Xylose Monomer and Oligomer Yields for Uncatalyzed Hydrolysis of Sugarcane Bagasse Hemicellulose at Varying Solids Concentration

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Pretreatment is an essential, but expensive, step in biologically converting biomass to fuels and chemicals, and acids added or released during the reaction hydrolyze hemicellulose to sugars and expose cellulose for enzymatic digestion with good yields. Pretreatment by liquid flow past solids increases hemicellulose removal yields particularly at higher flow rates, but current first-order homogeneous kinetic models indicate that the amount of water should not be important. However, these models suffer from inconsistencies, and the effect of varying sugarcane bagasse concentrations on xylose monomer and oligomer yields was experimentally measured in a batch reactor without adding acids or other chemicals at 200 °C. A greater drop in pH was observed at higher solids concentrations, as anticipated. Furthermore, only about 7−13% of the total xylose recovered in solution was as monomers at the maximum total xylose yield point, with the rest being oligomers, and although monomer yields could be increased at longer hold times, overall yields declined. These results and the general yield versus time profiles are consistent with the predictions of first-order models. However, a possible trend toward greater yields was observed at lower solids concentrations, but a paired difference test showed that these yield differences were only statistically significant between the extremes in biomass concentrations.

Introduction

Producing fuels and chemicals from vast, inexpensive sources of lignocellulosic biomass, such as agricultural and forestry residues and dedicated crops, in large biorefineries would essentially eliminate greenhouse gas emissions, dispose of problematic solid wastes, create rural agricultural and manufacturing jobs, secure energy supplies, reduce our trade deficit, help meet growing energy demand by developing countries, and improve air quality, particularly for pure biofuels and fuel cell applications.[1−5] Furthermore, biomass provides a unique sustainable feedstock for making liquid organic fuels that have inherent convenience, infrastructure, cost, and efficiency advantages; no other sustainable resource can be converted into organic chemicals.

About 40−50% of dry biomass is the glucose polymer cellulose, much of which is in a crystalline structure. Another 25−35% is hemicellulose, an amorphous polymer usually composed of arabinose, galactose, glucose, mannose, and xylose. The remainder is mostly lignin plus lesser amounts of minerals, oils, and other compounds.[4] Enzymatic hydrolysis of cellulose achieves nearly theoretical yields of glucose that are vital to success.[2,4] Furthermore, enzymatic processing costs have been reduced about 4-fold,[2] and the powerful tools of biotechnology promise additional improvements to make the technology competitive for biologically manufacturing ethanol[6] and commodity chemicals.[3,5]

Pretreatment is essential to realize high enzymatic hydrolysis yields. Although no one pretreatment technology has been shown to be clearly superior,[4,7] many favor dilute acid technologies for releasing hemicellulose sugars at high yields and for enhancing cellulose digestibility by enzymes[2,8] as well as for recovering hemicellulose before acid hydrolysis of cellulose.[2] Yet, dilute acid hemicellulose hydrolysis is the most expensive single processing step. Pretreatment also substantially impacts the cost for converting cellulose into sugars that collectively comprise about 40% of the total.[6] Thus, pretreatment must be improved if costs are to compete with conventional products. Innovative pretreatment could also recover coproducts that enhance revenues and increase the impact of the resource.[2,5]

Continuously flushing water through biomass achieves high sugar yields from hemicellulose without adding acid;[9,10] others have shown that adding very dilute acid achieves similar results.[11] Furthermore, about half the lignin is removed in such flow-through systems, and the remaining cellulose is highly digestible. The liquid hydrolyzate also appears to be less inhibitory to fermentative organisms, potentially reducing conditioning costs.[12] Unfortunately, high volumes of water are used, diluting product concentrations and resulting in high-energy costs for both pretreatment and product recovery. In addition, the frequently used countercurrent configurations are difficult to implement commercially.

The challenge is to achieve yield and fermentability advantages of flow-through approaches in a commercially viable configuration without high water usage, and a better understanding of the relationship between flow-through systems and conventional steam gun systems[13,14] can be important in achieving this goal. Because much more water is applied in flow-through reactors, this paper focuses on how recovery of xylose from hemicellulose is impacted by solids concentrations in batch reactors based on predictions by existing hemicellulose hydrolysis models and new experimental data.

Hemicellulose Hydrolysis Models

Biomass hydrolysis kinetics have been studied for over 5 decades, and nearly all models are based on

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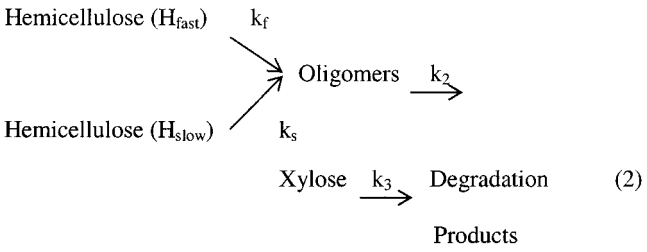
reactions in series with first-order dependence on reactant concentration and Arrhenius temperature dependence for the rate constants k_i. Saeman developed the first of these models in the mid-1940s for cellulose hydrolysis according to the reaction sequence:[15]

$$\text{cellulose} \xrightarrow{k_a} \text{glucose} \xrightarrow{k_b} \text{degradation products} \quad (1)$$

Such models predict the tradeoff between glucose release from cellulose and glucose degradation. On the basis of such models, various groups have shown that yields for chemical hydrolysis of cellulose are limited to about 60−70%, with these higher values at high temperatures of about 260 °C.[16]

Hemicellulose hydrolysis models have been built from these simple cellulose hydrolysis sequences, such as eq 1, to those that consider fast- and slow-hydrolyzing portions of hemicellulose. Most have assumed that sugar monomers form directly from hemicellulose,[17] but a few have included oligomer intermediates to reconcile with experimental observations, particularly for flow-through systems.[18] In either model, xylose reacts further to furfural and other degradation products, with the overall sequence pictured as



(2)

in which the k's represent the kinetic constants for each step and are Arrhenius functions of temperature.

Simple first-order homogeneous kinetic equations have been developed and integrated based on sequence (2) to predict the time-dependent yield of either the fast or slow unreacted hemicellulose as a function of time t:

$$H_i/H_{i0} = \exp(-k_i A^{n_i} t) \quad (3)$$

where H_{i0} is the initial amount of fast (i = f) or slow (i = s) hydrolyzing fraction, k_i is the rate constant for the fast- or slow-hydrolyzing fraction, A is the acid concentration measured in weight percent in most existing models, n_i is a power determined for either the fast or slow fraction, and t is the time in minutes. If oligomeric species are included in eq 2, their yield is predicted to be

$$\frac{O}{H_0} = \frac{k_f A^{n_f} H_{f0}}{(k_2 A^{n_2} - k_f A^{n_f}) H_0}\{\exp(-k_f A^{n_f} t) - \exp(-k_2 A^{n_2} t)\} + \frac{k_s A^{n_s} H_{s0}}{(k_2 A^{n_2} - k_s A^{n_s}) H_0}\{\exp(-k_s A^{n_s} t) - \exp(-k_2 A^{n_2} t)\} \quad (4)$$

where $H_0 = H_{f0} + H_{s0}$, O is the amount of oligomers, k_2 is the rate constant for oligomer conversion to monomers, and n_2 a constant for the acid concentration. Similarly, for production from oligomers, as in eq 2, the xylose yield is predicted to be

$$\frac{X}{H_0} = \frac{k_f A^{n_f} k_2 A^{n_2} H_{f0}\{\exp(-k_f A^{n_f} t) - \exp(-k_3 A^{n_3} t)\}}{(k_f A^{n_f} - k_2 A^{n_2})(k_f A^{n_f} - k_3 A^{n_3}) H_0} + \frac{k_s A^{n_s} k_2 A^{n_2} H_{s0}\{\exp(-k_s A^{n_s} t) - \exp(-k_3 A^{n_3} t)\}}{(k_s A^{n_s} - k_2 A^{n_2})(k_s A^{n_s} - k_3 A^{n_3}) H_0} - \frac{k_f A^{n_f} k_2 A^{n_2} H_{f0}\{\exp(-k_2 A^{n_2} t) - \exp(-k_3 A^{n_3} t)\}}{(k_f A^{n_f} - k_2 A^{n_2})(k_2 A^{n_2} - k_3 A^{n_3}) H_0} - \frac{k_s A^{n_s} k_2 A^{n_2} H_{s0}\{\exp(-k_2 A^{n_2} t) - \exp(-k_3 A^{n_3} t)\}}{(k_s A^{n_s} - k_2 A^{n_2})(k_2 A^{n_2} - k_3 A^{n_3}) H_0} \quad (5)$$

in which X is the amount of xylose formed, k_3 is the rate constant for degradation of xylose, and n_3 is the power for the acid concentration. Thus, eq 5 predicts the change in monomeric sugar yield based on the tradeoff between xylose formation and degradation, and the total sugar and oligomer yield is found by combining eqs 4 and 5. Most studies only consider direct reaction of hemicellulose to monomeric sugars, and the appropriate expression for the xylose yield can be obtained by replacing O with X along with the appropriate rate constants in eq 4. These models have been modified to improve their predictive ability over the years to include the neutralizing capacity of the substrate, reversion reactions, use of hydrogen ion concentration, and parasitic pathways.[19]

Such first-order kinetic models are the current foundation for predicting hemicellulose sugar recovery, and all indicate that solids concentration would not impact the reaction rates for fast- or slow-hydrolyzing solids, oligomers, or monomers. Thus, these models would not attribute performance variations between batch and flow-through reactor configurations to the large amount of water used. However, existing hemicellulose hydrolysis models suffer from important limitations. For example, some predict little change in hemicellulose sugar yield with temperature, and others suggest that the yield is sensitive to temperature.[19] As another example, Figure 1 compares the yield of sugars predicted by various kinetic models developed over the years versus the yield predicted for a model that was based on degradation of pure xylose sugar solutions at the exact same conditions.[20−23] The fact that none of the predictions fall on the diagonal line suggests that the xylose degradation constants apparently change from one study to the next to improve the overall fit for hemicellulose hydrolysis data but compromise the accuracy of describing xylose degradation itself. Thus, although first-order models are useful for correlating data, most are not based on independent experiments and apparently do not capture the true mechanism of these two-phase reactions. Such limitations raised doubt as to the ability of the models to predict the effect of water usage on hemicellulose hydrolysis, and experiments were conducted in batch tubes with changing solids concentrations to determine the impact on hydrolysis yield. No acid was used to provide insight into mechanisms for flow-through and steam gun technologies that add no chemicals for hemicellulose hydrolysis.

Materials and Methods

Raw Material and Preparation. Sugarcane bagasse from a single lot harvested in Louisiana was provided by BC International of Dedham, MA. The

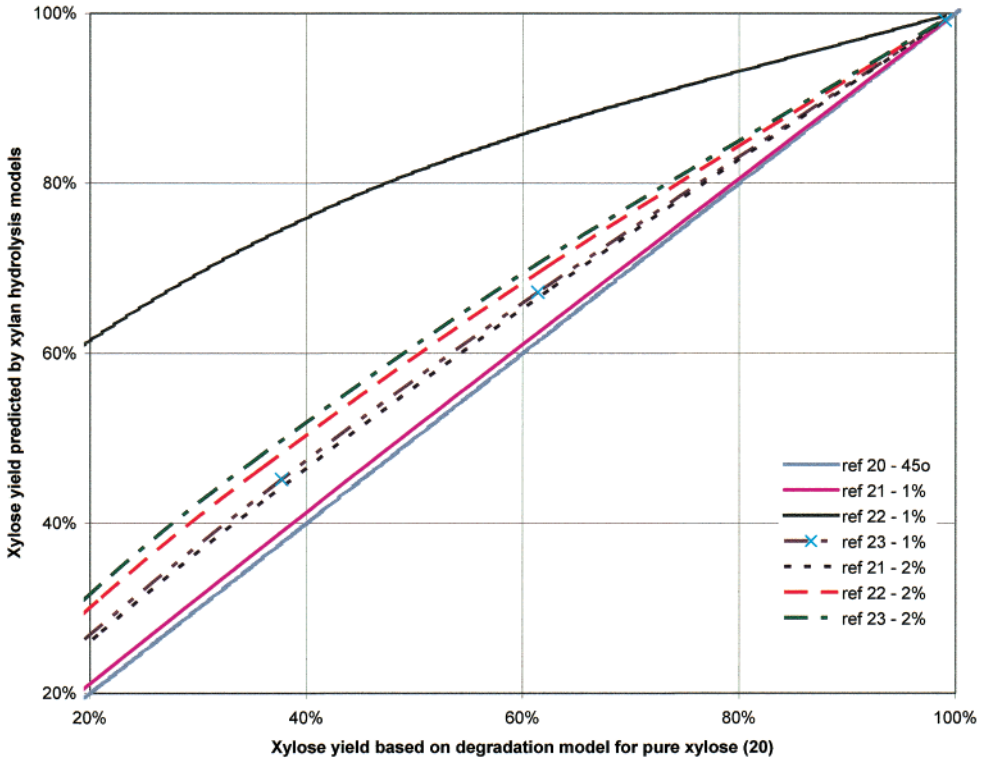


Figure 1. Model predictions of the fraction of initial xylose remaining for 1 and 2% sulfuric acid at 160 °C using constants derived from hemicellulose hydrolysis (ordinate) compared to a model derived for degradation of pure xylose solutions (abscissa) (refs 20−23).

bagasse was milled to 40-mesh (1-mm) size in a Thomas-Wiley Laboratory Mill model 4 and refrigerated at 10 °C until used. Samples of bagasse were periodically analyzed for xylan and glucan contents by standard methods.[24] However, the duration of the concentrated acid digestion (72% sulfuric) at 30 °C was decreased from 2 to 1.5 h and the duration of the second digestion decreased from 1 h to 40 min to reduce the degradation of the sugar recovery standard (SRS) to within a range of 5−15%. Since the time of the work reported here, these times have been further adjusted by their developers to optimize the recovery of sugars for herbaceous materials and agricultural residues versus the woody species for which many of these methods were developed originally. The moisture content (typically 10−15%) was measured for each experiment[24] and used in our yield calculations.

Biomass Hydrolysis. The batch reactors consisted of six 0.5-in.-diameter, 4-in.-long cylindrical Hastelloy C276 steel tubes with a 0.035-in.-thick wall and an internal volume of 9 mL. Prior modeling showed that radial heat transfer should have little effect on hemicellulose conversion for tubes of that diameter.[25] To facilitate mass balances, both ends of each tube were sealed with Swagelock caps. To minimize temperature transients during heat up, the tubes were heated using two sand baths (Techne model SBL2D). The first bath was at 300 °C to speed the heat up to the target temperature of 200 °C before the tubes were quickly transferred to a second bath held at 200 °C for the remainder of the reaction time. Our heat-transfer analysis and measurements of centerline temperatures in our tubes showed that this procedure would reduce the effect of heat-up on reaction yields.[25]

Each reactor was loaded with appropriate weights of bagasse and water to give final solids contents of 0.5, 1.0, 3.0, 7.0, and 10.0 wt %. The reaction tubes were held at 200 °C for the desired reaction time as described and then quickly transferred to an ice−water bath to terminate the reaction. For 0.5, 1.0, and 3.0% solids concentrations, the liquid hydrolyzate was recovered by filtering the product through a screen. However, for the 7.0 and 10.0% solids experiments, the product was pressed with a small kitchen garlic press because so little free water was present.

Analysis. After cooling to room temperature, the pH of the liquid obtained from each hydrolyzate by the protocol above was measured using a VWR gel filled combination probe (model 33221-040) within 2 h of the reactions. Then, 1 part of each hydrolyzate sample was diluted with 1, 2, or 3 parts water by weight to achieve sugar concentrations within 50% of the standard high-performance liquid chromatography (HPLC) solutions based on theoretical maximum yields. Each diluted hydrolyzate sample was neutralized with calcium carbonate (Sigma; 99% purity) to pH 5−9, with the amount added dependent on the volume and original pH of the hydrolyzate. After neutralization, 1 mL was centrifuged for 10 min at 13 000 rpm and the liquid analyzed for sugars by HPLC using an Alcott 728 autosampler, a Knauer differential refractometer, a Waters 510 pump at a flow rate of 0.6 mL/min, and a BioRad HPX-87P column heated to 85 °C. Standard 1 g/L solutions of glucose and xylose were run as every sixth sample as a reference.[24]

Total sugars in solution as both monomers and oligomers were measured by bringing the acid concentration of 2−4-mL samples of hydrolyzate in crimp-sealed pressure bottles to 3% (w/w) and autoclaving them at 120 °C for 30 min. Sugar recovery factors of about 0.95 for glucose and 0.90 for xylose were determined by subjecting known solutions to the same conditions. The measured sugar concentrations after posthydrolysis were then divided by these sugar recov-

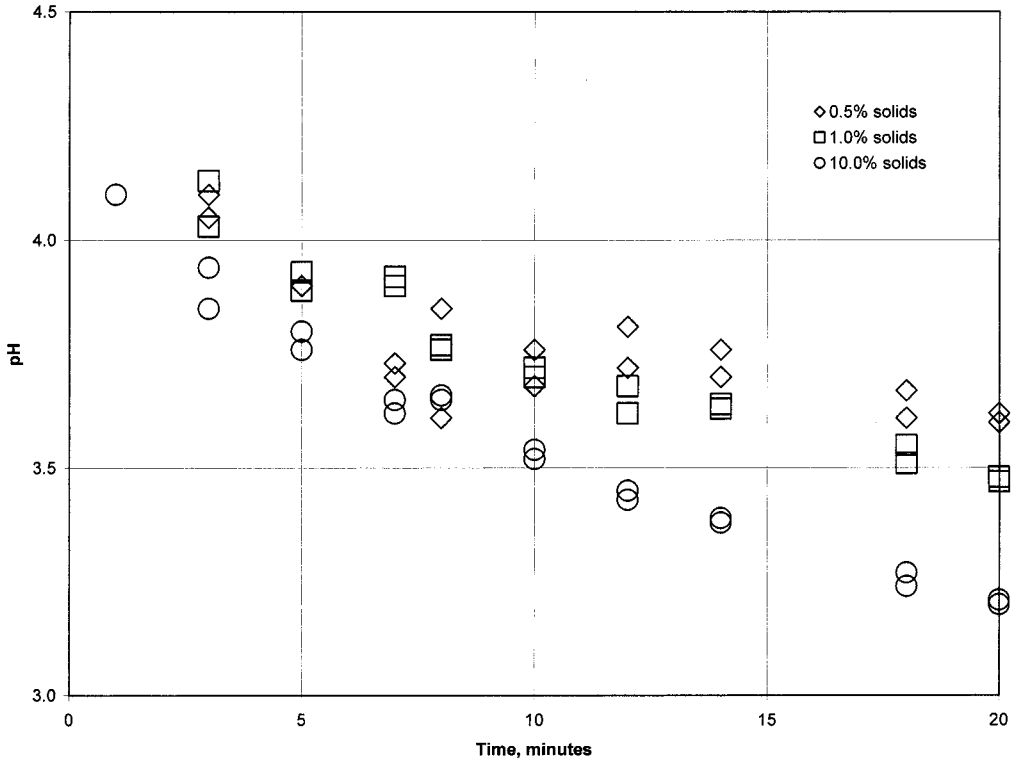


Figure 2. pH measured at room temperature versus reaction time for replicates of sugarcane bagasse hydrolysis at 200 °C with 0.5, 1.0, and 10.0% solids concentrations (wt %) and without acid addition.

ery factors to correct for sugar degradation. The composition of a number of solid residues was also measured according to standard procedures[24] and used to calculate the amount of unreacted xylose. This value was then added to the quantity of total xylose in solution to provide a check on material balances, and total xylose balances of between 92.5 and 101.0% were obtained, with only one check being at 84.3%.

Results

Figure 2 shows the pH history measured at room temperature for the liquid squeezed directly from the solids without water addition for replicate measurements for uncatalyzed hydrolysis of bagasse at 0.5, 1.0, and 10.0% solids concentrations. In all cases, the pH dropped rapidly from the initial value of about 7.0 to less than 4.5 early in the reaction and then continued to decrease with increasing time. Except for a few instances, the pH at any time is less for higher solids than for lower solids concentrations. This result is expected because the concentration of acetyl groups and other organic acids should be greater at higher solids concentrations, increasing the hydrogen ion concentration and dropping the pH, and Figure 2 suggests that the hydrogen ion concentration continues to increase throughout the reaction. It is important to note that the dissociation equilibrium for acetic and many other acids shifts toward less hydrogen ion release with increasing temperature, and the hydrogen ion concentration during the reaction should be somewhat less than that indicated by the pH at room temperature. However, the effect of temperature should be similar for all points. According to a few models that picture the rate of each step in hemicellulose hydrolysis to be proportional to the product of hydrogen ion and reactant concentrations, the rate would be expected to increase with increasing solids concentrations.

Figure 3 presents the combined yield of xylose monomers and oligomers for varying solids concentrations and time for the average of two replicates at each data point. The general trajectories are similar for all solids concentrations, reaching a maximum value of between 75 and 80% in approximately 10 min for 1.0% solids concentrations and greater. For comparison, large-scale biomass hydrolysis at solids levels of around 40% realizes maximum total yields of about 65%,[13] whereas the yields for flow-through and dilute-acid-catalyzed hydrolysis tend to be over 90%.[9−12] The peak yield appears to be somewhat higher at 0.5% solids concentrations, with a value of about 86% in 10−12 min. In addition, the average yields are generally greater at lower solids concentrations, and it appears that the yield increases faster at lower solids levels. However, the data for 1.0% solids counters that trend, particularly as time progresses beyond 5 min, and a statistical paired-difference analysis based on the Student's *t* showed that only the 0.5% data was significantly different from all other data points at the 95% confidence limit.

Figure 4 summarizes oligomeric xylose data obtained by averaging the differences between the total sugar recovery values and the monomer yields for the replicates at each run time and solids concentration. The majority of the xylose is released in oligomeric form, consistent with data reported for hemicellulose hydrolysis by others;[13] a posthydrolysis step would thus be required for sugar utilization. The oligomer time trajectories are quite similar for all solids concentrations, and the maximum oligomer yield of between 70 and 75% occurs at about the same time as that for the maximum total sugar recovery shown in Figure 3: 10 min. A more consistent trend toward higher oligomer yields is evident for lower solids concentrations, particularly before the maximum yield is reached, than was displayed for total sugar release in Figure 3. Oligomer yields also

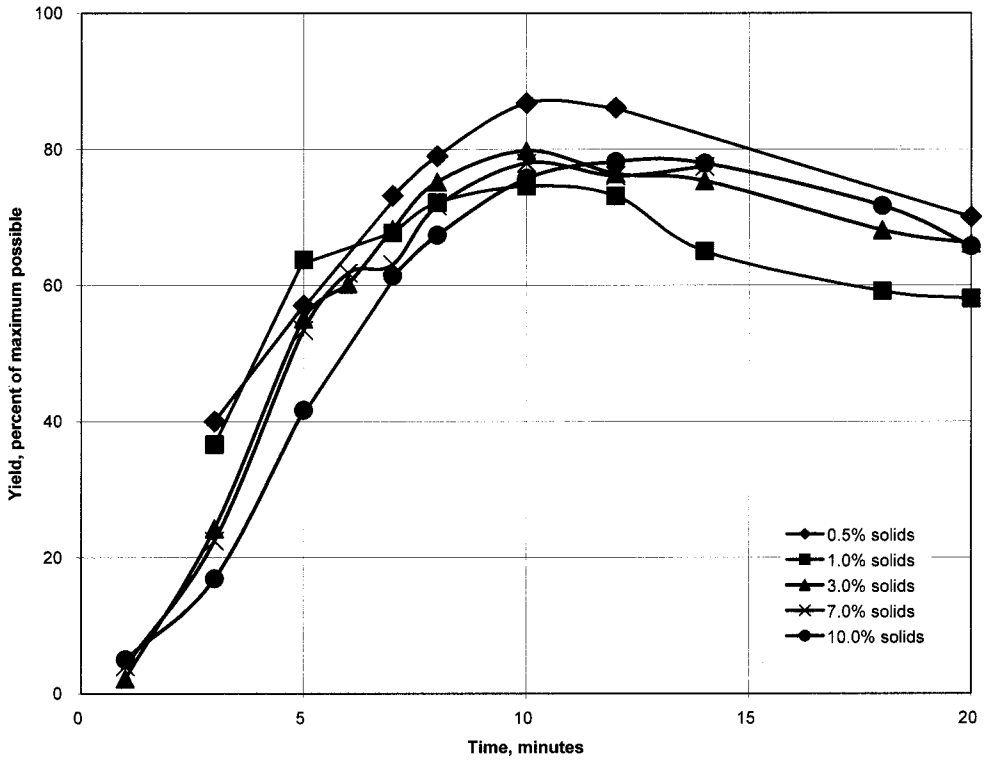


Figure 3. Total soluble xylose yield as monomers and oligomers versus reaction time for batch hydrolysis of sugarcane bagasse with varying solids concentrations without acid addition at 200 °C.

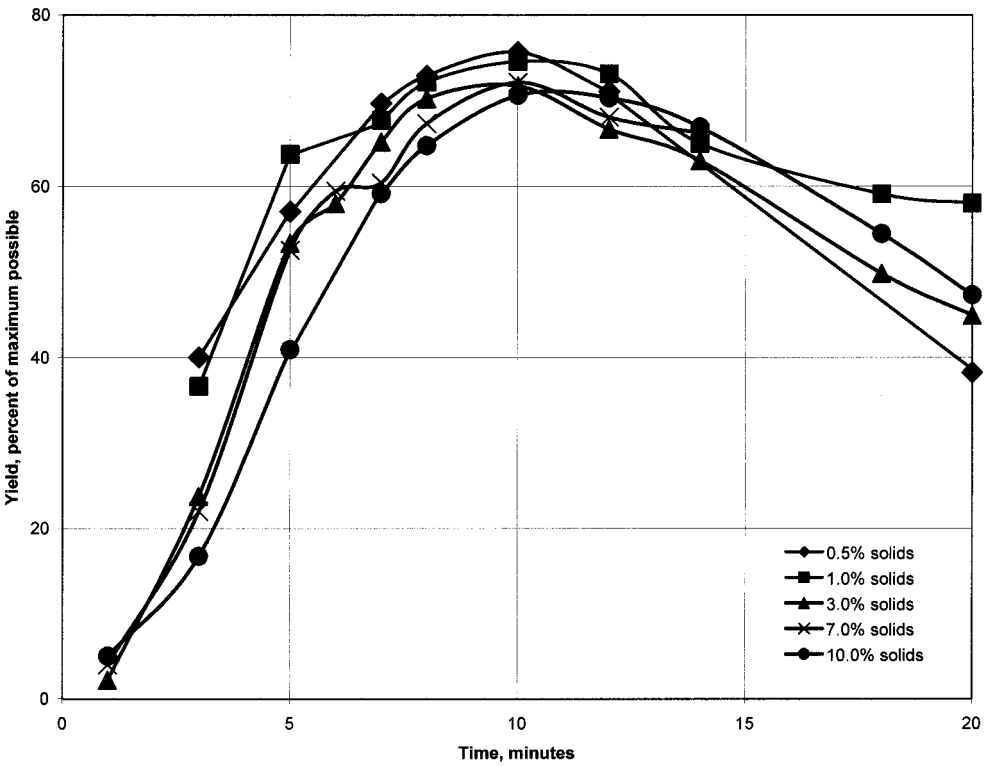


Figure 4. Oligomeric xylose yield (defined as the amount of xylose oligomers recovered divided by the total amount of xylose potentially available from bagasse) versus reaction time for hydrolysis of sugarcane bagasse with varying solids concentrations without acid addition at 200 °C.

seem to increase more rapidly at lower solids concentrations and then fall more rapidly beyond their maxima. A paired-difference analysis shows that the differences in oligomer yields for the following solids concentrations are statistically significant at the 95% confidence limit: 0.5 and 7.0%, 1.0 and 3.0%, and 1.0 and 10.0%; the difference for 1.0% and 7.0% solids concentrations is also very close to being statistically significant at the 95% confidence level. Thus, although not true for all pairs, these data indicate that the lower solids concentrations tend to give higher oligomer yields.

Figure 5 presents the average yield of monomeric xylose versus time and solids concentrations for the same series of replicate experiments, and Figure 6

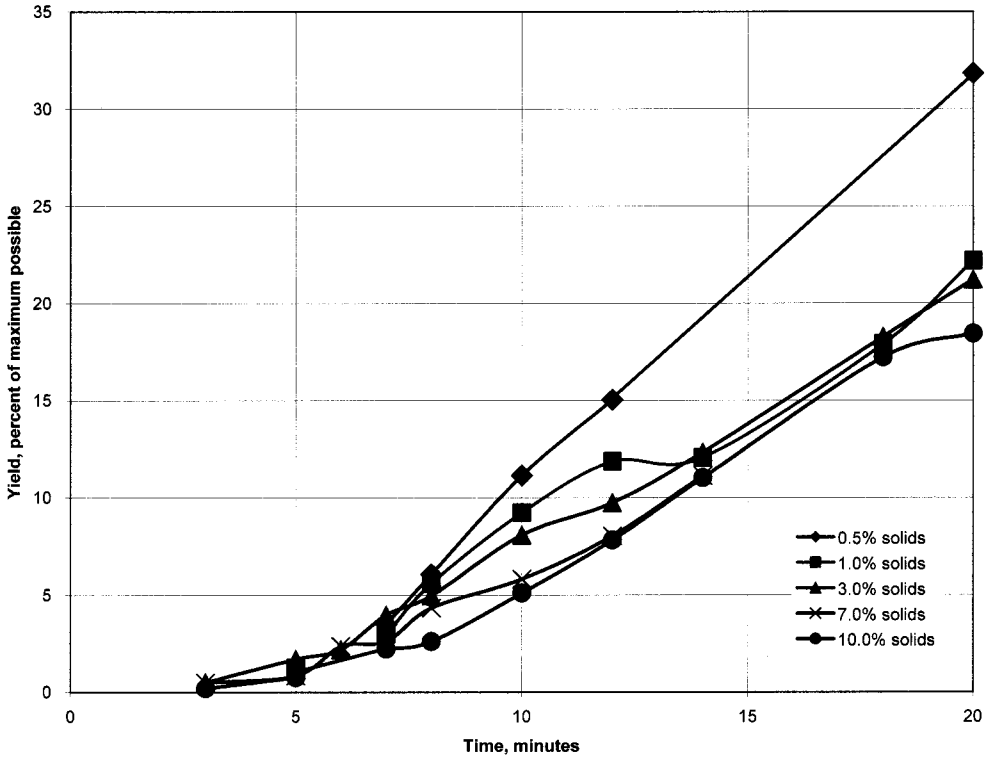


Figure 5. Monomeric xylose yield (defined as the amount of xylose recovered as monomers from the reaction divided by the total amount of xylose potentially available from bagasse) versus reaction time for hydrolysis of sugarcane bagasse with varying solids concentrations without acid addition at 200 °C.

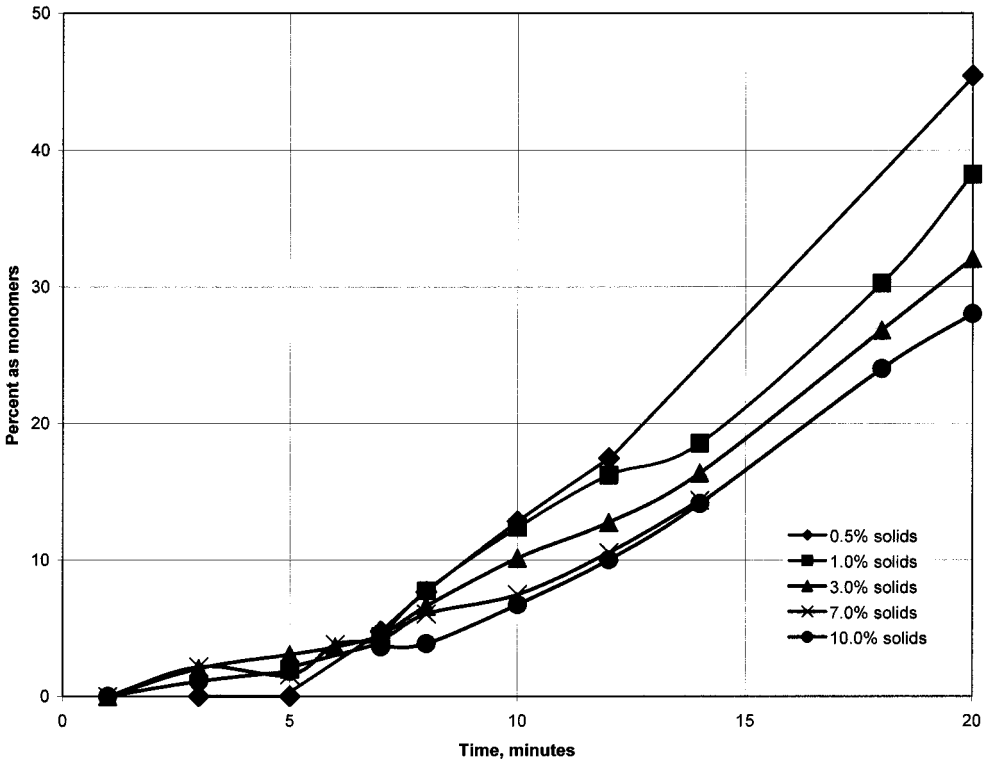


Figure 6. Fraction of soluble xylose recovered as monomers compared to total xylose solubilized for hydrolysis of sugarcane bagasse with varying solids concentrations without acid addition at 200 °C.

provides the ratio of xylose monomers to xylose monomers plus oligomers based on these average values. The general trend shows that the yield of monomers continues to increase with time well beyond the point where maximum overall and oligomeric sugar yields peaked at 10 min. This result is consistent with the mechanism depicted in eq 2 that oligomers provide a pool for formation of monomers and that, as hemicellulose concentrations drop, the rate of formation of oligomers slows enough that they cannot be replenished as fast as they react to monomers. Thus, monomer yields in uncatalyzed hydrolysis can only be increased beyond

about 7−13% of the total by sacrificing overall yields at the conditions run. The implication is that a posthydrolysis procedure is needed if high yields are important and monomers are targeted from hydrolysis.

It is interesting to observe that the spread in the monomer yields with solids concentration in Figure 5 is the greatest at about 10 min, the time where the maximum total sugar and oligomer yields occur. After that, the measured monomer yields converge for the 1.0, 3.0, 7.0, and 10.0% solids concentrations, while the yields at the 0.5% solids level continue to increase to a larger value. A paired-difference test shows the differences in monomer yields to be only statistically significant between the 10.0% solids concentrations and the results for experiments at 0.5, 1.0, and 3.0% solids. This result implies that monomer yields increase faster for lower solids concentrations even though the pH is higher. However, although repeated experiments were run to obtain the data reported, the extreme divergence of monomer yields for the lowest solids concentrations in Figure 5 is so different from the other trends as to deserve more scrutiny in the future so that we can better understand whether solids concentrations play a role in hemicellulose hydrolysis.

Conclusions

Traditional kinetic models based on batch experiments predict that monomer and oligomer yields are independent of solids concentrations and that the differences in results for flow-through or countercurrent reactors would be due to other factors such as rapid removal of oligomers by fluid flow. However, such models also suffer from inconsistencies that bring into question their mechanistic accuracy. Thus, although current models can be useful for data interpolation, their ability to describe different systems such as flow-through reactors is unproven.

Organic acids liberated from biomass during pretreatment are thought to play an important role in water-only hydrolysis of hemicellulose by increasing the concentration of hydrogen ions that drive hydrolysis. Consistent with this concept, our results showed that room-temperature pH decreased with reaction time and increasing solids concentrations. Others have also proposed that organic acids catalyze the reaction of soluble oligomers to monomers but do not affect hemicellulose solubilization as much.[26] However, contrary to the expectation that the lower pH observed for higher solids concentrations would promote hydrolysis to monomers, this work at worse showed no difference and at best suggests that the trends may be reversed: lower monomeric and oligomeric xylose yields occur at the lower pH measured for higher solids concentrations. This pattern would suggest that hydrogen ion concentration is not the only significant factor in hemicellulose hydrolysis.

Our batch data showed similar trajectories for concentration versus time profiles for release of monomeric xylose, oligomeric xylose, and total xylose at the solids concentrations tested at 200 °C, with the maximum total and oligomeric xylose yields occurring at about the same time, 10 min, for all solids levels. Most of the xylose released into solution was in oligomeric form, particularly at the maximum total yield points, requiring posthydrolysis to obtain monomers. Longer hold times increased xylose monomer recovery but at the expense of decreasing total yield. This result is consistent with the conventional first-order homogeneous kinetic model based on series reaction of hemicellulose solids to oligomers and on to monomers and then degradation products.

The data showed a possible decrease in yields with increasing solids concentrations, although statistically significant results could only be demonstrated between the extremes in solids concentrations. Thus, more extensive data are needed at a few times and solids concentrations to resolve the importance of these differences. We also plan to further evaluate our reactor design and operational strategies to ensure that heat transfer and other nonkinetic effects are not influencing these results. Although material balances were used to verify the validity of our procedures, careful attention must continue to be given to tracking the fate of xylose. These results could further clarify governing hydrolysis mechanisms and help build the foundation for a unifying model that could explain the differences in performance between batch and flow hemicellulose hydrolysis reaction systems and other poorly understood observations in biomass hydrolysis.[27] Such information could suggest novel approaches to biomass hydrolysis that overcome current process limitations as well as build greater confidence in applications of existing technologies.

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