Contract No. R-010-022
"Developing a Biomass Industry in North Dakota"
Submitted by North Dakota State University
Principal Investigators: Dr. F. Larry Leistritz and Dr. Nancy M. Hodur

PARTICIPANTS

Sponsor	Cost Share
MBI International	$371,982
North Dakota State University	$ 24,138
Great River Energy	$ 10,000 (in-kind)
North Dakota Industrial Commission	$406,120
Total Project Cost	$812,240

Project Schedule – 15 months
Contract Date – April 12, 2011
Start Date – April 1, 2011
Completion Date – July 31, 2013

Project Deliverables:
Status Report: June 30, 2011 √
Status Report: November 30, 2011 √
Status Report: February 28, 2012 √
Status Report: November 30, 2012
Status Report: February 28, 2013
Final Report: July 31, 2013

OBJECTIVE/STATEMENT OF WORK:
Funds for this project will be used to demonstrate a new pretreatment process for densifying biomass. The pretreated biomass could feed an integrated biorefinery that would produce fuels, chemicals, and composites. In addition to providing feedstock to a biorefinery the pre-treated material could also be used as fuel for a power plant or for animal feed. The main source of feedstock for this project will be wheat straw.

The ultimate benefit of this project will be to de-risk a new biofuels technology, leading to larger investment. Because transportation costs are high, this project would provide a way of locating the industry next to the source of biomass. If successful, the project will have a large impact on rural economic development.

The main objective of the project is to scale up the process, called Packed-Bed Ammonia Fiber Expansion (PB-AFEX), to a three reactor semi-continuous system that operates at 4.5 kg per cycle. Data from operating this system will be used to design a pilot scale system operating at one ton per day. The scope of work includes:

- Design and build a three reactor continuous PB-AFEX laboratory system.
- Operate the reactor system to collect mass and energy balances necessary to design a pilot plant for the process.
- Use the PB-AFEX reactor to generate sufficient quantities of AFEX-treated material for applications testing of fermentation products systems and initial animal feeding trials.
- Develop a pilot scale plan including:
    - Process flow diagram
    - Proforma of anticipated capital and operating costs
    - Plan for product development
- Develop a proforma for regional biomass processing centers using the PB-AFEX reactor and determine rural development implications for the project.

STATUS
Contract has been executed and work is underway

<u>June 30, 2011 Status Report</u>
Packed Bed AFEX reactor system design, build, test – Design of a 10 kg per day AFEX 3 test skid is complete. The skid will be able to treat wheat straw, corn stover, switchgrass, etc. under AFEX conditions in a three-bed configuration with NH_3 transport from bed to bed

Bed Mass – The design basis for the test skid bed tubes is approximately 1.5 kg of biomass per bed, and about 10 kg of treated biomass per day. The bed tube volume will be fixed at about 9.1 liter per bed. Consequently, the actual amount of biomass treated in each bed will depend on the bed density. Recently published data provides relationships between particle size and bed density for various biomass types, which allows us to calculate the expected bed masses for the AFEX skid. The dry mass of treated biomass may be as high as 1.2 kg/bed for fine ground switchgrass, or as low as 0.3 kg/bed for coarse wheat straw. Output of AFEX-treated biomass (kg/day) from the test skid will depend on both the bed mass (kg/bed), and the number of bed cycles that can be completed per day. For wheat straw at 4 mm particle length, for example, we can expect about 0.5 kg/bed, so completion of 20 bed cycles per day will generate 10kg/day of AFEX-treated wheat straw.

Safety Review – The test skid design was reviewed by MBI safety committee. The recommended revisions have been incorporated into the design. The design has been approved for fabrication.

<u>November 15, 2011 Status Report</u>
As reported in the last status report, the design of the PB AFEX reactor has been completed. Since then a PB-AFEX skid consisting of three 9.1 L reactors, an ammonia compressor, and ammonia vaporizer has been built and successfully tested with both corn stover and wheat straw.

Material procurement, reactor assembly and ammonia recovery assembly. – The reactor assembly was successfully completed during this reporting period. The reactors are vertically mounted on a single skid and can be opened from the top or bottom for biomass entry, removal or for cleaning. In addition, biomass can also be transferred to the reactors using a vacuum blower through ports located at the top of each reactor. A digital temperature display showing the temperature at the top and bottom of each reactor is also mounted on the skid, as is a pressure gauge for each reactor. Low pressure (20 psi) steam is added via an injection nozzle at the top of the reactor, as is ammonia. The ammonia compressor and vaporizer is located behind the skid and connected to ammonia pump. The inlet and outlet lines of the compressor can be easily transferred from one bed to the next by a series of valves placed at the front of the skid.

Reactor System Shakedown. – The reactor has been successfully tested with both corn stover and wheat straw. The Contractor has successfully demonstrated complete ammonia desorption, successful transfer of ammonia, continual reuse of ammonia, and successful pretreatment of biomass.

Ammonia recovery measurement and calculation. – In order to be economical, nearly all nonreacted ammonia must be transferred from bed to bed. It should be possible to replace any NH_3 lost to irreversible interaction with the biomass by the addition of makeup NH_3 vapor during the recompression and transfer of vapor from bed to bed. Three different options were evaluated for stripping ammonia from biomass:

- Using only hot N_2 – efficient ammonia removal, however it is very slow;
- Using a mixture of N_2 and steam – This method is fast with great recovery. However, N_2 will complicate the process and increase the operating cost.
- Using only steam – efficient ammonia removal was possible in a reasonable time.

Steam was chosen as the ammonia stripping gas, as it is a simpler process that does not require any ammonia/N_2 separation. While three beds were initially designed for the laboratory scale reactor, the steam process can be designed to effectively recycle ammonia with only two beds.

Experiments with corn stover in the PB AFEX skid (running 6 beds in series) demonstrated that NH3 could be charged to the biomass in one bed, stripped off as vapor, and the vapor recompressed and charged to a subsequent bed. More than 95% ammonia was recovered and recycled. The Contractor believes that the difference is in ammonia reacting with the biomass and a small amount of ammonia remaining within the lines. As the system is scaled up, the latter problem will be greatly reduced leading to nearly complete recovery of unreacted ammonia. Samples of the recovered ammonia were analyzed by GC/MS and no measurable impurity was detected. Performance of the PB AFEX system in treating corn stover was evaluated via enzyme hydrolysis and was bench marked with the corn stover treated in the Contractor's 1 gallon stirred batch AFEX reactor. Results are available in the Commission files.

Operate the reactor to provide sufficient material for downstream testing. – Considering 85-90 minutes processing time for treating corn stover or wheat straw with a particle size of (-5mm), allowed the Contractor to process approximately 8-10 kg of biomass per day in the Contractor's lab scale PB AFEX system. This allowed the generation of enough biomass for hydrolysis, fermentation and preliminary animal feed tests.

The resulting hydrolysis and fermentation studies demonstrated that the conditions in PB AFEX can provide pretreatment performance equal to a laboratory-scale stirred batch reactor.

Provide sufficient materials for animal feed studies and energy analysis – The Contractor indicates that they are capable of producing enough material for an energy analysis. AFEX-treated corn stover and wheat straw will be sent to an outside company to assess their nutritional value, including crude protein content, fiber content and digestible energy content.

The Contractor concludes in this status report that: "We have generated enough information to scale up to pilot scale. Further refinement of the data based on later experiments will be performed as improvements in the process become known. Based on the collected data, mass and energy balances were developed for our lab scale PB AFEX system. During this reporting period preliminary mass and energy balances were also developed for PB AFEX systems for 1 ton-per-day (TPD) and 50 TPD scales. Reactor dimensions and the number of reactors needed to process 1 TPD of corn stover or wheat straw were calculated based on the data [temperature, pressure, biomass bed density (100 KG/m^3), and cycle time (85 min.)] collected from our lab scale PB AFEX system. In order to reduce the capital cost, it is essential to increase the throughput rate of the system by increasing the bed density or/and decreasing the cycle time. Based on our current work, there is evidence that corn stover or wheat straw can be processed at a higher bed density and shorter cycle time compared to what was observed in the lab scale system. The preliminary mass and energy balances for a 50 TPD system have been developed assuming bed density of 125 kg/m^3 and cycle time of about 72 min."

January, 2012

North Dakota State University and MBI have requested a one-year no-cost extension due to the availability of additional funding ($4.3 million) being provided to MBI by the Department of Energy for construction of a pilot scale processor. Alignment with the DOE grant will enable MBI to develop a much more detailed design and plan for a pilot scale AFEX reactor. This will require additional time for work on the lab scale unit designed and built with funding from the Commission. The overall result will be a much more rigorous pilot scale design and techno-economic analysis (pro-formas) for the process which will ensure an accelerated timeline toward a functioning pilot scale reactor (expected to be completed and operational in 2013). The request is currently under consideration.

February 14, 2012 Interim Status Report

Ammonia recovery measurement and calculation

One of the distinguishing features of the AFEX 3 process is that a significant amount of the residual ammonia can be recovered and directly recompressed and recycled as substantially pure vapor. Overall ammonia recovery is > 95%. During this reporting period, 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 will be used in the future 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 was used and the ammonia released from the bed in the depressurizing step 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 was kept cold using an ice bath. The amount of collected ammonia was 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 is 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 was 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 was developed for the steam stripping step. These results show that the steam stripping process can be well- controlled.

Operate the reactor to provide sufficient material for downstream testing

During this reporting period more AFEX 3 treated corn stover and wheat straw were generated. AFEX-treated corn stover and wheat straw have been sent to an outside lab to assess their nutritional value, including crude protein content, fiber content, and digestible energy content. Results will be reported later.

Pilot-scale PB-AFEX Design

During this reporting period, MBI engineers met with representatives of three engineering and fabrication firms to discuss the AFEX 3 scale-up project. Each of these groups has expressed interest in the project and will provide both budgetary cost estimates and preliminary project plans for MBI's review.

April, 2012

The no-cost one-year extension has been approved and the contract amendment executed. The amendment also approved the change of the Principal Investigator from Dr. Larry Leistritz to Dr. Nancy Hodur.

April 13, 2012