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Impact of Fluid Velocity on Hot Water Only Pretreatment of Corn Stover in a Flowthrough Reactor

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Abstract

Flowthrough pretreatment with hot water only offers many promising features for advanced pretreatment of biomass, and a better understanding of the mechanisms responsible for flowthrough behavior could allow researchers to capitalize on key attributes while overcoming limitations. In this study, the effect of fluid velocity on the fate of total mass, hemicellulose, and lignin was evaluated for hot water only pretreatment of corn stover in tubular flowthrough reactors. Increasing fluid velocity significantly accelerated solubilization of total mass, hemicellulose, and lignin at early times. For example, when fluid velocity was increased from 2.8 to 10.7 cm/min, xylan removal increased from 60 to 82% for hot water only pretreatment of corn stover at 200°C after 8 min. At the same time, lignin removal increased from 30 to 46%. Dissolved hemicellulose was almost all in oligomeric form, and solubilization of hemicellulose was always accompanied by lignin release. The increase in removal of xylan and lignin with velocity, especially in the early reaction stage, suggests that chemical reaction is not the only factor controlling hemicellulose hydrolysis and that mass transfer and other physical effects may also play an important role in hemicellulose and lignin degradation and removal.

Index Entries: Pretreatment; hot water; hemicellulose hydrolysis; fluid velocity; corn stover.

Introduction

Lignocellulosic, often termed cellulosic, biomass is the most abundant renewable resource on Earth, and large-scale production of organic fuels and chemicals from this low-cost sustainable resource would provide unparalleled environmental, economical, and strategic benefits *(1–5)*.

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However, cellulosic biomass must be pretreated prior to biologic conversion to achieve the high yields vital to economical success, because a complex hemicellulose-lignin structure shields cellulose in native cellulosic biomass and limits cellulose accessibility to organisms or enzymes. Pretreatment is the most expensive single step in conversion of biomass to ethanol and other products and also greatly influences the cost of biological steps that collectively comprise the largest costs *(5)*. Thus, low-cost advanced pretreatment technologies must be developed if biomass conversion is to be economical *(5).*

Many favor dilute sulfuric acid pretreatment because both high hemicellulose recovery and good cellulose digestibility can be achieved *(6–8)*. Moreover, most of the soluble sugars from dilute-acid pretreatment are released as monomers that can be readily fermented to ethanol by recombinant organisms *(9,10)*. Pretreatment with just hot water or steam, termed *uncatalyzed hydrolysis* or *autohydrolysis*, eliminates chemical additives, lowers the cost of materials of construction, and generates less waste, but hemicellulose and cellulose yields from batch systems are limited.

Passing hot water continuously through a stationary biomass bed could result in higher hemicellulose sugar recoveries, more lignin removal, more digestible cellulose *(11–15)*, and less inhibitors in the hydrolysate liquid *(16)* compared to conventional systems. Antal and colleagues also reported complete xylan dissolution and >90% recovery of pentosans for hot water pretreatment of sugarcane bagasse in their flowthrough reactor *(17,18)*. Torget and colleagues *(19,20)* achieved both high xylan recovery and high simultaneous saccharification and fermentation conversion while applying extremely dilute sulfuric acid (0.07 %[w/w]) in a countercurrent flowthrough configuration.

Using water instead of steam *(21)* also increases yields for just water pretreatment. However, the high quantities of water used increase energy demands in pretreatment and product recoveries, and equipment selection presents challenges. A better understanding of the mechanisms responsible for flowthrough behavior could allow researchers to capitalize on its key attributes while overcoming its limitations. Our previous study showed that increasing flow rate can not only significantly increase hemicellulose solubilization but also increase recovered hemicellulose sugar yields and lignin removal, and high flow rate is especially favorable for runs at high temperatures *(22)*. Bobleter et al examined the effect of flow rate in a small range with a maximum flow rate less than one-third of reactor volume per minute *(12)* and reported that increasing flow rate can enhance total mass solubilization. However, no one has systematically evaluated the impact of fluid velocity on pretreatment of biomass. In the present study, the effect of fluid velocity on the fate of total mass, hemicellulose, and lignin was evaluated for hot water only pretreatment of corn stover in a flowthrough reactor.

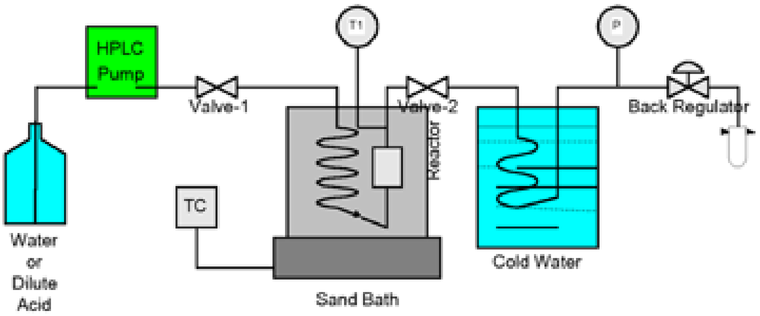

Fig. 1. Schematic diagram of flowthrough system. TC, Thermal controller; T1, thermal couple; P, pressure gauge.

Materials and Methods

Substrate

Corn stover was graciously provided by the National Renewable Energy Laboratory (NREL) in Golden, CO, from a large maintained supply that it obtained from Harlan, IA. Material was ground to a particle size of 250–420 µm using a laboratory knife mill (Model 4, Arthur H. Thomas Company, Philadelphia, PA) and passed through 35-mesh sieves to produce a particle small enough size to facilitate additions to the small reactors used. Samples prepared in this manner were kept in a freezer at –4°C for use in all tests. The composition of a representative sample was 36.1% glucan, 21.4% xylan, 2.5% galactan, 3.5% arabinan, 1.8% mannan, and 17.2% Klason lignin, as determined by the NREL according to its published methods *(22)*.

Flowthrough Apparatus and Experiments

A schematic of the flowthrough system is shown in Fig. 1. We used a set of 10.9 mm id × 180 mm long, 15.7 id × 87 mm long, and 21.2 id × 47 mm long tubular reactors with the same internal volume of 16.8 mL to investigate the impact of fluid velocity at constant residence time. Each reactor was constructed of VCR fitting parts with two gasket filters with an average pore size of 5 µm at each end of the reactor body. All of these parts were made of 316 stainless steel and obtained from the Maine Valve and Fitting Co. (Bangor, ME). We used 316 stainless steel tubing for a 1/4 in. od × 0.035 in. wall thickness preheating coil and a 1/8 in. od × 0.028 in. wall thickness cooling coil as well as to connect the reactor with other system components. The preheating coil was long enough to allow the incoming water to reach the desired temperature before it entered in the reactor, as measured experimentally. A 1/8 in. stainless steel thermocouple (Omega Engineering, Stamford, CT) was installed at the outlet of the reactor to monitor temperature. A high-pressure pump (Acuflow Series III Pumps;

Fisher, Puerto Rico) with a flow rate range of 0–40 mL/min, a pressure gage (Cole-Parmer, Vernon Hills, IL) with a pressure range of 0–1500 psi, and a back-pressure regulator (Maine Valve and Fitting, Bangor, ME) were used to control water pressure and flowthrough the system.

To operate the flowthrough unit, about 2.5 g of corn stover was loaded into the reactor, and the reactor was then connected to the preheating and outlet coils. Distilled water at room temperature was pumped through the reactor for a few min to purge air, completely wet the biomass in the reactor, and pressurize the system to a pressure of 350–400 psig by controlling the back-pressure regulator. Next, the preheating coil was submerged in a 4-kW model SBL-2D fluidized sand bath (Techne, Princeton, NJ) set at the target temperature for 3 min to make sure the preheating coil reached the desired temperature. Then the reactor was also submerged in the same sand bath. At the same time, defined as time zero, the pump was turned on, and liquid fractions were collected continuously over 4-min intervals. When the target reaction time was reached, the pump was turned off, and the reactor and preheating coil were immediately transferred to an ice-water bath to quench the reaction. Once the temperature in the reactor dropped to about 50°C, cold water was pumped through the system to purge liquid remaining in the reactor and coils until about 10 mL of additional effluent was collected.

Sample Analysis

The pH of each liquid fraction was promptly measured on cooling to room temperature. Then, a portion of each was dried under vacuum at 60°C until weight loss ceased to determine the fraction of the total mass dissolved in the liquid fraction. The rest of the sample was used for sugar analysis. The entire solid residue in the reactor was washed into a glass vial, dried at 105°C, and weighed for sugar analysis and determination of Klason lignin as described below. The amount of lignin removed was calculated as the difference between the dry mass of Klason lignin in the feed material and that in the solid residue and expressed as the percentage of the dry mass in the feed material.

Compositional analyses of all solid samples were carried out by the standard methods as provided by NREL *(23,24)*. Sugar monomers in the liquid portion were analyzed quantitatively by a Waters high-performance liquid chromatography (HPLC) model no. 2695 system equipped with a 2414 refractive index detector and a Waters 2695 autosampler using Millenium[32] chromatography manager 3.2 software (Milford, MA). A Bio-Rad Aminex HPX-87P column (Hercules, CA) was employed for sugar analysis. Total xylose as both monomers and oligomers in the liquid fraction was determined after post-hydrolysis with 4 wt% sulfuric acid at 121°C for 1 h *(25)*. Xylooligomers in the liquid were calculated as the difference between the total xylose and monomeric xylose measurements and expressed as a percentage of the original total xylose in the feed solids. All the experiments were performed in duplicate, with the average value reported.

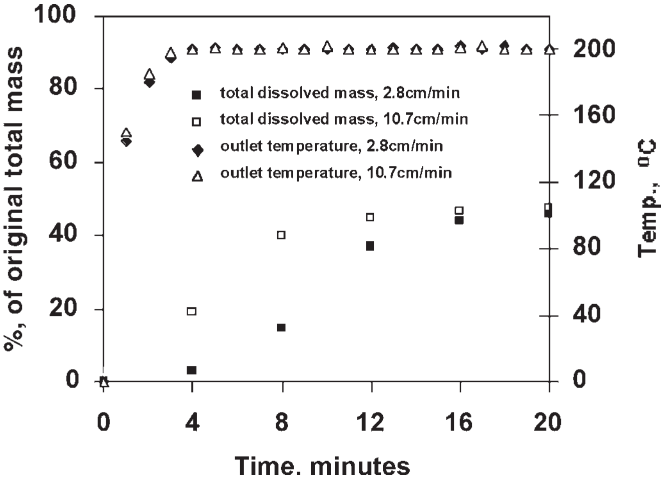

Fig. 2. Overall dissolved mass profiles for hot water only pretreatment of corn stover at 200°C.

Results and Discussion

Our previous research showed that increasing flow rate can significantly enhance solubilization of hemicellulose, lignin, and total mass *(22)*. Research by several teams has recently shown that hemicellulose solubilization and sugar recovery increase with water content in batch systems, suggesting that flowthrough behavior may benefit from the large amounts of water used *(21,26–28)*. However, water quantities alone cannot explain the differences between batch and flowthrough operation, because even at low flow rates (1 mL/min), more total mass, hemicellulose, and lignin was removed under otherwise identical conditions. To investigate whether factors other than water quantities could be responsible for the behavior of flowthrough operations, we examined the effect of fluid velocity during hot water only pretreatment of corn stover in a flowthrough reactor. Hot water without the addition of acid at 200°C was applied in the three reactors described earlier with the flow rate kept constant at 10 mL/min. Thus, fluid velocities of 10.7, 5.2, and 2.8 cm/min result, and average liquid residence time is the same for each reactor (1.68 min).

Solubilization of Total Mass

Figure 2 presents total dissolved mass yields as a function of reaction time for hot water only pretreatment of corn stover in the smallest-diameter and largest-diameter reactors. Total dissolved mass yields increased with reaction times with about 45% of the original total mass dissolved after 20 min for hot water only flowthrough pretreatment of corn stover at 200°C.

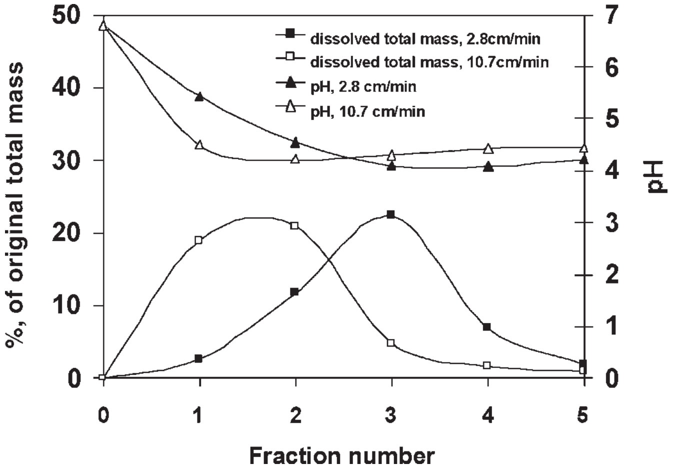

Fig. 3. Total dissolved mass in liquid fraction and pH of each fraction collected over 4-min intervals for hot water pretreatment of corn stover at 200°C.

The important finding is that total mass solubilization for the high-fluid-velocity (10.7 cm/min) run is more rapid than that for the low-fluid-velocity (2.8 cm/min) run, especially in the first 8 min. The heating rate is the same for all reactors for these small flowthrough systems, suggesting that delayed solubilization of total mass at lower fluid velocity did not arise from heat transfer effects (Fig. 2). The effect of velocity is more obvious when one examines changes in total dissolved mass and pH for each liquid fraction collected over 4 min intervals for flowthrough pretreatment (Fig. 3). The peak in total mass removal was delayed by about 4 min for the lowest-velocity run, although the maximum value was about the same as for the highest velocity. The pH for each fraction first dropped as total dissolved mass yield increased and then increased as total dissolved mass yield decrease for both runs, suggesting that acetyl groups are released with solubilization of biomass.

Hemicellulose Hydrolysis

Figure 4 present sugars concentration of each liquid fraction (collected in 4-min intervals) after posthydrolysis. Most of the hemicellulose dissolved in flowthrough operations was in oligomeric form, and very little monomeric sugars were produced for hot water only pretreatment of corn stover under the conditions run. This is in a good agreement with our previous results and those of other researchers *(21,26,27)*. As expected, most of the sugar was xylose, but some glucose, galactose, arabinose, and mannose were also detected in some fractions. As for total mass, the xylose concentration for lower-velocity operation peaked about 4 min after that for higher-velocity operation. However, the maximum xylose concentration for

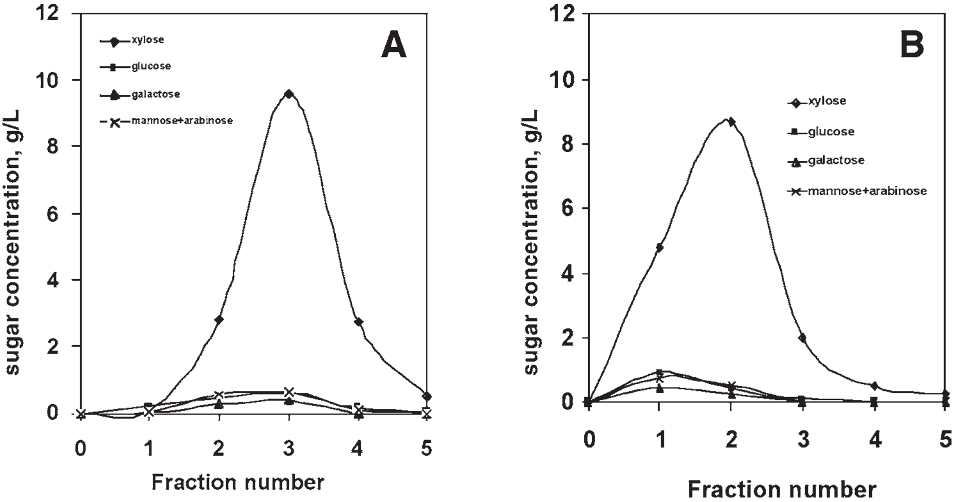

Fig. 4. Sugar concentrations in liquid fractions collected over 4-min intervals for hot water only pretreatment of corn stover at 200°C at velocities of **(A)** 2.8 cm/min and **(B)** 10.7 cm/min.

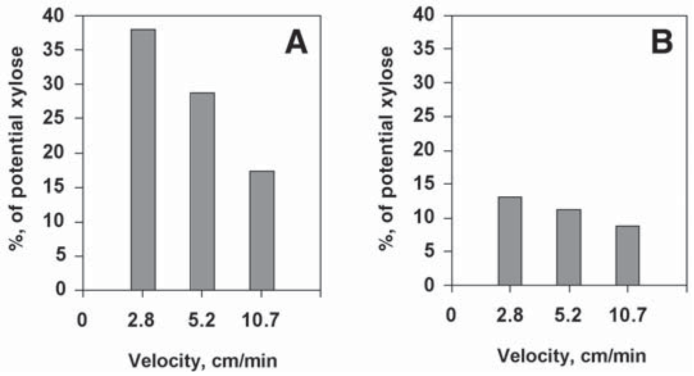

Fig. 5. Xylan remaining in solid residue for hot water only pretreatment of corn stover at 200°C after **(A)** 8 min and **(B)**16 min.

lower-velocity runs (about 9 g/L) was higher than that for higher-velocity runs (about 8 g/L) at the same flow rate. The hydrolysis rate of other hemicellulose sugars (glucan, arabinan, and mannan) increased with fluid velocity (Fig. 4B).

Xylan remaining in solid residues was also analyzed. As seen in Fig.5, increasing velocity significantly increased xylan removal, especially in the first 8 min. For example, xylan removal for operation at 2.8, 5.2, and 10.7 cm/min was 60, 70, and 82% for hot water only pretreatment of corn stover at 200°C after 8 min. However, after 16 min, the differences in xylan removal were less for all velocities run, suggesting that fluid velocity has less impact on the overall degree of hemicellulose hydrolysis.

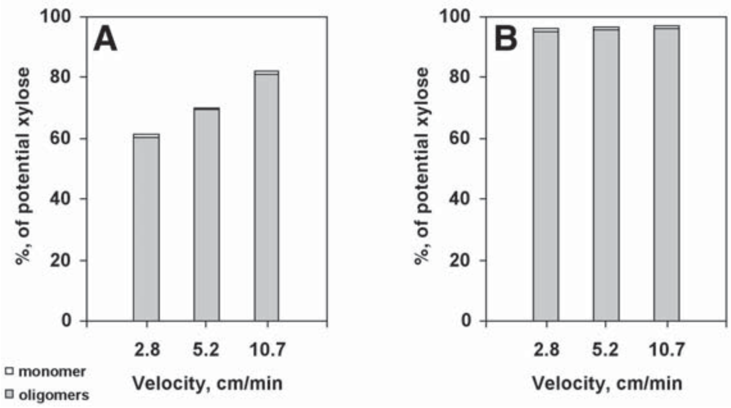

Fig. 6. Monomeric and oligomeric xylose yields for hot water only pretreatment of corn stover at 200°C after **(A)** 8 min and **(B)** 16 min.

Total xylose (monomeric and oligomeric xylose together) yield also increased with fluid velocity early in the reaction (Fig. 6). For example, when fluid velocity was increased from 2.8 to 10.7 cm/min, total xylose yield was increased from 60 to 82% for hot water only pretreatment of corn stover at 200°C after 8 min. Thus, the dissolved xylan was virtually completely recovered for all velocities. In addition, increasing reaction time increased total xylose yields, and about 95% of the potential xylose was recovered for all runs at this temperature after 16 min.

Lignin Removal

Figure 7 displays changes in lignin removal with fluid velocity. Lignin removal increased significantly with increasing fluid velocity in a manner similar to that for xylose removal. For example, when fluid velocity was increased from 2.8 to 10.7 cm/min, lignin removal increased from 30 to 45% after 8 min. However, the maximum lignin removal was almost the same (65% of the original Klason lignin) for both low- and high-velocity operations after 16 min, implying that fluid velocity has less impact on the degree of delignification of biomass than on the rate.

Figure 8 shows the change in total sugar and nonsugar compound concentrations collected in the liquid fractions at 4-min intervals. Total sugar concentration is defined as the sum of xylose, glucose, galactose, arabinose, and mannose concentration analyzed after posthydrolysis of each liquid fraction. Nonsugar compounds are defined as the difference between the total dissolved mass and the total sugar concentration in each fraction. The nonsugar fraction could also be roughly referred to as “dissolved” lignin, because most of the nonsugar compounds are lignin. The total sugar concentration for the highest-velocity operation peaked 4 min ahead of that for the lowest-velocity run, but the maximum total sugar

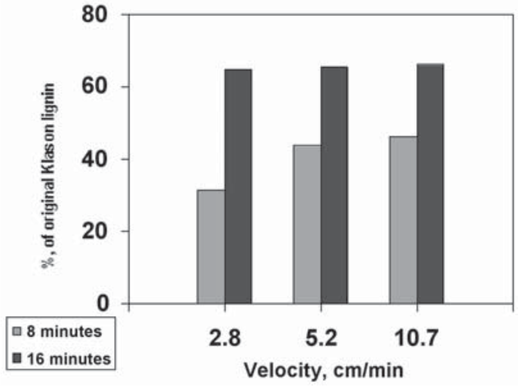

Fig. 7. Change in lignin removal with fluid velocity for hot water only pretreatment of corn stover.

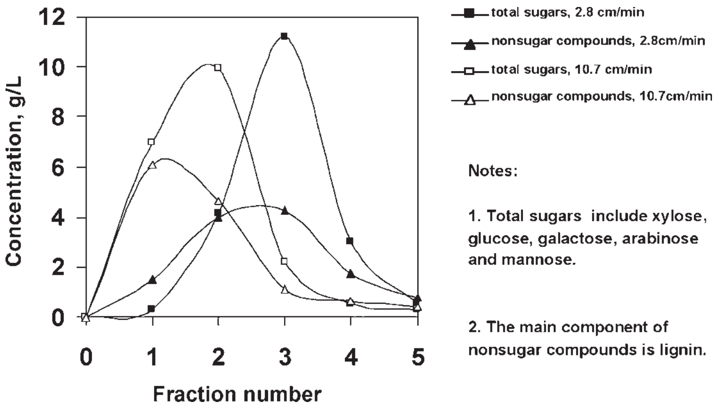

Fig. 8. Sugar and nonsugar collected in liquid fractions over 4-min intervals for hot water only pretreatment of corn stover at 200°C.

concentration was lower (10 g/L) compared with that for the low-velocity run (11 g/L), at the same flow rate. The important finding is that the nonsugar compound concentration peaks much earlier (about 8 min ahead) for high- vs low-velocity runs. However, unlike xylose, the maximum nonsugar compound concentration for the higher-fluid-velocity run was much higher than for lower velocity (6 vs 4 g/L). This strongly suggests that increasing fluid velocity significantly accelerates delignification of biomass in a flowthrough reactor with hot water only pretreatment. In addition, the nonsugar compound concentration increased as total sugar concentration increased, showing that lignin release always accompanies hemicellulose solubilization. Furthermore, at low fluid velocity, nonsugar compounds were extracted ahead of any sugar, suggesting that some nonsugar compounds such as tannin, protein, fat, and even a small portion of lignin are easily extracted.

Conclusion

Fluid velocity has a significant impact on hot water only pretreatment of biomass in a flowthrough reactor. Increasing fluid velocity significantly accelerated solubilization of total mass, hemicellulose, and lignin for hot water only pretreatment even at the same liquid residence time. For example, when fluid velocity was increased from 2.8 to 10.7 cm/min, xylan removal increased from 60 to 82% for hot water only pretreatment of corn stover at 200°C after 8 min. At the same time, total xylose yield increased from 60 to 82% and lignin removal increased from 30 to 46%. The dissolved hemicellulose is almost all in oligomeric form and always accompanied by lignin removal. The increase in xylan removal and lignin with velocity, especially in the early reaction stage, cannot be explained by traditional first-order reaction models developed from batch experiment data in which rate should only change with temperature and acid concentration. All these results suggest that chemical reaction factors (temperature, acid concentration) are not the only ones controlling hemicellulose hydrolysis and delignification reactions, and that mass transfer and other physical effects may play an important role in hemicellulose and lignin degradation. It is also important to note that these effects were all observed at the same residence time, suggesting that more time for xylose degradation or lignin reactions did not dominate compared to the influence of velocity. This result could be attributed to the influence of velocity on the thickness of the liquid film surrounding biomass particles and supports a possible role for mass transfer.

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