Contract No. R-009-021
"Promoting Standardization of Combustion Characteristics for Biofuels"
Submitted by Energy and Environmental Research Center
Principal Investigator: Carolyn Nyberg

PARTICIPANTS

Sponsor	**Cost Share Final**
Department of Energy	$ 69,400
Metso Power	$ 9,995
EPRI	$ 9,995
North Dakota Industrial Commission	$ 48,506
Total Project Cost	$137,896

Project Schedule – 15 months
Contract Date – December 7, 2010
Start Date – January 1, 2011
Completion Date – March 31, 2012

Project Deliverables:
Status Report: March 31, 2011√
Status Report: June 30, 2011√
Status Report: September 30, 2011 √
Status Report: December 31, 2011 √
Final Report: March 31, 2012 √

OBJECTIVE/STATEMENT OF WORK:
The goal of this project is to establish appropriate test methods and Standard Reference Materials (SRMs) for the chemical characterization of biomass to assess combustion and fuel quality parameters. Project deliverables will include:

- A list/book of standard test methods for the detailed chemical and combustion characterization of biofuels,
- Detailed chemical characterization information, including slagging behavior for select biofuels, of which a minimum of 5 will be dominant ND materials,
- Dissemination of information and promotion of standardized testing methods for biofuels (attendance at 1 committee meeting and 2 conferences), and
- Initial development of biomass SRMs.

This project will benefit North Dakota by setting a standard of chemical and combustion properties for a minimum of 5 ND dominant feedstocks, as well as establish standard methods to test those characteristics. Having standards that establish the quality of feedstocks will help advance the biomass industry.

STATUS
Contract is in the process of being executed and matching funds confirmed.

December 30, 2010
Contract has been executed – waiting for confirmation of matching funds.

April, 2011
EERC received word that the Department of Energy will be providing an additional $30,000 for this project. The additional money will not change the scope of work of the project. The additional money

will be used within the current scope of work by analyzing more replicates of the samples that will already be collected for the project. This will allow for better statistical analysis of the data.

The first status report was received. The report states:

During this quarter, all agreements with cost-share partners were put in place. Several methods for biomass characterization have been obtained and reviewed. The methods were obtained from ASTM International, the European Committee for Standardization, and the International Organization for Standardization. Contacts were also made with some of the sponsors and collaborators to discuss the list of biomass fuel candidates that will be characterized for this project. The biomass fuels currently being considered, along with their respective locations, include the following:

1. Switchgrass (North Dakota)
2. Wheat straw (North Dakota)
3. Corn stover (North Dakota)
4. Flax straw (North Dakota)
5. Beet pulp (North Dakota/Minnesota)
6. Woody biomass (to be determined)

Further discussions with sponsors and collaborators will take place during the second quarter in order to finalize the list of biomass candidates.

An abstract to present the findings of this project was submitted to the Biomass '11 Conference which will be held July 26 and 27, 2011 in Grand Forks.

July, 15, 2011
The second status report was received. The status report states:

During this quarter, nine of the ten biomass samples proposed for the project have been acquired. They include the following:

1. Switchgrass (North Dakota)
2. Corn stover (North Dakota)
3. Wheat straw (North Dakota)
4. Dried distillers grain (North Dakota)
5. Beet pulp (North Dakota/Minnesota)
6. Aspen (southeastern United States)
7. Cottonwood (southeastern United States)
8. Eucalyptus (southeastern United States)
9. Loblolly Pine (southeastern United States)

The biomass methods that were obtained and reviewed last quarter have been compiled into a table format. (A copy of that compilation is available in the Commission files.) These methods were obtained from ASTM International (ASTM), the European Committee for Standardization (CEN), the International Organization for Standardization (ISO), and the American Society of Agricultural and Biological Engineers (ASABE).

Planned activities for the next quarter include acquisition of a tenth biomass sample, bulk density determination on all samples, particle-size reduction to <2 mm, and the initiation of chemical

characterization of the samples. A presentation of project information is scheduled at the Biomass '11 Conference in Grand Forks, North Dakota, July 27, 2011.

October 15, 2011

The third status report was received for the quarter ending September 30, 2011. The status report states:

During this quarter project information was presented at the Biomass '11 Conference in Grand Forks, ND, July 27, 2011. Because of the timing of the conference, analytical data for the biomass samples were not available and, therefore, not presented. The presentation focused on the objectives of the project and emphasis on biomass analytical methods.

Also, this quarter the last proposed biomass sample was obtained which completes the sample acquisition task. The final sample is waste wood from Nebraska.

Bulk density, air drying, particle-size reduction, and some physical and chemical tests have been performed on nine of the ten project samples. The results of the analyses completed to date are available in Table 1. Major, minor, and trace element analysis are also under way but not completed. The data in Table 1 show that this suite of biomass samples varies in composition for some key fuel quality parameters. The most obvious are the ash content and chlorine content, with the ash ranging from 0.41% to 12.68% and the chlorine ranging from 0.0016% to 0.21%. Sulfur is relatively low in all of the biomass samples, which is to be expected. However, this is a key parameter to evaluate regarding the capability of analytical methods to quantitate at the low levels seen in most biomass samples.

March 29, 2012

The fourth status report was received for the quarter ending December 31, 2011. The status report summarized the activities that had taken place to date. In regards to the ***Characterization of Project Biomass Samples*** the report states:

The analytical characterization of the biomass samples is nearly complete. Still pending are bromine, fluorine, and some of the minor and trace elements.

In regards to ***Interlaboratory Comparisons*** the report states:

Five of the ten project samples were selected for a small interlaboratory comparison of the biomass methods used in this project. These samples included switchgrass, corn stover, wheat straw, cottonwood and eucalyptus. This suite of samples represents a range of varying concentrations for several of the parameters tested in these fuels. After the project samples were prepared to <1 mm in size as described above, a 30-g portion of each sample was packaged and sent to an independent laboratory of comparative analysis. The independent laboratory chosen for this work was based on the ability of the laboratory to employ biomass methods that are similar to those used by the EERC. Results were recently received from the independent laboratory. However, they were not reviewed in time for this interim report. A detailed comparative analysis of the two laboratories will be presented in the final report.

In regards to ***Thermodynamic Modeling and Plant Performance Estimations*** the report states:

The results of the analytical characterization of the different biomass materials can be used to help evaluate these materials as potential fuels in a combustion boiler. Equilibrium thermodynamic modeling is used to predict the amount and composition of gases, liquids, liquid solutions, solids, and aqueous liquids present in a system over a range of temperatures and pressures. This composition is then used to calculate the slag viscosity. The modeling program is called FactSage, which is a commercial integrated thermodynamic database coupled to programs developed to calculate multicomponent, multiphase equilibria based on a minimization of Gibbs free energy. The FactSage calculation results help estimate the effects that the biomass fuels may have on boiler operation. These include:

- Slag viscosity and the percentage of liquid slag indicate what effect the biomass ash may have on high-temperature silicate-based fouling. The viscosity and percentage of liquid fly ash is related to the amount of fouling that may occur on tube surfaces in the hotter section of the convective pass.
- The percentage of solid sulfates present is related to the propensity for calcium sulfate fouling in the lower-temperature economizer region of the boiler.
- The percentage of liquid sulfates, such as sodium and potassium sulfate, is related to the potential for forming a sticky liquid that would significantly increase deposition in the temperature range where it forms.
- The percentage of solid phosphates is related to the propensity for an increased number of cleaning cycles and higher-pressure drops in a baghouse. Fine phosphates tend to "blind" bags more than the usual fly ash.
- The percentage of solid chlorides and carbonates are related to the formation of fine particulates, which have a similar effect as phosphates on baghouse performance.

Using the proximate, ultimate, calorific value, chlorine, and mercury analytical results, estimations of overall plant performance and emissions can also be determined for the different biomass fuels. These include the following:

- Fuel feed rates expressed in pounds/MMBtu.
- Ash loading in pounds/MMBtu.
- SO_2, Hg, and chloride emissions can be estimated, since these species transform to gas-phase forms during combustion. However, no account is made for pollution control devices, such as scrubbers.
- NO_x emissions can be estimated from the fuel nitrogen but are highly dependent on plant operating conditions. A rule of thumb is that approximately half of the total NO_x arises from fuel nitrogen and half from thermally generated NO_x. No account is made for pollution control devices.

Results from the modeling and plant performance estimations are pending and will be presented and discussed in detail in the final report.

<u>April, 2012</u>

The final report has been received and is posted on the Industrial Commission/Renewable Energy Program website. The following is an excerpt from the Final Report Project Summary:

Work Accomplished: More than 50 analytical methods for biomass materials were collected from various organizations and reviewed. These included the International Organization for Standardization (ISO), the European Community for Standardization (CEN), ASTM International, and the American

Society of Agricultural and Biological Engineers (ASABE). The methods included those used to determine parameters typically associated with fuel quality, such as proximate analysis (moisture, ash, volatile matter, and fixed carbon). ultimate analysis (carbon, hydrogen, nitrogen, sulfur, and oxygen), calorific value, halogens (bromine, chlorine, and fluorine), ash chemistry (major and minor elements), trace elements (arsenic, lead, mercury, etc.), ash fusibility, and bulk density. The final numbers of methods used in this project was narrowed down to 16.

A total of ten different biomass samples were collected for this project. They included switchgrass, corn stover, wheat straw, dried distillers grain, beet pulp, aspen, cottonwood, eucalyptus, loblolly pine, and waste wood pellets. Several of these biomass types are acutely applicable to future North Dakota renewable energy development. The intent was to select candidates that are predominantly being used or have the potential to be used in the United Sates as feedstocks for energy production. Another factor that was considered when selecting these fuels was to choose materials that had varying chemical characteristics to better evaluate the test methods selected. Five of the ten samples collected for this project were from North Dakota sources.

Project Results: The analytical results showed that the materials selected did indeed represent a wide range of chemical and physical characteristics. The ash and chlorine content varied greatly among the ten fuels analyzed. The alkali and alkaline-earth metals (K, Na, Ca, Mg) were much higher in the herbaceous biomass materials than in the woody biomass. Many of the trace metals, including mercury, were very low in all of the materials, which make these materials an attractive energy source to help reduce overall emissions. However, the low levels pose an analytical challenge to biomass testing laboratories, if appropriate test methods are not available.

Another analytical issue that was investigated in this project was the availability of biomass SRMs for use in biomass testing labs. It was determined that very few of these materials are commercially available; however, discussions began with the National Institute of Standards and Technology during this project, and development work will begin in 2012 to characterize and certify biomass materials.

This project is now complete.

June 12, 2012