Final Report

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Recipient Organization: Michigan Biotechnology Institute d/b/a MBI (MBI)
Project Location: MBI – Lansing, MI; Michigan State University (MSU) – Lansing, MI; Idaho National Laboratory (INL) – Idaho Falls, ID

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Principal Investigator: Farzaneh Teymouri, Ph.D.; teymouri@mbi.org; 517.336.4622

Executive summary

MBI, a 501c(3) company focusing on de-risking and scaling up bio-based technologies, has teamed with Michigan State University and the Idaho National Laboratory to develop and demonstrate process improvements to the ammonia fiber expansion (AFEX) pretreatment process. The logistical hurdles of biomass handling are well known, and the regional depot concept - in which small, distributed bioprocessing operations collect, preprocess, and densify biomass before shipping to a centralized refinery - is a promising alternative to centralized collection.

AFEX™ (AFEX is a trademark of MBI) has unique features among pretreatments that would make it desirable as a pretreatment prior to densification at the depot scale. MBI has developed a novel design, using a packed bed reactor for the AFEX process that can be scaled down economically to the depot scale at a lower capital cost as compared to the traditional design (Pandia type reactor). Thus, the purpose of this project was to develop, scale-up, demonstrate, and improve this novel design

The key challenges are the recovery of ammonia, consistent and complete pretreatment performance, and the overall throughput of the reactor. In this project an engineering scale packed bed AFEX system with 1-ton per day capacity was installed at MBI's building. The system has been operational since mid-2013. During that time, MBI has demonstrated the robustness, reliability, and consistency of the process. To date, nearly 500 runs have been performed in the reactors. There have been no incidences of plugging (i.e., inability to remove ammonia from biomass after the treatment), nor has there been any instance of a major ammonia release into the atmosphere. Likewise, the sugar released via enzyme hydrolysis has remained consistent throughout these runs. Our economic model shows a 46% reduction in AFEX capital cost at the 100 ton/day scale compared to the traditional design of AFEX (Pandia type reactor).

The key performance factors were demonstrated; >94% ammonia recovery, >75% sugar yields at high solid loading, and complete utilization of the sugars for ethanol production at the 2500 liter scale. Fermentation tests were performed using *Zymomonas mobilis 8b* and densified AFEX-treated corn stover at >20% solid loading. The obtained titer (~60g/l), productivity (2.5 g/L-h), and yield (330 L/tonne of biomass) exceeded the performance targets set out by NREL. The key findings from these efforts are: no contamination was observed, no cleanup of the sugar stream was required, and no major nutrient addition was required. Our economic model shows that using a packed bed design for the AFEX process and pelleted AFEX-treated biomass reduces the ethanol production cost by 24% when compared to using the traditional AFEX design.

1.0 Introduction

The U.S. Department of Energy (DOE), Office of Energy Efficiency & Renewable Energy's (EERE) Biomass Multi-Year Program Plan (November 2010) details plans for achieving two major goals: 1) enable the production of biofuels nationwide and reduce dependence on oil through the creation of a new domestic bioenergy industry supporting the Energy Independence and Security Act (EISA) goal of domestic production of 36 billion gallons per year of renewable transportation fuels by 2022, and 2) increase biopower's contribution to national renewable energy goals through increasing biopower generating capacity. Critical technology barriers identified in EERE's plan are 1) feedstock supply, including logistics systems and sustainable high quality feedstock supply, and 2) conversion technology development. Market barriers include 1) feedstock availability and cost, 2) agricultural sector-wide paradigm shift, 3) high risk of large capital investment, and 4) inadequate supply chain infrastructure. The EERE's Biomass Program activities in conversion R&D are aimed at reducing processing costs for advanced biofuels. Expected outcomes of this program are pre-commercial advances in next generation technologies and biomass feedstocks that are available both sustainably, and cost effectively. MBI and project partners have addressed these challenges and work toward these outcomes through improvements to a single unit operation in a process to speed commercialization and economic attractiveness of biofuels.

Challenges Facing Lignocellulosic Biorefineries

Large centralized biorefineries (50-100 million gallons/yr) face a significant challenge in feedstock supply logistics (Hess et al., 2009; Richard, 2010; Carolan et al., 2007); specifically, the high cost of transporting the vast amounts of lignocellulosic biomass required to supply the production of fuels and chemicals at this scale. To be viable these biorefineries would combine all of the operations of biomass storage, pretreatment, hydrolysis and fermentation in a large facility which would process around 2,000-5,000 tons of biomass per day. The logistical, contracting and storage issues connected with supplying these large bioconversion plants with consistent feedstock material are formidable. These facilities are also tied irrevocably to whatever biomass exists in their immediate collection areas, since it is prohibitively expensive to ship low bulk density biomass more than a few dozen miles. The resulting feedstock supply uncertainties add to the risk and expense of cellulosic biofuels.

Potential Solution: Decentralized Preprocessing and Pretreatment

One of the leading concepts for addressing the feedstock logistics challenge is the relocation of preprocessing and pretreatment operations closer to biomass feedstock harvest locations through a system of Regional Biomass Processing Depots (RBPDs). In this decentralized concept a series of small, geographically dispersed RBPDs would preprocess, pretreat, and densify locally available biomass prior to transport to a central biorefinery for final conversion into advanced biofuels/chemicals. This decentralized approach offers substantial benefits to cellulosic biofuel production including:

- Aligns biomass production scale with the scale of cellulosic biorefineries
- Incentivizes rural interests to participate in the biofuel value chain, potentially including ownership in the RBPDs
- Utilizes conventional equipment to store and handle densified biomass
- Reduces transportation costs by increasing the density of the material prior to transport
- Enables the biorefinery to contract with a few RBPDs instead of thousands of farmers
- Reduces biorefinery capital costs by removing the pretreatment operation
- Produces a stable, highly densified feedstock commodity of consistent quality
- Eliminates the need to treat dust and fines as industrial waste at the central biorefinery

The RBPD concept has the potential to significantly accelerate the commercialization of cellulosic biofuels and chemicals through improved-feedstock logistics systems and the establishment of a consistent feedstock commodity for use by integrated biorefineries. The positive impact that this system could have on rural development is substantial as it would create regional jobs and establish a flexible commodity product that will have multiple uses in several markets and thereby tempers the effects of volatility in a single market (Carolan et al., 2007).

AFEX technology has a significant advantage, as it is one of the few pretreatments that is a dry biomass in/dry biomass out process. AFEX can produce a dry, stable, conversion-ready feedstock of high bulk density and quality for efficient conversion to fuels and chemicals in a biorefinery. The RBPD concept is a key element for successfully addressing supply-chain challenges that impact cost-effectiveness. However, an inexpensive pretreatment, suitable to a wide variety of feedstocks and fermentation systems, is essential to enable the RBPD concept and achieve our commercial goals.

Pretreatment Challenge: The economics of conventional dilute acid, AFEX, steam explosion, and other corn stover pretreatment technologies have been compared in detail (Eggeman and Elander, 2005). Dilute acid and AFEX were found to be among the most cost-effective pretreatment methods; however, both were still found to be very capital-intensive due to a design based on Pandia-type reactors. This type of reactor has been used for many years in the pulp and paper industry and has been adopted for a variety of pretreatment processes including AFEX, dilute acid and steam explosion. The Pandia reactor system was not specifically designed for ammonia catalyzed pretreatment and therefore has several drawbacks. Sensitivity analyses show that the primary cost drivers for an AFEX system based on this reactor are:

- Capital cost
- Equipment lifespan
- Ammonia recovery and recycle not inherent to the system
- Energy cost of moving biomass against a pressure gradient
- Complexity of operation (requiring highly skilled operators)

Additionally Pandia-type reactor systems cannot be economically scaled down to a size compatible with RBPDs. This scale-down is a critical factor in RBPDs achieving a feedstock production cost that is commercially viable. Aside from capital cost, moving the pretreatment step to a decentralized location requires a pretreatment that will provide a dry, stable, conversion-ready feedstock of high bulk density and quality for efficient conversion to fuels and chemicals in a biorefinery. The AFEX process can meet these criteria.

Project scope:

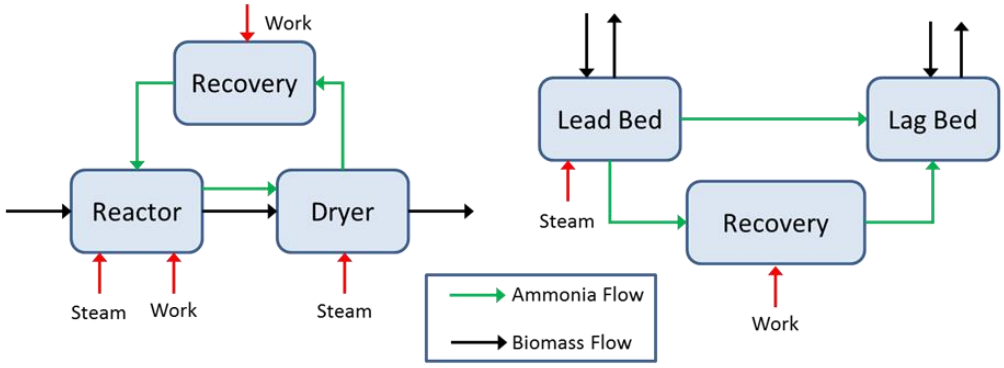
This project was designed to address the barriers noted above and to meet the goals of DOE's funding program DE- FOA-0000337 – Integrated Process Improvements for Biochemical Conversion of Biomass Sugars. The technology under development was aimed at advanced biofuels (ethanol) from corn stover. The focus of the project was to reduce the cost of conversion-ready biomass through improvements to the unit operation of AFEX pretreatment.

The team worked collaboratively to achieve the project's objectives with participant roles including: INL provided feedstock and analytical support; INL, along with MBI, used rheological and compositional analyses to ensure consistency of feedstock used in research and development efforts; MBI performed the pretreatment improvements study and oversaw quality

assurance and safety; MBI, along with MSU and INL, provided modeling and engineering support; MBI, along with MSU, conducted "use tests" of AFEX-treated material as a quality control measure to ensure fermentability of processed biomass.

AFEX Technology

The conventional AFEX process (AFEX 1) utilizes a Pandia-type reactor to produce the specific temperature and pressure required for optimal biomass feedstock pretreatment. This project addressed the high capital costs of AFEX 1 by replacing the Pandia-type reactor with a new design that is simpler in equipment requirements and operation (fewer moving parts) and incorporates ammonia recovery and reuse directly in the reactor (not an additional unit operation as with the AFEX 1 Pandia-type reactor) (Figure 1).



AFEX 1

- Initial design created in early 2000s
- Based on Pandia-type reactors
- Continuous treatment process
- High capital cost, desirable for high (1000+) tons/day

AFEX 3

- Vertical packed bed batch reactors in pairs
- Ammonia recovered directly within beds
- Low capital, simple design suitable for small (100) tons/day

Figure 1. Simple process diagram for AFEX1 and AFEX3 system

To address the primary cost drivers of the AFEX 1 system cited above, the MBI team has developed an approach to the AFEX process that exploits the chemical and physical characteristics of ammonia. This includes loading ammonia in the gaseous rather than liquid phase and using moist biomass to recover the ammonia in a cyclical fashion. Because this approach is not possible with the Pandia-type reactor, MBI developed an alternative reactor design (AFEX 3) as a test bed to evaluate process improvement strategies.

The AFEX 3 process consists of seven primary steps: 1) load biomass, 2) pre-steam, 3) charge ammonia, 4) soak, 5) depressurize, 6) steam strip, and 7) remove biomass (Campbell et al., 2013). This process is performed using pairs of reactors to pass the ammonia from one reactor to the next. While biomass is loaded into one reactor and pre-steamed (steps 1 and 2), biomass in a second reactor is in the soak phase (step 4). After pre-steaming reactor 1, reactor 2 undergoes depressurization (step 5) and steam stripping (step 6), which removes ammonia from the reactor. Simultaneously, this ammonia is repressurized and charged into the first reactor (step 3). The first reactor is then charged with

ammonia and biomass and begins the soak phase (step 4), while the treated biomass is removed from the second reactor (step 7), and new biomass is loaded and pre-steamed (steps 1 and 2). The first reactor is then depressurized and steam stripping performed, and the cycle repeats. A diagram of the ammonia and steam flow of these steps is shown in Figure 2. A detailed description of each of these steps is given by Campbell, et al, 2013 (Appendix A).

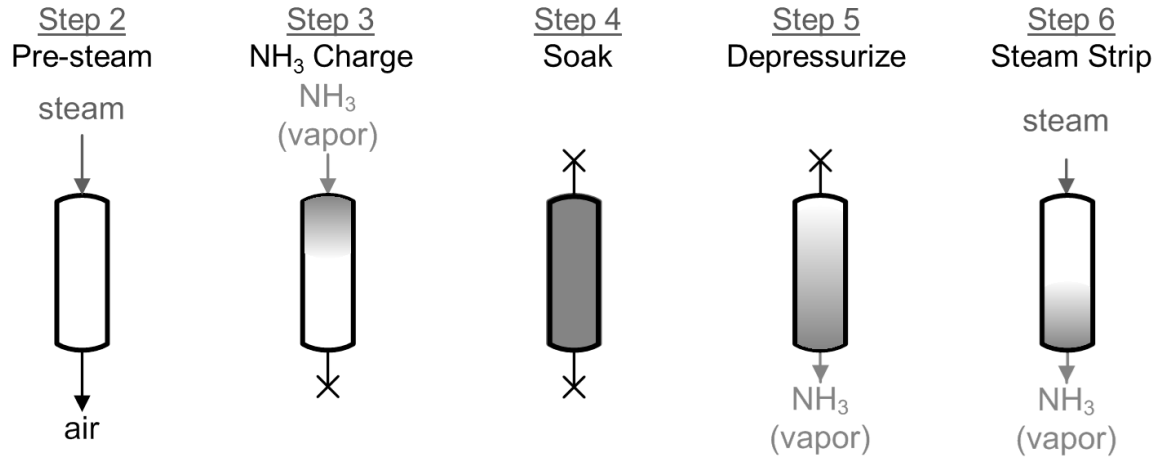


Figure 2: Diagram showing ammonia and steam flow during the major processing steps of AFEX. Loading (step 1) and unloading (step 7) biomass are not shown. The "X" at the top and bottom of reactors indicates the valve is closed and sealed.

With the AFEX 3 concept, a single charge of ammonia can be used to AFEX-treat sequential packed beds of biomass. The treatment cycle may be repeated indefinitely. Unlike AFEX 1, which requires the use of a dryer to recover NH3, NH3 recovery and re-use is accomplished in AFEX 3 without the use of a dryer. Loss of NH3 by irreversible reactions with biomass may be compensated as needed by addition of makeup NH3.

To investigate the AFEX 3 concept shown in Figure 2, MBI designed and fabricated a test skid with three 4-inch outside diameter (OD) by 48-inch long bed vessels. Figure 3 is a photograph of the fabricated skid. The skid is equipped with a small NH3 compressor and all of the valves, manifolds, and instruments needed to practice the process shown in Figure 2.

Prior to this project, using our AFEX 3 lab skid unit, the initial proof of concept for AFEX 3 design was demonstrated by showing a) acceptable pretreatment efficacy, releasing >75% sugars in subsequent hydrolysis process and b) 98% recovery of ammonia from the biomass. While running the lab skid AFEX 3 unit, the following primary challenges associated with the AFEX 3 concept for large scale operation were identified: 1) efficient biomass transfer through the system; 2) efficient interaction of the ammonia with the biomass; and 3) efficient ammonia recovery and reuse.

The overall objective of this project was to develop improvements to mitigate the primary risks associated with this approach at engineering scale.

Figure 3. AFEX 3 lab-scale test skid at MBI

Objectives:

The objective of this DE-FOA-0000337 Topic Area 1 (Process improvements to a single unit operation to be incorporated into an integrated system) project was to develop AFEX process improvements that lower capital and operating costs by:

- Altering the AFEX pretreatment system design to exploit the physical and chemical characteristics of the ammonia catalyst and enable:
  - Improved ammonia loading and activity efficiency
  - Improved biomass transfer efficiency within the system
  - Improved ammonia recovery and reuse efficiency

Project's goals:

High level goals for the project were:

- Design and build an engineering scale AFEX 3 system
- Develop process parameters and performance data for AFEX 3 engineering scale unit
- Develop a techno-economic model to validate the process improvement targets
  - Milestone: using techno economic model, data collected from AFEX 3 engineering scale system must show cost reduction of ≥ 43% for capital and operating costs compared to conventional AFEX 1 at commercial scale (100 TPD).
- Verify fermentability of the generated sugars from biomass treated in the AFEX 3 engineering scale unit for production of ethanol
  - Milestone: using techno economic model, data collected from AFEX 3 engineering scale system and fermentation test must show cost reduction of ≥ 16% for production of ethanol by replacing AFEX 1 design with AFEX 3 design.

Project activities:

The conceptual logic diagram shown in Figure 4 was followed to demonstrate corn stover AFEX pretreatment in lab and engineering scale packed bed reactor systems, to demonstrate the cost saving over conventional AFEX based on techno-economic modeling, and to assess the fermentability of the AFEX-treated corn stover hydrolysate. The logic diagram indicates the decision points that were used to determine whether to continue or end each iterative loop in the development process. The detail description of each task is provided below.

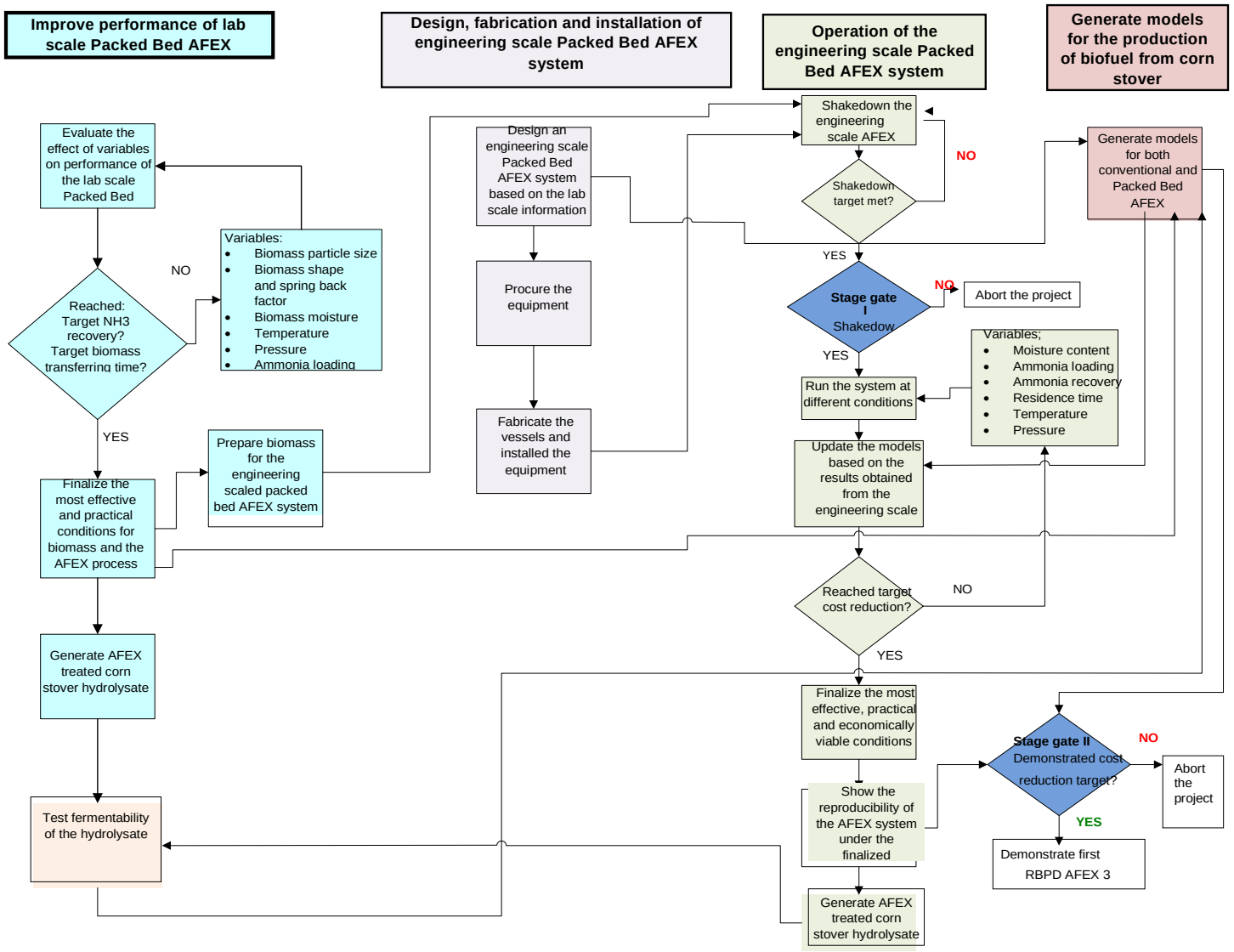


Figure 4. Conceptual logic diagram to demonstrate AFEX treatment of corn stover in lab and engineering scale AFEX 3 system

Tasks description and accomplishments:

Task A. Determine the effects of feedstock specifications (particle size, shape factor, moisture) and reactor design on pretreatment efficacy (sugar yield and feedstock throughput) and ammonia recycle at lab scale

Description:

The existing AFEX 3 lab skid is used to address the risks associated with biomass throughput, NH3 interaction with the biomass packed bed, and NH3 recovery and reuse. INL provides feedstock with consistent specifications to evaluate the effect of parameters such as corn stover particle size, shape and moisture. Statistical sampling of the feedstocks ensures that feedstock variability does not confound test results. Enzyme hydrolysis is used to assess the effects of feedstock specifications and the impact of improvements on sugar yield.

Accomplishments:

Subtask A.1. Produce ground corn stover for lab scale tests

An experimental design was developed that included a feedstock matrix with three levels of median/average particle size, narrow or wide particle size distributions, and two shape factors. Particle shape (shape factor) was varied by using two different grinder designs, a hammer mill and a knife mill (chipper). Particle size was varied by changing the collection screen mesh on the grinder (3/16, 5/16, and ½-inch screens for the hammer mill; 2 mm and 3/16 and ½-inch screens for the knife mill). Finally, grinding was conducted both with and without pneumatics to determine if the width of the resulting particle size distribution could be improved upon.

Low-cob corn stover was procured as described in Task B below. Four stover bales were randomly selected and weighed, and the weights and bale identifications were recorded. The Idaho National Laboratory (INL) Process Development Unit (PDU) was used to prepare the samples for the feedstock matrix. The samples were prepared as described below.

For the hammer milled samples, the stover was first ground to 2-inch minus using Vermeer BG 480. The 2-inch minus stover was conveyed into the drum dryer, and dried stover exiting the dryer was conveyed into a Bliss hammer mill fitted with the appropriate collection screen and operated with pneumatic assist. Material passing the screens was conveyed from the collection chamber and fed directly into separate 55-gal drums for each sample. Care was taken to clear material remaining in the system both before and after each run by passing a quantity of stover through the system before beginning sample collection.

For the knife milled samples, the stover bales were hand-fed into a HG 200 hammer mill that had been retrofitted with a chipper drum to convert the mill into a chipper mill. The HG 200 with the chipper drum was fitted with the appropriate collection screen and operated both with and without pneumatic assist. Material passing through the screens was fed directly into separate 55-gal drums for each sample. Care was taken to clear material remaining in the system both before and after each run by passing a quantity of stover through the system before beginning sample collection.

After each group of samples was prepared, the buckets from each sample run were mixed to ensure homogeneity and riffle split into a 10-kg sample which was aliquotted to four five-gallon buckets and sealed and shipped to MBI. The second split, comprising 3-10 kg, were aliquotted to additional buckets and stored indoors at INL for analysis. Table 1 summarizes the description of the samples that were sent to MBI.

Table 1. Samples prepared by INL

Number	Identifier	Description
1	H 3/16 N	Hammermill with 3/16 screen with pneumatics
2	H 5/16 N	Hammermill with 5/16 screen with pneumatics
3	H 1/2 N	Hammermill with 1/2 inch screen with pneumatics
4	H 3/16 W	Hammermill with 3/16 screen without pneumatics
5	H 5/16 W	Hammermill with 5/16 screen without pneumatics
6	H 1/2 W	Hammermill with 1/2 inch screen without pneumatics
7	K 2mm N	Chipper drum with 2mm screen with pneumatics
8	K 3/16 N	Chipper drum with 3/16 screen with pneumatics
9	K 1/2 N	Chipperdrum with 1/2 inch screen with pneumatics
10	K 2mm W	Chipper drum with 2mm screen without pneumatics
11	K 3/16 W	Chipper drum with 3/16 screen without pneumatics
12	K 1/2 W	Chipper drum with 1/2 inch screen without pneumatics

Feedstock characterization, water activity, permeability, moisture content, loose bulk density, compressibility, percent springback, wall friction, particle size/shape distributions, unconfined yield (shear) strength, and total percent ash content for all of the corn stover samples listed in the Table 1 were measure by INL team. The detail report for this activity is provided in Appendix B.

MBI evaluated the effect of particle size, shape factor and particle size distribution on the performance of AFEX 3 process. Performance was evaluated based on the efficiency of ammonia recovery/recycling and the reactivity level of the treated biomass in enzyme hydrolysis. Hydrolysis was performed using the method provided as part of the validation package. The benchmark for enzyme hydrolysis was to obtain greater than 75% glucose yield and the benchmark for ammonia recovery was to recover and recycle more than 95% of the ammonia with purity higher than 85%. INL provided corn stover samples with different specifications in two campaigns. The particle size distribution for most of the samples processed in the first round (Table 1) of the campaign was excessively skewed toward fines. Several of these samples were tested in the AFEX 3 lab scale system. All of the samples treated in the AFEX 3 system showed higher than 75% glucose yield in hydrolysis. However, with one exception, all of them showed poor ammonia recovery (an example is provided in Figure 5). A sample prepared using a chipper drum with 1/2" screen (largest screen size used in the first campaign) without pneumatic assist showed better ammonia recovery, in the acceptable range (Figure 6).

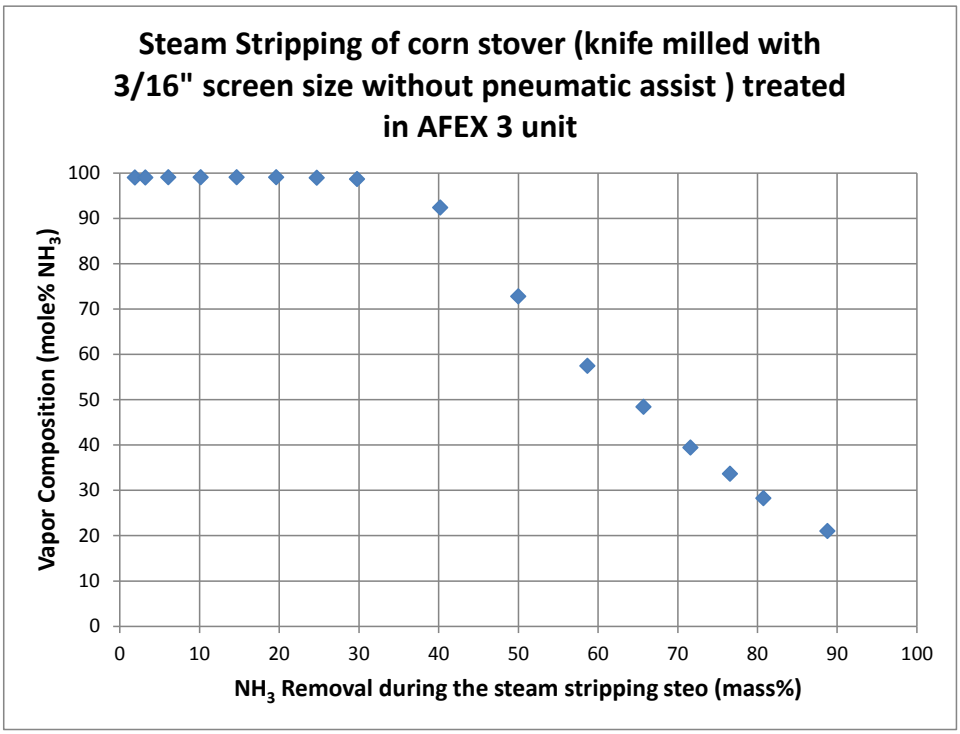


Figure 5. Composition of the vapor recovered during steam stripping of corn stover (knife milled with 3/16" particle size without pneumatic assist) treated in AFEX 3 lab skid unit.

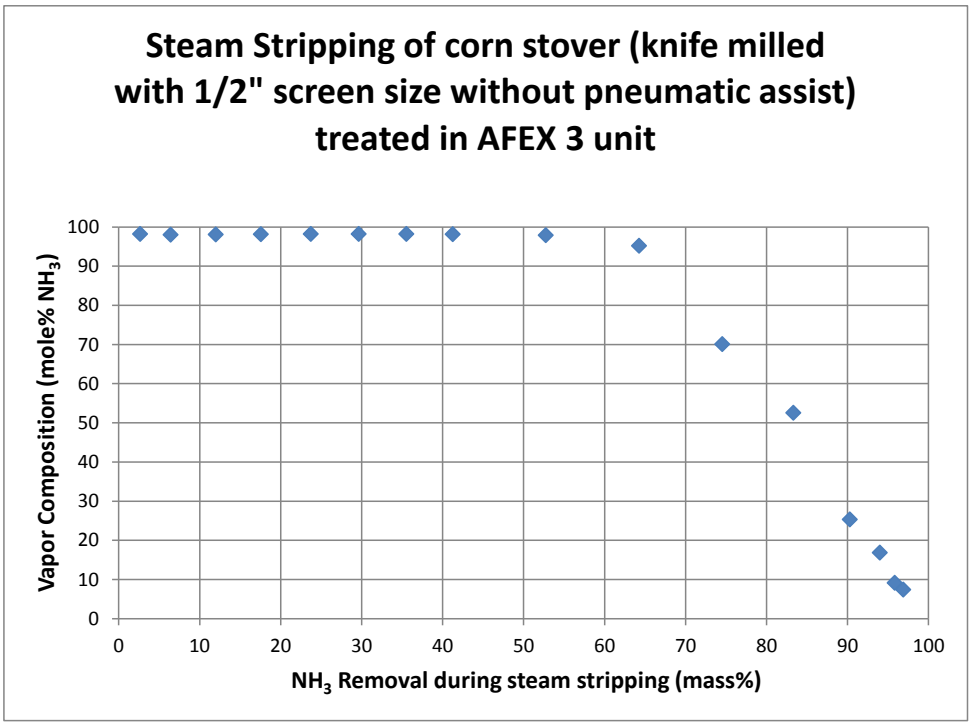


Figure 6. Composition of the vapor recovered during steam stripping of corn stover (knife milled with 1/2" particle size without pneumatic assist) treated in AFEX 3 lab skid unit.

Based on this observation, samples for the second round of the campaign were prepared using a mill with a larger screen size. The standard configuration for the INL feedstock PDU has an intermediate drying step between the two grinders. INL prepared a series of samples using various configurations of these steps in an attempt to minimize particles smaller than 1 mm. The preparation included two-stage grinding with and without intermediate drying, using a variety of screen sizes. It was expected that when the stover was dried between grinds, the percentage of fines would be higher, which was confirmed. It was ultimately determined that the first stage grind size had little effect on the distribution of fines and that this was dominated by the second grind size. Single stage grinding was then explored as a method of reducing the fines. Because the first stage grind is used to break the bale, a larger screen size is usually utilized to allow a reasonable throughput. The bale was broken and a good throughput was maintained using a 1-inch screen size. 50 kg of this material was prepared and shipped to MBI for testing. Evaluation of these samples showed that single stage grinding using a hammer mill with a 1" screen produced a sample that showed the best performance in terms of both ammonia recovery and hydrolysis. The ammonia recovery analysis for this sample is provided in Figure 7.

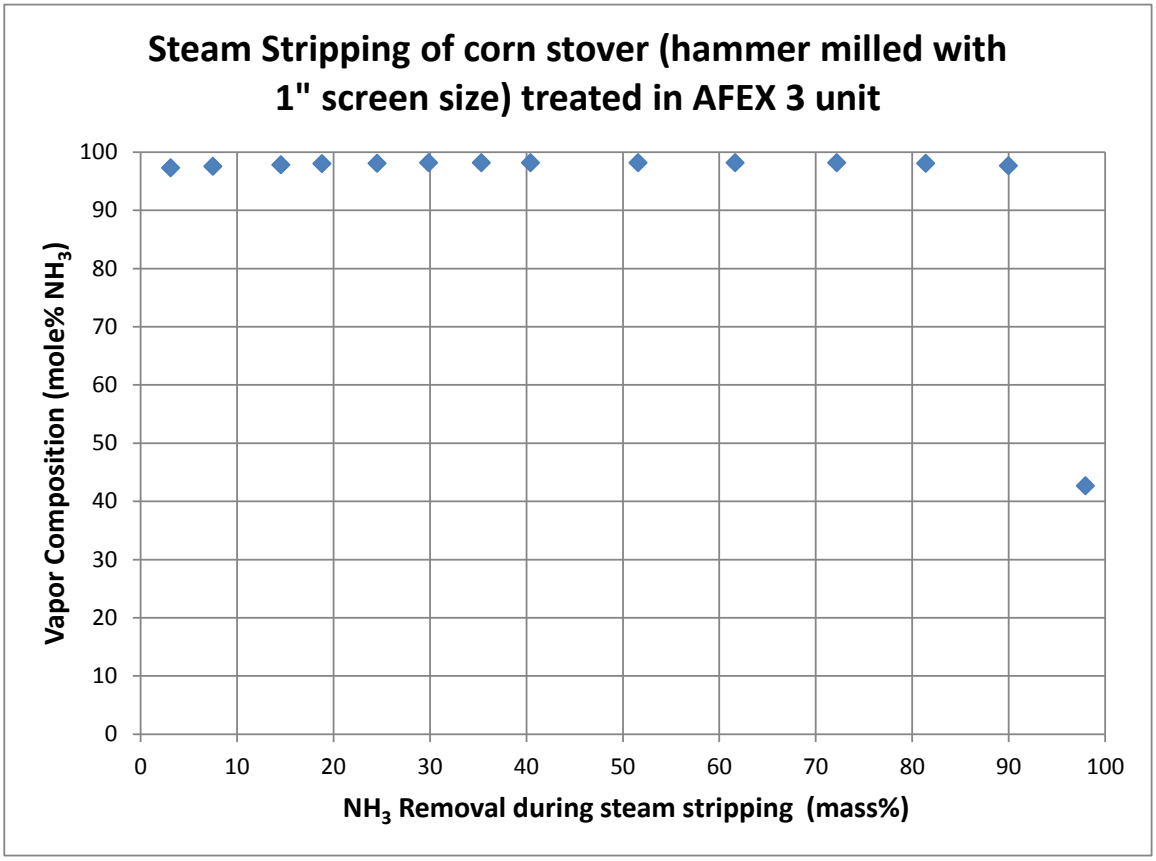


Figure 7. Composition of the vapor recovered during steam stripping of corn stover (hammer milled with 1" particle size) treated in AFEX 3 lab skid unit.

Subtask A.2. Loading and unloading of the vessels

Our preliminary cost analysis has shown that at an acceptable performance level (ammonia recovery and reactivity of the treated biomass as documented in Appendix F of our contract), the two factors that have the most impact on the capital cost of the AFEX 3 system are bed density and the processing time. Considering our current AFEX 3 system performance and processing time, the bed density in each reactor must be at least 100 kg/m^3 in order to meet our cost reduction target.

The original plan was to use a vacuum blower to load the biomass into the AFEX 3 reactor vessels and to unload the reactors by dropping the treated biomass out of fast-opening closures at the bottoms of the reactors. However, testing biomass such as corn stover and wheat straw in our AFEX 3 lab skid showed that the target bed density (100 kg/m^3) in the reactor is not achievable using a vacuum blower to load the biomass. Therefore, an alternative method, using a cylindrical basket for loading and unloading the biomass into and out of the reactor was developed. Six cylindrical baskets (each 4" diameter and 12" long) were fabricated (in-house) out of stainless steel mesh sheets. The end plates of the baskets were made out of stainless steel perforated sheets with 41% open area to allow axial flow of vapor in and out of each basket (figure 8 shows a picture of one of the baskets made by MBI team). As it has been explained in detail by Campbell et al. 2013 biomass is manually compressed into the baskets at a bed density of approximately 100kg/m^3. Using this method, each AFEX 3 lab skid reactor is loaded with three baskets filled with biomass.

Figure 8. One of the baskets made for our AFEX 3 lab scale unit

The effect of using the baskets on the performance of AFEX 3 process was evaluated in the treatment of corn stover and oat hulls. Oat hulls were used as the model biomass. MBI has extensive experience with processing oat hulls in the lab-scale AFEX 3 system and has thoroughly characterized the performance of the AFEX 3 system in the treatment of oat hulls. Additionally, the narrow particle size distribution of unground oat hulls allows the results of these evaluations to be interpreted without the confounding influence of a particular grind method. These tests were also carried out with the corn stover used for our initial validation visit. These experiments showed that using baskets in the AFEX 3 process does not compromise the performance of AFEX in terms of ammonia recovery level (Figure 9), processing time and reactivity of the treated biomass. However, while working with the baskets it was observed that the biomass was not uniformly compressed in the baskets. Having a uniformly packed biomass bed is critical for efficient performance of the AFEX 3 system. Therefore shorter baskets (each with 4" diameter and 6" length) were fabricated to address this issue and to eliminate the chance of bridging during packing the baskets with biomass. Using the shorter basket, each AFEX 3 lab skid reactor is loaded with 6 baskets filled with biomass.

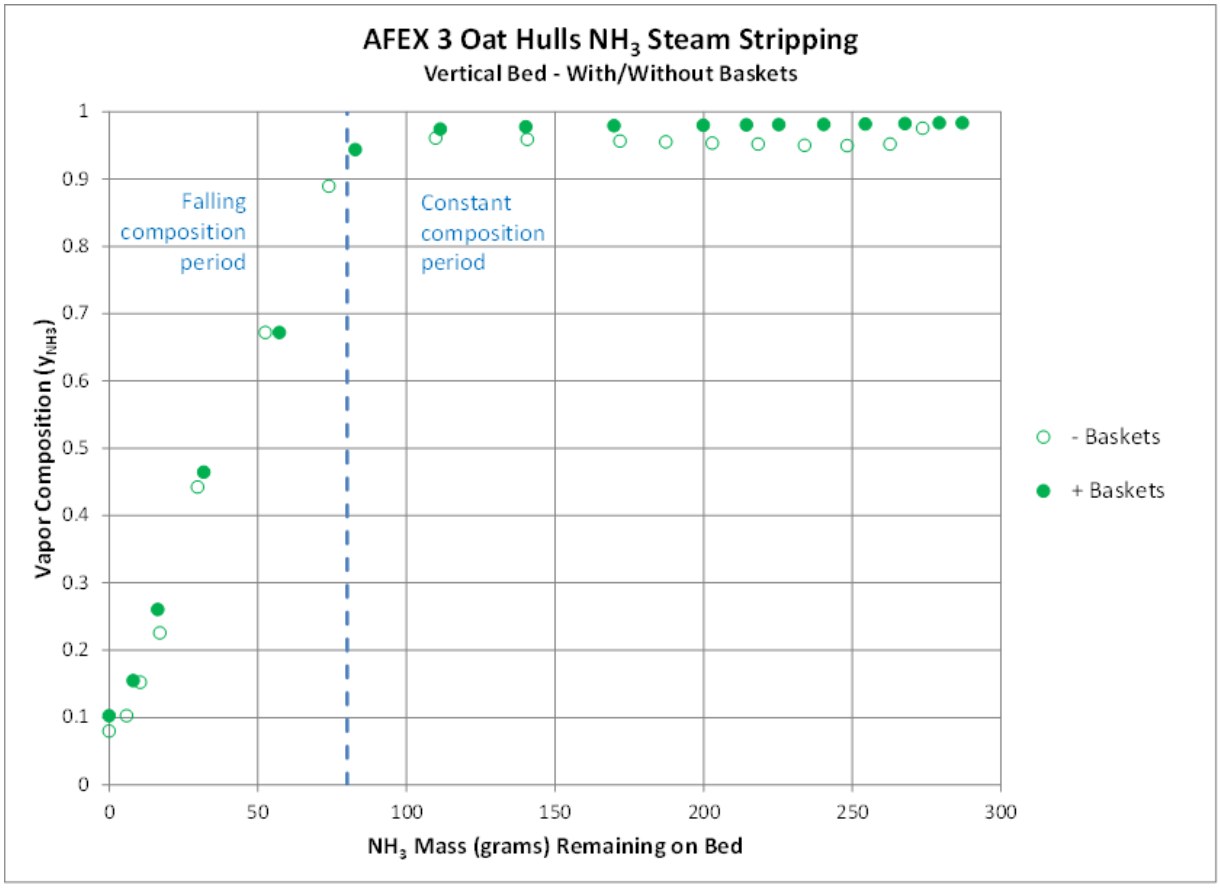


Figure 9. Composition curves for vapor collected during steam stripping of a bed of AFEX-treated oat hulls packed in the reactor tube using the baskets or without the baskets

Conceptual design for loading/unloading the reactor beds:

The loading process at a depot includes adding moisture to the biomass inside a mixing hopper, feeding material from the mixing hopper into perforated baskets, compressing the material into the baskets, and loading the baskets into the large vertical reactor. The unloading process includes removing the treated biomass from the baskets and placing the material inside a hopper/conveyor system to prepare the material for subsequent processes, such as drying.

The equipment that will compress the material inside the perforated baskets will resemble a VP-400 four-station compression bagger (Premier Tech Chronos, Quebec, Canada) that is used to compress super sack quantities of material into dense packages that reduce costs of shipping and storage. The exact details of the design depend on the rheological properties of the wetted corn stover material. These properties, including shear (unconfined yield), wall friction, bridging, compression, and elastic recovery tests were measured by the INL team on both untreated and AFEX-treated material in order to properly design the material loading/unloading system. To validate the feeding properties of the materials as predicted by the rheological properties tests, smaller perforated baskets with diameter of 1 ft and 2 ft, respectively, were fabricated, and used for experiments to evaluate the loading performance of the material. Results of these experiments (presented below) were used for the design of a conceptual feedstock and product handling and formatting system for a full-scale AFEX 3 depot.

Detail of flowability and compressibility test conducted by INL:

MBI processes corn stover in perforated baskets. The biomass material is compressed in the baskets to a dry density of 100kg/m^3. This has been determined to be an optimal packing density, allowing flow of ammonia and steam through the biomass bed, while ensuring maximal packing

density. The packing method that is currently practiced by MBI includes the use of a lever arm and packing plunger to compress biomass into the test baskets. The process is planned to be scaled up to a depot-scale processing operation, which will necessitate the use of larger baskets, currently planned for 5' diameter (60 inches diameter).

INL worked to determine the forces and pressures necessary to pack biomass into small and medium scale baskets to enable prediction of the forces, and equipment that will be necessary to pack biomass into the full scale baskets. This testing was conducted in two sections, the small scale testing was conducted in the Instron system on two different basket diameters (12 inch and 18 inch diameter), and the large scale testing was conducted with a custom fixture. An image of the testing setup for the 18" diameter basket is included in Figure 10.

This testing was also used to determine the propensity of the biomass to be retained in the basket, and the propensity to resist being dumped out. This was identified by MBI as a potential problem for biomass processing on a larger scale.

Test Method:

Testing was conducted as follows: First, the moisture content of the biomass was adjusted to be 20% wet basis by mass. This was determined to be optimal for subsequent processing. The moisture adjusted biomass was placed in the basket to be used for testing, and this biomass was then compressed. Force and displacement were recorded during testing, and this data was used to determine the maximum pressure to compress biomass, and the dry density achieved. These data were tracked and plotted to enable comparison between the different tests conducted, and to visualize the trends in the data. This was then used to predict an expected pressure for the full-scale basket.

Because of the size limitations of the Instron, a larger scale test was conducted with a custom designed fixture that was 36 inch diameter. This testing was plotted with the other data collected. Limitations on the ability to apply the forces necessary in the large size basket resulted in lower densities than were desired; however, the general trend in the data is identified.

It is also important to note that current testing at MBI is conducted in perforated wall baskets. The small scale INL testing included perforated wall baskets, however, it is expected that the final basket design will be a smooth wall basket with a perforated bottom, and so the 36 inch diameter test was conducted with a smooth wall basket. It was noted that the data for the small diameter Instron tests enables an estimation of the relative contribution of the wall friction (which is higher with a perforated wall) and the material compression resistance.

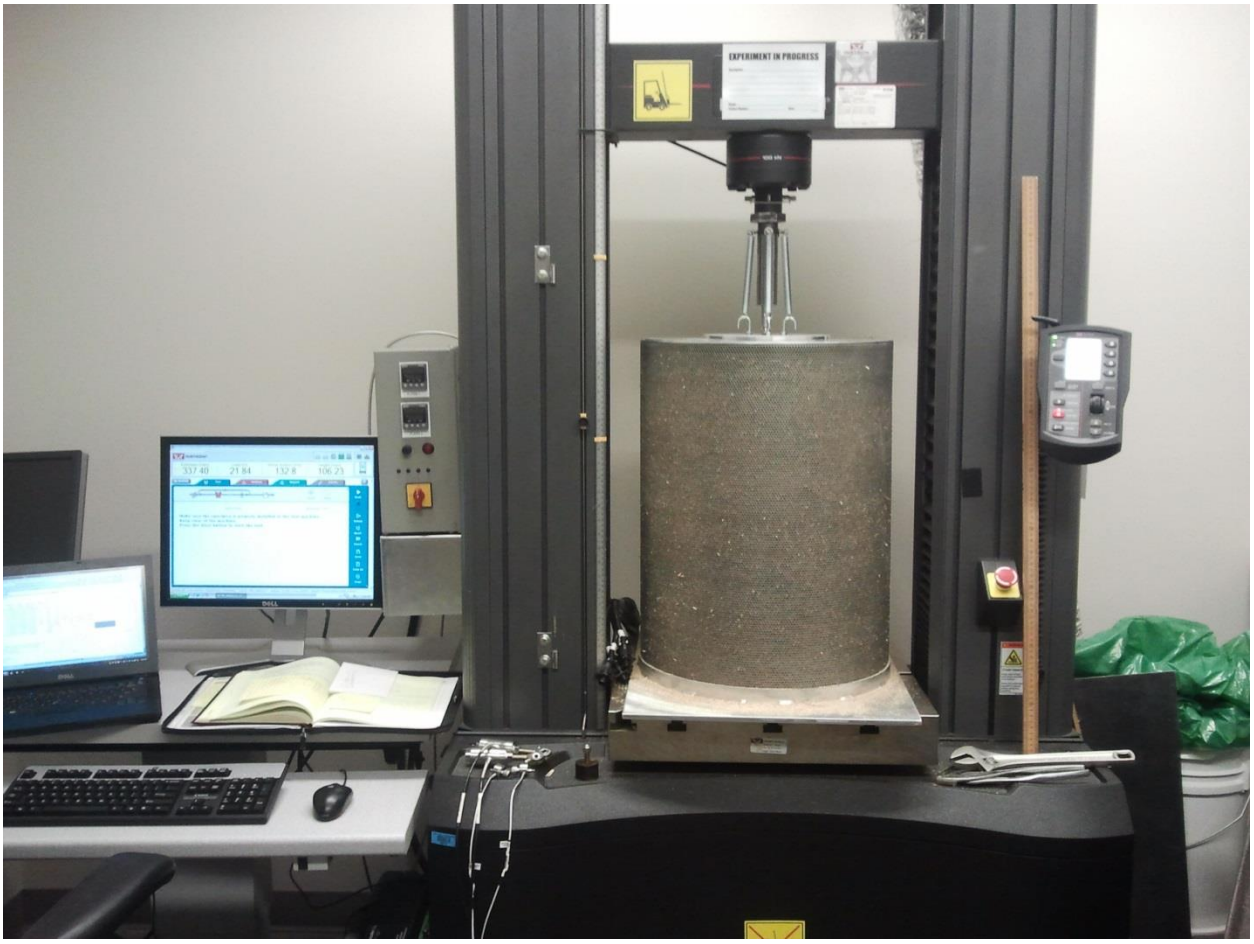


Figure 10. Small scale Instron testing

Compression Testing Results:

All of the data collected were summarized and compiled in a graph shown in Figure 111. This graph illustrates the decrease in compression pressures required for successively larger baskets. This illustrates the diminishing contribution of the wall friction (which is a function of basket radius r) as compared to the biomass compression pressure (which is a function of r^2).

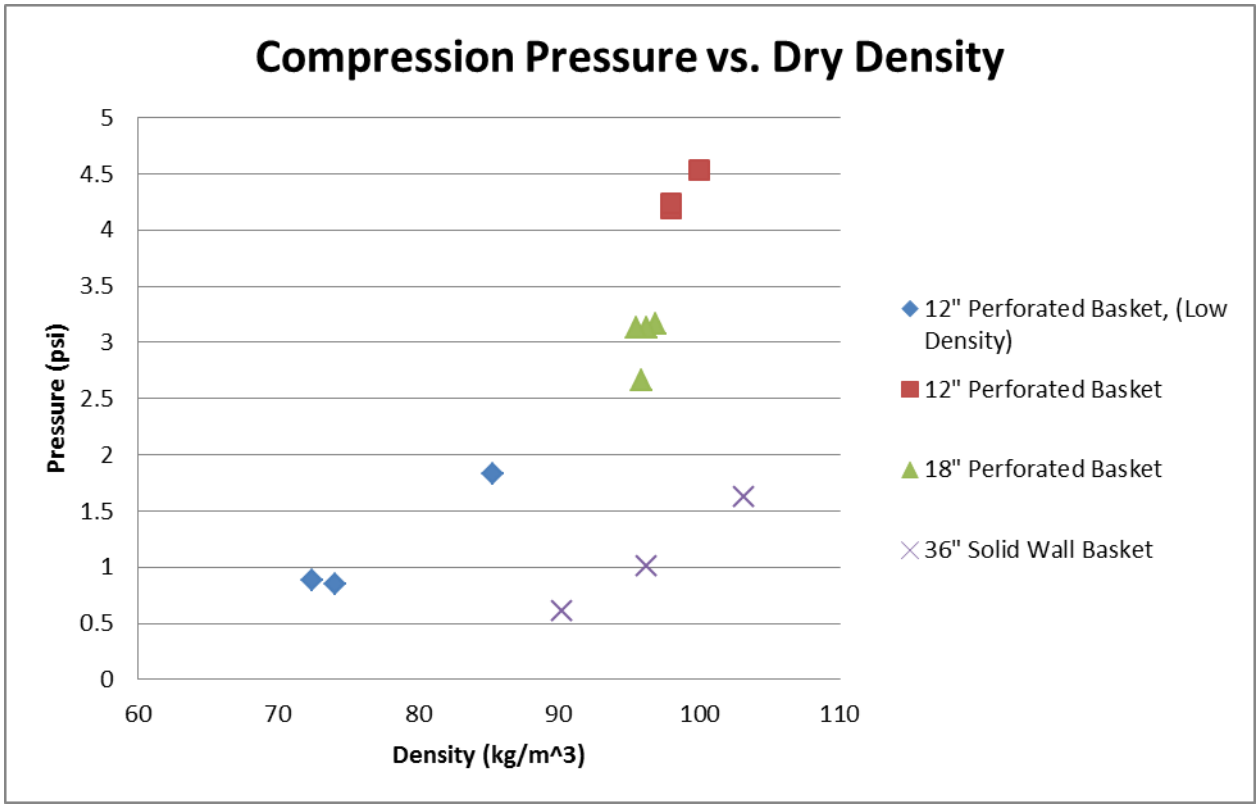


Figure 11. Compression pressure vs. achieved dry density.

Based on this testing, it was determined that on a large scale, a compression system capable of exerting a pressure of roughly 1.5psi would be sufficient to achieve the desired packing density. A margin will be designed into the final system to account for possible variations in biomass, and potential changes in desired packing density. As a rough basis for the conceptual design, a system capable of up to 4psi was designed.

Flowability Testing Results:

After compression of the biomass, the baskets were dumped into a separate receptacle to determine the propensity of the biomass to be retained in the basket after compression. With the 12 inch diameter baskets it was qualitatively observed that there was some propensity to bridge and be retained in the basket, but the 18 inch diameter baskets showed no such issues. Testing was conducted with both raw biomass and processed biomass. The treatment process renders the biomass somewhat stickier, and so the propensity to be retained in the basket is higher with the processed biomass, however, the lab testing conducted here was with material that had been removed from baskets by MBI, and did not exhibit the propensity to be retained in baskets that had been observed by MBI.

This observational data was shared with MBI, and it was expressed that there may be a significantly higher propensity of the biomass to bridge and adhere to itself directly upon being removed from the processing reactor. To enable INL to observe and compare the characteristics of the material directly post-processing, MBI shipped a full as-processed basket to INL for comparative qualitative testing. It was observed that the material did have a significant propensity to form matted clumps which adhere to the basket. This observational data informed the design of the device to dump the baskets, and the capability was conceptually designed (detail of the design is presented later in this section) into the system to enable the baskets to be shaken to remove

material that may be retained in the basket, as well as the capability to scrape the bottom of the basket between batches to dislodge any retained material.

Conceptual design developed by INL for automated biomass handling system:

The main objective of the project was to develop a design for a depot capable of processing up to 5 tons per hour of biomass. A system capable of processing these amounts of biomass requires a substantial amount of automated biomass handling, and so INL was asked to develop a conceptual design for this process.

The operations necessary to handle biomass were carefully considered in the context of an automated process. Because the process being considered is a batch process, it is necessary to load and unload biomass from reactors. These reactors are sized to handle a basket that is 60 inches in diameter, and 64 inches tall. The reactors are sized to hold 6 of these baskets. The cycle time for the reactors was considered in terms of the total desired throughput, and a spreadsheet was developed with each piece of equipment to determine the total cycle time required, and the resulting time allowable for each biomass handling operation.

After much consideration of the automation of each operation, and the time afforded for each step in the process, it was determined that the best configuration for the reactors was to load and unload each reactor from underneath. This enables the baskets to be quickly placed in the reactor, and quickly removed. Consideration was given to loading the reactors from above, but the challenges associated with using either a crane or gantry type robot to retrieve and place baskets in the reactor were substantial when compared with the challenges associated with a bottom-load reactor design.

Based on the above considerations, a flow sheet was developed for the process, and is included below in Figure 12.

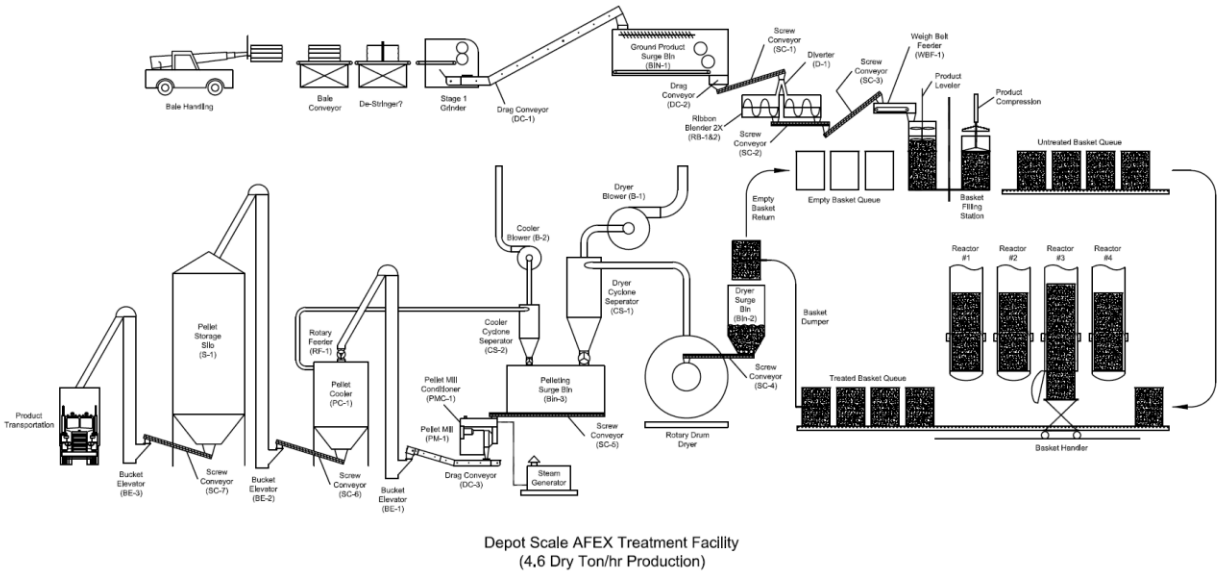


Figure 12. Conceptual system flow diagram

Conceptual CAD Model:

Based on the above conceptual flow diagram a conceptual CAD model of a system was assembled. The components are representative of what would be necessary in such a system, are primarily for illustration, and are not optimized for this process. This does, however, enable a consideration of the rough floor footprint, and an illustration of equipment necessary for the throughput desired, as well as the capacity necessary for storing the products.

Equipment that is more-or-less stock and available from a vendor is not covered here in great detail. This includes the pellet mill, dryer, grinders, associated surge bins and cyclone separators, and pellet storage bins, as well as the front end equipment such as the initial grinder and ribbon blender (the detailed cost estimate for the referenced equipment is provided under Task E). The ribbon blender is used to adjust the moisture content to the desired level.

A plan view of the conceptual system model is included in Figure 13, and an isometric view in Figure 14. The custom elements included to fill and pack baskets, load and unload baskets in the reactors, and dump the processed baskets for subsequent processing are also illustrated in more detail below.

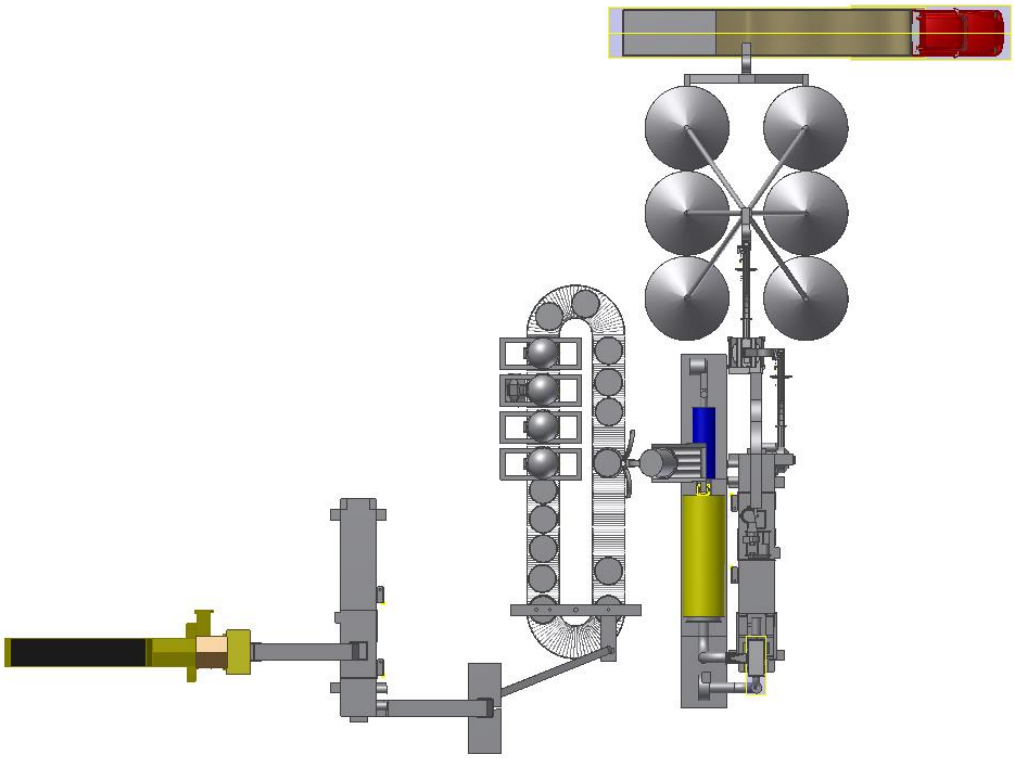


Figure 13. Plan view of conceptual system

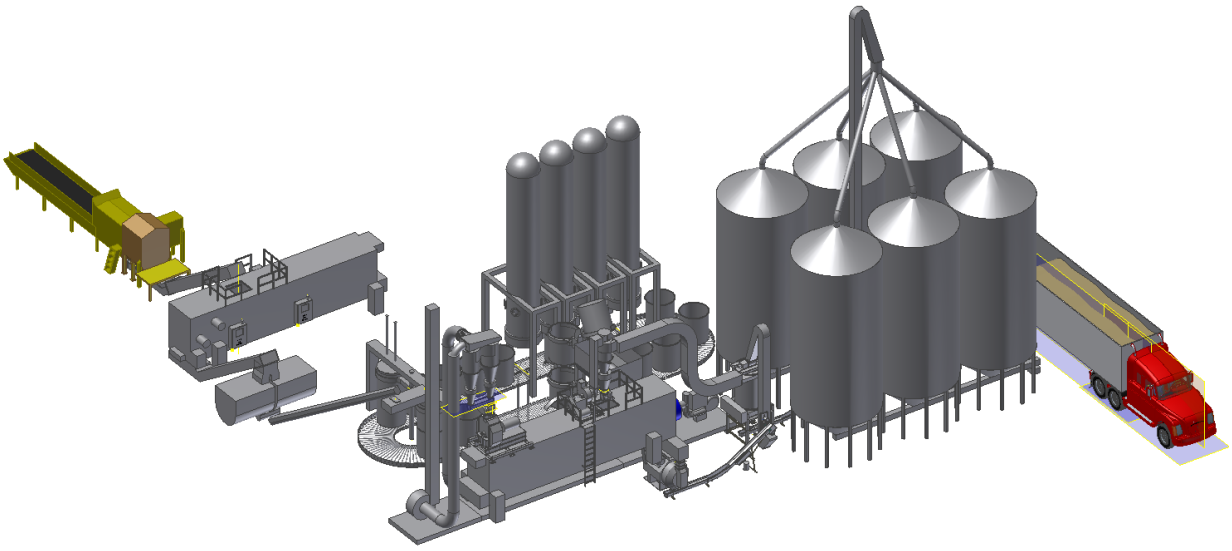


Figure 14. System overview - pelleting side

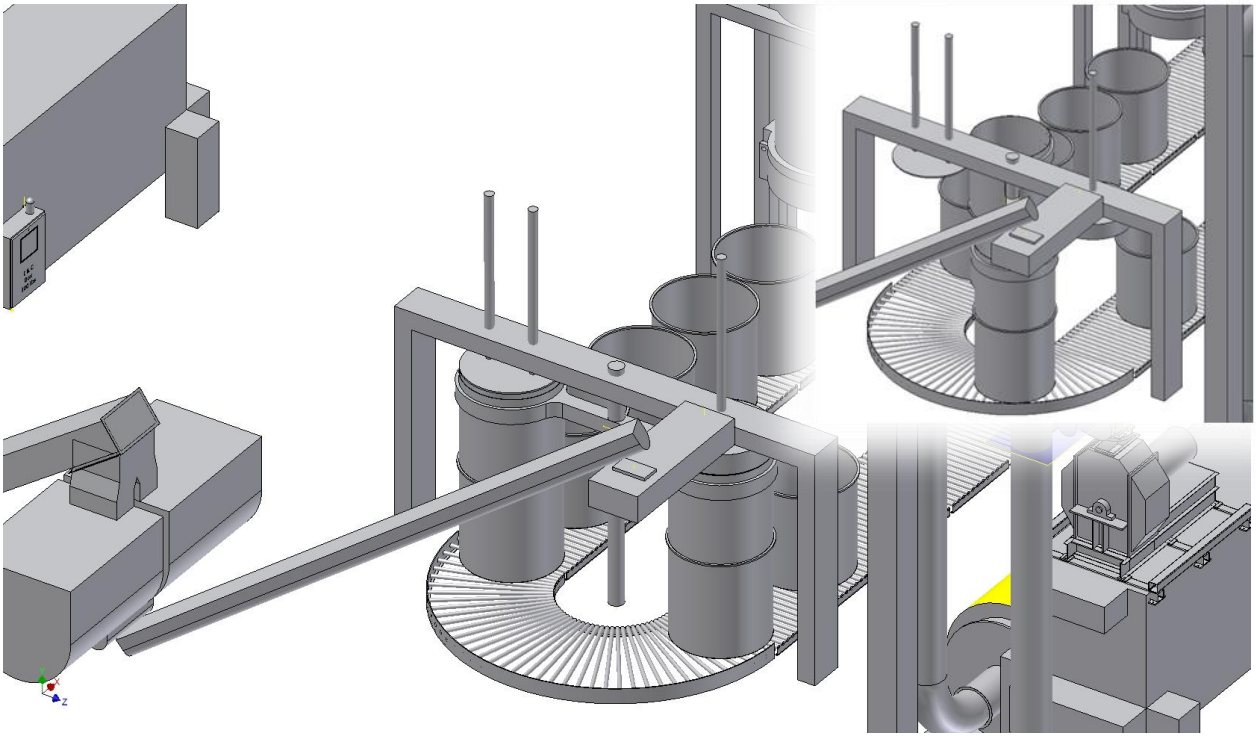


Figure 15. Ribbon blender and basket filler

The basket filler and stuffer are shown at one end of the roller conveyor in Figure 15. The filling of baskets is facilitated by a leveling bar that is extended into the basket during filling, and rotates to ensure a level fill. This bar also scours the bottom of the basket to dislodge any material left adhering to the basket after dumping. A sleeve follows the baskets around the corner of the race track conveyor to the filling station. This is necessary because the density of biomass is low, and requires nearly twice the compressed volume. After compressing, the basket is conveyed on to the reactor loader, and the sleeve cycles around to the filling station for the next basket. This is illustrated in the inset of Figure 5.

Baskets are loaded into the reactor chamber by means of a hydraulic lift shown in Figure 16. This lift moves each basket in succession into the reactor. The baskets stack, and when loading the last basket, the lift is lifting all 6 baskets into position. The baskets are retained in the reactor by means of a passive latch system illustrated in 17. This system makes it possible to load and remove baskets from the reactor without the need of active actuators inside the reactor vessel. The passive catch system relies on the hydraulic lift to move baskets into position. The catch system is made to be removable from outside the reactor in the event that the system encounters problems, enabling the baskets to be removed.

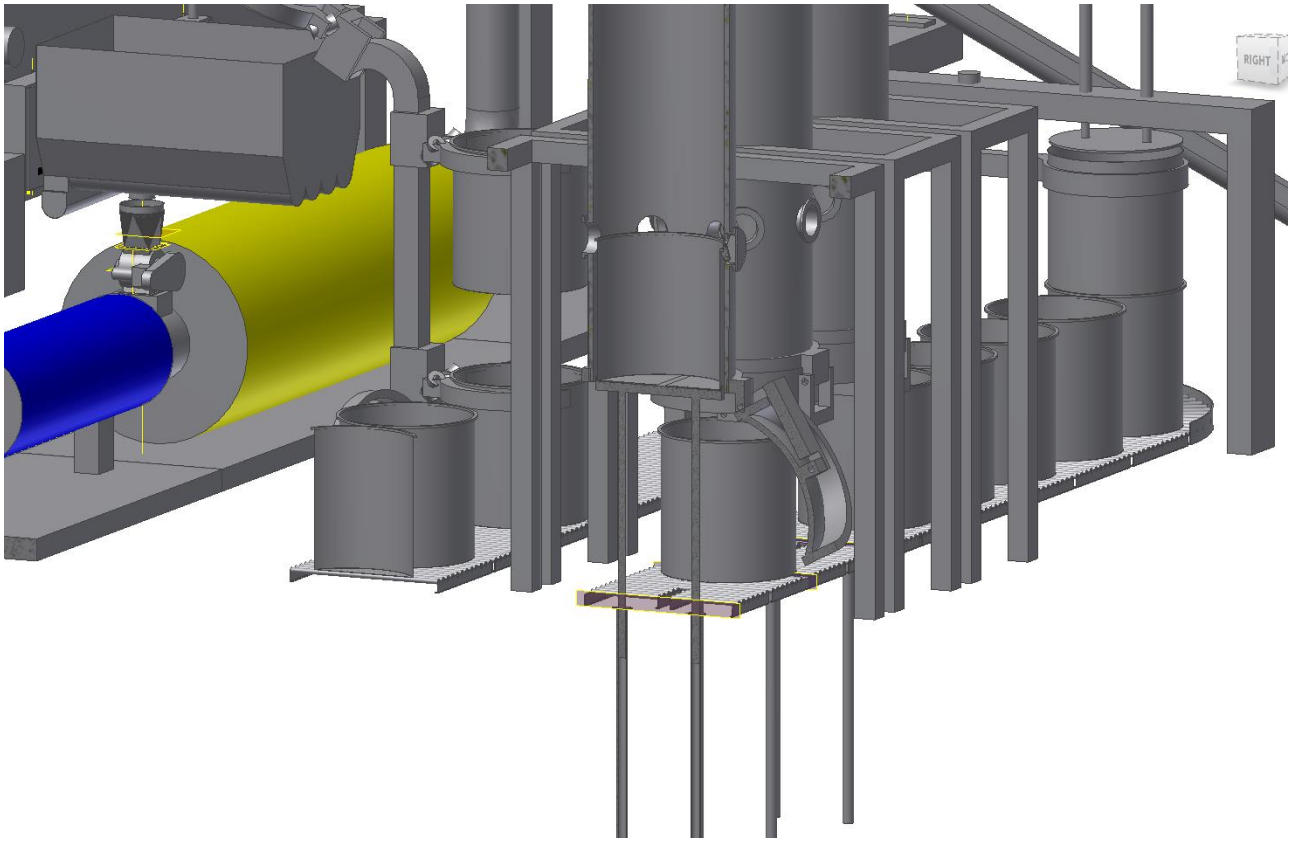


Figure 16. Section view showing basket loading and basket dumper

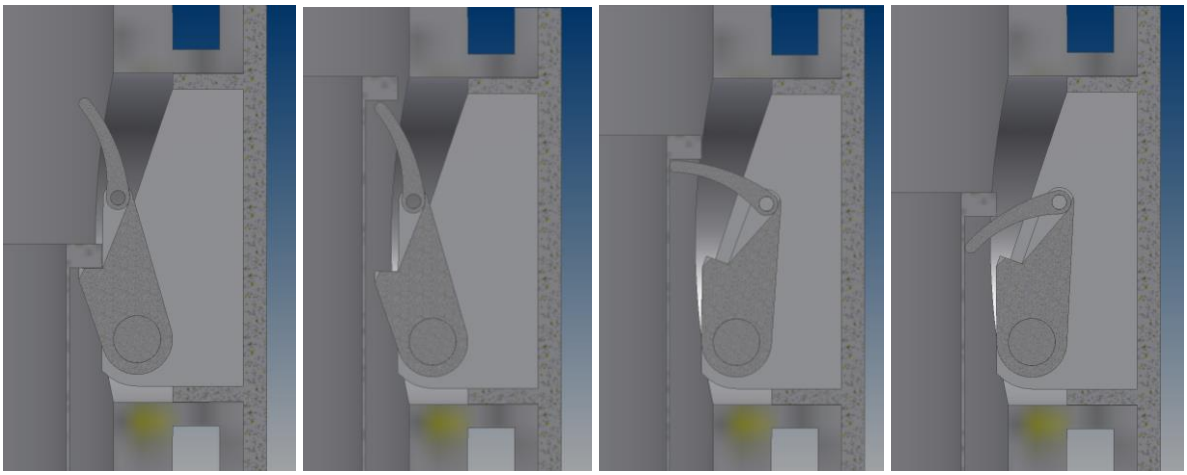


Figure 17. Basket catch operation

After the baskets are processed, the biomass material is dumped into the hopper that feeds the dryer, which is the next operation in the process. This is illustrated in Figure 8. The mechanism is only illustrative, but demonstrates the basket being moved into position in front of the dumper, being grasped, lifted, overturned and dumped into the bin. The basket may need to be shaken or given some sort of mechanical impulse to dislodge biomass, and the final system design will need a hard stop against which the basket can be driven to impart this impulse.

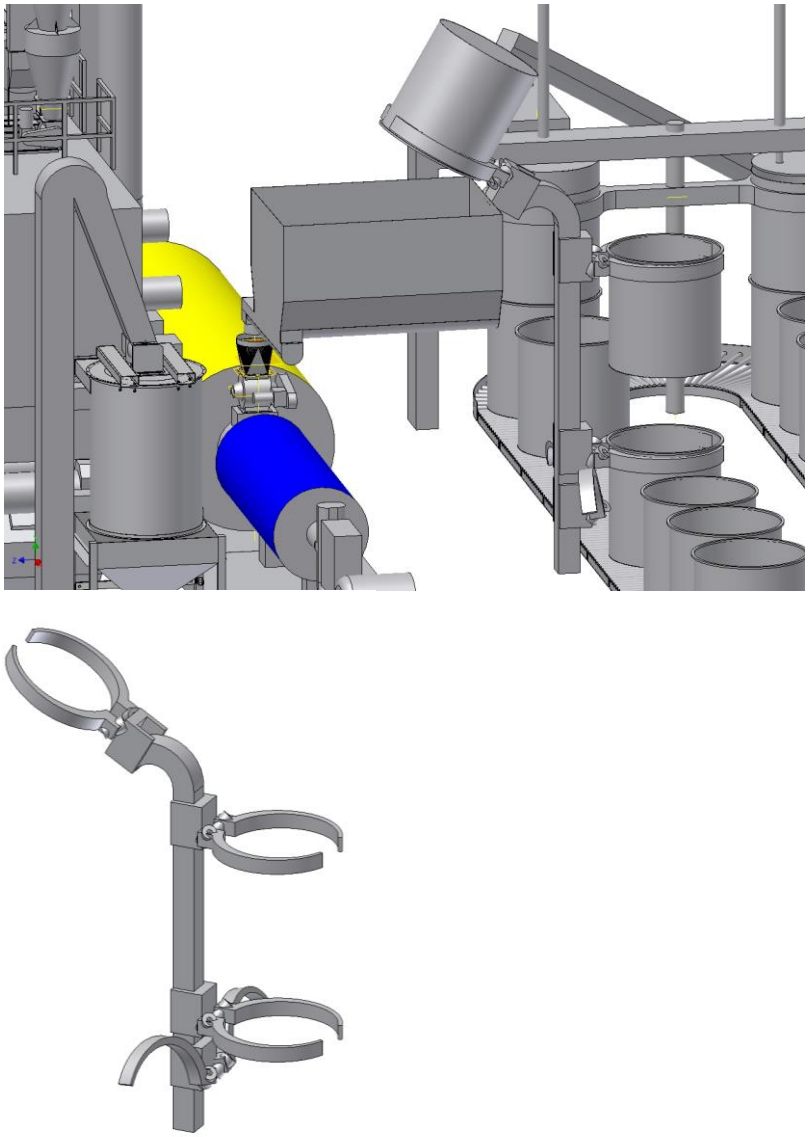


Figure 18. Basket dumper, in system and stand alone

Upon emptying, the baskets are returned to the racetrack roller conveyor where they are cycled back to the filling station. After drying, the biomass is placed in a surge bin upstream of the pellet mill. The surge bin enables a constant flow into the pellet mill, and averages out the surges in material caused by the basket dumping. After pelleting, the final product pellets are conveyed to the storage bins.

Subtask A.3. Vessel size, aspect ratio, and construction material for engineering scale vessels

To develop a detailed engineering design for the AFEX 3 engineering scale unit, the following information and specifications must be determined:

a. Maximum working pressure
b. Maximum working temperature
c. Processing time
d. Reactor volume
e. Aspect ratio of the reactor

f. Construction material
g. Compressor specification
h. Method of loading and unloading of the biomass in and out of the reactor
i. Initial moisture content of the biomass
j. Orientation of the reactor, vertical or inclined
k. Number of the reactor
l. Number of baskets for each reactor

The effect of aspect ratio on the performance of the AFEX 3 system was evaluated using oat hulls as the model biomass. (These experiments were not repeated with corn stover due to delayed delivery of biomass). In these experiments three different aspect ratios - 3, 6 and 9 were tested. Since the aspect ratio of the reactor bed vessels in the lab-scale AFEX 3 unit is fixed at 12 (4" diameter and 48" length), the aspect ratio was varied by using the three long baskets (each with 4" diameter and 12" length) in the reactor tube. The aspect ratio of 3 was assembled by inserting two empty baskets into the reactor tube, then placing the third basket filled with biomass on top of the empty baskets. For an aspect ratio of 6, one empty basket was first inserted into the reactor bed, and then two baskets filled with biomass were placed on top of the empty basket. For the aspect ratio of 9, the reactor bed was filled with three baskets packed with biomass. These tests were carried out following MBI's regular AFEX 3 run procedure and the amount of ammonia left in the biomass after the steam stripping step was measured via citric acid titration (detail explanation of the method is provided in Subtask A.4). Based on the obtained results, it is apparent that aspect ratio has an impact on the efficiency of the ammonia recovery; runs with an aspect ratio of 3 showed very poor ammonia recovery. Runs with aspect ratios of 6 and 9 exhibited acceptable ammonia recovery levels. Based on these data, an aspect ratio of 6 was chosen for the AFEX 3 engineering scale design.

MBI's original conceptual design for the AFEX 3 engineering scale system was based on using two vertical reactor pressure vessels. One of the engineering firms with whom we discussed the AFEX 3 design suggested using inclined pressure reactors instead of vertical reactors to reduce the installation cost. Generally installation cost for a vertical reactor is higher than that for an inclined reactor. To evaluate the impact of the orientation of the reactor on the performance of AFEX 3 process, MBI rearranged the orientation of one of the three reactor beds on the AFEX 3 lab-scale skid from a vertical to an inclined position with a 45 degree angle. For these experiments corn stover and wheat straw were used and AFEX runs were carried out following the regular AFEX 3 procedure. Ammonia recovery was evaluated using the method presented in Subtask A.4. Collected data are presented in Figure 19.

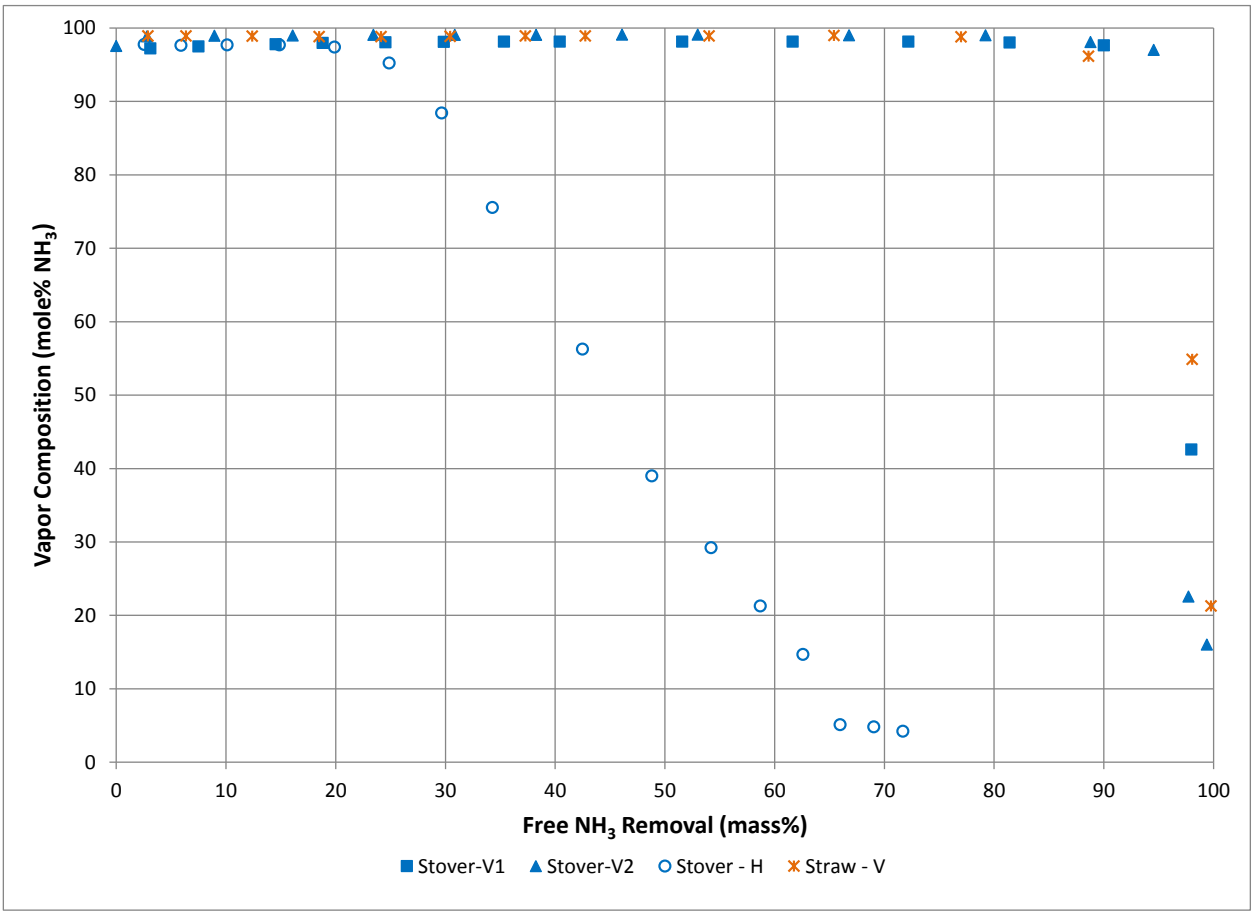


Figure 19. Composition of vapor removed during steam stripping of corn stover and wheat straw packed beds. V: Reactor oriented vertically; H: Reactor oriented horizontally.

The significant difference in steam stripping efficiency between horizontal and vertical beds is evidence of a buoyant effect in the stripping process. Figure 20 shows compositions and densities of ammonia-water vapor mixtures at atmospheric pressure over the range of temperatures encountered during ammonia steam stripping from biomass packed beds. As the vertical beds were stripped, steam entered the top of the bed and condensed on the cold biomass, liberating heat to generate vapor. The density of saturated steam at atmospheric pressure is indicated for reference by the dashed line in Figure 10. As cold, ammonia-rich vapor is released from the bed, that vapor is denser than the incoming steam. The buoyancy effect due to the density difference between the steam entering the top of the bed and the vapor exiting the bottom of the bed increases the efficiency of the stripping process by segregating the steam and ammonia vapor, so that only substantially dry vapor leaves the bed. When the bed is oriented horizontally, this beneficial buoyancy effect is lost. The incoming steam penetrates rapidly across the top of the horizontal bed and quickly breaks through to the bed exit, so that more than half of the residual ammonia is recovered as wet vapor. Recovery of ammonia as wet vapor is less efficient that recovery as dry vapor, both because more steam is required to completely strip the bed, and because more ammonia must be condensed to dry the vapor before re-compression. The condensed wet ammonia can be recovered by steam purging the condensate, but purging requires additional energy. Based on this information the vertical orientation was finalized for our AFEX 3 engineering scale design.

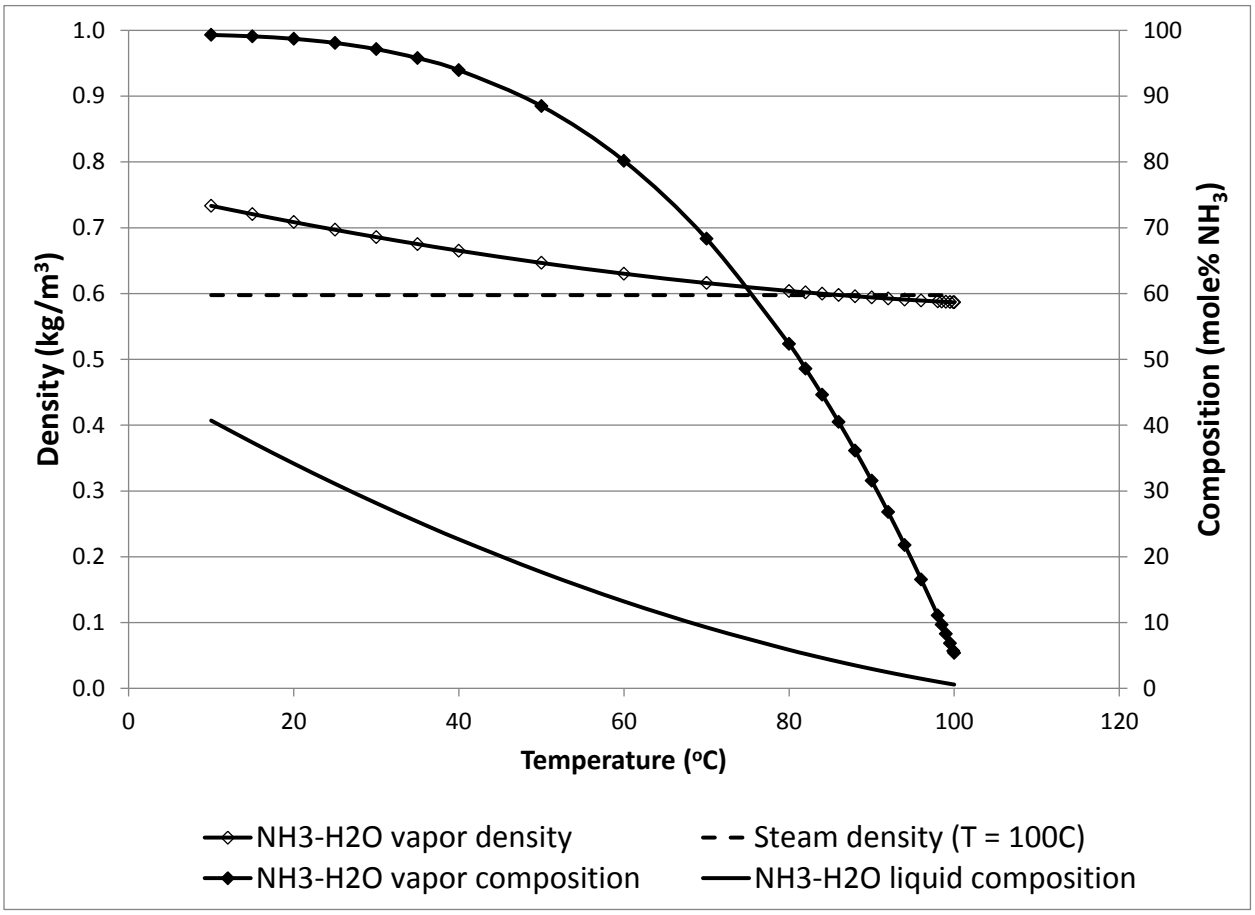


Figure 20 – Composition and density of ammonia-water liquid and vapor at atmospheric pressure (data from [Tillner-Roth R, Friend DG , 1998]).

Subtask A.4. Ammonia removal and recycling

One of the distinguishing features of the AFEX 3 process is that a significant amount (> 70%) of the residual ammonia can be recovered and directly recompressed and recycled as substantially pure (≥ 90%) vapor. In this task, a method was developed to measure quantity and quality of the ammonia removed from the biomass in both the depressurization and steam stripping steps. This method has been used in other tasks to generate data to develop mass balance for the ammonia used in the system.

Measuring ammonia collected in the depressurizing step:

For this experiment, one reactor bed tube of the lab-scale AFEX 3 system is used and the ammonia released from the bed in the depressurizing step is collected in a citric acid trap containing a known amount of citric acid with a known initial concentration and pH. To minimize ammonia loss during collection, the citric acid trap is kept cold using an ice bath. The amount of collected ammonia is calculated based on the final pH of the solution in the citric acid trap and the citric acid-ammonia titration curve. The amount of water collected in this stage will be equal to the final weight of the citric acid trap minus initial weight of citric acid trap minus weight of the collected ammonia calculated above.

Measuring ammonia collected during the steam stripping:

During the steam stripping step the vapor expelled from the bottom of the bed is collected in fractions (every 30 second for the first few fractions and every minute for the rest) in containers

containing 1 liter of 1M citric acid. By following the method explained above, the amount of the collected ammonia and water for each fraction can be calculated. Based on these measurements a breakthrough curve can be developed for the steam stripping step. Figure 9 shows the composition curves generated based on the amount of ammonia and water measured in each fraction collected from steam stripping of a bed of AFEX-treated oat hulls packed in the reactor tube using the baskets or without the baskets. These results show:

- The effect of the baskets is negligible for oat hulls under these stripping conditions.
- The steam stripping process can be well-controlled and is reproducible.
- There is little room for improvement during the constant composition period; vapor is already ≥ 95% NH3 during this period.
- There is room for improvement by delaying the transition to the falling composition period. Slower stripping may help with this.

Subtask A.5. Evaluate the performance of the AFEX system via enzyme hydrolysis of the treated biomass and finalize the most effective and practical conditions

Performance of the AFEX 3 system in treatment of corn stover was evaluated via high solid hydrolysis of treated biomass. Hydrolyses were carried out at 18% solid loading in accordance with the method provided in the validation package. The results showed that corn stover processed in a hammer mill with a 1" screen and treated in the AFEX 3 lab scale unit was able to match the benchmark performance, and released approximately 75% of the glucose in the enzyme hydrolysis step (Figure 21). Based on the hydrolysis and ammonia recovery results, the feedstock characteristics were finalized as one stage hammer mill grinding with 1" screen size.

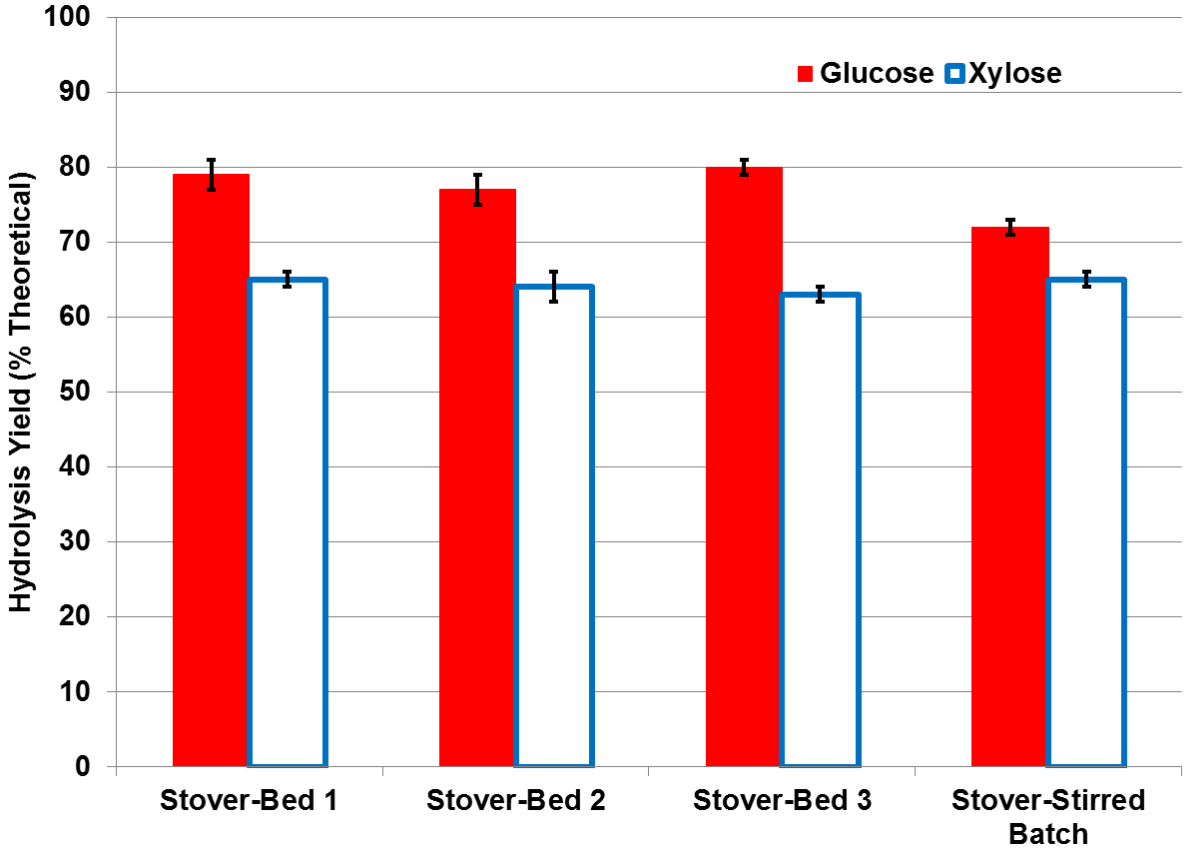


Figure 21. Hydrolysis results of corn stover processed in a hammer mill with a 1" screen and treated in the AFEX 3 lab scale unit

Task B. Preparation of biomass feedstock for engineering scale AFEX 3

Description:
INL will develop feedstock specifications relative to material handling, packing density, and rewetting for AFEX 3 system design and optimization. To accomplish this task INL will draw upon its biomass preprocessing equipment, characterization tools, and its Biomass Research & Development Resource Library. Statistical sampling methods will be employed to select samples for flowability, chemical composition, and thermo-chemical conversion characterization to assure feedstock quality and consistency. Flowability will be tested in engineering- scale handling equipment instrumented to measure feedstock flowability performance include a pneumatic flow loop, a flow hopper, and conveyor systems. INL's drying and environmental chambers and water activity meters will be used to develop the drying, rewetting curves and sorption and desorption isotherms. The experimental data will be further modeled to discover parameter values like monolayer moisture content, and drying and wetting rate constants. In order to improve ammonia recovery, sugar yields and lower capital, labor, and energy costs INL will grind, pelletize, dry, and/or wet material as necessary to prepare biomass feedstock material that is optimized for transportation, handling, and biochemical conversion in the AFEX reactor. Effects of parameters will be assessed via enzyme hydrolysis and fermentation.
INL will provide feedstock with consistent and reproducible specifications for running the engineering scale AFEX 3 system. Statistical sampling of the feedstocks will ensure that feedstock variability does not confound test results.

Accomplishments:
Subtask B.1. Biomass preparation and shipment

Fifty-four large square bales (3-ft x 4-ft x 8-ft) – approximately 30 tons (wet wt.)–of conventional multi-pass, low cob corn stover were harvested and baled by Iowa State University (ISU) on 10/23/2011. The stover was sourced from a field located at the GPS coordinates (42.213953, -93.742377), and was harvested later than expected due to wet weather. Following grain harvest, the stover was winnowed using a Hiniker 5600 Series side discharge winnowing stalk chopper, and baled using a Massey Ferguson MF2170XD large square baler. Several of the bales were cored at harvest and the average moisture and ash contents were determined to be 16.9% and 7.7%, respectively. The average bale weight was 922 lb. The bales were stored under tarps at ISU unitl delivery to INL. The bales were tarped during shipping to INL. Once received, the bales were stacked on pallets and tarped. Four of these bales were utilized for Subtasks A.1.1 and A.1.2 above.

Smaller supersacks were purchased at the request of MBI to more closely reflect their ability to handle formatted stover at their pilot facility. The addition of the larger number of supersacks and the logistics of filling them versus filling larger sacks (shorter time between bag switches) necessitated reconsideration of staffing requirements and was determined to significantly increase the cost of preparing multi-ton quantities of ground stover. A multi-supersack filler (Figure 22) that allows the same number of staff to operate the system with the smaller volume supersacks was purchased. Tests were performed to determine a more cost-effective way of packaging the smaller supersacks to reduce storage and shipping costs. A three-high stacking configuration (Figure 23) with the sacks banded to a single pallet was chosen as the most cost-effective method that allowed safe storage and moving of the sacks.

Figure 22. Multi-supersack filler located at INL

Figure 23. Three-high stacking configuration for storing and shipping the supersacks

INL ground roughly 30 tons (dry weight) of corn stover for this task during the third week of October 2012, using the single stage grinding (Figure 24) method developed for this project. Custom custom plastic-lined bottom-opening supersacks were procured and where filled by about 150 +/- 20 lbs of ground biomass. To minimize costs due to lower throughput when using the dryer, bales containing less than 15 wt% moisture (as determined by a moisture probe) were not dried; this value was chosen using the moisture sorption data determined earlier in the project and was 2 wt% below the moisture content at a water activity of 0.7 (will not support fungal growth). Bales above 15 wt% moisture were dried in the PDU. The filled supersacks, each containing ca. 150 lb (dry weight), numbered 448 sacks. These were banded three high onto pallets and shipped to WestOne Logistics (Figure 23) in Idaho Falls where they were placed in temperature-controlled indoor storage awaiting shipment to MBI. The first shipment of 24 pallets (72 supersacks, roughly 5.4 tons dry weight) was shipped to MBI in mid-December 2012. The feedstock was delivered to MBI in 6 shipments and the last one was in February 2015.

Figure 24. Hammer mill used at INL for grinding the feedstock

Subtask B.2. Test biomass flowability in engineering scale handling equipment
Accomplishments for this subtask were reported under Subtask A.2

Subtask B.3. Conduct experiments to evaluate sorption and desorption isotherm for the biomass

Sorption and desorption isotherm characteristic for both wetted untreated and AFEX treated biomass were measured. Material drying kinetics were also analyzed for the formatted raw corn stover and AFEX treated corn stover. This analysis provided an estimate of the time required to dry to target moisture contents suitable for pelletization and allowed dryer specification to be completed. In addition, moisture adsorption analysis was performed on the pelleted material to assess the final product's stability relative to a traditional corn stover pellet. The detail of the analysis and the results have been summarized and published by Bonner et al. 2015 (Appendix C)

The scale-up of AFEX pretreatment systems to the depot level depends on the ability to efficiently dry biomass for pelleting. The results of this work demonstrated decreased equilibrium moisture content to water activity relationship and improved rates of drying as a result of AFEX pretreatment. As a result, drying operations suitable for raw corn stover are expected to perform similarly or better with AFEX pretreated stover. Observational evidence of pellet degradation indicates that the pretreated pellets are more resilient under humid conditions than raw pellets despite a lower equilibrium moisture content to water activity relationship. This finding has direct impacts on pellet shelf-life and value within a commodity system.

The data developed under this task was used for Task E for technoeconomic analysis of the commercial scale AFEX 3 depot.

Task C. Design and fabrication of engineering scale AFEX™ 3 system.

Description:

An engineering scale (30 kg reactor capacity) AFEX 3 system will be designed, fabricated, and operated. MBI will employ standard procurement practices, compliant with federal regulations, to purchase individual pieces of prefabricated equipment required for the engineering scale system. The engineering scale unit will be assembled and located in the MBI facility at 3815 Technology Blvd, Lansing, Michigan.

Accomplishments:

Subtask C.1. Design

Selecting engineering firm for the project:
MBI engineers met with representatives of three engineering and fabrication firms and discussed the AFEX 3 scale-up project:

- Piping Technology & Products – A Houston, TX-based manufacturer of custom industrial piping systems and processing equipment. PT&P has experience fabricating vessels using the kind of fast-opening high-pressure closures that will be required for the AFEX 3 reactor vessels.
- Eisenmann Corp. – Clear Lake, IL-based engineering and construction firm with extensive biomass solids handling experience.
- EPS – South Bend, IN-based engineering services firm with both biomass solids handling experience and past experience with the AFEX process.

Each of these firms provided both budgetary cost estimates and preliminary project timeline. Based on the provided information EPS from South Bend, Indiana was selected to provide engineering consultation and services on the AFEX 3 project.

Developing detailed engineering design for AFEX 3 process:

Based on the floorplan, availability of ventilation system, accessibility of the necessary utilities, availability of ammonia monitoring system, MBI selected Room D209, located on the second floor of the MBI building as the most suitable location for housing the AFEX 3 system. Vertical clearance from the floor to bottom of the roof bar joists in Room D209 is 13'. Limitations in Room D209 height ultimately constrained the size (height) of the engineering scale reactor design. In particular, this appears to have resulted in reactors somewhat smaller – on a biomass capacity per reactor bed basis – than originally intended. Overall height of the vessels, including the closure davit, is 12'-1". The relatively limited overhead area above the reactors also requires that squatter aspect ratio baskets be used (7 baskets per bed) compared to the lab scale system (6 baskets per bed). Baskets, approximately 16.5"diameter and 14-3/4" long, packed with ground corn stover, are raised and lowered from a pallet to the reactor top openings using an air hoist. Figure 24 shows a simplified flow diagram of the engineering scale AFEX 3 system. This flow diagram was used as a starting point for detailed engineering design of the system.

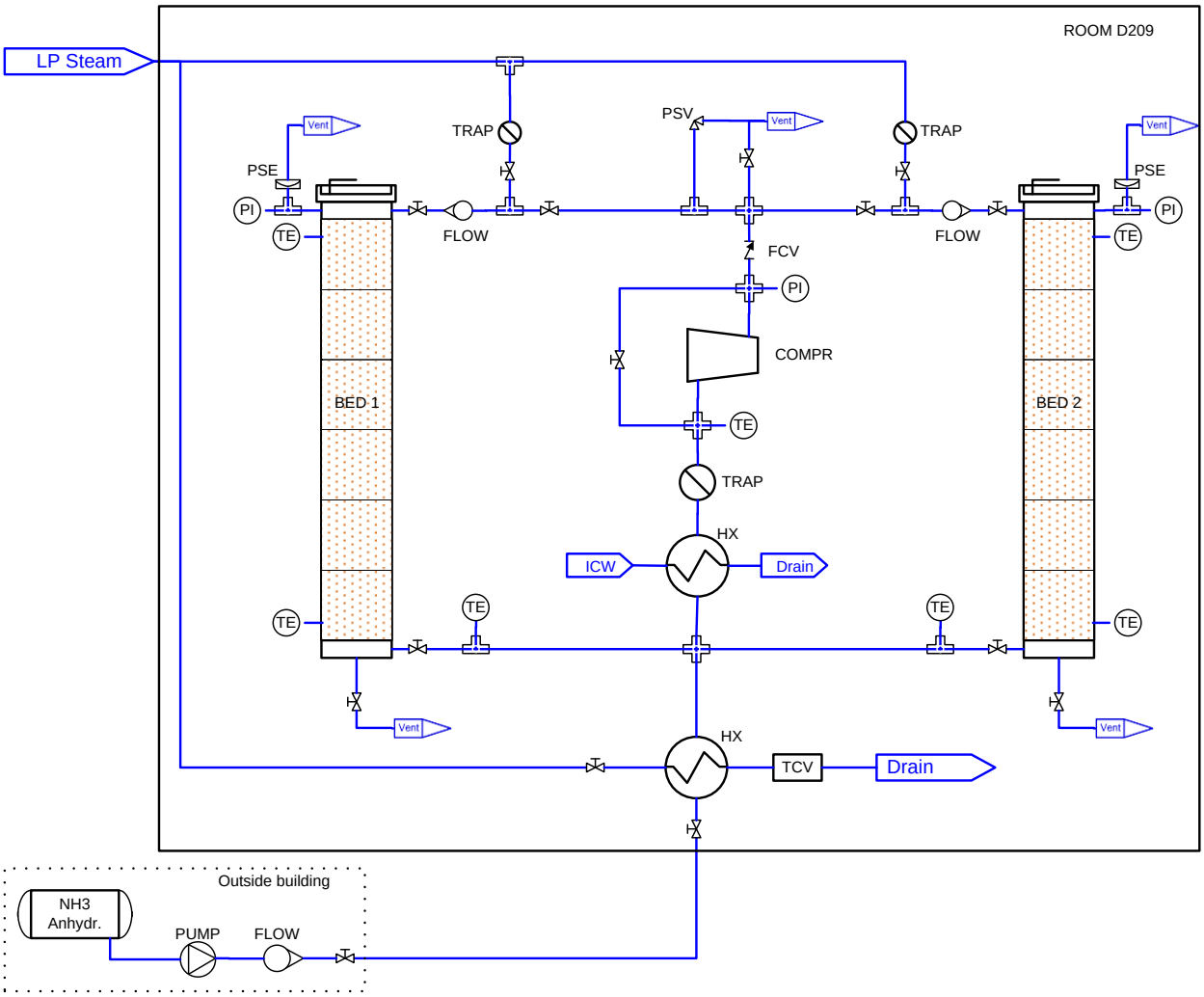


Figure 24 – Simplified flow diagram for AFEX 3 reactor system.

Hazards presented by ammonia release from reactor systems were identified and addressed through increased ventilation and appropriate personal protective equipment (PPE) (full-face respirators with appropriate cartridges), as well as extensive monitoring of ammonia concentrations in the reactor enclosure and surrounding areas. The detail of the ammonia release hazard analysis including the location of the sensors, type of sensors, and response for different ppm detection level of ammonia was reviewed and finalized with the MSU Environmental Health & Safety team and City of Lansing officials.

Specifications of the major equipment:

Reactor

Based on the process conditions in the AFEX reactor, the specifications listed in the Table 1 were selected for AFEX 3 reactors. The process includes two of these reactors.

Closure type options include simple manual T-bolt closures, quick-opening closures, and double-bolt yoke type closures with automatic activation. After reviewing approximately ten different closure types from several vendors, the Sypris Tube Turns T-Bolt type closure was selected. The selection was based on the low cost and adequate opening/closing time of the T-Bolt closure. It was decided that while other types of closures offered slightly faster open/close times, they added too much cost to the vessels. The 18-inch diameter Class 300 closure is joined to the vessel tube by a single butt weld. Sealing of the closure head to the matching hub is achieved by compression of an

EPDM elastomer O-ring seal as the bolts are tightened. Opening of the T-Bolt closure head is assisted by a spring-loaded hinge. In the full open position, the closure permits full access into the reactor vessel, to facilitate insertion and removal of biomass baskets. Each vessel is fabricated from 304 stainless steel as a stamped pressure vessel rated to 495 psig at 400°F (204°C).

Table 1. AFEX 3 engineering scale reactor specifications

Reactor	
Manufacture	Kennedy Tank and Manufacturing Co, Indianapolis, IN
Diameter (in)	18
Height (in)	144
Material	304 Stainless steel
Maximum pressure	495 psig@400°F
Top closure type	Sypris Tube Turns T-Bolt
Bottom head	Standard weight pipe cap
Tank shell	1/2" thick rolled and welded stainless steel plate

Using the detailed vessel design, EPS specified the reactor fabrication (Table 1) and prepared bid packages, which were sent out to several fabrication shops. Kennedy Tank and Manufacturing located in Indiana was selected for manufacturing the vessel. Figure 25 shows a picture of one of the fabricated vessels.

Figure 25. Picture of one of the fabricated vessels.

Ammonia compressor

The ammonia compressor was specified at 300 psig discharge pressure, with 0 psig suction, and up to 10% moisture in the ammonia working fluid. Several compressor vendors provided budgetary quotes based on these specifications, but the vendors pointed out that these are not ordinary specs for refrigeration system equipment. MBI's original displacement requirement for the engineering

scale compressor was 5 lb/min, to allow charging of 100 pounds of ammonia in 20 minutes. However, the information from vendors indicated that a compressor with that displacement and 300 psig discharge pressure may be outside the project budget.

A suitable compromise may be to use a 2-stage compressor with an intercooler, but having somewhat lower displacement. A number of reciprocating and screw-type ammonia compressors from various vendors were reviewed. In addition to cost, the selection criteria included displacement, maximum pressure, and willingness of the vendor to customize a compressor for our unique process conditions. Compressor vendors indicated that the 300 psig discharge pressure requirement, combined with the unique condition that up to three percent moisture may be present in the vapor, made the compressor specification a challenge. A Frick RXF Rotary Screw Compressor (Figure 26) was chosen as the most suitable for our AFEX application. In addition to the compressor itself, the compressor package includes an integrated control panel, lubrication system, oil separator, and oil cooler. Food-grade oil was specified so that the treated biomass is usable in future animal feed trials, if necessary. The compressor control panel interfaces with the AFEX system PLC.

Compressor	
Type	Screw compressor
Model	Frick model RXF 15H
Suction pressure	0 psig
Discharge pressure	300 psig
Flow	3 lb/min

Figure 26. Compressor and its specifications

Corn stover is prepared at INL (Task B) and shipped to MBI in supersacks, each containing 150 pounds of dry biomass. In order to minimize the level of dust in the main building, it was decided to build a temporary construction (Figure 27) adjacent to the MBI Building east wall, to be used as a dedicated location for staging the biomass prior to AFEX treatment. Equipment and devices required for staging the biomass prior to AFEX treatment including hoist, trolley, mixer, and the basket packer were installed in this building. The ribbon mixer (Figure 28) is large enough (~60ft^3) to contain the entire contents of one suppersack. A hoist with trolley and rail is used to raise a supersack and move it over the mixer to be dumped into the mixer. Mixing of any settled fines and addition of moisture is done in the mixer. Contents of the mixer is then dispensed into baskets (Figure 29) and packed to the target density using our in-house fabricated basket packer device (Figure 30). The packed baskets are moved to Room D209 for being processed in the AFEX 3 system. Baskets were fabricated by MBI

team using stainless steel perforated sheet, with 16.5"diameter and 14-3/4 inch height. Seven baskets are needed for each reactor. During the project more than 40 baskets were fabricated to enable consecutive runs.

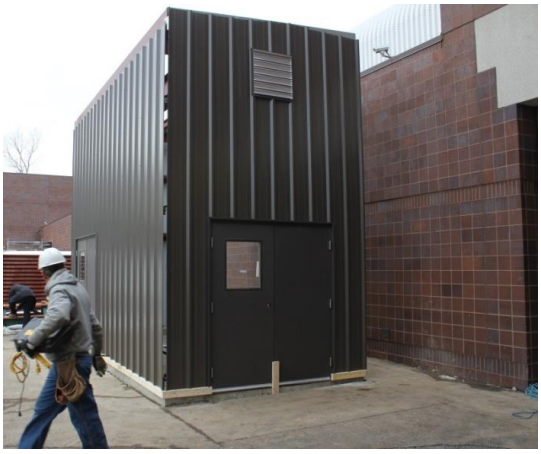


Figure 27. Biomass staging building, adjacent to the MBI Building east wall

Blender	
Type	Ribbon blender
Manufacture	Colorado Mill Equipment
Model	RB-2000
Mixing capacity	60 ft^3
Mixer motor	7.5 HP
Agitator RPM	18

Figure 28. Ribbon blender and its specifications

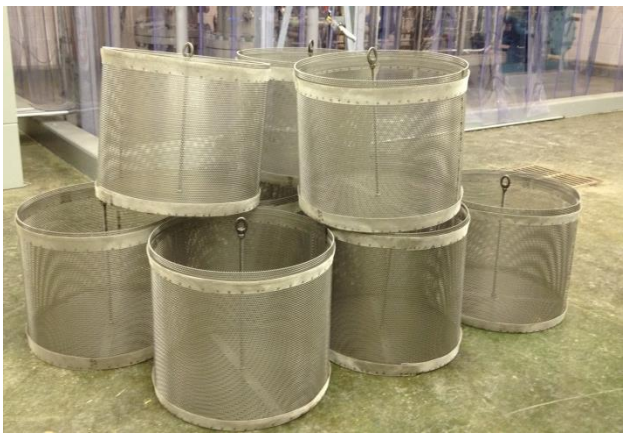


Figure 29. Baskets fabricated by MBI team

Figure 30. Manual basket packing device, designed and fabricated by MBI team

In addition to the major equipment, the AFEX 3 engineering scale system consists of several auxiliary equipment (listed in Table 2). The specifications for the auxiliary equipment depending on their function were defined by MBI, EPS, MSU Environmental Health & Safety or City of Lansing officials.

Table 2. List of the auxiliary equipment used in the AFEX 3 engineering scale system

Auxiliary Equipment	Purpose
Heat exchanger	Vaporizing ammonia arriving from liquid storage
Condenser	Removing excess water from ammonia stream
Ammonia tank/pump	Provide initial charge of ammonia and makeup ammonia
Scrubber	Removes ammonia vapor from vented fluids
Flow control valves	Allows for control over steam and ammonia inputs
Allen Bradley control system	Simple process control during operation
Ammonia sensor/monitor	Provides alarm in case of ammonia release
Ventilation system	Removes ammonia from atmosphere in case of leak or release
Hoist	Lifts baskets of biomass from floor to reactor
Waste tank	Allows for all drained liquids to be neutralized before being disposed of

Prior to installation of the AFEX3 system Room D209 was modified to provide sufficient ventilation and adequate ammonia safety monitoring. To add an extra layer of containment and protection vinyl strip curtains were installed around the area that the AFEX 3 system is housed. Running the process in an enclosed area minimizes the chance of ammonia leak into the room.

Installation of the AFEX 3 engineering scale system started in mid-February 2013 and was completed by mid-March 2013. Figure 31 shows the AFEX 3 engineering scale system installed in MBI building.

Figure 31. Installed AFEX 3 engineering scale system in Room D209 in MBI building

Task D. Process improvement development at engineering scale

Description:

Operation of the engineering scale system through multiple cycles will provide data on reliability and variability of the treated biomass. Composite samples of AFEX-treated biomass will be hydrolyzed for fermentation use testing (Task F). Measurements of mass and energy streams will be used in the process techno-economic model (Task E). The overall rate of biomass pretreatment that can be achieved with the economic scale system will be used in the techno-economic model to calculate capital costs for vessels and other equipment at commercial scale.

Accomplishments:

The EPS team developed a programmable logic controller (PLC) to be used for operation of the AFEX 3 system. Figure 32 shows the control panel for our AFEX 3 system. Two reactors, the compressor (COM-1A6), the condenser (HX-1A6), and the vaporizer (HX-2A6) are shown. In addition, lines show access to a scrubber (which connects to a low pressure waste reservoir), ammonia line, steam line, and air line. The 17 valves shown on the screen are all pneumatic control valves that can be opened and closed via the touch screen control panel, and are sufficient to perform the seven steps of the AFEX process as outlined in detail in AFEX technology section of this report. The control system also includes numerous safety systems as well, which prevents accidental discharge of ammonia or errant flow of air and steam from other lines. EPS also provided us with an instruction for sequence of operation for AFEX 3 system as an initial protocol for our shakedown operation.

Based on the observations made during the shakedown runs, the initial protocols were modified and finalized as MBI's standard of operation (SOP) for operation of AFEX 3 system. The final SOPs were provided to the validation team prior to intermediate on-site validation visit.

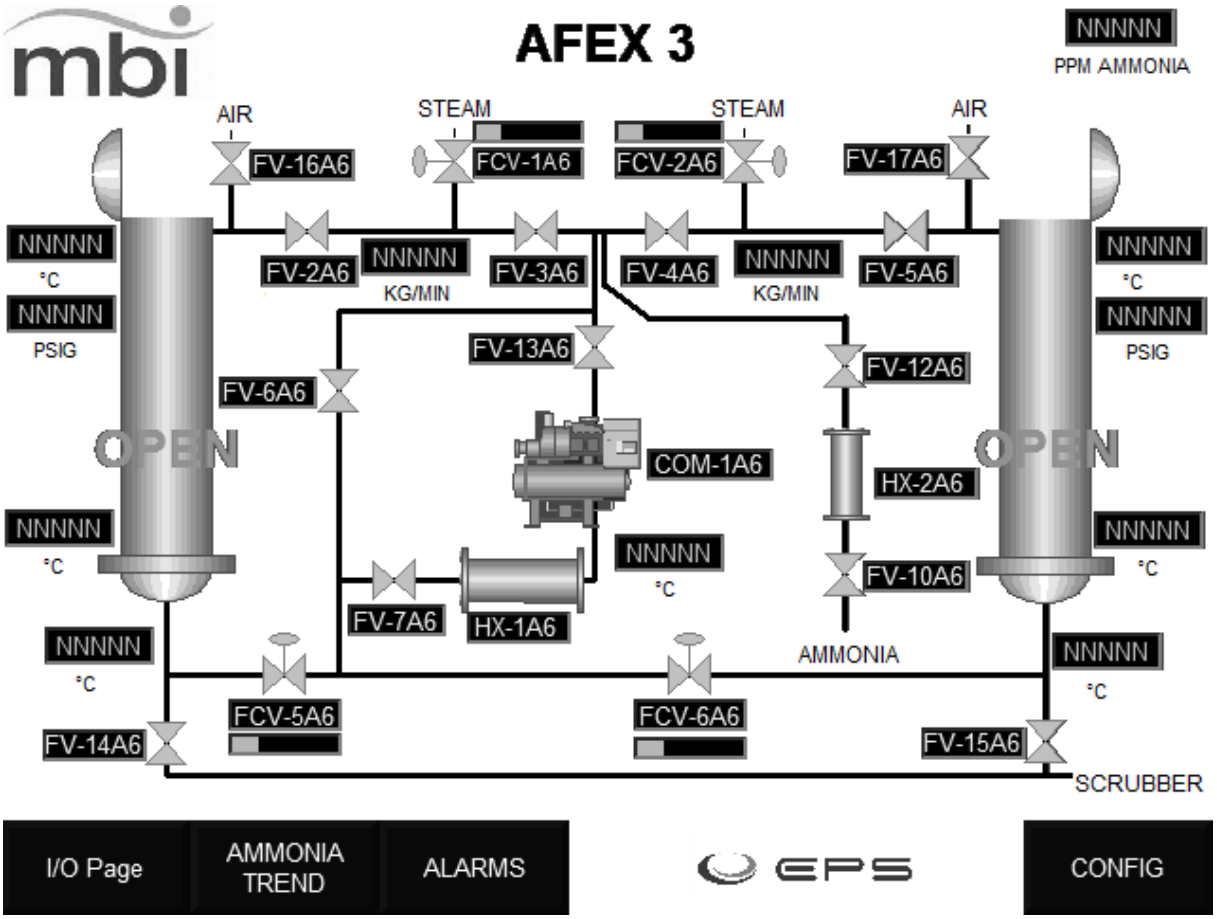


Figure 32. Screenshot of the control panel for the AFEX 3 control system. This system shows the control for two reactors, a condenser, compressor, and ammonia vaporizer, as well as inlet ports for steam, ammonia, and air and an outlet port to a scrubber connected to a waste vessel. Each of the valves can be opened and closed to allow for all seven processing steps for both reactors.

AFEX 3 engineering scale operation

For MBI's reactor, only the top of the reactor opens and the baskets are lowered in from the top. Seven baskets are used, which fill the entire reactor. The baskets are nearly the same diameter as the reactor itself, and fit snugly against the walls of the reactor. The baskets sit on top of each other. Once all seven baskets are loaded into the reactor, the top is closed and sealed.

Once the reactor is sealed, the presteaming step starts by opening the bottom valve on the reactor and introducing a low pressure (15 pigs) steam to the reactor from the top. During the presteaming process, air is forced out of the reactor through the bottom port and displaced by saturated water vapor. The reactor is also heated. The process continues until a temperature sensor at the bottom of the reactor reaches 90°C, at which point the steam is turned off and the valves at both the top and bottom of the reactor are closed. The average temperature in the reactor is approximately 95°C at this point, and the pressure remains at or near atmospheric.

After presteaming, ammonia is added to the reactor. This ammonia can come from one of two sources: a liquid reservoir of highly concentrated ammonia, or from a previously treated reactor. In

both cases, ammonia is added to the reactor in a vapor form. This ammonia reacts with the water within the biomass, which raises the temperature.

When obtained from a liquid reservoir, the reservoir is first connected to a vaporizer. The ammonia is pumped out of the reservoir to the vaporizer. There it is heated to using indirect contact with low pressure steam, which also evaporates the liquid. The valve at the bottom of the AFEX reactor is closed while the top is open and connected to the vaporizer, allowing ammonia to flow into the reactor. As ammonia is added, the pressure rises. If the pressure reaches above 300 psig (pressure limit for our reactor), the ammonia pump is turned off and the pressure in the reactor is allowed to decrease until the pressure decreases to 250 psig. At that point, the pump is turned back on and more ammonia is added. This process continues until the desired amount of ammonia is added.

When obtained from a different reactor, the process is similar. The valve at the bottom of the reactor is closed while the top valve remains open to allow ammonia to enter. Initially, ammonia flows rapidly into the reactor during the depressurization stage (step 5), during which the pressure and temperature in the reactor rapidly rises. The valve remains open after this stage during the steam stripping process. The incoming ammonia is not sent through a vaporizer but rather a compressor to increase the pressure to 300 psig. Once all ammonia is removed from the second reactor, the valve between the compressor and the first reactor is closed. At this point, a small amount of makeup ammonia is required to account for ammonia that is lost in the process or reacted with the biomass in the previous reactor. This makeup ammonia is added in the same method as described in the step above.

Once all ammonia is added to the reactor, it is allowed to soak. Valves at the top and bottom of the reactor are closed, and the ammonia reacts with the biomass. During this time, the pressure within the reactor gradually decreases, as ammonia enters the liquid phase. Likewise, the temperature gradually decreases as heat is lost to the ambient air. The residence time of this soaking period can be between 30 min and several hours. In pilot scale operations, the residence time is approximately one hour, which is the amount of time needed to allow the second reactor to cool sufficiently to open and remove the treated biomass baskets and add new untreated baskets.

After soaking, ammonia depressurization occurs. The bottom valve is opened to the second reactor. The valve is opened slowly and the pressure is released to the second reactor. During this time, approximately half of the ammonia is removed from the biomass. When transferred to another reactor, the pressure is approximately 60 psig after the pressure in the two reactors is equalized. At this stage, a compressor between the two reactors is turned on, drawing the pressure in the first reactor down. In addition to the compressor, a condenser is also included prior to the compressor. The condenser reduces the temperature via indirect cooling with water, which condenses out most of the residual water in the ammonia. The ammonia removed from the reactor is repressurized by the compressor and is added to the second reactor.

The remaining ammonia is removed via steam stripping. Once the pressure in the first reactor is below 10 psig, the top of the reactor is connected to a low pressure (15 psig) steam line. The valve at the bottom of the reactor remains open. Steam is added to the top of the reactor to evaporate the residual ammonia. The ammonia has a higher density than the steam, and is thus pushed out the bottom of the reactor. The temperature at the top of the reactor rapidly increases to over 100°C as the ammonia is removed. This increase in temperature gradually moves down the reactor, corresponding to the ammonia line in the reactor. Once the temperature at the bottom of the reactor reaches 90°C, it is assumed that all ammonia has been removed from the reactor. At this point, the bottom valve is shut off. The pressure in the reactor remains below 10 psig. Once the residual ammonia is removed, the reactor can be opened. At the end of the steam stripping the baskets are too hot (about 100°C) for manual handling and are left in the reactor with air sweeping through the reactor for approximately 1-1.5 hours for cooling prior to removal. The reactor is allowed to cool to 55°C before opening the reactor. The reactor is opened by removing the bolts and opening

the hatch at the top, at which point the baskets can be removed. Baskets are removed using a hoist system. The AFEX treated biomass is approximately 40 to 45 percent moisture at this stage. Depressurizing and steam stripping steps for the lead reactor cannot be started until the baskets containing the treated biomass are removed from the lag bed and replaced by baskets containing untreated biomass. Due to the long cooling time, the soak time for the beds (other than the first bed) is usually about 1.5 hr. For beds with longer soak time, less ammonia loading is normally used.

Operating parameters and performance data for AFEX 3 engineering scale system
Since commissioning in May of 2013, more than 500 beds of corn stover have been treated in the AFEX 3 engineering scale system. Figure 33 shows cumulative stover treatment since commissioning. Each symbol in the figure represents one bed of stover treated.

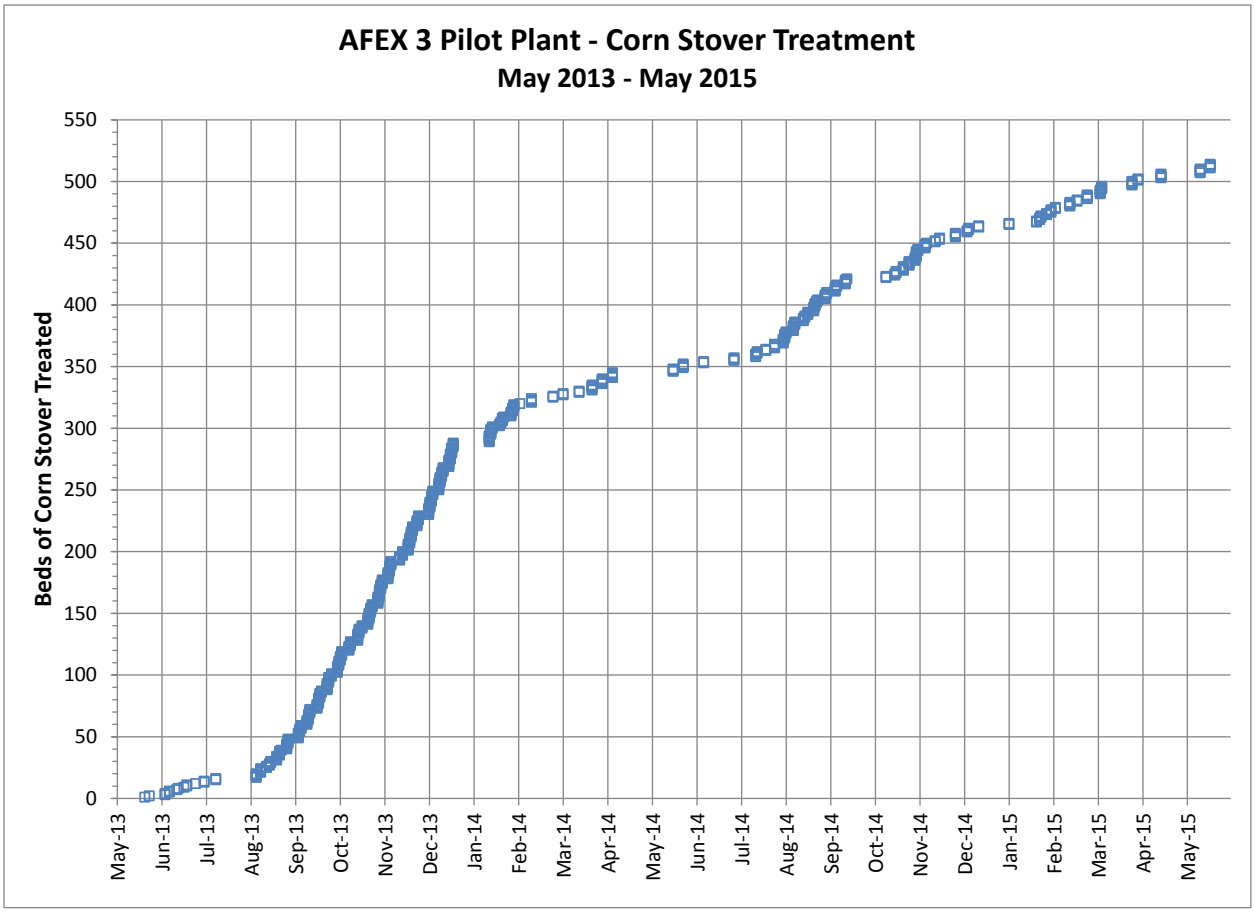


Figure 33. Corn stover treatment in the AFEX 3 system, May 2013 to May 2015.

Figure 34 shows the temperature and pressure profile within a reactor during a typical AFEX run. All steps except for loading the reactor (step 1) and unloading the reactor (step 7) are shown. The pressure within the reactor remains at atmospheric pressure during steps 1 and 2, and then increases rapidly during step 3. The pressure slowly declines during the soak phase, and then is decreased to below 15 psig during the depressurization phase. Meanwhile, the temperature increases during pre-steaming, and increases further as ammonia is loaded. Since steam is loaded from the top, the top of the reactor increases in temperature faster than the bottom of the reactor. During ammonia addition, the ammonia cools the top of the reactor as the vapor flows down, but increases the temperature at the bottom of the reactor as it reacts with water. The temperature then gradually decreases through the soaking step and depressurization, but increases again during steam stripping.

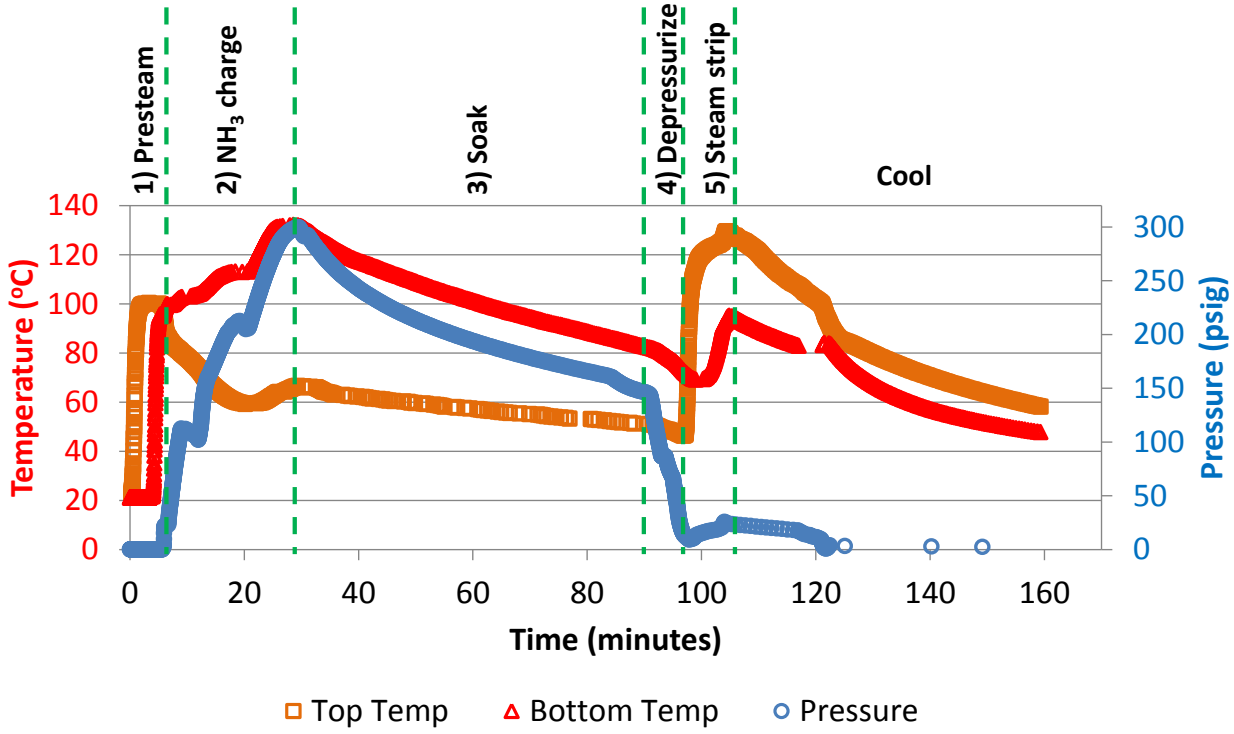


Figure 34. Temperature and pressure profile within a reactor during a typical AFEX run

The moisture gained during the process was closely monitored for each basket. The initial moisture content of biomass packed in each basket is measured. Total weight of biomass in each basket is measured before and after the process to calculate the moisture gained in the process. Data collected from more than 500 runs showed that moisture content of the biomass was increased from 18-20% before the treatment to 41-45% after the treatment. This information was used in Task E for development of mass and energy balance for the process.

Process performance of each run is evaluated via enzyme hydrolysis of the composite sample that is obtained by mixing samples from each of the 7 baskets of each bed. Hydrolysis is done at 3% solid loading for 72 hr using 10 mg of each Ctec3 and Htec3 per gram of glucan. Hydrolysis sugar yields are calculated based on the available sugars in the biomass (measured by following NREL – Lab-002) and sugar released during hydrolysis measured by HPLC.

Since the biomass for this project was stored for a long time, the composition of the biomass was measured periodically (2 times per year) to monitor the quality of the feedstock. No major changes were observed in the composition of the biomass. Table 3 shows the glucan and xylan composition of corn stover used in this project.

Table 3. Composition of biomass based on dry weight

	Glucan	**Xylan**
Corn Stover	36.27%	18.86%

MBI has demonstrated the robustness, reliability, and consistency of the process. Nearly 500 runs have been performed in the reactors with no incidences of plugging (i.e., inability to remove

ammonia from biomass after the treatment), nor any safety incidence related to ammonia. Data presented in Figure 35 demonstrates that the AFEX 3 engineering scale system, a 50-fold scale up from the lab scale, has achieved pretreatment performance equivalent to that obtained in the lab scale system, as assessed by enzymatic hydrolysis.

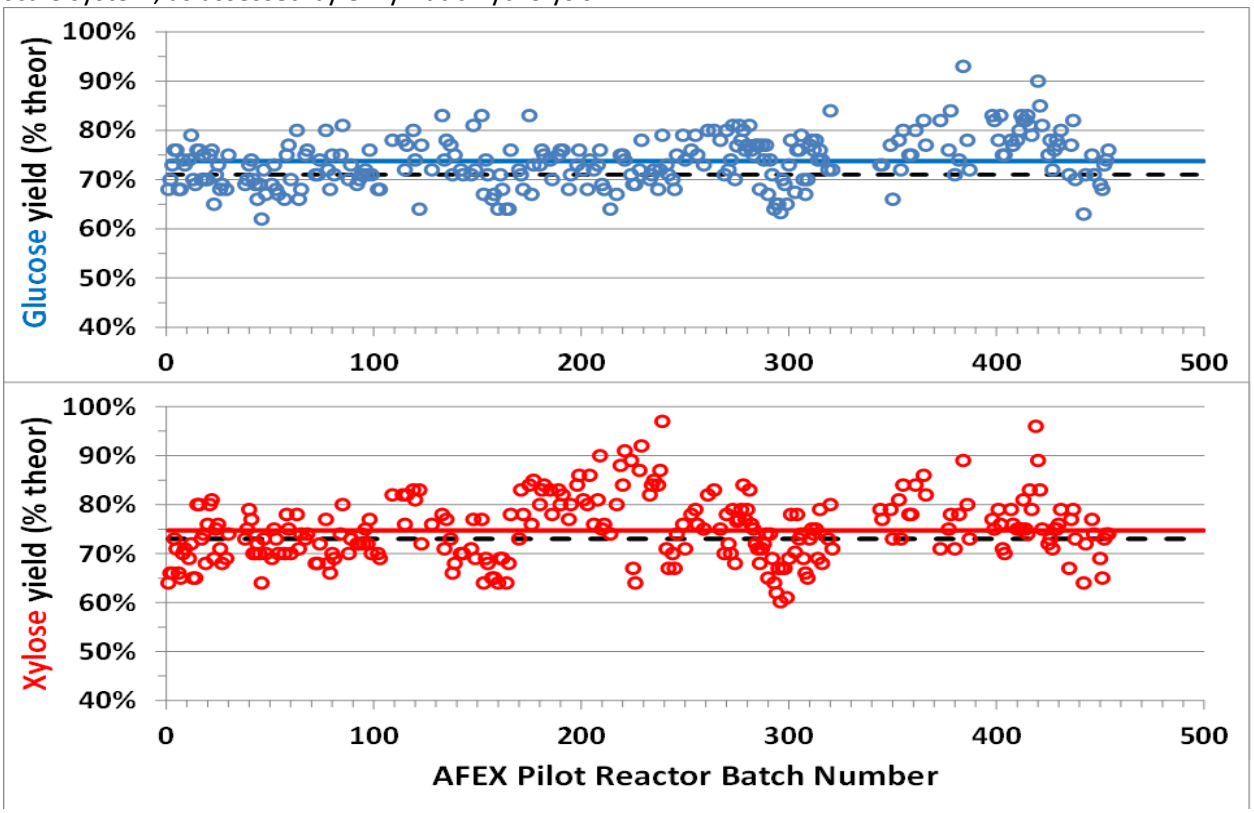


Figure 35. Trend showing the glucose and xylose yield from more than 500 pilot scale runs. The solid line represents the average while the dashed line represents the laboratory scale AFEX 3 reactor benchmark

The reported yields (figure 35) for the lab scale AFEX 3 system are achieved by treating each kg of biomass with 1 kg of ammonia, whereas in the pilot scale AFEX 3 the equivalent performance was achieved with 30% less ammonia, each kg of biomass was treated with 0.7 kg of ammonia. Collected data from the pilot scale run showed that the larger reactor retains heat better than the lab scale system. As a result, the operating temperature in the larger reactor is higher (50-130°C in pilot scale system vs 36-100°C in lab scale system). This putatively enables it to achieve equivalent pretreatment reaction performance at lower ammonia loading.

Ammonia recovery performance in AFEX 3 engineering scale system

The performance of ammonia removal and recovery steps were evaluated in accordance with the method described under Task A and was used to evaluate the lab scale AFEX 3 performance. Figure 36 compares the steam stripping performance of the pilot scale vs. the lab scale AFEX 3 system.

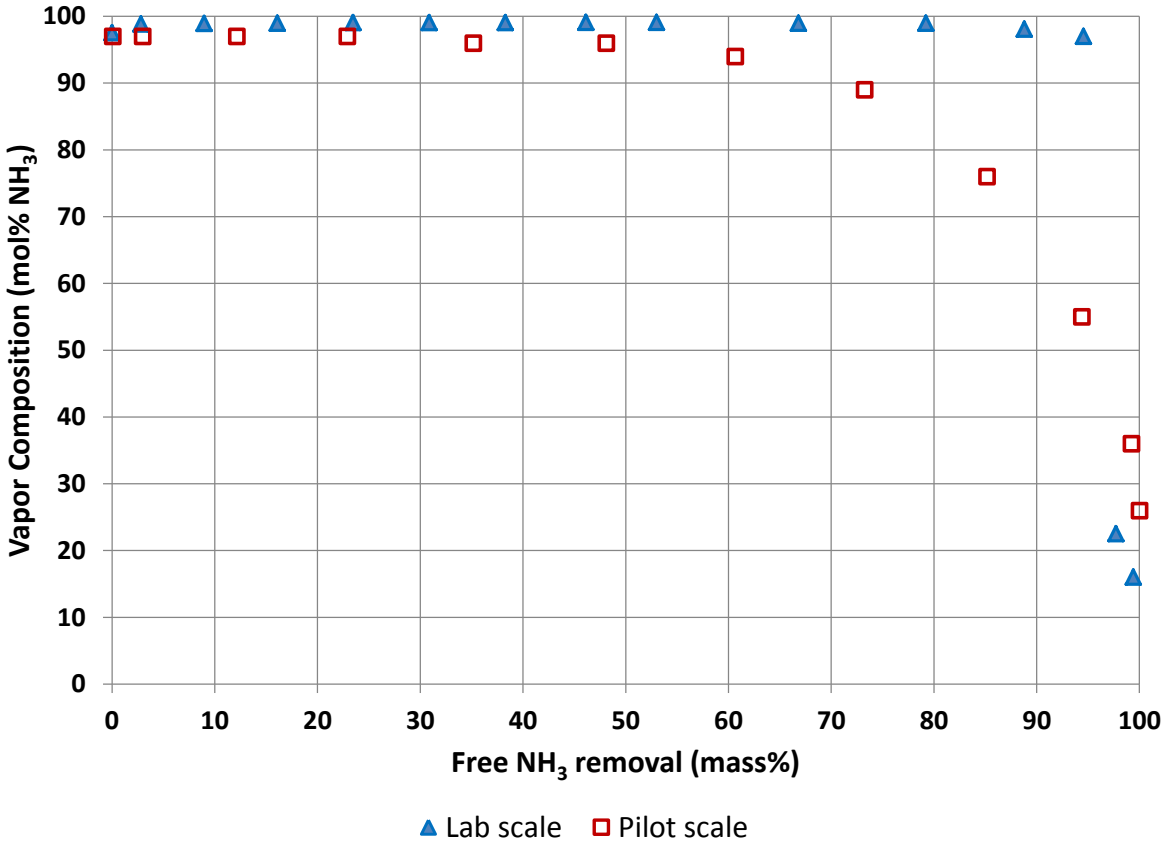


Figure 36. Steam stripping performance of pilot vs. lab scale unit

Following the method described under Task A the ammonia mass balance was calculated for the engineering scale AFEX 3 run. The data showed that the total ammonia recovery for the pilot run was about 94% which is lower than the performance target (98%) set for the project. Detail of the calculation and measurement was presented to the validation team during the third on-site validation visit.

Cycle time and the effect of bed soak time on the process performance

In current operation of the AFEX pilot plant, baskets of treated biomass are removed from the reactors by hand. This means that following steam stripping, each treated bed must cool for a period of time before the baskets can be handled safely. While one bed is cooling, the other bed is soaking. In a commercial-scale AFEX operation, the baskets will be too heavy to move by hand, so the cooling requirement will be avoided, and the cycle time may be shortened if the soak time can also be shortened. Figure 37 shows that bed soak time has no measurable effect on enzyme hydrolysis sugar yields for corn stover treated at pilot scale. This result may be explained by the observation that bed-to-bed NH3 transfer takes approximately 19 minutes, makeup NH3 addition to each bed takes another 10 minutes, and then steam stripping takes another 8 minutes. Some portion of each bed is in contact with NH3 for 37 minutes even without any soak time, so allowing additional soak time has negligible effect on the bed treatment. Overall bed cycle time at pilot scale is approximately 110 minutes (Figure 38), which includes at least 25 minutes of soak time to allow the opposite bed to cool. In a commercial-scale AFEX plant, the cooling requirement should be unnecessary, so that the soak time may be greatly reduced or even eliminated, with one bed of each reactor pair being unloaded and re-loaded while makeup NH3 is added to the opposite bed. In this way the bed cycle time could be shortened to < 60 minutes, and throughput for the reactor pair could be increased from 26 to as much as 50 beds per day.

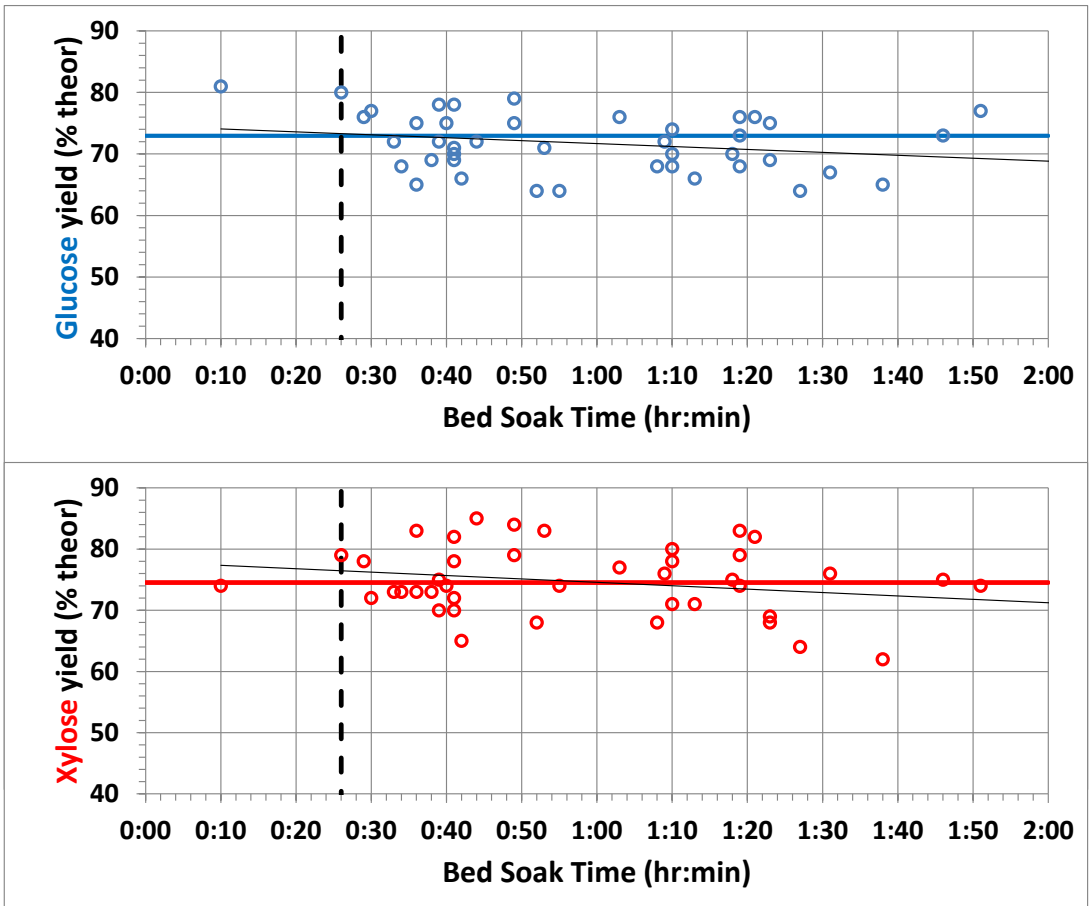


Figure 37. AFEX Pilot Plant, effect of bed soak time on glucose and xylose enzyme hydrolysis yields

Steps	NH_3 Charge	Makeup NH_3 Add → Soak	DePressurize → Steam Strip	Unload → Reload → PreSteam
Time (minutes)	19	36	19	36
	← Reactor Cycle Time = 110 minutes →			

Figure 38. Cycle time based on pilot plant runs

Compressor repairs

Perhaps the most important technical development made during operation of the AFEX pilot plant has been the modifications made to the system to allow an off-the-shelf refrigeration compressor to be used in the AFEX treatment cycle. After a year of operation, the Frick RXF-15 compressor used in the AFEX 3 engineering scale was found to have suffered substantial corrosion damage due to water accumulation in the compressor oil. A leaking shaft seal led to the discovery of a disintegrated shaft bearing cage. Subsequent removal of the compressor core by the vendor in July 2014 (Figure 39) and inspection by the manufacturer revealed badly corroded bearings, rotors, and other internal parts. The compressor core was determined to be too damaged for repair. A replacement core was ordered and installed in October 2014. After installation of the new core, the compressor separator vessel was cleaned to remove accumulated rust and scale, and a new coalescer element was installed, along with new oil and filter.

Figure 39. Pieces of shaft bearing cage removed from Frick RXF-15 compressor.

Installation of compressor hot gas bypass line

To prevent damage to the new compressor core caused by further water accumulation and corrosion, the manufacturer recommended installation of a hot gas bypass line. In concept, the bypass line would allow isolation of the compressor after bed-to-bed ammonia transfers, so that the compressor could run continuously. By operating continuously, the compressor temperature can be maintained above the dew point of water, so that any water entering the compressor suction as vapor would be discharged as vapor, preventing water from accumulating in the compressor oil. A back-pressure regulator in the hot gas bypass line would provide discharge-suction differential pressure > 150 psid, which is sufficient to maintain hydraulic control of the compressor slide valve. A schematic diagram of the hot gas bypass line and a photo of the installed piping are shown below (Figure 40). During bed-to-bed ammonia transfer, the isolation valve HV-n1A6 is fully open, and the bypass shutoff valve HV-n2A6 is closed. Between transfers, HV-n1A6 is closed, and HV-n2A6 is open, which allows recirculation flow through the bypass line with the compressor isolated from the AFEX reactors and the rest of the valve skid. Installation of the hot gas bypass line was completed in October 2014.

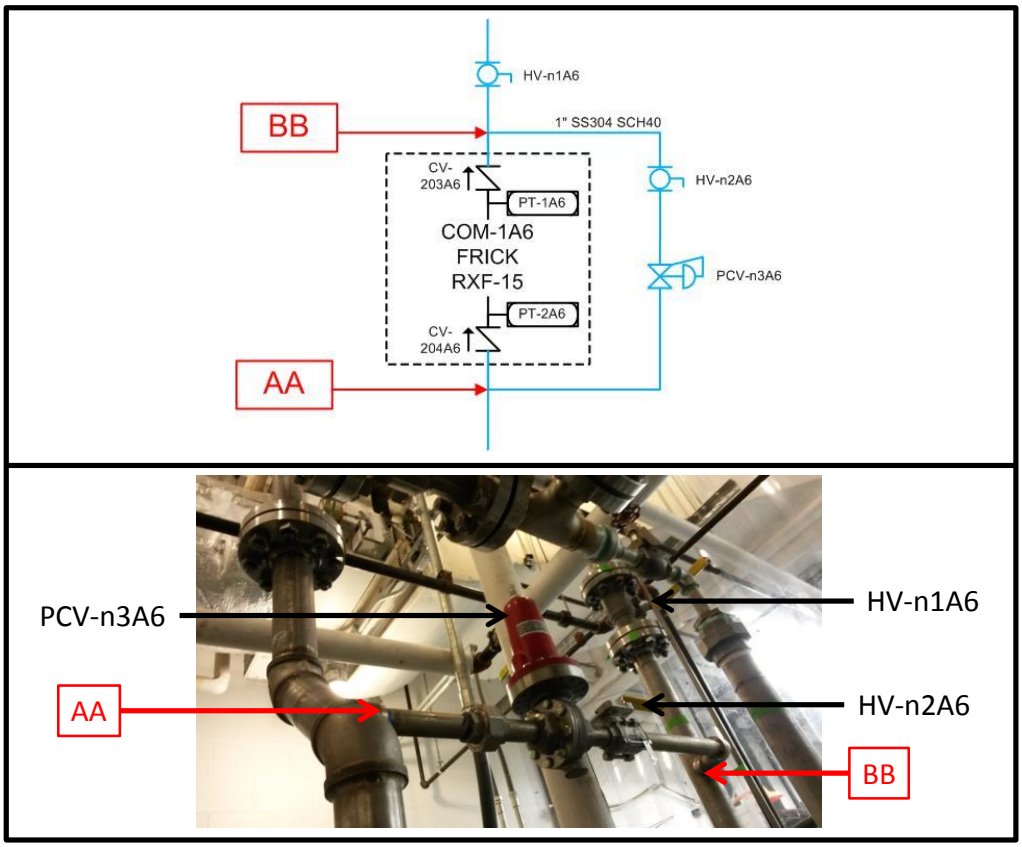


Figure 40 - Hot gas bypass line schematic (top), and photo (bottom), showing locations of suction (AA) and discharge (BB) weld connections, isolation valve HV-n1A6, bypass shutoff valve HV-n2A6, and backpressure regulator PCV-n3A6.

Shakedown compressor continuous operation

The first shakedown run of the new compressor core and hot gas bypass line piping was conducted in October 2014. After inerting and leak checking with N2 gas, a single bed-to-bed transfer was performed with continuous compressor operation. During this run, a high discharge temperature reading forced automatic shutdown of the compressor. In subsequent testing it was discovered that the temperature control mixing valve that diverts oil to the oil cooling heat exchanger on-board the compressor package had never been configured correctly; when the correct parameters were entered in the arcane depths of the Quantum software, the mixing valve functioned correctly, and the discharge over-temperature problem was solved.

With the compressor temperature under control, a series of more than 30 beds were treated between October 2014 and January 2015. During this period, automatic compressor shutdowns were a recurring problem, with error messages indicating high differential pressure across the filter. We speculated that residual rust and scale left in the oil tubing and separator vessel were causing the filter to foul rapidly. After three filter changes, the oil pressure finally stabilized, and the compressor began to perform reliably.

Task E. Generate and update techno-economic models of the biomass-to-fuel process (this task was completed by collective efforts of INL, MSU and MBI team)

Description:

A techno-economic model of the overall biomass-to-fuel process will be developed and regularly updated with new data generated from tasks C, D, and F to determine and quantify the effects of technical improvements on process costs.

MBI and a subcontractor will perform modeling and analyses to determine the costs to supply and produce feedstocks of the various specifications required by the AFEX 3 reactor design. This analysis will utilize the INL feedstock logistics model and the data generated in Task A to provide feedstock cost estimates associated with AFEX reactor design and operation.

MBI and a subcontractor will develop the process flow diagram of each AFEX method with the relevant details to each stream and unit operation being presented in accompanying Microsoft Excel spreadsheets. The design will be based on the data collected from Task A from the lab scale AFEX equipment and a detailed analysis of the ammonia recycle process developed by MBI in 2009 for the conventional AFEX 1 scheme. Appropriate data from the experimental work will be included to develop material and energy flows. Mass balances around all pieces of equipment will be performed for major components.

Multiple facility sizes will be considered. Industrial partners will provide information on the maximum and minimum size of these vessels and other pieces of equipment. Economies of scale for these pieces of equipment will be assessed, as well. With material and energy inputs as well as capital equipment, both the capital and operating costs of the facility can be determined.

Feedstock handling, milling, and densification will also be included in the model, and the economics of these processes handled in a similar method as the pretreatment facility. Although a detailed life cycle analysis will not be performed, it is necessary to provide an analysis of the energy requirements for a Regional Biomass Processing Depot (RBPD). Because the system is decoupled from the main biorefinery, where it is assumed that lignin would be burnt for heat and power, all heat and power requirements for an RBPD facility may require fossil energy. Thus, energy requirements will be used to determine the fossil energy use of an RBPD, which may be an important metric for economic and environmental sustainability. Downstream processes, including hydrolysis, and fermentation, will also be included in the model, with process economics determined through contacts with vendors, established literature, and expertise from MBI and subcontractors.

Accomplishments:

Under this task MBI in collaboration with INL and MSU team developed an Excel model for estimating the capital and operating costs for a depot with either AFEX 3 or AFEX 1 system as the biomass treatment option. A simplified block diagram of a depot operation is shown in Figure 41. The Blocks that are out of the dashed border are the operations that are common in depot with AFEX 3 system or AFEX 1 system.

This model is for a 100 metric ton/day AFEX depot. It assumes a brownfield facility that is owned by another entity, whether it be the biorefinery itself or a local grain elevator or cooperative. Material enters the depot as large square bales and leaves as dry, dense pellets. The depot operates 24 hours per day, 350 days per year. Material is assumed to be brought to the depot year round; only temporary storage is present at the depot. Likewise, pellets are assumed to be sold year round, with only temporary storage at site.

This model is based primarily on data obtained during the operation of MBI's engineering scale reactor. In addition, quotes from vendors are used for most of the pieces of equipment present. Capital investment is determined by obtaining a purchase price for each piece of equipment and estimating an installation factor for it, followed by an estimate for indirect costs. Cash costs include labor, maintenance, raw materials (biomass and ammonia), and utilities. Tax and royalties are not

included in this model. Labor requirements were estimated with help from the Idaho National Laboratory, and salaries were estimated based on comparable salaries in the rural Midwest. Energy requirements for each piece of equipment were determined, as was the total ammonia use.

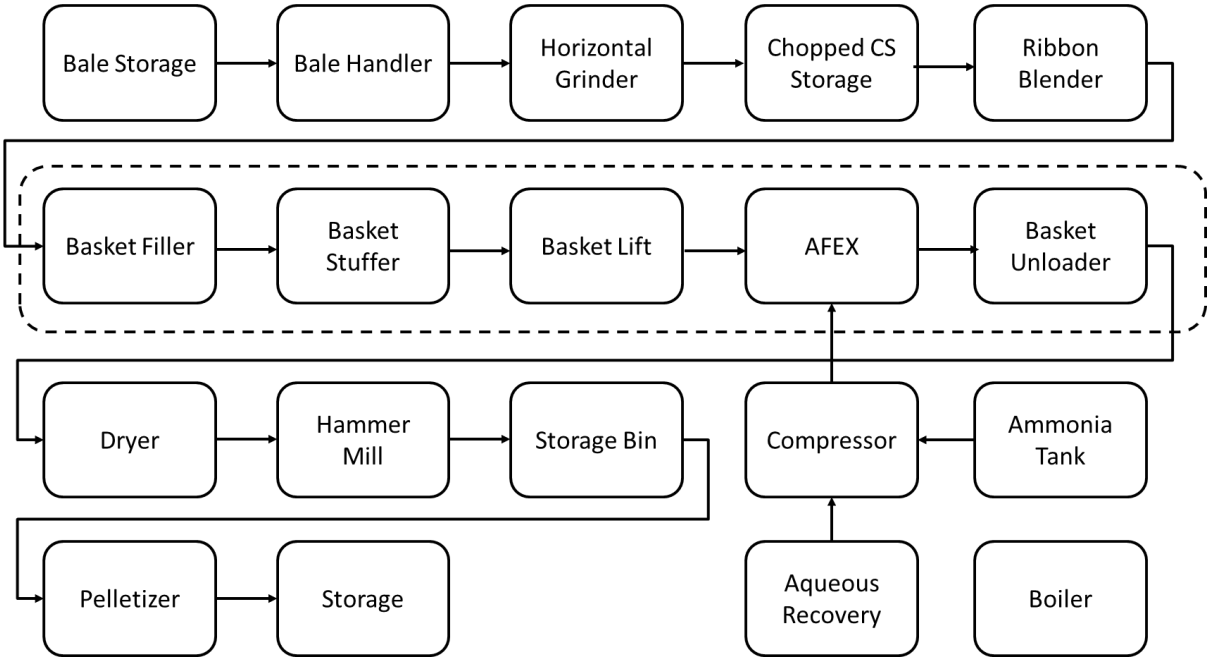
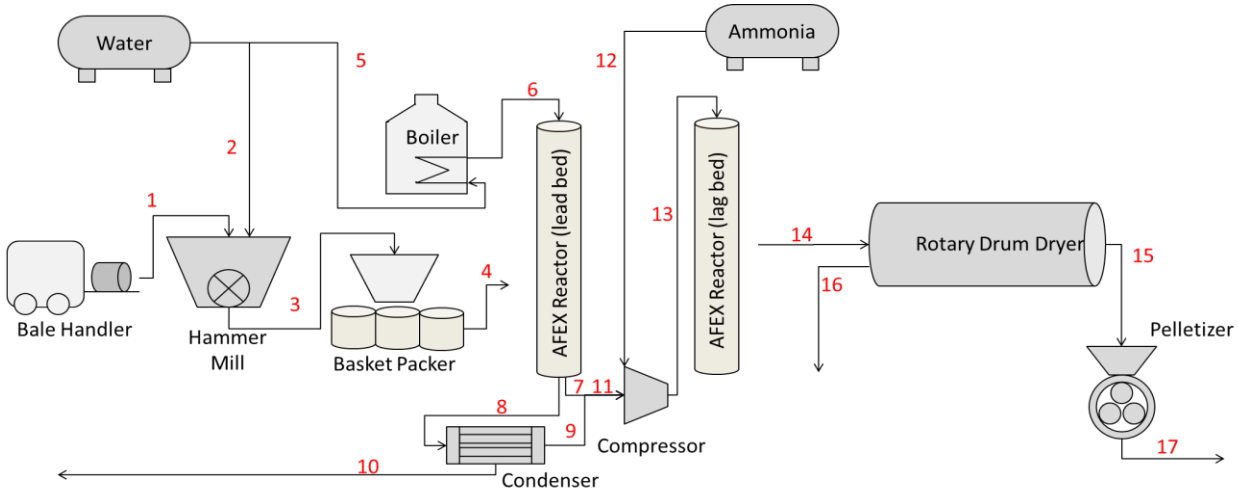


Figure 41. Simplified block diagram of operations in an AFEX depot

During the third validation visit the final version of the developed Excel technoeconomic model was presented and shared with the validation team (NREL and DOE representatives) for their evaluation. The details of the calculations and assumptions were presented and explained to the validation team. Figure 42 shows the process flow diagram for a depot operation with the high level mass balance for the process.



	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Biomass (kg)	1000		1000	1000										1000	1000		1000	
Water (kg)	150	100	250	250	640	640	45	80	4	76	49		49	814	333.3	480.7	180	153.3
Ammonia (kg)							900	80	80		980	20	1000					
Acetamide (kg)														20	20		20	
Temperature °C	25	25	25	25	25	120												
Pressure (psig)	0	0	0	0	0	15	0	0	0	0	0	100	200	0	0	0	0	

Figure 42. Process flow diagram and high level mass balance

Cost estimate for AFEX 1 depot

The Pandia-style ("AFEX 1") AFEX reactor and ammonia recovery system was designed for a full scale (1000+ tons/day) cellulosic biorefinery. This reactor design uses a continuous screw fed horizontal reactor similar in design to those used in the pulp and paper mills. It is also similar in style to steam and dilute acid pretreatment reactors. The goal is that, at the depot scale, the packed bed AFEX reactor ("AFEX 3") will reduce costs relative to AFEX 1 by at least 43%.

AFEX 1 can be conceptualized as three separate blocks. The first is the reactor itself, in which biomass is pressurized, mixed with ammonia, and allowed to sit at the desired temperature for the desired residence time. The biomass then enters the second block, the ammonia dryer, which removes the ammonia via evaporation. The biomass exits the ammonia dryer substantially free of ammonia, and at the depot would then enter the main dryer to remove water. The third block is the ammonia recompression block, where a series of compressors and condensers convert the ammonia to a pressurized state.

Price Estimates for Pandia design

In 2005 and 2009, MBI obtained installed capital cost quotes for two separate sizes of AFEX reactors. The prices (adjusted to 2010 dollars) for each of the three components, as well as the throughput, are shown below in Table 4.

Table 4. Price for each major component of AFEX 1 design

	2005 Design	**2009 Design**	**Scale Factors**
Feedstock	Corn Fiber	Corn stover	
Throughput	1360 kg/h*	50 kg/h	
Reactor	$3,813,000	$3,561,000	0.024
Dryer	$1,027,000	$312,000	0.43
Recompression	$1,696,000	$1,676,000	0.004

* Because corn stover is less dense than corn fiber, the equivalent throughput for the reactor and dryer is 820 kg/h. The recompression system is still 1360 kg/h, as it is based on the amount of ammonia only.

Typically, scale factors are on the order of 0.6 for commercial scale operations. While the dryer is at the right scale factor between these two designs, the reactor and recompression system are not. Essentially, there is no difference in price between the 100 kg/h system and the 1360 kg/h system. Projecting from these values would suggest that a commercial scale 2000 ton/day AFEX reactor would only cost $4.4 million, which is clearly false. The reason for the extremely low scale factors is most likely due to the fact that commercial scale Pandia style reactors are still much larger than the 100-1000 kg/h scale presented here. In contrast, dryers are used at these scales, hence why the dryer prices quoted above can be directly extrapolated to a full scale.

To account for the extremely low scaling factors for the reactor and recompression system, a gradually increasing scaling factor was used. Beginning at 0.014 (the average of the two scaling factors) at 50 kg/hr, the scaling factor gradually increased to a final factor of 0.6 at 5200 kg/hr. This was determined by discretely increasing the throughput by 2% at each iteration, calculating the new price using the previous scaling factor, and then calculating an increased scaling factor. This allowed both the reactor and recompression system to reach the quoted prices at the correct throughputs as shown above. For the dryer, a constant 0.43 scaling factor was used until 6200 kg/hr, at which point a constant 0.6 scaling factor was used.

Auxiliary equipment at the AFEX 1 Depot.

Two pieces of equipment are needed at an AFEX 1 Depot that are not required at the AFEX 3 depot. AFEX 1 requires a smaller particle size than AFEX 3, and so a secondary hammer mill is included. This must be included prior to AFEX (as stated later, AFEX 3 will require a second mill if pelletization occurs). In addition, AFEX 1 requires cooling large streams of concentrated ammonia, whereas AFEX 3 has only a very small condenser. Thus, AFEX 1 will require a cooling tower based on the large quantities of cooling water required. In contrast, there are two pieces of equipment that AFEX 3 requires that AFEX 1 does not. The first is a basket packing station, as AFEX 1 is a continuous process. The second is a rotary drum dryer to reduce biomass moisture after AFEX. The ammonia dryer in AFEX 1 reduces both the water and ammonia content in the biomass, and so no additional dryer is needed. Table 5 presents the total capital cost for AFEX1 system.

Table 5. Capital Cost estimate for a 100 TPD AFEX 1 depot

	Base cost	**Base size**	**Scaling**	**Cost**
Bale handler	$208	4200	1	$ 208
First stage grinder	$230	4200	0.6	$ 230
Hammer mill	$127	4200	0.6	$ 127
Metering				$ 126
AFEX Reactor	$3,813	820	N/A	$ 5,715
Ammonia Dryer	$1,027	820	N/A	$ 2,101
Ammonia recompressior	$1,894	1360	N/A	$ 2,841
Cooling tower	$225	1360	0.6	$ 443
Ammonia tank	$90	4200	0.6	$ 90
Pelletizer	$474	4200	0.6	$ 474
Pellet storage	$208	4200	1	$ 208
Boiler	$90	4200	0.6	$ 90
Building				$288
Bucket Elevators				$21
Storage	$15	4200	1	$ 15
Surge Bins				$ 122
Balance				$ 655
Engineering and Construction (30% of total costs)				$ 4,126
Total				**$ 17,878**

Estimating operating costs for AFEX 1 depot

Utilities decrease for AFEX 1 relative to AFEX 3. This is due to the decreased moisture content in the biomass, as steam is not directly contacted with the biomass to remove ammonia. While more steam is used within the AFEX reactor itself (approximately 800 kg/tonne biomass compared to 700 kg/tonne for AFEX 3), this is offset by the elimination of all energy use in the biomass dryer. In total, only ~280 kg of water must be removed from a ton of biomass treated in the AFEX 1 process, considerably more than the 670 kg that must be removed from AFEX 3.

While natural gas consumption is decreased in AFEX 1 relative to AFEX 3, the opposite is true for electricity. AFEX 1 has more material run through the compressors, which increases the electrical load. In addition, screw feeding the reactors is a significant electrical load. Combining natural gas and electricity costs, AFEX 1 utility cost is about at $21/tonne.

We expect labor costs to be higher for AFEX 1 than AFEX 3. We expect AFEX 3 to be simpler, but that AFEX 1 will be fully automatic throughout the process. AFEX 1, by virtue of having more moving parts, being a continuous process, and having a more complex ammonia recovery process, will require more process control, and may require two operators to fully supervise and control the process. AFEX 3 likely only needs 1, but will require another person monitoring the basket packing operation. AFEX 1 may also require monitoring of feed input, although this is not entirely known. Other labor requirements are identical between the two depots. The total estimated labor cost for AFEX 1 is about $21.72/tonne.

Maintenance costs will undoubtedly be higher in an AFEX 1 depot than in an AFEX 3 depot. AFEX 3 reactors will have very low maintenance costs due to a lack of moving parts, and there is only one compressor to service. The basket packing station may also have moderate maintenance cost associated with it. In contrast, the AFEX 1 reactor has several screws that come in contact with biomass, causing abrasions and requiring the screws to be periodically replaced. In addition, the compressors are dealing with more water in the process, which could shorten the lifespan of the

compressors or increase the maintenance requirements. In contrast, because the biomass is already milled, there may be less wear on the pelletizer. Annual maintenance on the pelletizer was assumed to be 10% of its installed cost, maintenance on the reactor was 5%, and maintenance was 2.5% for all other pieces of equipment. The total maintenance cost for the AFEX 1 depot is $11.88/tonne.

Cost estimate for AFEX 3 depot

One major area of depot design is the biomass handling. Based on INL's studies on the compression required to pack baskets to a density of 100 kg/m3 dry weight, there appear to be no problems with using a pneumatic press system. Furthermore, there is no need for a press to remove the biomass from the basket after AFEX. This vastly simplifies the biomass handling aspect of the depot operations. Based on these findings, INL team designed a latching mechanism inside AFEX reactor to load/unload the baskets into and out of the reactor from the bottom of the reactor. Details of this design are presented under Task A. In addition to the schematics for 100TPD depot (Figure 43) INL developed schematics for systems to meter, load, pack, and unload the biomass and the carousel system for moving baskets between the reactors. These schematics were used in estimating the footprint of the depot and sizing the equipment. In order to refine our estimates for pricing the hammer mill, pelletizer and their auxiliary equipment, the INL team made an arrangement with Bliss Industry to test our AFEX-treated corn stover in their hammer mill and pelletizer. Approximately 600 lb of AFEX treated corn stover at two different moisture content levels was shipped to Bliss Industry in two shipments. Based on the results obtained from this trial for the energy consumption and throughput, Bliss Industry provided us with quotes for the hammer mill and pelletizer for the 100 TPD depot design.

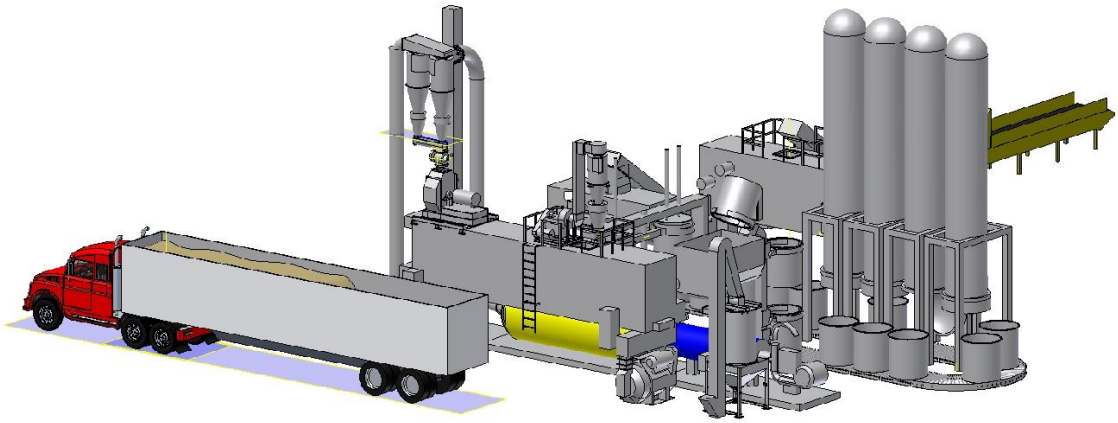


Figure 43. 100 TPD AFEX 3 depot CAD drawing

Major Equipment

Bale storage

Purchase price: $15,000 (Source: Integrated Biomass Supply and Logistics (IBSAL) model) No installation factor (Final cost: $15,000). Bale storage is temporary and will consist of a gravel pad and tarps. Total area is 11,000 square feet, which is sufficient to store 400 tons of square bales.

Bale handler

Purchase Price: 2X$104,000 = $208,000 (Source: IBSAL model)
Installation Factor: 1 (Final cost: $208,000).

The bale handler must be capable of moving ~26 bales per hour from the temporary storage area to the grinder. Many bale handlers can handle up to 3 bales at one time, which would mean that a full trip for taking bales would be 7 minutes, which is quite doable. The temporary storage area would be located near the initial stage grinder. Two bale handlers are included in the model to

insure no down time if one breaks down. During peak harvest season, both may be in operation to unload incoming bales.

Grinder
PurchasePrice: $164,000 (Source:Warren&BaergQuote)
Installation factor: 1.4(Final cost: $230,000)

This grinder is capable of grinding 8 US dry tons/hr to a 1 inch particle size. It is oversized for the depot, but would allow the depot to only operate the grinder for ~16 hours per day. A larger grinder was considered, but would be difficult to store ~65 tons of milled material. Such a large amount would require ~40,000 cubic feet of storage space, which would be an unnecessary expense.

Storage bin
Purchaseprice: $51,000 (Source: Internal estimate)
Installation factor: 1.6 (Final cost:$82,000)

This is a simple enclosed and possibly ventilated storage bin that would be in place after the grinder. It is approximately 4500 cubic feet in size and has the capacity to hold 10 tons of biomass. This will allow the grinder to only be in service 10 hours a day, which would reduce peak electricity use and reduce labor. The bin can be made of relatively simple materials, and thus should not be prohibitively expensive.

Ribbon blender
Purchase price: 2 X $37,000 = $74,000 (Source: Colorado Mill Equipment)
Installation Factor: 1.4 (Final cost: $104,000)

Two ribbon blenders will be used, each with ~300 cubic feet of mixing capacity. Biomass would be added to the blender, mixed with water for 5 minutes, and metered to baskets. Assuming 5 minutes for loading, 5 for mixing, and 10 for unloading, two blenders could supply a steady state of biomass to the basket packer. Each would then need to be able to hold ~1500 lb of corn stover at one time.

Biomass metering, packing baskets, loading and unloading the baskets:

Based on INL's studies on the compression required to pack baskets to a density of 100 kg/m3 dry weight, there appear to be no problems with using a pneumatic press system. Furthermore, there is no need for a press to remove the biomass after AFEX. This vastly simplifies the biomass handling aspect of the depot operations. In order to refine our estimates for pricing the hammer mill, pelletizer and their auxiliary equipment, the INL team made an arrangement with Bliss Industry to test our AFEXTM-treated corn stover in their hammer mill and pelletizer. During this reporting period approximately 600 lb of AFEX treated corn stover at two different moisture content levels was shipped to Bliss Industry in two shipments. The results of this effort are being analyzed and the final results will be discussed in the next quarterly report.

Metering:
Purchase price: $90,000 (Source: INL estimate)
Installation Factor: 1.4 (Final cost: $126,000)

The metering station will consist of a weigh belt conveyor and a basket filler. The weigh belt conveyor will accurately dispense a known amount of biomass to each basket. The basket filler will insure that the biomass is level throughout the basket. It will also include a sheath that allows biomass to be filled above the basket line. This sheath will be on an arm that can be moved between the filler and the plunger. The price estimate is based on equipment purchased by INL for the weigh belt conveyor and internal estimates for the leveler.

Baskets:

Purchase price: 35 X $2,000 = $70,000 (Source: INL estimate) No installation needed (Final cost: $70,000)

Baskets are 60" tall and 60" diameter and produced from 304 stainless steel. A thick (0.12") perforated plate can be used for the bottom of the basket and a thinner solid sheet can be used for the sides. Stainless steel bars can be added for structural support. Cost is estimated based on stainless steel cost. A total of 28 baskets will be in use at one time; an additional set is included as reserve.

Basket piston:

Purchase price: $55,000 (Internal estimate)

Installation factor: 1.4 (Final cost: $77,000)

The basket piston does not need a significant amount of pressure to force the biomass into position. A relatively small piston can thus be used. The piston would be connected to the hydraulic system also in use for lifting the baskets.

Carousel:

Purchase price: $75,000 (Source: Gilmore-Kramer company)

Installation factor: 1.6 (Final cost: $121,000)

Cost is based assuming a total carousel length of 180 ft and 61 inch wide live roller conveyor. Cost is $400/ft. Each basket after AFEX could be up to 1200 lb, and thus the price may need to be increased to adjust to additional weight.

Lift:

Purchase price: $60,000 (Source: INL estimate)

Installation Factor: 1.6 (Final cost: $96,000)

Each reactor will have its own lift, and be connected to a central hydraulic system. The lift will be under the carousel and grab the baskets from the bottom. It is not expected that multiple reactors will need to be loaded/unloaded at the same time, so the hydraulic system will not be overtaxed.

AFEX reactors:

Purchase Price: 4X$267,000 = $1,068,000 (Source: Kennedy Tank Quote)

Estimated Installation Factor: 2.4 (Installed Cost: $2,563,000)

AFEX reactors are 5x35 ft and able to contain 1.95 metric tons per batch. Throughput for each reactor is calculated based on the total residence time and the bed density of the biomass in each reactor which were demonstrated during our final validation visit (Table 6). Each reactor is stainless steel with a closed end at the top and a quick opening hatch at the bottom. The quick opening hatch may be automated, but will more likely require manual labor. The hatches will be pneumatic and thus not require significant effort to open. The installation factor of 2.4 used is identical to the installation costs of towers and columns in NREL's cellulosic ethanol model. This high number is due to the need to build supports for the vertical column.

Table 6. Reactor throughput and residence time demonstrated during the last validation visit

Reactor Throughput				**Residence time**		
Reactor diameter	5	ft		Material unload	10	min
Reactor height	35	ft		Material load	12	min
Biomass bed density in reactor	100	kg/m^3		Presteaming	6	min
kg biomass per reactor	1946	dry wt		Ammonia addition	28	min
min residence time	112			Soak time	28	min
tonnes per reactor per day	25.0			Depressurization	20	min
Tonnes per day	**100.1**			Ammonia stripping	8	min
				Total Time	112	min

Compressor:
Purchase Price: $600,000 (Source: scale up of pilot scale reactor)
Estimated installation factor: 1.6 (Final cost: $960,000)

The design of the compressor may be different from the design used for the pilot plant, and thus this cost may change. MBI is currently working with an ammonia expert to develop a new design for a commercial scale compressor. The installation factor is based on values from NREL's model. The compressor must be able to move ~50 kg/min ammonia.

Ammonia Recovery:
Purchase Price: $36,000 (Source: Peters and Timmerhaus Engineering Textbook)
Estimated Installation Factor: 2.4 (Installed Cost: $86,000)

Due to the high relative vapor pressure of ammonia compared to water, a relatively small column can be used to vaporize 99.9% of the ammonia to 95+% purity. This design is for a 0.5 m diameter column and 4 m height for a 304 SS column. Exiting ammonia can then be sent to the compressor. Although this price is based solely on design calculations, ammonia-water mixtures are well understood. A thorough design calculation will be performed prior to the next scale-up.

Basket unloader:
Purchase Price: $135,000 (Source: Material Transfer and Storage)
Estimated Installation Factor: 1.4 (Final cost: $189,000)

The basket loader design is a simple design that can be easily adapted to the depot. The design is similar to a barrel dumper, but scaled to a 5 ft diameter basket. The quote above includes the dumper as well as a surge bin to meter the biomass into the dryer. The cost is based on a rough estimate from a company that builds similar equipment. Because this is currently a design unique to the depot and not an off-the-shelf item, the price may decrease in the future.

Dryer:
Purchase Price: $350,000 (Source: Baker Rullman Quote)
Estimated Installation Factor: 2 (Installed Cost: $700,000)

The dryer quoted has the ability to remove 3.8 metric tons/hr of water with a throughput of 4.1 metric tons/hr dry weight of biomass. Actual process conditions are 2.1 metric tons/hr water removed and 4.2 metric tons/hr dry weight of biomass. While the throughput of biomass is slightly higher than the quoted value, this throughput is predicated on the total amount of water removed. Because we are only removing half as much water as the dryer is designed for, biomass throughput can be increased (alternatively, air flow can be decreased). Thus, this is actually a conservative size, but one that may be necessary if stripping performance decreases and the biomass has higher moisture exiting the reactor.

Scrubber:
Purchase Price: $180,000 (Source: Pollution Systems Quote)
Estimated Installation Factor: 1 (Final cost: $189,000)

Current information on the scrubber is limited due to uncertainties in the drying performance. This quote is for a 20,000 cubic feet/min air flow and 1000 ppm ammonia. It is likely that the actual requirements are much less. In particular, air flow may be decreased with the low (<40%) moisture in the biomass. The quote includes installation.

Hammer mill:

Purchase Price: $91,000 (Source: Bliss Quote)
Estimated Installation Factor: 14 (Installed Cost: $127,000)

The hammer mill is required to keep the cost of the pelletizer low by milling the biomass to pass through a 1/4 inch mesh. The motor is purchased and installed by the vendor, which keeps installation costs low. A significant percentage of the cost is a magnetic plate to remove metals. However, this may not be necessary as metals can be caught in the first stage grinder.

Storage bin:
Purchase price: $25,000 (Source: IBSAL model)
Installation factor 1.6 (Final cost: $40,000)

This storage bin would be similar in style to the storage bin after the initial grinder. However, a much smaller size is needed, approximately 1500 cubic feet. This would allow ample time to perform routine maintenance on the pelletizer as well as prevent any surges into the pelletizer due to inconsistent flow in the hammer mill.

Pelletizer:
Purchase Price: $296,000 (Source: Bliss Quote)
Estimated Installation Factor: 1.6 (Installed Cost: $473,000)

The pelletizer is sized assuming a 3 inch thick pellet die. This produced pellets that were extremely durable, meaning a thinner die should be possible. This would increase the throughput of the pelletizer, meaning a less expensive pelletizer may be used. The quote is for 120 tons/day, and so is slightly conservative. However, this allows for downtime due to changing the die or rotor, removing plugging, etc.

Storage:
Purchase price: $40,000 x 4 = $160,000 (Source: Meridian Bins)
Estimated installation factor: 1.3 (Final cost: $208,000)

Each storage bin would be able to hold ~100 metric tons of pellets. Thus, four storage bins would support ~4 days' worth of production. It is expected that biorefineries will also be running continuously throughout the year, and thus would need a continual supply of material. Thus, storage on site would not need to be significant. If supply chain problems exist, off-site storage may be possible as well.

Ammonia Storage:
Purchase price: $45,000 (Source: National Renewable Energy Laboratory 2011 Biorefinery Model)
Estimated installation factor: 2 (Final cost: $90,000)
This tank is sufficient to store 24 tonnes of ammonia, which is enough for nearly two weeks' worth of continuous operation. The price estimate is similar to that of the NREL biorefinery model as well as design equations obtained from Peters and Timmerhaus chemical engineering textbook.

Boiler:
Purchase price: $45,000 (Source: REI Boilers quote)
Estimated installation factor: 1.8 (Final cost: $81,000)

The boiler only needs to produce approximately 1.5 kg/s steam at a low pressure (15-60 psi). Thus, a relatively low cost boiler can be used.

Building cost is $288,000; this represents 4800 square feet and $60/square foot. An additional $2,204,000 is budgeted for engineering and construction. Because this is an Nth plant, engineering costs are low; it is expected that little engineering work is needed, as much of the depot will be a preexisting design. The costs are only for adapting the design to the existing landscape. Likewise, a brownfield is assumed here. This means that much of the utilities and land development is already in place. Thus, construction costs are also relatively low. This cost also includes contingencies and so forth.

The summary of the total cost of all the major equipment in an AFEX 3 depot (100 TPD) is presented in Table 7.

Table 7. Capital cost estimate for an AFEX 3 depot (100 TPD)

All costs below are in thousands of US dollars					
List of Equipment	**Number needed**	**Purchase cost**	**Installation factor**	**Installed Cost**	**Final Cost**
Bale handling	2	$104	1	$104	$208
Bale Storage	1	$15	1	$15	$15
Initial Grinder	1	$164	1.4	$230	$230
Surge bin	1	$51	1.6	$82	$82
Ammonia hold tank	1	$45	2	$90	$90
Ribbon Blenders	2	$37	1.4	$52	$104
Metering station	1	$90	1.4	$126	$126
Basket Piston	1	$55	1.4	$77	$77
Carousel	1	$75	1.6	$121	$121
Lift	1	$60	1.6	$96	$96
AFEX Reactor	4	$280	2.4	$672	$2,688
Compressor	1	$600	1.6	$960	$960
Ammonia recovery	1	$36	2.4	$86	$110
Baskets	35	$2	1	$2	$70
Unloader	1	$135	1.4	$189	$189
Dryer	1	$350	2	$700	$700
Scrubber	1	$180	1.4	$252	$252
Hammer mill	1	$91	1.4	$127	$127
Surge bin	1	$25	1.6	$40	$40
Pelletizer	1	$296	1.6	$474	$474
Pellet storage	4	$40	1.3	$52	$208
Boiler	1	$45	1.8	$81	$81
Screw Conveyors	5	$10	1.4	$14	$70
Bucket elevators	3	$5	1.4	$7	$21
Building	1	$288	1	$288	$288
Total Installed Costs					$7,426
Engineering + Construction					$2,228
Total capital investment					$9,653

Labor

The facility will be operating 24 hours a day, 8400 hours per year. In this model, the depot is not a separate entity, but rather owned by a group (such as a farm co-operative) that also owns other agricultural resources in the area (such as a grain elevator). Thus, certain labor concerns, particularly administration, are lessened. Labor costs are dependent on location. Generally speaking, rural labor costs are less than urban costs. For this study, a flat labor cost per hour is used, with an additional 30% cost for overhead. Labor costs are as follows:

Shift Supervisor: $17.50/hr x 8400 hr/yr = $150,000

The shift supervisor will also be the main control operator for the AFEX3 unit. The AFEX 3unit is simple to run, and would not require highly skilled personnel. Most operations would be performed at a control panel. Based on current estimates for residence times, the operator will likely only need to monitor one reactor at a time. There will also be ample time in between transferring ammonia for short breaks.

Operators: $12/hr x 8400 hr/yr x 2/shift = $208,000

Two operators are seen as needed for the process. Essentially, these can be seen as being upstream and downstream of AFEX. One operator will be monitoring the grinding and basket packing, while the second will be monitoring the pelletizer. In addition, one operator may be required to open the reactors. These are quick opening pneumatic hatches, and so will not require significant manpower to open. These operations are all unskilled labor.

Bale handler: $15/hr x 2000 hr/yr = $31,000

The bale handler has less hours working than the other operators. Bale handlers will work 14 hours per day during weekdays placing bales on the grinder as well as removing bales from incoming trucks. Trucks will be unloaded for 8 hours/day and bales must be added to the grinder for 10 hours per day, so there is some overlap between them. During weekends, only 8 hours per day is needed, as no trucks will be incoming at that time.

Administrator: $20/hr x 2000 hr/yr = $40,000

The administrator will be responsible for sales receipts and payroll, as well as general office administration and upkeep. The administrator would work a conventional 40 hr/week shift.

Total labor salaries: $434,000

Total labor cost: $564,000

This cost represents nearly $20 per metric tonne of biomass, a significant investment. It does not appear likely that costs can be greatly reduced. It is unlikely that less than 3 operators could run the whole depot (not including bale handling), as the reactors, basket handling, and pelletizer will need fairly consistent monitoring. Instead, cost reductions would require a larger depot. A 200 tonne/day depot would not need much more labor than a 100 tonne/day, thus significantly reducing labor costs per tonne biomass.

Maintenance

Maintenance on the pelletizer is assumed to be 10% of the installed cost of the pelletizer annually. This is due to the perception that the die and roller will need to be replaced periodically. For all other pieces of equipment except storage, the annual maintenance cost is 2% of the installed cost. This number is in line with traditional estimates for maintenance cost for production facilities. This leads to an annual maintenance cost of $185,000.

Utilities

Electricity:

Electrical requirements will be mostly constant throughout the day. The key exception is the initial stage grinder, which is only run 16 hours/day. Likewise, lights would only be required at night. Major electricity consumers are as follows:

First stage grinder: 15 kW*hr/tonne. Based on Warren & Baerg quote.

Ribbon Blender: 10 kW*hr/tonne. Based on stated motor size.

Compressor: 45 kWh/tonne. Estimate based on current compressor.

Dryer: 15 kWh/tonne. Based on Baker-Rullman specifications

Hammer Mill: 35 kWh/tonne. Based on tests performed on Bliss specifications

Pellet mill: 55 kWh/tonne. Initial tests with Bliss showed 80 kWh/tonne, but the resulting pellets were too hard. These were performed with a 12:1 L/D ratio for the die, which is necessary for untreated material but not AFEX. It is expected that an 8:1 ratio is possible, which should significantly reduce the energy required to pelletize the material. This number is a placeholder until the value can be confirmed.

Boiler: 25 kW*hr/tonne. Based on motor size of a quoted boiler of the proper size.

Other: 10 kWh/tonne. Estimate.

Total: 210 kWh/tonne. At an estimated industrial electricity price of 6.5 cents/kWh, the total cost at the biorefinery is $444,000 per year.

Steam:

Presteaming: 207 kg steam per tonne biomass. This number is based on the latest runs in the pilot scale reactor, which is an average of the amount recorded in both reactors for runs not starting at room temperature. It is expected that the amount of steam needed per ton of biomass will decrease as the reactor size increases due to better insulation.

Steam stripping: 452 kg steam per tonne biomass. This number is also based on latest runs in the pilot scale reactor looking solely at runs where the ammonia is transferred from one reactor to the next. This number may also decrease as the scale increases. Furthermore, tests at different bed density showed little difference in the steam per bed ratio used. If bed density can be further increased, steam/tonne ratio may decrease further.

Ammonia recovery: Approximately 271 kg water/metric ton is condensed during the process, and an assumption of ~81 kg ammonia condensed as well. Assuming 1 kg steam needed per kg ammonia condensed, this means 81 kg ammonia are required.

Total: Total steam usage is 740 g steam per kg biomass. At an estimated cost of $3/1000 lb steam, this equates to $4.90/tonne biomass.

Natural Gas:

Natural gas to the boiler is included in the steam calculations, and so not included here. The only other application that requires natural gas is the dryer. For this process, we assume 41% moisture as an input (the moisture of the biomass exiting the reactor) and 14% as an output. Because we are assuming a triple pass dryer, we assume the output biomass will be reasonably consistent. The 41% moisture value is based on current results in the pilot scale reactor, although this may change as the reactor is scaled up. In particular, the top basket is significantly wetter than the next few, which is likely due to the low quality steam in the process.

We are assuming 1500 BTU/lb water removed. Exiting moisture content should be tuned to ~14% moisture to provide efficient operation of the hammer mill and pelletizer. Entering moisture is approximately 41% moisture. Thus, 535 kg water must be removed per tonne biomass. At a cost of $4/million BTU, that is equivalent to $7.08/tonne biomass.

Condenser:

Based on the mass balance of water throughout the process, approximately 240 kg water/tonne biomass is condensed in the process. This means approximately 540 MJ/tonne cooling energy needed. Assuming a 20°C temperature rise in the cooling water, that means 6.5 tonnes cooling water needed per tonne biomass. This is a relatively small cooling water requirement, on the order of 0.5% the size of that required in the NREL 2011 biorefinery report.

Ammonia:

Ammonia is assumed to cost $400/tonne, and with a loss of 30 kg ammonia per metric tonne of biomass.

Financial Summary

Financial summary of the AFEX 1 and AFEX 3 depot is presented in Table 8. As seen in the Table below, AFEX 1 is a worse value proposition in a depot setting relative to AFEX 3. This is primarily due to the very high capital cost of the AFEX 1 depot, which is nearly twice as high as the AFEX 3 depot. This is likewise reflected in the maintenance costs. However, utility costs are lower, while labor costs are higher. When capital costs are taken into account, the minimum pellet selling price is 25% lower for AFEX 3 depot compared to AFEX 1.

Table 8. Financial summary for the two depot designs

AFEX 3 Depot			
Depreciation length	25	years	
Return on investment	0.07	%	
Ammonia price	400	$/tonne	
Ammonia use	4%	%	
Corn stover purchase price	63.85	$/tonne	
	$/tonne	$/US ton	$thousand/yr
Capital cost	$18.37	$16.66	$643.56
Return on investment	$5.28	$4.79	$184.80
Labor	$17.07	$15.48	$597.94
Electricity	$13.65	$12.38	$478.13
Steam for AFEX	$4.90	$4.44	$171.47
Heat for drying	$7.08	$6.42	$247.93
Maintenance	$5.31	$4.82	$186.10
Ammonia	$16.80	$15.24	$588.47
Corn stover	$63.85	$57.91	$2,236.53
Subtotal (no CS or transport	$88.45	$80.23	$3,098.39
Subtotal (operating costs)	$128.66	$116.70	$4,506.57
Total	$152.30	$138.15	$5,334.93
Total capital investment	$9.65	million dollars	

AFEX 1 Depot			
Depreciation length	15	years	
Return on investment	0.07	%	
Ammonia price	400	$/tonne	
Ammonia use	0.02	%	
Corn stover purchase price	63.85	$/tonne	
	$/tonne	$/US ton	$thousand/yr
Capital cost	$34.05	$30.89	$1,191.88
Return on investment	$22.01	$19.97	$771.05
Labor	$21.72	$19.70	$760.18
Electricity	$16.58	$15.03	$580.59
Steam for AFEX	$4.35	$3.95	$152.35
Maintenance	$11.88	$10.78	$415.80
Ammonia	$8.00	$7.26	$280.22
Corn stover	$63.85	$57.91	$2,236.53
Subtotal (no CS or transport	$118.59	$107.56	$4,152.07
Subtotal (operating costs)	$126.37	$114.62	$4,425.67
Total	$182.44	$165.48	$6,388.60
Total capital investment	$17.88	million dollars	

The objective for the project was to demonstrate at least 43% reduction in the pretreatment cost relative to established AFEX 1 technology. The total capital investment for a 100 TPD depot using the conventional AFEX 1 technology is estimated to be approximately $17.9 million. In comparison, an AFEX 3 depot is estimated to be $9.7 million, or **46%** less than the AFEX 1 technology. This is primarily due to the very high cost of the AFEX system itself, which is 87% of the total installed cost. The final validated AFEX 3 pilot-scale process exceeded its goal to reduce pretreatment capital cost as well as to maintain cost values associated with reasonably good process performance. The estimated total pretreatment cost was $88/metric ton for the AFEX 3 depot compared to $119/metric ton for the AFEX 1 depot, which is a 26% reduction in overall cost. This is less than the initial goal of the project. However, this is primarily due to the higher than expected cost for the biomass handling for both the AFEX 1 and AFEX 3 depot.

Using these results, the estimated total installed capital cost for the AFEX 1 equipment at different depot size was calculated. For estimating the AFEX 3 installed capital cost for different depot size, a linear increase was used, as it assumes that reactors will be scaled by number. AFEX 1 is more expensive than AFEX 3 until ~850 tons/day capacity. This is equivalent to ~20-25 million gallons of ethanol per year, similar in throughput to several early generation cellulosic ethanol refineries (Dupont, POET, Abengoa, and Beta Renewables are all planning or building refineries of this size). Thus, it is unlikely that depots will actually reach this size. This demonstrates that at the biorefinery scale, the AFEX 1 design is appropriate, but the AFEX 3 design is more appropriate for depots.

Task F. Determine the quality of pretreated biomass through fermentation use tests (this task was completed by collective effort of both MSU and MBI team)

Description:

Fermentability test of the sugars generated by enzyme hydrolysis of the AFEX-treated corn stover will be conducted via ethanol fermentation. For this fermentation use test *Zymomonas mobilis* 8b, which utilizes both C6 and C5 sugars will be used. Our prior works have shown that this microorganism can effectively utilize sugars generated from AFEX treated biomass. The fermentation will be carried out as fed batch high solid loading (up to 20%) SHF. As part of this task most practical pattern for batch feeding the biomass and enzyme to the fermentor (5-10 liter) and most practical contamination control method will be determined. The fermentation test will provide data on ethanol titers, productivity, yield, nutrient and mixing power requirement. These data will be used in the techno-economic model to obtain realistic estimates of process costs.

Subtask F.1. Evaluate fermentability of corn stover treated in AFEX 3 lab scale unit

- Determine the most practical method of controlling contamination
- Develop a method for hydrolyzing AFEX-treated corn stover at high solids
  - Using loose treated biomass
  - Using densified treated biomass

Accomplishments:

Contamination Testing

The regional biomass processing depot concept relies on AFEX-treated biomass being shipped to a centralized refinery. Thus, the biomass will not be sterile when entering the hydrolysis reactor. To simulate this, dried AFEX-treated corn stover was exposed to the atmosphere for two weeks. The biomass was then added to shake flask fermenters at 10% solid loading and both hydrolysis (50°C, pH = 5.0) and fermentation (30°C, pH = 5.5) conditions. Sugar and corn steep liquor were added as nutrients to facilitate contaminated growth. For fermentation, the solution was inoculated with *Z. mobilis* at initial inoculum of 5-10%. If necessary, glass flasks, nutrients, and buffers were sterilized via autoclaving prior to adding to the simulated hydrolysate.

A summary of results is in Table 9. Fungal growth was seen when non-sterile water and sugar were used and also when fermentation nutrients were added during hydrolysis. This fungal growth was above the water line, and was only seen to occur in shake flask reactors, not stirred reactors. Thus, it is not expected that such fungal growth would occur during scale-up. Some bacterial contamination during hydrolysis also occurred at this point. When sterilized water and sugar were used, no contamination was seen during hydrolysis, and no lactic acid was produced. Fermentation also went well, and microscopic observations revealed no other microbes besides *Z. mobilis*. Lactic acid production was between 1.5-3 g/L for a 40 g/L ethanol fermentation, or less than 2% of total sugars were consumed by lactic acid producing bacteria. Increasing the inoculum tended to decrease lactic acid production as well.

Table 9. Contamination Evaluation during hydrolysis and fermentation Of AFEX-3 treated biomass

	Fungal Growth	Bacteria observed in microscope	Lactic Acid
Nutrients added during hydrolysis, no sterilization of sugars, water, or flask	Yes	Many	7.1 g/L
No nutrients added, no sterilization of sugars, water, or flask	Yes	Few	4.2 g/L
No nutrients added, sterile water and flask	No	None	1.9 g/L
All material, including biomass, sterilized	No	None	2.3 g/L
Sterile water, actual hydrolysis performed with enzymes	No	None	2.6 g/L

Based on these results, contamination of AFEX-treated biomass is not expected to be a significant concern. Bacterial growth does not occur during enzymatic hydrolysis if nutrients are not present,

and sugars consumed for lactic acid are minimal during fermentation. An economic optimum for inoculation can be obtained by balancing reduced contamination from higher inoculum levels with the increased cost of the seed train.

Method for hydrolyzing loose AFEX-treated corn stover at high solids

Because AFEX does not greatly increase the soluble solids content of biomass, the initial stage of hydrolysis (liquefaction) must be carefully controlled to keep the hydrolysate in suspension. At high solids, the biomass can absorb all of the liquid, thus preventing adequate mixing of enzymes and biomass. Therefore, the biomass must be loaded in a fed batch manner to keep the insoluble solids content low throughout the initial liquefaction.

Different methods of fed-batch addition of biomass and enzymes were investigated. Three factors were considered: the amount of biomass added in each batch (33%/33%/33%, 50%/50%, or 50%/25%/25%), the time between each batch addition (1-6 h), and the method of adding enzymes (all enzyme added initially, enzyme added proportionally with biomass, or 50% initially and 50% after 24 h). Hydrolysis was performed in shake flasks. Samples were visually inspected during the liquefaction stage to determine if the biomass was free flowing. In addition, glucose and xylose concentration were measured after 72 h. When each batch of biomass was added 1 h apart, the material did not have time to fully solubilize, and lower sugar yields were observed. Likewise, when 50% of the biomass was added initially without all of the enzyme, the mixture was difficult to fully liquefy in the first 6 h.

Given these results, the optimal fed batch loading method for loose biomass was determined to be three equal parts of biomass added 2 h apart, with all of the enzyme added initially. The previous tests were performed on corn stover milled to less than 5 mm particle size. The fed batch method was retested with coarse (1") corn stover, and was found to still be sufficient to effectively liquefy biomass during the first 6 h of hydrolysis.

Method for hydrolyzing densified AFEX-treated corn stover at high solids

High Solid hydrolysis of densified AFEX-treated corn stover: Similar experiments as explained above were conducted using pelleted AFEX treated corn stover. For these experiments AFEX treated corn stover biomass was pelletized using a Buskirk Engineering (Ossian, IN) flat die pellet mill with ¼-inch pore size. Pelletized AFEX treated corn stover was shown to be easily mixable and digestible at high solid loadings (up to 30%) during enzymatic hydrolysis. Pelletization of lignocellulosic biomass has traditionally been considered for the purpose of improving logistics, both in increasing the bulk density and the ease of handling. However, the ease of mixing during liquefaction for pellets of AFEX treated biomass may offer another advantage. Conventional stirred tank reactors cannot be used at insoluble solid loadings above 10-15% (Hodge et al., 2009). Increasing solid loading also increases the power input on these reactors (Palmqvist and Liden, 2012). Various liquefaction reactor designs have been proposed for liquefying high solid biomass slurries, including horizontal paddle mixers (Jorgensen et al., 2007), vertical high shear mixers with anchor and/or ribbon impellers, or a vertical plug flow reactor (Humbird et al., 2011). However, these designs are either expensive, cannot be scaled to high volumes, or unproven. In contrast, liquefaction of pelletized AFEX treated biomass can be performed in conventional stirred tank reactors using a marine or pitched blade turbine due to the high free water to insoluble solids ratio. These reactors are relatively inexpensive, scalable, and may be identical to the reactors used for hydrolysis and anaerobic fermentation. Given the extreme differences in free water available during initial liquefaction for pellets and loose biomass, pelletization could significantly reduce power requirements for mixing at the biorefinery (Bals et.al.2013).

In this study, experiments were done at different solids loading (18%, 24%) with equal amounts of Ctec3 and Htec3 enzymes with a total enzyme loading of 20 mg/g of glucan. For the 18% and 24%

solid loadings experiments both fed batch biomass loadings (i.e., adding biomass two loadings) and adding all biomass at the beginning of hydrolysis showed similar conversions.

Pelletized AFEX-treated corn stover was shown to be easily mixable and digestible at high solid loadings during enzymatic hydrolysis. Using 20 mg enzyme protein per g glucan, over 70% of the total sugars were liberated in monomeric form at 18% solid loading and 72 hours. Hydrolysis yields were virtually identical between pelletized and milled, non-pelletized AFEX-treated stover, while pelletization improved sugar yields over unmilled material by approximately 3%. Thus, AFEX treatment at a local depot followed by pelletization and transportation to a centralized biorefinery may be a viable approach to solve the logistical issues with biofuel from herbaceous cellulosic materials.

Fermentation of AFEX- treated corn stover:

Pellets were hydrolyzed at 18% solid loading for 48 hours using 10 mg of each Ctec3 and HTec3 per gram of glucan. After hydrolysis, the pH was adjusted to 6, and 1% potassium phosphate and corn steep liquor was added. The hydrolysates (without removing the unhydrolyzed solids) were inoculated with Z. mobilis and fermented for 48 hours. In addition, a control using pure sugars (58 g/L glucose and 31 g/L xylose) was included. These experiments were carried out in shake flask following the method described below.

Shake Flask Hydrolysis and Fermentation

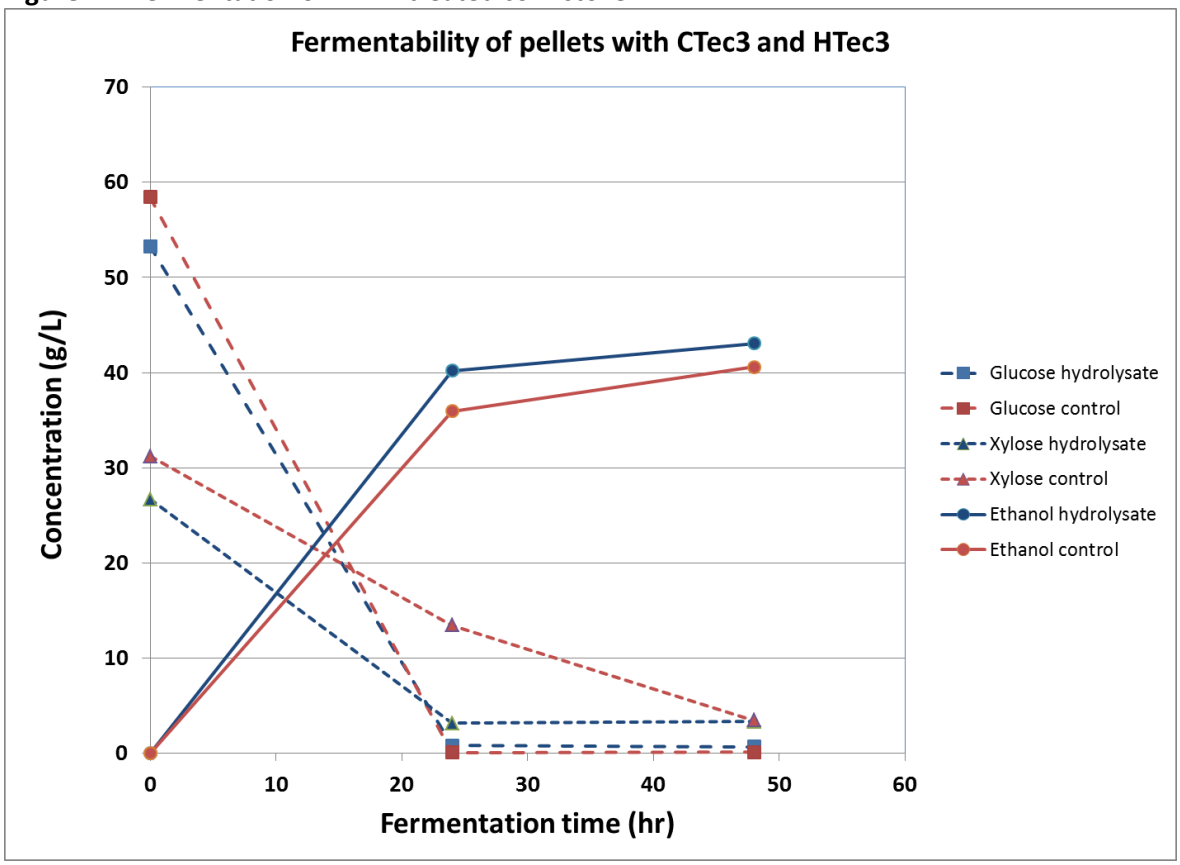
The hydrolysis and fermentation were performed in 250 mL baffled Erlenmeyer flasks. The biomass pellets were added at 20% solids loading using a total reaction mass of 100 grams. The empty flasks were first covered with foil and an aluminum culture cap with no added water before being autoclaved at 121°C for 20 minutes. Autoclaved distilled water was added to reach the 100 gram final reaction mass minus the future enzyme, nutrient, and inoculum requirements. The pH was adjusted to 5.0 using 72% sulfuric acid. CTec3 and HTec3 enzymes were added at a 10 mg protein/g glucan loading for each. The enzymes were diluted using distilled water due to their high viscosity and filtered through a 22 micron filter for sterility. The flasks were incubated in a shaker at 50°C and 250 RPM for 48 hours.

The seed culture preparation involved stages. For the first stage, a glycerol stock of the strain was used to inoculate a “rich media” composed of 100 g/L glucose, 20 g/L xylose, 10 g/L yeast extract, and 2 g/L potassium phosphate. This stage was performed in 125 mL erlenmeyer flasks with a 50 mL reaction volume under anaerobic conditions. Future seed culture stages were performed in 125 mL Erlenmeyer flasks using a reaction volume of 50 mL. The media for the second stage was identical to the first stage and 5, 10, 25, or 50 g/L corn steep liquor (CSL), the amount of the CSL was varied to investigate the optimal level. Seed cultures were incubated in a shaker at 32°C and 100 RPM until late exponential phase.

Prior to fermentation, pH was adjusted to 6.0 using 10M potassium hydroxide. Inoculation was performed by directly adding the Z. mobilis seed culture on a percent weight basis assuming a density of 1 g/mL. Inoculum size was 10% of the total reaction mass. Corn steep liquor (CSL) was added to the fermentation as a nutrient source. The CSL was weighed onto plastic dishes to the nearest 0.01 g and washed into the fermentation using the inoculum broth. The fermentations were incubated in a shaker at 30°C and 100 RPM.

As seen in Figure 44, the hydrolysate fermentation performed better than the control. In both cases, glucose consumption was complete within 24 h. However, xylose consumption was faster for the hydrolysate than the control, although the final extent of xylose consumption was similar in both. Likewise, the ethanol productivity was higher for the hydrolysate, a higher concentration of ethanol (43 g/L) in the hydrolysate than in the control (41 g/L) was obtained. Due to the high xylose consumption and high productivity, we can conclude that pelletization will not harm the fermentability of AFEX-treated biomass. For this test the AFEX treated corn stover was generated using the AFEX 3 lab scale. Fermentability of corn stover treated in our AFEX 3 pilot scale has been demonstrated in Subtask F.2

Figure 44. Fermentation of AFEX- treated corn stover



Subtask F.2. Evaluate fermentability of corn stover treated in AFEX 3 engineering scale unit

Fermentability of the corn stover treated in the AFEX 3 engineering scale was evaluated using 5-L fermentor and later the results were verified at larger scale 2500l fermentor. For this study AFEX treated corn stover were pelletized using our flat die pellet mill. The detail of the study is provided below.

(Note: The 5-L experiments were supported by this project. The 2500-l run was supported with another project, however the collected data were used in our techno economic model to estimate the ethanol production cost from AFEX treated corn stover pellets)

5-L Hydrolysis and fermentation

Hydrolysis and fermentation was carried out in a Bioflo 3000 (Eppendorf, Inc, Enfield, CT) 5-L fermentor equipped with a single marine impeller and no baffles. Temperature was controlled via an external jacket connected to a water bath. Hydrolysis was performed at 50˚C and 22% solid loading. The fermentor and water were autoclaved prior to use; enzymes, biomass, and acid were not sterilized. AFEX pellets were added from a port at the top of the reactor in a fed batch manner; two-thirds of the pellets were added initially and the remaining one-third were added after 3 hours. Enzyme loading was 10mg CTec3 and 10 mg HTec3 per g glucan and added proportionally with the pellets. The pH was maintained at 5.25 +/- 0.25 by addition of 4M sulfuric acid as needed. The impeller speed was increased to 900 RPM during liquefaction and later maintained at 400 RPM. Total hydrolysis time varied from 30-36 hours.

After hydrolysis was complete, the vessel was cooled to 30˚C and pH adjusted to 6.0 using 4M KOH prior to inoculation. *Z. mobilis* was first grown in 15 mL tubes for 8 hours in order to reach an OD600

of 0.7 before transferring to pleated 1000 mL flasks for 24 hours. Both seeds were incubated at 30C and shaken at 100 RPM. The seed media included 105 g/L glucose, 20 g/L xylose, 10 g/L Bacto yeast extract (Becton, Dickinson and Co, Franklin Lakes, NJ), and 2 g/L potassium phosphate. The inoculum was 10% of the total weight, reducing the AFEX biomass solid loading to 20%. The only nutrient was Fermgold corn steep liquor (Cargill, Minneapolis, MN) at 2.5 g/L. The fermentation was performed for 24 hours.

The data collected from this study is presented in Figure 45. To evaluate the performance of *Z. mobilis* in utilization of the sugars derived from AFEX pellets, a fermentation using clean sugar (at a concentration similar to the AFEX pellets hydrolysate) was also conducted. The results are presented in Table 10.

Important observations and results:

- There was no sign of contamination
- Both glucose and xylose were utilized
- Controlling pH and temperature was not aproblem
- Productivity was high = >2.0 g/Lh
- High hydrolysis yield: 89% glucose and 76% xylose yield
- Ethanol Yield = 0.50 g/g glucose and xylose
- Good ethanol titer=60 g/L
- The titer, productivity, and yield exceeded the performance targets set out by NREL (Table 10)
- AFEX fermentation performs better than clean sugars

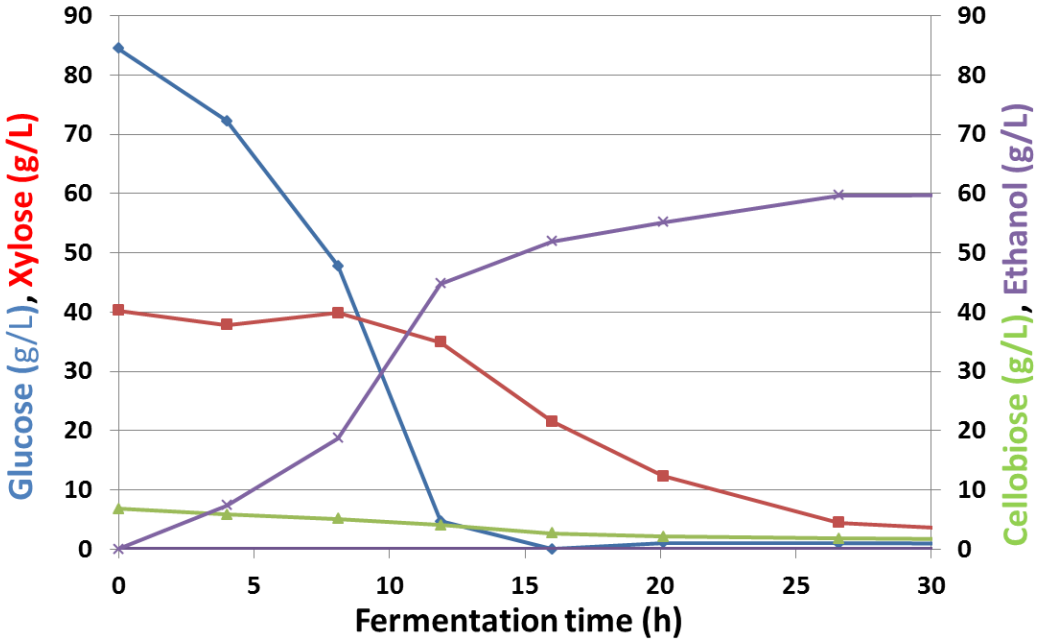


Figure 45. Saccharification and fermentation of AFEX pellets at a final solid loading of 20% at the engineering (5-L) scale. Hydrolysis was performed at 22% solid loading and 7 g enzyme protein/kg biomass, 50°C, and pH 5.5. Fermentation occurred with a 10% inoculum, 2.5 g/L corn steep liquor, 30°C, and pH 6.

2500-L Hydrolysis and fermentation

The scale-up was performed in a 3800-L jacketed stainless steel reactor equipped with a single marine impeller and a variable speed 20HP motor. The desired amount of water was added to the reactor and then sterilized at 120˚C for 30 min prior to beginning hydrolysis. AFEX pellets were poured into the reactor from a port at the top of the reactor. Identical conditions (22% solid loading, 7 g enzyme protein/kg biomass, fed batch approach, 4 M H2SO4 for pH control) was used as with the 5-L reactor. Two separate pH probes were used, and the average of the two was used to provide pH. In addition, a sample at 3 h was taken and pH tested to insure that the calibration remained correct on these probes. The impeller speed was 110 RPM. Adequate mixing was determined by monitoring the pH and monitoring the temperature at the bottom of the reactor. The total hydrolysis time was 48 hours. The first two stages of the fermentation seed train were identical to the 5-L reactor. The third stage was performed in 10-L glass Bioflo 3000 fermenters (Eppendorf, Inc, Enfield, CT) for approximately 8 hours, and the last stage in a 100-L and 150-L stainless steel stirred tank reactor. The optical density was measured prior to transferring to each successive stage. Fermentation continued in the 2500-L reactor under the same conditions as the 5-L reactor. Nitrogen overpressure at 2 psig was used to minimize contamination. Total fermentation time was 36 hours with an impeller speed of 90 RPM. The results are presented in Figure 46.

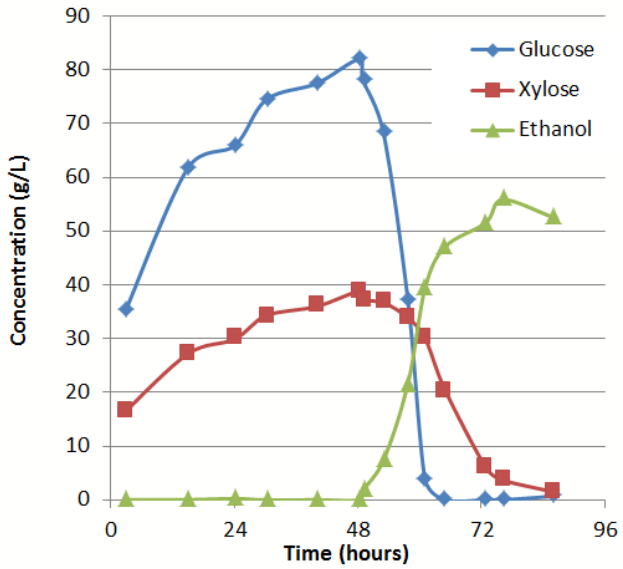


Figure 46. Saccharification and fermentation of AFEX pellets at a final solid loading of 20% at the engineering (2500-L) scale. Hydrolysis was performed at 22% solid loading and 10 mg total enzyme protein/g glucan, 50°C, and pH 5.5. Fermentation occurred with a 10% inoculum, 2.5 g/L corn steep liquor, 30°C, and pH 6.

Important observations and results:

- There was no sign of contamination
- AFEX pellets were not sterilized before added to fermentor
- No evidence of inhibitory compounds in the sugar stream
- Very similar trends and performance as at 5-L scale
- Both glucose and xylose were utilized
- No additional processing of the pellets (such as washing or grinding) was required prior to enzyme addition

- During the first few hours of the hydrolysis, due to a poor mixing, the pH and temperature deviated from the set targets. However after a few hours (4-5 hr) the problem was resolved and everything was controlled at the target
- No major nutrient addition was required, as all minerals and nitrogen are provided by the AFEX pellets. By avoiding the need for nutrient supplementation, AFEX pellets can provide a considerable cost advantage over competing pre-treatment processes.
- Productivity was high = >2.0 g/Lh
- Hydrolysis yields were slightly lower than the 5-L experiment: 81% glucose and 69% xylose yield, most probably due to the pH deviation
- Ethanol Yield = 0.46 g/g glucose and xylose
- Good ethanol titer=51 g/L

Results shown in Figure 45 and 46 confirmed that AFEX pellets can be successfully hydrolyzed into a sugar stream that can be fermented to ethanol at high yield and productivity. In comparison with the 2011 NREL biorefinery model performance targets the AFEX fermentation actually meets/exceeds the targets (Table 10).

Table 10. Summary of fermentation results

	Clean sugars	**5L**	**2500 L**	**NREL Target***
Fermentation time (hr)	40	24	24	36
Seed size (%)	10	10	10	10
Nutrient addition (CSL % w/w)	0.25	0.25	0.25	0.25
Ethanol titer (g/l)	51	60	51	56
Ethanol metabolic yield (g/g sugar)	0.44	0.5	0.45	0.45
Productivity (g/Lh)	1.24	2.53	2.1	1.57
Ethanol yield (gallon/ MT of corn stover)	N/A	87	71	87
Hydrolysis performance				
Hydrolysis time		30	36	84
Enzyme loading (mg/g glucan)		20	20	20
Solid loading(%)		22	22	20
Glucose yield (%)		90	81	90
Xylose yield (%)		76	69	90

One of our project milestones was to demonstrate that using AFEX 3 design for a commercial scale depot instead of the traditional AFEX design can reduce the cost of ethanol production in a biorefinery (processing 2000 tonne biomass per day) by 16%. Using the techno economic model developed based on NREL biorefinery and applying the fermentation parameters and performance data collected from our large scale fermentation test showed, 24% reduction (exceeding our target) in the ethanol production cost.

Task G. Project management and reporting

Description:

Reports and other deliverables will be provided in accordance with the Federal Assistance Reporting Checklist following the instructions included therein. MBI will accommodate and facilitate

two to three technical and commercialization validations to be conducted by National Renewable Energy Laboratory (NREL), under guidance of the Department of Energy (DOE), with confidentiality agreements in place.

The validation plan will be sent to MBI well in advance of the validations. This plan will contain additional definition of the validation protocol. The validation plan will also outline the process that will be followed if any saccharification experiments fail to meet or exceed the performance baselines and targets presented in the recipient's application as well as the procedure to be followed for return visits.

MBI will provide NREL and DOE with requested documents related to the validations in a timely manner. Failure to provide requested information in a timely manner could result in DOE requesting corrective action or lead to termination of the award.

A Stage Gate Review is to be incorporated into the Project Management Plan (PMP), that coincides with the end of the Research and Development (R&D). The Stage Gate Review will be used to analyze project progress, as it relates to the initial performance data produced before the award, and provided within the application. The data used in the analysis will be provided from the recipient, as well as the validation gathered by NREL after initiation of award. NREL will provide the Stage Gate Review Committee with the results of the technical and commercial audits of the projects, to be performed at the project facilities in the months leading up to the Stage Gate.

Accomplishments:

- On-site initial validation was completed in October 2011
- On-site intermediate validation was completed in July 2013
- Stage gate review was completed in July 2013
- Final on-site validation was completed in February 2015
- All of the reporting requirements were fulfilled according to the agreed schedule

Patents: US Patent Application No. 13/458,568, Process for Treating Biomass, was applied for on April 27, 2012.

Publications/Presentations:

Campbell TJ, Teymouri F, Bals B, Glassbrook J, Nielson CD, Videto J (2013). A packed bed Ammonia Fiber Expansion reactor system for pretreatment of agricultural residues at regional depots. Biofuels 4: 23-34.

Thompson DN, Campbell T, Bals B, Runge T, Teymouri F, Ovard LP (2013). Chemical preconversion: Application of low-severity pretreatment chemistries for commoditization of lignocellulosic feedstock. Biofuels, 4:3, 323-340

Bals BD, Gunawan C, Moore J, Teymouri F, Dale BE. Enzymatic hydrolysis of pelletized AFEX™-treated corn stover at high solid loadings. Biotechnology and Bioengineering 111: 264-271 (2014).

Campbell T, Teymouri F, Glassbrook J, Senyk D, Bals BD, Nielson CD, Videto JJ, Moore JM. Development of a pilot-scale packed bed Ammonia Fiber Expansion (AFEXTM) process. Presented at 35th Symposium for Biobased Fuels and Chemicals, Portland, OR, May 2, 2013.

Bals BD, Gunawan C, Moore J, Teymouri F, Pardonnet A, Campbell T, Nielson C, Videto J, Dale B. Pelletization and high solids enzymatic hydrolysis of AFEX treated corn stover. Poster presented at 35th Symposium for Biobased Fuels and Chemicals, Portland, OR, April 29, 2013.

Campbell T, Teymouri F, Glassbrook J, Senyk D, Bals BD, Nielson CD, Videto JJ, Moore JM. Pilot-Scale De-Risking of AFEX Performance and Applications. Presented at 36th Symposium for Biobased Fuels and Chemicals, Clearwater, FL April 30, 2014.

Amber N. Hoover, Jaya Shankar Tumuluru, Farzaneh Teymouri, Janette Moore, Garold Gresham. Effect of pelleting process variables on physical properties and sugar yields of ammonia fiber expansion pretreated corn stover. Bioresource Technology 164 (2014) 128–135

Ian J. Bonner, David N. Thompson, Farzaneh Teymouri, Timothy Campbell, Bryan Bals, Jaya Shankar Tumuluru. Impact of Sequential Ammonia Fiber Expansion (AFEX) Pretreatment and Pelletization on the Moisture Sorption Properties of Corn Stover. Accepted for publication in Drying Technology

Cory Sarks, Bryan D. Bals, Mingjie Jin, Farzaneh Teymouri, Bruce E. Dale, and Venkatesh Balan. Fermentation condition optimization and economic analysis for ethanol production from pelletized AFEX™ corn stover using commercial enzymes and Zymomonas mobilis 8b. Manuscript submitted to Bioresource Technology

References

Bals BD, Gunawan C, Moore J, Teymouri F, Pardonnet A, Campbell T, Nielson C, Videto J, Dale B. Pelletization and high solids enzymatic hydrolysis of AFEX treated corn stover. Poster presented at 35th Symposium for Biobased Fuels and Chemicals, Portland, OR, April 29, 2013.

Campbell, T.J., Teymouri, F., Bals, B., Glassbrook, J., Nielson, C.D., Videto, J., 2013. A packed bed AFEX reactor system for pretreatment of agricultural residues at regional depots. Biofuels 4, in press, DOI 10.4155/BFS.12.71.

Carolan, J., S. Joshi, and B. Dale. 2007. Technical and financial feasibility analysis of distributed bioprocessing using regional biomass pre processing centers. Journal of Agricultural and Food Industrial Organization, Volume 5, Article 10 (2007) SPECIAL ISSUE: Explorations in Biofuels Economics, Policy, and History.

Eggeman, T. and R.T. Elander. 2005. Process and economic analysis of pretreatment technologies. Bioresource Technology. 96: 2019-2025.

Hess, R.J., K.L. Kenney, L.P. Ovard, E.M. Searcy, and C.T. Wright. 2009. Commodity-scale production of an infrastructure-compatible bulk solid from herbaceous lignocellulosic biomass. Vol. A: Uniform-format vision and conventional-bale supply system. Uniform-format bioenergy feedstock supply system design report series. INL/EXT-09-17527.

Hodge, D.B., Karim, M.N., Schell, D.J., McMillan, J.D., 2009. Model-based fed-batch for high-solids enzymatic cellulose hydrolysis. Appl. Biochem. Biotechnol. 152, 88-107.

Humbird, D., Davis, R., Tao, L., Kinchin, C., Hsu, D., Aden, A., et al., 2011. Process design and economics for biochemical conversion of lignocellulosic biomass to ethanol. National Renewable Energy Laboratory, NREL Report tp-5100-47764.

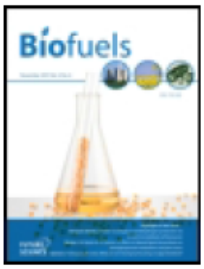
Jorgensen, H., Vibe-Pedersen, J., Larsen, J., Felby, C., 2007. Liquefaction of lignocellulose at high-solids concentrations. Biotechnol. Bioeng. 96, 862-870.

Palmqvist, B. and Liden, G., 2012. Torque measurements reveal large process differences between materials during high solid enzymatic hydrolysis of pretreated lignocellulose. Biotechnol. Biofuels 5, 57.

Richard, T.L. 2010. Challenges in scaling up biofuels infrastructures. Science. 329: 793-796

Tillner-Roth R, Friend DG. A Helmholtz free energy formulation of the thermodynamic properties of the mixture {water + ammonia}. J. Phys. Chem. Ref. Data. 27(1), 63–96 (1998). *Provides fundamental property data for ammonia/water mixtures

Appendix A



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A packed bed Ammonia Fiber Expansion reactor system for pretreatment of agricultural residues at regional depots

Timothy J Campbell[b], Farzaneh Teymouri[a], Bryan Bals[a], John Glassbrook[a], Chandra D Nielson[a] & Josh Videto[a]
[a] MBI, 3815 Technology Boulevard, Lansing, MI 48910-8596, USA
[b] MBI, 3815 Technology Boulevard, Lansing, MI 48910-8596, USA.
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Appendix B

Summary of Characterization Test of Corn stover
Campaigns 1 & 2

Tyler Westover, Neal Yancey, Dave Thompson, Debby Bruhn
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1.0 Background/Objectives/Description
The primary objective is to determine the effects of feedstock specifications (particle size, shape factor, moisture) and reactor design on pretreatment efficacy (sugar yield and feedstock throughput) and ammonia recycle at lab scale. Another objective is to demonstrate a lower the financial cost of AFEX3 treatement than was attained with earlier designs (AFEX1). The tests to be performed at INL include water activity, permeability, moisture content, loose bulk density, compressibility, percent springback, wall friction, particle size/shape distributions, unconfined yield (shear) strength, and total percent ash content.

2.0 Material
This experiment involved twelve corn stover samples as listed in Table 1. These samples were subjected to several characterization tests, the results of which are briefly summarized in experiments listed in the logic diagram shown in Table 2. Each of the characterization tests is discussed in greater detail in the paragraphs that follow.

Table 1. Sample label information.

Campaign 1 (Jan. 2012)

Number	Identifier	Description	INL bar code
1	H 3/16 N	Hammermill with 3/16 screen with pneumatics	
2	H 5/16 N	Hammermill with 5/16 screen with pneumatics	
3	H 1/2 N	Hammermill with 1/2 inch screen with pneumatics	
4	H 3/16 W	Hammermill with 3/16 screen without pneumatics	
5	H 5/16 W	Hammermill with 5/16 screen without pneumatics	
6	H 1/2 W	Hammermill with 1/2 inch screen without pneumatics	
7	K 2mm N	Chipper drum with 2mm screen with pneumatics	
8	K 3/16 N	Chipper drum with 3/16 screen with pneumatics	
9	K 1/2 N	Chipperdrum with 1/2 inch screen with pneumatics	
10	K 2mm W	Chipper drum with 2mm screen without pneumatics	
11	K 3/16 W	Chipper drum with 3/16 screen without pneumatics	
12	K 1/2 W	Chipper drum with 1/2 inch screen without pneumatics	

Campaign 2 (Feb. 2012)

2a.	(1/2")	Discussed below	
2b.	(BG480 1")	" "	
2c.	(BG480 2")	" "	
2d.	(6"→1/2")	" "	
2e.	(4"→1/2")	" "	
2f.	(1"→1/2")	" "	
2g.	(3.375")	" "	
2h.	(3.375"→>1/2"→1.75")	" "	
2i.	(3.375"→>1/2"→1.25")	" "	
2a.	(1/2")	" "	

Table 2. Brief Summary of Physical and Chemical Characterization Tests

Test→		**H_2O Act.**	**Perm.**	**Moist.**	**LBD**	**Comp.**	**SprBk**	**Wall Fr.**	**Camsizer**	**Sieve**	**Shear**	**Ash**
Priority→		1	2	3	4	5	6	7	8	9	8	9
Replicates→		3	3	3	3	3		1	3	2	1	3
Parameter→				MC	ρ_{LB}	CR	SprBk		d_{50}	d_{50}		
Unit→		Equil. MC @ 90% R.H.		% w.b.	kg/m^3	C.R. @ 4 kPa	%SprBk @ 4kPa		mm	mm		% ash (d. b.)
#	Code											
1	H 3/16 N	19.7%		5.6%	135.4	1.13	5%	*	0.39	0.29	*	8.7
2	H 5/16 N	19.7%		10.4%	126.5	1.18	4%	*	0.54	0.43	*	6.9
3	H 1/2 N	18.9%		7.1%				*	0.75	0.51	*	9.0
4	H 3/16 W	14.5%		11.8%	126.5	1.22	5%	*	0.58	0.38	*	4.7
5	H 5/16 W	18.9%		6.5%	117.5	1.15	5%	*	0.56	0.63	*	5.6
6	H 1/2 W			4.8%	102.1	1.22	8%	*	0.70	0.39	*	6.2
7	K 2mm N	19.7%		9.2%	134.6	1.18	4%	*	0.46	0.54	*	7.8
8	K 3/16 N	17.7%		9.5%	134.3	1.23	5%	*	0.51	0.35	*	9.6
9	K 1/2 N	21.2%		9.1%	101.4	1.31	11%	*	0.72	0.32	*	7.5
10	K 2mm W	18.3%		9.1%	139.9	1.21	4%	*	0.49	0.37	*	6.9
11	K 3/16 W	16.5%		9.5%	121.2	1.29		*	0.55	0.38	*	8.8
12	K 1/2 W	19.7%		8.8%	101.0	1.31	8%	*	1.00	0.42	*	7.3

Note: H2O Act. – Water activity; Perm. = Permeability; Moist. (MC) – Moisture content; LBD. = Loose Bulk density; Comp. – Compressibility; CR – Compressibility ratio; SprBk – Spring back (elastic wind-up); Wall Fr. = wall friction; Sieve – Sieve size distribution using Ro-tap sieve separator ; Camsizer – Particle size/shape distribution with camsizer; Shear = Jenike shear ratio from unconfined yield (shear) test; * indicates tests that have been completed but the data has not yet been fully analyzed.

3.0 Water Activity

Figure 1 presents the sorption isotherms of 10 samples (samples tested to date), while Fig. 2 present the sorption isotherms of samples hammer and knife milled separately. The data in Figures 1 and 2 indicate that except for the vapor-saturated conditions (distilled water ~100% RH) the two grind sizes exhibited similar sorption performance. The results in Figures 1 and 2 are based upon a single test per sample, and additional test will be necessary to determine if there are significant differences in the moisture sorption of the samples.

Figure 3 contains sorption isotherms for samples ground using a 3/16" screen and at different temperatures. Again, the different grinder and pneumatic conveyance techniques do not exhibit a clear impact on the sorption curves. Figure 3 does indicate that water content goes DOWN as temperatures increased from 40° to 90° C. The data in Figures 1-3 indicate that 25% water content (wet basis) may be achieved using a relative humidity in the range 80-100%; however, considerable uncertainty still exists. We may find additional benefit by injecting steam directly onto the materials, which would allow condensation on the material's surfaces as well as vapor-phase water adsorption.

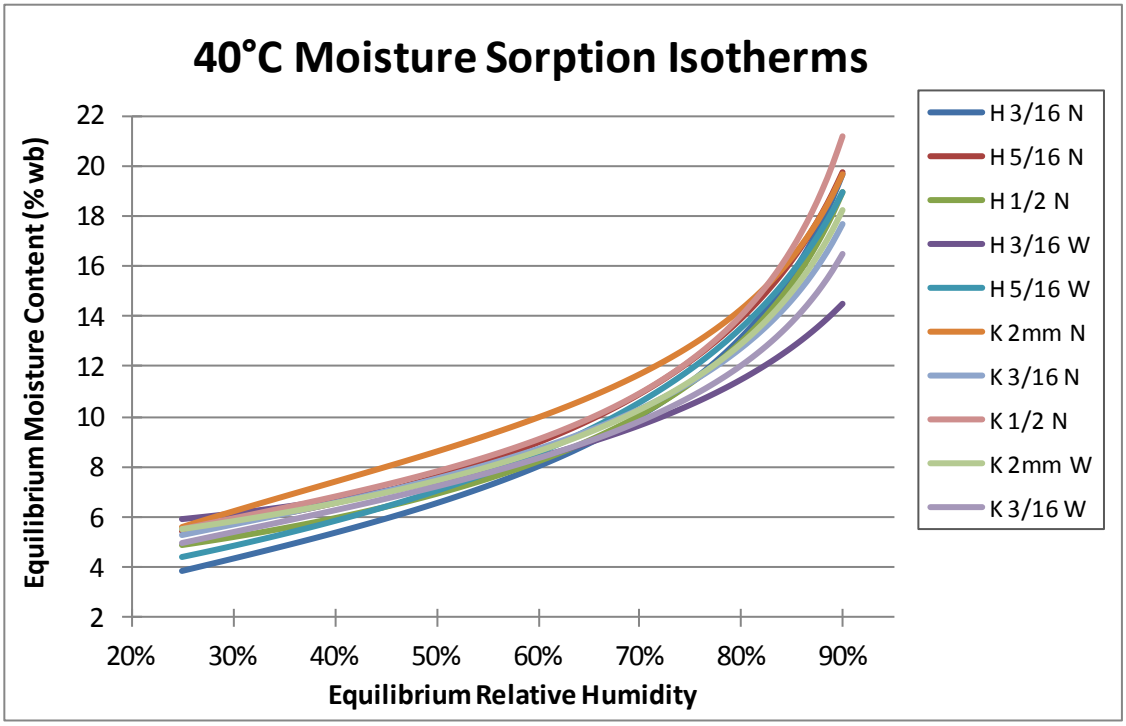


Fig. 1. Sorption isotherms of 10 samples (samples tested to date).

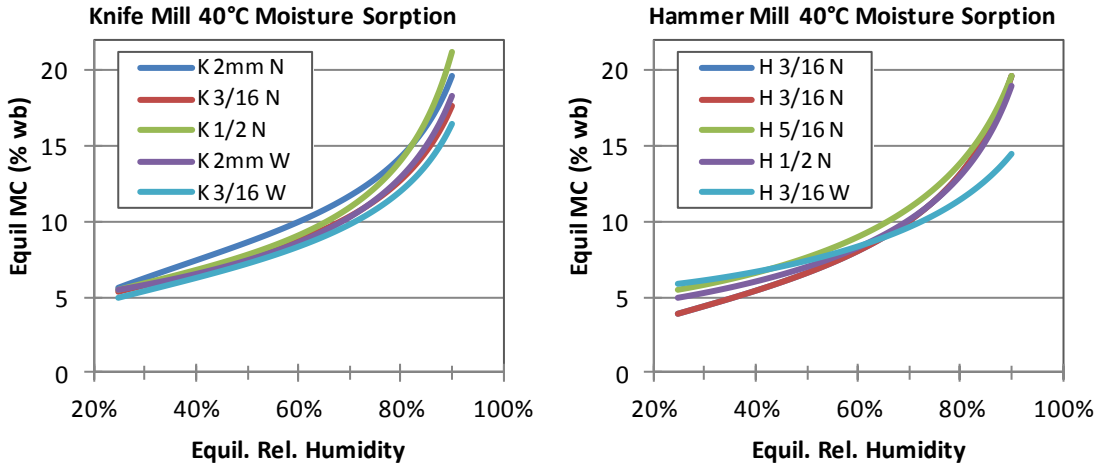


Fig. 2. Sorption isotherms of samples hammer and knife milled separately.

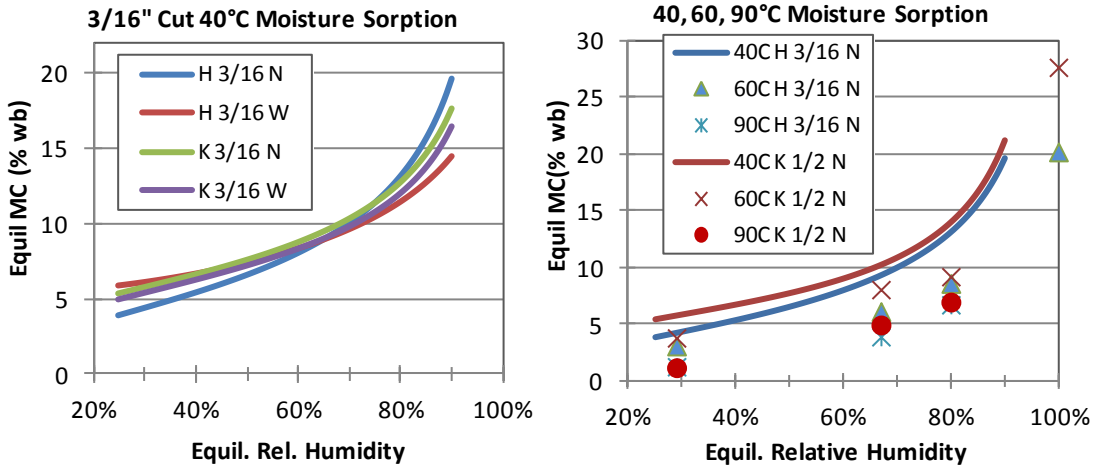


Fig. 3. Sorption isotherms for samples ground using a 3/16" screen and at different temperatures.

4.0 Moisture

For moisture measurements, one specimen from each sample (labelled 'A') was grabbed from each primary sample immediately after the grinding operation. Two additional specimens were also split from each of the primary samples using a rifflesplitter. The specimens were dried using NREL oven drying standard methods, which involves drying the specimens for 24 hours at 105°C. The percent moisture measurements on a wet basis are reported in Table 3 for each of the three replicates.

Table 3. Measured percent moisture for all samples, including three replicates.

#	Code	A (% wb)	B (% wb)	C (% wb)	Average (% wb)
1	H 3/16 N	4.9%	6.0%	6.0%	5.6%
2	H 5/16 N	13.0%	9.1%	9.1%	10.4%
3	H 1/2 N	4.5%	8.5%	8.3%	7.1%
4	H 3/16 W	11.7%	12.0%	11.8%	11.8%
5	H 5/16 W	6.6%	6.5%	6.3%	6.5%
6	H 1/2 W	4.8%	4.8%	4.8%	4.8%

7	K 2mm N	9.1%	8.8%	8.8%	8.9%
8	K 3/16 N	9.6%	9.4%	9.4%	9.5%
9	K 1/2 N	9.7%	9.3%	9.3%	9.4%
10	K 2mm W	9.0%	9.1%	9.2%	9.1%
11	K 3/16 W	9.3%	9.6%	9.5%	9.5%
12	K 1/2 W	9.2%	8.6%	8.6%	8.8%

5.0 Loose and consolidated bulk densities

For bulk density measurements, specimens were split from each of the primary samples using a rifflesplitter. Each specimen was then uniformly loaded into a compression cell (diameter = 7.75 in. and height = 2.5 in.) and compressed slowly to 0.38, 0.76, 1.54, and 2.68 kPa in sequence. The pressure was maintained constant at each target pressure for a minimum of 15 minutes, and the compression history of the sample was recorded every 20 seconds to verify that a steady state consolidated bulk density had been very nearly achieved for each measurement before the consolidation stress was advanced to the next measurement. The pressure sequences were 0.38, 0.76, 1.54 kPa (performed 1 time to measure percent spring back after 4 kPa consolidation stress) and 0.0, 0.38, 0.76, 1.54, and 2.68 kPa (performed 2 times to measure percent spring back after 2.68 kPa consolidation stress).

After the final consolidated bulk density was recorded, the pressure on the sample was relaxed and maintained at a small value (approximately 0.05 kPa) until steady state after spring back had been nearly achieved (minimum of 15 minutes, based on the relaxation history of the sample). Percent spring back is calculated as the percent increase in volume of the sample after the consolidation stress is relaxed from its maximum value to a very small value of approximately 0.05 kPa. The measured bulk densities and percent spring back for the samples characterized thus far are listed in Table 3 (data that has not yet been collected are blank in Table 3).

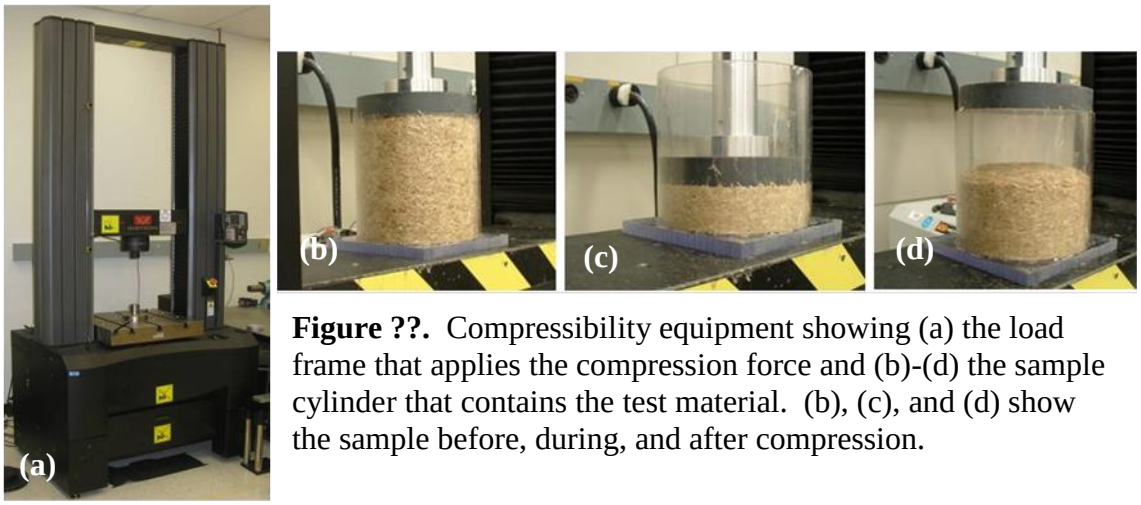


Figure ??. Compressibility equipment showing (a) the load frame that applies the compression force and (b)-(d) the sample cylinder that contains the test material. (b), (c), and (d) show the sample before, during, and after compression.

6.0 Particle size and shape distributions

Two methods were employed to assess particle size distribution. First, a standard sieve analysis using a set of nine sieves and a pan. The sizes of the sieves were 2.38, 1.68, 1.2, 0.85, 0.60, 0.42, 0.30, 0.25, and 0.18 mm. Secondly, a Camsizer^{TM} digital image processing system was employed to characterize the particle size/shape distributions. For the sieve analyses, two specimens were split using rifflesplitters from each primary sample and both samples were

separately characterized. For the camsizer characterizations, three specimens were split from each primary sample using a combination of riffle splitters and rotary splitters.

Figure 4 displays the cumulative particle passing distributions (CPDs) for the four samples that were ground with a ½ inch screen (knife mill and hammer mill each with and without pneumatic assist) as measured using the Camsizer^{TM}. The associated probability density distributions (PDDs), which represent the derivative of the CPDs are also shown as dashed lines. Interestingly, three of the CPDs appear very similar, and only the sample that was knife milled without pneumatic assist (#12 in Table 1) exhibits a significantly larger particle size distribution. The corresponding data obtained from the mechanical sieve test (Fig. 5) displays the same general trend, although the standard sieve analysis indicates that the sample that was hammer milled without pneumatic assist (#6 in Table 1) is the sample that is most different from the others.

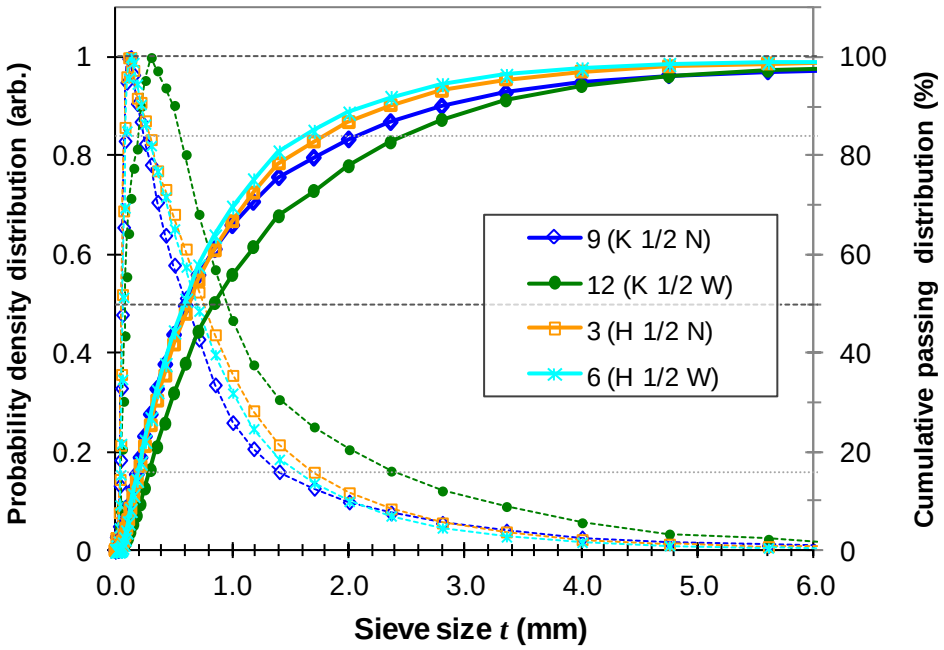


Fig. 4. Cumulative particle passing distributions (CPDs) and associated probability density distributions (PDDs) for the samples that were ground with a ½ inch screen (knife mill and hammer mill each with and without pneumatic assist) as measured using the CamsizerTM. Horizontal dashed lines indicate the 16, 50, and 84% marks on the CPD axis.

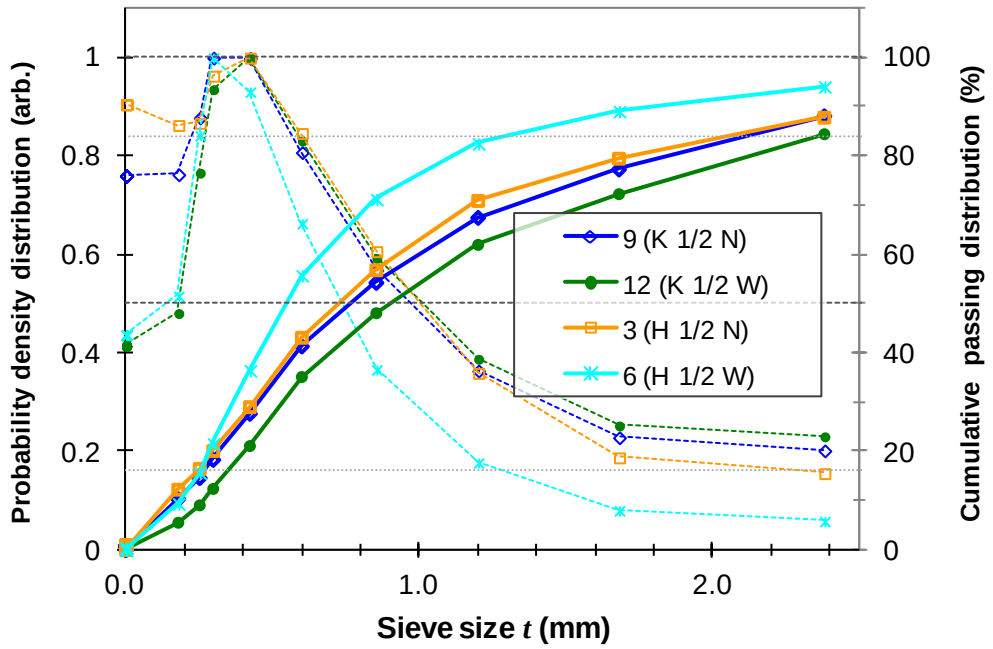


Fig. 5. Standard sieve analysis results of the samples featured in Fig. 4 (knife mill and hammer mill each ground with a ½ inch screen with and without pneumatic assist). Note that the sieve scale is smaller from that in Fig. 4.

For all of the analyses, the 50% cumulative passing percentile sieve size, t_{50}, was calculated by interpolation to find the theoretical sieve size that corresponds to retaining 50% of the particles by mass (by approximated particle volume for the Camsizer™). This sieve size corresponds to the 50% height on the cumulative passing distribution (CPD). Similarly, the 16% and 84% cumulative passing percentile sieve sizes (t_{16} and t_{84}, respectively) were also interpolated from the percent cumulative passing plots from both the Camsizer™ and standard sieve analyses. These parameters are plotted graphically in Fig. 6 for all of the samples, and the actual data values are presented in Table 4, along with their estimated standard deviations (three replicates for the Camsizer™ and two replicates for the sieve analyses). Two other parameters, the mean sphericity and the mean aspect ratios of the particle distributions are also available from the Camsizer™ and are listed in Table 4. The definitions of these parameters are provided in the Appendix. Note that from the standard deviations calculated from the replicate measurements (see Table 4) that the Camsizer™ and standard sieve analyses are both highly repeatable with small variation between replicate measurements. The data indicate that standard sieve analyses tend to yield somewhat larger particle size distributions than Camsizer™ analyses of the same samples. Figure 6 and Table 4 also indicate that the samples ground with the ½ inch screens are the samples with the largest particles and the fewest fines.

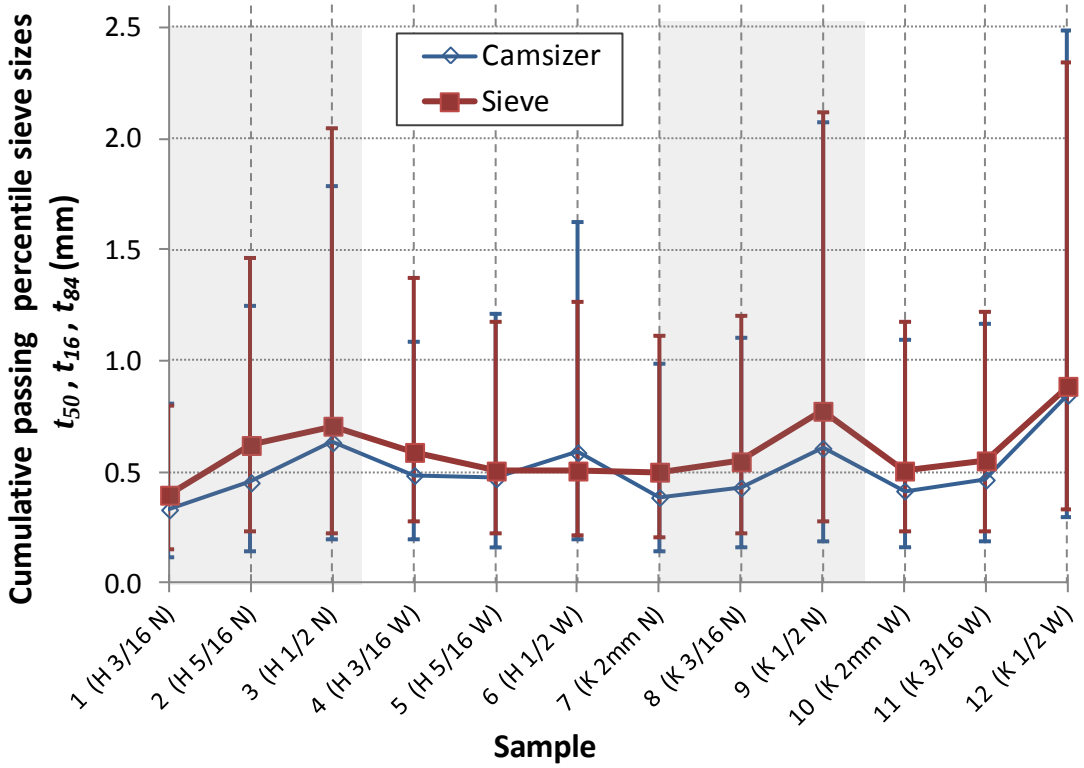


Fig. 6. 50% cumulative passing percentile sieve sizes t_{50}) estimated from the Camsizer™ and standard sieve analyses. The error bars represent t_{16} and t_{84} (the 16% and 84% cumulative passing percentile sieve sizes). This data is the average of three replicate Camsizer™ measurements and two replicate sieve analyses.

Table 4. Bulk density measurements of Campaign 1 samples at different levels of consolidation stress.

		Consolidation stress													**Spring back**		
		0 kPa			**0.38 kPa**			**0.76 kPa**			**1.54 kPa**			**2.68 kPa**	**1.54 kPa**	**2.68 kPa**	
#	Code	A	B	C	A	B	C	A	B	C	A	B	C	A	B	A	A	B
1	H 3/16 N	135.4			143.2			147.5			153.0					5%		
2	H 5/16 N	126.3	126.7		139.3	135.6		144.5	140.7		151.0	147.3		153.6		4%	8%	
3	H 1/2 N																	
4	H 3/16 W	127.9	125.0		140.9	140.3		147.0	146.1		154.5	153.2		160.5		5%	7%	
5	H 5/16 W	117.0	117.5	118.1	125.5	125.4	126.6	130.4	130.2	130.1	136.4	136.3	134.5			5%		
6	H 1/2 W	101.6	102.6		112.8	112.5		117.9	117.7		124.1	124.0		130.1		8%	10%	
7	K 2mm N	133.8	135.3		145.1	142.8		151.4	151.1		159.5	159.0		166.8		4%	7%	
8	K 3/16 N	139.3	129.4		149.3			156.1			164.6					5%		
9	K 1/2 N	99.8	103.0		115.9	118.1		123.0	125.3		131.8	134.2		142.8		11%	12%	
10	K 2mm W	143.8	136.0		156.4	151.7		162.9	159.1		171.2	167.9		176.4		4%	9%	
11	K 3/16 W	121.5	120.9		139.4	138.7		147.0	146.2		156.3	155.3		164.8				
12	K 1/2 W	104.2	97.8		118.8	113.9		126.2	121.2		135.2	130.2		139.0		8%	13%	

Table 5. Particle size and shape distributions from Camsizer™ and sieve analyses. Standard deviations for the analyses are shown in parantheses.

		Camsizer					**Sieve**		
#	Code	t_{50}	t_{16}	t_{84}	1/SPHT	Aspect Ratio	t_{50}	t_{16}	t_{84}
1	H 3/16 N	0.33 (0.01)	0.12 (0)	0.8 (0.01)	1.7 (0)	0.52 (0)	0.4 (0.01)	0.16 (0.01)	0.8 (0.01)
2	H 5/16 N	0.45 (0.02)	0.14 (0)	1.25 (0.06)	1.84 (0.02)	1.48 (0)	0.61 (0.01)	0.22 (0)	1.46 (0.03)
3	H 1/2 N	0.63 (0.02)	0.2 (0.01)	1.78 (0.09)	1.87 (0.02)	2.08 (0)	0.73 (0.02)	0.24 (0.02)	2.06 (0.04)
4	H 3/16 W	0.48 (0.01)	0.2 (0)	1.09 (0.01)	1.8 (0)	1.27 (0)	0.6 (0.01)	0.28 (0)	1.38 (0.03)
5	H 5/16 W	0.47 (0.01)	0.16 (0)	1.21 (0.03)	1.85 (0.01)	1.44 (0)	0.52 (0.02)	0.23 (0)	1.18 (0.02)
6	H 1/2 W	0.59 (0)	0.2 (0)	1.63 (0.01)	2.05 (0.02)	1.92 (0)	0.55 (0.08)	0.25 (0.03)	1.3 (0.2)
7	K 2mm N	0.39 (0.01)	0.14 (0)	0.98 (0.03)	1.85 (0.02)	1.16 (0)	0.5 (0)	0.2 (0)	1.11 (0.01)
8	K 3/16 N	0.43 (0.01)	0.16 (0)	1.1 (0.04)	1.92 (0.06)	1.3 (0.01)	0.55 (0)	0.22 (0)	1.2 (0)
9	K 1/2 N	0.61 (0.04)	0.19 (0.01)	2.07 (0.2)	2.14 (0.11)	2.44 (0.02)	0.77 (0.01)	0.27 (0)	2.12 (0)
10	K 2mm W	0.42 (0.01)	0.16 (0)	1.09 (0.03)	2.02 (0)	1.28 (0)	0.5 (0)	0.23 (0.01)	1.17 (0)
11	K 3/16 W	0.47 (0)	0.19 (0)	1.16 (0.01)	1.93 (0)	1.37 (0)	0.55 (0)	0.24 (0)	1.22 (0)
12	K 1/2 W	0.85 (0.03)	0.3 (0.01)	2.48 (0.12)	2.5 (0.04)	2.94 (0)	0.9 (0.02)	0.35 (0.01)	2.35 (0.02)

After the initial set of 12 samples were prepared and analyzed, a second set of samples were prepared using specially selected grinder configurations based on the results of the first set of measurements. These samples have been labelled 2a, 2b, 2c, etc., and the particle size distributions of these samples were characterized using standard sieve analyses (characterizations using the Camsizer™ were not performed because many of the samples included particles with lengths exceeded the 30 mm upper range of the Camsizer™). Figure 7 displays standard sieve analysis results of three samples each ground with a single pass through a hammer grinder employing ½, 1, and 2 inch screens, respectively. Note that the samples that were ground with the 1 and 2 inch screens (samples '2b' and '2c') have very similar particle distributions for particles passing through sieves smaller than 2.5 mm, although the sample ground with the 2 inch screen ('2c') has a higher concentration of very large particles that were retained by a 19 mm screen (not shown in Fig. 7). The sample ground with a ½ inch screen ('2a) exhibited a similar particle size distribution for small particles that passed through a 1 mm sieve but had few large particles.

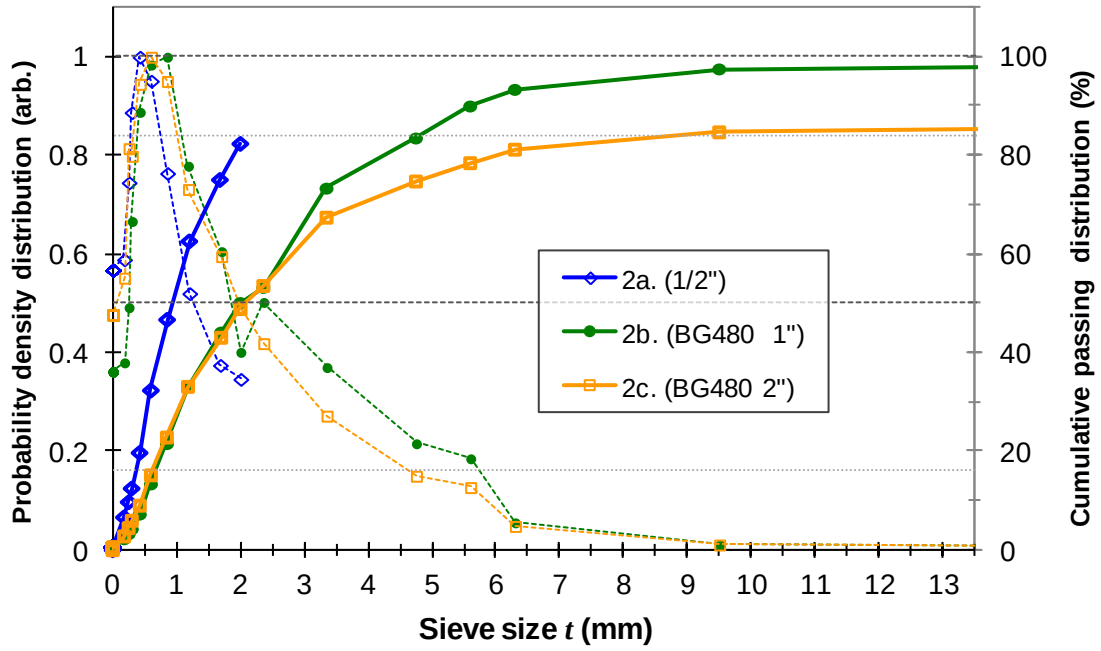


Fig. 7. Standard sieve analysis results of three samples each ground with a single pass through a hammer grinder. Blue, green, and gold curves represent particle size distributions obtained from samples ground with a Bliss mill with a ½" screen, and a BG480 using 1" and 2", screens, respectively.

In another set of experiments, three additional samples were ground using two passes in two separate hammer mills. The first hammer mill employed 6", 4," and a 1" screens for the different samples, and the second hammer mill employed a ½" screen for all samples. Figure 8 displays the standard sieve analysis results of these sample ground along with the sample that was ground in a single pass in the Bliss hammer mill with a ½" screen ('2a'). Surprisingly, all of the distributions appear similar except for the sample that was ground using the 1" and 1/2" screen combination, which contained more fines as expected. This test indicates that the screen size in

the first hammer mill has little effect upon the final particle size distribution as long as the screen in the first hammer mill is substantially larger than that in the second hammer mill.

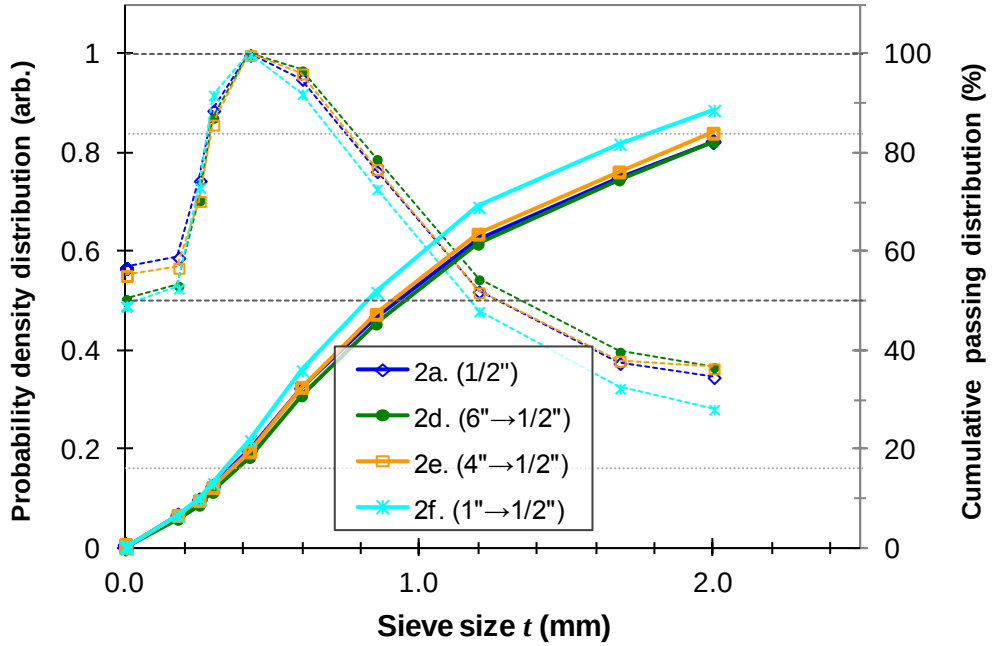


Fig. 8. Standard sieve analysis results of a sample ground using a single pass in a hammer mill with a ½" screen (same as that featured in Fig. 7) and three samples ground using two passes in two separate hammer mills. The first hammer mill employed 6", 4," and a 1" screens for the different samples, and the second hammer mill employed a ½" screen for all samples.

In another set of experiments, several kilograms of material were ground using a hammer mill retrofitted with a chipper drum to simulate a knife mill. The sample was first ground using a 3.375 inch screen, resulting in particle size distribution represented by the blue curve, labelled '2g' in Fig. 9. Some of the material was then split with a rifflesplitter and sieved into two fractions using a 1/2 inch sieve. The material retained on the sieve was further split and reground using 1.75 inch (green curve, '2h') and 1.25 inch (orange curve, '2i') screens in the same mill. Notably, the material that was ground using a single pass with a 3.375 inch screen consisted of approximately 25% of particles by mass that were retained on a 12.7 mm (1/2 inch) sieve. The two samples that were further sieved and whose large particles were subjected to additional grinding steps (curves 'B' and 'C') exhibited very similar particle size distributions with very few particles retained on a ½ inch sieve.

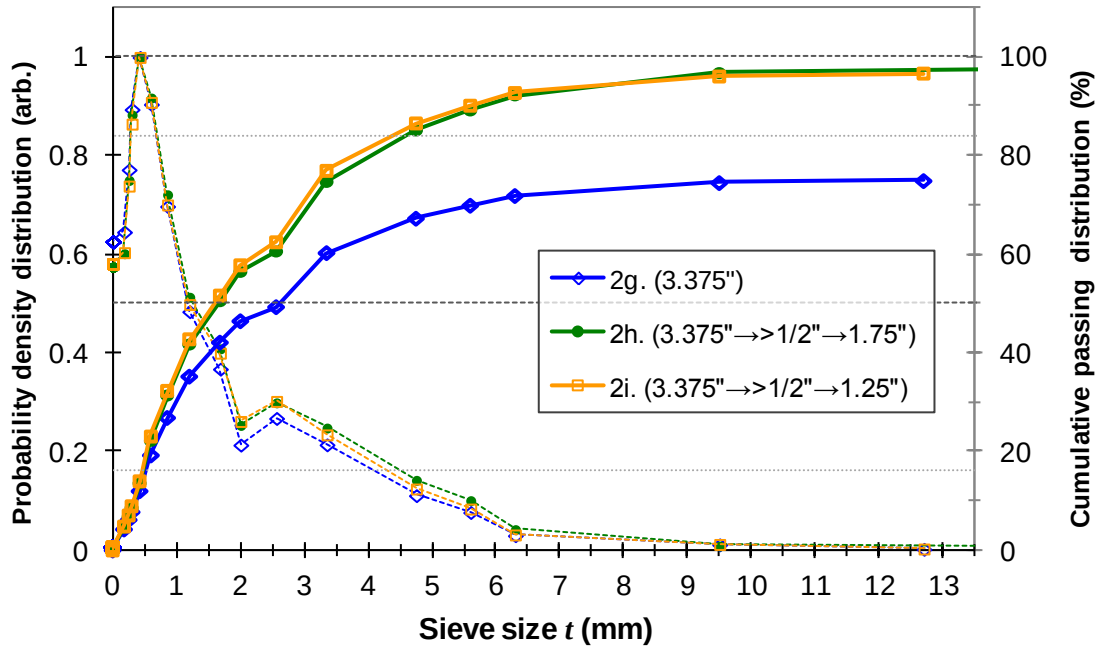


Fig. 9. Standard sieve analysis results of three sample ground using a hammer mill retrofitted with a chipper drum to simulate a knife mill. The three combined samples were first ground using a 3.375 inch screen, resulting in a particle size distribution represented by the blue curve. Some of the material was then split with rifflesplitter and sieved into two fractions using a 1/2 inch sieve. The material retained on the sieve was further split and reground using 1.75 inch (green curve) and 1.25 inch (orange curve) screens, respectively.

For the second set of samples the 16, 50, and 84% cumulative passing percentile sieve sizes (t_{16}, t_{50}, and t_{84}) are plotted graphically in Fig. 10, which indicates that the most promising of these samples appear to 2b, 2h and 2i because these samples appear to have particle size distributions with the largest mean particle size without an excessive amount of very large particles.

7.0 Additional Experiments on Samples 2b, 2d, 3a and 3b

Sample 2b was ground with a single hammer mill (BG480) employing a 1" screen before being dried in a rotary drum drier. However, for high-volume production in the biomass PDU at INL, it is more convenient to pass the material through a second hammer mill before the material enters the drier, due to the arrangement of the PDU equipment. Additional grinding experiments were conducted that employed a second hammer mill without a screen to determine if a material similar to Sample 2b (which only passed through a single hammer mill) could be produced using the more convenient PDU configuration with two hammer mills in place. For the first experiment (Sample 3a), the second hammer mill was turned off (rotor not spinning, no screen), while for the second experiment (Sample 3b), the second hammer mill was turned on (rotor spinning, no screen) to facilitate feeding material.

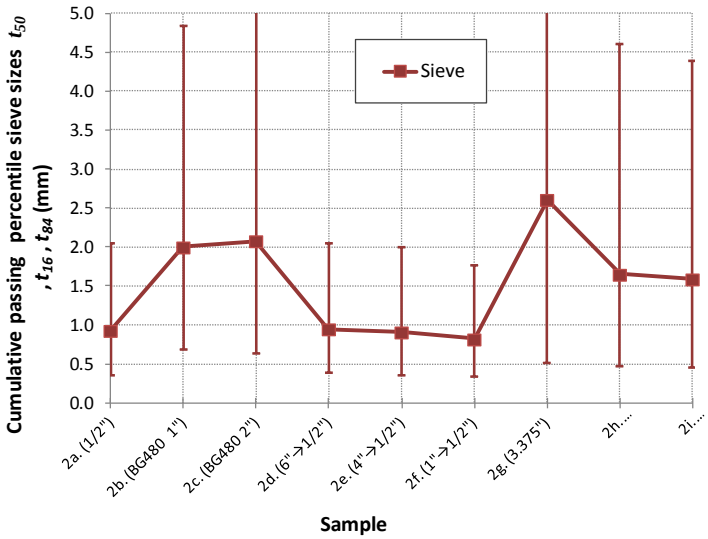


Fig. 10. 16, 50, and 84% cumulative passing percentile sieve sizes (t_{16}, t_{50}, and t_{84}) estimated from standard sieve analyses. The error bars represent t_{16} and t_{84} (the 16% and 84% cumulative passing percentile sieve sizes). For most samples, this data is estimated from a single sieve analysis.

Particle Size Characterization

Standard sieve analyses of both new materials (3a and 3b) are shown in Fig. 11, which also includes the sieve results of Sample 2b (same as in Fig. 7) did not employ a second mill. Note that 3a is similar to 2b within sampling error, demonstrating that the second hammer mill had little effect on the material if the rotor was not turning. Additional replicates of sieve analysis were also conducted for samples 2b and 2d as requested by MBI. The measured values of 16, 50, and 84% cumulative passing percentile sieve sizes (t_{16}, t_{50}, and t_{84}) are listed in Table 6.

Table 6. Particle size and shape distributions from duplicate sieve analyses. Standard deviations for the analyses are shown in parenthesis.

#	Code	t_{50}	t_{16}	t_{84}
2b.	BG480 1"	2.78 (0.03)	0.78 (0.08)	5.46 (0.21)
2d.	(6"→1/2")	0.9 (0.01)	0.33 (0.01)	3 (0.01)

Bulk Density, Percent Spring Back, and Air Permeability

Bulk densities and percent spring back for the samples 2b and 2d were measured as described in Section 5, and the measured values are shown in Table 7 and Fig. 12. The air permeability of sample 2b was measured following ASTM Standard 6539 by compressing the material inside a vertical cylindrical vessel. Compressive stresses ranging from 0 to 15 kPa were applied using an aluminium piston that featured an array of 1/8” holes to allow air passage during the permeability tests. The experiment was conducted two times using different heights of material, *L*, inside the cylindrical vessel, and similar results were obtained both times as shown in Table 8 and Figures 13 and 14. Moisture contents of samples 2b and 2d were also re-measured are provided in Table 9.

Table 7. Bulk density measurements of samples 2b and 2d at different levels of consolidation stress. Includes three replicates of 2b and two replicates of 2d.

		Consolidation stress														Spring back		
		0 kPa			1.0 kPa			3.0 kPa			7.0 kPa			15.0 kPa			15.0 kPa → 0 kPa		
#	Code	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C
2b.	BG480 1"	64.6	66.6	66.7	89.0	83.4	84.6	100.5	100.1	96.7	113.8	111.3	110.7	130.6	128.0	128.5	25%	23%	25%
2d.	(6"→1/2")	102.8	103.9	-	118.0	121.2	-	131.4	135.2	-	147.4	152.2	-	168.1	174.2	-	13%	14%	-

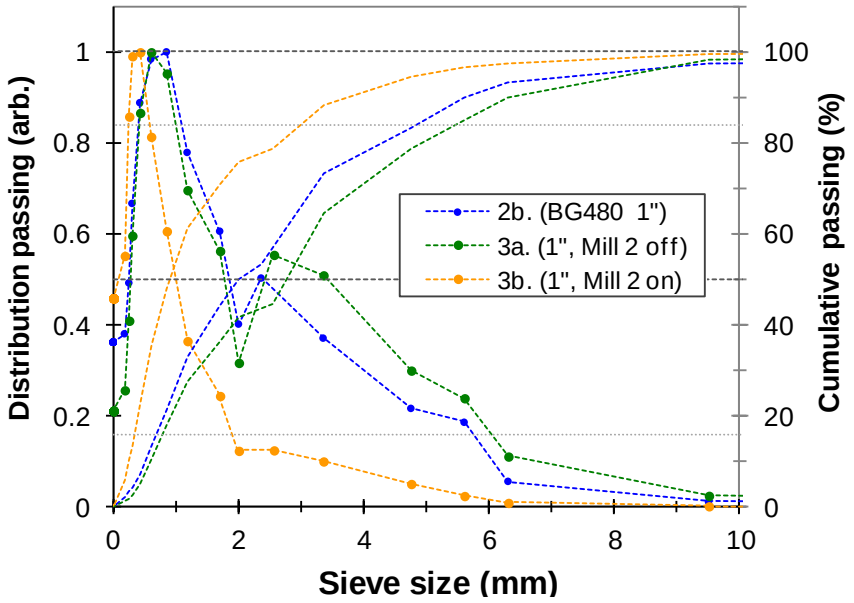


Fig. 11. Standard sieve analysis results of three samples all ground with a 1" screen on the BG480 (first mill). Sample 2b (same as in Fig. 7) did not employ a second mill, while samples 3a and 3b passed through a second mill which was turned off and on, respectively. Note that 3a is similar to 2b within sampling error, as expected.

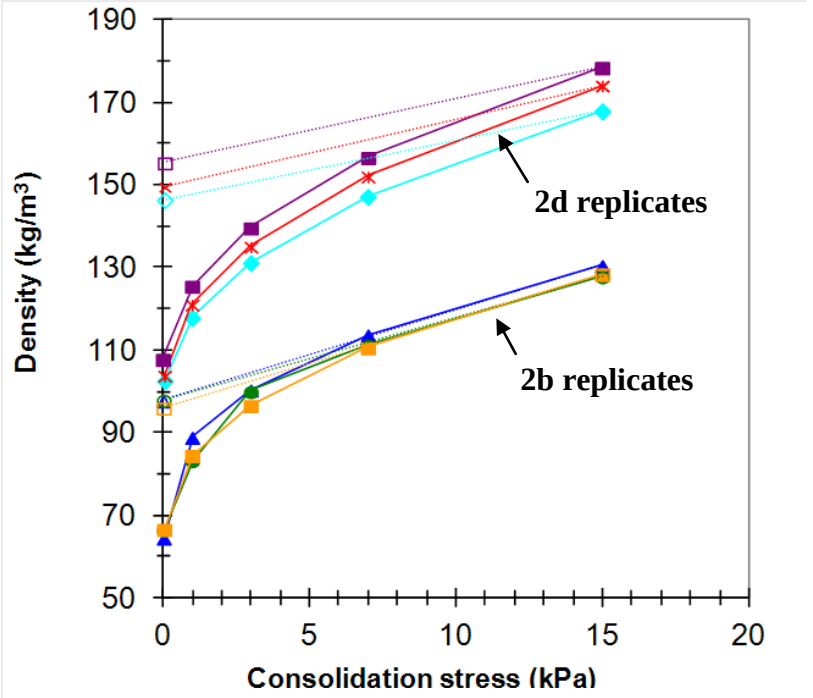


Fig. 12. Measured bulk density as a function of consolidation stress for samples 2b and 2d. Data is from Table 7. Solid lines represent sample compression while dashed lines indicate expansion.

Table 8. Permeability coefficient values and associated parameters for sample 2b (BG480 1”). Symbols are defined in ASTM Standard 6539.

#	Code	Replicate	σ_1 (kPa)	L (m)	ΔP (Pa)	Q_{AV} (m^3/s)	K_P (m^2)	K_P (Darci)
2b.	BG480 1"	A	0	0.138	10.0	$1.97x10^{-3}$	$1.7x10^{-8}$	$1.7x10^{4}$
			0	0.138	14.6	$3.05x10^{-3}$	$1.7x10^{-8}$	$1.7x10^{4}$
			1	0.104	9.31	$1.30x10^{-3}$	$8.5x10^{-9}$	$8.6x10^{3}$
			1	0.104	15.1	$1.95x10^{-3}$	$8.2x10^{-9}$	$8.3x10^{3}$
			3	0.088	9.60	$8.68x10^{-4}$	$4.9x10^{-9}$	$4.9x10^{3}$
			3	0.088	14.7	$1.44x10^{-3}$	$5.3x10^{-9}$	$5.3x10^{3}$
		B	1	0.186	3.92	$3.06\ x10^{-4}$	$8.9\ x10^{-9}$	$9.0\ x10^{3}$
			1	0.183	11.18	$7.31\ x10^{-4}$	$7.3\ x10^{-9}$	$7.4\ x10^{3}$
			3	0.152	20.00	$9.50\ x10^{-4}$	$4.4\ x10^{-9}$	$4.5\ x10^{3}$
			7	0.132	19.54	$6.96\ x10^{-4}$	$2.9\ x10^{-9}$	$2.9\ x10^{3}$
			15	0.113	19.99	$4.86\ x10^{-4}$	$1.7\ x10^{-9}$	$1.7\ x10^{3}$
			15	0.110	10.38	$2.21\ x10^{-4}$	$1.4\ x10^{-9}$	$1.5\ x10^{3}$
			15	0.110	23.59	$4.52\ x10^{-4}$	$1.3\ x10^{-9}$	$1.3\ x10^{3}$

Table 9. Measured percent moisture for all samples, including three replicates.

#	Code	A (% wb)	B (% wb)	C (% wb)	Average (% wb)
2b.	BG480 1"	10.2%	6.6%	-	16.2%
2d.	(6"→1/2")	15.5%	16.2%	17.0%	8.4%

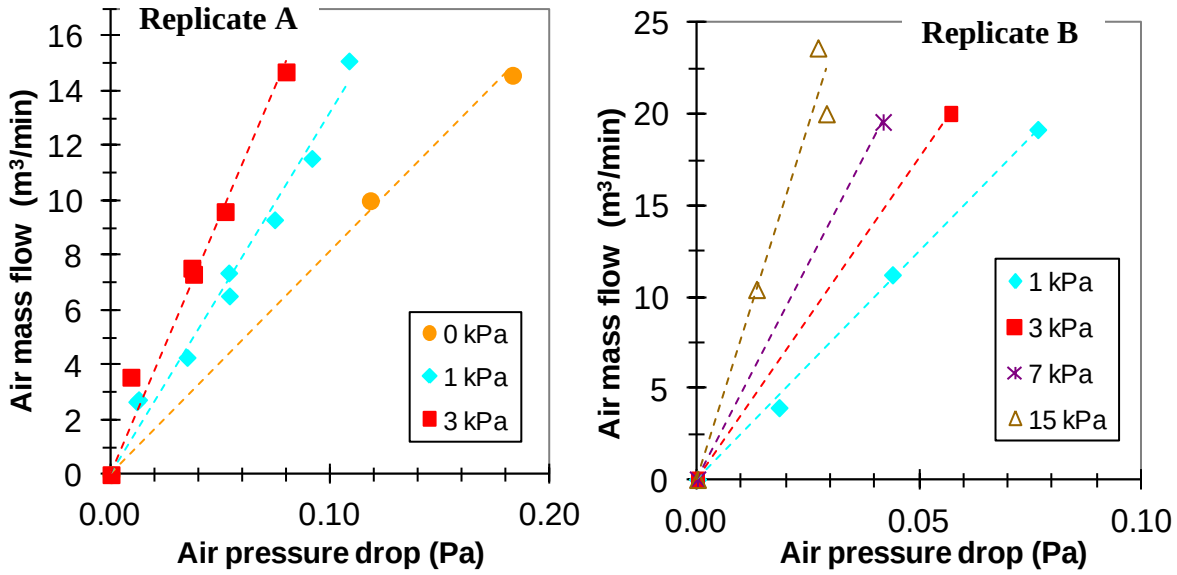


Fig. 13. Air mass flow measurements as a function of pressure drop across sample 2b (BG480 1”), including replicates A and B.

8.0 Conclusions

The tests performed at INL included water activity, moisture content, loose bulk density, compressibility, percent springback, wall friction, particle size/shape distributions, unconfined yield (shear) strength, and total ash content. Twelve initial samples were produced and characterized. Permeability measurements were not performed on the first twelve samples due to equipment failure but are now available if this test is desired for any samples.

In a second set of experiments, additional samples were produced labelled 2a, 2b, 2c, etc., using specially selected grinder configurations. Standard sieve analyses of the second set of samples were performed, and the results are summarized in Figures 7-9. **The most promising of these second set of samples appear to be samples to be 2b, 2h and 2i** because these samples appear to have particle size distributions with the largest mean particle size without an excessive amount of very large particles.

Appendix: Test Methods

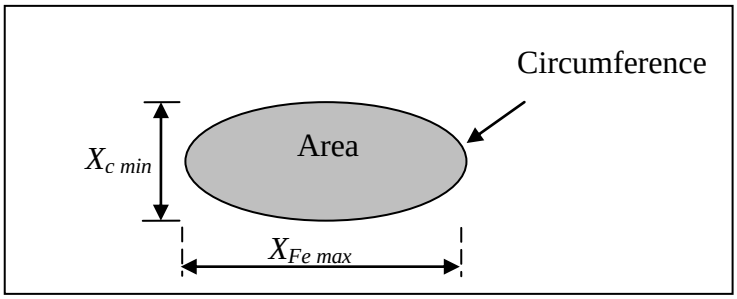
Particle Size Characterization using Camsizer

A dynamic image analyzer Camsizer (HORIBA Instruments, Inc., Irvine, CA) equipped with two digital cameras was used to analyze particle characteristics. This method was reported to be highly correlated with a well accepted static/quantitative technique using light microscopy (r>0.9 for both aspect ratio and sphericity) (Miller).

Average particle size and size distribution were determined based on the ASABE forage sieve method (ASABE. 2008). Shape quantification was determined according to a standardized method developed by the International Organization for Standardization (ISO 9276-6, 2006; ISO 13322-2, 2008). Particle distribution was calculated based on volume, which was defined using an ellipsoid model (Fig. 1, Eq. 3.1). $X_{c\ min}$ is the greatest width of a particle projection at a right angle; this measurement is equivalent to the result obtained from sieving analysis because, with sieving, the particle passes through the mesh with its smallest dimension. $X_{Fe\ max}$ is the maximum Feret-diameter of the measured set of Feret diameter of a particle projection (Feret diameter is the distance between two tangents placed perpendicular to the measuring direction (Hawkins, 1993)).

$$V_{Ellipsoid} = \frac{\pi}{6} * X_{c\ min}{}^{2} * X_{Fe\ max} \qquad (3.1)$$

Figure 1 Two dimensional-particle model.



The series of sieves followed the Standard ANSI/ASAE S319.4 (ASABE. 2008), and were set in the software as follows: 6.7, 6.3, 5.6, 4.75, 4, 3.5, 2.8, 2.36, 2, 1.7, 1.4, 1.18, 1, 0.85, 0.71, 0.6, 0.5, 0.425, 0.355, 0.3, 0.25, 0.212, 0.18, 0.15, 0.125, 0.106, 0.09, 0.075, 0.063, 0.053, 0.045, 0.038, 0.032, 0.025 mm, and 0.02 mm (corresponding to sieve numbers 0.265", 0.25", #3.5, #4, #5, #6, #7,#8, #10, #12, #14, #16, #18, #,20, #25, #30, #35, #40, #45, #50, #60, #70, #80, #70, #80, #100, #120, #140, #170, #200, #230, #270, #325, #400, #450, #500, and # 635). Four parameters were analyzed, including:

i) Geometric mean diameter *(d_{gw})*, mm – the size at the 50% point on the plot of cumulative percentage under size (percentage of particles passing through a given sieve) versus particle size.

ii) Geometric mean diameter standard deviation (*S_{gw})*, mm – dimensions d_{84} and d_{16} are particle diameters at 84% and 16% probability, respectively.

$$S_{gw} = 0.5*[d_{84} - d_{16}] \quad (3.2)$$

iii) Aspect ratio (dimensionless) – essentially a ratio of the width to the length of the ellipsoid silhouette, indicating elongation of particles (ISO 9276-6:2008).

$$\text{Aspect ratio} = \frac{X_{c\,min}}{X_{Fe\,max}} \quad (3.3)$$

$0 \leq \text{value} \leq 1$; the ratio lesser than one indicates elongated particle, departing from equi-dimensional.

iv) Sphericity (dimensionless), (Retsch Technology, Haan, Germany).

$$\text{SPHT} = \frac{4\pi * \text{Area}}{\text{Circumference}^2} \quad (3.4)$$

The name sphericity suggested the comparison of surface area of a sphere, of the same volume as the particle, and the actual surface area of the particle (Wadell, 1932). However, Eq. 3.4 was proposed using two dimensional measurements and in fact related more on the circumference of particle projections. Cox (Cox, 1927) considered the calculation was more appropriate as roundness as it involved edges and corners of surface, instead of sphericity, which rather explained a form of a particle. Wadell also explained that roundness was a matter of the sharpness of corner, while shape had to do with the form of the particle. Pons (Pons et al., 1999) similarly considered roundness as it was more sensitive to the variations in surface roughness, and used it in the comparison of surface of the object to the surface of the disc of the same perimeter. In ISO 9276-6:2008, the square-root term of this Eq. 3.4 was referred to as circularity, indicating the degree to which the particle (or its projection area) is similar to a circle and therefore the smoothness of the perimeter. Miller (Miller) related this calculation to the qualitative angularity/roundness as it was strongly involved in particle surface irregularities. Today, the reciprocal (*1/SPHT*), value ≥ 1 is widely used; the names circularity shape factor or surface factor were given (Hausner; Hawkins, 1993). The factor increasing from unity designates a particle with a corrugated/irregular surface.

Appendix C

Material Sorption Testing

Material Thermodynamics

Desorption isotherms of formatted raw corn stover and AFEX treated corn stover were completed across a range of temperatures (40, 50, and 60°C). The results of the analyses are used to describe the thermodynamic properties of each material, particularly how the material properties change as a result of pretreatment. This research aimed to explore the potential drying energy requirements of the pretreated biomass relative to conventional raw corn stover.

The scale-up of the AFEX pretreatment system to the depot level depends on the treated material's ability to easily dry to a moisture content suitable for pelletization (i.e., 10% to 20% moisture wet basis). If the pretreatment were to result in a material that is difficult to dry, a more costly drying operation may be required that could disrupt the proposed process economics. The research conducted was poised to answer the question of whether or not the AFEX treated corn stover requires more, less, or equal energy to dry compared to raw formatted stover. In these experiments, the low moisture formatted stover created by INL was rewetted to 45% moisture (wet basis) to best capture only the impact of the AFEX pretreatment on the feedstock's thermodynamic properties. Isotherms were determined to best fit the Peleg Model:

$$Me\ (db) = b_1 \cdot aw^{b_2} + b_3 \cdot aw^{b_4}$$

Where *Me* is the equilibrium moisture content, *aw* is the water activity, and b_1-b_4 are model coefficients (Table 1). Moisture sorption analyses show that the treated corn stover has consistently lower equilibrium moisture contents at equal values of water activity across the three temperatures tested

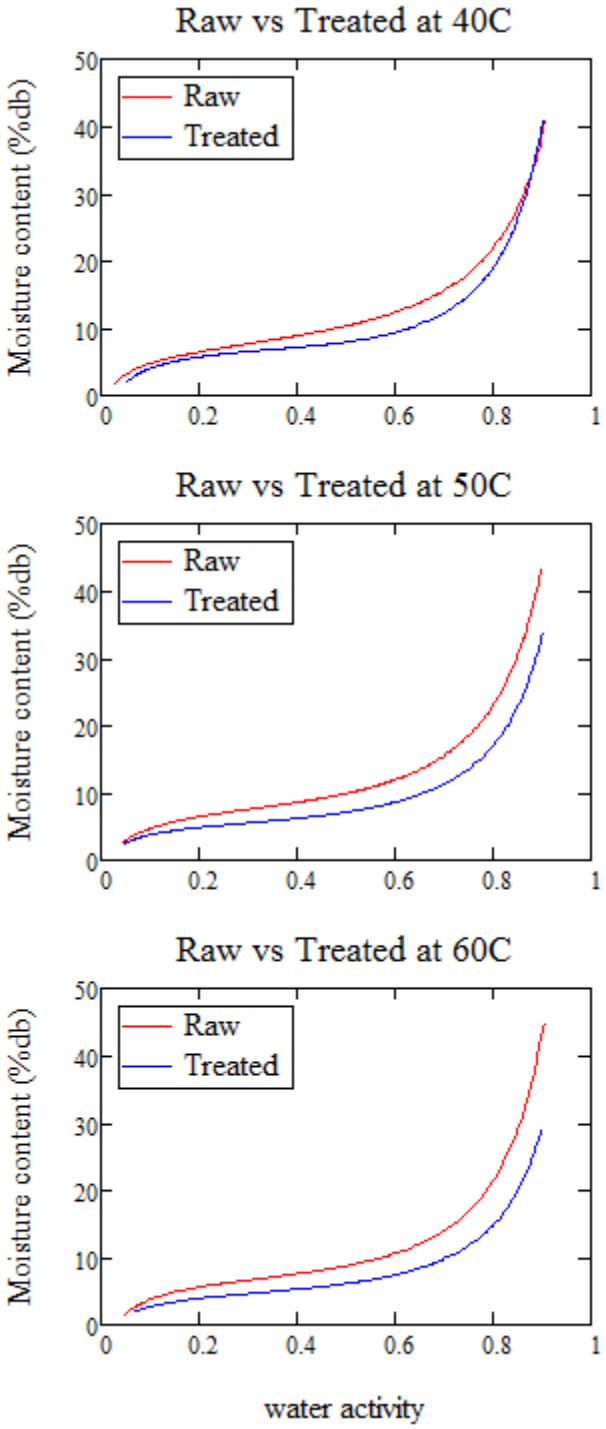


Figure 1 Desorption isotherms for raw formatted corn stover and AFEX pretreated corn stover at three test temperatures.

(Figure 1). This means that the treated material is not able to hold as much water as the raw material at any given equilibrium condition of temperature and relative humidity. While this result bodes well for the material's affinity to dry, it also tells us that the treated material must reach a lower moisture content to be stored safely (i.e., the equilibrium moisture content corresponding to a water activity of about 0.7). It should be noted that neither of the materials appear to behave like a naturally wet feedstock, that is to say, the process of rewetting (either through surface moisture application for the raw material or the steam injection during pretreatment of the AFEX treated material) has not entirely removed the hysteresis phenomena observed between an initial desorption and a second desorption. While this effect is not of particular concern for this analysis, it should be kept in mind that the "raw" material may not be adequately representative of a natively high moisture corn stover, but does stand as a good comparison for understanding the impact of pretreatment on the materials' thermodynamic properties.

The monolayer moisture content, water-binding surface area, and net isosteric heat of sorption was calculated using the moisture sorption isotherms of both materials. The monolayer moisture content is the point at which a single layer of water molecules is believed to cover a material's surface and is widely used in the food industry as a point of premier storage stability. While the feedstocks being handled here do not require storage at this level of stability, the monolayer moisture content can be used to describe changes in the material's surface area due to pretreatment. Interestingly the monolayer moisture content of the raw material is slightly higher than that of the treated material (Figure 2). Because surface area is proportional to the monolayer moisture content, this result suggests that the AFEX pretreatment is lowering the water-binding surface area of corn stover. This notion is contradictory to previous work where nitrogen sorption surface area analysis was used to show pore volume and surface area increasing as a result of AFEX pretreatment. The results of the water vapor sorption analysis here suggest that a portion of the treated material's surface area is hydrophobic, resulting in a lower apparent surface area.

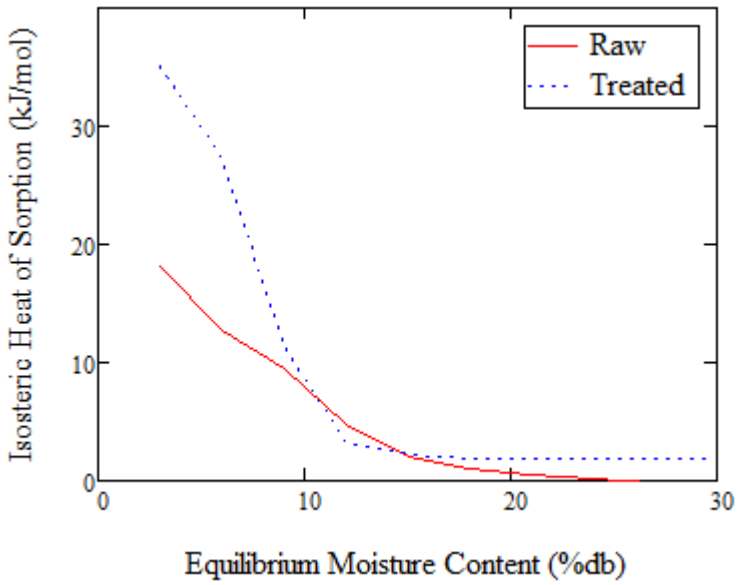


Figure 3 Isosteric heat of sorption for raw and AFEX treated corn stover, describing the amount of energy required to dry each material from 3 to 30% moisture, dry basis.

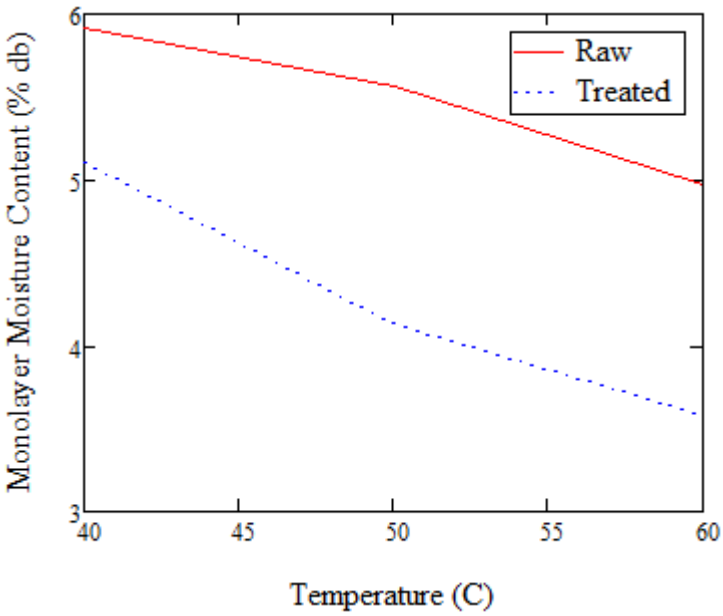


Figure 2 Monolayer moisture content of raw and AFEX treated corn stover using the GAB model, describing the relative relationship of surface area between each material with temperature.

Net isosteric heat of sorption describes the amount of energy required to remove moisture from each of the materials across a range of equilibrium moisture contents (Figure 3). At moisture contents greater than 15% dry basis both materials are within the range of pure water and would be expected to dry as such. At moisture contents below this range the two materials show important trends and differences. The raw material's isosteric heat of sorption gradually increases as moisture content is decreased, meaning more and more energy is required to remove the final fractions of water. The AFEX treated material has a distinctly different behavior in that the isosteric heat of sorption remains near zero (i.e., requiring no more energy to dry than pure water) until about 12% dry basis and then begins to climb rapidly. This behavior suggests there is some critical point in the interaction between the treated stover and water where the moisture at contents of < 10% dry basis is much more tightly bound to the stover. As a result, removing moisture beyond this point would require much more energy than that required to reach this critical point, and more when compared to the raw stover at equal moisture content. It is unlikely that such low moisture contents would be necessary from the perspective of the pelletization process however. With this practical consideration in mind, these results demonstrate that a drying operation targeting final moisture contents in the range of 12 to 20% wet basis would not require a more robust drying method than would conventionally be prescribed.

Drying Kinetics

The untreated and AFEX treated formatted corn stover was dried at 40, 50, and 60°C under a constant flow of 100 mL/min and relative humidity of 2% (desiccant dried air). This type of drying analysis is similar to thin-layer drying where an even, thin layer of material is exposed to constant drying conditions to better understand the kinetics of moisture loss. The resultant drying curves were fit to the Page's Modified Equation:

$$MR\ (Moisture\ Ratio) = \frac{M - Me}{Mo - Me} = e^{-k \cdot t^n}$$

Where *M* is the moisture content at any time (*t*) in minutes, *Mo* is the moisture content at the beginning of drying, and *Me* is the equilibrium moisture content. The drying coefficient *k* and empirical modifier *n* were solved for each of the three drying conditions for each material with a high degree of fit (Table 1). Both the raw and AFEX treated materials displayed a temperature relationship, though the raw material appeared more sensitive (Figure 4). When the data is used to predict drying curves for each material beginning at identical initial moisture contents (82% dry basis, or 45% wet basis) we can see that the rate of drying is slightly greater for the AFEX treated material compared to the raw stover at 40 and 50°C early in the drying process (up to about one hour)(Figure 5). Beyond this point (and for the entire duration at 60°C) the untreated and AFEX treated materials have similar rates of drying. The drying rates are clearly temperature dependent, with peak rates of 0.5 % moisture loss per minute at 40°C and 1.25 % moisture loss per minute at 60°C for both materials. It should be noted that the model underestimates the rate of drying at the very early stages of drying (i.e., < 20 minutes), though the general trend of the falling rate period represents the drying behavior well.

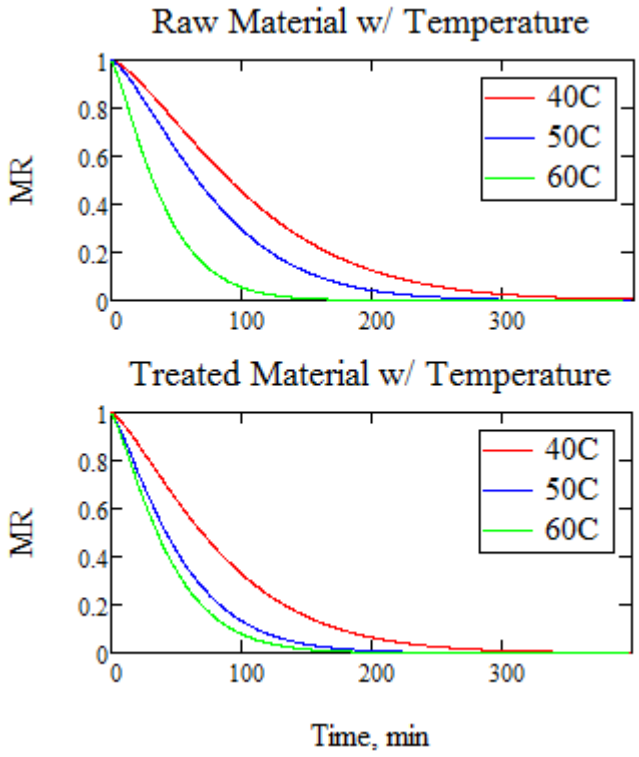


Figure 4. Drying curves for raw and AFEX treated corn stover fitted using the Page's Modified equation.

The drying rate behavior of both materials reflects the isotherm findings discussed previously, principally that the AFEX pretreatment has little to no effect on the drying rate of corn stover at moisture contents suitable for pelletization. In terms of the thin-layer drying tests conducted here, the time required to reach a range of moisture contents can be easily calculated and compared between materials. For example, if we assume both materials begin at 82% moisture, the AFEX treated material requires on average 19% less time to reach a moisture content between 25% and 10% than the raw material at 40C, 30% less time at 50°C, but 13% *more* at time at 60°C. Again it is worth noting that the two materials have a net isosteric heat of desorption near that of pure water within this moisture content range, and comparisons of this nature should be taken lightly as the true difference is likely minimal.

Overall the results of this testing demonstrate that drying technologies suitable for conventional high moisture biomass would be suitable for AFEX treated corn stover. When comparing the two materials the treated corn stover dries more favorably at lower temperatures than the untreated stover as a result of lower equilibrium moisture contents compared to raw stover, though higher temperatures intuitively result in increased drying rates. Low temperature drying may be of interest if the high temperatures encountered in a rotary drum dryer (i.e., >200°C) result in (1) unfavorable chemical or physical changes to the material or (2) unacceptable levels of volatiles.

Economics of the drying process should be explored to determine if these concerns merit further review. Immediate drying and pelletization of the material following pretreatment will alleviate concerns of material degradation in storage, however, if drying and/or pelletization are delayed, the AFEX treated material is potentially more unstable than raw stover based on the water activity relationships shown here. It is possible that the pretreatment process offers a degree of stabilization though partial sterilization of the material, though this hypothesis is only supported by anecdotal evidence.

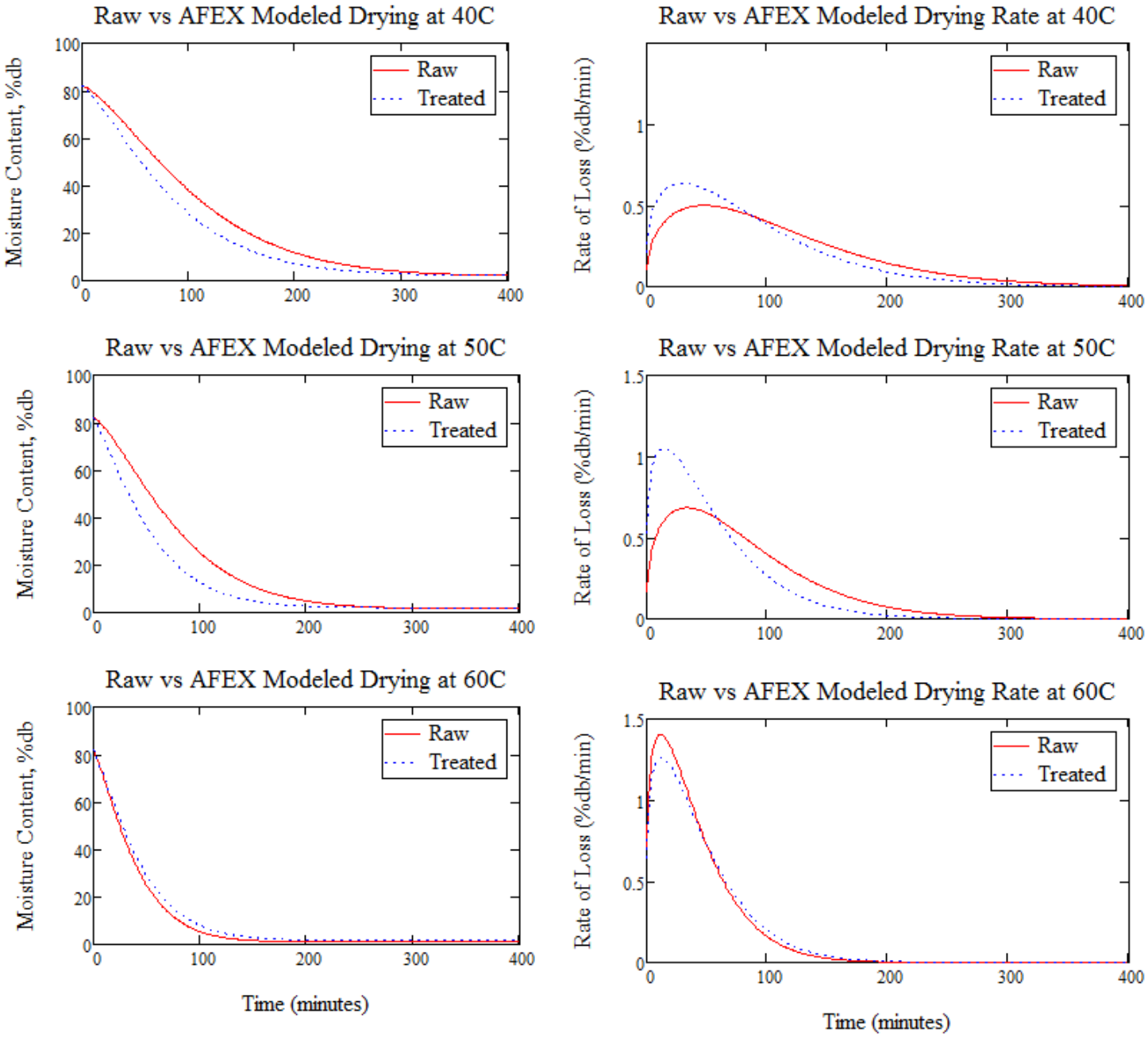


Figure 5. Modeled drying curves beginning at a fixed initial moisture content (left) and modeled rate of drying (right) for

raw and AFEX treated corn stover across a range of temperatures.

Table 1. Best fit model parameters for the desorption isotherms and kinetics of raw and AFEX treated corn stover.

		Desorption Isotherm Peleg Model Parameters				
Material	Temperature, °C	B1	B2	B3	B4	RMSE
Raw Corn Stover	40	15.691	0.567	63.053	9.341	0.801
	50	15.249	0.561	85.666	10.069	0.784
	60	14.542	0.633	94.887	11.014	0.356
AFEX Treated Corn Stover	40	12.381	0.507	104.153	12.045	1.161
	50	10.145	0.472	61.631	9.305	0.485
	60	9.529	0.583	57.107	9.95	0.496
		Drying Kinetics Page's Modified Model Parameters				
		k		n		RMSE
Raw Corn Stover	40	0.00129		1.396		0.044
	50	0.00212		1.380		0.042
	60	0.00886		1.259		0.044
AFEX Treated Corn Stover	40	0.00269		1.308		0.029
	50	0.00668		1.240		0.037
	60	0.00808		1.249		0.039