A novel mechanism and kinetic model to explain enhanced xylose yields from dilute sulfuric acid compared to hydrothermal pretreatment of corn stover

Jiacheng Shen [a,c,*], Charles E. Wyman [a,b]

[a] Center for Environmental Research and Technology, Bourns College of Engineering, University of California, 1084 Columbia Avenue, Riverside, CA 92507, USA
[b] Chemical and Environmental Engineering Department, Bourns College of Engineering, University of California, 1084 Columbia Avenue, Riverside, CA 92507, USA
[c] Northwest Irrigation and Soils Research Laboratory, Agricultural Research Service, United States Department of Agriculture, 3793 N. 3600 E. Kimberly, ID 83341, USA

ARTICLE INFO

ABSTRACT

Pretreatment of corn stover in 0.5% sulfuric acid at 160 °C for 40 min realized a maximum monomeric plus oligomeric xylose yield of 93.1% compared to a maximum of only 71.5% for hydrothermal (no added mineral acid) pretreatment at 180 °C for 30 min. To explain differences in dilute acid and hydrothermal yields, a fast reacting xylan fraction (0.0889) was assumed to be able to directly form monomeric xylose while a slow reacting portion (0.9111) must first form oligomers during hydrothermal pretreatment. Two reactions to oligomers were proposed: reversible from fast reacting xylan and irreversible from slow reacting xylan. A kinetic model and its analytical solution simulated xylan removal data well for dilute acid and hydrothermal pretreatment of corn stover. These results suggested that autocatalytic reactions from xylan to furfural in hydrothermal pretreatment were controlled by oligomeric xylose decomposition, while acid–catalytic reactions in dilute acid pretreatment were controlled by monomeric xylose decomposition.

© 2011 Published by Elsevier Ltd.

1. Introduction

Corn stover is an abundant agricultural residue in the United States (about 75 million dry tones in 2005) (http://pdf.wri.org/corn_stover_for_ethanol_production.pdf), and has significant potential as a feedstock for conversion to liquid fuels such as ethanol and biodiesel (Kadam and McMillan, 2003). However, for biological conversion, corn stover, like most lignocellulosic materials, must first be pretreated to increase cellulose accessibility by cellulase (Wyman et al., 2005a,b). Hydrothermal pretreatment, in which biomass is treated with either hot-water or steam without adding a mineral catalyst, is attractive due to the simplicity and minimization of chemical additives, but yields tend to be limited. However, dilute sulfuric acid pretreatment has proven to be a very effective in recovering most of the hemicellulose sugars from corn stover as well as other biomasses during pretreatment, while exposing cellulose to enzymes for high yields from subsequent hydrolysis (Wyman et al., 2005a, 2008). Some recent applications of these pretreatments to corn stover include dilute-sulfuric acid in a high-solids percolation reactor (Zhu et al., 2005), steam (Varga et al., 2004), and

controlled pH liquid hot water (Mosier et al., 2005). A vital consideration is that conditions to maximize the total yield of xylose from hemicellulose and glucose from cellulose in the combined operations of pretreatment and enzymatic hydrolysis are different from those that maximize the yield of either sugar alone (Lloyd and Wyman, 2005).

In addition to enhancing sugar yields for fermentation to ethanol and other products, pretreatment can generate reactive compounds from which to make other products from the cellulose and hemicellulose portions of biomass. For example, Jae et al. (2010) recently proposed a process to utilize xylan, glucan, and lignin in biomasses to produce furfural, 5-(Hydroxymethyl)furfural (HMF), and pyrolysis products, respectively. In such an approach, the pretreatment objective would be to maximize xylose yields and minimize glucose losses to maximize furfural and HMF yields. In addition, this application also requires minimizing lignin losses during pretreatment to maximize availability for downstream pyrolysis.

Kinetic models are valuable for testing mechanisms and process design, and several have been applied to pretreatment to describe hemicellulose release and degradation such as xylan decomposition during dilute acid pretreatment of cellulosic biomass (Jacobsen and Wyman, 2000). Some models assumed that hemicellulose follows homogeneous reaction kinetics to form xylose and other sugars (Aguilar et al., 2002; Bustos et al., 2003; Morinelly et al., 2009). Another type of hemicellulose decomposition model
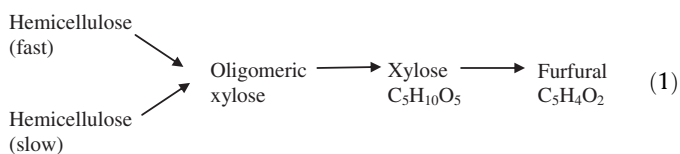
---

* Corresponding author. Address: Northwest Irrigation and Soils Research Laboratory, Agricultural Research Service, United States Department of Agriculture, 3793 N. 3600 E. Kimberly, ID 83341, USA. Tel.: +1 208 423 6565; fax: +1 208 423 6555.
   E-mail address: shenj417@yahoo.com (J. Shen).

Nomenclature

A	pre-exponential factors for reaction (L/(mol min))
c_p	glucose or xylose concentration measured by HPLC (g/L)
E_a	activation energies for reaction (J/mol)
F_X	concentration of fast reacting xylan (mol/L)
FS_X	total amount of xylan in corn stover
F_U	concentration of furfural (mol/L)
f_{FX}	fraction of fast reacting xylan in the total xylan (dimensionless)
f_{SX}	fraction of slow reacting xylan in the total xylan (dimensionless)
f_{xsp}	xylan fractions in the pretreated residue (dimensionless)
f_0	total carbohydrate content (glucan plus xylan) in the raw corn stover (dimensionless)
H	concentration of proton (mol/L)
K	first-order rate constant for reaction integrating the proton concentration (min^{-1})
k''	rate constant not including the proton concentration (L/(mol min))
m_0	weight of the dried corn stover added to the reactor (g)
m_p	weight of pretreated dry corn stover solid (g)
O_{FX}	concentrations of oligomeric xylose formed by the fast xylan reaction (mol/L)
O_{SX}	concentration of oligomeric xylose formed by the slow xylan reaction (mol/L)
R	gas constant (J/(mol K))

R_h	modified reaction ordinate including the effect of proton (dimensionless)
r	conversion factor from glucose and xylose to glucan and xylan (0.9 and 0.88)
S_X	concentration of slow reacting xylan (mol/L)
T	reaction temperature (K)
T_b	is a base temperature (100 °C)
T_r	pretreatment temperature (°C)
t_s	reaction time (s)
v_p	liquid volume including moisture of the raw corn stover (L)
X_Y	concentration of monomeric xylose (mol/L)
y_{FU}	furfural yield (dimensionless)
y_{FX}	fraction of the remaining fast reacting xylan (dimensionless)
y_{OSX}	yield of oligomeric xylose (dimensionless)
y_{SX}	fraction of slow reacting xylan in the total xylan (dimensionless)
y_{XY}	yield of monomeric xylose (dimensionless)
y_p	sugar yields (dimensionless)
y_{sp}	solid yield (dimensionless)

Subscript

I	reaction number
0	initial state

partially accounted for the heterogeneous structure of hemicellulose in biomass by considering two types of hemicelluloses, one of which reacts faster than the other (Kobayashi and Sakai, 1956), and several investigators have applied this type of model (Jacobsen and Wyman, 2002; Schell et al., 2003; Lu and Mosier, 2008). The fast and slow fractions in these models were postulated to form oligomeric xylose and then monomeric xylose (called just xylose in following text) and finally furfural by irreversible, first-order reactions, as in Eq. (1):

$$
\begin{array}{c}
\text{Hemicellulose (fast)} \\
\text{Hemicellulose (slow)}
\end{array}
\searrow\nearrow
\begin{array}{c}
\text{Oligomeric} \\
\text{xylose}
\end{array}
\longrightarrow
\begin{array}{c}
\text{Xylose} \\
C_5H_{10}O_5
\end{array}
\longrightarrow
\begin{array}{c}
\text{Furfural} \\
C_5H_4O_2
\end{array}
\qquad (1)
$$

However, this model does not distinguish differences in reaction mechanisms between fast and slow reacting hemicelluloses, i.e., both are irreversible first-order. Hemicelluloses in biomass are polysaccharides with a backbone of pentoses to which are attached different side-groups of hexoses and pentoses. As the side-groups are hydrolytically removed, the longer chained xylans and others in the backbone can be hydrolyzed more effectively. These side-groups may directly form monomeric sugars.

In this paper, data was developed on xylose release from corn stover hemicellulose for both hydrothermal and dilute sulfuric acid pretreatments to support development of a novel mechanism and kinetic model that could explain why dilute acid gives higher xylose yields. On that basis, our objectives for this study were to (1) experimentally measure sugar release from corn stover in hydrothermal and dilute acid pretreatments to maximize total xylose yields for subsequent furfural production or fermentation to ethanol or other products, (2) determine the proportions of fast and slow reacting hemicelluloses in corn stover according to our proposed definition, (3) develop kinetic rate expressions for

hemicellulose hydrolysis based on these fast and slow reactions, and (4) determine parameters for the kinetic model to best describe experimental hemicellulose hydrolysis data for both hydrothermal and dilute acid pretreatment of corn stover

2. Modeling hemicellulosic hydrolysis kinetics

2.1. Definition and determination of initial fractions of fast and slow reacting hemicelluloses
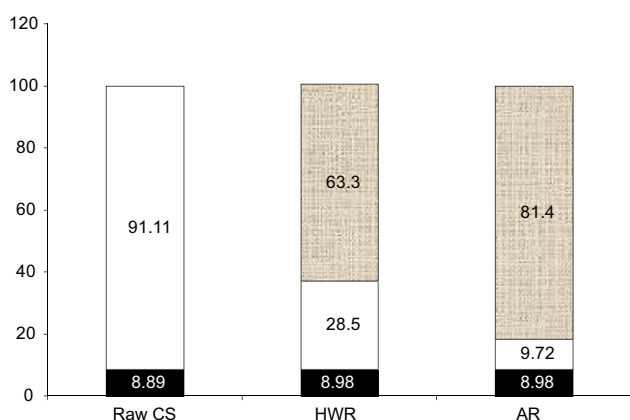
Although the concept has been applied for several decades (Kobayashi and Sakai, 1956), the fast and slow reacting hemicelluloses in biomass have not been distinctly defined. Because of complex hemicellulose structure and limitations in analytical methods to understand its structure, it is still difficult to identify the fast and slow reacting hemicelluloses at the molecular level. In a review, Wyman et al. (2005c) reported that the fast and slow fractions of hemicellulose were around 65% and 35%, respectively, for many biomasses, based on the observation that the hydrolysis rate slowed when the hemicellulose fraction dropped below 35%. Maloney et al. (1985) determined the percent of fast reacting xylan in white birch treated by sulfuric acid as between 59.5% and 72.4% by fitting the data to their model. A summary of data by Esteghlalian et al. (1997) showed the fast reacting xylan fraction to be between 67% and 84.3%. Based on their experimental data, Esteghlalian et al. (1997) also calculated the fast reacting xylan portion to make up 64.4%, 76.8%, and 83.8% of the total xylan in corn stover, switchgrass, and poplar, respectively, by fitting the data to a model that assumed direct conversion of xylan to xylose without considering oligomer intermediates.

It may be noted that the values of fast and slow reacting xylan fractions obtained by fitting of constants were not consistent with experimental break points in the decomposition of two types of xylans. For example, Kim and Lee (1987) and Chen et al. (1996)

reported the average percent of fast reacting xylan in hardwood was 69.7% using best-fit technology, but the break point between the two straight lines from their experiments was between 2% and 4%, leaving open the possibility that the fraction of fast reacting xylan in hardwood was between 96% and 98%. Kobayashi and Sakai (1956), the originators of the two fraction model, reported the break points for dilute sulfuric acid pretreatment of hardwood were lower than 10%.

In addition to this inconsistency, two additional considerations led us to not apply the best-fit approach to estimate the fractions of fast and slow reacting xylans (corresponding to the parameters $f_{FX,0}$ and $f_{SX,0}$ (= $1 - f_{FX,0}$) in Eqs. (21)–(25)). First, because $f_{FX,0}$ and $f_{SX,0}$ are properties of biomass, which should be initial conditions in the model, and not kinetic parameters (such as rate constants), they should not be derived from a fitting program because the model cannot be used to determine initial conditions, but determined by experimental data. Second, increasing the number of model parameters to be fit to the data in addition to the rate constants, for example, from 4 parameters in our model to 5 parameters, increases the uncertainty in the fitted parameters values.

In this paper, we hypothesize that the response of hemicellulose to different environments could be used as an indicator of hemicellulose structure. In this context, two catalytic mechanisms can breakdown hemicellulose: hydrothermal (water only) pretreatment in which protons released from acetyl groups in biomass and from water at high temperatures promote hemicellulose hydrolysis, and dilute acid pretreatment in which protons released from added mineral acids accelerate hydrolysis. Hydrothermal pretreatment of hemicellulose in corn stover forms three products: monomeric sugars such as xylose, a much larger portion of oligomeric sugars such as oligomeric xylose, and unreacted hemicelluloses left in the biomass. Most of the sugar released from dilute acid pretreatment is as monomers. We categorized the portion released easily in hydrothermal pretreatment as the fast reacting hemicellulose. On the other hand, the extra hemicellulose sugars released by dilute acid were considered as coming from the slow reacting fraction. The hemicellulose remaining in the solids after dilute acid pretreatment were taken to be recalcitrant (unreacted) hemicellulose. Thus, we can defined the fast reacting hemicelluloses to be the portion that directly forms monomeric sugars (reaction 2′ in Eq. (2) dotted line) by an autocatalytic mechanism, and the slow reacting hemicel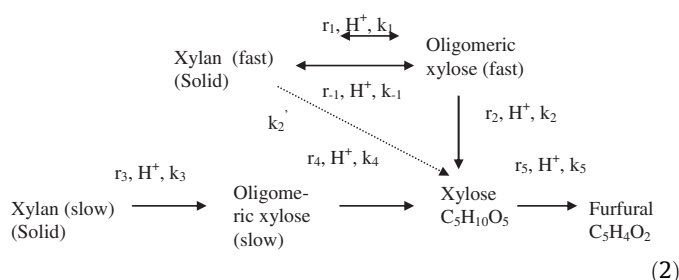luloses to be the portion that reacts to oligomeric sugars by an autocatalytic mechanism plus the portion that remains in the solid hemicellulose in biomass. Therefore, our definition of fast reacting and slow reacting hemicelluloses combined may be equivalent to the fast reacting hemicellulose defined by other investigators, and our unreacted hemicellulose may be equivalent to the slow reacting hemicellulose defined by others. In any event, our definition provides a clear approach to determine the fast and slow reacting hemicellulose fractions in biomass.

Based on these definitions and our hydrothermal experimental data, the percent of fast and slow reacting xylan in the corn stover we used were 8.9% and 91.1%, respectively. Fig. 1 presents the fast and slow reacting portions of xylans in the raw corn stover and their changes during hydrothermal and dilute acid pretreatments. The sum of the fast plus slow reacting fractions of xylan that eventually reacted equals 0.715 (= 0.0889 + 0.633), leaving 0.285 as the unreacted fraction, close to the values for the data (0.65 and 0.35) summarized by Wyman et al. (2005c).

2.2. Development of a hemicellulose hydrolysis kinetic model

Because the fast reacting hemicellulose reacts more rapidly than the slow reacting portion, some smaller macromolecules of fast reacting hemicelluloses, such as side groups, may directly form monomers such as xylose by a irreversible first-order reaction, and some larger macromolecules may first form oligomers such as oligomeric xylose by a reversible first-order reaction. These oligomers could quickly equilibrate with the larger macromolecules, and then further breakdown to monomers such as xylose by an irreversible first-order reaction that becomes rate-controlling. Therefore, our kinetic model assumes that chemical equilibrium is rapidly reached between the fast reacting hemicelluloses in biomass and the oligomers, such as oligomeric xylose, by a pseudo-homogeneous, reversible first-order reaction. Further conversion from oligomers to monomers, such as xylose, follows an irreversible first-order reaction, which is slower than the reversible reaction, and controls the reaction rate. The slow reacting hemicellulose is converted into mono-molecular compounds, such as xylose, through oligomers, such as oligomeric xylose, by two irreversible first-order reactions. Reactions from monomers, such as xylose, to decomposition products, such as furfural, are taken to be irreversible first-order reactions. The proton concentration that catalyzes reactions is integrated into all rate constants. Another key assumption is that resistance to mass transfer in the interior of biomass particles and mass transfer from the bulk liquid to the solid surface is small for the agitated reactors used at high reaction temperatures.

It would be desirable to apply the below reaction mechanism to the entire hemicellulose and not just the xylan portion. However, we focused on just determining the fast and slow reacting xylan, oligomeric xylose, xylose, and furfural in the following text because only xylose and its derivatives can be measured accurately enough for meaningful analysis, and the results are likely a good proxy for fast and slow reacting hemicelluloses and their oligomers, mono-compounds, and decomposition products. In any event, the following reaction mechanism results from these assumptions (Eq. (2)):

Fig. 1. Fast and slow reacting fractions of xylan in raw corn stover and their changes in residues following pretreatments. Column 1: black: fast reacting xylan; white: slow reacting xylan in raw corn stover (Raw CS). Column 2: black: reacted fast reacting xylan; white: remaining slow reacting xylan; texture: reacted slow reacting xylan in residue after hydrothermal pretreatment (HWR). Column 3: black: reacted fast reacting xylan; white: remaining slow reacting xylan; texture: reacted slow reacting xylan in residue after 0.5% sulfuric acid pretreatment (AR).

(2)

According to the law of mass action, the rate equations for these reactions can be, respectively, expressed as

$$\frac{dF_X}{dt} = -k_1 F_X + k_{-1} O_{FX} \tag{3}$$

$$\frac{dO_{FX}}{dt} = k_1 F_X - k_{-1} O_{FX} - k_2 O_{FX} \tag{4}$$

$$\frac{dS_X}{dt} = -k_3 S_X \tag{5}$$

$$\frac{dO_{SX}}{dt} = k_3 S_X - k_4 O_{SX} \tag{6}$$

$$\frac{dX_Y}{dt} = k_4 O_{SX} + k_2 O_{FX} - k_5 X_Y \tag{7}$$

$$\frac{dF_U}{dt} = k_5 X_Y \tag{8}$$

$$k_i = k_i'' H = A_i H \exp\left(-\frac{E_a}{RT}\right) \quad i = 1-5 \tag{9}$$

where F_X, S_X, O_{FX}, O_{SX}, X_Y, F_U, and H are the concentrations of fast reacting xylan, slow reacting xylan, oligomeric xylose formed by the fast xylan reaction, oligomeric xylose formed by the slow xylan reaction, xylose, furfural, and protons, respectively, all in mol/L. The first order rate constants for each reaction are k_1, k_{-1}, k_2, k_3, k_4, and k_5 in units of min^{-1} with the proton concentrations integrated into each. On the other hand, k_i'' represents the corresponding rate constants that do not include the proton concentration, with units of L/(mol min) and subscripts $i = 1–5$ corresponding to the appropriate reaction step in expression (4). Furthermore, A_i and E_{ai} are the Arrhenius pre-exponential factors and the activation energies for each reaction with units of L/(mol min) and J/mol, respectively. Finally, R is the gas constant with units of J/(mol K), and T is the reaction temperature in K. Because reaction 2 is assumed to be rate-controlling step, the pseudo steady state hypothesis can be applied to Eq. (4), and substituting the result into Eqs. (3) and (7), respectively, results in:

$$\frac{dF_X}{dt} = -k_1' F_X \tag{10}$$

$$\frac{dX_Y}{dt} = k_4 O_{SX} + k_2' F_X - k_5 X_Y \tag{11}$$

where

$$k_1' = k_2' = \frac{k_1 k_2}{k_{-1} + k_2} \tag{12}$$

Application of the pseudo-steady state hypothesis to the reversible first-order reaction makes the two-step reaction equivalent to an irreversible first-order reaction. Therefore, both pathways of direct and indirect formation of monomers can be combined as one pathway (dotted line), as in Eq. (2). Moreover, an analytical solution is more easily developed after application of the pseudo-steady state hypothesis.

Integration of Eqs. (5), (6), (8), (10), and (11), in that order, with the initial conditions $F_X = F_{X,0}$, $S_X = S_{X,0}$, and $O_{SX} = X_Y = 0$ at $t = 0$ results in the analytical expressions given by Eqs. (13)–(17) to describe fast reacting xylan, slow reacting xylan, oligomeric xylose, xylose, and furfural concentrations over time.

$$F_X = F_{X,0} \exp(-k_2' t) \tag{13}$$

$$S_X = S_{X,0} \exp(-k_3 t) \tag{14}$$

$$O_{SX} = \frac{k_3 S_{X,0}}{k_4 - k_3} [\exp(-k_3 t) - \exp(-k_4 t)] \tag{15}$$

$$X_Y = \frac{k_4 k_3 S_{X,0}}{k_4 - k_3} \left[\frac{\exp(-k_3 t) - \exp(-k_5 t)}{k_5 - k_3} - \frac{\exp(-k_4 t) - \exp(-k_5 t)}{k_5 - k_4} \right] + \frac{k_2' F_{X,0}}{k_5 - k_2'} [\exp(-k_2' t) - \exp(-k_5 t)] \tag{16}$$

$$F_U = \frac{k_5 k_4 k_3 S_{X,0}}{k_4 - k_3} \left\{ \frac{1}{k_5 - k_3} \left[\frac{\exp(-k_5 t)}{k_5} - \frac{\exp(-k_3 t)}{k_3} \right] - \frac{1}{k_5 - k_4} \left[\frac{\exp(-k_5 t)}{k_5} - \frac{\exp(-k_4 t)}{k_4} \right] \right\} + \frac{k_5 k_2' F_{X,0}}{k_5 - k_2'} \left[\frac{\exp(-k_5 t)}{k_5} - \frac{\exp(-k_2' t)}{k_2'} \right] \tag{17}$$

The total amount of xylan FS_{X0} in biomass initially must equal the sum of the initial fast and slow reacting fractions:

$$FS_{X,0} = F_{X,0} + S_{X,0} \tag{18}$$

Thus, the fractions $f_{FX,0}$ and $f_{SX,0}$ of fast and slow reacting xylans in the total xylan in biomass at an initial time, were, respectively, defined as:

$$f_{FX,0 \text{ or } SX,0} = \frac{F_{X,0} \text{ or } S_{X,0}}{F_{X,0} + S_{X,0}} \tag{19}$$

As the reaction proceeds, the fractions of the remaining fast reacting xylan as y_{FX}, and slow reacting xylan as y_{SX}, in the total xylan of biomass, and yields of oligomers as y_{OSX}, xylose as y_{XY}, and furfural as y_{FU} can be, respectively, expressed as:

$$y_{FX, \text{ or } SX, \text{ or } OSX \text{ or } XY \text{ or } FU} = \frac{F_X \text{ or } S_X \text{ or } O_{SX} \text{ or } X_Y \text{ or } F_U}{F_{X,0} + S_{X,0}} \tag{20}$$

Therefore, the corresponding fractions of fast and slow reacting xylans, and yields of oligomeric xyloses, xylose, and furfural can be determined at any time by dividing the results from Eqs. (13)–(17) by the total amount of xylan contained initially in the raw biomass.

$$y_{FX} = f_{FX,0} \exp(-k_2' t) \tag{21}$$

$$y_{SX} = f_{SX,0} \exp(-k_3 t) \tag{22}$$

$$y_{OSX} = \frac{k_3 f_{SX,0}}{k_4 - k_3} [\exp(-k_3 t) - \exp(-k_4 t)] \tag{23}$$

$$y_{XY} = \frac{k_4 k_3 f_{SX,0}}{k_4 - k_3} \left[\frac{\exp(-k_3 t) - \exp(-k_5 t)}{k_5 - k_3} - \frac{\exp(-k_4 t) - \exp(-k_5 t)}{k_5 - k_4} \right] + \frac{k_2' f_{FX,0}}{k_5 - k_2'} [\exp(-k_2' t) - \exp(-k_5 t)] \tag{24}$$

$$y_{FU} = \frac{k_5 k_4 k_3 f_{SX,0}}{k_4 - k_3} \left\{ \frac{1}{k_5 - k_3} \left[\frac{\exp(-k_5 t)}{k_5} - \frac{\exp(-k_3 t)}{k_3} \right] - \frac{1}{k_5 - k_4} \left[\frac{\exp(-k_5 t)}{k_5} - \frac{\exp(-k_4 t)}{k_4} \right] \right\} + \frac{k_5 k_2' f_{FX,0}}{k_5 - k_2'} \left[\frac{\exp(-k_5 t)}{k_5} - \frac{\exp(-k_2' t)}{k_2'} \right] \tag{25}$$

3. Methods

3.1. Feedstock and reagents

Raw corn stover supplied by the National Renewable Energy Laboratory (NREL) to the Biomass Refining Consortium for Applied Fundamentals and Innovation (CAFI) was used as the feedstock, and sulfuric acid was purchased from Sigma–Aldrich (St. Louis, MO). The composition of the raw corn stover as determined in

our laboratory by standard NREL methods was 36.1% glucan, 21.4% xylan, 1.72% arabinan, 0.93% galactan, 13.6% lignin, 2.8% ash, and 23.5% others. D-(+)-glucose and xylose (both Sigma–Aldrich, 99.5%) were used as standard materials for HPLC analysis. Calcium carbonate (Fisher Scientific, 99.0%) was used to neutralize acid in samples before HPLC analysis.

3.2. Pretreatment of corn stover in hydrothermal and dilute sulfuric acid

The raw corn stover was ground to less than 1 mm using a laboratory mill with an internal sieve (model 4, Arthur H. Thomas Company, Philadelphia, PA). The milled corn stover was stored in plastic bags in a freezer at −18 °C until used for pretreatments.

A one-liter stainless steel Parr reactor with two stacked pitched blade impellers (Model 4525, Parr Instruments Company, Molline, Illinois) was used for monomeric and oligomeric sugar production from the raw corn stover by hydrothermal and dilute sulfuric acid pretreatments. The reactor was heated in 4 kW fluidized sand baths (Model SBL-2D, Techne Co., Princeton, NJ), and the internal temperature was monitored with a type K thermocouple (Omega CASS-18U-12, Omega Engineering Co., Stamford, CT). For hydrothermal pretreatments, typically, 50 g of dry corn stover and 650 mL of deionized water were loaded into the Parr reactor to provide a total suspension volume of 700 mL in the reactor, and the Parr reactor was sealed. The temperature of the sand bath was taken to 450 °C, and the Parr reactor was lowered into it. After about 5 min, the temperature of the Parr reactor approached to within 5 °C of the target temperature, and the Parr reactor was raised to keep the temperature stable at the target temperature, at which point the reaction time was set as zero. When the desired reaction time was reached, the Parr reactor was quickly moved to a water bath to cool it and stop the reaction. When ambient pressure was reached, the Parr reactor was opened, and the pretreated corn stover slurry was filtered through filter paper (Fisher Brand Glass Fiber Filter Circles). The filtrates were analyzed by HPLC as described below. The pretreated solids were transferred to a glass filter and washed three times with hot-deionized water. The washed solids were measured for moisture using an automatic system (HB43-S, Mettler Toledo) and weighed to calculate solid yields. For dilute sulfuric acid pretreatment, the milled corn stover was soaked in a predetermined solution volume with the required dilute sulfuric acid concentration (for example, 0.5 wt.%) overnight.

The rest of the experimental procedures were the same as the hydrothermal pretreatment described above. The sugar yields y_p (dimensionless) from pretreatment was defined by the following equation:

$$y_p = \frac{r c_p v_p}{m_0 f_0} \tag{26}$$

where c_p is the glucose or xylose concentration measured by HPLC (g/L), v_p is the liquid volume including moisture of the raw corn stover (L), m_0 is the weight of the dried corn stover added to the reactor (g), r is the conversion factor from glucose and xylose to glucan and xylan (0.9 and 0.88), respectively, and f_0 is the total carbohydrate content (glucan plus xylan) in the raw corn stover (dimensionless). The solid yield y_{ps} (dimensionless) from pretreatment is defined as:

$$y_{ps} = \frac{m_p}{m_0} \tag{27}$$

where m_p is the weight (g) of pretreated dry corn stover solids following pretreatment for a particular time.

The modified severity factor including pH was calculated to facilitate comparison of the effect of various dilute sulfuric acid pretreatment conditions on sugar yields (Chum et al., 1990):

$$\log(R_h) = \log \left[\int_0^{t_s} \exp \left(\frac{T_r - T_b}{14.75} \right) dt \right] + \log(H^+)$$
$$= \log \left[t_s \exp \left(\frac{T_r - T_b}{14.75} \right) \right] - pH \tag{28}$$

where R_h is the modified reaction ordinate including the effect of protons, t_s is the reaction time (s), T_r is the pretreatment temperature (°C), and T_b is a base temperature (100 °C). In Eq. (28) it was assumed that the pretreatment temperature T_r is constant, i.e., the time for temperature rise could be ignored in the initial pretreatment period for heating-up reactor. Final pH values measured at room temperature after pretreatment were used in Eq. (28).

3.3. Analysis of components in the liquid fraction

Xylose and glucose concentrations in the liquid fraction were measured using an Agilent HPLC equipped with an RI detector and a Bio-Rad Aminex HPX-87H column (Bio-Rad Laboratories, Hercules, CA) at 65 °C. The mobile phase was 0.005 M sulfuric acid with a flow rate of 0.6 mL/min. The identities of the compounds were authenticated by comparing their retention times with those
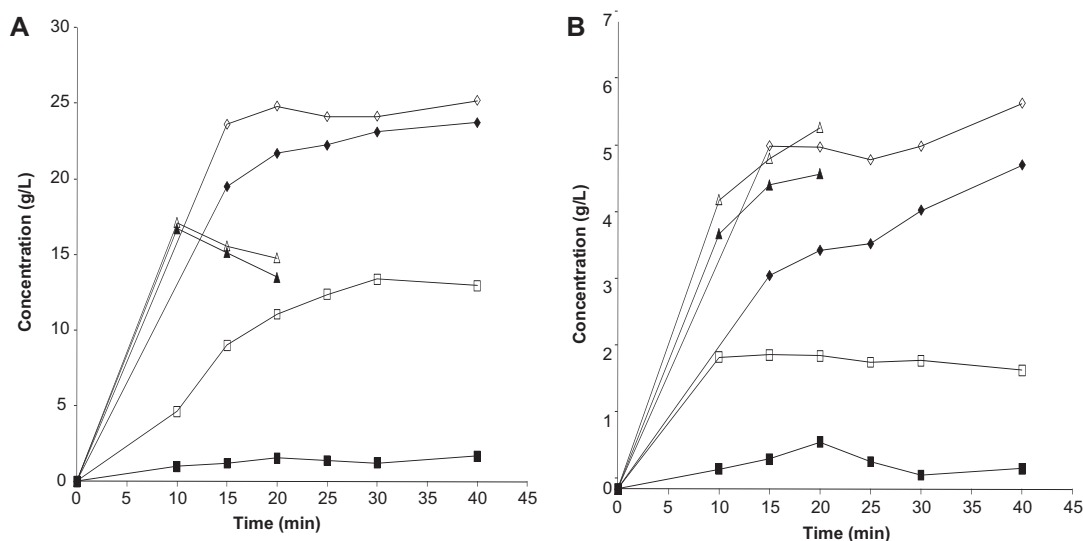
Fig. 2. Total xylose (A) and glucose (B) concentrations over reaction time. Closed points show results before post hydrolysis, and open points show the results after post hydrolysis, with the difference being oligomers. Square points: hydrothermal at 180 °C; rhombus: 0.5% sulfuric acid at 160 °C; and triangles: 0.5% sulfuric acid at 180 °C.

of pure compounds (Sigma–Aldrich, St. Louis, MO). Before injecting into the HPLC, the acid in the filtrates was neutralized with calcium carbonate to pH 5–6, and then the suspensions were centrifuged at 15,000 rpm for 5 min through a 0.2 µm member filter. The supernatants were used for HPLC analysis.

3.4. Analysis of components in the solids

The components in the solids were analyzed according to NREL standard procedures (Selig et al., 2008; Sluiter et al., 2008, 2005) with the carbohydrates expressed in terms of the corresponding sugars. Briefly, about 0.3 g of the pretreated residue or the raw corn stover was added to 3 mL of 72 wt.% sulfuric acid, and the suspension was hydrolyzed at 50 °C for 1 h. Then, the slurry was diluted to 4 wt.% sulfuric acid by adding 84 mL deionized water followed by autoclaving at 121 °C for 1 h. After cooling, the slurry was filtered through a crucible, and the filtrate was used in HPLC analysis. A Waters HPLC model 2695 system equipped with a 2414 refractive detector, a Waters 2695 autosampler, a Bio-Rad Aminex HPX-87P column (Bio-Rad Laboratories, Hercules, CA), and Millenium32 chromatography manager 3.2 software (Waters Co., Milford, MA) were employed for analyzing the compounds. The column temperature was 85 °C, and the mobile phase was deionized water at a flow rate of 0.6 mL/min.

3.5. Post hydrolysis

After pretreatments of the raw corn stover, 72% sulfuric acid was added to samples of the liquid fractions derived from both hydrothermal and dilute acid pretreatments to make a 4% acid solution according to NREL standard procedures (Sluiter et al., 2006). The solution was autoclaved at 121 °C for 1 h and further prepared for HPLC analysis of the sugars as described above.

3.6. Determination of the remaining fractions of fast and slow reacting xylans over the pretreatment period

An important aspect of modeling xylan decomposition based on experimental data was to determine the remaining fractions of fast and slow reacting xylans as a function of time during pretreatment (y_{FX}, and y_{SX} in Eqs. (21) and (22) vs. time). For dilute acid pretreatment, these could be directly calculated because the xylan fractions f_{xsp} (Fig. 4 A) in the pretreated residues and solid yields y_{sp} (Fig. 4 E) were measured vs. time, i.e.,

$$y_{FX} = \frac{0.0889 f_{xsp} y_{sp}}{FS_{X0}} \tag{29}$$

$$y_{SX} = \frac{0.911 f_{xsp} y_{sp}}{FS_{X0}} \tag{30}$$

in which FS_{X0} is equal to 15.2 for hydrothermal pretreatment and 21.4 for dilute acid pretreatment at 160 °C (0.214 of xylan fraction in the raw corn stover times the initial corn stover weight in the Parr). For hydrothermal pretreatment, y_{FX} and y_{SX} were calculated by subtracting monomeric and oligomeric xylose yields vs. time from the fast and slow reacting xylans (0.0889 and 0.9111) in the raw corn stover (Fig. 4 C), i.e.,

$$y_{FX} = 0.0889 - \text{monomeric xylose yield in liquid fraction} \tag{31}$$
$$y_{SX} = 1 - 0.0889 - \text{oligomeric xylose yield in liquid fraction} \tag{32}$$

The yields of oligomeric xylose required to be fitted in Eq. (23) were determined by the xylose yields after post hydrolysis minus the xylose yields before post hydrolysis.

4. Results and discussion

4.1. Effect of pretreatment time and temperature on concentrations and yields of glucose and xylose

The raw corn stover was pretreated at the following three conditions: (1) hydrothermal (just water without acid added) at a solids concentration of 71 g/L and temperature of 180 °C, (2) 100 g/L solids with 0.5 wt.% sulfuric acid at 160 °C, and (3) 71 g/L solids with 0.5 wt.% sulfuric acid at 180 °C. Fig. 2 presents xylose and glucose concentrations before and after post hydrolysis plotted against time for these three cases. As expected, the relative concentrations of glucose were low, while the total xylose (xylose plus oligomeric xylose) concentrations for both pretreatments were
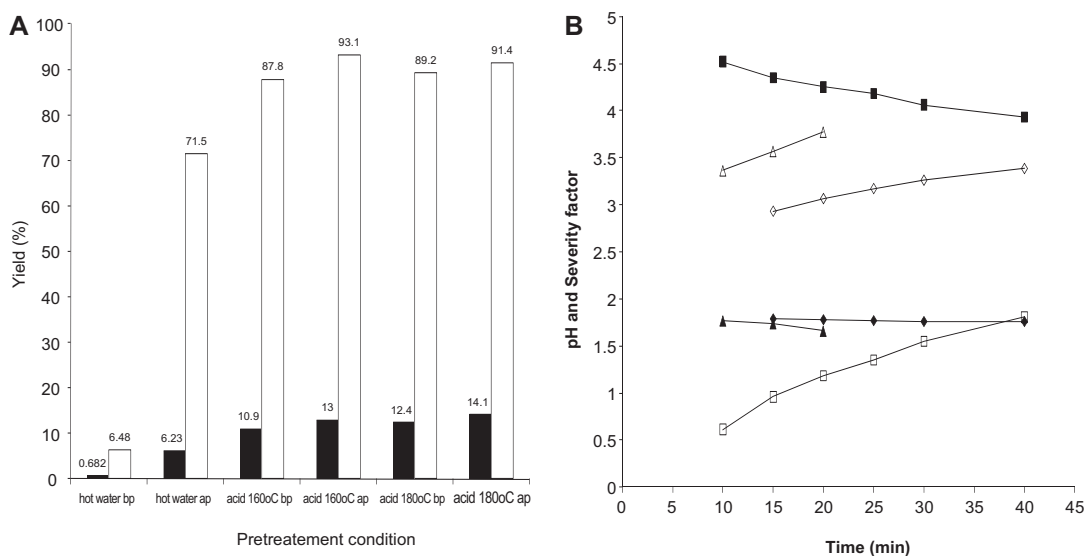
Fig. 3. (A) Yields of total glucose and xylose at the optimal conditions. Black bars refer to glucose, and white bars refer to xylose. Columns 1 and 2: hydrothermal at 180 °C and 30 min before post hydrolysis (bp). Columns 3 and 4: hydrothermal at 180 °C and 30 min after post hydrolysis (ap). Columns 5 and 6: 0.5% sulfuric acid at 160 °C and 40 min before post hydrolysis. Columns 7 and 8: 0.5% sulfuric acid at 160 °C and 40 min after post hydrolysis. Columns 9 and 10: 0.5% sulfuric acid at 180 °C and 10 min before post hydrolysis. Columns 11 and 12: 0.5% sulfuric acid at 180 °C and 10 min after post hydrolysis. (B) Final pH values and severity factors vs. time at three pretreatment conditions: hydrothermal at 180 °C and 30 min (squares); 0.5% sulfuric acid at 160 °C and 40 min (rhombus); 0.5% sulfuric acid at 180 °C and 20 min (triangle). Solid symbols refer to measured pH, and open symbols are the severity factor.

higher because hemicellulose in corn stover, like most plants, was more easily decomposed than cellulose. For hydrothermal pretreatment, the maximum total xylose concentration was about 13.4 g/L following reaction for 30 min at 180 °C. However, adding 0.5% sulfuric acid increased the maximum xylose concentration to a much higher value of 25.2 g/L for reaction at 160 °C for 40 min and 17.1 g/L after pretreatment for 10 min at 180 °C. Three reasons could explain the lower xylose concentration at 180 °C
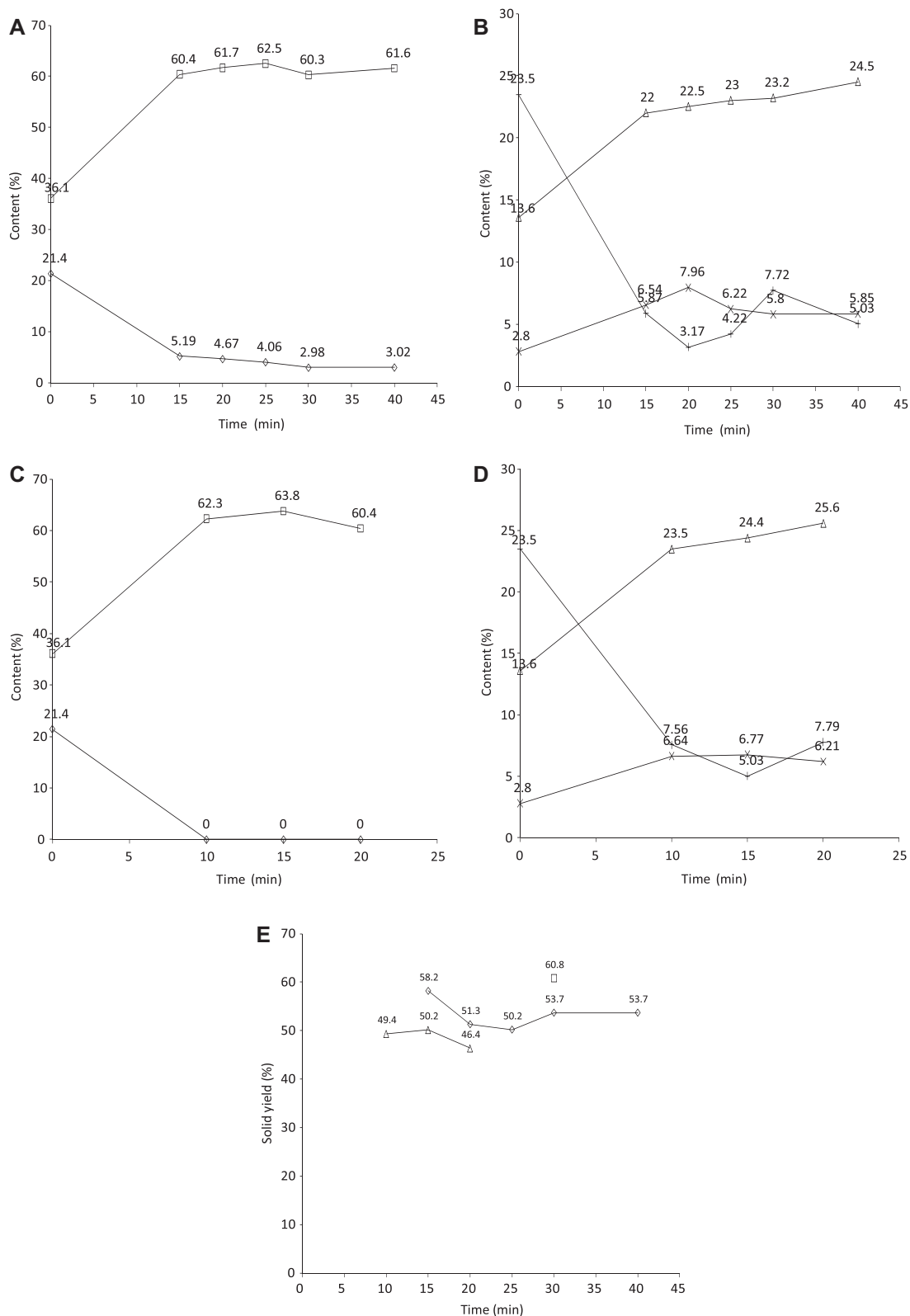
Fig. 4. (A and B) Change in composition of corn stover solids following pretreatment with 0.5% sulfuric acid at 160 °C vs. time: (A) squares: glucan; rhombus: xylose; (B): triangle: lignin; multi symbol: ash; cross: others. (C and D) The change in composition of corn stover solids following pretreatment with 0.5% sulfuric acid at 180 °C vs. time: (C) squares: glucan; rhombus: xylose; (D) triangle: lignin; multi symbol: ash; cross: others. (E) Solid yields following three pretreatments: squares: hydrothermal pretreatment at 180 °C; rhombus: 0.5% sulfuric acid at 160 °C; triangle: 0.5% sulfuric acid at 180 °C.

than at 160 °C: (1) a higher initial corn stover concentration of 100 g/L at 160 °C vs. 71 g/L at 180 °C, which accounts for most of the difference; (2) differences in the modified severity factor of 3.29 for 40 min at 160 °C vs. 2.77 for 10 min at 180 °C; and (3) more degradation products at higher temperatures even for the same severity. The times to achieve the maximum total glucose (monomer plus oligomer) concentrations (10 min for hydrothermal, 40 min for dilute acid at 160 °C, and 20 min for dilute acid at 180 °C) for both hydrothermal and dilute acid pretreatments were different than those for xylose (30 min for hydrothermal, 20 min for dilute acid at 160 °C, and 15 min for dilute acid at 180 °C).

Fig. 3 A summarizes the highest xylose yields as well as glucose yields at the same times, before and after post hydrolysis for hydrothermal and dilute acid pretreatments; as noted above, these do not correspond to the highest glucose yields due to the different optimal times for xylose and glucose. From this figure, we can see that the highest total xylose yield for hydrothermal pretreatment was about 71.5% and the highest total glucose yield was 6.51% (data not shown in Fig. 3), with about 91% of the total xylose and 65% of the total glucose as oligomers. However, oligomers made much lower contributions to the total xylose and glucose yields for dilute acid pretreatment (5.6% and 16% for 160 °C, and 2.4% and 12% for 180 °C, respectively). Furthermore, dilute acid produced higher total sugar yields than hydrothermal pretreatment, with the highest total xylose and glucose yields being 93.1% and 13% at 40 min and 160 °C and the highest total xylose and glucose yields being 91.4% at 10 min and 17.6% (data not shown in Fig. 3) at 20 min and 180 °C. The maximum xylose yield of 93.1% from dilute acid pretreatment was close to those (90% and 95%) reported by Lloyd and Wyman (2005) and Tucker et al. (2003), respectively. However, our highest xylose yield of 71.5% from hydrothermal pretreatment is much greater than the 46.8% value reported in the limited study of these conditions by Lloyd and Wyman (2005). The reason may be that they used steam explosion for hydrothermal pretreatment, an open system in which, some xylose might be released the air due to the sudden drop in pressure, while we used a closed Parr reactor. In addition, increasing temperature reduced reaction times needed to reach maximum xylose yields because higher temperature accelerated hemicellulose degradation. These results confirmed that the maximum xylose yield is governed by both temperature and time, as expected.

Fig. 3 B shows final pH values measured after pretreatment and severity factors calculated from Eq. (28) vs. time for hydrothermal pretreatment and 0.5% sulfuric acid pretreatment at the two temperatures. Increasing pretreatment time reduced the final pH for all three cases, likely due to greater proton release from acetyl compounds in hemicellulose. The final proton concentrations in the liquid fractions for the three cases increased by 1.86, 1.05, and 1.29 times from 10 to 40 min, respectively. Hydrothermal pretreatment was more sensitive to longer reaction times than dilute acid pretreatment because the former depended on proton release from acetyl compounds and not from external proton addition.

4.2. Composition of corn stover solids pretreated with 0.5% sulfuric acid at 160 and 180 °C

Fig. 4 presents the composition of acid pretreated corn stover solids at 160 °C (A and B) and 180 °C (C and D) over the reaction times. Generally, xylan (xylan fraction f_{xsp}) and lignin contents in the pretreated corn stover solids at both temperatures decreased and increased monotonically, respectively, with increasing pretreatment time for the period studied due to (1) significant release of hemicellulose, mainly xylan, from corn stover into the liquid phase; (2) limited release of glucan; (3) limited lignin loss; and (4) likely formation of pseudo-lignin by degradation. The maximum glucan contents in the solids occurred at intermediate pretreatment times (62.5% at 160 °C for 25 min and 63.8% at 180 °C for 15 min), and the highest lignin contents were 24.5% at 160 °C for 40 min and 25.6% at 180 °C for 20 min. Higher temperature was more effective in xylan removal from corn stover, with almost all of the xylan removed at 180 °C after 10 min (corresponding to a log of the modified severity factor of 3.36), while xylan was still detected in the pretreated solids at 160 °C even for 40 min of reaction time (a log of the modified severity factor of 3.39). This outcome implies that temperature was the most significant factor for xylan removal among the three parameters of temperature, time, and proton concentration that comprise the modified severity factor (Eq. (28)) and that the same severity does not necessarily realize the same pretreatment effect.

Fig. 4E presents the total solid yields for the three pretreatments run. The 60.8% solid yield from hydrothermal pretreatment at 30 min was higher than any of the total solid yields for the two dilute acid pretreatments. In addition, the solid yields for lower temperature (160 °C) pretreatment with dilute acid was higher than for dilute acid pretreatment at the higher temperature (180 °C). Both outcomes can be attributed to sulfuric acid and high temperature increasing solubilization of corn stover.
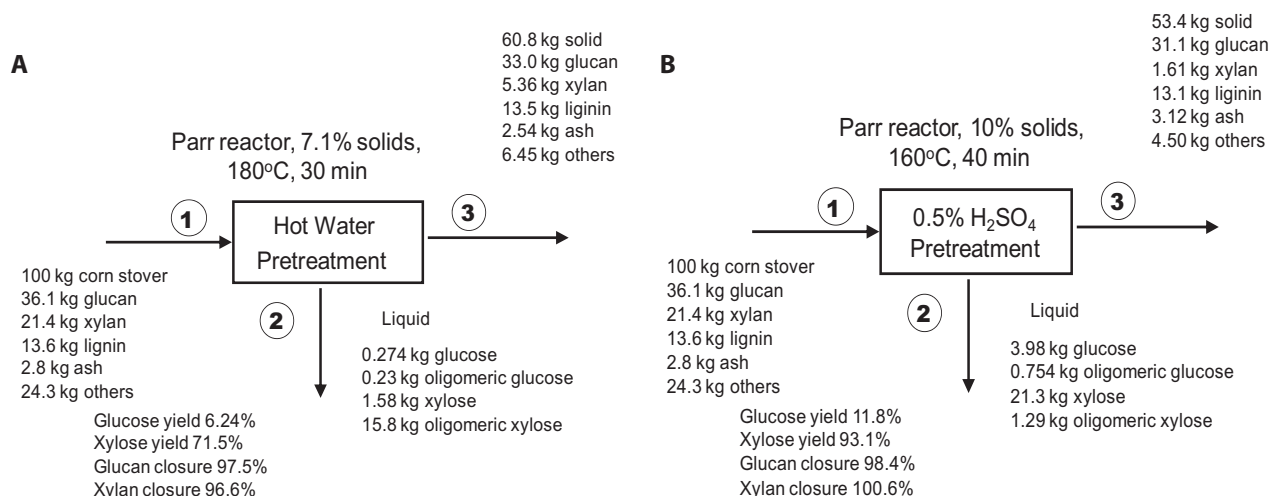
A

100 kg corn stover
36.1 kg glucan
21.4 kg xylan
13.6 kg lignin
2.8 kg ash
24.3 kg others

Parr reactor, 7.1% solids, 180 °C, 30 min

① → Hot Water Pretreatment → ③

② ↓

60.8 kg solid
33.0 kg glucan
5.36 kg xylan
13.5 kg liginin
2.54 kg ash
6.45 kg others

Liquid
0.274 kg glucose
0.23 kg oligomeric glucose
1.58 kg xylose
15.8 kg oligomeric xylose

Glucose yield 6.24%
Xylose yield 71.5%
Glucan closure 97.5%
Xylan closure 96.6%

B

100 kg corn stover
36.1 kg glucan
21.4 kg xylan
13.6 kg lignin
2.8 kg ash
24.3 kg others

Parr reactor, 10% solids, 160 °C, 40 min

① → 0.5% H₂SO₄ Pretreatment → ③

② ↓

53.4 kg solid
31.1 kg glucan
1.61 kg xylan
13.1 kg liginin
3.12 kg ash
4.50 kg others

Liquid
3.98 kg glucose
0.754 kg oligomeric glucose
21.3 kg xylose
1.29 kg oligomeric xylose

Glucose yield 11.8%
Xylose yield 93.1%
Glucan closure 98.4%
Xylan closure 100.6%

Fig. 5. Xylan and glucan mass balances for corn stover pretreatment for hydrothermal at 180 °C (A) and 0.5% sulfuric acid at 160 °C (B).
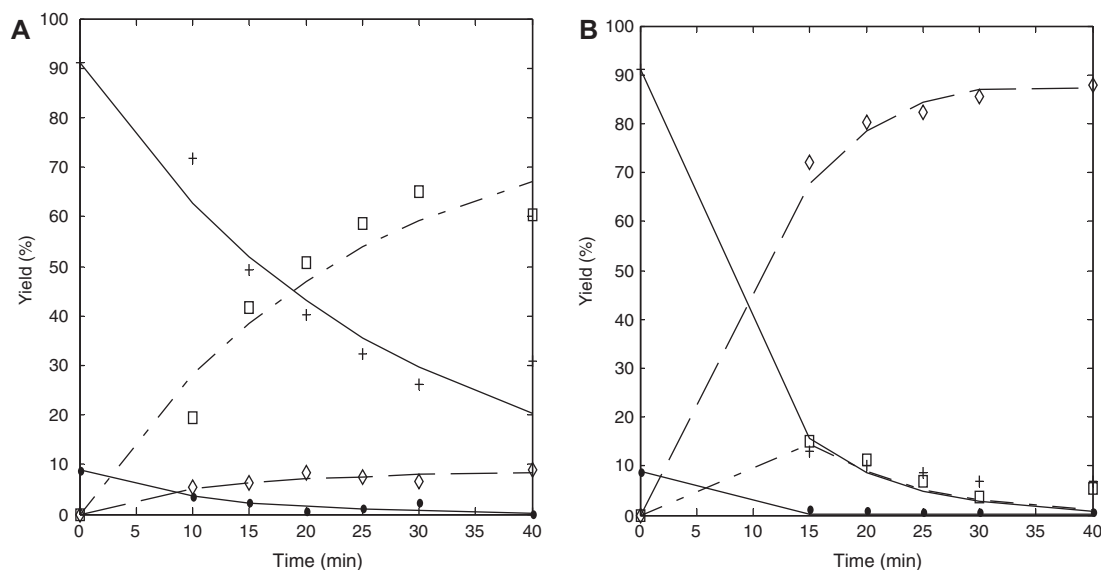
Fig. 6. Experimental data and model results for xylan decomposition by 180 °C hydrothermal (A) and 160 °C, 0.5% sulfuric acid (B) pretreatments. Fast reacting xylan: data (solid points) and model (solid lines); slow reacting xylan: data (crosses) and model (dot lines); oligomeric xylose: data (squares) and models (dot/dash lines); xylose monomer: data (rhombus) and models (dashed lines).

4.3. Mass balances of sugars from pretreated corn stover

Fig. 5 presents mass balances for hydrothermal pretreatment of corn stover at 180 °C for 30 min (A) and 0.5% sulfuric acid pretreatment at 160 °C for 40 min (B), both being conditions that realized the highest xylose release. Based on projecting our results to a basis of 100 kg of dry corn stover, 17.4 kg of total xylose (1.58 kg of monomeric xylose and 15.8 kg of oligomeric xyloses), 2.50 kg of total glucose (0.274 kg of monomeric glucose and 2.23 kg of oligomeric glucose), and 60.8 kg of total solids would result from hydrothermal pretreatment at 180 °C. Application of 0.5% sulfuric acid at 160 °C increased the amounts released into solution to 22.6 kg of total xylose (21.3 kg of monomeric xylose and 1.29 kg of oligomeric xylose) and 4.73 kg of total glucose (3.98 kg of monomeric glucose and 0.754 kg of oligomeric glucose), while reducing the total solids left to 53.4 kg. Thus, dilute acid pretreatment produced much higher glucose and xylose yields (11.8% and 93.1%) than hydrothermal pretreatment (6.24% and 71.5%). Weight losses of 20.9% and 20.2% in the overall mass balances of the solid and liquid fractions combined were also measured for hydrothermal and dilute acid, respectively, possibly because the filter paper was not fine enough to capture all the particles in the slurry after pretreatment. In addition, some solids were adsorbed in the filter paper and funnel wall during filtration and could not be collected. Another possible cause of losses could be lack of detection by HPLC of unknown compounds formed by decomposition of hemicellulose and cellulose. Despite the losses in overall solids, most of the xylan and glucan in the raw corn stover fed to pretreatment could be accounted for, with deviations of only −3.4% for xylan and −2.5% for glucan for hydrothermal pretreatment and 0.6% of xylan and −2.1% of glucan for 160 °C dilute acid conditions in Fig. 5.

4.4. Simulation of fast and slow reacting xylan hydrolysis

Once the fractions of the remaining fast and slow xylan (y_{FX} and y_{SX}), and the yields of oligomers and xylose (y_{OSX} and y_{XY}) were known over time from the experiments reported above, the rate constants in Eqs. (21)–(24) were fit to these data, with Fig. 6 showing the results for hydrothermal (A) and dilute acid (B) pretreat-

ments and Table 1 reporting the fitted parameters for each pretreatment. The rate constant k_4 in Table 1 is the smallest among all four rate constants for pretreatment without added acid, implying that reaction of oligomeric xylose to monomers controlled the rate of xylan conversion to furfural for hydrothermal pretreatment. However, the rate constant k_4 in Table 1 is greater than k_5 for dilute acid pretreatment, suggesting the acid addition resulted in the rate-controlling step conversion to xylose decomposition to furfural from oligomeric xylose decomposition in hydrothermal pretreatment, which explains the reason of higher yield of dilute acid pretreatment than hydrothermal pretreatment from reaction mechanism. The results also demonstrate that autocatalysis occurred in hydrothermal pretreatment has a different rate-controlling mechanism with acid–catalysis occurred in dilute acid pretreatment. Furthermore, the rate constant k_4 (0.0021 min^{-1}) for hydrothermal pretreatment was only about 1/100 of that (0.2165 min^{-1}) for dilute acid pretreatment, suggesting that reaction from oligomeric xylose to xylose was much slower for hydrothermal than for dilute acid pretreatment and further providing a quantitative explaining of why dilute acid pretreatment gives higher yields than hydrothermal pretreatment. The rate constant k_2' (0.090 min^{-1} for hydrothermal pretreatment and 0.4413 min^{-1} for dilute acid pretreatment) was greater than k_3 and k_4 (0.0375 and 0.0021 min^{-1} for hydrothermal pretreatment, and 0.1177 and 0.2165 min^{-1} for dilute acid pretreatment), confirming that

Table 1
Parameters for models in Eqs. (21)–(24) for hydrothermal pretreatment at 180 °C and dilute acid pretreatment at 160 °C.

Rate constant	k_2 (min^{-1})	k_3 (min^{-1})	k_4 (min^{-1})	k_5 (min^{-1})	SSD
Hydrothermal	0.090	0.0375	0.0021	0.0156	552
Dilute acid	0.4413	0.1177	0.2165	0.0042	141

	k_2'' L/(mol min)	k_3'' L/(mol min)	k_4'' L/(mol min)	k_5'' L/(mol min)	
Hydrothermal	1033	431	24.1	179	
Dilute acid	25.4	6.77	12.4	0.242	

SSD: sum of square deviation.
The initial fractions of fast and slow reacting hemicelluloses are 0.0889 and 0.9111, respectively.

the pathway represented by k'_2 is the reaction path for the fast reacting xylan. On the other hand, the value of the rate constant k'_2 for dilute acid pretreatment is 4.9 times that for hydrothermal pretreatment, meaning that the reaction rate for the path from xylan to xylose was faster for dilute acid than for hydrothermal pretreatment. Interestingly, the k''_2 value that excludes the proton concentration with dilute acid was only 2.5% (25.4/1033%) of that for hydrothermal conditions. From this, we could conclude that external protons supplied by dilute acid are the primary reason that reaction 2′ is so much faster for dilute acid pretreatment.

5. Conclusions

The maximum total xylose yield was only 71.5% after 30 min for hydrothermal pretreatment of corn stover in a one-liter Parr reactor at 180 °C. However, the maximum total xylose yield increased significantly to 93.1% for pretreatment with 0.5% sulfuric acid at 160 °C for 40 min. A model with a fast xylan reaction to monomeric xylose and a slow xylan reaction to monomeric xylose via oligomeric xylose could fit experimental xylan release data well for both hydrothermal and dilute acid pretreatments. The results predicted that xylose formation from oligomers was rate-controlling for hydrothermal pretreatment, while xylose decomposition to furfural was rate-controlling for dilute acid pretreatment.

Acknowledgements

References

Aguilar, R., Ramirez, J.A., Garrote, G., Vazquez, M., 2002. Kinetic study of the acid hydrolysis of sugar cane bagasse. Journal of Food Engineering 55, 309–318.

Bustos, G., Ramirez, J.A., Garrote, G., Vazquez, M., 2003. Modeling of the hydrolysis of sugar cane bagasse with hydrochloric acid. Applied Biochemistry and Biotechnology 104, 51–68.

Chen, R.F., Lee, Y.Y., Torget, R., 1996. Kinetic and modeling investigation on two-stage reverse-flow reactor as applied to dilute-acid pretreatment of agricultural residues. Applied Biochemistry and Biotechnology 57–8, 133–146.

Chum, H.L., Johnson, D.K., Black, S.K., Overend, R.P., 1990. Pretreatment catalyst effects and the combined severity parameter. Applied Biochemistry and Biotechnology 24–25, 1–14.

Esteghlalian, A., Hashimoto, A.G., Fenske, J.J., Penner, M.H., 1997. Modeling and optimization of the dilute-sulfuric-acid pretreatment of corn stover, poplar and switchgrass. Bioresource Technology 59, 129–136.

Jacobsen, S.E., Wyman, C.E., 2000. Cellulose and hemicellulose hydrolysis models for application to current and novel pretreatment processes. Applied Biochemistry and Biotechnology 84 (6), 81–96.

Jacobsen, S.E., Wyman, C.E., 2002. Xylose monomer and oligomer yields for uncatalyzed hydrolysis of sugarcane bagasse hemicellulose at varying solids concentration. Industrial & Engineering Chemistry Research 41, 1454–1461.

Jae, J.H., Tompsett, G.A., Lin, Y.C., Carlson, T.R., Shen, J.C., Zhang, T.Y., Yang, B., Wyman, C.E., Conner, W.C., Huber, G.W., 2010. Depolymerization of lignocellulosic biomass to fuel precursors: maximizing carbon efficiency by combining hydrolysis with pyrolysis. Energy & Environmental Science 3, 358–365.

Kadam, K.L., McMillan, J.D., 2003. Availability of corn stover as a sustainable feedstock for bioethanol production. Bioresource Technology 88, 17–25.

Kim, S.B., Lee, Y.Y., 1987. Kinetics in acid–catalyzed hydrolysis of hardwood hemicellulose. Biotechnology and Bioengineering Symposium 17, 71–84.

Kobayashi, T., Sakai, Y., 1956. Hydrolysis rate of pentosan of hardwood in dilute sulfuric acid. Bulletin of the Agricultural Chemical Society of Japan 20, 1–7.

Lloyd, T.A., Wyman, C.E., 2005. Combined sugar yields for dilute sulfuric acid pretreatment of corn stover followed by enzymatic hydrolysis of the remaining solids. Bioresource Technology 96, 1967–1977.

Lu, Y.L., Mosier, N.S., 2008. Kinetic modeling analysis of maleic acid–catalyzed hemicellulose hydrolysis in corn stover. Biotechnology and Bioengineering 101, 1170–1181.

Maloney, M.T., Chapman, T.W., Baker, A.J., 1985. Dilute acid–hydrolysis of paper birch – kinetics studies of xylan and acetyl-group hydrolysis. Biotechnology and Bioengineering 27, 355–361.

Morinelly, J.E., Jensen, J.R., Browne, M., Co, T.B., Shonnard, D.R., 2009. Kinetic characterization of xylose monomer and oligomer concentrations during dilute acid pretreatment of lignocellulosic biomass from forests and switchgrass. Industrial & Engineering Chemistry Research 48, 9877–9884.

Mosier, N., Hendrickson, R., Ho, N., Sedlak, M., Ladisch, M.R., 2005. Optimization of pH controlled liquid hot water pretreatment of corn stover. Bioresource Technology 96, 1986–1993.

Schell, D.J., Farmer, J., Newman, M., McMillan, J.D., 2003. Dilute-sulfuric acid pretreatment of corn stover in pilot-scale reactor – investigation of yields, kinetics, and enzymatic digestibilities of solids. Applied Biochemistry and Biotechnology 105, 69–85.

Selig, M., Weiss, N., Ji, Y., 2008. In: Laboratory Analytical Procedure No. TP-510-42629. National Renewable Energy Laboratory, Golden, CO.

Sluiter, A., Hames, B., Ruiz, R., Scarlata, C., Sluiter, J., Templeton, D., Crocker, D., 2008. In: Laboratory Analytical Procedure No. TP-510-42618. National Renewable Energy Laboratory, Golden, CO.

Sluiter, A., Hames, B., Ruiz, R., Scarlata, C., Sluiter, J., Templeton, D., 2005. In: Laboratory Analytical Procedures No. TP-510-42622. National Renewable Energy Laboratory, Golden, CO.

Sluiter, A., Hames, B., Ruiz, R., Scarlata, C., Sluiter, J., Templeton, D., 2006. In: Laboratory Analytical Procedures No. TP-510-42623. National Renewable Energy Laboratory, Golden, CO.

Tucker, M.P., Kim, K.H., Newman, M.M., Nguyen, Q.A., 2003. Effects of temperature and moisture on dilute-acid steam explosion pretreatment of corn stover and cellulase enzyme digestibility. Applied Biochemistry and Biotechnology 105 (1–3), 165–178.

Varga, E., Reczey, K., Zacchi, G., 2004. Optimization of steam pretreatment of corn stover to enhance enzymatic digestibility. Applied Biochemistry and Biotechnology 113, 509–523.

Wyman, C.E., Dale, B.E., Elander, R.T., Holtzapple, M., Ladisch, M.R., Lee, Y.Y., 2005a. Coordinated development of leading biomass pretreatment technologies. Bioresource Technology 96, 1959–1966.

Wyman, C.E., Dale, B.E., Elander, R.T., Holtzapple, M., Ladisch, M.R., Lee, Y.Y., 2005b. Comparative sugar recovery data from laboratory scale application of leading pretreatment technologies to corn stover. Bioresource Technology 96, 2026–2032.

Wyman, C.E., Decker, S.R., Himmel, M.E., Brady, J.W., Skopec, C.E., Viikari, L., 2005c. Hydrolysis of cellulose and hemicellulose. In: Dumitriu, S. (Ed.), Polysaccharides: Structural Diversity and Functional Versatility. CRC Press, Boca Raton, FL, pp. 995–1034.

Wyman, C.E., Dale, B.E., Elander, R.T., Holtzapple, M., Ladisch, M.R., Lee, Y.Y., Mitchinson, C., Saddler, J.N., 2008. Comparative sugar recovery and fermentation data following pretreatment of poplar wood by leading technologies. Biotechnology Progress 25, 333–339.

Zhu, Y.M., Lee, Y.Y., Elander, R.T., 2005. Optimization of dilute-acid pretreatment of corn stover using a high-solids percolation reactor. Applied Biochemistry and Biotechnology 121, 1045–1054.