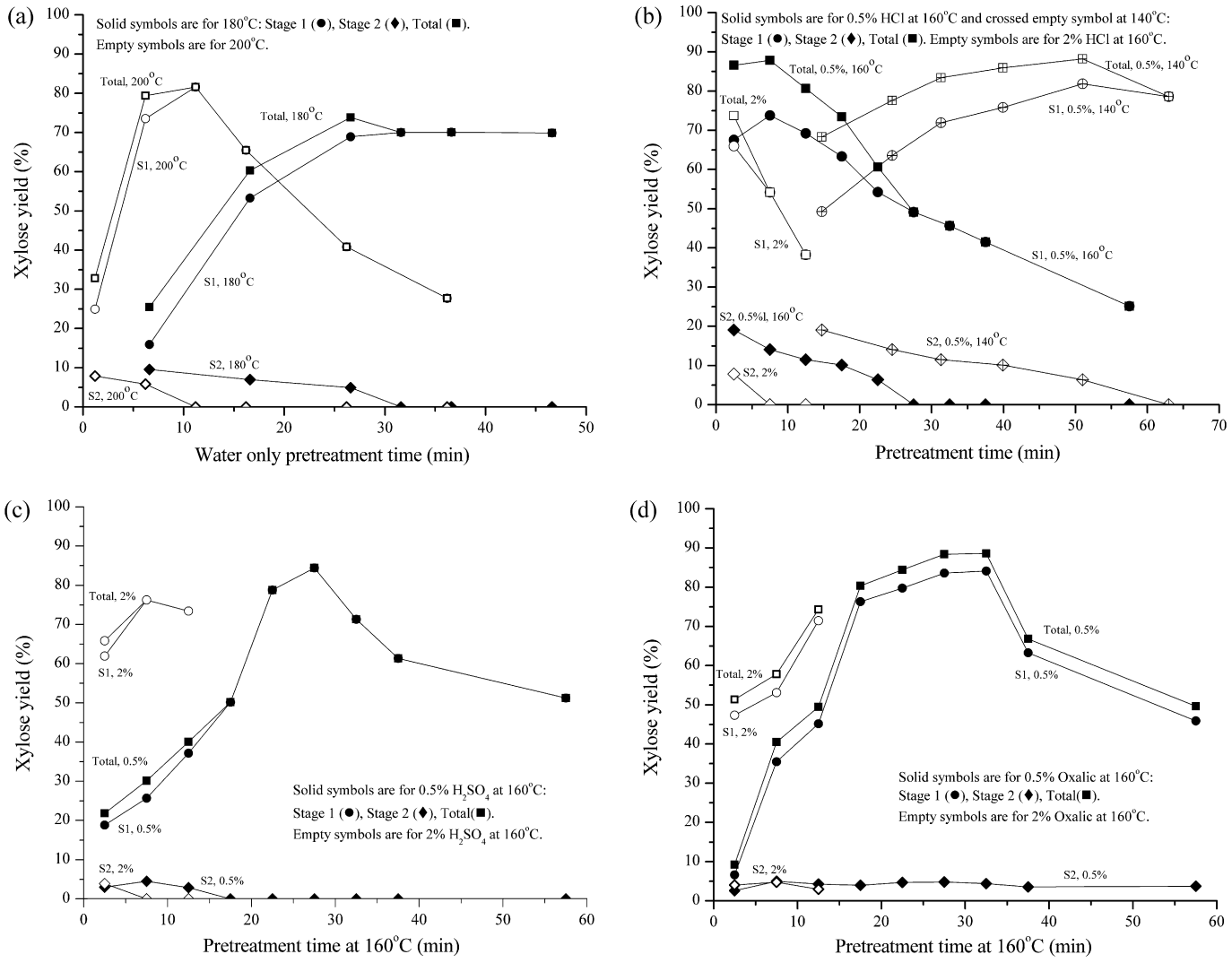

Fig. 3. Xylose yields (stage 1, stage 2, and combined total) vs. pretreatment time for (a) hydrothermal, (b) dilute hydrochloric acid, (c) dilute surfuric acid, and (d) dilute oxalic acid pretreatments.

released in stage 1 due to the low pH and its ability to hydrolyze hemicellulose to sugars. Thus, the trends in total xylan yields from pretreatment combined with enzymatic hydrolysis followed closely the respective patterns in xylose yields shown for stage 1 alone. Yet, there are some important differences in release patterns. Stage 2 xylan yields of about 10%, calculated as a percent of the xylan contained in raw maple wood, were obtained following hydrothermal pretreatment at 180 °C for up to 26.6 min but were less than 5% for 0.5% sulfuric acid pretreatment at 160 °C. However, somewhat higher stage 2 xylose yields were observed for 0.5% hydrochloric acid and oxalic acid pretreatment at 160 °C, but the values dropped from ~20% to ~6% as the pretreatment time was extended from 2.5 min to 22.5 min. The lower stage 2 xylose yields for hydrochloric acid pretreatment at 160 °C compared to yields from other acids at 160 °C and hydrothermal pretreatments at comparable reaction conditions at 200 °C suggest that xylose degradation is accelerated faster than xylan hydrolysis for hydrochloric acid at 160 °C. Therefore, the lower pH for hydrochloric acid resulted in the need to drop the temperature to 140 °C to realize the highest xylose yield of 81.8% in 53 min from maple wood. Overall, hydrothermal pretreatment left a larger fraction of xylose in the solids near the maximum stage 1 xylose yield

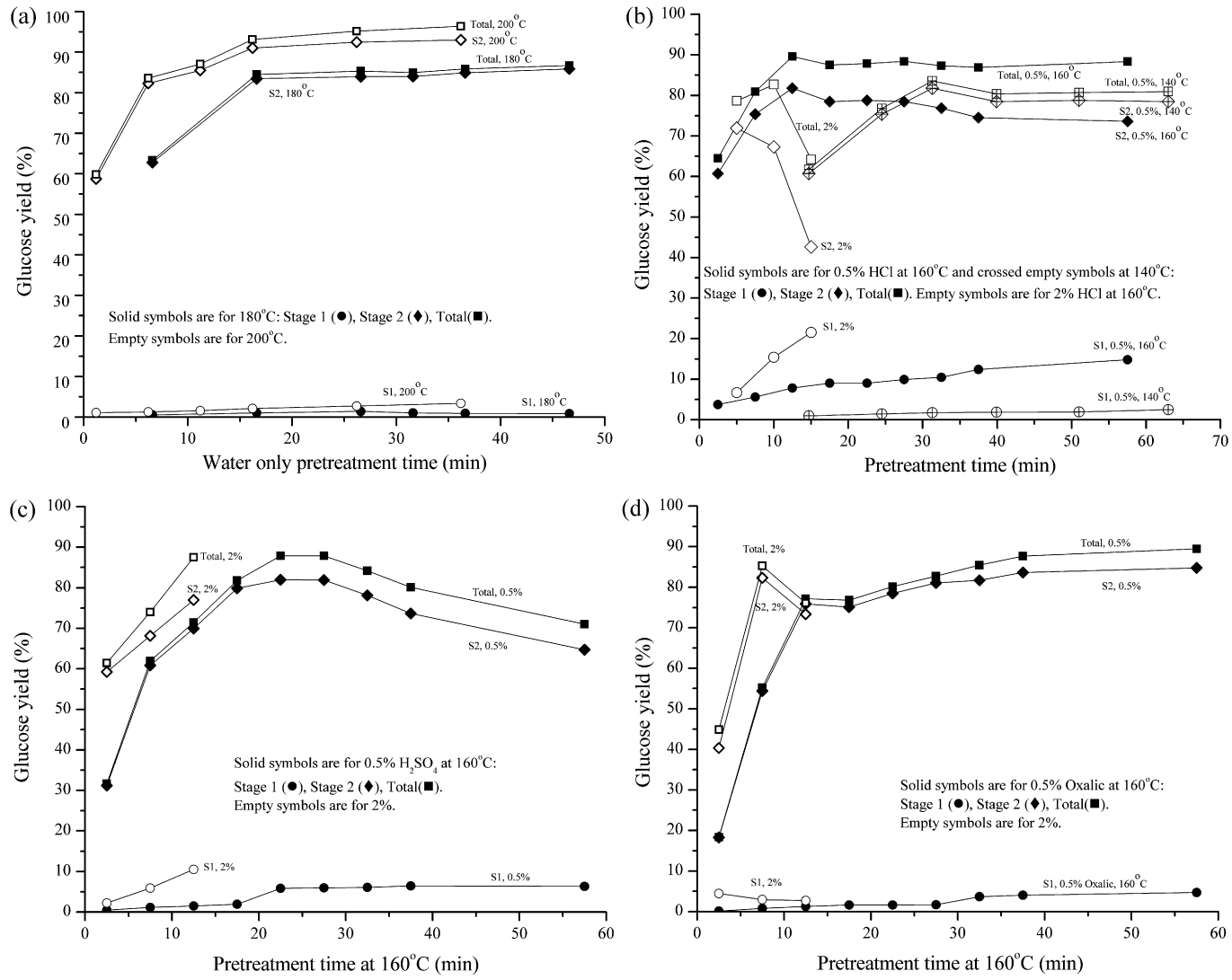

Fig. 4. Glucose yields (stage 1, stage 2, and combined total) vs. pretreatment time for (a) hydrothermal, (b) dilute hydrochloric acid, (c) dilute sulfuric acid, and (d) dilute oxalic acid pretreatments.

point that were available for stage 2 hydrolysis compared to the dilute acid approaches. However, oxalic acid left a similar amount of xylose in the solids that was released in stage 2 over virtually the entire range of times applied. Further characterization of the pretreated solids would be useful to better understand barriers to more effective enzymatic hydrolysis.

In almost total contrast to the xylose yield results, Fig. 4a–d shows that stage 1 glucose yields were less than 10% for all pretreatments except for pretreatment at both hydrochloric acid concentrations and for pretreatment with 2% sulfuric acid for more than 12.5 min. However, because of the high release in stage 2, total glucose yields from pretreatment combined with enzymatic hydrolysis reached ~90% for all pretreatments, consistent with the pretreatment goal. Thus, these results suggest that these pretreatments are able to disrupt cellulose structure effectively and improve its digestion. Combined total glucose yields for hydrothermal pretreatment at 200 °C and pretreatment with 0.5% hydrochloric acid at 160 °C increased with time and then remained constant, while combined total glucose yields increased initially and then dropped with time for pretreatment for 0.5% sulfuric acid and 0.5% oxalic acid at 160 °C. The highest glucose yield from pretreatment (stage 1) of 21.5% was achieved with 2% hydrochloric acid at 12.5 min, and the highest glucose yield of ~93% from enzymatic hydrolysis (stage 2) was obtained following pretreatments with 0.5% oxalic acid at 160 °C for 17.5 min or 22.5 min and hydrothermal pretreatment at 200 °C for 26.2 min. The latter conditions also corresponded to those for the highest combined total glucose yields of ~95% for these pretreatments.

Fig. 5a–d shows the total glucose plus xylose yields from stage 1 and 2 combined. The highest combined glucose plus xylose yields from all four pretreatments were very close (about 86%). However, although the values dropped slowly from their peaks with longer pretreatment times for 0.5% sulfuric acid and 0.5% hydrochloric acid pretreatments at 160 °C, they remained nearly constant after reaching the peak values for hydrothermal pretreatment at 180 °C and 0.5% oxalic acid pretreatment at 160 °C. Furthermore, total glucose and xylose yields from pretreatment and enzymatic hydrolysis were lower at longer pretreatment times for hydrochloric acid pretreatment at 160 °C than for other pretreatments.

Table 3 summarizes the optimal glucose and xylose recoveries from Fig. 5 for the different pretreatments together with enzymatic hydrolysis as. The combined sugar recoveries were all above 85% of the maximum possible for all pretreatments. As reported elsewhere, the pretreatment hydrolysates from these four pretreatments were used for direct catalytic conversion to drop-in-hydrocarbons by a novel thermocatalytic technology developed

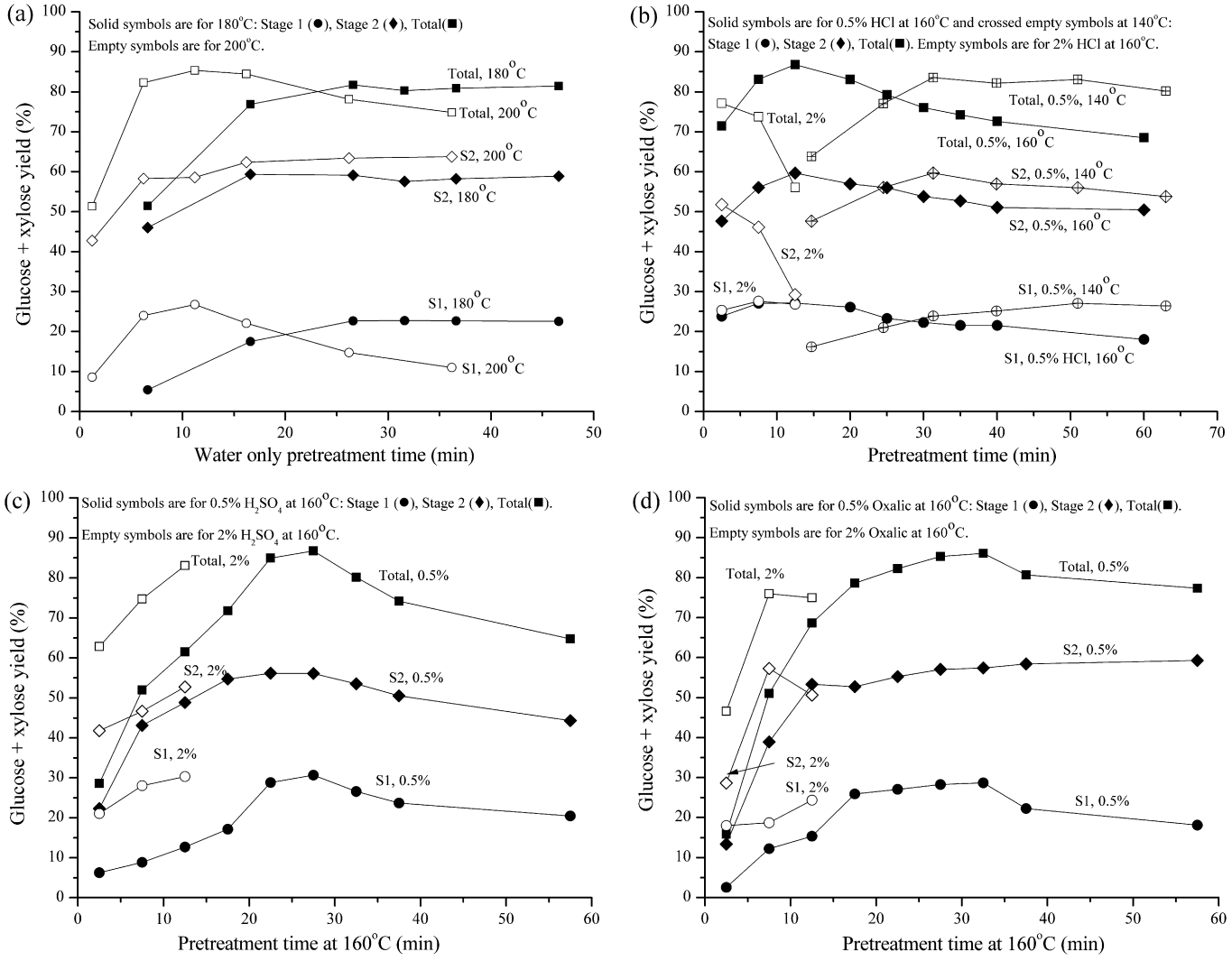

Fig. 5. Glucose plus xylose yields (stage 1, stage 2, and combined total) vs. pretreatment time for (a) hydrothermal, (b) dilute hydrochloric acid, (c) dilute surfuric acid, and (d) dilute oxalic acid pretreatments.

Table 3
Optimal glucose and xylose recovery of different pretreatments followed by enzymatic hydrolysis on the basis of 100 g dry maple wood.[a]

Liquid hydrolysates from pretreatments			Solid yield and composition (%)			Enzymatic hydrolysis		Combined sugar recovery (%)		
Condition	Glu (g)	Xyl (g)	Yield	Glu	Xyl	Glu (g)	Xyl (g)	Glu	Xyl	Glu + Xyl
Hydrothermal, 200 °C, 11.2 min	0.7	17.1	70.9	56.9	0.0	39.8	0.0	87.1	81.6	85.3
0.5% sulfuric acid, 160 °C, 27.5 min	2.8	17.6	69.0	56.2	0.0	38.1	0.0	87.8	84.4	86.8
0.5% hydrochloric acid, 140 °C, 51 min	2.2	17.1	65.5	62.3	1.2	40.5	0.7	91.7	85.0	89.6
0.5% Oxalic acid, 160 °C, 27.5 min	1.9	17.4	71.3	56.2	2.5	38.9	0.8	87.7	86.9	87.4

[a] 100 g dry maple wood has 46.5 g glucose, 20.9 g xylose, and 24.9 g lignin.

at the University of Massachusetts (Li et al., 2011). However, hydrolysate from hydrothermal pretreatment was not effectively utilized due to its high oligomer content, while the monomeric xylose from the acid pretreatments was (Li et al., 2011). Unfortunately, hydrolysates produced with hydrochloric acid and sulfuric acid pretreatments deactivated catalysts in subsequent conversion of xylose to monofunctional jet fuel (Huber et al., 2005). However, oxalic acid was effective in producing high yields of monomeric xylose while maintaining catalyst activity better, making it more compatible with downstream catalytic conversion (Huber et al., 2005). Thus, although high yields from the coupled operations of pretreatment and enzymatic hydrolysis are very important, it is vital to also consider the impact of pretreatment on other operations in the overall conversion process (Wyman, 2007).

4. Conclusions

Dilute sulfuric acid and dilute oxalic acid achieved similar maximum total xylose yields (~85%) in pretreatment, while the maximum yields from hydrothermal pretreatment at 200 °C and dilute hydrochloric acid at 140 °C were slightly lower (81%) and dropped even lower to ~70% for hydrothermal pretreatment at 180 °C and dilute hydrochloric acid at 160 °C. As expected, all three dilute acid pretreatments resulted in almost all monomeric xylose

while most of the xylose was oligomeric for hydrothermal pretreatment. The highest combined total xylose yields from the different acid pretreatments were observed to occur at combined severities of 1.81 for oxalic acid, 2.00 for hydrochloric acid, and 2.05 for sulfuric acid. Glucose yields from pretreatment at 160 °C were lower than 10% except for 2% concentrations of the strong acids hydrochloric acid and sulfuric acid. Although the pretreatment temperatures, times, and acid concentrations differed, all four pretreatments were effective in disrupting the cellulose structure and producing high glucose release, as shown by comparable combined glucose and xylose yields.

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