Design and Initial Operation of a High-Solids, Pilot-Scale Reactor for Dilute-Acid Pretreatment of Lignocellulosic Biomass

TEH-AN HSU,[*,1] MIKE HIMMEL,[1] DAN SCHELL,[1]
JODY FARMER,[1] AND MARK BERGGREN[2]

[1]Alternative Fuels Division, National Renewable Energy Laboratory,
Golden, CO 80401-3393; and [2]Hazen Research, Inc., Golden, CO

ABSTRACT

A recently installed 100-L horizontal shaft custom-fabricated mixer/reactor, made of Carpenter 20 Cb-3 stainless steel and designed for high-solids, dilute-acid pretreatment of lignocellulosic biomass, is described. Several preliminary runs with a hardwood and a herbaceous feedstock are reported; the results show the operation to be reliable with good reproducibility. No significant differences between comparable pretreatments in the high-solids reactor and a 1-L laboratory-scale reactor are apparent. Pretreatment efficiency is not affected by 10–15% (w/w) solids loading or biomass particle size of up to –10 mm. Mass balances are closed reasonably well, with improvement in reactor contents handling and biomass analytical methods desirable.

Index Entries: Dilute sulfuric acid pretreatment; high-solids reactor; pilot-scale reactor; ethanol from biomass; prehydrolysis.

INTRODUCTION

A pretreatment step is necessary to overcome the recalcitrant nature of the native cellulose to facilitate subsequently enzymatic conversion of cellulose in lignocellulosic biomass into glucose that can be fermented into alternative fuels and chemicals. The numerous pretreatment techniques reported in the literature can generally be grouped into physical, chemical, and biological methods (1–7). Some consider thermal pretreatments to form a fourth family (8), which is considered by others as either physical (1,3–5,7) or chemical (2,6) pretreatment. Chemical pretreatment has received the most attention by far (2), probably because physical pretreatment is generally too costly and not very effective, whereas biological pretreatment is in its developmental infancy (9).

*Author to whom all correspondence and reprint requests should be addressed.

Among various chemical techniques, dilute-acid pretreatment has been studied for the past two decades, including sulfuric *(10–20)*, hydrochloric *(21–23)*, nitric (D. L. Brink, Forest Products Laboratory, University of California, Richmond, personal communication, 1993; *24,25)*, phosphoric *(21)*, and peracetic *(26)* acid. Sulfuric acid, apparently because of its low cost and high effectiveness in removing the recalcitrant nature of native cellulose, has been most extensively investigated. Laboratory studies *(11,12,17–19,27,28)* of a dilute sulfuric acid pretreatment process have shown that it significantly enhances the enzymatic digestibility of many forms of lignocellulosic feedstocks, including hardwoods, herbaceous crops, and agricultural residues. At the same time, hemicellulosic sugar yields are reasonably high from pretreatment. Yields of xylose (or, more precisely, soluble xylose equivalents), for example, have reached as high as 80% of theoretical. Therefore, although it suffers from the need for corrosion-resistant construction materials for reactors, generation of gypsum during postpretreatment neutralization, and formation of saccharification and fermentation inhibitors during pretreatment, dilute sulfuric acid pretreatment is still one of the most, if not the most, promising techniques.

All except two *(12,16)* of the dilute sulfuric acid pretreatment studies cited used reactor dry solids loadings of 10% or lower. However, the dry solids loading needs to be substantially higher to reduce reactor size, limit acid use, and reduce steam consumption. For example, the ethanol production cost estimates by the National Renewable Energy Laboratory (NREL) *(29)* employ a dry solids loading of 35%, because ethanol production costs increase prohibitively with lower solids loadings (R. Elander, NREL, personal communication, 1995). Nevertheless, literature data on high-solids, dilute-acid pretreatment are extremely limited. Grohmann et al. *(12)* extended the solids loading to 40% using small (13-mm [1/2-in.] od × 100-mm [4-in.] long) pipe reactors with indirect heating, and Schell et al. *(16)* extended it to 30% using open trays in a cylindrical reactor with direct steam injection aided by indirect heating. In both studies, the biomass was completely static during pretreatment, and heat and mass transfers would likely be severely uneven at a large scale.

To gather higher solids data in a system that can be applied at a commercial scale, we designed and fabricated a 100-L horizontal shaft mixer/reactor. This reactor was designed to demonstrate the feasibility of the dilute sulfuric acid pretreatment technique at high-solids levels, provide scale-up data, and produce large quantities of pretreated solids for fermentation research. The reactor was recently installed and tested with a hardwood and a herbaceous feedstock. This article describes the high-solids, pilot-scale pretreatment reactor and its initial operation, and compares the results to those obtained from a bench-scale reactor.

MATERIALS AND METHODS

Materials

The woody and herbaceous lignocellulosic feedstocks were obtained by the NREL Alternative Fuels Program feedstock interface project. The woody material was primarily hardwood hybrid poplar DN34 *(Populus eugenei)* (mixed with minor other clones), whole tree, purchased from Domtar Paper Company (Cornwall, Ontario, Canada) as commercial chips. The chips were then air-dried, knife-milled, and sieved to –2-mm to +0.25-mm (–1/16-in. to +60-mesh) size range. The herbaceous

material was switchgrass (*Panicum virgatum L.*, Alamo cultivar), purchased from Auburn University (Auburn, AL). It was field-dried and baled before being shipped to NREL. On receipt, it was knife-milled to either –3-mm (–1/8-in.) or –10-mm (–3/8-in.) particles for use in this study.

Chemicals used for pretreatment and sample analysis were all of reagent grade. The cellulase enzyme used was a Genencor Cytolase CL preparation.

Pretreatment Reactor

The pilot-scale reactor (dubbed the "paddle reactor," Fig. 1) was designed based on classical paddle-blender designs, with mixing elements (arms) placed along a horizontal shaft in such a manner as to ensure that all surfaces inside the reactor shell are contacted by the element tips. Teflon™ wiping blades are attached to each mixing element (including special arms designed to wipe the end plates) to ensure the biomass is effectively removed from the hot inner walls. This system of gentle, positive mixing combined with extensive wall scraping ensures minimal biomass overheating and maximum overall heat transfer of high-solids slurries.

The reactor vessel was constructed (by Sterling Machine Company, Sterling, CO) entirely of Carpenter 20 Cb-3 stainless steel to provide resistance to hot dilute sulfuric acid. The reaction vessel, about 100 L, is approx 610-mm (24 in.) long × 460-mm (18 in.) in diameter and is surrounded axially by a 25-mm (1-in.) wide steam/cooling fluid jacket with one 19-mm (3/4-in.) bottom port and two 19-mm (3/4-in.) top ports. All penetrations into the reaction vessel are made through the primary head plate, a 250-mm (10-in.) diameter manway. The vessel is constructed with only one removable end plate, located on the hand-crank side of the vessel, and this plate is dismantled during major repair only. All routine cleaning is done through the manway. A unique vessel handling system allows the vessel to be rotated in the support frame from the operating/loading position with the manway facing up to a position 180° around axially with the manway facing down for cleaning and product removal. To allow the vessel to rotate, a dual support system was employed. Whereas the reactor shaft and electric motor are one independent unit driven from one side of the framework, a hand wheel and gear box drive a lug attached to the reactor housing on the other (the hand-crank) side. This reactor housing lug is bolted to the framework during normal operation. Thus, the electric motor-side train drives the reactor shaft, and the hand wheel rotates the reactor vessel.

The reactor shaft is sealed by two annular stuffing box seals packed with 13-mm (1/2-in.) GFO® packing rings. This type of seal was found to be very practical for biomass pretreatment, in which the mixed material is often abrasive as well as corrosive. The drive shaft is Carpenter 20 Cb-3 stainless steel, 56 mm (2–3/16 in.) in diameter, and is supported by four "Seal Master"-type, double-row ball bearing blocks. The drive motor is a U.S. Motors 750-W (1-HP), 208 maximum rpm, adjustable-speed gear motor. The overall unit footprint and weight are 1.6 (65 in.) × 1.0 m (40 in.) and 680 kg (1500 lb), respectively. The reactor is insulated where practical.

Originally, the reactor was built for a maximum allowable working pressure (MAWP) of 720 kPa (90 psig), but later altered (by Eaton Metal Products Company, Denver, CO) to 1.1 MPa (150 psig). Assuming that the vapor pressure for dilute-acid pretreatment could be estimated from the vapor pressure of saturated steam, the original 720-kPa (90-psig) pressure limit constrained the operating tempera-
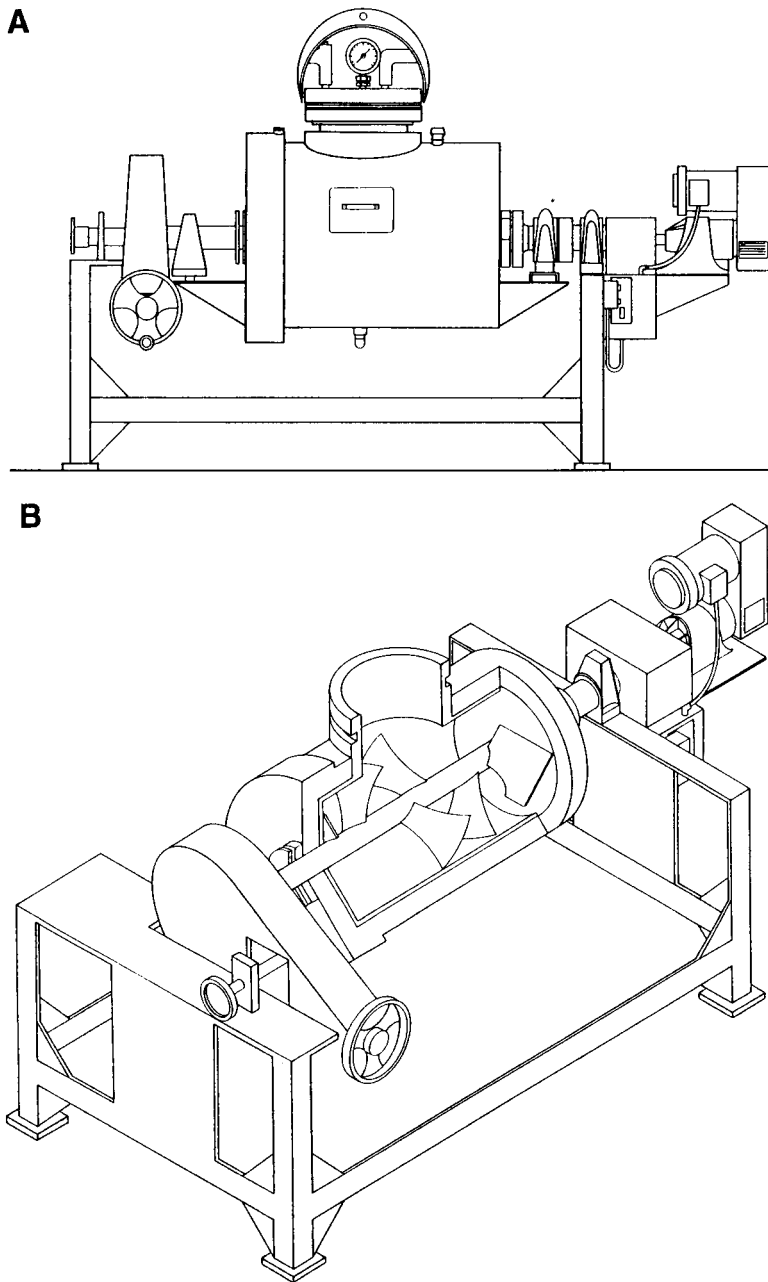
Fig. 1. Schematics of paddle reactor: **(A)** front view and **(B)** cut-away view showing inside of reactor.

ture for dilute-acid prehydrolysis to about 166°C (331°F) or below. According to our previous observations (data not shown), however, the actual reactor pressure was consistently slightly higher than the corresponding saturated steam pressure—possibly caused by a small amount of residual air in the reactor, volatile gases generated during pretreatment, or both. With this consideration and the consideration of the installation of a rupture disk, prior to the pressure rating

alteration, we were planning on limiting pretreatment temperature in the paddle reactor to approx 160°C (320°F).

The modification of the MAWP was necessary, because, as study of the dilute sulfuric acid pretreatment technique progressed (using a laboratory-scale reactor), it became desirable to operate the paddle reactor at temperatures higher than the originally projected maximum of 160°C. Early NREL studies showed that temperatures up to 160°C were effective *(11,12)*. More recent studies, however, suggest that higher temperatures (as high as 180°C) might be desirable for some feedstocks *(17,19)* or certain temperature strategies *(13)*. Without the modification and with the installation of a rupture disk having a typical tolerance margin of 5% of the rated pressure to ensure the vessel not to be overpressured accidently, the maximum pretreatment temperature allowed of the reactor would be approx 160°C (320°F). As a result, the vessel was modified to an MAWP of 1.1 MPa (150 psig). The reactor can now be safely operated at 175°C. Without the alteration, the original design would have restricted operation of the vessel to temperatures possibly below those necessary for effective pretreatment of many of the feedstocks of interest. The pressure rating alteration involved changing of the removable end plate to a heavier flange and redoing the welds of the reactor. The reactor jacket is now rated at 960 kPa (125 psig).

To our knowledge, this is the only reactor of its kind ever reported in the literature for high-solids, dilute-acid pretreatment of lignocellulosic biomass.

Pretreatment Reactor Utility Skid

A utility skid was built by a subcontractor (Interpro [now Colorado Minerals Research Institute], Golden, CO) to allow the paddle reactor to be operated. The skid provides a centralized and portable location for all support equipment and external utility connections (e.g., steam, water). Flexible stainless-steel hoses are used to make connections between the skid and the reactor using quick-disconnect and Swagelok fittings. A flow diagram for the system is shown in Fig. 2. Not shown in the figure are the rupture disk and a pressure gage that are tapped to the manway lid, and a tee fitting between the lid and the quick coupling in the reactor condensate valve (RCV) line that houses a thermocouple (the tip of which protrudes into the reactor head space). The skid is equipped with a high-pressure metering pump (Cheminjector Diaphragm Metering Pump, Hydroflo Corporation, Plumsteadville, PA, 55.3 L/h [14.6 gal/h] maximum flow rate and 1.1 MPa [150 psig] maximum delivery pressure), steam pressure regulator, pressure relief valve, steam traps, heat exchanger, and (regular) valves. All connectors, tubing, tankage, and valves used to construct the system are either Carpenter 20 Cb-3 or 304 stainless steel.

Pretreatment Runs

To conduct a dilute-acid pretreatment run, a known amount of biomass is loaded into the paddle reactor through the manway, and then mixed with a predetermined amount of deionized water to form a slurry of the desired solids content. The manway lid is then closed and connections to the utility skid made. Next, the biomass in the reactor is deaerated by heating by steam to 75°C for 10 min. Following deaeration, the reactor is sealed by closing the vent valve (the reactor condensate valve, RCV) and then heated to the target pretreatment reaction temperature, either by injecting steam into the reactor jacket or directly into the reactor. For this study, we applied indirect heating of the jacket. The steam used is filtered to remove par-
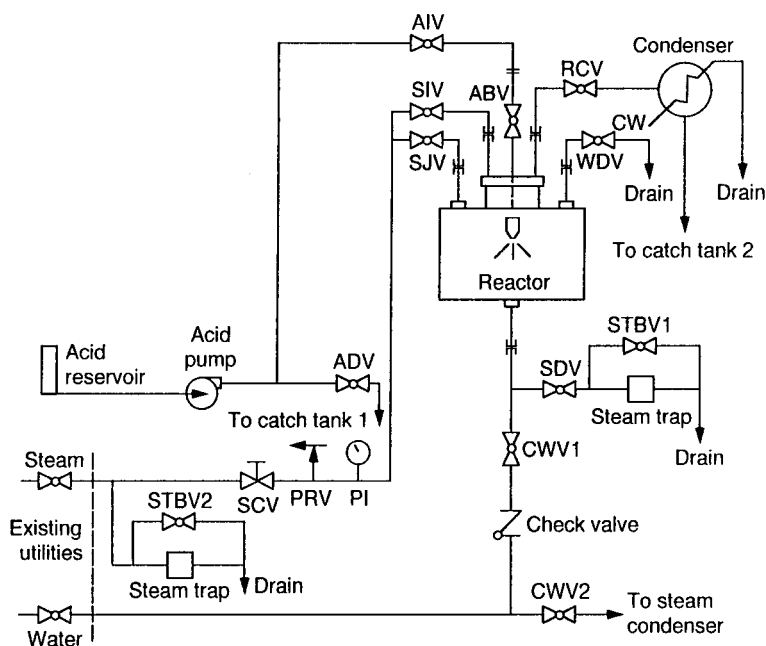
Fig. 2. Paddle reactor process diagram. ⊠, ball valve; ⊠, needle valve; �H, quick coupling; =, swagelok connector; ABV, acid block valve; ADV, acid drain valve; AIV, acid injection valve; CWV, cold water valve; PI, pressure indicator; PRV, pressure relief valve; RCV, reactor condensate valve; SCV, steam control valve; SDV, steam drain valve; SIV, steam injection valve; SJV, steam jacket valve; STBV, steam trap bypass valve; WDV, water drain valve.

ticulates and reduced to an appropriate pressure by a control valve, and then further controlled by a steam control valve at the utility skid. Steam traps drain condensate from the steam lines on the skid and from the reactor jacket.

When the target reaction temperature is reached, a calculated amount of 72 wt% sulfuric acid is injected quickly (in 20–40 s, depending on the amount of acid injected) into the reactor by the metering pump through a spray nozzle (Fig. 2). At the completion of the pretreatment time, cooling water is injected into the bottom port of the jacket to cool the reactor rapidly. When the reactor temperature drops to 95°C, the vapors are vented through a condensing heat exchanger and collected in a separate tank (Catch Tank 2). At 80°C, the manway lid is opened. Although the reactor can also be cooled by venting it immediately after the predetermined pretreatment time is reached, this cooling method was not used in this study. To discharge the reactor, it is rotated about 180° and the contents removed by gravity. A filter pan under the reactor collects the discharged reactor contents, which can be filtered to separate the prehydrolysate from the pretreated solids and the prehydrolysate sampled for compositional analysis. For runs to determine dry biomass solids yield, the wet filter cake of pretreated solids and residual prehydrolysate is washed until the filtrate pH rises to 5.0 or higher and then partially air-dried before determining the dry solids weight. A solids sample is collected for compositional analysis before air-drying. If the dry biomass solids yield is not needed, the filter cake is partially washed until the filtrate pH turns to 4.0 or higher and a sample is then collected for analysis.

For initial operation of the paddle reactor, a total of two hybrid poplar and six switchgrass runs was conducted. The pretreatment conditions are summarized in Table 1, and include both 10 and 15% solids loadings. The higher acid concentrations for switchgrass were needed to compensate for the higher buffering capacity of switchgrass or the higher solids loading, or both, so that the prehydrolysate pH was controlled to about 1.3. Throughout the runs, the rotational speed of the reactor shaft was maintained at 90 rpm. During loading and discharging, the shaft speed was set at a much lower level of approx 25 rpm (the lowest speed without incurring undesirable noise, possibly owing to belt slippage, in the gear box) to facilitate loading and discharging. The reactor temperature during heating was manually controlled by the steam control valve (SCV, Fig. 2); the steam supply upstream of the steam control valve was regulated to 930 kPa (120 psig).

For investigating scale-up differences, the results obtained from a laboratory-scale (1-L) reactor were compared to the paddle reactor results under the same pretreatment conditions. The laboratory-scale reactor operation has been previously described (19), except that the acid injection was achieved by using a high-performance liquid chromatography pump.

Analytical Methods

All samples generated were refrigerated until analyzed. To analyze the composition of prehydrolysates and solids, NREL standard analytical procedures as described by Ehrman and Himmel (30) were followed. All pretreated solids were washed extensively to ensure the soluble sugars and acids were removed before analysis for enhanced accuracy (30,31). Solids were analyzed for glucan, xylan, arabinan, galactan, mannan, Klason lignin, acid-soluble lignin, and ash. The extractives content was also determined for raw switchgrass. Prehydrolysates were analyzed for glucose, xylose, arabinose, galactose, mannose, acetic acid, furfural, 5-hydroxymethylfurfural (HMF), and acid-soluble lignin.

For enzymatic digestibility tests, a modified NREL standard analytical procedure was followed. The NREL standard protocol (Laboratory Analytical Procedure no. 009, Ethanol Project, Alternative Fuels Division, NREL) calls for using 1% cellulose loading with 60 filter paper units (FPU) cellulase/g cellulose in pH 4.8 sodium citrate buffer at 50°C and determining digestibility by following glucose concentrations. In the modified procedure, instead of following only glucose concentrations that take, at times, 6–7 d to reach the final values, 3-d samples were analyzed for glucose and cellobiose, and total glucose equivalents were calculated by summing total glucose units in glucose and cellobiose to represent the ultimate digestibility. Some digestibility tests were conducted after the pretreated solids were size-reduced in a laboratory blender (Waring Commercial Lab Blender, Dynamics Corporation of America, New Hartford, CT). The blending procedure has been described elsewhere (32).

Reactor Mass Balances

Overall mass balances were estimated for three paddle reactor runs. The entire reactor discharge was filtered immediately following discharge. The total weight of the reactor contents after pretreatment was obtained by adding the weights of filtrate (prehydrolysate), wet filter cake, vent condensate, and reactor clean-out (residual material in reactor on discharging), and compared to the total weight of materials (biomass, water, and acid) loaded into the reactor. The ratio, expressed as a percentage of total reactor charge, is referred to as the reactor mass recovery. The filter

Table 1
Paddle Reactor and 1-L Laboratory-Scale Reactor Pretreatment Runs[a]

Run no.	Sulfuric acid concentration,[b] wt%	Dry solids loading		Biomass particle size	Reactor mass recovery, %	Dry biomass solids yield, %
		%	g			
Hybrid poplar DN34						
Paddle reactor run 1	0.73	10	6000	−2 mm +0.25 mm (−1/16 in. +60 mesh)	nd	nd
Paddle reactor run 2	0.73	10	5830	−2 mm +0.25 mm (−1/16 in. +60 mesh)	nd	nd
1-L lab-scale reactor	0.73	10	50	−2 mm +0.25 mm (−1/16 in. +60 mesh)	nd	nd
Switchgrass						
Paddle reactor run 1	0.88	10	6000	−10 mm (−3/8 in.)	nd	nd
Paddle reactor run 2	0.88	10	6000	−10 mm (−3/8 in.)	nd	nd
Paddle reactor run 3	0.88	10	6000	−3 mm (−1/8 in.)	nd	nd
Paddle reactor run 4	0.88	10	6000	−3 mm (−1/8 in.)	101.0	54.0
Paddle reactor run 5	0.88	10	6000	−3 mm (−1/8 in.)	93.3	53.8
Paddle reactor run 6	1.11	15	9000	−3 mm (−1/8 in.)	99.7	56.0
1-L lab-scale reactor	0.88	10	60	−3 mm (−1/8 in.)	nd	52.0

[a]Pretreatment temperature was 170°C for all runs; pretreatment time was 10 min for all hybrid poplar runs and 5 min for all switchgrass runs. nd, not determined.
[b]Acid concentration calculated based on weight of liquid phase of reactor contents.

cake dry weight, plus reactor clean-out dry weight, relative to the dry weight of the feedstock biomass, expressed as a percentage, is referred to as the dry biomass solids yield.

Furthermore, the mass balance for major biomass components, including glucan, xylan, and Klason lignin, was established for these runs. In doing so, the generation of the small amounts of volatiles during pretreatment was ignored (most or all of the volatiles would result in the vent condensate, which was observed to be negligible in all cases—data not shown). Moreover, HMF and furfural were assumed to be generated from glucose and xylose, respectively.

RESULTS AND DISCUSSION

All paddle reactor runs conducted thus far have operated satisfactorily. We have encountered only very minor and predictable operating issues, such as the need for tightening the packing seals and fittings during a run. Figure 3 shows the temperature profiles of the two hybrid poplar DN34 runs. Apparently, except for a time shift, the two profiles are very similar and can be superimposed almost exactly on each other. The time shift resulted from the difference in the starting points when the first temperature point was recorded. This observation of reproducibility of heating course was also true for the switchgrass runs (data not shown). Thus, the control of the steam heating was quite reproducible.

The compositions of the pretreated solids and prehydrolysates resulting from the hybrid poplar runs, along with that of the raw feedstock, are presented in Table 2. Comparison of the duplicate paddle reactor runs (runs 1 and 2) shows good reproducibility, including solids and prehydrolysate compositions and pretreated solids enzymatic digestibility. Hemicellulose was removed effectively, and the cellulose digestibility of the pretreated solids was approx 80% (based on available cellulose in the pretreated solids) for both runs.

In comparison with the laboratory-scale reactor, the solids digestibility seems to be significantly higher, and more glucan seems to have been solubilized for the smaller reactor. These results, however, may be somewhat misleading— because, as noted in Table 2, the pretreated solids sample from the laboratory-scale reactor was only partially washed before the composition was analyzed. This inadequate washing probably resulted in the carbohydrate (specifically, glucan) content being underestimated *(31)*. Thus, the significantly lower pretreated solids glucan content (58.8%) for the laboratory-scale reactor was likely higher than that reported, and accordingly, the digestibility of the solids is likely to be somewhat lower than that (89%) shown in the table.

Table 3 shows the compositions of raw and pretreated switchgrass and the enzymatic digestibility of the pretreated solids, as well as the corresponding prehydrolysate compositions. Based on these data, two points are worth noting. First, the enzyme digestibility shown for Run 2 is based on the glucan content reported in the table, but these values are somewhat biased, because they were obtained from a partially washed solids sample *(31)*. Thus, the true glucan content was somewhat higher, and the true digestibility lower, perhaps in the neighborhood of 60%. As a result, the digestibilities of runs 1 and 2 are considered comparable to each other. Second, the laboratory-scale reactor run represents the average of six runs of the laboratory-scale reactor, and pertinent statistical analysis results of these six runs are included in the table to allow meaningful data comparison.
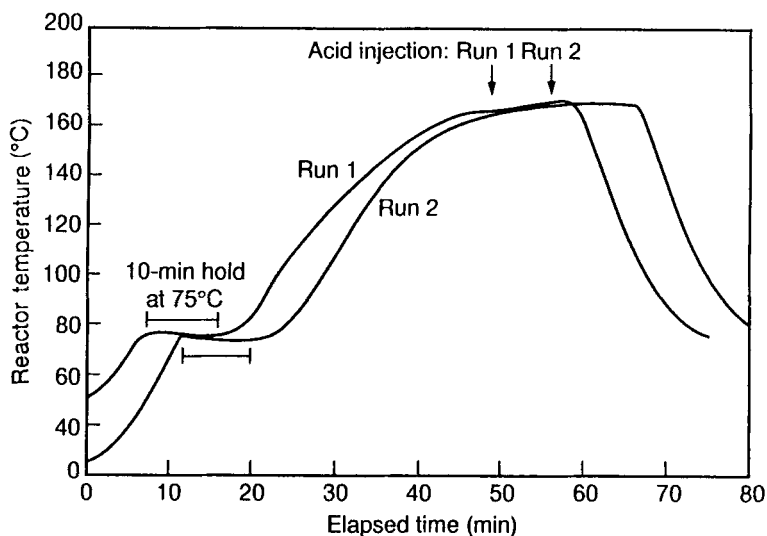
Fig. 3. Temperature profiles of hybrid poplar DN34 pretreatment runs.

It is apparent from Table 3 that the 10% solids loading runs agree well for the paddle and the laboratory-scale reactors. The difference in feedstock particle sizes (Table 1) did not significantly affect the pretreatment efficiency. The enzyme digestibility, before size reduction of the pretreated solids, of the larger (–10-mm or –3/8-in.) particles was significantly lower than that of the smaller (–3-mm or –1/8-in.) particles (cf runs 1 and 2 vs runs 3–6 and laboratory-scale reactor run). However, the paddle reactor 10 and 15% solids loadings and the laboratory-scale reactor, all being of the same smaller particle size, showed comparable digestibilities between 78 and 83% (cf runs 3–6 and laboratory-scale reactor run). For the smaller particle size, size reduction after pretreatment showed no effect (cf digestibilities of run 6 solids with and without blending). Because the solids from runs 1 and 6 showed similar digestibilities after laboratory blending, we conclude that the same pretreatment efficiency was achieved for both feedstock particle sizes.

In comparison, the two reactors resulted in comparable pretreatments (cf runs 1–5 vs laboratory-scale reactor run). Only the Klason lignin content appears to differ in product obtained from the two reactor designs. This small difference, however, is probably not statistically significant. A larger data base will have to be established for a definitive answer.

Because the preliminary paddle reactor runs showed acceptable reproducibility, agreed reasonably well with the laboratory-scale reactor runs, and resulted in no significant differences for low (10%) and high (15%) solids loadings, we have placed the reactor into service for producing large quantities of dilute-acid pretreated biomass for fermentation research. The reactor is also ready for pretreatment research. Solids loadings higher than 15% are now being tested.

Interestingly, Tables 2 and 3 indicate a tendency for the total accounting of mass to be slightly (up to 6%) more than 100% for pretreated solids. This is suspected to be largely owing to the built-in variabilities and weaknesses in the analytical methods employed (C. I. Ehrman, NREL, personal communication, 1995). For raw feedstocks, the approx 5% composition unaccounted for is likely to be a combination of acetyl groups and uronic acids that were not specifically analyzed.

Table 2
Results of Dilute Sulfuric Acid Pretreatment of Hybrid Poplar DN34

| | Pretreated solids composition[a] (% dry weight) | | | | | | | | | |
Run no.	Glucan	Xylan	Galactan	Arabinan	Mannan	Klason lignin	Acid-soluble lignin	Ash	Total	Enzymatic digestibility, %
Feedstock	43.7	16.0	1.0	1.8	3.1	25.2	2.7	1.4	94.9	nd[b]
Paddle reactor run 1	65.1	2.6	0.0	0.0	0.0	32.6	1.3	0.2	101.9	78
Paddle reactor run 2	65.0	2.5	0.0	0.0	0.0	33.8	1.7	0.2	103.2	79
1-L lab-scale reactor[c]	58.8	2.5	0.9	0.6	1.2	33.7	1.9	0.2	100.4	89[d]

| | Prehydrolysate composition, g/L | | | | | | | |
Run no.	Glucose[e]	Xylose[e]	Galactose[e]	Arabinose[e]	Mannose[e]	Acetic acid	HMF	Furfural
Paddle reactor run 1	4.4	16.2	0.0	0.7	2.1	4.3[e]	0.1	1.4
Paddle reactor run 2	4.2	13.8	0.0	0.4	1.8	4.5[e]	0.1	1.2
1-L lab-scale reactor	6.0	15.5	0.0	3.2	2.9	3.0	0.2	1.7

[a]Except for run noted as feedstock.
[b]nd, not determined.
[c]Compositional analysis performed on a partially washed solids sample.
[d]Determined with NREL standard procedure.
[e]Analyzed after hydrolysis (4% H_2SO_4 at 121°C for 1 h) of prehydrolysates; sugars reported should therefore be interpreted as monomeric sugar equivalents, such as glucose equivalents.

Table 3

Results of Dilute Sulfuric Acid Pretreatment of Switchgrass

Run no.	Extractives	Glucan	Xylan	Galactan	Arabinan	Mannan	Klason lignin	Acid-soluble lignin	Ash	Total	Without blending	With blending
			Pretreated solids composition,[b] % dry weight								Enzymatic digestibility, %	
Feedstock	12.2	33.6	20.0	2.0	3.3	0.0	17.7	2.5	3.1	94.4	nd	nd
Paddle reactor run 1	nd	59.8	3.2	0.0	0.0	0.0	38.2	1.5	2.9	105.6	63	84
Paddle reactor run 2	nd	53.3[c]	3.3[c]	0.0[c]	0.0[c]	0.0[c]	37.7[c]	1.0[c]	4.1[c]	99.8	64[d]	nd
Paddle reactor run 3	nd	57.5	3.5	0.0	0.0	0.0	37.9	1.4	3.7	104.0	81	nd
Paddle reactor run 4	nd	nd	nd	nd	nd	nd	nd	nd	nd	—	nd	nd
Paddle reactor run 5	nd	57.5	4.6	0.0	0.4	0.0	35.6	1.6	3.7	103.3	83	nd
Paddle reactor run 6	nd	54.6	5.1	0.0	0.0	0.0	32.5	0.9	4.8	97.9	78	80
1-L lab-scale reactor[e]	nd	57.2	3.3	0.0	0.6	0.2	34.2	1.9	4.3	101.1	78	nd

pH Prehydrolysate composition, g/L

Run no.	pH	Glucose[f]	Xylose[f]	Galactose[f]	Arabinose[f]	Mannose[f]	Acetic acid	HMF	Furfural	Acid-soluble lignin
Paddle reactor run 1	nd	5.2[g]	20.8[g]	nd	nd	nd	3.0	0.6	0.9	nd
Paddle reactor run 2	nd	5.2[g]	20.7[g]	nd	nd	nd	2.8	0.5	0.8	nd
Paddle reactor run 3	1.3	5.5	20.7	2.1	3.7	0.7	0.6	0.4	0.9	3.7
Paddle reactor run 4	1.3	nd	nd	nd	nd	nd	nd	nd	nd	nd
Paddle reactor run 5	1.4	5.8	21.6	1.8	3.7	0.7	2.8	0.5	0.7	5.0
Paddle reactor run 6	1.4	6.6	26.6	0.6	4.6	1.4	1.2	0.3	0.5	5.3
1-L lab-scale reactor[h]	1.3–1.4	5.7	19.7	2.6	3.9	1.2	2.7	0.4	0.6	5.1

[a]nd, not determined.
[b]Except for run noted as feedstock.
[c]Analysis performed on a partially washed solids sample.
[d]Obtained based on glucan content analyzed from a partially washed solids sample.
[e]Data presented are averages of six duplicate runs; statistical analyses for glucan, Klason lignin, acid-soluble lignin, and ash resulted in coefficients of variation (CVs) <10%; CV for xylan was 29.6%.
[f]Analyzed after hydrolysis (4% H_2SO_4 at 121°C for 1 h) of prehydrolysates; sugars reported should therefore be interpreted as monomeric sugar equivalents, such as glucose equivalents.
[g]Analyzed without further (secondary) hydrolysis of prehydrolysate.
[h]Data presented are averages of six duplicate runs; statistical analyses resulted in coefficients of variation <10% for all components, except for HMF and furfural (CVs for HMF and furfural were 23.6 and 26.3%, respectively).

Table 4
Paddle Reactor Pretreatment Mass Balances
for Switchgrass Runs[a]

Run no.	Mass balance closure, %		
	Glucan	Xylan	Klason lignin
Paddle reactor run 3	107.5	101.5	115.5
Paddle reactor run 5	108.4	106.7	108.2
Paddle reactor run 6	102.5	87.8	103.1
1-L lab-scale reactor[b]	104.4	94.8	100.5

[a]The small amounts of volatiles generated during pretreatment were neglected, and HMF and furfural were assumed to be generated from glucose and xylose, respectively.

[b]Data presented are averages of six duplicate runs; statistical analyses resulted in CVs equal to or lower than 5% for all components.

Table 4 summarizes the mass balance closures for the major components: glucan, xylan, and Klason lignin. For run 3 (dry biomass solids yield not available, *see* Table 1), calculations were made based on the average dry biomass solids yield of runs 4 and 5. It shows that comparisons between the two duplicate runs (runs 3 vs 5), between the 10 and 15% solids loading runs (runs 3 and 5 vs run 6), and between the paddle and laboratory-scale reactor runs (runs 3, 5, and 6 vs laboratory-scale reactor run) all appear to agree reasonably well. However, in general, there was an overaccounting of glucan (by up to 8%) and Klason lignin (by up to 16%). Xylan recovery was not as consistent, in that the two 10% solids loading runs resulted in an average 104% recovery, whereas the 15% solids loading run resulted in only 88%, and the laboratory-scale reactor run achieved 95%.

It should be noted that three assumptions were used to derive the numbers in Table 4:

1. The volatiles generated in pretreatment were negligible;
2. HMF and furfural were generated from glucose and xylose, respectively; and
3. Regardless of the reactor mass recoveries (Table 1) determined, the total amount of prehydrolysate in each run was calculated by subtracting the weight of the dry biomass solids recovered after pretreatment from the total reactor loading.

The first assumption was justified from our consistent observations of the negligible amount of vent condensates. The second should not introduce any significant errors because of the low levels of the minor sugars. The third was also considered justifiable, because handling the large quantities of the paddle reactor contents was difficult, and the reactor mass recovery numbers that showed some scattering served only to provide an indication of how consistent this reactor discharge handling was.

The consistent mass balance overaccounting is likely to be, at least in part, owing to the overaccounting of mass discussed. It thus appears desirable to improve the mass balance closures by improving the handling of the reactor contents (before and after pretreatment) and, possibly, the various biomass analytical methods. We are currently working on improving reactor contents handling.

Improving biomass analytical methods is a continual goal of the NREL ethanol project chemical analysis and testing (CAT) task (C. I. Ehrman, NREL, personal communication, 1995).

CONCLUSIONS

A 100-L, custom-fabricated paddle pretreatment reactor has been constructed, which provides a valuable tool for high-solids operation. The reactor is useful for both producing pretreated biomass and allowing study of high-solids pretreatment. No significant scale-up differences in pretreatment efficiency are apparent between a 1-L laboratory-scale reactor and the paddle reactor. The paddle reactor, designed to be able to handle high-solids dilute-acid pretreatment, has thus far been successfully tested for solids loadings up to 15%, and different solids loadings do not appear to affect pretreatment efficiency. Moreover, different biomass particle sizes, up to –10 mm (–3/8 in.), do not appear to affect pretreatment efficiency.

Material balances estimated for the reactor resulted in reasonably good closures, although it is desirable to have the overall accuracy further improved.

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REFERENCES

1. Chang, M. M., Chou, T. Y. C., and Tsao, G. T. (1981), *Adv. Biochem. Eng.* **20,** 15–42.
2. Dale, B. E. (1985), *Ann. Rep. Fermentation Processes* **8,** 299–323.
3. Datta, R. (1981), *Process Biochem.* **June/July,** 16–19.
4. Fan, L. T., Lee, Y., and Gharpuray, M. M. (1982), *Adv. Biochem. Eng.* **23,** 157–187.
5. Han, Y. W. (1978), *Adv. Appl. Microbiol.* **23,** 119–153.
6. Millett, M. A., Baker, A. J., and Satter, L. D. (1976), *Biotechnol. Bioeng. Symp.* **6,** 125–153.
7. Shimizu, K. (1981), *JARQ* **14,** 4244–4248.
8. Ghosh, P. and Singh, A. (1993), *Adv. Appl. Microbiol.* **39,** 295–333.
9. Grohmann, K., Wyman, C. E., and Himmel, M. E. (1992), *ACS Symp. Ser.* **476,** 354–392.
10. Grethlein, H. E., Allen, D. C., and Converse, A. O. (1984), *Biotechnol. Bioeng.* **26,** 1498–1505.
11. Grohmann, K., Torget, R., and Himmel, M. (1985), *Biotechnol. Bioeng. Symp.* **15,** 59–80.
12. Grohmann, K., Torget, R., and Himmel, M. (1986), *Biotechnol. Bioeng. Symp.* **17,** 135–151.
13. Grohmann, K. and Torget, R. W. (1992), US Patent No. 5,125,977.
14. Knappert, D., Grethlein, H., and Converse, A. (1980), *Biotechnol. Bioeng.* **22,** 1449–1463.
15. Knappert, D., Grethlein, H., and Converse, A. (1981), *Biotechnol. Bioeng. Symp.* **11,** 67–77.
16. Schell, D. J., Water, P. J., and Johnson, D. K. (1992), *Appl. Biochem. Biotechnol.* **34/35,** 659–665.
17. Torget, R., Werdene, P., Himmel, M., and Grohmann, K. (1990), *Appl. Biochem. Biotechnol.* **24/25,** 115–126.

18. Torget, R., Walter, P., Himmel, M., and Grohmann, K. (1991), *Appl. Biochem. Biotechnol.* **28/29,** 75–86.
19. Torget, R., Himmel, M., and Grohmann, K. (1992), *Appl. Biochem. Biotechnol.* **34/35,** 115–123.
20. Torget, R. and Hsu, T. (1994), *Appl. Biochem. Biotechnol.* **45/46,** 5–21.
21. Israilides, C. J., Grant, G. A., and Han, Y. W. (1978), *Appl. Environ. Microbiol.* **36(1),** 43–46.
22. Mehlberg, R. L. (1977), MS Thesis, Purdue University, West Lafayette, IN.
23. Mehlberg, R. L. and Tsao, G. T. (1979), Paper presented at the 178th ACS National Meeting, Washington, DC.
24. Brink, D. L. (1993), US Patent No. 5,221,357.
25. Brink, D. L. (1994), US Patent No. 5,366,558.
26. Fan, L. T., Gharpuray, M. M., and Lee, Y. (1981), *Biotechnol. Bioeng. Symp.* **11,** 29–45.
27. Grohmann, K., Himmel, M., Rivard, C., Tucker, M., Baker, J., Torget, R., and Graboski, M. (1984), *Biotechnol. Bioeng. Symp.* **14,** 137–157.
28. Torget, R., Himmel, M., Wright, J. D., and Grohmann, K. (1988), *Appl. Biochem. Biotechnol.* **17/18,** 89–104.
29. Hinman, N. D., Schell, D. J., Riley, C. J., Bergeron, P. W., and Walter, P. J. (1992), *Appl. Biochem. Biotechnol.* **34/35,** 639–649.
30. Ehrman, C. I. and Himmel, M. E. (1994), *Biotechnol. Tech.* **8(2),** 99–104.
31. Hsu, T. and Nguyen, Q. (1995), *Biotechnol. Tech.* **9(1),** 25–28.
32. Torget, R., Hatzis, C., Hayward, T. K., Hsu, T., and Philippidis, G. P. (1995), Paper presented at the 17th Symposium on Biotechnology for Fuels and Chemicals, Vail, CO, May 7–11.