Application of a Depolymerization Model for Predicting Thermochemical Hydrolysis of Hemicellulose

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Abstract

Literature data were collected and analyzed to guide selection of conditions for pretreatment by dilute acid and water-only hemicellulose hydrolysis, and the severity parameter was used to relate performance of different studies on a consistent basis and define attractive operating conditions. Experiments were then run to confirm performance with corn stover. Although substantially better hemicellulose sugar yields are observed when acid is added, costs would be reduced and processing operations simplified if less acid could be used while maintaining good yields, and understanding the relationship between operating conditions and yields would be invaluable to realizing this goal. However, existing models seldom include the oligomeric intermediates prevalent at lower acid levels, and the few studies that include such species do not account for the distribution of chain lengths during reaction. Therefore, the polymeric nature of hemicellulose was integrated into a kinetic model often used to describe the decomposition of synthetic polymers with the assumption that hemicellulose linkages are randomly broken during hydrolysis. Predictions of monomer yields were generally consistent with our pretreatment data, data reported in the literature, and predictions of other models, but the model tended to overpredict oligomer yields. These differences need to be resolved by gathering additional data and improving the model.

Index Entries: Hemicellulose; hydrolysis; kinetic model; dilute acid; depolymerization.

Introduction

Ethanol made from cellulosic biomass has the potential to displace a significant fraction of petroleum in the United States, reducing the dependence on foreign imports and improving the environment. Biologic process-

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ing routes offer particular promise of reducing costs sufficiently to make ethanol cost competitive *(1)*. However, biomass must be pretreated if we are to realize the high yields vital to commercial success by such processes, and pretreatment is among the most costly steps *(2,3)*. Several pretreatment approaches have been and are currently being developed with the intent of reducing overall processing costs *(4)*, and results for many technologies are reported in the literature. Yet, it is challenging to compare performance of these options because different feedstocks have been used and testing and analytical methods are not always the same. Thus, a research project funded by the US Department of Agriculture (USDA) Initiative for Future Agricultural and Food Systems Program seeks to evaluate leading biomass pretreatment technologies using a common feedstock and standardized methods. Specifically, the technologies being evaluated include ammonia percolation, dilute-acid, water-only, ammonia fiber explosion, neutral hot water, and lime pretreatment. Corn stover from Iowa is currently being used as feedstock by all of the investigators involved.

Our effort in this project focuses on pretreatment by removal of hemicellulose either with the addition of acid or in water-only thermochemical processes. During these operations, hemicellulose is solubilized to monomeric and oligomeric saccharides that can degrade to furfural, tars, and other products *(5)*. It is desirable to minimize acid use, produce highly digestible cellulose, and maximize the yield of monomers that are most easily fermented to fuels and chemicals. The approach we applied to achieve these goals began with an extensive search of the literature data to define favorable dilute-acid and water-only pretreatment conditions. Several reported pretreatment studies present data on water-only pretreatment of corn stover *(6–10)* and corncob *(5)*, and others provide data on dilute-acid pretreatment of corn stover *(11–13)* (M. Tucker, personal communication, 2002), and a combination of corncob and corn stover *(14)*. Next the severity parameter and a newly developed modified severity parameter that integrates the weight percent acid concentration were applied to estimate optimal operating conditions from the literature data gathered over a wide range of times, temperatures, and acid levels, and experiments were then conducted to verify the predicted performance. Finally, because oligomers are found to be important at the low acid levels targeted and existing analyses do not consider the range of oligomer chain lengths expected, a model used to describe the breakdown of synthetic polymers was applied to predict the yield of soluble monomeric and oligomeric sugars and to help guide definition of conditions to reduce acid use while maintaining high sugar yields.

Materials and Methods

Preparation of Corn Stover

Corn stover collected by BioMass Agri-Products in Harlan, IA, was supplied by the National Renewable Energy Laboratory (NREL) for all of our experiments. Samples were drawn from a lot created for all partici-

pants in the multi-institutional investigation and ground in a Mitts and Merrill Model 10× 12 rotary knife mill (Harvard, IL) to less than 6-mm particle size, air-dried to about 5% moisture, and stored at –4°C.

For the water-only steam gun tests, about 10 kg of this material was placed into a Hastelloy basket and immersed in a circulation tank containing water at 60°C. Water was pumped through the basket for 4 h to thoroughly wet it, the basket was then removed from the water, and the contents were allowed to drain. Next, soaked corn stover was transferred in approx 1-kg batches to a hydraulic press and dewatered to a nominal moisture content of 50%. Dewatered stover was coned and quartered and separated into 740-g (dry) batches.

For dilute-acid experiments with small reaction tubes, frozen corn stover was taken from the lot and ground further to pass through a 2-mm screen. This material was separated using a model RX-29 Ro-tap with 8-in. Tyler screens (Soiltest, Chicago, IL) to recover the –590 + 420µm fraction, and 1% (w/w) H_2SO_4 (made from a stock 72 ± 0.1% H_2SO_4 solution) was added to this material to achieve a solids concentration of about 5%. Excess liquid was drained after letting this slurry sit overnight at room temperature, and the moist solids were pressed in a 4-in. stainless steel cylinder with a 1-in. diameter hydraulic piston to a final resting pressure of the hydraulic fluid of 1000 psig. The moisture content of this pressed corn stover was determined to be 35% in a Precision 1800W drying oven (Winchester, VA) following NREL LAP 001 *(15)*. A 1% H_2SO_4 solution was added back to bring the final solids content to 25%. Because corn stover has some neutralizing power, a sample was checked for acid content. Seventy-five grams of water was added to a 1-g sample and agitated for several minutes. The pH was determined to be 2.68 using a model 8000 VWR Scientific (West Chester, PA) pH meter and combination electrode (model 511050; Beckman Coulter, Fullerton, CA). This pH corresponds to an actual acid concentration of 1.02% (assuming total dissociation).

Steam Gun Tests

The large batch water-only tests were performed using the 4-L, vertical steam gun at the NREL *(16,17)*. The insulated and heat-traced vessel was preheated for several h to ensure that it was completely up to temperature. Prepared corn stover sample was then loaded into the vessel through a funnel, and the contents were sealed by actuated ball valves on either end of the 10-cm-diameter pipe. Next, live steam was introduced at the top and bottom of the vessel, raising the temperature of thermocouple probes to the target temperature in about 15 s. The temperature was maintained at a target value by controlling steam pressure in the vessel with a valve on the line from the boiler. The reaction time was defined as the period from when steam was introduced to the reactor until the contents were explosively discharged.

A total of 10 steam gun "shots" were performed at various temperatures and a range of times. Three tests were performed at 210°C, one each

for 2, 6,and 18 min. Four tests were performed at 190°C, one each at 7, 14, 22, and 74 min. Two tests were performed at 170°C, one each at 27 and 87 min. One test was performed at 150°C for 107 min.

When a run was completed, the discharge valve on the bottom of the steam gun was opened, and the contents were blown into a 300-L flash vessel to rapidly bring the temperature to below 100°C and quench the reaction. Next, the contents were removed, placed in double plastic bags for storage at 4°C, and shipped in a cooler to Dartmouth College for analysis. After arriving at Dartmouth, the pretreated biomass was pressed to obtain about 100 mL of liquid hydrolysate, the remaining material was slurried with tap water in a 19-L poly bucket, the supernatant was decanted, and fresh water was added. This procedure was repeated until the pH of the supernatant reached 6.0. Then the solids were filtered and weighed, and their moisture content was determined before rebagging and refrigerating them.

Tube Reactor Batch Tests

Batch tube reactors were assembled from 12.5-mm OD Hastelloy (C276) tubing with a 0.8255-mm wall thickness cut into 10-cm lengths. About 6 g of the acid-soaked corn stover described earlier was loaded into each reactor tube using a small spatula and a specially designed plastic funnel and tamped lightly with a glass rod. The tubes were capped with inexpensive 304 stainless steel end caps protected from the acid by inserting machined Teflon plugs into the tube ends based on the kind suggestion of Professor Y. Y. Lee of Auburn University. The tubes were immersed in a 22.8 cm id × 35 cm deep 4-kW model SBL-2D fluidized sand bath (Techne, Princeton, NJ) controlled at the target temperature, held for a specified amount of time, removed from the sand bath, and immediately immersed into a room temperature water bath to quench the reaction. Reaction time was determined as the moment of immersion into the heated sand bath until the moment of quenching. After cooling, the contents of the tubes were removed and filtered with 100 mL of deionized water through a medium-porosity fritted glass filter crucible, and the solids were dried in a vacuum oven at 45°C.

Runs were made at the following temperatures and times: 180°C for 1, 2, 5, 10, 20, and 40 min; 160°C for 5, 10, 20, 40, and 80 min; and 140°C for 5, 10, 20, 40, 80, and 120 min. Temperature transients to be expected using batch tubes during heat-up were analyzed using the method developed by Stuhler and Wyman *(18)*. This showed that at 160°C it could be expected that the center-line temperature of a 0.5-in. ID tube would be 153°C (.95 Δ $T + T_0$) after approx 90 s. This simulation suggests that the longer run times at lower temperatures would not be affected significantly although transient effects could be greater at 180°C.

Analyses

Dried solids and filtered hydrolysates were analyzed for their monomeric sugar content according to NREL LAP-002 *(19)* and LAP-013 *(20)*

protocols, respectively. LAP-014 was applied to quantify soluble oligomers in the hydrolysates *(21)*.

The corn stover used contained 36.1% glucan, 21.4% xylan, 3.5% arabinan, 1.8% mannan, 1.6% galactan, 17.2% lignin, 4.0% protein, 3.2% acetyl, 3.6% uronic acid, and 7.1% ash.

Development of Kinetic Models for Hemicellulose Hydrolysis

Severity Parameter Models

In the mid-1940s Saeman *(22)* modeled the saccharification of wood cellulose during pulping by assuming that the reaction followed first-order homogeneous kinetics, and this model has become the basis for describing hemicellulose hydrolysis and subsequent sugar degradation *(23)*. In the mid-1950s, this model was refined by assuming that hemicellulose was composed of two distinct fractions, one that is relatively easy to hydrolyze and the other more difficult *(24)*. A few recent articles have refined this model to include one or two species of oligomers as intermediates in the reaction's sequence *(5)*:

Hemicellulose (fast)
$\searrow k_f$

$\searrow$
Monomers $\underrightarrow{k_o}$ Oligomers $\underrightarrow{k_d}$ Degradation
$\nearrow$

$\nearrow k_s$
Hemicellulose (slow)
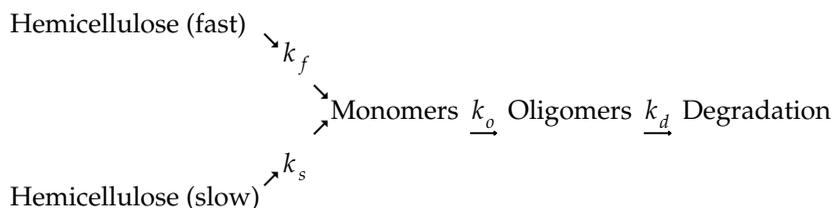
Another approach has been to apply severity models that combine operating conditions such as time and temperature to the following single expression for water-only hydrolysis *(25)*:

$$R_0 = t \cdot \exp\left([T_H - T_R]/14.75\right) \tag{1}$$

in which t is reaction time in minutes; T_H is hydrolysis temperature; and T_R is reference temperature, most often 100°C. When acid is used, a combined severity parameter, *CS*, that includes the effect of added acid catalyst during organosolv treatments has been applied by Chum et al. *(26)*:

$$\log CS = \log R_0 - \text{pH} \tag{2}$$

When Eq. 1 is substituted into this expression, the following relationship results:

$$CS = t \cdot \left(H^+\right) \cdot \exp\left([T_H - T_R]/14.75\right) \tag{3}$$

Because most of the literature data available on corn stover only reported weight percent acid addition but not pH, we modified this expression by assuming that the hydrogen ion concentration is proportional to the percent acid:

$$\left(H^+\right) \propto nA \tag{4}$$

in which *A* is the acid concentration in weight percent and *n* is a proportionality constant close to 10. This is consistent with many of the Saeman-based models applied to hemicellulose hydrolysis. Substituting relationship 4 into 3 and assuming the proportionality constant *n* = 10 gives a result we term the modified severity parameter, M_o:

$$M_o = t \cdot 10A \cdot \exp([T_H - T_R]/14.75) \tag{5}$$

Although not identical to the *CS* defined by Eq. 3, the modified severity parameter provides a useful tool for correlating a diverse array of literature data that only provides weight percent acid addition and not pH.

Depolymerization Model

Most kinetic models for hemicellulose hydrolysis do not consider the presence of oligomers in the reaction sequence at all, and the few that include such species lump them into one or two compounds that ignore the range of chain lengths expected as hemicellulose decomposes from larger chains to smaller ones. However, kinetic models have been devised to describe the distribution of chain lengths that occur in the decomposition of plastics *(27)* and size reduction operations in the grinding of mineral ores *(28)* based on both continuous *(29,30)* and discrete *(31–33)* product distributions. Furthermore, Agarwal et al. *(34)* applied discrete depolymerization kinetics to predict hemicellulose and cellulose degradation in alkaline pulping. The discrete depolymerization approach of Simha *(32)* was applied here to capture the range of chain lengths that are expected during pretreatment by hemicellulose hydrolysis.

Consider the breaking of one bond of a polymer composed of *n* monomer units to form two new molecules:

$$N_n \rightarrow N_j + N_{n-j} \tag{6}$$

Subsequently, these products can degrade further as follows:

$$N_{n-j} \rightarrow N_k + N_{n-j-k} \tag{7}$$

$$N_j \rightarrow N_i + N_{j-i} \tag{8}$$

If we assume that all the bonds linking monomer units have the same probability of being broken, then the rate of change in concentration of any *j*-mer can be expressed by the following differential equation:

$$\frac{dN_j}{dt} = 2k_h \sum_{i=j+1}^{n} N_i - k_h(j-1)N_j \tag{9}$$

in which k_h is the hydrolysis rate constant that is now assumed to be the same regardless of chain length, in which the first term on the right side is the rate of creation of *j*-mers from the scission of molecules larger than a *j*-mer (note that there are two scission events that result in identical products) and the second term describes the rate at which existing *j*-mers disappear when any one of the (*j*–1) bonds present are broken. When this

expression is extended to the longest polymer chain of length n that can only be broken but not formed, the rate of change in its concentration is described by the following expression:

$$\frac{dN_n}{dt} = -k_h(n-1)N_n \tag{10}$$

Integrating Eq. 10 based on the initial condition that at time $t = 0$, $N_n = N_n^0$, we obtain the following result:

$$N_n = N_n^0 \exp\left(-k_h[n-1]t\right) \tag{11}$$

To solve for the concentration of the $(n–1)$-mer, Eq. 11 is substituted into Eq. 9 to give

$$\frac{dN_{n-1}}{dt} = 2k_h N_n^0 \exp\left(-k_h[n-1]t\right) - k_h(n-2)N_{n-1} \tag{12}$$

The result of integrating this linear first-order differential equation with the initial condition $N_{n-1} = 0$ is

$$N_{n-1} = 2N_n^0 \left(\exp\left[-k_h\{n-2\}t\right] - \exp\left[-k_h\{n-1\}t\right]\right) \tag{13}$$

Following this procedure for successively smaller j-mers, we can arrive at a generalized equation to describe the concentration of any j-mer ($j \neq n$) at any time:

$$N_j = N_n^0(1-\alpha)^{(j-1)}\alpha(2 + [n-j-1]\alpha) \tag{14}$$

$$\text{with} \quad \alpha = 1 - e^{-k_h t} \tag{15}$$

Figure 1 illustrates the distribution of products predicted by applying Eqs. 11 and 14 to describe the decomposition of a hypothetical pentamer. The concentration of oligomers of chain length 5 rapidly drops while the concentrations of oligomers with 2, 3, and 4 monomer units build up and then drop off as monomer is formed. Furthermore, because shorter chains can be formed in more ways than longer chains, the concentration of oligomers with a chain length of 4 is less than that of chain length 3, which is, in turn, less than the concentration of chain length 2. Ultimately, depolymerization results in monomer being the only remaining species.

An additional consideration for predicting hemicellulose hydrolysis kinetics is the reaction of monomer to furfural and other degradation products *(35)*. Assuming a single degradation reaction that can be described by a first-order dependence on monomer concentration, the differential equation describing the rate of monomer formation and consumption becomes

$$\frac{dN_1}{dt} = 2k_h \sum_{i=2}^{n} N_i - k_d N_1 \tag{16}$$

in which k_d is the rate constant for decomposition of the monomer. This equation can be integrated to obtain the following result:

$$N_1 = \frac{2k_h}{n}\left(\frac{[n-1]\left[e^{\{-k_h t\}} - e^{\{-k_d t\}}\right]}{k_d - k_h} - \frac{[n-2]\left[e^{\{-2k_h t\}} - e^{\{-k_d t\}}\right]}{k_d - 2k_h}\right) \tag{17}$$
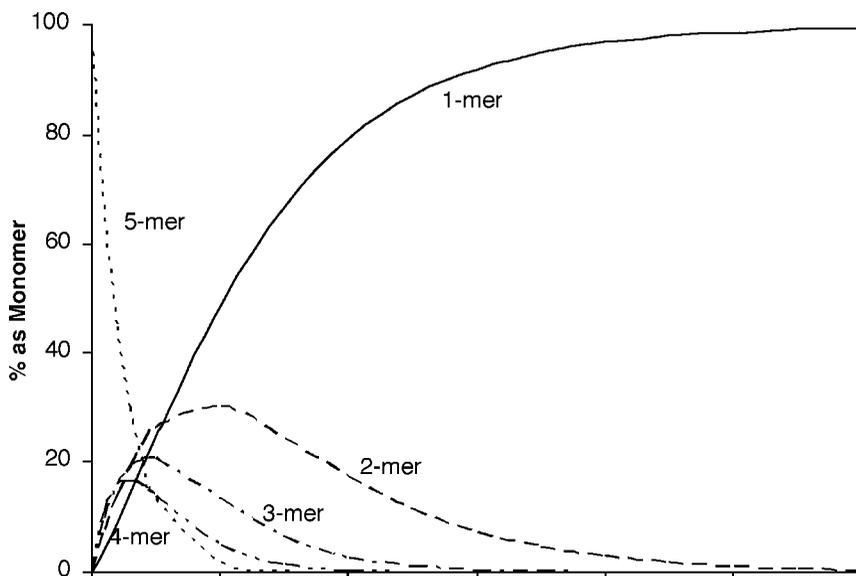
Fig. 1. Distribution curves for depolymerization of a hypothetical 5-mer containing 5 monomer units assuming random scission and arbitrary rate constant.

We now have expressions that describe the concentrations of each fragmentation product expected for hemicellulose hydrolysis at any time.

Results and Discussion

Water-only hydrolysis data for corn stover from Rubio et al. *(6)*, Tortosa et al. *(9)*, and Schultz et al. *(10)*, and corn cobs from Garrote et al. *(15)* were plotted against log severity parameter to provide a basis for selecting pretreatment conditions. The fraction of potential xylose remaining in the solids is presented in Fig. 2, and the yield of oligomers only and oligomers plus monomers plotted in Fig. 3. Based on these results, conditions were defined for additional runs with our controlled source of corn stover, and trends were found that are consistent with the literature data, as shown in Figs. 2 and 3. The maximum yield of xylose in the hydrolysate including monomers and oligomers was about 60% and occurred at a log severity factor of between 3.8 and 4.0. In addition, we note that xylooligomers predominated, accounting for as much as 90% of solubilized species at lower severities and about 80% at the conditions corresponding to the maximum yield.

For dilute-acid hemicellulose hydrolysis, the hydrolysate data of Lee et al. *(14)* for corncob/cornstover mix and Tucker (personal communication, 2002) for corn stover were plotted against the log modified severity parameter to guide our definition of run conditions. Figure 4 shows that the yields reported in the literature and those obtained in our tests are very similar. In this case, the maximum yield of monomers and oligomers was
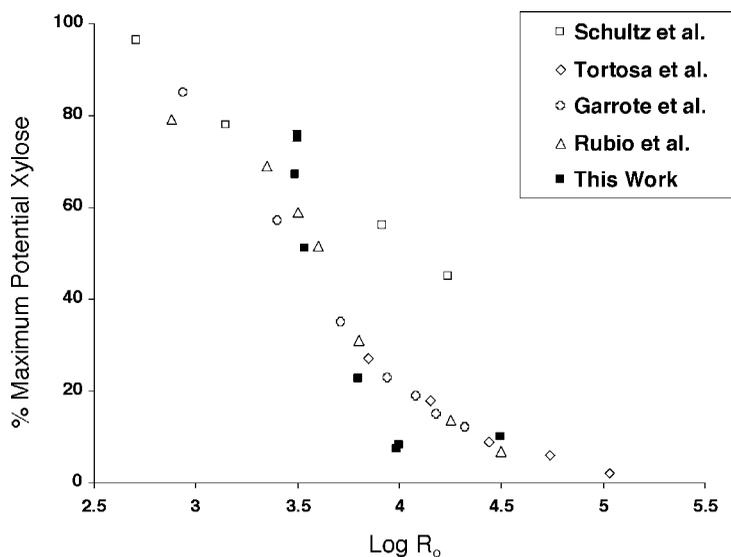
Fig. 2. Percentage of potential xylose remaining in solid residue vs log R_0 (R_0 + t · exp[{T_H - T_R}/14.75]) for various investigators and data from this study for water-only hydrolysis.
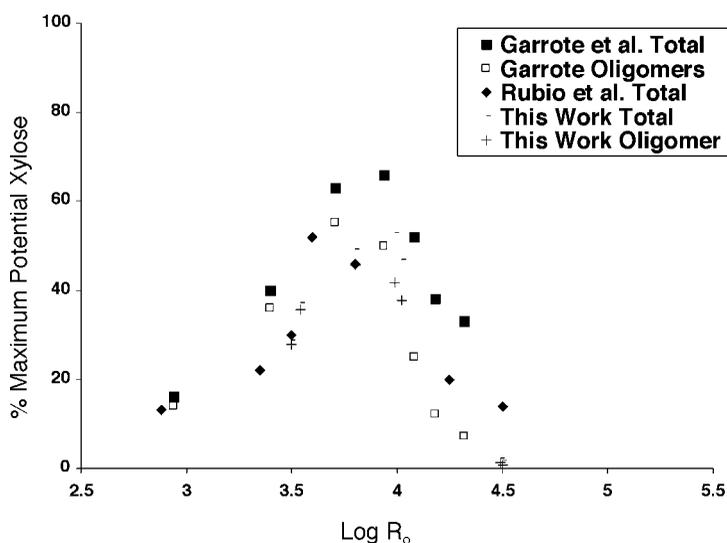
Fig. 3. Percentage of potential xylose as monomers plus oligomers (total) and as only oligomers in liquid hydrolysate vs log R_0 (R_0 = t · exp[T_H - T_R/14.75]) for various investigators and data from this study for water-only hydrolysis.

about 90% and occurred at a log modified severity parameter of about 3.8. However, xylooligomers represented a much lower fraction of the total solubilized sugars than for the water-only case, with only about 20% of the total being oligomers at the optimum yield point.
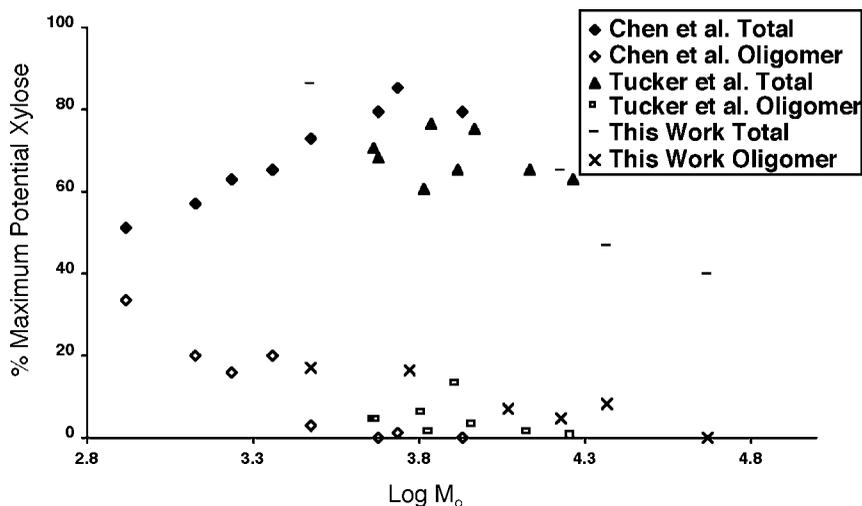
Fig. 4. Percentage of potential xylose in hydrolysate as monomers plus oligomers (total) and oligomers only vs long M_o ($M_o = t \cdot A^n \cdot \exp[T_H - T_R]/14.75]$) for various investigators and data from this study for kilute-acid hydrolysi.

Next, model curves based on Eqs. 11, 14, and 17 were fit to our steam gun data in Fig. 5 and to literature data as shown in Fig. 6 for Garrote et al.'s *(5)* data for water-only hydrolysis of corncobs. The kinetic constant for monomer degradation was calculated from the Arrhenius expression reported by Converse et al. *(35)*. Then, the hydrolysis constant was determined to minimize the sum of the squares of the differences between monomer data and model predictions. Use of the monomer for predicting xylan partitioning is somewhat arbitrary but was chosen because it could be fit well with an arbitrary hydrolysis rate constant. In addition, oligomers with nine or more monomer units were arbitrarily assumed to remain in the residual solids, and those of length 2 through 8 as well as monomers were assumed to be all in the liquid phase. If the cutoff between soluble and insoluble oligomers is decreased, the oligomer curve moves closer to the data but never reaches it even at a cutoff degree of polymerization (DP) of 2. A cutoff above DP-8 tends to increase the divergence between data and model, but only slowly, as the contribution from higher-chain oligomers diminishes rapidly with increasing DP.

As shown in Figs. 5 and 6, the data and predictions agree reasonably well initially, but xylooligomers are overestimated and residual xylan underestimated at later times. This divergence could be explained, at least in part, by an accelerated decomposition of xylose, but only analysis could confirm or deny this. Unfortunately, no analyses of degradation products were available, and the decomposition kinetics of Converse et al. *(35)* were used unmodified.
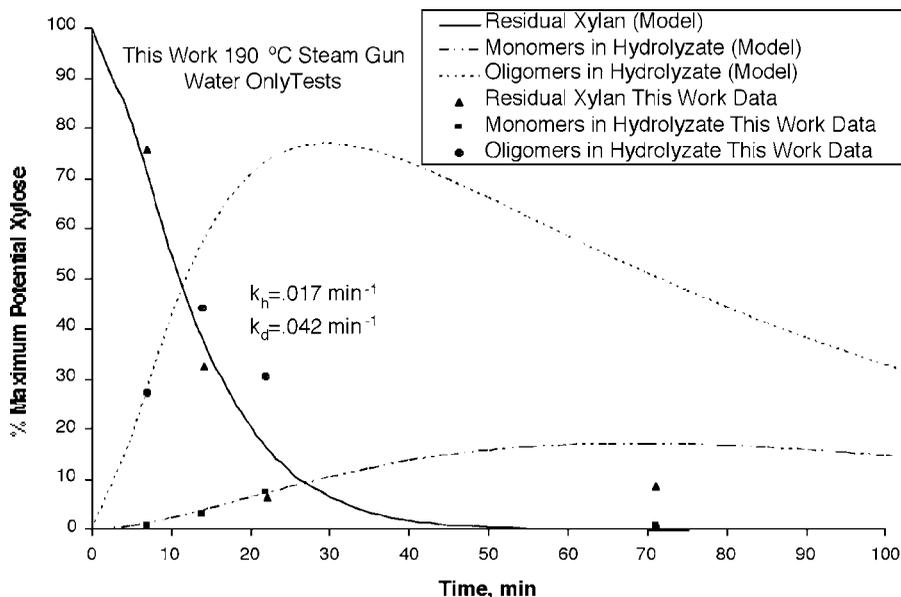
Fig. 5. Comparison of data and depolymerization model predictions for water-only hydrolysis of corn stover for this work.
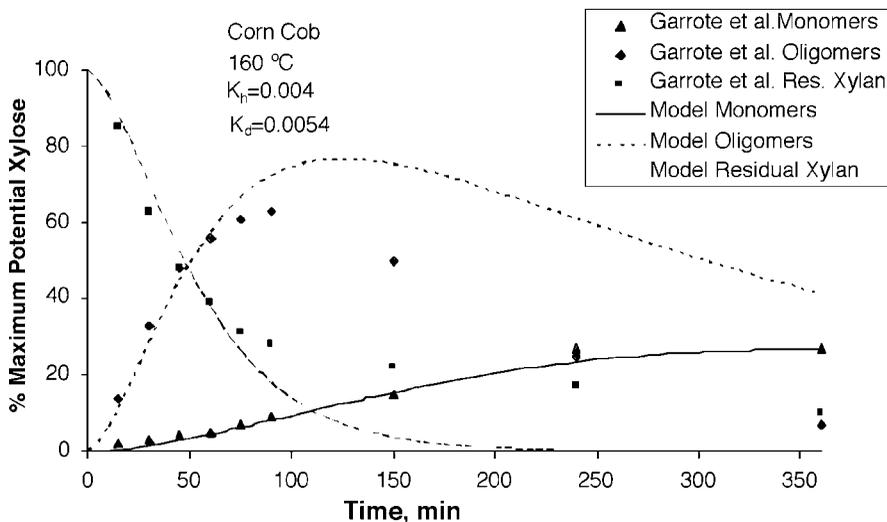
Fig. 6. Comparison of data and depolymerization model predictions for water-only hydrolysis of corncobs.

Of note, Fig. 5 shows that the maximum experimental yield (monomers plus oligomers) occurred at about 14 min, corresponding to a log severity factor of about 3.8, and Fig. 6 shows that the maximum yield occurred at about 100 min, also corresponding to a log severity factor of about 3.8.
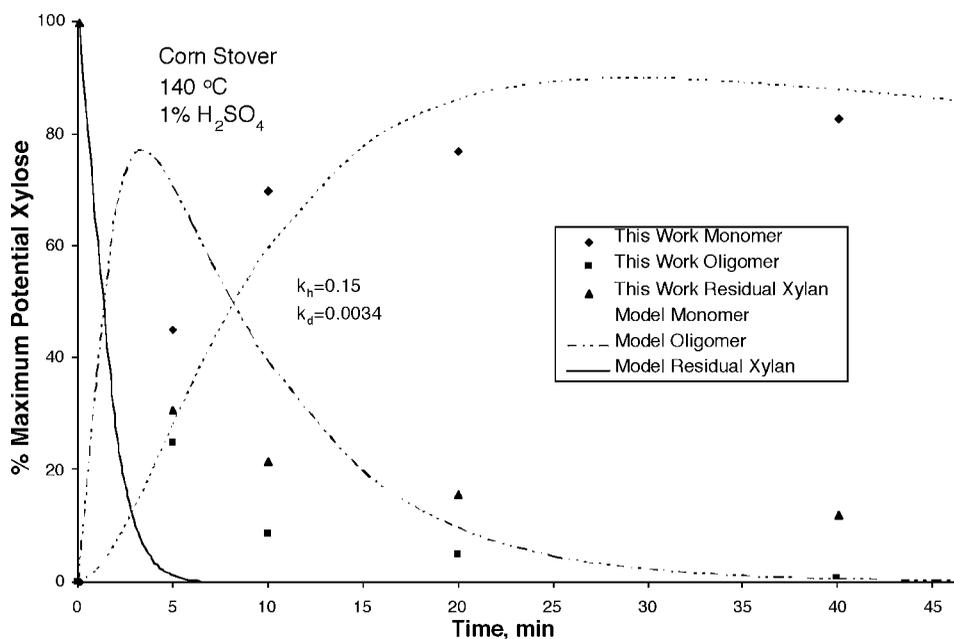
Fig. 7. Comparison of data and depolymerization model predictions for dilute-acid hydrolysi of corn stover for this work.

The same procedure was applied to develop the depolymerization model for dilute H_2SO_4 hydrolysis using some of our batch tube data and the data of Lee and Chen for a corncob/corn stover mix *(14)*. A comparison of the models and data are presented in Figs. 7 and 8, respectively. There is a particularly large misfit between the oligomer and residual xylan data and model in both figures. This is apparently a consequence of the addition of acid catalyst. Figure 7 shows that the maximum experimental yield occurred at about 40 min, which corresponds to a log modified severity parameter of about 3.8. In Fig. 8 the maximum yield appears to be near, but beyond, the limit of the data provided by the literature source (50 min). At 50 min, the log modified severity parameter is about 3.7.

Conclusions

The highest yields of total solubilized corn stover xylose in our steam gun, water-only hydrolysis was 53% at a log severity parameter near 4.0, consistent with results reported in the literature. With H_2SO_4 addition, the modified severity parameter was found to provide a useful means for comparing data from different studies, and the highest yield of solubilized hemicellulose, using our batch tube apparatus, was measured to be 89% at a log modified severity of 3.8, again consistent with literature values. Oligomeric xylan comprised about 80% of the total soluble monomers and oligomers at the maximum total yield point without acid present but contributed only about 20% of the total sugars in solution when 1% H_2SO_4 was added.
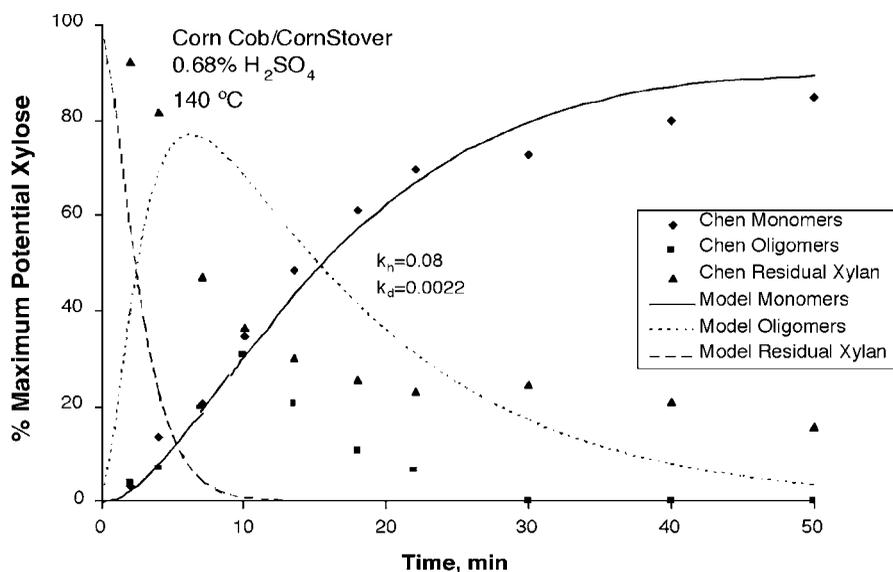
Fig. 8. Comparison of data and depolymerization model predictions for dilute-acid hydrolysis of corncob/corn stover mixture.

The severity parameter was found to provide a valuable tool to predict the combination of conditions that maximize hemicellulose yield. Although not as useful for predicting quantitative results, the ability of the severity parameter to relate performance at different times, temperatures and acid levels is very valuable for selecting run conditions for specific kinetic studies.

An important goal of our research is to reduce acid use while maintaining high yields, and oligomers are expected to become more important at lower acid levels. Thus, predicting oligomer histories will be very useful in defining promising paths to this end, but available hemicellulose hydrolysis kinetic models, including the severity parameter, do not describe the time course distribution of oligomeric species of varying chain lengths. A depolymerization model was found to predict monomer trends well using an arbitrary hydrolysis rate constant. In the case of uncatalyzed hydrolysis, the model-data fit was reasonable during the early stages of reaction, but oligomer yields were overestimated and residual xylan was underestimated by the depolymerization model at later stages. In the case of catalyzed hydrolysis, the fit between oligomer and residual xylan and the model was not particularly good at any point during the reaction. Thus, further refinements are needed for a depolymerization model to be useful as a predictive tool. For instance, the assumption that all bonds react at equal rates may be modified to include differences in end bonds; to consider changes in kinetic constant due to chain heterogeneity; or to account for the "gel" effect observed in polymer synthesis, in which the accessibility of molecules changes with chain length. In addition, we plan to focus on improving our methods of capturing oligomers to ensure that oligomer data accurately

reflect their history during hydrolysis and are not affected by heat transfer or other effects that could influence the profiles. It will also be valuable to determine the range of oligomer sizes that are released into solution to determine whether the definition of soluble and insoluble chain lengths we arbitrarily assigned is reasonable.

Acknowledgments

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