

Dilute–Sulfuric Acid Pretreatment of Corn Stover in Pilot-Scale Reactor

*Investigation of Yields, Kinetics,
and Enzymatic Digestibilities of Solids*

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Abstract

Corn stover is a domestic feedstock that has potential to produce significant quantities of fuel ethanol and other bioenergy and biobased products. However, comprehensive yield and carbon mass balance information and validated kinetic models for dilute–sulfuric acid (H_2SO_4) pretreatment of corn stover have not been available. This has hindered the estimation of process economics and also limited the ability to perform technoeconomic modeling to guide research. To better characterize pretreatment and assess its kinetics, we pretreated corn stover in a continuous 1 t/d reactor. Corn stover was pretreated at 20% (w/w) solids concentration over a range of conditions encompassing residence times of 3–12 min, temperatures of 165–195°C, and H_2SO_4 concentrations of 0.5–1.4% (w/w). Xylan conversion yield and carbon mass balance data were collected at each run condition. Performance results were used to estimate kinetic model parameters assuming biphasic hemicellulose hydrolysis and a hydrolysis mechanism incorporating formation of intermediate xylo-oligomers. In addition, some of the pretreated solids were tested in a simultaneous saccharification and fermentation (SSF) process to measure the reactivity of their cellulose component to enzymatic digestion by cellulase enzymes. Monomeric xylose yields of 69–71% and total xylose yields (monomers and oligomers) of 70–77% were achieved with performance level depending on pretreatment severity. Cellulose conversion yields in SSF of 80–87% were obtained for some of the most digestible pretreated solids.

Index Entries: Pretreatment; dilute–sulfuric acid; enzymatic conversion; corn stover; xylan conversion; kinetics; pilot scale.

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Introduction

The potential of biomass-derived ethanol for use as a transportation fuel has been previously documented (1,2). One promising technology for conversion of biomass to ethanol is an enzyme-based process utilizing a pretreatment process to enhance the enzymatic conversion of cellulose to soluble glucose. A variety of pretreatment processes utilizing mechanical, thermomechanical, and thermochemical processing have been developed to alter the structural and chemical composition of biomass to improve enzymatic conversion (3,4). One pretreatment that has been extensively explored is a high temperature, dilute-sulfuric acid (H_2SO_4) process, which also effectively hydrolyzes the hemicellulosic portion of the biomass to soluble sugars.

Extensive work has been done on dilute- H_2SO_4 pretreatment of a variety of feedstocks (3), however, relatively little work has been done using corn stover. Corn stover, which includes the leaves, stalks, and cobs of the corn plant, may be available in quantities that could support significant production of ethanol and other bioenergy and biobased products. Several groups have investigated dilute- H_2SO_4 pretreatment of corn stover at low solids concentrations in batch, bench-scale reactors (5,6), but little information on xylan hydrolysis is reported. The primary focus of previous work has been on obtaining good enzymatic conversion of the pretreated solids.

More recently, Esteghlalian et al. (7) performed dilute- H_2SO_4 pretreatments at 10% solids concentration in a Parr reactor at conditions of 140–180°C, 0.6–1.2% (w/w) H_2SO_4 , and estimated residence times spanning 1–60 min. They modeled biphasic xylan hydrolysis and determined the rate constants using Arrhenius-type expressions with preexponential factors dependent on the effective acid concentration (i.e., acid concentration after neutralization by ash contained in the feedstock) to determine the rate constants. The model-predicted monomeric yields of 80–90% could be achieved at temperatures of 170–180°C with effective acid concentrations >1.0%.

Chen et al. (8) determined the kinetic parameters for dilute- H_2SO_4 xylan hydrolysis modeled with biphasic xylan hydrolysis and formation of intermediate xylo-oligomers. Pretreatments were performed in a Parr reactor at 6% solids concentration using temperature conditions of 120–150°C, acid concentrations of 0.44–1.9%, and residence times of 2–90 min. These investigators calculated that maximum xylose yields were about 89% regardless of reaction temperature.

The goal of the present work was to investigate dilute- H_2SO_4 pretreatment of corn stover in a pilot-scale (1 dry t of biomass/d) continuous reactor at high solids concentrations (20% [w/w]). We wished to work at conditions and with equipment that would generate more commercially relevant results than have been reported previously. The results produced during our study were xylan yields with carbon mass balance closure data

and enzymatic cellulose digestibilities at a variety of pretreatment conditions. In addition, rate parameters were determined from the data for a kinetic model based on biphasic xylan hydrolysis that incorporates intermediate xylo-oligomer formation.

Calculating carbon mass balance across the pretreatment process is a useful technique for assessing the accuracy of performance measurements. Obtaining good carbon mass balance closure indicates internal data consistency and provides a higher level of confidence in the accuracy of the underlying data. This is increasingly important as technology moves toward commercialization, because confidence in performance data is essential for engineering companies to commit to guaranteeing process performance. If carbon mass balance closures near 100% cannot be obtained, then process stoichiometry or the accuracy of measuring one or more of the carbon-containing process streams is suspect.

Materials and Methods

Corn Stover

Corn stover was obtained directly from Biomass AgriProducts (Harlan, IA). The tub-ground material was approx 9 mo old (harvested in fall 1999) when received at National Renewable Energy Laboratory (NREL) (summer 2000) and was then used over a period of 9 mo. As received, corn stover was washed by mixing with water in an agitated 6000-L conical tank to remove dirt and other foreign matter. The washed corn stover was then dried to approx 10% moisture before use. The composition of the washed corn stover (on a dry basis) from an average of five randomly selected samples from the lot was 37.1% cellulose, 19.8% xylan, 2.5% arabinan, 1.6% galactan, 1.4% mannan, 20.7 % lignin (acid soluble and insoluble), 7.8% protein, 5.2% ash, and 2.4% acetate.

Pretreatment System

Dilute-H₂SO₄ pretreatments were conducted in a continuous pilot-scale reactor operating at a feed rate of approx 32 kg (dry basis)/h. The process flow diagram of the pretreatment system is shown in Fig. 1 and Schell et al. (9) describe in more detail the pilot plant and the data acquisition and control system. Biomass is conveyed to the pretreatment system from a feed hopper via a weigh belt and belt conveyor. The continuous pretreatment system consists of acid supply tanks; a biomass mixer; a high-temperature, high-pressure reactor system; and a flash tank. The pretreatment reactor system is a vertical pulp digester supplied by Sunds Defibrator, (now Metso Paper USA, Norcross, GA) and includes the reactor and material feed (plug feeder) and discharge (reciprocating poppet valves) systems. The reactor is steam heated and can operate at temperatures of 150–200°C, and residence times of 3–20 min can be achieved by controlling feedstock level in the reactor. A gamma-ray level sensor measures the level of biomass in the pretreatment reactor. The acid delivery system consists of

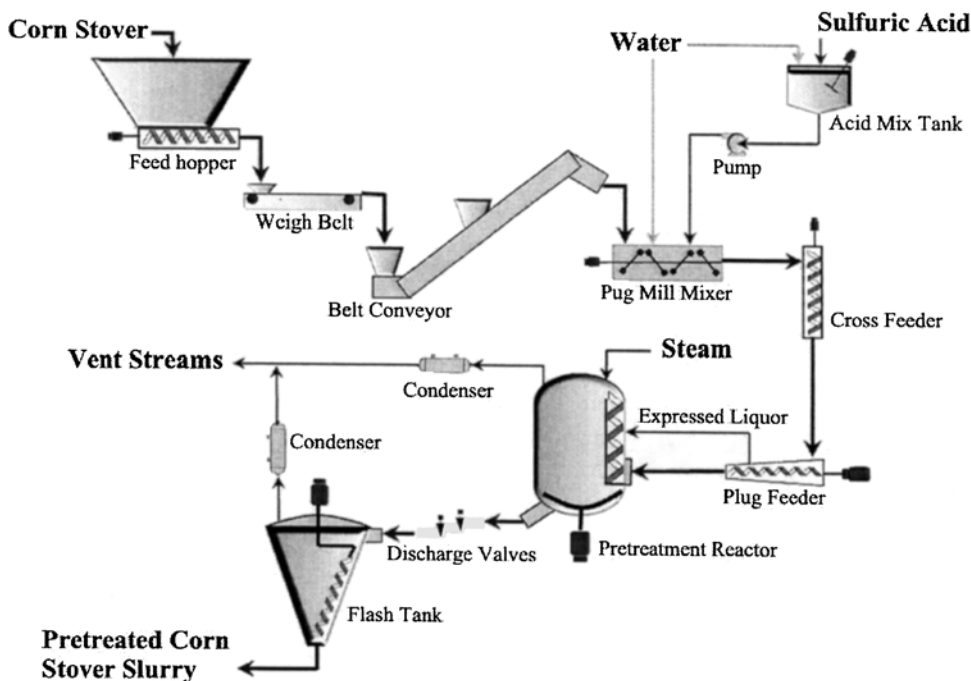


Fig. 1. Diagram of pilot-scale dilute-H₂SO₄ pretreatment system.

two fiberglass-reinforced plastic tanks (only feeding from one tank at a time) and associated pumps. Acid is diluted to 5–12% (w/w) in the acid tank, and a calibrated conductivity probe measures acid concentration.

Continuous operation of the pretreatment system begins at the feed hopper. Washed and dried corn stover in totes is dumped into the feed hopper. Feedstock is continuously metered from the hopper onto a weigh belt that controls feed rate. A signal from the weigh belt provides feedback control to the screw on the bottom of the hopper that controls weigh belt loading. The feed rate is also used to control other additions of material (e.g., acid and water). The corn stover then exits the weigh belt onto a belt conveyor that delivers it to the pug mill mixer for mixing with dilute acid and water. Water is added as needed to adjust the solids concentration in the pretreatment reactor. The wetted feedstock is screw conveyed to a plug feeder that compresses the material into an impermeable plug that is then forced into the pretreatment reactor. Liquid pressed out of the material by the plug feeder is pumped into the pretreatment reactor to maintain desired acid and water concentrations. The corn stover enters the side of the reactor and is conveyed by twin screws to the top of the reactor, where it flows over a weir and enters the main body of the reactor. There is no mixing in the main reactor body and the material essentially moves by plug gravity flow to the reactor discharge port at the bottom of the reactor. A rotating scraper on the bottom of the reactor facilitates movement of mate-

rial to the discharge port. Two reciprocating popet valves operating as a pressure lock direct the pretreatment material into the flash tank. The reactor is vented to remove non-condensables and this stream is sent to a condenser. The flash tank is a conical screw mixer, and vapor exiting from the top of the tank is also sent to a condenser. The noncondensable fraction from both of these streams is sent to a scrubber. The pretreated feedstock exits the bottom of the flash tank.

Pretreatment Experimental Protocol

Pretreatments were performed by first establishing steady-state conditions in the pretreatment reactor, i.e., ensuring that the feed rates of biomass, acid, water, and steam were all stable for at least 10–15 min after a change in operating set points. After steady-state conditions were established, the reactor was emptied and then allowed to fill to establish a level vs residence time calibration. The reactor residence time was then set to the desired value and the system was again allowed to come to steady state. After approximately three residence times, the flash tank was reemptied and pretreated material was collected over a period of three (or more) residence times. During this collection period, the corn stover was sampled before entering the pretreatment reactor, and its moisture content was measured using a Denver Instruments (Arvada, CO) Model IR-100 Infrared Moisture Balance. Additionally, samples of the vent streams from the reactor and the flash tank were condensed and collected. At the end of the collection period, the flash tank was emptied and a sample of the pretreated slurry was obtained. The data acquisition and control system collected data on flow rates, pressures, temperatures, and level every 30 s. These data were averaged and used to define operating conditions and calculate yield and mass balance results.

A total of 41 pretreatment runs were completed, including some replicates, as summarized in Table 1. Conditions were varied from temperatures of 165–183°C, residence times of 3–12 min, and acid concentrations in the liquid phase of 0.5–1.41% (w/w). All runs were conducted using a 20% total solids concentration in the pretreatment reactor on an unhydrolyzed feed solids basis. Five of the runs (nos. 37–41) were carried out at conditions outside of these ranges and are discussed separately. Table 1 shows the nominal acid concentration, which is different from the effective acid concentration. Variability in the effective acid concentration may occur because the neutralizing capacity of the stover may not be constant within a batch of material. The final pH of the post-pretreatment liquor was used in this work rather than the effective acid concentration because pH inherently accounts for the feedstock's neutralizing capacity.

Chemical Analysis

The composition of raw and pretreated corn stover was measured using methods reported by NREL for determining biomass carbohydrates (10), acid insoluble lignin (11), acid soluble lignin (12), ash (13), and acetate con-

Table 1
Pretreatment Run Conditions and Enzymatic Cellulose and Xylan Conversion Results

Run no.	Pretreatment Conditions				Xylan conversion						
	Temperature (°C)	Time (min)	Acid concentration (% [w/w])	Final pH	CSF	Cellulose conversion (%)	Monomeric xylose yield (%)	Total xylose yield (%)	Furfural yield (%)	Unconverted xylan (%)	Mass closure (%)
1	165	8.1	1.37	1.28	1.55	79	64	67	14	10	92
2	165	8.1	1.37	1.28	1.55		63	67	19	11	97
3	165	6.0	1.37	1.14	1.57	63	57	65	9	15	89
4	165	8.2	0.71	1.85	0.99		35	55	7	27	90
5	165	8.1	1.35	1.17	1.66		70	71	14	11	95
6	165	8.0	1.39	1.19	1.64	82	71	71	13	11	95
7	165	6.4	0.71	1.84	0.90		31	53	10	34	97
8	165	10.1	1.37	1.16	1.77		59	61	13	8	82
9	165	8.0	1.41	1.05	1.78	83	66	63	15	13	90
10	166	10.2	0.71	1.74	1.20		44	59	16	24	99
11	166	8.0	1.37	1.14	1.69		62	63	21	9	93
12	169	3.9	0.71	1.52	1.12		56	65	7	22	94
13	170	8.3	0.74	2.10	0.89		33	54	6	40	100
14	170	6.1	0.74	2.05	0.81		27	57	7	39	103
15	171	5.1	0.73	2.22	0.57		17	43	9	34	86
16	174	5.8	1.37	1.18	1.78		63	67	18	9	94
17	174	2.9	1.37	1.27	1.38		63	68	6	11	85
18	175	3.8	1.38	1.29	1.49		66	72	7	13	92
19	175	2.9	1.37	1.17	1.49		64	70	12	15	97
20	175	8.1	0.94	1.52	1.59	81	59	61	17	7	85
21	175	8.1	0.95	1.76	1.36	71	50	63	17	23	103
22	175	4.2	0.94	1.71	1.13	70	49	67	8	18	94
23	175	5.0	0.94	1.63	1.28	78	59	70	10	21	101
24	175	6.1	0.95	1.60	1.41	67	62	69	17	12	98

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Pretreatment Run Conditions and Enzymatic Cellulose and Xylan Conversion Results

Run no.	Pretreatment Conditions				Xylan conversion						
	Temperature (°C)	Time (min)	Acid concentration (% [w/w])	Final pH	CSF	Cellulose conversion (%)	Monomeric xylose yield (%)	Total xylose yield (%)	Furfural yield (%)	Unconverted xylan (%)	Mass closure (%)
179	8.1	0.97	1.40	1.83		52	56	11	9	77	
26	179	4.7	1.03	1.78	1.22		50	53	24	19	97
27	179	6.2	1.16	1.50	1.63		68	70	16	14	100
28	180	8.1	0.80	1.42	1.83	87	55	60	16	10	86
29	180	4.0	1.18	1.47	1.48		66	70	10	11	91
30	180	10.1	0.80	1.48	1.87	78	54	60	14	9	83
31	180	12.2	0.80	1.47	1.96	80	55	58	19	9	86
32	180	10.1	0.99	1.33	2.02	81	54	55	17	7	79
33	180	5.1	1.18	1.56	1.50		56	63	13	9	86
34	180	3.1	1.19	1.49	1.34		66	71	11	13	95
35	180	6.0	0.99	1.37	1.76		54	58	14	11	82
36	180	5.8	1.27	1.39	1.74		66	63	31	7	101
37	181	4.1	^c	1.46	1.52		65	65	27	13	105
38	183	5.3	^c	1.49	1.69	84	67	66	27	13	106
39	190	^b	1.39	1.08			67	70	19	10	99
40	191	^b	1.17	1.43		76	65	77	5	18	99
41	195	^b	1.35	1.13			68	61	19	7	87
Average ^a	165.4	8.28	1.38	1.19	1.65	81.3	66.1	67.0	15.8	10.9	93.7
SD	0.1	0.06	0.02	0.09	0.09	2.3	3.7	3.5	3.1	1.3	2.6

^aAverages and SDs for runs 1, 2, 5, 6, 9, and 11 all were targeted for the same run conditions.

^bPretreatment reactor operated at zero level in a mode that achieves a short but unknown residence time estimated at 45–75 s.

^cCorn stover preimpregnated with acid before pretreatment; actual acid concentration in the pretreatment reactor was not controlled but targeted to achieve an acid concentration equivalent to 1.2% (w/w).

tent (14). Protein content was calculated as 6.25 times the nitrogen content, which was measured using a Perkin-Elmer Series 2400 CHNS/O Elemental Analyzer (Norwalk, CT).

Concentrations of soluble components in the hydrolysate liquors (monomeric and oligomeric sugars, acetic acid, 5-hydroxymethanol furfural, and furfural) were measured using techniques previously reported (9). Total xylose is defined as the sum of monomeric and oligomeric xylose. Measurements of hydrolysate liquor pH were made the following day with the liquor at ambient temperature (approx 25°C). The amount of insoluble solids in the hydrolysate was measured using a technique (procedure A) reported by NREL (15).

Enzymatic Digestibility

Enzymatic digestibility or cellulose conversion was determined by hydrolyzing the cellulose contained in washed pretreated solids using a simultaneous saccharification and fermentation (SSF) process. The washed solids were produced by the aforementioned procedure for measuring insoluble solids. SSF was conducted in a laboratory-shaking incubator (150 rpm) at a working volume of 100 mL in 250-mL baffled flasks with water traps. The washed solids were loaded to a level of 6% (w/w) cellulose (cellulose measured as discussed above) and Iogen (Ottawa, Canada) cellulase enzyme (lot no. BRC 191095) was added to a level of 15 filter paper units (FPU)/g of cellulose. The medium consisted of yeast extract (1% [w/v]), peptone (2% [w/v]), and citrate buffer (0.05 M). The initial pH was adjusted to 5.2 using NaOH, and then the culture was inoculated with the yeast, *Saccharomyces cerevisiae* D₅A, to achieve an initial optical density (at 600 nm) of 0.5. The flask was maintained at 32°C for 7 days and sampled daily. Ethanol concentration was measured by high-performance liquid chromatography using a Bio-rad (Richmond, CA) HPX-87H column operating at 65°C with a 0.01 N H₂SO₄ solution mobile phase and a refractive index detector. Ethanol yield was calculated based on the theoretical ethanol concentration from cellulose after subtracting the ethanol added from the inoculum. The theoretical ethanol yield number is assumed to be a conservative estimate of cellulose conversion but is also a number that represents realistic conversion results, since the SSF test is done at conditions roughly similar to those that might be encountered in an actual process (i.e., 6% cellulose concentration, 32°C, and a low enzyme loading of 15 FPU/g of cellulose).

Xylan Conversion Yields and Mass Balance Calculations

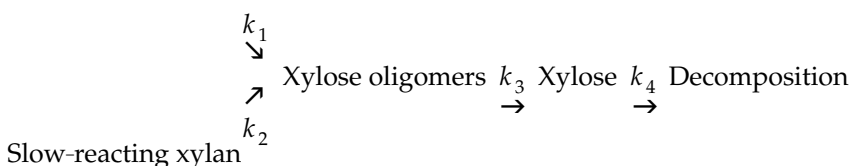
Calculation of xylan conversion yields (i.e., monomeric xylose, oligomeric xylose, furfural, and unconverted xylan) and carbon mass balances followed a previously reported methodology (16) and relies on accurate measurements of flow rates and component concentrations in the inlet and outlet streams. We measured flow rates for corn stover (weigh belt), acid, and water to the pug mill mixer (Magnetic flowmeter and Coriolis mass flowmeter, respectively), and the pretreatment-reactor vent stream

(Coriolis mass flowmeter). The flash-tank vapor flow rate was calculated from an energy balance around the pretreatment reactor and flash tank. The hydrolysate slurry flow rate was calculated from an overall mass balance. Component concentrations were measured for corn stover (moisture and composition), vapor vent streams (furfural and acetic acid), and the hydrolysate (fraction insoluble solids, solids composition, liquor composition). Components yields based on the amount of xylan contained in the corn stover and xylan mass balance closure are reported as the mass of output xylan products (monomeric xylose, oligomeric xylose, furfural, and unconverted xylan) over the mass of input xylan.

Kinetics of Hemicellulose Hydrolysis

Xylan hydrolysis kinetics was modeled as biphasic hemicellulose hydrolysis with a hydrolysis mechanism incorporating formation of intermediate xylo-oligomers (8) as follows:

Fast-reacting xylan



The kinetic rate parameters, k_i , were modeled using Eq. 1, which applies the Arrhenius relationship and general acid-base catalysis:

$$k_i = (k_i^o + k_i^H[H^+] + k_i^{OH}[OH^-]) \exp\left(\frac{-E_i}{RT}\right) \quad (1)$$

Since all pretreatments were conducted at very low pH (<2.25), the hydroxyl ion term was ignored and rewriting the hydrogen concentrations in terms of the pH gives

$$k_i = (k_i^o + k_i^H[10^{-pH}]) \exp\left(\frac{-E_i}{RT}\right) \quad (2)$$

Using pH is more appropriate than using the effective acid concentration (i.e., acid concentration after neutralization by ash), which could effectively be zero if there is insufficient acid.

The model contains 13 parameters (4 each of k_i^o , k_i^H , E_i , and the fraction of fast-reacting xylan) that must be determined. A genetic algorithm (Evolver, an Excel add-in from Palisade, Newfield, NY) adjusted the 13 parameters to minimize an error term (E):

$$E = X + O + XI \quad (3)$$

in which X , O , and XI are the sum of the square of the errors between the measured yield and the predicted yield for monomeric and oligomeric xylose, and unconverted xylan, respectively. When the measured total xylose concentration was less than the measured monomeric xylose concentration, probably owing to measurement error, the value for oligomeric xylose yield was set to zero; this occurred in runs 9, 36, and 38.

Results

Table 1 summarizes run conditions and key results from each of the 41 runs. It presents the pretreatment run conditions (temperature, time, and acid concentration), the final pH of the hydrolysate liquors, the combined severity factor (CSF), cellulose conversion determined by SSF testing, and xylan conversion results. The CSF is defined as (17,18)

$$\text{CSF} = \log_{10} \left(t \times \exp \left[\frac{T - 100}{14.75} \right] \right) - \text{pH} \quad (4)$$

in which t and T are pretreatment residence time (min) and temperature ($^{\circ}\text{C}$), respectively. The CSF provides a method for consolidating the effects of pretreatment temperature, residence time, and acid concentration into a single parameter, which can be useful for analyzing results.

Replicate runs at the same targeted operating conditions were performed to assess reproducibility. At the bottom of Table 1, averages and SDs are given for six runs (1, 2, 5, 6, 9, and 11) that were all targeted for the same pretreatment conditions (165 $^{\circ}\text{C}$, 8 min, 1.4% [w/w] acid concentration). The runs were performed on four different days spanning a period of 6 mo with two runs performed on the same day for two of the different dates. Although there is little variability in the operating conditions, there is more variability in the yields, cellulose conversion, and carbon mass balance results. One SD was approx 5% of the average value for many of these results, except for furfural and unconverted xylan yields, for which the value of the SD was much higher (up to 20%). This information is useful for accessing the overall reproducibility of results from our pretreatment system.

As noted in Table 1, runs 37 and 38 were performed with acid pre-impregnated corn stover using an impregnation device previously described (18). After acid soaking, the stover was dried to approx 10% moisture. This material was fed to the pretreatment reactor but no additional acid was added at the pug mill mixer. The acid-impregnated stover was used to test the hypothesis that mass transfer of acid into the feedstock may limit performance. These runs were performed at conditions close to those of runs 29 and achieved similar xylan conversion yields, which suggests that acid mass transfer was not limiting performance.

Runs 39–41 were performed without a detectable level in the pretreatment reactor in a “flowthrough” mode that achieves a short but unknown residence time estimated to be 45–75 s. This operating mode was achieved by cycling the reciprocating popet valves at a high frequency so that no solids built up within the reactor. The short residence time required us to conduct pretreatments at higher temperatures (190–195 $^{\circ}\text{C}$) than were used in the other experiments in order to achieve high yields. In general, the cellulose and xylan conversion results obtained under these conditions are similar to those achieved in the lower-temperature pretreatments. However, a particularly high total xylose yield of 77% was achieved in run 40, which was performed at 191 $^{\circ}\text{C}$ and 1.17% (w/w) acid. This result is intriguing, but

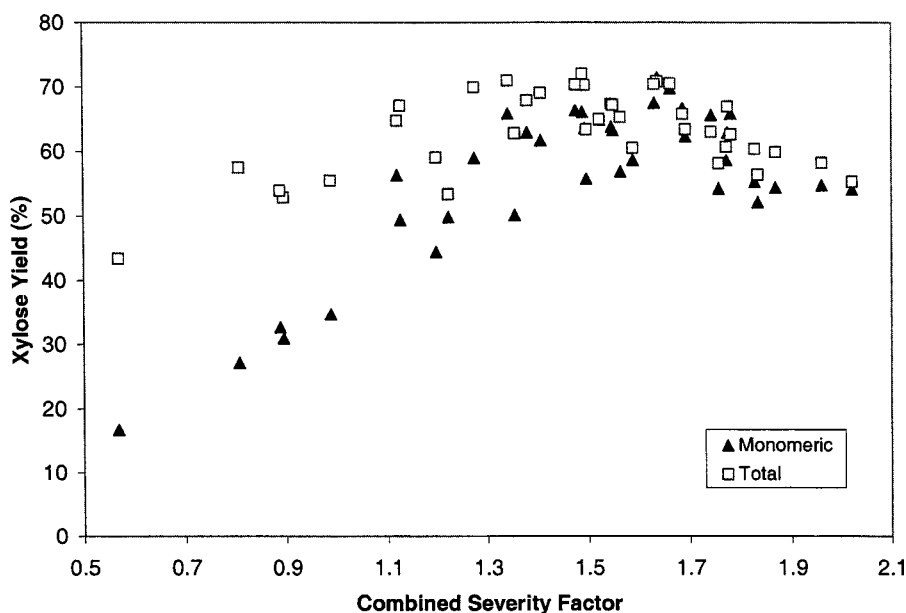


Fig. 2. Monomeric and total xylose yields of pretreated corn stover as function of CSF.

additional work needs to be performed to confirm that better performance can be obtained at this higher temperature and shorter residence time.

Xylan Conversion

Figure 2 presents monomeric and total xylose yields as a function of the CSF. The results show peaks in monomeric xylose yield at CSF (1.6–1.7 and total xylose yield at CSF (1.4–1.5, with both yields reaching highs of 70 to 71%. At lower severities, total xylose yields were much greater than monomeric xylose yields, but the two values were nearly equal above a CSF of 1.6. In addition, above a CSF of 1.7, both monomeric and total xylose yields declined, presumably because the harsher pretreatment conditions at these higher severities degraded more of the xylose to furfural and other degradation products.

The fractionation of xylan into monomeric and oligomeric xylose, furfural, and unconverted xylan, as well as the overall xylan mass balance is shown in bar chart form in Fig. 3, which plots run numbers in order of increasing pretreatment severity. In addition to the trends just discussed, Fig. 3 shows the predicted trend of increasing furfural and decreasing xylan with increasing pretreatment severity. The top of the bar shows the overall mass balance closure for xylan, which is usually in the range of 90–100%, except at the higher pretreatment severities, where mass balance begins to drop below 90%. We believe that other unmeasured degradation products are being produced under these conditions that are not included in the mass balance calculation.

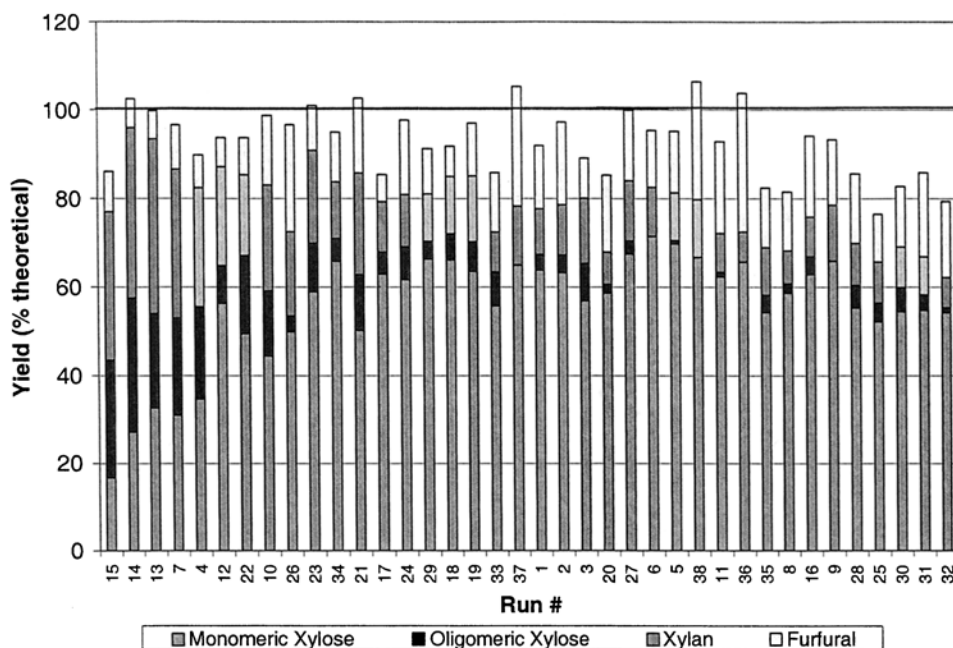


Fig. 3. Yields of monomeric and oligomer xylose, furfural, and unconverted xylan plotted by run number in order of increasing severity. The height of each bar represents the total xylan mass balance closure.

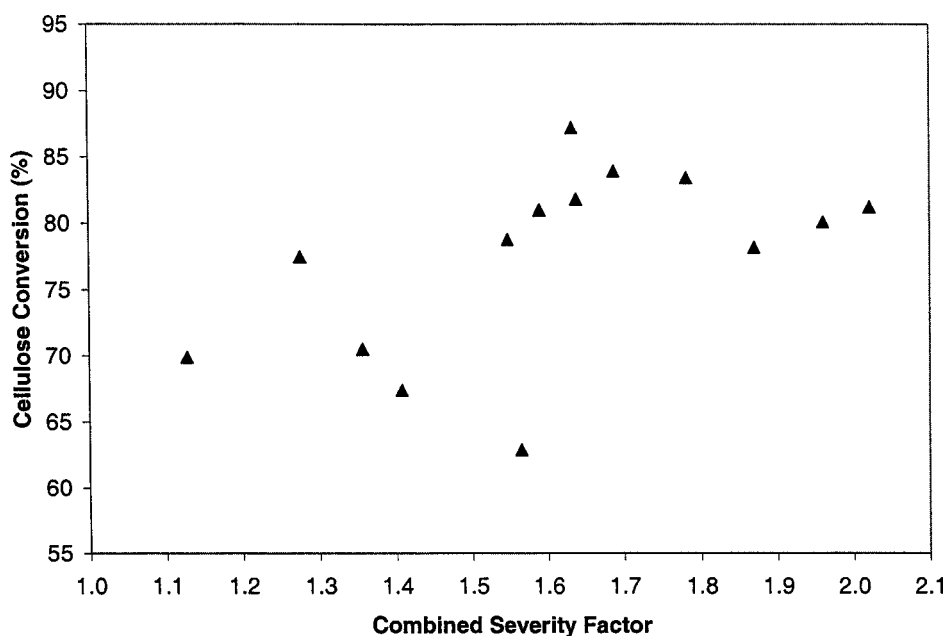


Fig. 4. Enzymatic digestibility of pretreated and washed corn stover cellulose as function of CSF.

Table 2
Estimated kinetic parameters

	k_1	k_2	k_3	k_4
k_i^o (min^{-1})	2.61×10^{25}	1.00×10^{15}	1.03×10^{28}	1.00×10^{15}
k_i^H ($\text{min}^{-1} \cdot \text{M}^{-1}$)	8.54×10^{29}	4.59×10^{29}	1.00×10^{30}	1.00×10^{15}
E_i (kcal/g mol)	57.4	59.9	58.6	33.4

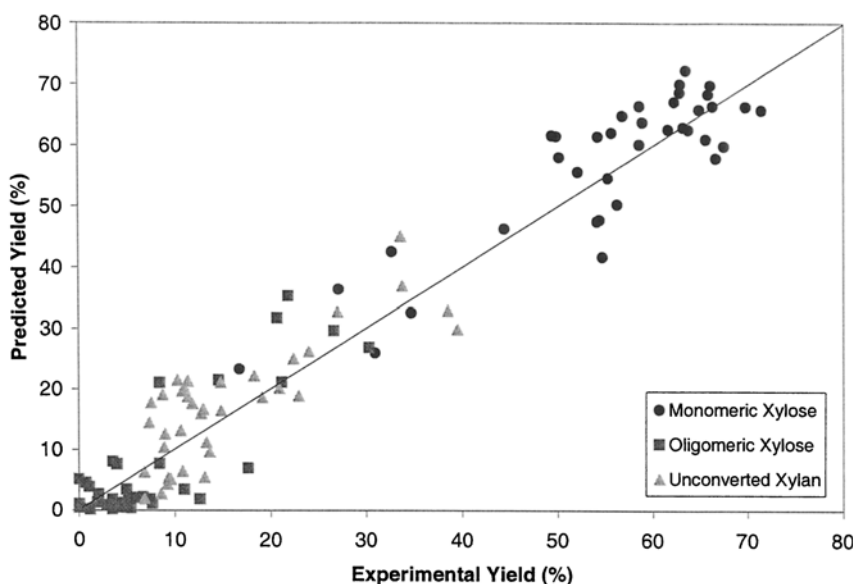


Fig 5. Predicted (kinetic model) vs measured values of monomeric and oligomeric xylose and unconverted xylan.

Cellulose Conversion

Figure 4 shows cellulose conversion or enzymatic digestibility of the pretreated solids plotted against the CSF. In general, there appears to be a trend of increasing cellulose digestibility with increasing pretreatment severity, particularly at CSFs <1.6 . At CSFs >1.6 , digestibilities $>80\%$ were routinely obtained, and the highest value obtained was 87%. The typical composition (dry basis) of well-pretreated corn stover was 55–60% cellulose, 3–7% residual xylan, and 27–31% lignin.

Pretreatment Kinetics

Kinetic parameters were estimated using data from runs 1–38 and are shown in Table 2. The ability of the kinetic model to fit the xylan hydrolysis data is presented in Fig. 5, which shows that the model predicts xylan hydrolysis performance across the data set fairly well. The best fit estimated value of the fast-reacting xylan fraction was 0.72, slightly higher than previous estimates (7, 8).

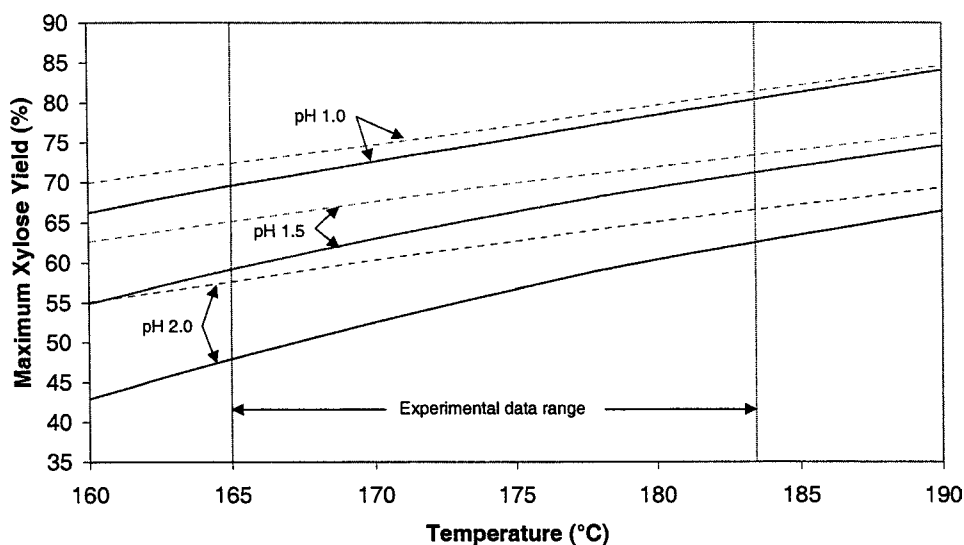


Fig. 6. Predicted maximum monomeric and total xylose yields as function of temperature and pH when maximizing based on monomeric xylose yield.

The kinetic model was used to predict both maximum monomeric and total xylose yields as a function of temperature and pH (at 1.0, 1.5, and 2.0) by adjusting residence time (i.e., calculating the residence time that maximizes xylose yield at a fixed temperature and pH). The results using monomeric xylose yield as the criterion to maximize are shown in Fig. 6. The vertical dotted lines at temperatures of 165 and 183°C show the range investigated in the experiments, thus demonstrating that the graph includes some extrapolation beyond the range within which the model parameters were estimated. The graph highlights several interesting results. First, maximum yields increase with increasing temperature and decreasing pH. Second, maximum total xylose yields are always greater than monomeric xylose yields, but the differences become small (0.5–2.0 percentage points) at low pH and high temperature. Third, the model predicts that the time required to achieve maximum xylose yield is always shorter for total xylose yield than for monomeric xylose yield (not shown).

Figure 7 presents the maximum monomeric and total xylose yields when either maximum monomeric xylose or maximum total xylose is used as the maximization criterion. The results are presented as a function of temperature at pHs of 1.0 and 2.0. For clarity, the lines of monomeric and total xylose yield when monomeric xylose is the maximization criterion are not shown at pH 1.0, since these lines lie very close to (almost on top of) the lines based on maximizing total xylose yield. Figure 7 highlights the following results: At pH 1.0, the maximum yields are similar regardless of which criterion is used to maximize yield. At pH 2.0, maximizing on total xylose yield gives higher overall total xylose yields than

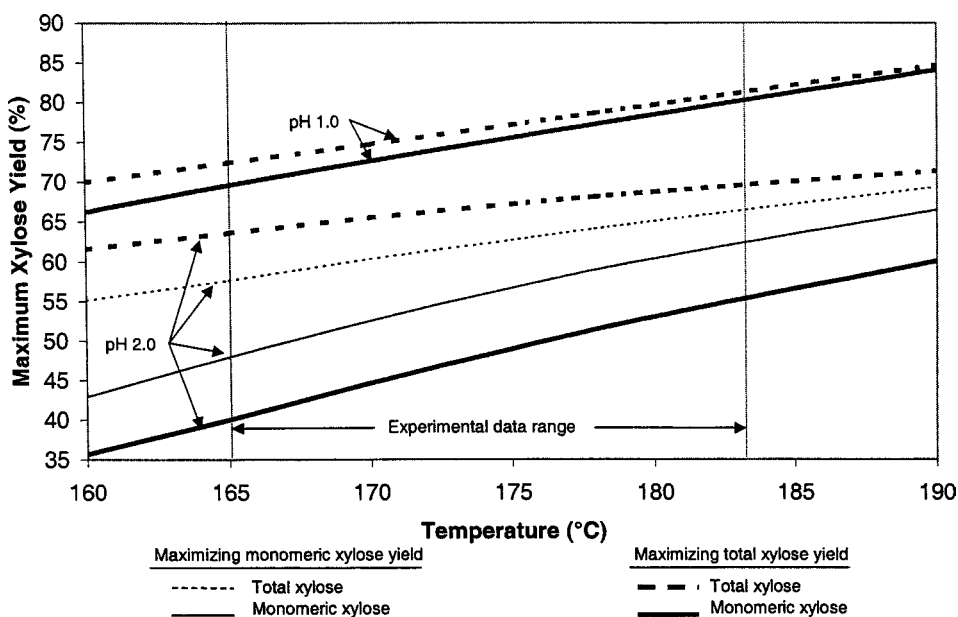


Fig. 7. Predicted maximum monomeric and total xylose yields as function of temperature and pH when maximizing based on either monomeric or total xylose yield.

when maximizing on monomeric xylose yield but produces significantly lower yields of monomeric xylose than when maximizing based on monomeric xylose yield.

Discussion

Our highest xylose yields obtained with corn stover (70–77%) are significantly lower than the best results reported by Esteghlalian et al. (7) and Chen et al. (8) (85–90%). However, our results were obtained at pilot scale using significantly higher solids concentrations (20% compared with 10%). Besides the obvious differences in dilute-acid pretreatment reactor systems (small-scale batch agitated systems compared with a continuous unagitated pilot-scale system), the higher solids concentration also produces higher sugar concentrations in the hydrolysate that may be affecting yields because the reaction rates (k_3 and k_4) depend on xylose concentration. We believe one or both of these factors contribute to the differences observed between our results and those previously reported.

Performance variability and scatter in the data are apparent from the results presented in Figs. 2–5 and the previous discussion of reproducibility. Several factors possibly contribute to this variability, including uncertainties in the residence time calibration, temperature nonuniformities within the reactor, changes in feedstock acid-neutralizing capacity that affect the final measured acid concentration, as well as normal measure-

ment and control errors associated with operating continuous pilot-scale equipment. The high degree of scatter in the performance results reflects a combination of these factors. Kinetic modeling was used to develop an overall representation of performance trends.

The most important predictions from the kinetic modeling are that low pHs are required to achieve the highest xylose yields and that yields improve at higher temperatures (although shorter residence times are required). Esteghlalian et al. (7) reported similar kinetic behavior, although other investigators have reported that temperature has little effect on maximum xylose yields (8,19). Differences in reactor systems, solids concentrations, and accounting for acid neutralization, as well as measurement uncertainties may explain some of the discrepancies. The highest total xylose yield, 77% achieved in run 40, was obtained using a higher temperature (190°C). However, this was only a single run and additional work is needed to confirm this finding. Although, it is outside the scope of this article, we are also seeing significant corn stover compositional variability, which may also be affecting both pretreatment and enzymatic hydrolysis kinetics (unpublished results).

Demonstrating effective pretreatment technology at pilot scale using economically attractive conditions is required to move lignocellulosic conversion technology toward commercialization. The work reported here, in which performance data were obtained with component mass balance closures near 100%, represents an initial effort to generate accurate and reliable pilot-scale performance data that can be used to more rigorously analyze process economics than have been performed in the past (20). Future work will examine the impact that compositional variability of corn stover has on performance and will apply measurement uncertainty analysis (21) to assess the accuracy of pretreatment yield and mass balance results.

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