DESIGN AND TESTING OF A PILOT-SCALE AQUEOUS AMMONIA SOAKING BIOMASS PRETREATMENT SYSTEM

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ABSTRACT. *Scale-up of the aqueous ammonia soaking (AAS) biomass pretreatment method to 75-L soaking vessel size was accomplished in this work. A novel, pilot-scale AAS system capable of pretreating 4 kg of switchgrass per cycle was designed, fabricated, and tested. The pretreatment process involved soaking biomass in 29.5% aqueous ammonium hydroxide at a liquid: solid ratio of 5 L/kg. Major vessel design criteria included (1) allowing thorough washing of the soaked biomass in the pretreatment reactor; (2) simple, low-cost fabrication; and (3) limiting safety hazards by minimizing ammonia fumes from the system. Based on these constraints, commercially available 75-L HDPE tanks were selected as the primary vessels for pretreatment. The pretreatments were conducted outside, without agitation during the summer months in Iowa, with ambient temperatures ranging from 15 °C to 33 °C. During the first experimental cycle, clogging of the outlet resulted in leakage from the vessel during rinsing, and led to redesign of the washout prevention system. The redesigned system used a "teabag" approach in which dry biomass was preloaded into a cylindrical mesh bag, and the filled bag was placed into the soaking vessel. This modification eliminated outlet clogging, simplified biomass loading and unloading, but slightly reduced washing efficiency. Through five soaking cycles, an average of 22% to 25% delignification was achieved (Klason lignin basis) compared to the 35% removal seen at the bench-scale as reported by our group. Approximately 50% to 60% of the pretreated switchgrass was recovered, dry basis, compared to 75% previously achieved at the bench-scale. Overall, the system successfully generated moderate quantities (10 kg/wk) of pretreated biomass for pilot-scale fermentation experiments while illustrating some of the materials handling challenges that must be addressed as pretreatment methods are scaled-up.*

Keywords. *Bioenergy, Pilot-scale, Pretreatment, Aqueous ammonia soaking, Switchgrass.*

Integrated biorefineries are expected to extract value from a complex feedstock through a variety of processing steps. In one possible embodiment of a biochemical/thermochemical biorefinery, lignocellulosic biomass would be pretreated, hydrolyzed, and fermented to produce ethanol. The fermentation residue would then be thermochemically converted to additional fuels, process heat, and a nutrient-rich ash residue suitable as a soil amendment. Returning this ash to crop fields closes nutrient cycles, reduces the energetic and economic costs of fertilization, and creates a more sustainable system (Anex et al., 2007). The authors were interested in contributing a proof-of-concept demonstration of this integrated biorefinery with nutrient recovery. This system used switchgrass as a feedstock, aqueous ammonia soaking (AAS) as a pretreatment method, simultaneous saccharification and fermentation (SSF) of pretreated switchgrass to ethanol, followed by gasification of the fermentation residue in a 5-kg/h air blown fluidized bed gasifier located on the campus of Iowa State University. This gasification system required a minimum of approximately 10 kg of dry fermentation residue to achieve steady-state operation (Do et al., 2007). Upstream of the gasifier, 50- and 350-L fermentors were available for the simultaneous saccharification and fermentation (SSF) (Isci et al., 2009). What was lacking was a means to pretreat sufficient quantities of biomass for fermentation that would meet the gasifier feed-rate requirements.

Pretreatment of cellulosic materials is required to break down its complex structure making the cellulose and hemicellulose more accessible to enzymatic hydrolysis (Heitz et al., 1991). A variety of pretreatment methods have been developed and tested at the lab scale (Mosier et al., 2005a), however, pretreatment of lignocellulosic biomass remains one of the most costly steps in biofuels production (Lynd et al., 1996). Ammonia fiber explosion (AFEX), hot water with pH control, dilute acid, and lime treatment are all pretreatment methods capable of increasing biomass digestibility, but most require high temperatures and/or pressure, increasing capital and operating costs. Some alkali pretreatments use lower temperature and pressure while adequately removing lignin from biomass and maintaining the polysaccharides required for conversion downstream in biological processing (Mosier et al., 2005a).

Aqueous ammonia soaking (AAS) – pioneered by Kim and Lee (2005) as a method of pretreating corn stover – was selected over other pretreatment methods for our work because of its relative simplicity and effectiveness at ambient temperatures and pressures. Kim et al. (2008) have recently explored the use of AAS to pretreat barley hull, while Isci et al. (2007) explored the use of AAS on switchgrass. In previously reported work (Isci et al. 2007), we designed and

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fabricated a system to soak and rinse switchgrass at the bench-scale (1-L vessel volume) and analyzed the effect of soaking time and liquid:solid ratios on lignin removal from switchgrass. We found a liquid to solids ratio of 5 L/kg and 5-d soaking time to be effective and selected this for our operational parameters for the scaled-up AAS pretreatment. To produce the 10 kg of dry residue required for the subject biorefinery concept demonstration using the bench-scale system described in Isci et al. (2007), would require approximately 1,000 runs of the 1-L AAS system, which would have been both time and cost prohibitive. To save time and reduce costs, a pilot-scale pretreatment system was developed and is described below.

Aqueous ammonia soaking and other pretreatment techniques have been explored at the bench-scale (Kim and Lee, 2005; Mosier et al., 2005a; Isci et al., 2007). However, pilot-scale experiments are a necessary intermediate step between bench- and full-scale experiments because they help estimate operational parameters and identify potential problems associated with scale-up prior to investing in expensive full-scale equipment. A handful of pilot-scale lignocellulosic biomass pretreatment systems using different pretreatment methods have been previously described. Thomsen et al. (2006) scaled-up a hydrothermal treatment process to coproduce both ethanol and electricity using a series of three reactors for pretreatment of wheat straw. Mosier et al. (2005b) scaled-up pH-controlled liquid hot water pretreatment for corn fiber from a 45-mL test tube to 163 L, using laboratory test as a baseline for loading rates. Similar studies by Schell et al. (2003) using dilute-sulfuric acid pretreatment of corn stover and Marchal et al. (1992) using steam explosion as a biomass pretreatment method were also explored at a pilot-scale. However, none of these systems could be easily adapted, without significant capital investment, to handle a volatile corrosive pretreatment chemical like aqueous ammonia. Therefore, the objective of this study was to design and fabricate a pilot-scale soaking and washing system to safely and effectively generate aqueous ammonia pretreated switchgrass, and to thereby identify critical factors affecting materials-handling and operation of pilot-scale pretreatment systems, to aid others in future work.

Materials and Methods

Sizing of Soaking Vessels

Operational parameters were based on bench-scale experiments evaluating solid-to-liquid loading ratio and soaking durations followed by fermentation of the pretreated biomass (Isci et al., 2007). A solid-to-liquid loading ratio of 5 L/kg ammonium hydroxide for 5 d was selected as the pretreatment condition for this study because it required less chemical inputs and a shorter durations. Accounting for lignin and hemicellulose removal, approximately 75% of the original dry biomass was collected after AAS pretreatment (Isci et al., 2007). This, in combination with the bench-scale operating system design, was used as a basis for scaling-up the AAS biomass pretreatment system to meet the 10-kg feedstock requirement of the gasification system.

Accounting for an anticipated reduction in recovery efficiency at pilot-scale (compared to bench-scale) yielded a target dry matter pretreatment capacity of 40 kg. Processing this amount of material could be done in a small number of large vessels or a large number of small vessels. Selecting the optimum number and size of vessels was done via an economic analysis with the goal of minimizing the total overall cost while taking into consideration less-quantifiable considerations such as safety and ease of material handling.

To begin the economic analysis, nine tank sizes were selected based on commercial availability and compatibility with ammonium hydroxide. The estimated price per container was determined for commercially available products, all of which were high-density polyethylene (HDPE) (Options 1-3: Nalgene, Fisher Scientific, Hanover Park, Ill.; Options 4-6: Plastic Drums, Dawg, Inc., Terryville, Conn.; Options 7-9: Schutz IBC Indusrun Totes, Theisen's, Dubuque, Iowa). Vessel fabrication time was estimated based on the number of shop operations required. Fabrication time was then converted to a cost based on an estimated labor rate of $9/h. Operational cost was again based upon an assumed labor rate ($9/h) multiplied by the total time needed to process the biomass. Factors such as the number of times a vessel would be reused, the vessel cleaning time, setup time, and monitoring time were included in this computation. The total cost to process the requisite 40 kg of switchgrass was found by summing the capital cost, fabrication cost, and operation cost estimates.

Not surprisingly, the economic analysis indicated that the 1- and 3-L vessels were the most expensive options due to the labor costs associated with fabricating 20 vessels and with operating and cleaning them all 50 to 100 times. At the other end of the spectrum, the high capital cost of the 2000-L vessel, and it's relatively low use rate, led to a high total cost. Furthermore, the safety risks associated with high volumes of ammonium hydroxide in the 2000-L vessel were deemed unacceptable. For these reasons, both the 1- and 2000-L vessels were eliminated from further consideration.

The remaining vessels were compared based on cost as shown in figure 1. Four of the options were estimated to cost less than $500 per use, and we believed the difference in these were negligible compared to the uncertainty inherent in these estimates. We selected the 75-L vessel, primarily based on the expected ease of transportation, fabrication, and operation as compared with the larger but slightly cheaper alternatives.

Biomass Washing System

Having selected a 75-L soaking vessel, the remainder of the system was designed and fabricated, with a goal of operating similarly to the bench-scale model described by Isci et al. (2007). A challenge in this regard was to ensure sufficient stirring of the biomass during the washing phase.

For proper stirring and washing of the switchgrass, agitation is needed. At the bench-scale, a magnetic stir bar augmented the mixing created by the wash-water flushing through the vessel, but implementing mechanical mixing at the pilot-scale would be expensive and hazardous due to the necessity of positioning the mechanical mixer directly in the aqueous ammonia. Therefore, agitation was provided solely by the flow of rinse-water through the reactor. For intense agitation, mixing power densities of 0.8 to 2.0 W/L are recommended (Geankoplis, 1993). Accounting for the pump losses, and aiming for the high end of this range because of the slurry-like nature of the soaked biomass, a 250-W pump

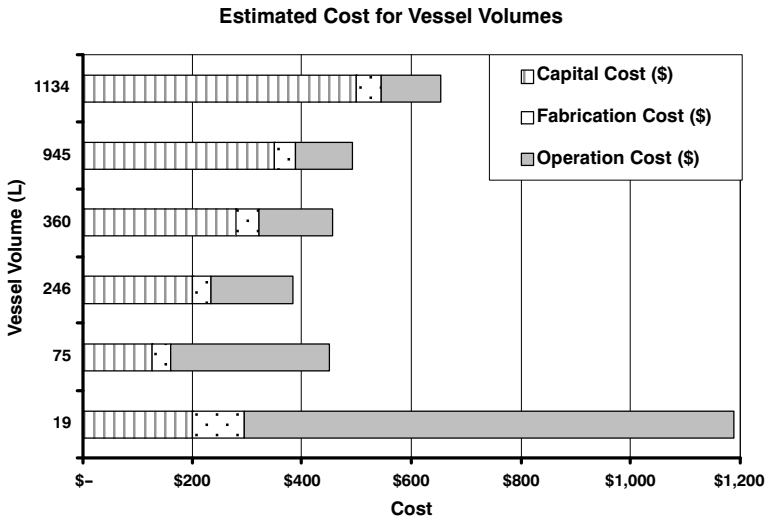


Figure 1. Total cost to process 40-kg dry biomass at six vessel sizes based on capital, fabrication, and operation costs.

(Model 43577, Wayne Reliant One, Harrison, Ohio) was selected to provide fresh water into the system and to agitate the solution. Wash water was introduced into the bottom of the soaking vessel via a PVC manifold with 3.2-mm (1/8-in.) holes on 2-cm centers (approx 60 total holes). Supplying rinse water on the bottom the vessel at high flow rates with a drain port near the top of the reactor provided thorough washing and agitation of the switchgrass. In preliminary testing, the effectiveness of this washing system was visually verified by adding red dye to the bottom of the system as water was pumped through the reactor (data not shown).

Additional Design Considerations

A 75-L container (Model PAK120, Dawg Inc., Terryville, Conn.) with a screw-top lid was used as the primary vessel for the soaking system. Since rinse-water was pumped into the soaking vessel it was necessary to evaluate the pressure limits of the vessel. Based on material properties for HDPE, the estimated burst pressure for the vessel was 82 psi. Because the supply pump was rated at 11 psi, the system was considered safe from a burst standpoint. However, the screw top lid would likely leak at significantly lower pressures, estimated to be around 0.1 psi. Considering this during the design of the system suggested placement of the water inlet and outlet below the 75-L containers' screw top lid rather than in the lid itself.

Safety Emphasis

Handling, storing, and disposing of ammonium hydroxide in a safe and environmentally acceptable manner was a major consideration at all stages of this experiment. Ammonia gas volatilized from the ammonium hydroxide solution poses a significant health hazard due to irritation or burning of skin or eyes. Inhalation of concentrated ammonia fumes causes similar damage to the upper respiratory tract and can be fatal at moderate exposure levels. A multi-step approach was employed to mitigate this risk, including the use of engineering controls, administrative controls, and personal protective equipment. Specifically, because the primary risk was due to the volatile nature of the ammonia, the soaking vessel and handling systems were designed to minimize the possibility of gaseous emissions. The experiment was carried out at a cordoned-off location away from buildings and populated areas. Major equipment was labeled with content and contact information, and the soaking vessels were placed in secondary containment vessels to avoid ground contamination if leaks occurred. Whenever ammonium hydroxide was handled, there were always more than two people on site with one serving as an observer and safety monitor. Full-face respirators (6000 series with ammonia cartridges, 3M, St. Paul, Minn.), ammonia compatible gloves (.016 in non-flocked nitrile gloves, Fisher Scientific), non-permeable aprons (cat. S47382, Fisher Reusable Vinyl Aprons, Fisher Scientific), and lab coats were worn by the personnel at all times working with the vessels while they contained ammonium hydroxide or when handling the fresh or spent ammonium hydroxide.

Experimental Procedure

The biomass used in these experiments was *Cave-in-Rock* cultivar switchgrass harvested from dormant mature stands in Chariton, Iowa. Switchgrass was harvested above a 5-cm height following killing frost. Dry switchgrass was ground to a size of 5-6 mm at the Biomass Energy Conservation Center, BECON, Nevada, IA using a hammer mill grinder (Model 400430, Art's Way, Armstrong, IA). Composition of the switchgrass was determined by the Iowa State University Department of Agronomy using the ANKOM method (ANKOM Technol. Corp., Fairport, N.Y.) as described by Vogel et al. (1999). This procedure uses hot, acidified detergent solution to dissolve cell solubles, hemicellulose and soluble minerals, leaving a residue of cellulose, lignin, and heat damaged protein and a portion of cell wall protein and minerals. Acid detergent fiber (ADF) is determined gravimetrically as the residue remaining after acid detergent extraction. Lignin is determined gravimetrically after the ADF residue is extracted with 72% H_2SO_4 and ashed. Cellulose is determined by subtracting the pre-ash lignin value from the ADF value. Klason lignin was determined as described by Crawford and Pometto (1988), slightly modified by Isci et al. (2007). Composition of the untreated switchgrass was 32% cellulose, 31% hemicellulose, 4.4% acid detergent lignin, 27% Klason lignin, and 0.7% ash.

The original intent was to operate the soaking system six times to treat the desired 40 kg of dry switchgrass. After the

soaking system had been designed and constructed, the estimated biomass requirement was reevaluated at 24-kg dry switchgrass. However, because of problems encountered during the first run, a design change was made. Because the operational problems did not reduce the quality of the pretreated biomass, biomass from the first run was used as the pretreated feedstock a for preliminary 50-L pilot-scale fermentation (Isci et al., 2009).

In the first soaking run (Run 1), switchgrass was loaded directly into the soaking system. After loading 4 kg of switchgrass into each soaking system, a screening system constructed of 2-mm fiberglass mesh (Fiberglass Screen, New York Wire, Mount Wolf, Pa.) was installed above the switchgrass to keep the switchgrass from clogging the outlet during rinsing. This screening system was attached above the inlet and below the outlet in the inside of the container with screen retainer strips (US Patent 6250040, Screen Tight, Georgetown, S.C.), with the hook retainer surface attached to the vessel interior using adhesive (Quick Gel Super Glue, Duro, Avon, Ohio). In addition to the bulk switchgrass loaded into the container, six mesh bags, constructed from 0.02-cm square pore, containing 20-g switchgrass each were installed in various locations (radially and at two heights) in the vessel to determine the spatial uniformity of the soaking and washing processes.

Because of problems encountered with the direct-loading method, in soaking runs 2 through 5, switchgrass was loaded into a large cylindrical mesh bag (0.02-cm fiberglass screen, New York Wire, Mount Wolf, Pa.) that was then placed in the soaking vessel (fig. 2). To test the uniformity of this method, sample bags containing 20 g of switchgrass each were placed in even increments along the length of the large cylindrical mesh bag; when the large bag was coiled into the vessel, this meant that the sample bags were distributed as shown in figure 3. Because the biomass was constrained within the bag, no screening system was installed over the vessel outlet for these runs.

In both methods of operation, the process began by removing the vessel top, loading 4.0 kg of switchgrass, and adding reagent grade 29.5% aqueous ammonium hydroxide to achieve a ratio of 5 L/kg, bringing the initial pH of the solution to approximately 12. The lid was then replaced and secured, and the switchgrass soaked for 5 d. The total working volume of the pretreatment vessel was approximately 25 L. The reagent grade aqueous ammonia was purchased in a 196-L drum (cat A669- 385LB, Fisher Scientific) and was pumped into the soaking vessels using a hand pump (PMP 101, Dawg Inc., Terryville, Conn.) with a buttress fitting (70-mm buttress adapter BRE, BA-Industrial, Muldrow, Okla.). During soaking, the PVC outlet of the system was covered using a plastic bag to reduce ammonia volatilization from the vessel. We intentionally avoided a truly airtight seal to avoid accidental pressurization of the vessel.

The experimental site was set up as shown in figure 3. Following the 5-d soaking process, the rinse pump was submerged in the 250-L full-scale reservoir; the pump was connected to the vessel inlet via a 3-cm diameter corrugated hose, energized, and used to flush the treated switchgrass. Ball valves on the inlet allowed for rinse-water flow rate control and simultaneous rinsing of both soaking vessels. During flushing, rinsate flowed into the 75-L outlet container via a 4-cm PVC pipe (PVC-1120, Silver-Line, Asheville, N.C.). A second 250-W pump was used to transfer the ammonia-laden rinsate to the 2000-L holding tank.

Approximately 250 L of fresh water flushed through each soaking vessel to remove the ammonia from the switchgrass, yielding a rinse volume of approximately 12x the initial aqueous ammonium hydroxide dose. This level of rinsing was demonstrated to be adequate for subsequent SSF

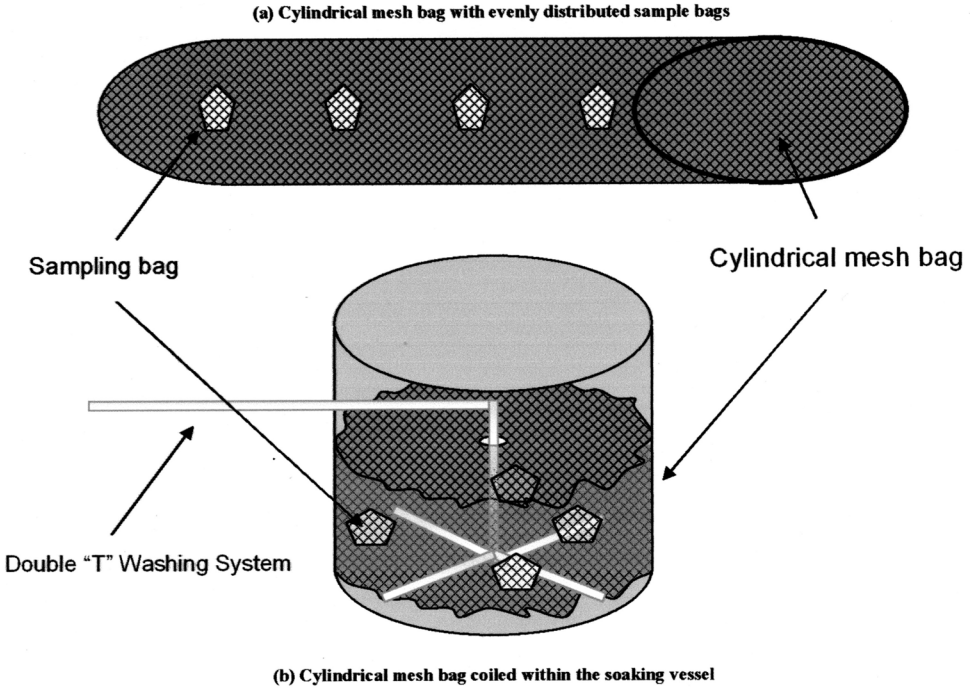
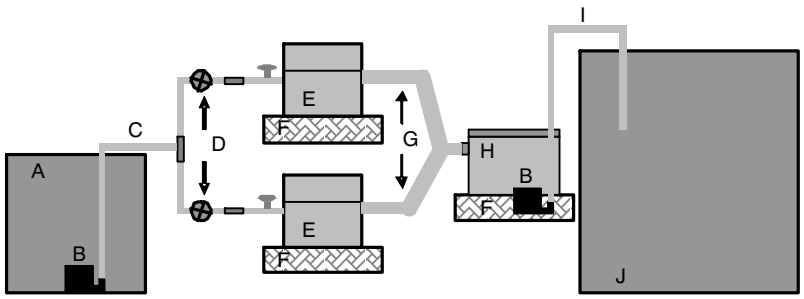


Figure 2a-b. (a) Cylindrical mesh bag was loaded with 4-kg switchgrass and sample bags at even increments and the end of the mesh bag was cinched closed by elastic drawstring. (b) The cylindrical mesh bag was loaded into the soaking vessel around the vertical inlet pipe of the double "T" washing system.



A: 250 L Fresh water containment
B: 250 W Submersible pump
C: Inlet hose
D: Flow Valve
E: 75-L Soaking vessel with screw top lid
F: Secondary vessel containment
G: Soaking outlet hose
H: 75-L Outlet container with cover
I: Rinsate outlet hose
J: 2000 L Rinsate containment

Figure 3. Pilot-scale soaking system.

experiments at the bench scale (Isci et al., 2007). At this rinsing level, a significant amount of nitrogen-rich (0.012 kg N/L) rinsate was generated which was land applied at an agronomic rate at the research site, with approval from the Iowa State University Environmental Safety and Health unit.

Following washing, the cylindrical mesh bags were removed from soaking vessels and drained. Pretreated switchgrass at approximately 80% moisture content was then transferred to 4-L poly bags (poly bag, cat. 288807, Associated Bag Company, Milwaukee, Wis.) and frozen at -20°C until needed for pilot-scale fermentation. The switchgrass sampling bags were oven dried and ground to 1 mm for fiber and Klason lignin analysis (Isci et al., 2007).

Results and Discussion

In Run 1, the screen, which had excess fabric, was forced into the outlet by the upwelling switchgrass and rinsate. This in turn partially clogged the outlet and caused pressurization of the vessel and leakage of rinsate from the cap seal. Placing a weight on top of the screen temporarily solved this problem during Run 1, but additional challenges in loading and unloading the switchgrass motivated a redesign. The six sample bags, containing 20 g of switchgrass from Run 1, were analyzed to determine cellulose and hemicellulose content (fig. 4). Consistent cellulose and hemicellulose content in various sample locations within the soaking vessel (fig. 4) demonstrated uniformity of both soaking and washing operations. In Run 1, the average post-soaking cellulose and hemicellulose concentrations were 48% and 23% respectively, with a variance among the samples of 2% and 4%, respectively. These results are similar to those we reported at the bench-scale: 56.6% cellulose and 23% hemicellulose (Isci et al., 2007). We attribute the slightly lower cellulose concentrations at the pilot-scale to the loss of fine particles from the system during washing. Aqueous ammonia pretreated switchgrass from Run 1 was subjected to simultaneous saccharification and fermentation (SSF) in a 50-L bioreactor. SSF was carried out using *Saccharomyces cerevisiae* (D_5A) resulting in 73% of maximum theoretical ethanol yield (Isci et al., 2009)

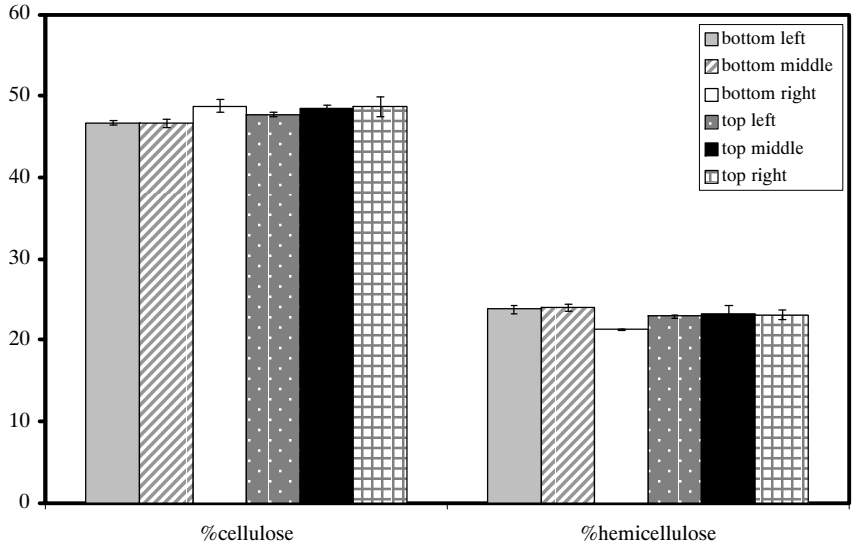


Figure 4. Percent cellulose and hemicellulose at various locations in one soaking vessel during the first run.

The redesigned vessel was operated with a cylindrical mesh bag into which the switchgrass was loaded (the "teabag" approach). The uniformity of pretreatment using the teabag method was evaluated by fiber analysis of small sample bags containing 20 g of switchgrass distributed throughout the biomass during pretreatment. Cellulose (45%) and hemicellulose (23%) content were slightly less consistent in the cylindrical mesh bag runs (fig. 5) with a variance among the samples of 6% for cellulose and 2% for hemicellulose. One disadvantage of the mesh bag approach used in Runs 2-5 was that agitation during rinsing did not appear to be as thorough as in the initial design. This was suggested by visual observations at the end of the rinsing (when ammonia concentrations were low), and by a faint smell of ammonia from the rinsed switchgrass which was not noted in Run 1. Future designs could overcome this by reducing the amount of switchgrass in each vessel or by providing better sealing on the vessel top and allowing for higher rinse-water flow rates for greater agitation.

As at the bench-scale, pilot-scale AAS proved to be an effective method for preserving the cellulose fraction in the switchgrass. Percent cellulose increased in both runs, from 32% to 48% in Run 1 and to 45% in Runs 2-5, these changes were similar to those reported by Isci et al. (2007) at the bench-scale. Percent hemicellulose decreased in all runs, from 31% to 23%, this decrease is an expected characteristic of AAS of switchgrass (Isci et al., 2007). Klason lignin decreased by nearly 25% in the pilot-scale experiments, a smaller drop than the 37% decrease seen at bench-scale (Isci et al., 2007). We attribute this reduced delignification to the less thorough rinsing, particularly with the teabag method implemented in Runs 2-5. Breaking the structure and partially removing lignin is a desired characteristic of biomass pretreatment because it allows the cellulose and hemicellulose to be more accessible to enzymatic hydrolysis. Isci et al. (2009) demonstrated that the pilot-scale aqueous ammonia soaking system adequately pretreated switchgrass for subsequent simultaneous saccharification and fermentation (SSF). Aqueous ammonia soaked switchgrass from Run 2 was subjected to SSF in a 350-L bioreactor using *Saccharomyces cerevisiae* (D_5A) resulting in 52% to 74% of maximum theoretical ethanol yield (Isci et al., 2009)

The redesigned vessel significantly improved the ease of fabrication and operation of the system over the initial design and only slightly reduced pretreatment efficacy. The cylindrical mesh bag vessel reduced safety hazards because the system was less likely to leak due to clogging. Clearly, the methods developed and described herein are not suitable to full-scale AAS systems, which will likely rely on metal vessels and automated solids handling systems. However, the methods described here work well for small pilot-scale projects needing AAS pretreated biomass.

CONCLUSION

A method for generating kilogram-quantities of aqueous ammonia soaked pretreated biomass was developed and demonstrated. The experiment showed that aqueous ammonia soaking can be operated at pilot-scale with relatively inexpensive equipment. Based on economic, safety, and convenience factors, a 75-L soaking vessel was selected and shown to be effective in pretreating 4 kg of switchgrass with 20 L of aqueous ammonia. Multiple such soaking vessels can be run at one time; in this study, we ran two simultaneously. Ammonia soaking for 5 d at 5 L/kg at the pilot-scale increased cellulose content and decreased hemicellulose and Klason lignin content of the remaining solids in a similar manner as observed in bench-scale experiments. The pretreated switchgrass was successfully used in subsequent pilot-scale fermentations (Isci et al., 2009). To our knowledge, this is the first description of a pilot-scale aqueous ammonia soaking biomass pretreatment system. Key challenges overcome in our effort included the handling of multi-liter quantities of aqueous ammonia, the separation of biomass from rinsate, and the disposal of over 1000-L of ammonia-enriched rinsate. Large-scale application of the AAS method will need to address safety, separation, and ammonia recycling issues that were encountered here.

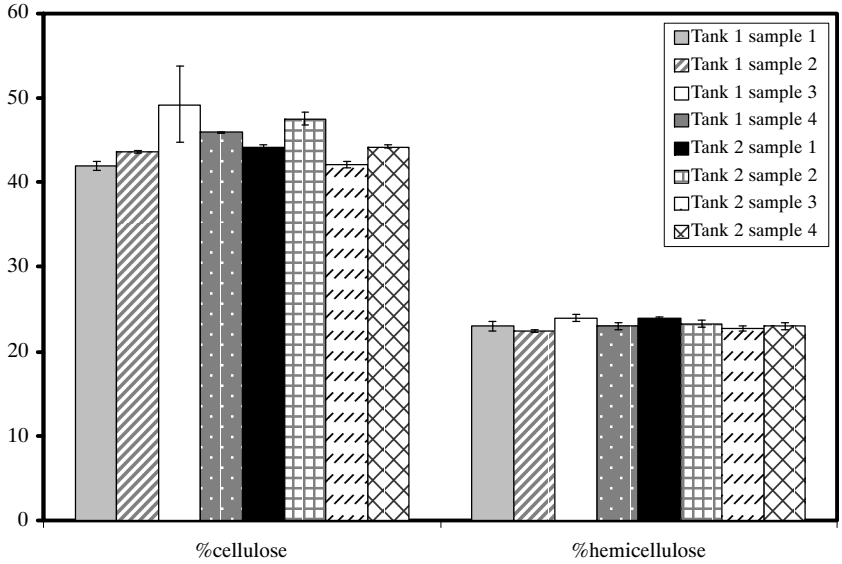


Figure 5. Percent cellulose and hemicellulose from various locations in two soaking vessels during the second trial.

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