Kinetic Characterization of Biomass Dilute Sulfuric Acid Hydrolysis: Mixtures of Hardwoods, Softwood, and Switchgrass

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The effects of woody biomass mixtures were investigated on the rates of hemicellulose hydrolysis by dilute acid. Very good agreement between the model predictions and single species acid hydrolysis data confirmed the validity of a pseudo first-order model approach. This model was then utilized to predict monomer sugar concentrations for mixtures of hardwood (aspen, basswood, and red maple), a softwood (balsam), and the energy crop switchgrass, with very good agreement. The results of this study show that there are not significant synergistic or antagonistic effects by mixtures of woody biomass species on the kinetics of hemicellulose hydrolysis by dilute acid. Kinetic parameters were developed for each woody biomass species with xylose formation activation energies ranging from 76.19–171.20 kJ/mol, and pre-exponential factors ranging from 2.19×10^8–7.73×10^{19} min^{-1}. Overall xylose yields for pure biomass species ranged from approximately 66–88% with balsam having the lowest yield and switchgrass producing the highest yield. © 2008 American Institute of Chemical Engineers *AIChE J,* 54: 1637–1645, 2008

Keywords: dilute acid hydrolysis, pretreatment, switchgrass, aspen, balsam, red maple, basswood, mixture effects

Introduction

The use of renewable sources of transportation fuel, such as ethanol derived from woody biomass, has great potential to be a solution to the problem of dependence on foreign petroleum. Other potential benefits of cellulosic ethanol include lowering the trade deficit, improvement of national energy security and price stability, as well as reducing greenhouse gas emissions.[1,2,3] Furthermore, cellulosic biomass, such as corn stover, forest products residue, and energy crops,[1] has the capability of being processed into ethanol without competing with a major food source.

Woody biomass is composed mainly of three types of material; cellulose, hemicellulose, and lignin. The conversion of woody biomass to ethanol begins with a pretreatment process followed by cellulose enzymatic hydrolysis, fermentation, and then finishes with product separation.[4] The pretreatment process continues to be one of the most expensive steps and improvements to pretreatment will have significant benefits for subsequent enzymatic hydrolysis and fermentation.[1,3]

The purpose of the pretreatment stage is to open up the biomass structure so enzymes can more easily access the cellulose by breaking down hemicellulose into primarily xylose, a five carbon sugar, which can be fermented into ethanol,

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while minimizing xylose degradation which generates inhibitory byproducts.[4,3] Pretreatment has been studied extensively in the past; however, until the formation of the Biomass Refining Consortium for Applied Fundamentals and Innovation (CAFI) in 2000, it was difficult to compare one pretreatment process to another. The CAFI groups all used corn stover as a feedstock and employed the same experimental methods, materials, and analysis techniques as much as possible to ensure good comparison between the approaches.[1] Pretreatment technologies, such as steam explosion, liquid hot water, pH controlled hot water, flow-through liquid hot water, dilute acid, flow-through acid, ammonia fiber/freeze explosion, ammonia recycled percolation (ARP), and lime were analyzed by the CAFI group.[4] Alkali swelling, steam explosion, AFEX, and ARP are not efficient for softwood biomass, and lime requires long pretreatment times, being hours to weeks rather than minutes to hours.[5]

Feedstocks to the ethanol production process will most likely contain a mixture of woody biomass species, rather than a single type. Forest feedstocks could be supplemented with the growth of an energy crop, such as switchgrass or hybrid willow to increase biomass yields per acre of land. Dilute acid hydrolysis was chosen for this study, because it is one of the most widely used and studied pretreatment processes,[4] and because experimental results can be directly compared to previous work in the literature. Therefore, the goal of this project is to determine the effect of feedstock mixtures on the dilute acid pretreatment kinetics. Five biomass species are included in this analysis. Four of the biomass samples are regional timber species, including three hardwoods (aspen, basswood, and red maple), and one softwood (balsam). The fifth sample of biomass is the energy crop switchgrass. We hypothesize that there will not be significant synergistic or antagonistic effects by mixtures of woody biomass species on the kinetics of hemicellulose hydrolysis by dilute acid, since the catalyst (protons) should access reactive sites on each species independent of the presence of other species. However, little work has been done in the area of mixtures, as most studies in the literature have utilized only one form of biomass, and therefore the mixture hypothesis has not been tested experimentally.

Research questions other than measuring mixture effects will be addressed in our work; for example, selection of an appropriate kinetic model, prediction of the xylose time course hydrolysis results of mixtures using single species kinetic parameters, and utilization of an improved modeling approach for the extraction of kinetic parameters (simultaneous xylose generation and degradation).

In prior literature, pretreatment kinetics was modeled by several different approaches. Some studies assumed that the hemicellulose contains two types of xylan (the polymeric sugar containing molecule of hemicellulose), a fast reacting fraction and a slow reacting fraction.[6,7] One model developed to account for this biphasic relationship[8,9,10] is shown in Eq. 1[6]

$$\underset{\text{(Xylan)}}{\text{Hemicellulose}} \left[\begin{array}{l}\text{Fast Reacting Xylan} \xrightarrow{k_f} \\ \text{Slow Reacting Xylan} \xrightarrow{k_s}\end{array}\right] \underset{\text{(In Liquid)}}{\text{Xylose}} \xrightarrow{k_2} \text{Degradation Byproducts} \tag{1}$$

This model includes two first-order rate constants for the forward reaction of hemicellulose to xylose, one for the fast reacting xylan, and one for the slow reacting xylan, represented as k_f and k_s, respectively, as shown in Eq. 1.

Other models incorporate an additional reaction step; the formation of xylose oligomers, intermediate polymeric sugars containing hemicellulose molecules of variable molecular weight, prior to the formation of xylose. This approach also depends on the biphasic relationship of biomass, and utilizes two first-order rate constants for the breakdown of fast and slow reacting xylan, and is shown in Eq. 2[11]

$$\text{Hemicellulose} \left[\begin{array}{l}\text{Fast Reacting Xylan} \xrightarrow{k_1} \\ \text{Slow Reacting Xylan} \xrightarrow{k_2}\end{array}\right] \mathrm{O} \xrightarrow{k_3} \mathrm{X} \xrightarrow{k_4} \mathrm{D} \tag{2}$$

where k_1 and k_2 refer to the rate constants of fast and slow reacting xylan, O represents soluble xylose oligomer, X is xylose, D represents decomposition products (mainly furfural), and k_3 and k_4 are first-order rate constants for the hydrolysis of xylose oligomers to xylose, and the further degradation of xylose to furfural, respectively.

A third kinetic modeling approach simplifies the aforementioned models, and utilizes a pseudo first-order rate constant[3] to describe the conversion of hemicelluloses and oligomers to xylose. Experimental data in some prior studies suggest that the biphasic nature of the substrates is negligible.[3,12] One study attributes the use of a pseudo first-order rate constant to approximately equal reactivities of the internal bonds of the polymer.[12] This model is shown in Eq. 3[3]

$$\left.\begin{array}{l}\text{Hemicellulose Xylan,}\\ \text{Xylose Oligomers}\end{array}\right\rangle (\mathrm{H}) \underset{\substack{\uparrow \\ H_2O}}{\xrightarrow{k_1}} \text{Xylose (X)} \underset{\substack{\downarrow \\ 3H_2O}}{\xrightarrow{k_2}} \text{Degradation Products (D)} \tag{3}$$

The hydrolysis takes place with the addition of water to xylan resulting in the production of xylose; and the main degradation product, furfural, is the degradation of a molecule of xylose by the release of three molecules of water.

An improved application of the kinetic model in Eq. 3, compared to Yat et al.,[3] was used in this work to determine the kinetic parameters for single species woody biomass pretreatment. This improvement to the model centers on the incorporation of the simultaneous xylose formation and degradation mechanisms, which are occurring in the early time of the experiment. Good agreement between the model predictions derived from Eq. 3, and single species pretreatment experimental data will be used to confirm the validity of the pseudo first-order model approach.

Using the kinetic parameters extracted from single species experiments, a model was developed to predict the effects of biomass mixtures on the generation and degradation of xylose. The agreement between the mixture model and experiments was used to test the mixture effects hypothesis stated above. In essence, we will show that the models developed from the individual species data can be used to predict xylose monomer sugar concentrations obtainable from various mixtures of biomass, as long as the percentage of each biomass species in the mixture is known. This simplifies the kinetic modeling of mixtures by eliminating the need for determining new kinetic parameters for each possible combination of mixtures.

Methods

Biomass materials

The biomass species used for these experiments include aspen, balsam, basswood, red maple, and switchgrass. The hardwood and softwood tree species were obtained from forests in close proximity to Michigan Technological University, and switchgrass was provided by the National Renewable Energy Laboratory (NREL). The samples were debarked, flaked, dried, and milled in preparation for pretreatment as according to Yat et al.[3] For uniformity, the size fraction was chosen to be +20–10 mesh. The carbohydrate structure of the individual species, as pertaining to initial glucan, xylan, galactan, arabinan, and mannan percentages, was determined by Yat et al.[3]

Dilute sulfuric acid hydrolysis reaction experiments

The dilute sulfuric acid hydrolysis was executed according to the methods and equipment specifications of Yat et al.[3] A well mixed Parr reactor, model 4571, and Parr controller, model 4842 were utilized for these experiments. The operating conditions were the following: a maximum temperature of 175°C, and acid concentration of 0.5% (wt.) H_2SO_4. The experimental approach included the analysis of five individual species and 10 mixtures, run in duplicate, equaling 25 experiments. The 10 mixtures included a 50/50 wt % mix of each possible combination of the five species. For the individual species experiments, 25.0 g of biomass was mixed with 500 mL of 0.5% (wt.) sulfuric acid. For the mixtures experiments, a biomass sample was prepared which consisted of 12.5 g of each individual species to obtain a total biomass sample of 25.0 g. The biomass species were kept separate until being mixed into the 500 mL solution. The glass liner containing the biomass slurry was placed into the reactor base, which was inserted into the oven, and the top of the reactor was securely closed. Compressed air flowing through a heat exchanger tube was used to manually control the maximum reactor temperature at 175°C. A thermocouple and pressure sensor were attached to the reactor and connected to a controller that measured their values. An angle-bladed impeller was used to stir the reactor at a speed of 50 rpm during the reaction. With the setup complete, the contents were then heated from room-temperature to a maximum temperature of 175°C.

Sample acquisition and preparation

Reactor temperature, oven temperature, oven output, pressure, and stirring speed were recorded every 5 min until the reactor reached a temperature of 100°C. At this time the sample port was purged of its contents (8 mL), and a 5 mL sample was taken and placed into an ice bath to stop the reaction. The aforementioned recordings were continued every 5 min until a reactor temperature of 135°C was reached. Again the sample port was purged, and a 5 mL sample was taken and added to the ice bath. After this point in time, reactor conditions were recorded and samples were taken every 3 min, and samples were placed in ice until the reactor reached the maximum temperature of 175°C. At this time, compressed air was used to manually control the temperature at 175°C, and four more readings of reactor conditions and samples were taken at 8 min intervals and placed in the ice bath. All the samples were then filtered through a 0.2 μm nitrocellulose filter to remove any particles that would interfere with the HPLC analysis. After the samples had been filtered, they were transferred into two different sets of HPLC vials. One set was analyzed for the total sugar content by undergoing an additional acidification procedure prior to using the HPLC, while the other set was analyzed for monomeric sugars. The set to be analyzed for monomeric sugars was prepared for HPLC by adding 6 N NaOH to a 1 mL sample resulting in a pH between 5 and 6.

Total sugar analysis

A total sugar analysis was performed on alternate samples starting with the first sample taken at a reactor temperature of 100°C according to the NREL laboratory procedure 002: "determination of structural carbohydrates and lignin in biomass".[13] To determine the total sugar content of the samples, the oligomers had to be broken down into monomers since HPLC only detects the sugars in their monomeric form. To accomplish this, samples were brought to a 4% acid concentration using H_2SO_4. After this acidification, the samples were placed in an autoclave for 60 min at 121°C. Samples were then placed in an ice bath to stop the reaction. After the samples had cooled, the samples were neutralized to a pH of 5–6, with the use of 6N NaOH. By neutralizing the already acidic samples, a precipitate was formed. The samples were centrifuged in a Marathon 21K centrifuge (Fisher Scientific) for 5 min, at a speed of 8,000 rpm, and carefully decanted into fresh vials using pipettes without disrupting the impacted precipitate on the bottom of the vials. Oligomeric sugar concentrations were calculated by taking the difference between the sugar monomer concentrations determined from the samples that did not undergo the autoclave acid treatment step from the concentrations determined from the samples that did undergo this step, and applying a "sugar recovery" factor as per NREL procedures.

HPLC analysis

High-performance liquid chromatography (Agilent 1200 Series HPLC) was used to determine the concentrations of the monomer sugars (xylose, glucose, galactose, mannose, and arabinose), as well as furfural, the main product of xylose degradation. The column used for the separation of the sugars was a bio-rad aminex HPX-87P column. A bio-rad deashing column was also connected prior to the P-column to remove interfering ions. The sugar concentrations were measured by the use of a refractive-index detector and furfural was determined with a diode-array detector, combined with suitable calibration of detector signals using known standards.

Kinetic model development

For the kinetic model describing the mechanisms in Eq. 3, both reaction steps are irreversible and follow a first-order kinetic dependence on reactant concentration. The kinetic constants $k_{1,2}(t)$ are a function of absolute temperature and time according to the Arrhenius expression as follows

$$k_{1,2}(t) = A_{1,2} \exp\left(-\frac{E_{1,2}}{RT(t)}\right), \; A_{1,2} = A_{1,2o} C^{m} \tag{4}$$

where $E_{1,2}$ = activation energy (kJ/mol) for reaction 1 and 2, respectively, $R = 8.3143 \times 10^{-3}$ (kJ/mol-K), $T(t)$ = temperature (K), $A_{1,2o}$ = pre-exponential factor (min^{-1}), C = acid concentration (% w), m = acid concentration exponent; m = 1.75 for xylose formation and approximately 1.0 for xylose degradation as determined by Yat et al.[3]

The following expressions are the mass balance equations for hemicelluloses/oligomers (H) and xylose (X), respectively, under the assumption of constant reactor liquid volume and first-order reaction for each species

$$\frac{dH}{dt} = -k_1 H \tag{5}$$

$$\frac{dX}{dt} = k_1 \frac{H}{0.88} - k_2 X \tag{6}$$

The constant 0.88 is the ratio of the hemicellulose molecular weight per sugar unit to the molecular weight of xylose.

During the constant temperature xylose degradation period, the first term of Eq. 6 can be neglected since hemicellulose concentration is negligible, and the degradation term dominates over the formation term. Therefore, Eq. 6 becomes

$$\frac{dX}{dt} = -k_2 X \tag{7}$$

The analytical solution to this differential equation with initial condition $X = X_{\max}$ at $t = 0$ (where $X_{\max}$ is measured) is given as follows

$$\ln \frac{X}{X_{\max}} = -k_2 t \tag{8}$$

A value for k_2 can be determined using experimental data at constant maximum temperature T_2. The xylose degradation kinetic parameters A_2 and E_2, were obtained using linear regression for the values of k_2 at different maximum temperatures according to Eq. 9[3]

$$\ln k_2 = \ln A_2 - \frac{E_2}{R} \frac{1}{T_2} \tag{9}$$

Xylose formation and degradation

A numerical integration for the xylose mass balance (Eq. 6) using the trapezoidal rule approximation[14] yields the following expression for xylose concentration at each new time step $i+1$

$$X_{i+1} = X_i + \frac{\Delta t}{2}\left[\frac{k_{1i}H_i + k_{1(i+1)}H_{i+1}}{0.88} - k_{2i}X_i - k_{2(i+1)}X_{i+1}\right] \tag{10}$$

where i = current time, $i + 1$ = new time, Δt = time step (0.01 min), H_{i+1} is the hemicelluloses concentration at the new time point obtained by numerical integration of Eq. 5. Rate constants k_{1i}, $k_{1(i+1)}$, k_{2i}, and $k_{2(i+1)}$ are evaluated at each time point using a quadratic expression for the temperature increase over the reactor heat-up period.

An explicit expression for X_{i+1} is obtained by algebraic manipulation of Eq. 10

$$X_{i+1} = \frac{\left(k_{1i}H_i + k_{1(i+1)}H_{i+1}\right) \cdot \frac{\Delta t}{2(0.88)} + X_i \cdot \left(1 - k_{2i}\frac{\Delta t}{2}\right)}{1 + k_{2(i+1)}\frac{\Delta t}{2}} \tag{11}$$

where $H_{i+1} = H_i - k_{1i} H_i \Delta t$, which is the numerical approximation to Eq. 5.

The sum of squared errors among model predictions and experimental data is minimized by adjusting the kinetic parameters A_1 and E_1 using the Microsoft Excel© Solver function with initial guesses.

Results

Single biomass species results

A representative reactor temperature vs. time profile for these dilute acid hydrolysis pretreatment experiments is shown in Figure 1. A near-linear temperature profile was observed in all experiments, but to achieve a better fit to the data, a quadratic formula was fit to each data set. This non-linear temperature equation was then utilized in obtaining kinetic parameters for xylose formation, as discussed next.

Excellent agreement for all biomass species is shown in Figure 2 between experimentally measured reactor xylose concentrations and the pseudo first-order model of Eq. 3. This agreement is a validation of the pseudo first-order

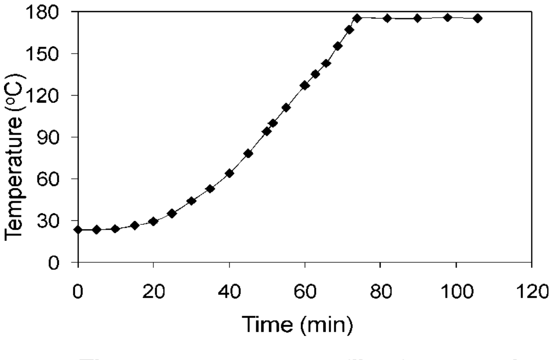

Figure 1. Time-temperature profile for experimental data from a pure species red maple experiment.

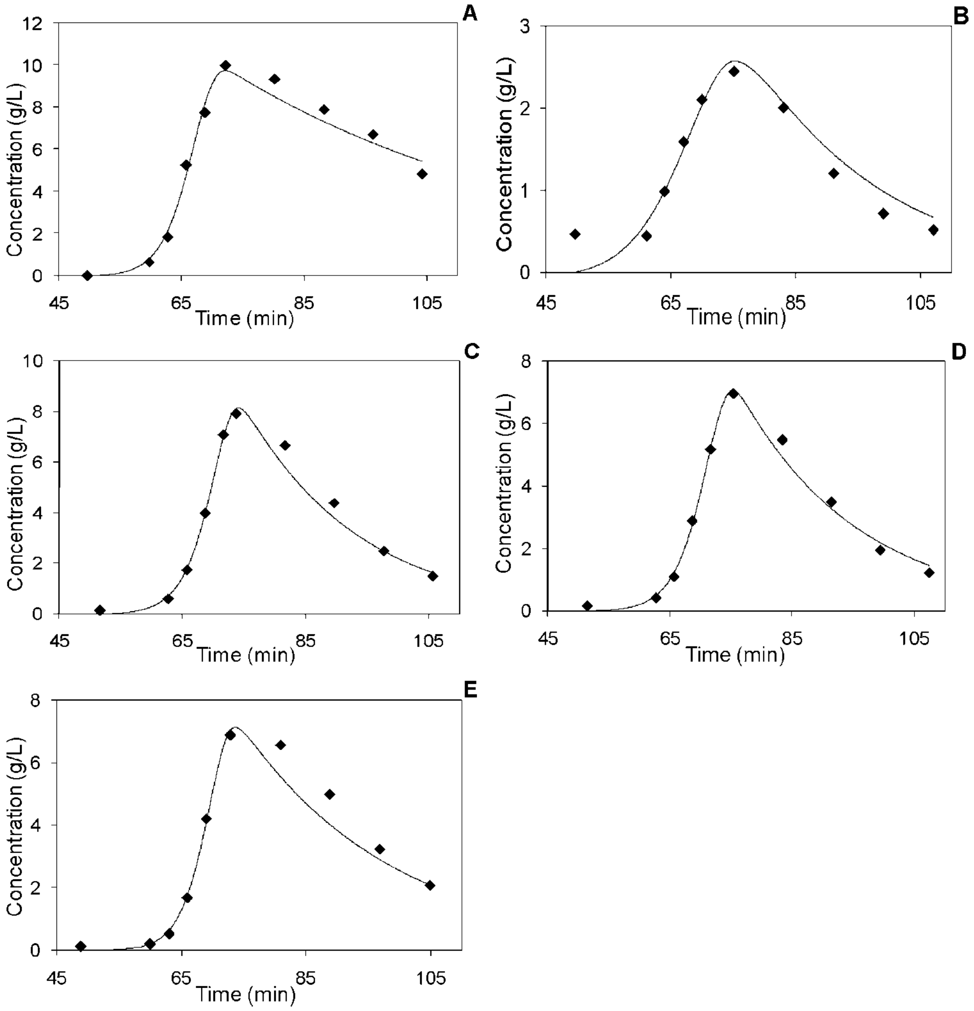

Figure 2. Single species xylose kinetic models and xylose experimental data: (A) Switchgrass, (B) balsam, (C) red maple, (D) aspen, and (E) basswood.

For all species: (◆) experimental data and (—) model.

model approach. As stated in the kinetic model development section, the xylose degradation kinetic parameters from Yat et al. [3] were used in this current modeling work (see Table 1), resulting in very good agreement between predictions and data. Table 2 summarizes all of the xylose formation kinetic parameters for each biomass species (right most column of numerical data), and compares these values with results reported in Yat et al.[3] The Yat et al.[3] model assumed that

Table 1. Kinetic Parameters for Xylose Degradation (Yat et al.[3])

	A_2 (min^{-1})	m_2	E_2 (kJ/mol)
Aspen	6.51×10^{16}	1.0	155.36
Balsam	7.59×10^{15}	0.9	147.56
Basswood	2.52×10^{13}	1.2	126.89
Red Maple	6.83×10^{13}	1.0	129.64
Switchgrass	3.73×10^{17}	1.4	165.59

Table 2. Kinetic Parameters for Xylose Formation for Reactor Conditions: Maximum Temperature of 175°C and Acid Concentration of 0.5% (Percent by Weight)

	Yat et al., 2008	Yat et al., 2008	This Study
Aspen			
A_1 (min^{-1})	5.47×10^{15}	7.55×10^{15}	4.67×10^{16}
E_1 (kJ/mol)	134.7	136.1	142.58
Balsam			
A_1 (min^{-1})	1.54×10^{7}	4.64×10^{7}	2.19×10^{8}
E_1 (kJ/mol)	67.83	71.74	76.19
Basswood			
A_1 (min^{-1})	2.42×10^{14}	2.58×10^{15}	7.73×10^{19}
E_1 (kJ/mol)	126.27	134.44	171.20
Red Maple			
A_1 (min^{-1})	6.42×10^{11}	5.77×10^{9}	3.18×10^{15}
E_1 (kJ/mol)	104.07	88.65	133.44
Switchgrass			
A_1 (min^{-1})	8.56×10^{7}	1.87×10^{8}	4.10×10^{16}
E_1 (kJ/mol)	70.75	74.36	141.30

The two sets of results from Yat et al.[3] represent duplicate experiments.

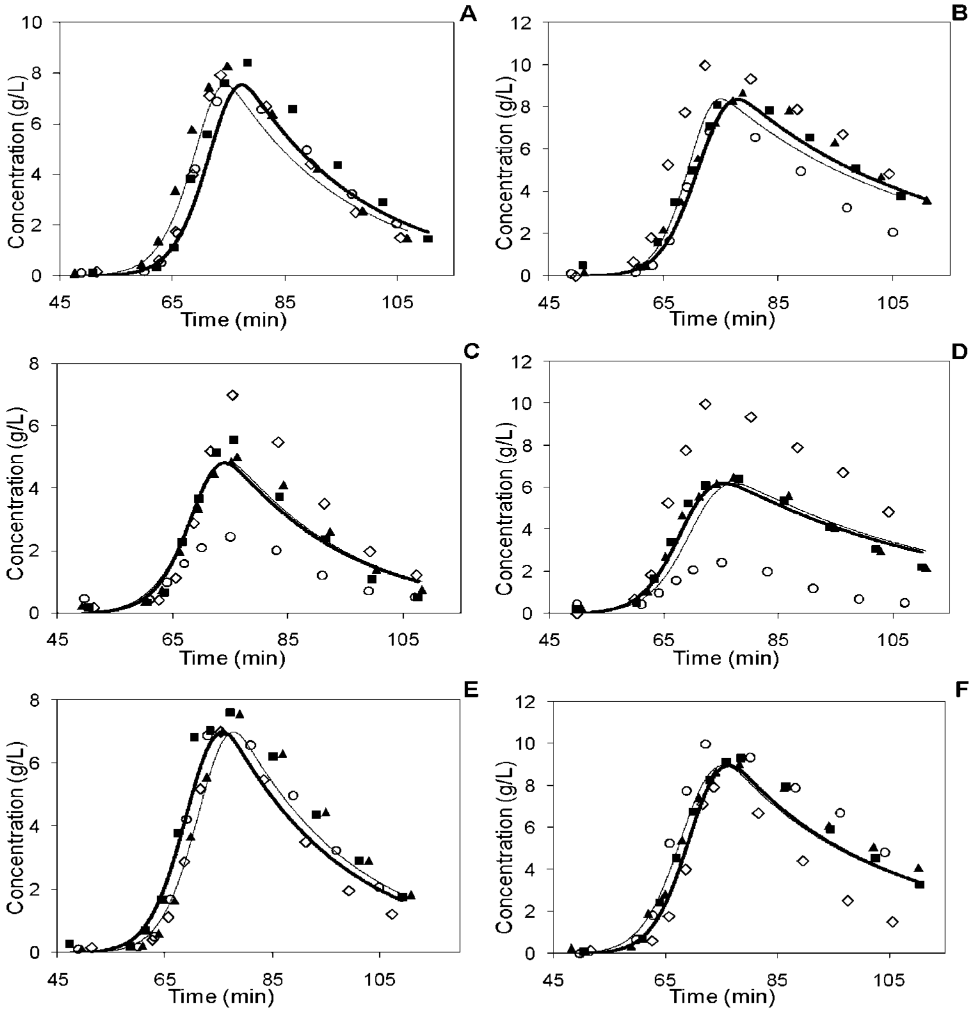

Figure 3. Single species xylose experimental data and mixtures xylose experimental data plotted with mixtures xylose model prediction for (A) basswood/red maple mixture, (B) basswood/switchgrass mixture, (C) aspen/balsam mixture, (D) balsam/switchgrass mixture, (E) aspen/basswood mixture, and (F) red maple/switchgrass mixture.

For A–F: ■ experimental data mixture 1, ▲ experimental data mixture 2, — (thick line) model mixture 1, — (thin line) model mixture 2. Single species experimental data: (A) ◇ red maple, ○ basswood, (B) ◇ switchgrass, ○ basswood, (C) ◇ aspen, ○ balsam, (D) ◇ switchgrass, ○ balsam, (E) ◇ aspen, ○ basswood, and (F) ◇ red maple, ○ switchgrass.

negligible xylose degradation occurred during xylose formation, an assumption we relax in generating the kinetic data in this work. In general, the kinetic parameters generated in this work are higher than those generated by the model application of Yat et al.[3]

Effects of biomass mixtures

The single species kinetic model, with parameters shown in Table 2, was combined with the appropriate weighting factors reflecting the mixture composition (50/50 wt.) to predict mixture xylose concentration in the reactor versus time. Each of the plots in Figure 3a–f shows xylose single species experiment results, xylose mixture experiment results, and xylose mixture model predictions. Figure 3 reports results for six of the 10 mixture combinations. The remaining four mixtures exhibited similar behavior to those shown in Figure 3. In general, the mixture model is an excellent match to the experimental data. There is a general trend, especially evident in Figure 3a and e, showing a slight tendency for the experimental data to be higher than the mixture model predicts, especially at the peak xylose concentration and during the xylose degradation time period, suggesting a slight rate enhancement for some of the mixtures. Overall, Figure 3 illustrates how the new model developed can accurately pre-

Table 3. Carbohydrate Analysis[3,5]

Species	Carbohydrate Structure (percent)					
	Glucan	Xylan	Galactan	Arabinan	Mannan	Lignin
Aspen	52.43	14.60	3.52	2.41	5.32	26.69
Balsam	47.09	6.23	5.45	5.41	11.49	36.04
Basswood	43.99	15.31	3.41	3.49	2.91	28.44
Red Maple	43.18	17.69	5.71	4.13	5.37	36.49
Switchgrass	47.72	19.06	4.18	8.11	6.30	26.04

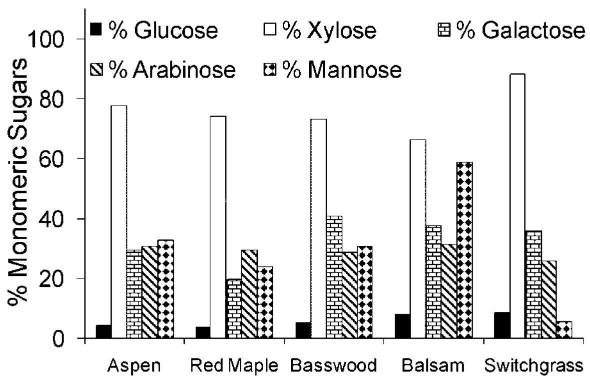

Figure 4. Monomeric sugar yields for dilute acid pretreatment of the five individual species.

Pretreatment conditions were 0.5% H_2SO_4 and maximum temperature of 175°C.

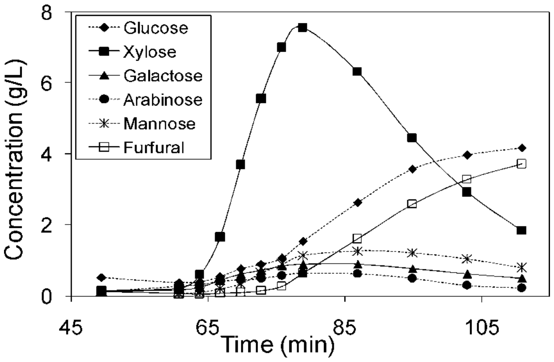

Figure 6. Aspen and basswood mixture dilute acid hydrolysis results.

The experimental data for all five sugars and furfural, the main degradation product, are shown in this plot.

dict the mixture xylose concentrations obtained from use of the individual species kinetic parameters.

Yields of monomer sugars

The carbohydrate analysis shows that there is between 6.23 and 19.06% xylan in the biomass species in this study,[3,5] as shown in Table 3. This amount of xylan allows for the formation of up to 3.4, 8.1, 8.4, 9.8, 10.3 g of xylose per L for balsam, aspen, basswood, red maple, and switchgrass, respectively; if there is 100% conversion of the xylan present in the biomass to xylose and no xylose degradation. Also, this is under the assumption that 100% of the xylan is converted to its monomeric form of xylose, and none is left in the oligomeric form. At the time point in the reaction when xylose concentration is at its maximum, when the reactor initially reaches 175°C, xylose yields between 66 and 88% are achieved. Xylose yields, as well as the yields of the other four sugars (at this time point, 175°C) are shown for individual biomass species in Figure 4, and for the mixtures in Figure 5. The percentages reported in Figure 5 are the averages of duplicate experiments.

Yields of xylose from biomass mixtures reached similar high values as in the single species experiments. However, the yields reported in Figures 4 and 5 for the other sugars, glucose, galactose, arabinose, and mannose, may not be at their maximum values. For instance, glucose continues to rise at the end of the reaction period as shown in Figure 6, whereas xylose has been almost completely degraded. Also, mannose concentration in this experiment achieves a maximum after xylose. Our results suggest that it may not be possible to optimize reactor conditions to achieve a maximum in the concentrations of all sugars simultaneously. However, achieving maximum reactor xylose monomer concentration is important, because it is the dominant hemicellulose sugar for the hardwoods and switchgrass.

Figure 5. Monomeric sugar yields for the 10 mixture combinations.

Each of these mixtures is a 50/50 mixture by weight.

Oligomeric sugar formation

Oligomeric sugars are generated early in the reaction, and would require further acidification to be converted to monomer sugars. For xylose, the oligomer concentration reaches a maximum and begins to decrease prior to the monomer peak. Figure 7 shows the experimental monomer concentration of xylose in comparison with its oligomer concentration throughout the sampling period. At the point where monomer xylose reaches its maximum, there is still approximately 1 g/L of oligomeric xylose left in solution. This trend is similar for all hemicellulose sugars except glucose. The presence of

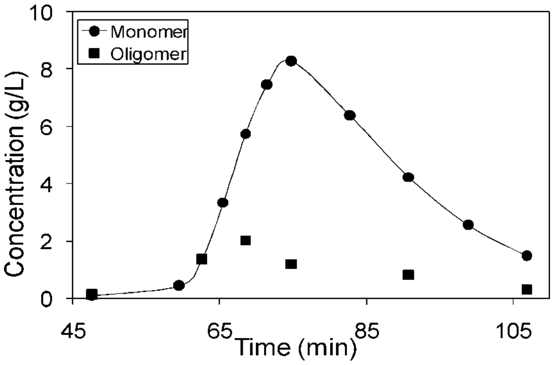

Figure 7. Basswood and red maple 50/50 mixture dilute acid hydrolysis xylose monomer and oligomer formation and degradation.

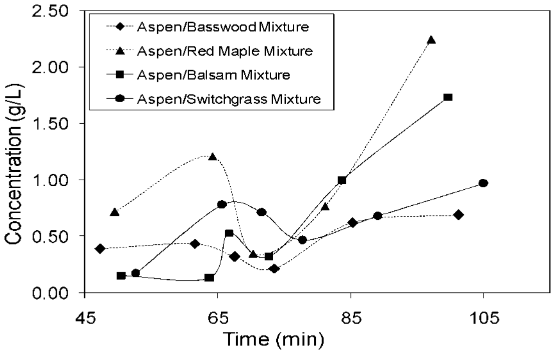

Figure 8. Glucan oligomer concentration from four of the aspen mixtures.

oligomers suggests that their reaction kinetics should be studied in more detail, since oligomers are not as fermentable as monomer sugars and reactor conditions for their efficient hydrolysis need to be identified.

There are clear trends for the oligomeric sugars throughout the experimental time period. The trend for xylan oligomers (as well as galactan, mannan, and arabinan oligomers), shows that the concentration reaches a maximum, and then diminishes to a very small value (Figure 7). Glucan oligomers, however, have an unexpected trend as they reach an initial maximum, decrease, and then begin increasing again to reach a new maximum throughout the remainder of the reaction period (Figure 8). Glucan oligomer concentrations higher than 2 g/L were observed, and this can lead to considerable amounts of additional fermentable glucose through subsequent enzymatic hydrolysis.

Discussion

Relatively little prior work has been completed in the area of pretreatment of biomass mixtures by dilute acid hydrolysis as compared to single woody biomass species. There has been some prior research with municipal solid waste,[15] other work with mixtures of softwoods, such as white fir and ponderosa pine[16] and spruce and pine,[17] as well as with mixtures of hardwoods, such as birch and maple,[18] and finally, with mixtures of hardwood and softwood species, such as oak, birch, maple, pine, and cedar.[19] However, none of these studies focused specifically on the effects of feedstock mixtures on hemicellulose hydrolysis kinetics with comparison to pure species data. One study on biomass mixtures[11] states that there are significant kinetic differences in the various types of biomass. According to that study, while mixtures, such as corn cobs and corn stover may be pretreated simultaneously because each has similar kinetics, hardwoods have much slower kinetics in comparison, and need higher acid concentrations and/or temperatures. This leads to the conclusion that there is a limit to which mixtures of biomass could be most efficiently utilized,[11] and that the dilute acid hydrolysis pretreatment process may still need to be optimized for different groups of mixtures. The high xylose yields obtained in our current study show that the kinetics of the five biomass species are similar, and that mixtures of these species may be pretreated to achieve the expected xylose yields obtained from single species experiments.

The differences in kinetic parameters (Table 2) between the work of Yat et al.,[3] and this study is due to differing assumptions in applying the kinetic model to fit the data. The kinetic parameters generated in this work are a result of the simultaneous mechanisms of xylose formation and degradation, whereas the kinetic parameters of Yat et al.[3] are purely for xylose formation with the assumption that degradation is negligible during the reactor heat-up period. The accurate fit of the model application used in this study to the experimental data leads to the conclusion that xylose degradation during the xylose formation period is not negligible and should be accounted for.

The kinetic parameters for k_1 generated in this study are considered preliminary and need to be validated with additional experimental work. In particular, the effect of different temperatures on the selectivity ratio ($K = k_1/k_2$) needs further investigation. From the values of E_1 and E_2 in Tables 2 and 1, respectively, K increases with increasing temperature for basswood and red maple (increasing yield of xylose with increasing temperature), while it decreases with increasing temperature for aspen, basswood and switchgrass. A review of the literature confirms similar contradictory behavior for selectivity ratio for dilute acid hydrolysis, with 12 cases having increasing K with increasing temperature, six cases with decreasing K, and one case with K relatively unchanged.[6,7,11,18,20–26] The effect of temperature on selectivity ratio is of great interest, not only for its impact on xylose monomer yield, but also on the degree of crystallinity and processibility of residual cellulose by enzymatic hydrolysis.

The pseudo first-order model approach for modeling the production of xylose from the dilute acid hydrolysis of hemicelluloses was validated by our single species and mixture data. Lumping hemicelluloses and xylan oligomers together in the model mechanism appears to be a valid way to describe the xylose formation process. Lumping in this fashion simplifies the modeling of xylose production from woody biomass, and provides an accurate prediction of reactor concentrations. We believe that this same modeling approach can be applied successfully to the other sugars in hemicelluloses; glucose, galactose, arabinose, and mannose.

This model not only represents an accurate fit for the individual species, but leads to an efficient model for predicting the concentrations and yields that would be obtained from mixtures of species. The good agreement between the mixture model and data validates the hypothesis that there is little to no mixture effect that enhances or inhibits the rate of hemicellulose hydrolysis to form xylose for biomass mixtures. This is a significant finding in that mixture behavior during dilute acid hydrolysis of hemicelluloses can be understood using single species experimental data and kinetic parameters.

Conclusion

This work investigated the effects of woody biomass and switchgrass mixtures on the kinetics of xylose production and degradation to the nonfermentable byproduct, furfural. The rates of xylose production and degradation for the 10 mixtures studied were predicted very well using the preliminary pure species kinetic parameters and a pseudo first-order mixture model. There was only a slight enhancement in rate of xylose production in the mixtures compared to the pure species. Each of the species exhibited similar xylose production kinetics (similar reaction time to achieve maximum concentration), suggesting that mixtures of these biomass species can be processed together and still achieve high xylose yields. The use of biomass mixtures for commercial cellulose ethanol production is important, because feedstock mixtures in the processing plant are much more feasible and likely than the use of individual species.

Our work also shows that, unlike some prior studies, the inclusion of detailed oligomer reaction kinetics is not necessary to accurately describe xylose monomer concentrations in the reactor during dilute acid hydrolysis. However, there are good reasons to study oligomer reaction kinetics, and to adjust reactor conditions to hydrolyze them to more fermentable monomer sugars. This aspect of woody biomass dilute acid hydrolysis, as well as a detailed understanding of the kinetics for the minor sugars in hemicellulose, are important topics of further research.

Experiments that study the effects of not only mixtures of biomass species, but also the inclusion of bark and other forms of biomass in these mixtures should be pursued. The effect of pretreated mixtures on the subsequent enzymatic hydrolysis and fermentation stages should be studied to determine if the use of mixtures creates unexpected behavior in these processes. Finally, imaging work, such as scanning electron microscopy (SEM), and fluorescence imaging should be conducted to visualize the structural differences in the untreated and pretreated biomass. This imaging could be an additional tool used to determine optimum dilute acid hydrolysis pretreatment conditions.

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