ACS Sustainable Chemistry & Engineering

Research Article

pubs.acs.org/journal/ascecg

Kinetic Modeling of Switchgrass-Derived Xylose Oligomers Degradation during Pretreatment in Dilute Acid or in Water

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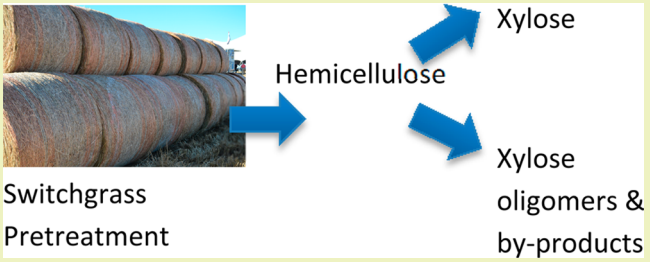
ABSTRACT: Switchgrass hemicellulose can be converted into sugars, such as xylose, for biobased product manufacturing. However, during pretreatment, the hemicellulose can also be converted into xylose oligomers, furfural and formic acid, which are detrimental to subsequent enzymatic hydrolysis and fermentation. Pretreatment conditions that maximize xylose production from hemicellulose, while also minimizing xylose oligomers, furfural, and formic acid generation, would improve the economics of biobased product manufacturing by increasing yields and reducing enzyme and microorganism costs. The current study utilized switchgrass purified-xylose oligomers as model compounds to follow xylose oligomers, and furfural generation during pretreatment, using 0 to 1 wt % acid sulfuric acid at temperatures of 160 and 180 °C. The resulting kinetic data were used in simple first order rate expressions. On the basis of the empirically derived Arrhenius models but not verified by experimental data, maximum xylose yields can be obtained at low temperatures and high acid concentrations. Pretreatment conditions with high temperatures yielded high reaction rates and shortened reaction times, but at the expense of increased concentrations of degradation compounds.



KEYWORDS: *Switchgrass, Hemicelluloses, Oligomers, Arrhenius, Degradation constants, Dilute acid pretreatment*

INTRODUCTION

The carbohydrate components of cellulosic feedstocks, cellulose and hemicellulose, need to be deconstructed into their monomeric components prior to being used as substrates for biobased manufacturing processes. Pretreatment is a common step that facilitates the release of carbohydrate from tightly woven plant cell wall structures prior to enzymatic hydrolysis. The integration of pretreatment and enzymatic hydrolysis steps is not seamless, where components formed during pretreatment inhibit enzyme activity. Pretreatment processing parameters can affect hydrolyzate compositions, and ensuing inhibitory potency.[1,2] Recent work performed with rice straw hydrolyzates compared the inhibitory effect of hot water pretreated hydrolyzate to those of dilute acid. Results showed that hot water pretreatment (220 °C, 52 min, at pH 7.0) hydrolyzates inhibited 77% to 82% of endo−cellulase and intact cocktail enzymes, respectively, as compared to 64% to 67% for dilute acid hydrolyzates.[3] Compositional analysis of the hydrolyzates showed that the xylose oligomers concentration was 28 times greater in hot water pretreatment hydrolyzate.[3]

Pretreatment-generated-xylose oligomers inhibition has previously been reported.[1,4] Furthermore, increased inhibition of enzymatic hydrolysis was associated with augmentation in loadings of mannan-derived oligomers.[2] In fact, incubation with as little as 0.1 g/L of mannan polysaccharides decreased by 50% the ability of cellulase to convert cellulose into glucose, indicating that cell wall carbohydrates can interfere with saccharification. Thus, an understanding of the depolymerization of cell wall carbohydrates, including hemicellulose, into monomeric components is important in minimizing the inhibitory effect of the hydrolysates.

In-house purified birchwood xylan oligomers, namely xylose (DP 1), xylobiose (DP 2), xylotriose (DP 3), and xylotetraose (DP 4), were depolymerized in acid or in water at temperatures of 120, 160, or 200 °C.[5] Degradation rates of DP 1, DP 2, DP 3, and DP 4 were calculated, and it was observed that acidic conditions favored the formation of DP 1 and DP 3 from DP 4. On the other hand, water conditions promoted the cleavage of the middle bond, forming two DP 2 units.[5] Results presented by Lau et al.[5] were aligned with the results of Kumar and Wyman,[1] indicating that acidic pretreatment conditions favored end bond cleavage. Thus, acid concentration affected the overall composition of the produced hydrolysate and ensuing inhibitory potential on enzymatic hydrolysis.

Switchgrass (*Panicum virgatum*, L.) is considered to be an important candidate as a dedicated bioenergy crop because it requires low inputs, produces high yields of biomass, provides good carbon sequestration, prevents erosion, and has a wide geographic distribution throughout North America.[6] Recently, switchgrass-derived xylo-oligomers, such as xylopentaose (DP 5) and xylohexaose (DP 6) were purified.[7] In this work, experiments were conducted with these switchgrass-produced

Received: April 12, 2015
Revised: July 19, 2015
Published: July 27, 2015

DOI: 10.1021/acssuschemeng.5b00298
ACS Sustainable Chem. Eng. 2015, 3, 2030−2035

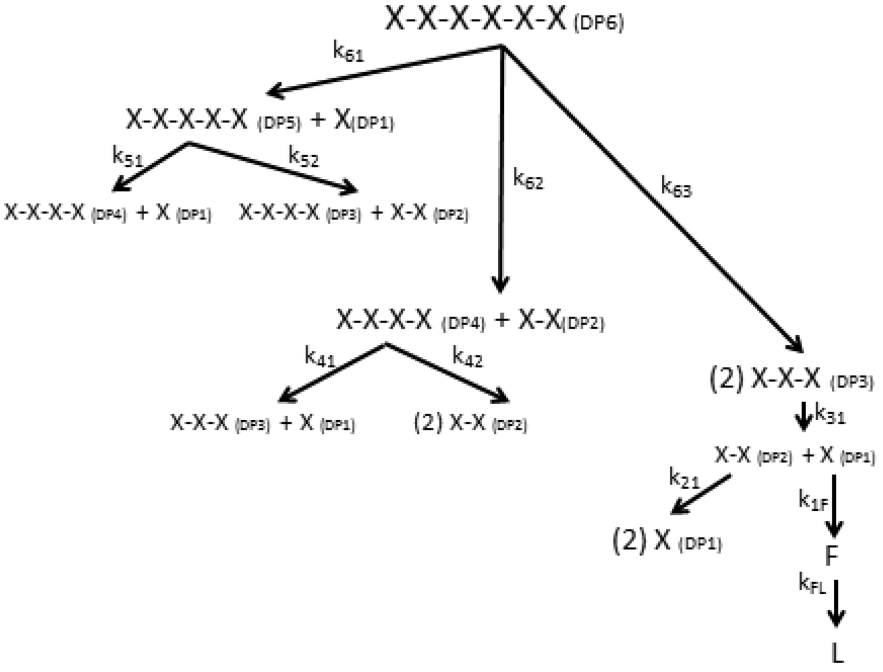


Figure 1. Reaction pathway for the degradation of xylose oligomers. k_{61}, k_{62}, k_{63}, k_{51}, k_{52}, k_{41}, k_{42}, k_{31}, k_{21}, and k_{1F} are the rate constants for the formation of DP 1 from DP 6, DP 2 from DP 6, DP 3 from DP 6, DP 1 from DP 5, DP 2 from DP 5, DP 1 from DP 4, DP 2 from DP 4, DP 1 from DP 3, DP 1 from DP 2, furfural from DP 1, and the degradation of furfural into unaccounted degradation products, respectively, in min^{-1}.

oligomers to describe their depolymerization using acidic and water pretreatment conditions. The rates of formation for monomeric sugars were calculated using first-order kinetics from which Arrhenius relations were derived. The Arrhenius relations permitted the expansion of pH and temperature conditions with respect to overall yield of xylose monomers and degradation products. The developed relations were useful in determining the effect of temperature and pH on overall DP 1 yields, establishing ranges in which processing parameter trade-offs could occur, which could minimize the inhibitory potential of hydrolyzates on enzymatic hydrolysis.

MATERIALS AND METHODS

Materials. Switchgrass (*Panicum virgatum*) was grown at the University of Arkansas Agricultural Research and Extension Center, Fayetteville, AR, 36.0906° N, 94.1828° W, as previously described.[6] The samples were dried, ground to a size 20 mesh, and stored in a 4 °C cold room until use.

Oligomer Generation and Purification. Hemicelluloses from switchgrass were prepared as previously described.[6] Oligomers were made by loading 800 mg of switchgrass hemicelluloses into stainless steel reactors (20.0 cm in length, interior diameter of 1.4 cm, and 32 mL capacity) with 20 mL of water and hydrolyzed at 160 °C for 60 min in a fluidized sand bath (Techne Ltd., Burlington, NJ). After hydrolysis, the reactors were immediately cooled by submersion in cold tap water. The hydrolyzate was then collected, filtered through a 0.45-μm syringe filter, and neutralized with 50% sodium hydroxide, using a Mettler-Toledo SevenEasy pH-meter (Columbus, OH). Neutralized hydrolyzate was then dried using a rotary vacuum dryer (Savant, Farmingdale, NY). Oligomers were separated by centrifugal partition chromatography (CPC), using a solvent system made from butanol:methanol:water (5:1:4, V:V:V), as described earlier.[8]

Depolymerization Experiments. Twenty milligrams of switchgrass-derived oligomers was hydrolyzed in stainless steel reactors (4.9 cm in length, interior diameter of 0.56 cm, and 1.2 mL capacity), in one mL of water or 1.0% wt sulfuric acid at 160 or 180 °C in the fluidized sand bath. When the reaction time had elapsed, the reactors were cooled by submersion in cold tap water. The hydrolyzate was collected, centrifuged at 7500*g* (Eppendorf MiniSpin Plus, Hamburg, Germany) and separated into two aliquots. One aliquot was directly filtered using a 0.2 μm nylon syringe filter, and analyzed for monomeric sugars as described below. Depolymerization experiments were conducted in duplicate.

Analysis of Oligomers and Furfural. Oligomers were identified using a high performance anion exchange chromatography with pulsed amperometric detection (HPAEC-PAD) system (Dionex ICS-5000, Sunnyvale, CA) equipped with an ICS 3/5 electrochemical detector, a CarboPac PA200 guard column, and a CarboPac PA200 analytical column (Dionex, Sunnyvale, CA). Separation was obtained using a two solvent gradient system. Solvent A was 100 mM sodium hydroxide, and solvent B was 100 mM sodium hydroxide with 320 mM sodium acetate. Both solvents were padded under helium gas. Elution began with 100% solvent A for 15 min, followed by a linear increase of solvent B to 50% over the next 40 min. Solvent B was then increased to 100% over one min and held constant for four min before returning to 100% solvent A over one min. Solvent A was then held at 100% for nine min. The flow rate was constant at 0.5 mL/min, and the compartment and columns were maintained at 35 °C. Oligomers were quantified based on peak area using calibration curves built using xylose oligomers purchased from Megazyme (Wicklow, Ireland). Furfural analysis was carried out as previously described.[5]

Kinetic Constant Determination. The reaction pathway for the degradation of xylose oligomers with accompanying rate constants is described in Figure 1. First order degradation rate constants for the experimental data in Table 1 were generated by the normalized least-squares method using the Excel Solver routine as applied to eqs 1 to 14.

$$\frac{dX_6}{dt} = -k_6X_6 \quad (1)$$

$$\frac{dX_5}{dt} = -k_5X_5 + k_{61}X_6 \quad (2)$$

$$\frac{dX_4}{dt} = -k_4X_4 + k_{62}X_6 + k_{51}X_5 \quad (3)$$

DOI: 10.1021/acssuschemeng.5b00298
ACS Sustainable Chem. Eng. 2015, 3, 2030−2035

Table 1. Summary of Degradation Rate Constants As Determined Using an Excel Solver Routine for Normalized Least Sum of Squares Method

rate constant (min^{-1})	160 °C water	1% acid 160 °C	180 °C water
k_6	0.0404	1.6137	0.0906
k_{61}	0.0001	1.6136	0.0393
k_{62}	0.0207	0.0001	0.0146
k_{63}	0.0196	0.0001	0.0366
k_5	0.0018	2.9794	0.0905
k_{51}	0.0018	1.1525	0.0900
k_{52}	0.0001	1.8268	0.0005
k_4	0.0408	0.8041	0.0600
k_{41}	0.0232	0.8040	0.0001
k_{42}	0.0176	0.0001	0.0599
k_3 (k_{31})	0.0409	0.5598	0.0594
k_2 (k_{21})	0.0413	0.0856	0.0492
k_1 (k_{1F})	0.0093	0.0009	0.0294
k_F (k_{FL})	0.1240	0.1379	0.1182

$$\frac{dX_3}{dt} = -k_3X_3 + 2k_{63}X_6 + k_{52}X_5 + k_{41}X_4 \quad (4)$$

$$\frac{dX_2}{dt} = -k_2X_2 + k_{62}X_6 + k_{52}X_5 + 2k_{42}X_4 + k_{31}X_3 \quad (5)$$

$$\frac{dX_1}{dt} = -k_1X_1 + k_{61}X_6 + k_{51}X_5 + k_{41}X_4 + k_{31}X_3 + 2k_{21}X_2 \quad (6)$$

$$\frac{dF}{dt} = -k_FF + k_{1F}X_1 \quad (7)$$

$$k_6 = k_{61} + k_{62} + k_{63} \quad (8)$$

$$k_5 = k_{51} + k_{52} \quad (9)$$

$$k_4 = k_{41} + k_{42} \quad (10)$$

$$k_3 = k_{31} \quad (11)$$

$$k_2 = k_{21} \quad (12)$$

$$k_1 = k_{1F} \quad (13)$$

$$k_F = k_{FL} \quad (14)$$

where X_1, X_2, X_3, X_4, X_5, X_6, and F were concentrations of DP 1, DP 2, DP 3, DP 4, DP 5, DP 6, and furfural, respectively, in mmol L^{-1}. The constants, k_{61}, k_{62}, k_{63}, k_{51}, k_{52}, k_{41}, k_{42}, k_{31}, k_{21}, k_{1F}, and k_{FL} were the rate constants for the formation of DP 1 from DP 6, DP 2 from DP 6, DP 3 from DP 6, DP 1 from DP 5, DP 2 from DP 5, DP 1 from DP 4, DP 2 from DP 4, DP 1 from DP 3, DP 1 from DP 2, furfural from DP 1, and degradation of furfural into unaccounted degradation products, respectively, in min^{-1}. The overall degradation rates for DP 6, DP 5, DP 4, DP 3, DP 2, DP 1, and furfural were k_6, k_5, k_4, k_3, k_2, k_1, and k_F, respectively.

RESULTS AND DISCUSSION

Generation of Oligomers Stemming from Switchgrass Hemicelluloses. Experiments to generate oligomers from switchgrass hemicellulose produced oligomers solutions with the following composition: 0.91 mg/mL (1.12 mmol/L) DP 6, 0.38 mg/mL (0.55 mmol/L) DP 5, 0.40 mg/mL (0.73 mmol/L) DP 4, 0.54 mg/mL (1.31 mmol/L) DP 3, 0.40 mg/mL (1.43 mmol/L) DP 2, 0.83 mg/mL (5.52 mmol/L) DP 1, and 0.02 mg/mL (0.23 mmol/L) furfural. The oligomers mixture was subsequently used in the kinetic modeling at 160 °C because this temperature was reported to yield the best results in dilute acid hydrolysis.[2,9] However, experiments were also conducted at 180 °C to determine the effect of a higher pretreatment temperature on oligomer generation. Accordingly, extracted switchgrass hemicelluloses were pretreated at 160 and 180 °C in water and in 1.0 wt % at 160 °C. Total hydrolysis times varied from 60 to 720 s, depending on the hydrolysis conditions. The hydrolysis times began 2 s after dipping the reactor tubes into the preheated sand bath. The 2 s time delay was determined by the reactor wall reaching the hydrolysis temperature using a heat gun. Results from Kumar and Wyman,[1] combined with this work, showed that pretreating, in liquid hot water, either for deacetylated hemicellulose or intact switchgrass, resulted in hydrolyzates that contained oligomers of various lengths.

Pretreatment of Switchgrass Hemicellulose-Derived Oligomers. In-house centrifugal partition chromatography (CPC) purified DP 6 was prepared according to the procedures of Bunnell et al.,[7] and pretreated in 160 or 180 °C water or in 160 °C 1.0 wt % sulfuric acid. The experiments were conducted in duplicate and averages are presented in Figures 2, 3, and 4.

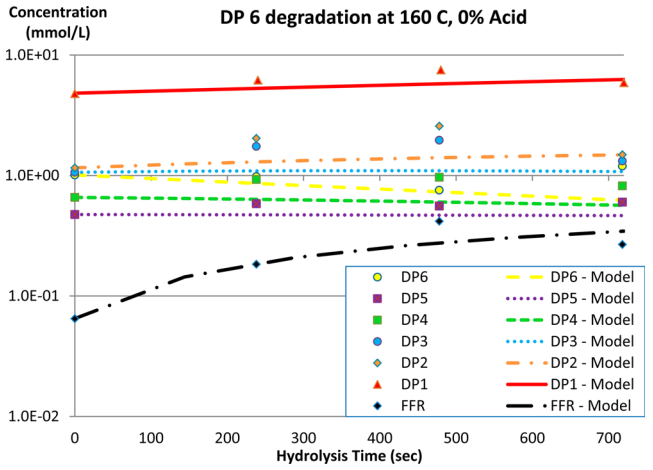


Figure 2. Experimental DP 6, DP 5, DP 4, DP 3, DP 2, DP 1, and furfural concentrations for the hydrolysis of DP 6 in 160 °C water.

During the course of the depolymerization experiments, samples were analyzed for oligomer content and reported in

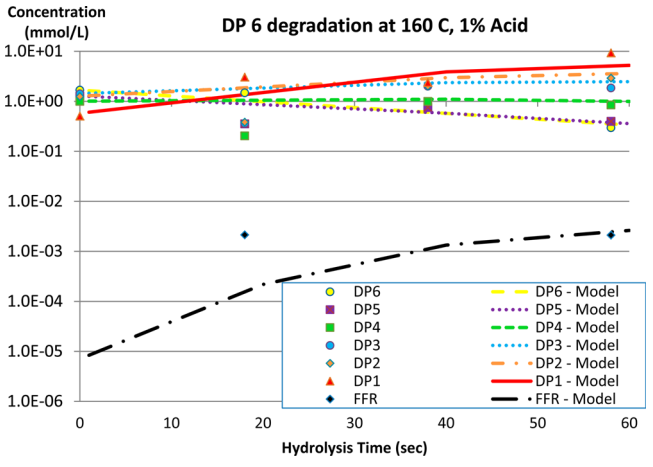


Figure 3. Experimental DP 6, DP 5, DP 4, DP 3, DP 2, DP 1, and furfural concentrations for the hydrolysis of DP 6 in 1.0 wt % sulfuric acid at160 °C.

DOI: 10.1021/acssuschemeng.5b00298
ACS Sustainable Chem. Eng. 2015, 3, 2030−2035

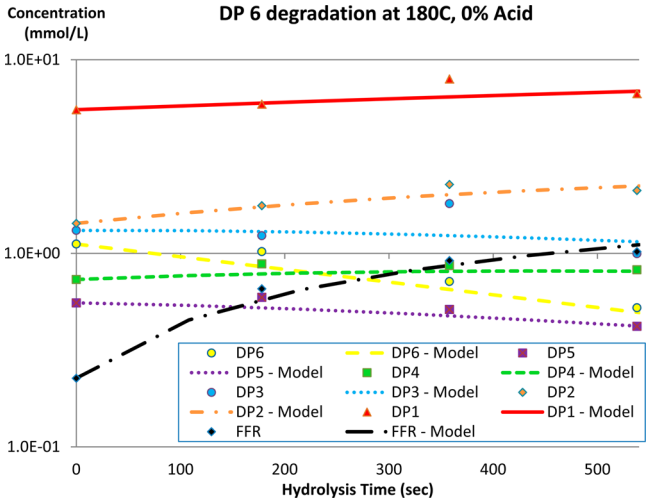


Figure 4. Experimental DP 6, DP 5, DP 4, DP 3, DP 2, DP 1, and furfural concentrations for the hydrolysis of DP 6 in 180 °C water.

terms of molar composition, as presented in Figures 2, 3, and 4. The depolymerization of DP 6 in 160 °C water was relatively slow; after 720 s, the molar composition was similar to the initial material. Maintaining the hydrolysis temperature at 160 °C, but conducting the reaction in 1.0 wt % sulfuric acid, resulted in almost complete loss of DP 6 to produce DP 1, DP 2, DP 3, DP 4, and DP 5. When depolymerizing DP 6 in 180 °C water, most of the DP 6 was converted to DP 1. Overall it was noted that, of the three conditions tested, a temperature of 160 °C combined with 1 wt % sulfuric acid for 60 s was the condition that was most conducive to maximize DP 6 depolymerization to DP 1 without the formation of furfural. It was interesting to note that all three tested conditions were performed on a much shorter time scale than those reported for birchwood-derived oligomers, where hydrolysis occurred in a time frame of minutes instead of seconds.[5]

Degradation rate constants, as presented in eqs 1 to 14, were calculated from the data presented in Figures 2 to 4. Degradation rate constants were generated by the normalized least-squares method using the Excel Solver routine. The parameters X_6, X_5, X_4, X_3, X_2, X_1, and F correspond to the concentrations of DP 6, DP 5, DP 4, DP 3, DP 2, DP 1, and furfural, in mmol L^{-1}, respectively. The parameters k_{61}, k_{62}, k_{63}, k_{51}, k_{52}, k_{41}, k_{42}, k_{31}, k_{21}, k_{1F}, and k_{FL} are the rate constants as described earlier. The overall degradation rates for DP 6, DP 5, DP 4, DP 3, DP 2, DP 1, and furfural were k_6, k_5, k_4, k_3, k_2, k_1, and k_F, respectively. Degradation rate constants were calculated for depolymerization of DP 6 in 160 °C water or in 1.0 wt % sulfuric acid, as well as in 180 °C in water. Model-predicted values for the degradation rate constants are presented in Table 1.

In analyzing the degradation of DP 6 in water and in acid, the following conclusions were drawn. In 160 °C water, k_{61} was 0.0001 min^{-1}, whereas k_{63} was 0.0196 min^{-1}, indicating a preference for middle bond cleavage in 160 °C water. When using 1 wt % at 160 °C, on the other hand, there was a preference for end bond cleavage by a factor of over 16 000. Finally, when carrying out the reaction in water, but at a temperature of 180 °C, there was no preference in the site of the cleaved bond. With DP 5 depolymerization, the use of acid at 160 °C did not result in a cleavage preference for middle or end bond. On the other hand, depolymerization of DP 5 in water at 180 °C favored the cleavage of the end bond. Overall, the degradation constant k_{61} was calculated to be greater than k_{41}, possibly indicating that end bond cleavage is less favorable during depolymerization of oligomers into smaller units, such as DP 3 and DP 2. With water-only hydrolysis conditions, cleavage of the interior bond was promoted, but as the oligomer length decreased, the degradation constants were somewhat similar in magnitude. With acidic conditions, DP 3 and DP 2 xylose equivalents are greater than those of the longer chain xylose oligomers, and there is a preference for end bond cleavage. Under water-only hydrolysis conditions, cleavage of the interior bond was promoted, but as the oligomer length decreased, the degradation constants were somewhat similar in magnitude. Results presented in this work concur with those of Kamyama and Sakai,[10] where the inclusion of acid in pretreatment promoted end bond cleavage over internal bond cleavage.

Temperature and acid effects were modeled using a modified Arrhenius equation as initially reported by Saeman.[11] The pre-exponential factor (k_0), acid concentration exponent (m), and activation energy (E_a) were generated by the least-squares method using the Excel Solver routine. This approach minimized the sum of squares of the differences between the degradation rate constants presented in Table 1 and model-predicted degradation rate constants. The model predicted degradation rate constants were once again determined based on the degradation conditions under three different hydrolysis conditions: 160 °C water, 1 wt % acid at 160 °C, and 180 °C water. The calculated Arrhenius parameters are presented in Table 2.

Table 2. Summary of Arrhenius Parameters for the Degradation Rate Constants

compound	k_0 (min^{-1})	m (unitless)	E_a (kJ/mol/K)
DP 6	2.71×10^7	0.249	58.24
DP 5	2.71×10^7	0.302	55.94
DP 4	2.54×10^7	0.225	60.88
DP 3	9.34×10^5	0.193	50.48
DP 2	4.45×10^3	0.064	38.77
DP 1	4.45×10^3	0.020	141.91
furfural	7.11×10^2	0.030	30.58

Using the parameters of Table 2, values, it was possible to model concentration profiles for xylose oligomers over a broader range of conditions. The acid concentration exponent (m) results were similar for DP 4, DP 5, and DP 6 (0.23 to 0.30), indicating that acid concentration is not a determining parameter for the depolymerization of oligomers of DP 4 or greater. On the other hand, the acid concentration exponents concentration were lower for DP 2, DP 1 and furfural (0.02 to 0.06), indicating that the degradation rates of these compounds were even less sensitive to changes in acid concentration. Activation energies for DP 2, DP 3, DP 4, DP 5, and DP 6 were comparative, whereas the activation energy of DP 1 was at least 2.3 times higher, indicating strong temperature-dependence of the degradation rate of DP 1. However, the activation energy for furfural, which was 30.6 kJ/mol/K, was lower than the previously reported value of 49.6 kJ/mol/K.[5] The lower activation energy values reported in this study possibly indicate that the degradation rate of furfural was less temperature dependent, in comparison to that of furfural stemming from birchwood oligomers.[5] It is important to note that the

DOI: 10.1021/acssuschemeng.5b00298
ACS Sustainable Chem. Eng. 2015, 3, 2030−2035

activation energy values for xylose have been documented in the literature to be 89.0 to 123.9 kJ/mol/K, as compared to 141.91 kJ/mol/K obtained in current study, whereas the activation energy for furfural are 49.6 to 106.0 kJ/mol/K.[12−17] Although the values determined from the current study were not within the reported range, they remained in general agreement with those reported in the literature.

Using the parameters of Tables 1 and 2, a model was developed for pretreatment with sulfuric acid (0 to 1.0% wt) over a temperature range of 140 to 180 °C to maximize xylose accumulation. In other words, the reaction model was developed to examine, in a theoretical space, the effect that expanded temperatures and acid conditions would have on xylose oligomer depolymerization. However, the authors are cognizant that the model needs to be validated with experimental data for asserting its robustness. Figure 5 depicts

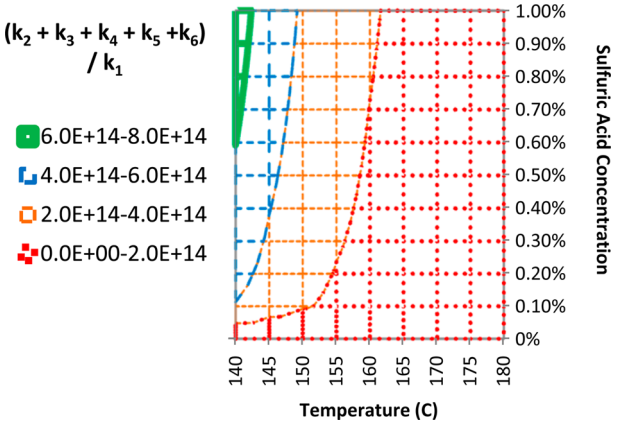


Figure 5. Kinetic model summarizing the optimum condition to maximize xylose yield. The data for the graph is calculated by determining the ratio of xylose oligomers depolymerization rate into xylose ($k_2 + k_3 + k_4 + k_5 + k_6$) and dividing by the degradation rate of xylose (k_1). A high value (as represented by the solid line region) is desired.

the reaction model for xylose accumulation rates over different temperatures and times. The objective of the model is to identify temperatures and times that lead to high xylose accumulation rates. It should be noted that xylose accumulates when the depolymerization rates of the oligomers ($k_2 + k_3 + k_4 + k_5 + k_6$) are faster than xylose degradation rates (k_1). On the other hand, Figure 6 portrays the reaction rate, $k_2 + k_3 + k_4 + k_5 + k_6$, as reflected by the degradation rates of xylose oligomers, where high degradation rates are preferred.

The optimum condition for xylose accumulation, as shown in Figure 5, was at low temperature and high acid concentration (140 °C in 1 wt % acid) where the ratio $(k_2 + k_3 + k_4 + k_5 + k_6)/k_1$ was between 6×10^{14} and 8×10^{14}. In using hydrolysis condition below 0.6 wt % acid but with temperatures above 145 °C, the rate of xylose degradation negated the benefit of faster reaction rates, with ratios between 4×10^{14} and 6×10^{14}. Overall, degradation of DP 1 was more temperature dependent than acid-dependent. Overall the degradation rate of DP 1 increased by an average factor of 17.5 when the temperature increased from 140 to 180 °C, or a factor of 0.44 for every 1 °C increment in temperature. In comparison, the degradation rate of DP 1 increased by an average factor of 0.86 when the acid concentration increased from 0 to 1%, or a factor of 0.09 for every 0.1 wt % acid increment in the hydrolysate. It is

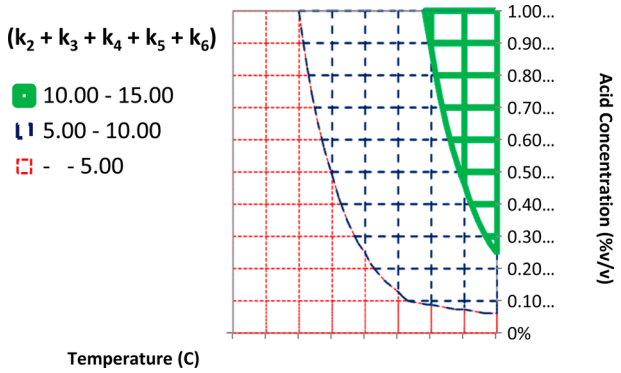


Figure 6. Kinetic model summarizing the reaction rate. The data for the graph is calculated by determining the xylose oligomers depolymerization rate into xylose ($k_2 + k_3 + k_4 + k_5 + k_6$). A high value (as represented by the solid line region) is desired.

important to note that the degradation rate of DP 1 was almost negligible, 10^{-14} min^{-1}, and remained constant throughout hydrolysis (all the way to maximum model conditions, corresponding to 180 °C and 1 wt % acid). In this work, increased acid concentrations and low temperatures led to maximum xylose accumulation. On the other hand, calculated xylose accumulation rates were orders of magnitude higher than those reported for birchwood-derived oligomer depolymerization.[5] Higher xylose accumulation rates could possibly be attributed to switchgrass DP 1 degradation rates that were 10^{14} slower than the degradation rates of oligomers.

Calculations corresponding to the sum of the constants, $k_2 + k_3 + k_4 + k_5 + k_6$, as a function of temperature and acid are presented in Figure 6. Interestingly, the conditions that favored maximum xylose accumulation were not similar to those that were conducive to the rapid reaction rates depicted in Figure 5. In Figure 6, reaction rates were greatest when both the acid concentration and temperature were at the highest level (in 1 wt % acid at 180 °C), where sum of the constants was between 10 and 15. The depolymerization rate increased by an average factor of 4.3 when the temperature increased from 140 to 180 °C, or a factor of 0.11 for every 1 °C increase in temperature. Similarly, the depolymerization rate of oligomers increased by an average factor of 39.8 when the acid concentration increased from 0 to 1 wt % or a factor of 3.98 for every 0.1% acid increment. In comparison to Figure 5, increases in acid concentration were more significant than those of temperature on reaction rates; the use of 0.1 wt % acid concentration was equivalent to an increase of 36 °C in temperature. This study is in agreement with Kumar and Wyman[1] and Lau et al.,[5] which highlighted that in the absence of acid, xylose oligomers degraded at faster rates into byproducts as compared to the accumulation rate of xylose. Therefore, the presence of acid is important for the depolymerization of xylose oligomers into monomers. Moreover, hydrolyzing in water conditions favored the accumulation of xylose oligomers, which are known to inhibit enzymatic hydrolysis.[4]

CONCLUSIONS

Current work extended previous depolymerization studies by including DP 5 and DP 6. Although it would have been sounder to have more than three experimental data points, results presented in this work indicated that oligomers, such as DP 6 and DP 5, depolymerized into xylose in different ways, depending on the hydrolysis conditions. End bond cleavage was

DOI: 10.1021/acssuschemeng.5b00298
ACS Sustainable Chem. Eng. 2015, 3, 2030−2035

favored in acidic conditions, while internal bond cleavage occurred in hot water pretreatment. Calculated DP 1 accumulation rates were orders of magnitude higher than those reported for birchwood-derived oligomers, indicating that switchgrass could show more promise as a feedstock to produce xylose. Furthermore, it was determined that if the conditions were acidic, depolymerization occurred rapidly, maximizing DP 1 accumulation. On the other hand, when depolymerization occurred in hot water, xylose oligomers were produced, contributing to conditions leading to enzymatic inhibition. Overall, current work indicated that pretreatment processing parameters, such as temperature and acid concentrations, affected the chemical composition of the pretreatment hydrolyzate.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors thank the National Science Foundation award number 0822275, United States Department of Energy award number GO88036, Arkansas Center for Plant Powered Production (P3), and the Department of Biological and Agricultural Engineering and Graduate School at the University of Arkansas for their funding and support. The P3 Center is funded through the RII: Arkansas ASSET Initiatives (AR EPSCoR) I (EPS-0701890) and II (EPS-1003970) by the National Science Foundation and the Arkansas Science and Technology Center.

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DOI: 10.1021/acssuschemeng.5b00298
ACS Sustainable Chem. Eng. 2015, 3, 2030−2035