

The Effect of Flow Rate of Compressed Hot Water on Xylan, Lignin, and Total Mass Removal from Corn Stover

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Flowing hot water through cellulosic biomass offers many promising features for advanced pretreatment, and a better understanding of the mechanisms responsible for flowthrough behavior could allow us to capitalize on its key attributes while overcoming its limitations. In this study, extensive data were developed to show the effect of flow on the fate of hemicellulose, lignin, and total mass for hot-water pretreatment of corn stover in a small tubular flowthrough reactor at 180, 200, and 220 °C. Solubilization of hemicellulose increased with flow, especially at high temperatures; a result that is inconsistent with traditional first-order kinetic models. The dissolved xylan in the hydrolyzate was mostly oligomers over this temperature range, and the fraction as oligomers increased with flow rate. Also of importance, lignin removal increased from less than about 30% for batch reactors to about 75% at high flow rates and was nearly linearly related to hemicellulose release for the flowthrough reactor. These observations suggest that mass transfer or other physical factors, and not strictly first-order homogeneous chemical kinetics, impact hemicellulose hydrolysis. In addition, lignin appears to be released throughout hydrolysis, but its fate may be governed by subsequent precipitation reactions unless it is removed first.

Introduction

Cellulosic biomass—including agricultural and forestry residues, large portions of municipal solid waste, and herbaceous and woody plants—is the most abundant renewable resource on earth. Production of fuels and commodity chemicals from low-cost cellulose would provide unparalleled environmental, economic, and strategic benefits.^{1–4} Enzymatic hydrolysis of cellulose, generally the largest fraction of cellulose, to glucose followed by fermentation to ethanol is very attractive for producing sustainable liquid transportation fuels because high yields are achievable with these low-cost feedstocks.^{5,6} However, in native cellulosic biomass, a complex hemicellulose–lignin structure shields cellulose and limits cellulose accessibility to enzymes. Therefore, pretreatment is essential to achieve high product yields from cellulose.

Considerable attention has been focused on dilute sulfuric acid pretreatment because both high hemicellulose recovery and good cellulose digestibility result.^{7,8} For instance, hemicellulose sugar yields are limited to less than 65% in batch or co-current systems when pretreated with just steam;⁹ however, adding about 0.7% sulfuric acid increases the yields to as high as 90% of the maximum possible.^{7,8} Further, dilute acid releases most of the soluble sugars as monomers that recombinant organisms can readily ferment to ethanol.^{10,11} Glucose yields from enzymatic digestion of the cellulose remaining in the solid residue usually reach about 90% or better when nearly all of the hemicellulose is removed.⁷ Despite these attributes, dilute acid pretreatment is one of the most expensive steps in biological conversion of cellulose to ethanol and other products; therefore, advanced pretreatment technologies are needed

if such products are to be made at costs that compete with conventional fuels.¹²

Passing hot water through cellulose offers important advantages compared to conventional batch or co-current systems including elimination of chemical additives, less costly materials of construction, and less waste generation. Flowthrough technologies can also recover almost all of the hemicellulose sugars and produce highly digestible cellulose.^{13,14} Bobleter and co-workers pioneered hot-water pretreatment and showed that passing hot water continuously through a stationary biomass bed resulted in far more digestible cellulose,¹⁵ higher hemicellulose sugar recoveries, greater lignin removal,^{16–18} and less inhibitors in the hydrolyzate liquid compared to conventional systems.¹⁹ Antal and co-workers reported complete xylan dissolution and more than 90% recovery of pentosans for hot-water pretreatment of sugarcane bagasse in their flowthrough reactor.^{20,21} Torget and his team achieved both high xylan recovery and high SSF conversion while applying extremely dilute sulfuric acid (0.07 wt %) in a counter-current flowthrough configuration.^{22,23} Others further investigated and extended passing hot water through biomass with or without acid for biomass pretreatment and other applications.^{24,25} Research by several teams has recently shown that sugar recovery increases with water content in batch systems, suggesting that flowthrough behavior benefits from the large amounts of water used,^{13,26–28} but a complete explanation is not yet established.

Despite some very important attributes, flowthrough and water-rich batch operations use large amounts of water, resulting in excessive energy costs for both pretreatment and product recovery, and flowthrough equipment configurations are challenging to implement commercially. However, improving the understanding of the mechanism responsible for their favorable features could suggest new economically viable systems.

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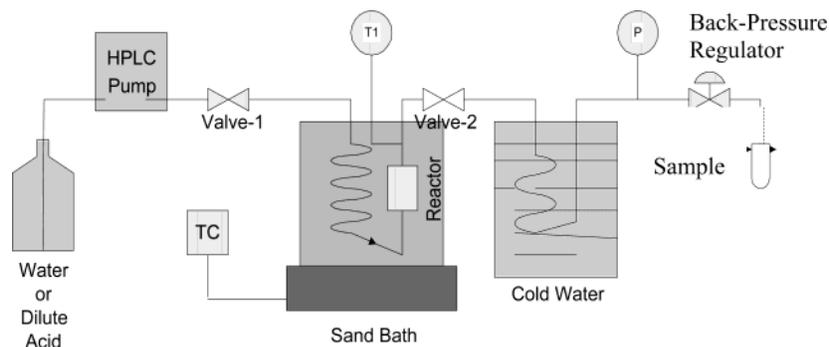


Figure 1. Schematic of the flowthrough reactor system.

Therefore, in this study, the fate of hemicellulose xylan, lignin, and total mass in corn stover was followed in a small flowthrough apparatus with changes in water flow rate of up to about three times the reactor internal volume per minute at 180, 200, and 220 °C to gain a more detailed perspective on the relationship between flow and biomass dissolution.

Materials and Methods

Substrate. Corn stover was graciously provided by the National Renewable Energy Laboratory in Golden, Colorado from a large supply obtained from Harlan, Iowa. Material for this study 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 obtain small particles appropriate for 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 38.6% glucan, 20.6% xylan, and 17.6% Klason lignin as determined by the standard method published by the National Renewable Energy Laboratory.²⁹

Flowthrough Apparatus and Experiments. A schematic of the flowthrough system is shown in Figure 1. The reactor body was a 10.2-mm-diam by 46.7-mm-long VCR fitting with a volume of 3.8 mL. The system also included one $1/2$ -in. VCR male union, two gasket filters with an average pore size of 5 μm , two $1/2$ -in. \times $1/2$ -in. VCR glands, two VCR nuts, and two $1/2$ -in. \times $1/8$ -in. VCR reducing fittings. All of these parts were made of 316 stainless steel and were obtained from the Maine Valve and Fitting Company (Bangor, ME). Type 316 stainless steel tubing was used for a $1/4$ -in. o.d. \times 0.035-in.-wall-thickness preheating coil and a $1/8$ -in. o.d. \times 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 the reactor, as measured experimentally. A $1/8$ -in. stainless steel thermocouple (Omega Engineering Co., Stamford, CT) was installed at the outlet of the reactor to monitor temperature. A high-pressure pump (Acuflo Series III Pumps, Fisher, Puerto Rico) with a flow rate range from 0 to 40 mL/min, a pressure gauge (Cole-Parmer Instrument Co., Vernon Hill, IL) with a range 0–10.3 MPa, and a back-pressure regulator (Maine Valve and Fitting Co., Bangor, ME) were used to control water pressure and flow through the system.

To operate the flowthrough unit, about 0.5 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 minutes to purge air, completely wet the biomass in the reactor, and pressurize the system to the set pressure of 2.1–2.4 MPa by controlling the back-pressure regulator. Next, the reactor and preheating coil were submerged in a 4-kW model SBL-2D fluidized sand bath (Techne Co., Princeton, NJ) set at a temperature of 100 °C for 2 min, and then quickly transferred to a second sand bath at the desired reaction temperature. At the same time, defined as time zero, the pump was turned on. 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 decreased to about 50 °C, cold water was pumped through the system to purge liquid remaining in the reactor and the exit tube until about 10 mL of additional effluent was collected.

Sample Analysis. The pH of each liquid sample was measured with a pH meter (model 8000, VWR Sci) promptly after the liquid cooled to room temperature. Then, to determine the fraction of the total mass dissolved in the liquid fraction, a portion of each was dried under vacuum at 60 °C until weight loss ceased. 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 and liquid samples were performed by standard methods documented by the National Renewable Energy Laboratory.²⁹ Sugar monomers in the liquid portion were analyzed quantitatively by a Waters HPLC model 2695 system equipped with a 2414 refractive index detector and a Waters 2695 autosampler using Millennium³² chromatography manager 3.2 software (Waters Co., Milford, MA). A Bio-Rad Aminex HPX-87P column (Bio-Rad Laboratories, Hercules, CA) was employed for sugar analysis. Total xylose as both monomers and oligomers in the liquid fraction was determined after posthydrolysis with 4 wt % sulfuric acid at 121 °C for 1 h.³⁰ Xylo-oligomers in the liquid were calculated as the difference between the total xylose and monomeric xylose measurements and expressed as a percent of the original total xylose in the feed solids. All the experiments were performed in duplicate, with the average value reported.

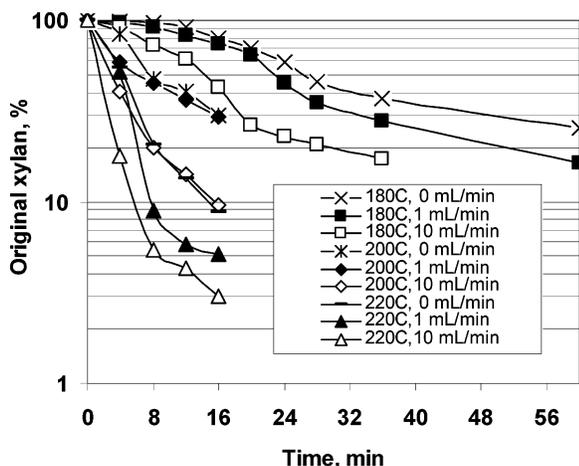


Figure 2. Effect of flow rate on removal of xylan from corn stover at different times and temperatures.

Results and Discussion

Xylan Remaining. Experiments were initially run at flow rates of 0, 1, 5, 10, 20, and 40 mL/min, but little difference in results was observed above 10 mL/min. In addition, the results at 5 mL/min did not offer significant new insight versus those at 1 and 10 mL/min. Thus, this paper focuses on results at 0, 1, and 10 mL/min to facilitate following key major trends.

Figure 2 shows the important result that flow rate enhances the removal of xylose from the solid residue for hot-water-only pretreatment of corn stover at 180, 200, and 220 °C. For example, at the lowest temperature (180 °C), about 60% of the original xylan dissolved after 16 min with a flow rate of 10 mL/min versus only 10% removal for batch operation (Figure 2). When the flow rate increased from 0 to 10 mL/min at 200 °C, the amount of xylan dissolved increased from 70% to 90%, again at 16 min. Thus, the impact of flow rate on enhancing xylan solubilization decreased with increasing temperature. Furthermore, the rate of xylan solubilization was especially enhanced by increasing flow rate in the early reaction stages for each temperature run.

Although data scatter makes it difficult to be sure of the exact trends, the results in Figure 2 suggest that the total xylose remaining in the solid residue at each temperature does not change exponentially with time as predicted by conventional kinetic first-order expressions that have been applied to model cellulose hydrolysis for years.³¹ In any event, the variation in xylose removal with flow rate is contrary to predictions of traditional kinetic models derived from batch data that are used to describe hemicellulose hydrolysis in terms of only acid levels, temperature, and time.^{32,33} Such a change in performance with flow suggests that mass transfer or other physical factors could play an important role in hemicellulose hydrolysis.

As expected, xylan solubilization increased significantly with temperature and reaction time (Figure 2). For example, more than 90% of original xylan was solubilized for batch conditions (flow rate of 0 mL/min) at 220 °C after 16 min, whereas less than 10% was solubilized without flow at 180 °C for the same time. In all batch runs, the initial solids concentration of corn stover in the reactor was around 20 wt %.

Glucan Solubilization. As shown in Table 1, from 0 to about 5.5% of the glucan in the feed was removed

in the liquid hydrolyzate over the range of temperatures and times studied, consistent with the average of about 6% for hot-water-only batch pretreatment of sugarcane bagasse at 200–220 °C reported by others¹³ and about 8% for flowthrough pretreatment of poplar wood at 200 °C.¹⁷ As expected, glucan dissolution increased with temperature and reaction time, although the impact was small over this range. However, increasing flow rate also enhanced glucan dissolution, especially at high temperatures, a result not predicted by current hydrolysis models. The impact of flow on cellulose solubilization has also been reported by others, with solubilization of amorphous cellulose impacted the most.^{30,34}

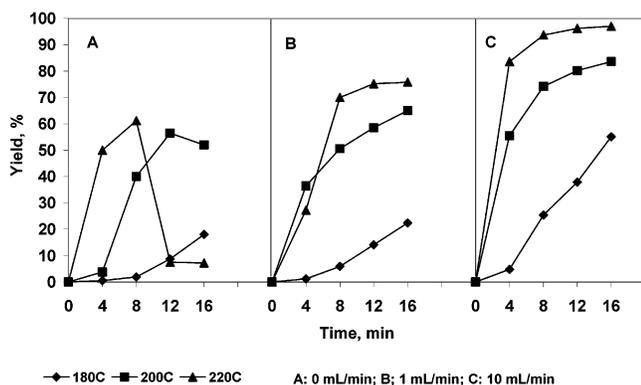
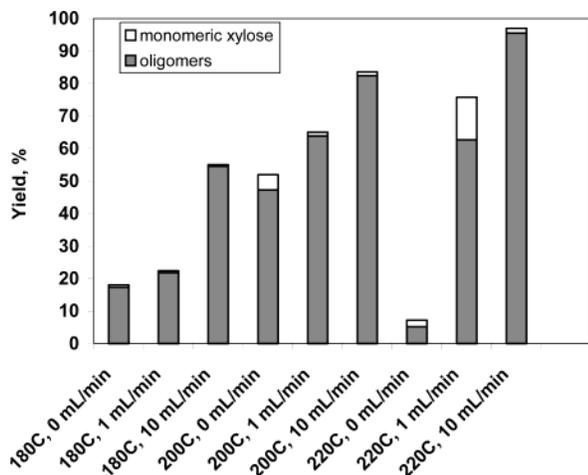
Recovery of Dissolved Xylan. Figure 3 presents the total yields of xylose monomer and oligomers in the liquid fraction determined after posthydrolysis for hot-water-only pretreatment of corn stover at varying flow rates and temperatures. For the batch runs in Figure 3A (0 mL/min), the maximum total xylose yield occurs within 16 min at 200 or 220 °C and is less than 60% for both runs even though most of the xylan is solubilized. Moreover, xylose recovery can only decrease for more extended reaction times especially at high temperature as the monomers and oligomers degrade to furfural and other undesirable products when held in a batch system. On the other hand, the total xylose yield increases with flow rate for all temperatures run in the flowthrough system (Figure 3B and C). For example, when the flow rate was increased to 10 mL/min for hot-water-only pretreatment of corn stover at 220 °C, the total xylose yield increased to 97% after 16 min, suggesting nearly all of the xylan was dissolved and recovered. This result is credited to enhanced dissolution of xylan with increasing flow rate (Figure 2) coupled with removal of dissolved xylose and oligomers before they can degrade. At the lowest temperature (180 °C), less corn stover xylan is dissolved over the time studied, reducing the total xylose yield. Overall, flow rate increases total xylose yield, especially at high temperatures.

The xylan dissolved in the hydrolyzate for batch runs was mostly oligomers (Figure 4), consistent with reported data for other batch runs.^{9,26} For example, a 47.3% yield of oligomers was measured for batch operation at 200 °C after 16 min, whereas the yield of xylose monomers was only 4.7%, about 10% of the xylose oligomer yield. However, the yield of xylose oligomers and fraction of total dissolved xylose in oligomeric form increased further with temperature and flow rate for all runs except for no flow or low flow rates at 220 °C. As one example, when the flow rate was increased from 0 to 10 mL/min, oligomer recovery increased from 47.3 to 82.7% after 16 min at 200 °C. At the highest flow rate of 10 mL/min, the yield of xylose oligomers increased to 95% after 16 min at 220 °C. On the other hand, it is apparent that holding the liquid hydrolyzate for 16 min at 220 °C degrades the sugars, resulting in very low yields for a batch operation at that temperature. These trends are similar to, but more pronounced than, the increased total xylose and oligomers yields reported for batch runs at very low solid concentrations.²⁶ Such increases in yields suggest that oligomers are important intermediates that need to be more fully accounted for during hot-water-only hemicellulose hydrolysis.

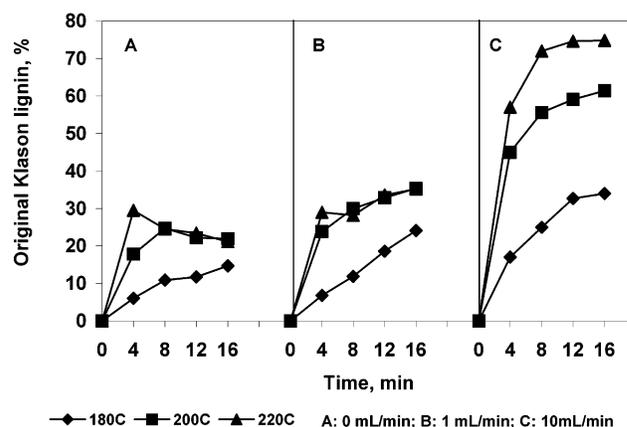
Lignin Removal. Figure 5 illustrates the time-dependent Klason lignin removal profiles for hot-water-only pretreatment of corn stover in our flowthrough

Table 1. Total Mass Dissolution (TMD), Total Mass Remaining (TMR), Overall Mass Balance (OMB), Xylan Remaining, Glucan Remaining, and Klason Lignin Remaining in Solid Residues for Hot-Water Pretreatment of Corn Stover

temp. (°C)	flow rate (mL/min)	time (min)	TMD (%)	TMR (%)	OMB ^a (%)	xylan remaining (%)	glucan remaining (%)	Klason lignin remaining (%)
180	0	12	13.3	82.7	96.0	91.3	102.3	88.3
		16	18.1	78.9	97.0	80.0	101.5	85.3
180	1	12	16.9	77.2	94.1	82.5		81.7
		16	20.8	70.9	91.7	73.3	99.8	75.9
180	10	12	27.0	66.5	93.5	60.8		67.3
		16	32.4	62.3	94.7	42.5	99.4	66.0
200	0	12	22.5	63.5	86.0	40.1	101.0	79.8
		16	23.4	62.2	85.6	29.9	99.9	79.1
200	1	12	28.4	56.6	85.0	36.4		67.1
		16	32.7	53.0	85.7	29.4	99.5	64.6
200	10	12	51.2	48.5	99.7	14.1	99.3	40.9
		16	52.4	43.3	95.7	9.5	98.5	38.6
220	0	12	28.7	55.2	83.9	13.5		76.6
		16	30.2	53.1	83.3	8.7	98.8	79.9
220	1	12	30.1	50.9	81.0	5.8		66.4
		16	30.3	47.8	78.1	5.1	97.2	64.8
220	10	12	52.8	44.2	97.0	4.3	96.0	25.4
		16	52.1	43.4	95.5	2.0	94.5	25.2

^a OMB = TMD + TMR.**Figure 3.** Effect of flow rate on yield of total xylose monomer and oligomers for different times and temperatures.**Figure 4.** Changes in xylose monomer and oligomer yields with flow rate at 180, 200, and 220 °C after 16 min.

reactor. It is particularly important to note that Klason lignin removal increased with flow rate for each temperature, but less than 30% was removed for all batch runs (0 mL/min). When the flow rate was increased from 0 to 1 and then to 10 mL/min at 200 °C, lignin removal increased from 30 to 35 and 60%, respectively, after 16 min. Furthermore, when the highest flow rate (10 mL/min) was combined with the highest temperature (220

**Figure 5.** Effect of flow rate on Klason lignin removal at different times and temperatures.

°C), more than 75% of the Klason lignin was removed after only 12 min (Figure 5C). On the other hand, lignin removal at 220 °C is less than 35% for 1 mL/min after 16 min. Thus, high flow rates resulted in much higher lignin removal, especially at high temperature. These trends are consistent with enhanced lignin removal observed by others for flowthrough reactors, although their studies did not relate lignin removal to flow rate.^{16,20,21}

Although lignin removal was limited to less than 35% for batch runs, flowthrough operation increased lignin removal to as high as 75%, and a virtually linear relationship was found between removal of lignin and xylan for all flowthrough operations in the temperature range studied (Figure 6). Furthermore, a small fraction of the Klason lignin (about 10%) was dissolved at the lowest temperature before any xylan was removed (Figure 6A). Although temperature transients made it difficult to obtain meaningful short-time data at higher temperatures, extrapolation of the lignin/xylan curves in Figure 6B and C suggests that some of the lignin may be more readily released than xylan at higher temperatures. It was also found that the lignin/xylan removal ratio decreased significantly with increasing tempera-

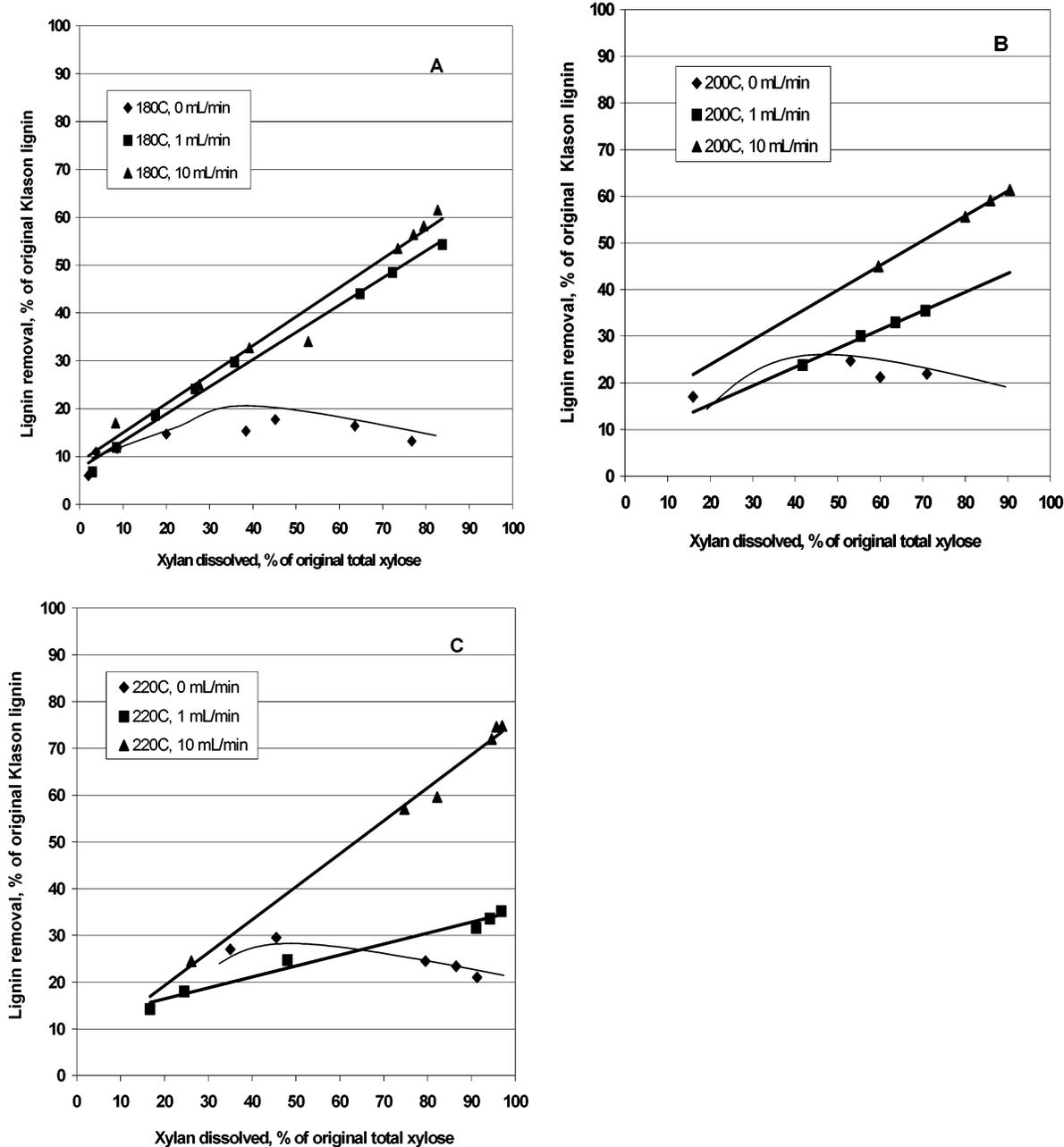


Figure 6. Lignin removal vs dissolved xylan for hot-water-only pretreatment of corn stover at different flow rates and temperatures.

ture at a low flow rate of 1 mL/min, whereas the ratio did not change with temperature at the highest flow rate.

Total Mass Solubilization. Figure 7 shows that both temperature and flow rate increased the removal of total mass, which is expected based on the patterns of lignin and hemicellulose removal. For example, raising the temperature from 180 to 220 °C under batch conditions increased total mass removal from 20% to about 40% after 16 min. However, the important finding is that introducing flow at any level greatly enhanced total mass solubilization for all temperatures. In one such instance, changing the flow rate from 0 to 1 mL/min at 200 °C increased total dissolution from 30 to 45% after 16 min. Furthermore, more total mass was removed as the flow rate was increased for each temperature run. Although total mass removal appeared to

level off for batch operations, for flowthrough operations, it continued to increase over the reaction period at high flow rates.

Overall mass balances were tracked throughout these experiments. As presented in Table 1, about 95% of the material was accounted for in all runs at 180 °C after 16 min, suggesting little loss of mass by decomposition at this temperature. However, the overall mass recovery decreased with increasing temperature, especially under batch and low-flow-rate runs. For example, only about 80% of the overall mass could be accounted for after 16 min with 0 and 1 mL/min flow rates at 220 °C, but about 95% could be captured at a flow rate of 10 mL/min at this temperature. At longer reaction times, this result is consistent with degradation of dissolved sugars to furfural and other volatile degradation products.

Proposed Mechanism for Enhanced Hemicellulose Hydrolysis. Hydrolysis of hemicellulose without

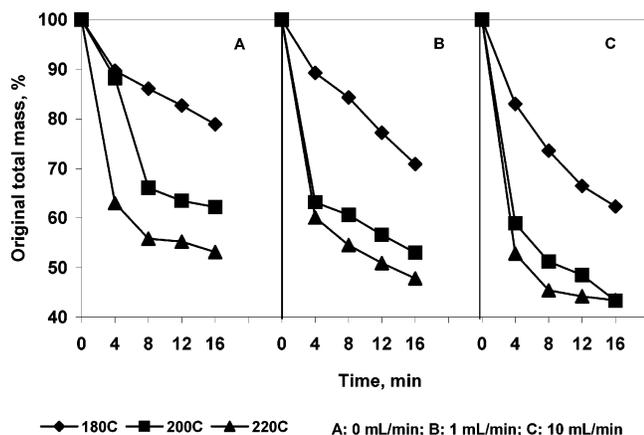


Figure 7. Effect of flow rate on total mass remaining in the solid residue at different times and temperatures.

acid addition is generally postulated to be catalyzed by acetic and other organic acids liberated during the breakdown of hemicellulose.³⁵ However, this explanation, which was developed from hot-water-only or steam batch hemicellulose hydrolysis, cannot explain the large difference in performance of flowthrough reactors that remove and recover much more xylan and lignin. First, the large amount of water used in flowthrough experiments quickly removed such acids, minimizing the time for them to act on the solid hemicellulose. In addition, these copious amounts of water dilute acetic acid so much that the organic acids concentrations were very low even at the low flow rate; for example, the pH in the total liquid collected from the flowthrough reactor was determined to be about 4.5 for a flow rate of 1 mL/min after 16 min of operation at 200 °C versus about 4.0 for the batch run at these conditions. Moreover, organic acid concentration would decrease with increasing flow rate whereas hemicellulose removal increased with flow rate, again bringing the importance of organic acid catalysis into question. In line with this reasoning, Bobleter et al.³⁶ found that adding acetic acid to the feed for a small flowthrough reactor had a negligible effect on performance, and another experiment showed that adding acetic acid to deacetylated biomass, even in far excess of the amount that would have been released naturally, did not give yields as good as those for the natural material.²⁷ Other measurements showed that 78% of the acetate remained bound to hemicellulose after aqueous steam pretreatment of poplar, further implying that liberated acetic acid is not a primary hydrolytic agent.³⁷ Another postulate is that organic acids catalyze the reaction of soluble oligomers to monomers but do not affect hemicellulose solubilization as much.¹³ In sum, these points all suggest that factors other than the liberated organic acids are likely responsible for accelerated hemicellulose and lignin removal in flowthrough operations.

Because the ionic product of water, k_w , decreases with increasing temperature to 1.86×10^{-12} at the critical point (374.15 °C, 22.12 MPa),³⁸ water itself can act as a hydrolytic catalyst, especially at high temperature. However, lignin, protein, and fat surrounding the hemicellulose are hydrophobic, resisting water and slowing its attack. On the other hand, the solubility of hemicellulose oligomers increases with decreasing chain length, and low-molecular-weight oligomers are very soluble in water.³⁹ Overall, these factors suggest that water will hydrolyze long-chain hemicellulose more slowly than short-chain oligomers. Furthermore, the

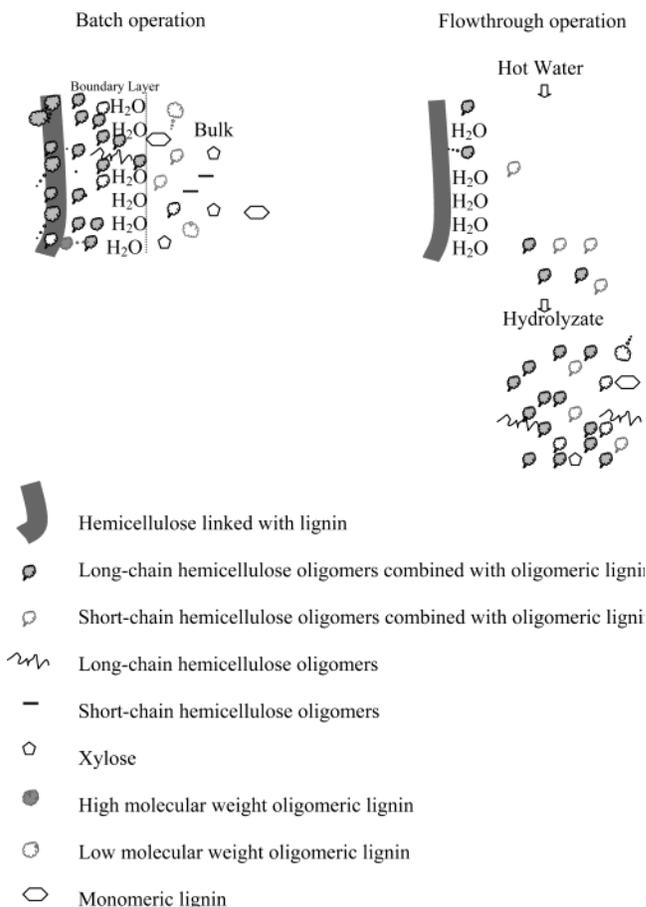


Figure 8. Possible effects of flow on reaction pathways that could differentiate performance of batch and flowthrough systems for hemicellulose hydrolysis in hot water.

dissolution and diffusion of longer oligomers to the bulk solution would be much slower than for shorter species, and long-chain oligomers could build up on the solid surface for batch operations (Figure 8). Compounding these effects, the long-chain oligomers and unreacted hemicellulose are rich in hydroxyl groups that could hydrogen bond with water molecules to form an “ice-like” layer that slows the access of water to hemicellulose.³⁰ Therefore, approaches that increase removal and degradation of long-chain oligomers would be favorable for enhancing hemicellulose hydrolysis, possibly explaining why increasing temperature and acid concentration are effective in this regard. On this basis, it is hypothesized that flow of liquid past the hemicellulose-containing solids would enhance removal of less-soluble oligomers and disturb the “ice-like” layer. In addition, flow would reduce the thickness of the stagnant fluid layer surrounding the solid particles, lowering resistance to penetration of water into the solids for hydrolysis and diffusion of oligomers into solution. The overall effect would be to accelerate hemicellulose removal with increasing flow rates.

Proposed Mechanism for Lignin Solubilization. Although the mechanism accounting for a change in lignin removal with flow rate is not yet clear, dissolved lignin in chemical pulping processes is known to react with itself and possibly other compounds such as oligomers to form larger molecules that precipitate on residual fiber,^{40,41} and high temperatures, high acid concentrations, and long residence times promote lignin condensation and precipitation.⁴² For organosolv pulping processes, Tirtowidjojo et al. found that even slow

removal of solvent from a flowthrough reactor caused a major increase in lignin removal versus a batch operation, further supporting the existence of self-condensation reactions.⁴³ Moreover, precipitation of dissolved lignin was further enhanced when the reactors were cooled to ambient temperature which resulted in less lignin removal for batch operations.⁴³ These observations support the idea that lignin breaks down to form solubles, which in turn react with themselves to form longer chains that precipitate out of solution, particularly if the contents are cooled. Flowthrough systems could remove lignin before it has the opportunity to react to less soluble compounds or condense, resulting in greater lignin removal than for batch systems that provide additional time for further reactions or allow precipitation on cooling.

Although release and reaction of lignin could explain why more lignin is removed for flowthrough than for batch reactors, it does not account for the nearly linear relationship between the lignin and xylan removal evident in Figure 6 at high flow rates. Hemicellulose and lignin are covalently linked in native materials, and the relationship in Figure 6 could be explained by the release of chemically bound compounds of lignin and hemicellulose oligomers into solution initially (Figure 8). The relatively high solubility of short-chain hemicellulose oligomers could promote dissolution of the attached lignin fragments that have more limited solubility, particularly for high-molecular-weight lignin fragments. Higher flow rates could promote more rapid dissolution of these compounds by providing more water to compensate for solubility limitations and by reducing the mass transfer resistance. The long-chain lignin-oligomer molecules first released into solution could also be less prone to recondensation reactions than subsequently formed shorter-chained lignin breakdown fragments, allowing greater removal of lignin at high flow rates. On the other hand, the longer hold time for hemicellulose oligomer-lignin compounds released in a batch reactor will allow their hydrolysis into short-chain hemicellulose oligomers and monomers and formation of short lignin fragments with limited solubility that either drop out of solution directly or react to form insolubles. The hold time could be adequate at lower flow rates for greater formation of such insolubles, resulting in lignin removal levels that are intermediate between the performance observed for batch and high flow rate systems. Increasing the temperature could first promote release of lignin into solution, but a further increase could promote reactions to form less soluble components with the result that less lignin is removed for the same degree of hemicellulose reaction for higher temperatures at lower flow rates (Figure 6). In addition, reaction of lignin to short-chain soluble products that react to long-chain species that precipitate from solution could be an ongoing process in which a high fraction of lignin participates but with little evidence unless the cycle is interrupted by flow.

Conclusions

For pretreatment of corn stover with addition of just hot water in a flowthrough reactor, increasing flow rate significantly enhanced hemicellulose removal and had an effect on xylose removal similar to that of raising temperature. This variation in xylose removal with flow rate cannot be predicted by simple first-order homogeneous kinetic models now used to describe hemicellulose

hydrolysis; these models include only temperature, acid concentration, or time, but not flow rate. Furthermore, these changes in hemicellulose removal with flow rate cannot be attributed to acetic acid released from biomass during hydrolysis, as this effect should decrease and not increase with flow rate. Because almost all of the dissolved xylan is oligomeric and oligomer yields increase with flow rate, xylose oligomers appear to play an important role in hot-water-only hemicellulose hydrolysis. It is hypothesized that increasing flow rate affects physical processes such as reducing the thickness of a liquid film surrounding biomass particles, thereby facilitating mass transfer of hydronium ions into the hydrophobic biomass surface to hydrolyze hemicellulose to short-chain oligomers or removal of these oligomers.

Although no more than 30% of the lignin was removed at any time during batch reactions, about 75% of the original Klason lignin could be released at high flow rates, and removal of xylan and lignin were nearly linearly related. The latter observation indicates that lignin and xylan are released together, possibly as covalently bound hemicellulose oligomer-lignin compounds formed during the hydrolysis of hemicellulose. Reaction of these compounds in solution could then continue with the formation of shorter-chained soluble hemicellulose oligomers and separate lignin fragments. The former could be hydrolyzed to short-chain oligomers and eventually monomers depending on how long they were held in the reactor. Lignin fragments could react to form insoluble species or have such low solubility that they directly precipitate out of solution. Consequently, hemicellulose can be completely removed in a batch operation, whereas lignin removal is limited to about 30% unless flow is introduced to sweep lignin from solution before it has time to precipitate. Increasing temperature could enhance lignin release from biomass and promote more complete removal with flow. However, excessive increases in temperature could accelerate the formation of precipitates enough to reduce net lignin removal.

Continued research is needed to better understand the properties and behavior of oligomers, lignin, and other components during hemicellulose hydrolysis and how they are affected by flow. Such insight will both facilitate commercial applications of hemicellulose hydrolysis and suggest advanced technologies that improve performance and achieve lower costs.

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