EERC

Energy & Environmental Research Center

UNIVERSITY OF NORTH DAKOTA

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March 30, 2012

Ms. Karlene Fine
Executive Director
North Dakota Industrial Commission
600 East Boulevard Avenue, Department 405
State Capitol, 14th Floor
Bismarck, ND 58505-0840

Dear Ms. Fine:

Subject: Final Report Entitled "Promoting Standardization of Combustion Characteristics For Biofuels"; Agreement No.: R-009-021; EERC Fund 16101

We certify that the Energy & Environmental Research Center (EERC) agreements for the project include the following:

Sponsor	Award	Expended
North Dakota Industrial Commission	$50,000	$49,900
U.S. Department of Energy	$70,000	$69,400
Electric Power Research Institute	$10,000	$9,995
Metso Power	$10,000	$9,995

Enclosed is the subject final report and final report summary. If you have any questions, please contact me by phone at (701) 777-5057 or by e-mail at cnyberg@undeerc.org.

Sincerely,

Carolyn M. Nyberg
Manager, Analytical Research Laboratory

CMN/kal

Enclosure

FINAL REPORT SUMMARY FOR "PROMOTING STANDARDIZATION OF COMBUSTION CHARACTERISTICS FOR BIOFUELS"
INDUSTRIAL COMMISSION OF NORTH DAKOTA CONTRACT NO. R-009-021

Purpose of the Project: This Energy & Environmental Research Center (EERC) project was conducted to help establish appropriate test methods for biomass characterization that are acceptable and reproducible and to promote their use among industry. The specific objectives included a review of existing standard methods used for determining combustion characteristics for biomass fuels; characterization of common biomass materials, which included thermodynamic modeling to help predict slagging behavior; promotion of these biomass methods among industry through involvement in standards committees and dissemination of information at conferences; and evaluation of suitable biomass candidates for the development of Standard Reference Materials (SRMs).

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 number 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 grains, 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 States 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.

Potential Applications of the Project: The EERC is committed to advancing the use of renewable energy resources and will continue to support efforts that began with this project. EERC researchers will stay involved in biomass standards development through continued membership in biomass committees and networking at various biomass workshops and conferences.

PROMOTING STANDARDIZATION OF COMBUSTION CHARACTERISTICS FOR BIOFUELS

Final Report

Submitted to:

Karlene Fine

North Dakota Industrial Commission
600 East Boulevard Avenue
State Capitol 14th Floor
Bismarck, ND 58505-0310

Agreement No.: R-009-021

Submitted by:

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EXECUTIVE SUMMARY

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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.

During this project, EERC personnel were able to present the findings of this project at various conferences, workshops, and meetings. The EERC is committed to advancing the use of renewable energy resources and will continue to support efforts that began with this project. EERC researchers will stay involved in biomass standards development through continued membership in biomass committees and networking at various biomass workshops and conferences.

PROMOTING STANDARDIZATION OF COMBUSTION CHARACTERISTICS FOR BIOFUELS

1.0   INTRODUCTION

Biomass or biofuel for power and electricity has been of great interest in the United States for the past two decades as more information has been developed on the world scale of greenhouse gas accumulation and global warming. Renewable energy, such as burning biomass in power generators, is still the number one energy form that coal-fired utility or industrial boilers can easily switch to in order to generate renewable power. However, the overall percentage of biopower in the United States remains a paltry 3% when totaled and normalized relative to other energy forms. In other parts of world, such as Europe, that percentage is much higher because many European countries have aggressive renewable energy mandates and even carbon taxes that make it difficult for coal power plants to continue operation and easy for biomass to be used at a much higher rate.

The primary driver for electricity and heat production from biomass in the United States remains individual-state-promoted renewable portfolio standards (RPS). Twenty-seven states mandate renewable energy production by their utilities. That leaves 23 states with no RPS or they have an alternate energy production standard, which includes energy from biomass technologies or from advanced fossil-fuel technologies such as coal gasification. Most renewable electricity production in the United States still comes from hydroelectric or wind resources. For some states, an RPS has attracted development of smaller (20–50 MW) baseload biomass power plants. For other regions, communities have incentivized new biomass plants using local venture drives and grassroots support. These new biomass power plants have essentially replaced older units related to the pulp and paper industry. This offset or build one–close one scenario is one reason why the level of biopower remains about 3% nationally.

In the future, the U.S. power industry may have to comply with federal mandates for renewable energy, in which case, biomass could very quickly become a very important fuel of choice. There could be regulations implemented for a national RPS or for greenhouse gas emission limits. In some future circumstances, incentives could be implemented such as categorizing biomass as a carbon-neutral fuel, eligible for CO_2 credits on the basis of displacement of CO_2 emissions associated with fossil fuel-based electricity. Coal boiler emissions limits are already somewhat of a driver for smaller biomass power plant installation since biomass generally has lower overall emissions of hazardous air pollutants such as sulfur, mercury, and other trace metals. These constituents are regulated by the U.S. Environmental Protection Agency (EPA) in the recently issued Mercury and Air Toxic Standard (MATS) rule (1).

Because biomass has become such a significant boiler fuel to either replace or be cofired with coal in European boilers, national standards have been devised to provide standard methods for characterizing biomass quality, much in the same way similar standards were devised for coal over a century ago. In the United States, biomass has not become so popular yet; however, as stated above, things could change quickly, and a demand for such characterization standards is being raised. In short, as more biomass is used in the United States, because of new incentives,

regulations, or mandates, standards will be necessary. Currently, the power industry and pellet fuel industry in the United States is already in need of such standards.

The project described in this report was conceived under the premise that the increased use of biomass in generating systems and the potential for greatly increased biomass use in the future warrants a systematic methodology for standardizing biomass physical and chemical properties, similar to standards already developed in Europe. The information and data generated through this project and detailed in this report are intended to advance the development of suitable biomass standard methods that would be widely available to the biomass industry.

2.0   BACKGROUND

The interest in biomass as a fuel source in the United States and even more internationally has led to a need for proper characterization of suitable biomass materials for energy production. However, the United States lacks consistency regarding the use of testing methods for biomass when evaluating combustion and fuel quality parameters. Many laboratories are relying on methods that have been developed and validated for fossil fuels, which may not be suitable for biomass fuels. Biomass varies greatly in composition, and the concentrations of some constituents are well outside the range of what is typically found in fossil fuels. Sulfur and trace metals are typically much lower in biomass fuels than in fossil fuels; however, some minor and major constituents such as phosphorus and potassium can be an order of magnitude higher. Many European countries have been utilizing biomass as a fuel source for decades and have relied mostly on draft standard test methods developed by the European Committee for Standardization (CEN), under the jurisdiction of a technical committee (CEN/TC 335), Solid Biofuels. Many of these standards have now been moved from the draft stage to provisional status and are published as national standards in Europe.

In 2007, the International Organization for Standardization (ISO) formed a new committee, ISO/TC 238, Solid Biofuels, that would help establish international standard test methods specific to biomass fuels that would be used in combustion systems. This committee has established six working groups that are reviewing the CEN standards and will adopt many of these standards for publication as ISO standards. The U.S. Technical Advisory Group (TAG) for ISO/TC 238 is the American Society of Agricultural and Biological Engineers (ASABE).

ASTM International (ASTM) standards are used by the United States for characterizing fuels, similarly to ISO standards in Europe. ASTM currently has several committees that oversee the development and publication of test methods for a variety of fuels, such as coal, coke, oil, natural gas, and refuse-derived fuels. There is also a committee dedicated to wood-based materials. However, ASTM does not have a committee or standard test methods that are solely applicable to evaluating biomass materials for fuel quality parameters. ASTM biomass methods for major, minor, and trace elements, including mercury, are nonexistent.

A key component in methods development and validation, for any type of material, is the analysis of standard reference materials (SRMs). SRMs supplied by the National Institute of Standards and Technology (NIST) and other agencies are a vital part of this process in analytical

laboratories when various materials are tested. Although many SRMs are available for fossil fuels, such as coal, petroleum coke, and oil, the availability of biomass SRMs is extremely limited. A few reference materials exist from biomass proficiency test programs and round-robin studies, but these are not widely available and many have expired. NIST currently has four biomass reference materials in stock; however, the reference parameters listed in the certificates of analysis are not the same parameters that are needed for the combustion characteristics and fuel quality parameters mentioned above and, therefore, are not applicable to biomass fuels, which are the subject of the work conducted under this project (2–5).

Since there is such a dearth of good reference methods and analyses for characterizing biomass types in the United States, the goal of this project was to help develop suitable biomass methods and reference materials that would be widely available to the biomass industry.

3.0 EXPERIMENTAL APPROACH

3.1 Task 1 – Assessment of Current Biomass Standards

To aid in the review of existing biomass standard methods and to follow the development of new methods, the Energy & Environmental Research Center (EERC) has taken an active role in two biomass committees. Currently, two EERC researchers are members of the ASABE FPE-709 committee, Biomass Energy and Industrial Products. One researcher is a member of the ISO/TC 238, Solid Biofuels. The FPE-709 committee has established a working group, X564, to assemble information and standards from several standards organizations such as ISO, CEN, and ASTM. Table 1 lists the standards that were reviewed for parameters that were determined for biomass fuels in this project.

Many of the CEN technical specifications listed in Table 1 were considered draft standards at the beginning of this project. However, during the course of the project, some of these standards were promoted to provisional status and eventually approved and published as European national standards. Throughout this process, the number designation of the standard didn't change, but the letter designation changed to reflect the status of the standard. For example, the ash standard began at the draft committee level as CEN/TS 14775, then was promoted to provisional status as prEN 14775, and finally was published as a European national standard under the designation EN 14775.

The ISO standards listed in the tables are currently under the jurisdiction of ISO Technical Committee ISO/TC 27, Solid Mineral Fuels. However, the Solid Biofuels ISO committee, ISO/TC 238, was formed to establish standard test methods that were more specific to biomass. This committee is reviewing the CEN standards and will adopt many of these standards for publication as ISO standards as well as develop new methods.

Table 1. Standard Methods Reviewed for Biomass Analysis

Parameter	Analytical Methods
Moisture Content	CEN/TS 14774-1, ASTM E871, ASTM D5142, ASTM D3302, ASABE S358.2
Ash Content	ISO 1171, CEN/TS 14775, ASTM D3174, ASTM D1102, ASTM E1534, ASTM E1755, ASTM E830
Volatile Matter	CEN/TS 15148, ASTM E872
Calorific Value	ISO 1928, CEN/TS 14918, ASTM D5865, ASTM E711
C, H, N Content	ISO 12902, CEN/TS 15104, ASTM D5373, ASTM E777, ASTM E778
Sulfur Content	CEN/TS 15289, ASTM D4239, ASTM E775
Bromine Content	CEN/TS 15289
Chlorine Content	CEN/TS 15289, ASTM D6721, ASTM D4208, ASTM E776
Fluorine Content	CEN/TS 15289, ASTM D5987, D4208
Ash-Melting Behavior	ISO 540, CEN/TS 15370, ASTM D1857
Major Elements (Na, K, Ca, Mg, Si, P, Fe, Al, Ti)	CEN/TS 15290, ASTM D4326, ASTM D6349
Minor and Trace Elements (As, Be, Cd, Cr, Co, Cu, Mn, Ni, Pb, Sb, Tl, V, Zn)	CEN/TS 15297, ASTM D6349, ASTM D6357
Mercury Content	CEN/TS 15297, ASTM D6414, ASTM D6722
Bulk Density	ISO 567, CEN/TS 15103, ASTM E873

3.2   Task 2 – Fuel Selection and Characterization

3.2.1   Fuel Selection

A second task was related to actual biomass analysis and characterization, using methods that were determined to be more appropriate for biomass. This task was also a crucial element in obtaining good average data on common biomass types which is of great interest to the clients of this project.

A total of ten different biomass samples were collected for this task. Their descriptions, locations, and collection information, are presented in Table 2. The intent was to select candidates that are predominantly being used in the United States as feedstocks for energy production or that could potentially be used as feedstocks. Another factor that was considered when selecting these fuels was to choose materials that had varying chemical characteristics. Typically, herbaceous materials have higher ash, potassium, and phosphorus contents than woody biomass. The presence of higher alkali concentrations, coupled with the usual silica content from phytoliths can become a combination for severe fouling and slag deposit development in a combustion boiler (6–8). In contrast, woody biomass materials can vary significantly in ash constituents, depending on how much bark and other forest material remains with the trees when harvested, but usually wood is lower in ash content compared to herbaceous biomass (9).

Table 2. Biomass Samples Characterized in This Project

Sample Type	State Collected	Collection Information
Switchgrass	ND	Collected at the Central Grasslands Research Extension Center in Kidder County. Cut with a swather and baled with a square baler.
Corn Stover	ND	Collected at the Central Grasslands Research Extension Center in Kidder County. Cut by hand after the corn harvest.
Wheat Straw	ND	Collected in Ward County and straight cut when harvested and baled with a round baler.
Dried Distillers Grain	ND	Coproduct of corn ethanol production. Collected at the ethanol plant after drying.
Sugar Beet Pulp	ND/MN	Fibrous by-product of beet sugar processing. Collected at the processing plant after pelletizing.
Loblolly Pine	GA	After harvesting 10-year-old trees, branches and leaves were removed, and the main trunks with bark were chipped with a brush chipper to 1-inch-size pieces.
Cottonwood	AL	After harvesting 5-year-old trees, branches and leaves were removed, and the main trunks with bark were chipped with a brush chipper to 1-inch-size pieces.
Aspen	AL	After harvesting 5-year-old trees, branches and leaves were removed, and the main trunks with bark were chipped with a brush chipper to 1-inch-size pieces.
Eucalyptus	AL	After harvesting 5-year-old trees, branches, leaves, and bark were removed, and the main trunks were chipped with a brush chipper to 1-inch-size pieces.
Waste Wood Pellets	NE	A combination of construction and demolition wood, packing or crating wood, and scrap pallets that were ground and pelletized.

Upon receipt of samples at the EERC, the bulk density test was performed promptly, and the samples were air-dried and reduced in size to −5 mesh (4 mm) using an AEC Nelmor granulator. Further size reduction to −18 mesh (1 mm) was done with a Bel-Art Micro-Mill® grinder. A particle size of 1 mm or less is the typical requirement for analytical methods used for biomass.

3.2.2 Analytical Characterization

Based on a thorough review of the methods presented in Task 1 and discussions with others in the biomass industry that have experience with biomass testing, the methods selected for characterizing the samples in this project are presented in Table 3.

Table 3. Standard Methods Used for Biomass Analysis

Parameter	Analytical Methods
Moisture Content	CEN/TS 14774-1
Ash Content at 550°C	CEN/TS 14775
Ash Content at 815°C	ISO 1171
Volatile Matter	CEN/TS 15148
Calorific Value	CEN/TS 14918
C, H, N Content	ASTM D5373
Sulfur Content	ASTM D4239
Bromine Content	CEN/TS 15289
Chlorine Content	CEN/TS 15289, ASTM D6721
Fluorine Content	CEN/TS 15289
Ash-Melting Behavior	ISO 540
Major Elements (Na, K, Ca, Mg, Si, P, Fe, Al, Ti)	CEN/TS 15290 (Part A)
Minor and Trace Elements (As, Be, Cd, Cr, Co, Cu, Mn, Ni, Pb, Sb, Se, Tl, V, Zn)	CEN/TS 15297
Mercury Content	CEN/TS 15297, ASTM D6722
Bulk Density	CEN/TS 15103

3.2.3   Interlaboratory Comparison

Five of the ten project samples were selected for a small interlaboratory comparison of the biomass methods used in this project. These samples included the switchgrass, corn stover, wheat straw, cottonwood, and eucalyptus. To help evaluate the results from both laboratories (i.e., the EERC laboratory and the independent laboratory), a biomass reference material, NJV 94-5 Wood Fuel, was also included as a blind sample. As discussed previously, biomass reference materials are extremely limited and not widely available; however, the EERC was able to acquire some materials that had been evaluated in a proficiency test program in Sweden in 1994. These materials are distributed in the United States by Alpha Resources; however, only a partial list of fuel quality parameters are certified in these materials, resulting in the need to produce more of these materials for use in biomass testing laboratories.

After project samples were prepared to <1 mm in size as described in Section 3.2.1, a 30-g portion of each sample was packaged and sent to the independent laboratory of comparative analysis. The laboratory was chosen, based on the ability of the laboratory to employ biomass methods that are similar to those used by the EERC. Table 4 lists the methods that each laboratory used. Bulk density was not done by the independent laboratory (Lab B) because the sample had already been ground to help ensure a homogenous representative sample for both labs. The ash-melting behavior parameter, which requires a large quantity of biomass material ashed at 815°C, was also not performed by Lab B because of the limited amount of material available.

Table 4. Methods Used by Participating Laboratories

Parameter	Analytical Methods	
	Lab A	Lab B
Moisture Content	CEN/TS 14774-2	EN 14774-3
Ash Content at 550°C	CEN/TS 14775	EN 14775
Volatile Matter	CEN/TS 15148	EN 15148
Calorific Value	ISO 1928	EN 14918
C, H, N Content	ASTM D5373	prEN 15104
Sulfur Content	ASTM D4239	CEN/TS 15289, 15408
Bromine Content	CEN/TS 15289	CEN/TS 15289
Total Chlorine Content	CEN/TS 15289, ASTM D6721	CEN/TS 15289
Fluorine Content	CEN/TS 15289	CEN/TS 15289
Major Elements (Al, Ca, Fe, K, Mg, Na, P Si, Ti)	CEN/TS 15290 (Part A), ASTM D6349	CEN/TS 15290 (Part A), ASTM D6349
Minor and Trace Elements (As, Be, Cd, Cr, Co, Cu, Mn, Ni, Pb, Sb, Se, Tl, V, Zn)	CEN/TS 15297	CEN/TS 15297
Mercury Content	CEN/TS 15297, ASTM D6722	CEN/TS 15297

3.3 Task 3 – Technology Transfer and Standards Promotion

The EERC will continue to have opportunities to promote biomass standards throughout the United States by presenting important information at biomass conferences and workshops. Also, through membership in biomass committees, EERC researchers are directly involved in the development and publication of biomass standards to be used throughout the industry. It was anticipated that two conferences and one committee meeting would be attended during this project, with continued membership in the standards committee as new methods are being evaluated.

3.4 Task 4 – Predicting Slagging Behavior of Biomass Fuels

Equilibrium thermodynamic modeling was used to predict the concentrations and compositions of gases, liquids, liquid solutions, and solids present in each biomass fuel's products of combustion as a function of temperature. The FactSage model (Version 6.2) was used (10). It is a commercially integrated thermodynamic database coupled to programs for calculating multicomponent, multiphase equilibria based on a minimization of Gibbs' free energy.

Prior to the FactSage calculations, a preliminary calculation was performed using each biomass ultimate analysis to estimate the major gas concentrations (N_2, O_2, CO_2, SO_2, and NO_2) produced per gram of ash. This preliminary calculation estimates the amount of air (oxygen and nitrogen) that would be consumed during combustion to produce a gaseous atmosphere (i.e., flue gas) that subsequently interacts with the ash components. After a chemical composition is input for each biomass, FactSage determines equilibrium concentrations of solid, liquid, aqueous, and gaseous species over a specified temperature range. Calculations were performed from 392°F to

2732°F (200° to 1500°C) at 45°F (25°C) increments. A pressure of 1 atmosphere and excess air of 20% was assumed. Small changes in pressure or excess air have an insignificant effect on the calculation results. Approximately 1400 elements and compounds were considered in the calculations.

FactSage will not only predict the amount of liquid in a combustion melt, it will also give a composition of that liquid that can be used to determine a viscosity of the liquid material. Viscosity of the liquid predicted by FactSage for each temperature was calculated using the Kalmanovitch–Frank modification of the Urbain equation (11). The calculation results provide the concentration (wt%) and viscosity of liquid in the slag as a function of temperature. Viscosity information is important for deducing whether fouling and slagging deposits will form and become potentially troublesome.

The FactSage calculation results are useful for predicting the effects that the biomass fuels may have on boiler operations. Five such predictive scenarios include the following:

1) Slag viscosity and the percentage of liquid slag, which are predicted calculations made by FactSage, 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 and slagging that may occur on steam tube surfaces in the hotter section of the convective pass. A high concentration of a low-viscosity slag is indicative of a severe slagging problem.

2) The percentage of solid sulfates present is related to the propensity for calcium sulfate-based, low-temperature fouling in the economizer region of the boiler.

3) The percentage of liquid sulfates (sodium or potassium sulfate, Na_2SO_4 or K_2SO_4) is related to the potential for forming a sticky liquid that would significantly increase deposit severity in the temperature range where it forms.

4) The percentage of solid phosphates is related to the propensity for an increased number of cleaning cycles and higher pressure drop in a baghouse. Fine phosphates tend to "blind" bags more than the usual fly ash.

5) The percentage of solid chlorides and carbonates are related to the formation of fine particulate, which has a similar effect as phosphates on baghouse performance.

3.5 Task 5 – Setting the Stage for the Development of Biomass Standard Reference Materials

At the beginning of this project, the intent was to use some of the same materials that were collected for this project as possible candidates for the development of SRMs by NIST. Unfortunately, the timing of the sample collection did not coincide with the product development stage at NIST, and an alternate plan for SRM development at NIST was discussed. NIST representatives agreed that biomass SRMs were needed and would begin development work in 2012. In order to ensure a 5-year supply of biomass SRMs at NIST, it will be acquiring at least

100 kg of each material considered. These large quantities were not attainable through the resources in this project.

4.0   RESULTS AND DISCUSSION

4.1   Task 1 – Assessment of Current Biomass Standards

After reviewing the various analytical methods for fuel characterization, it appeared that some of the methods were very similar in their procedures. Those included the methods for moisture, calorific value, and CHN (carbon, hydrogen, and nitrogen) testing. Given the similarity in the procedures, it is anticipated that all the methods reviewed for these parameters would produce similar results and be suitable for biomass materials. However, there were several methods that had significant procedural differences for the same parameter. Those included ash content, volatile matter, sulfur, chlorine, major elements, minor elements, and trace elements. These procedures will be discussed in detail below.

4.1.1   Ash Determination Methods

Table 5 lists the different ash methods that were reviewed for this project along with the sample types for which they were designed and the recommended operating temperature of the furnace. The most significant difference among the methods was the operating temperature of $725° \pm 25°C$ for the ASTM D3174 coal method compared to the other methods, which specify much lower temperatures. Because of the high levels of alkali (i.e., Na, K,) and alkaline-earth (i.e., Ca, Mg) metals found in some biomass materials, ash determination at lower temperature is recommended to avoid mass loss of these metals. Although biomass testing laboratories may be aware of this, there is still a 100°C difference in the range of operating temperatures specified in the other methods reviewed. This makes it difficult for the users of the data to compare biomass fuels if results are obtained from different laboratories employing different ash determination methods. At the very least, laboratories should specify the method and temperature used; however, one method with one temperature that would be used by all biomass testing laboratories would be ideal.

Table 5. Methods for Ash Determination in Various Fuel Types

Method	Sample Type	Ignition Temperature
ISO 1171	Solid mineral fuels	500°
CEN/TS 14775	Solid biofuels	$550° \pm 10°C$
ASTM D3174	Coal	$725° \pm 25°C$
ASTM D1102	Wood	$590° \pm 10°C$
ASTM E1534	Wood	$590° \pm 10°C$
ASTM E1755	Biomass	$575° \pm 25°C$
ASTM E830	Refuse-derived fuel	$575° \pm 25°C$

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4.1.2   Volatile Matter

There are similarities in the methods reviewed for volatile matter in that all methods call for a similar sample size of 1 gram and reducing atmosphere in the furnace. Again, the most significant difference is the operating temperature. Method CEN/TS 15148 specifies a temperature of 900° ± 10°C, and method ASTM E872 specifies a temperature of 950° ± 20°C, which is identical to ASTM coal methods. Based on the chemical differences between coal and biomass, the CEN/TS method, or an equivalent method with a 900°C operating temperature, would be recommended for biomass fuels.

4.1.3   Sulfur Methods

Each of the three sulfur methods reviewed has very different analytical approaches. The CEN/TS 15289 method is suitable for the determination of both total sulfur and total chlorine. The method describes two different approaches to decompose the sample and trap the acidic gas (i.e., HCl) in an absorbing solution: for Method A, a 1-g sample is prepped in a sealed oxygen bomb and combusted in the presence of water or an alkaline absorbing solution, and Method B describes digesting the sample with hydrogen peroxide (H_2O_2) in a closed vessel. The preferred method for detecting the sulfate in either solution is ion chromatography, however the method does mention other suitable analytical methods such as inductively coupled plasma atomic emission spectrometry (ICP–AES), coulometry, potentiometric titration, and photometric titration. It also allows for the use of automated equipment and x-ray fluorescence (XRF) spectrometry, provided a thorough validation is done using suitable biomass standard reference materials, if available. The estimated method detection limit (MDL) for sulfur is 50 mg/kg.

The ASTM D4239 method is a direct combustion method with infrared absorption detection. The estimated detection limit is dependent on the equipment and sample size, but 100 mg/kg is reasonable.

The ASTM E775 method was intended for refuse-derived fuels but is occasionally used for biomass. This method describes two different approaches: Method A, where the sample is mixed with magnesium oxide and sodium carbonate (Eschka mixture) and ignited at 800°C. The ignited sample is dissolved in water, and barium chloride is added to precipitate the sulfur, which is weighed. Method B is an oxygen bomb preparation followed by precipitation and weighting as described in Method B. The method did not have specific limits for ranges or detection limits but reported the repeatability (*r*) of an average value of 0.35% to be 0.03%. This method appears to be lengthy and time-consuming and is not suited for low-level sulfur determination, which is needed for many of the woody biomass materials.

4.1.4   Chlorine Methods

Details of the chlorine methods reviewed in this project are compared in Table 6. Three of the four methods specify a sample size of 1 g, which is significantly higher than the sample amount specified in ASTM D6721. A larger sample size would be more conducive to heterogeneous samples, if the samples are not ground fine enough. However, the ASTM D6721

Table 6. Chlorine Methods Comparison

Method	Sample Type	Sample Size	Sample Oxidation	Detection Method	Estimated MDL, ppm
ASTM D6721	Coal	10–50 mg	Tube combustion	Coulometric titration	5
ASTM D4208	Coal	1 g	Bomb combustion	Ion selective electrode	220
ASTM E776	Refuse-derived fuels	1 g	Bomb combustion	Potentiometric titration	Unknown
CEN/TS 15289	Solid biofuels	1 g	Bomb combustion	Ion chromatography	50

method clearly surpasses the other methods for low chlorine detection. The method detection limits listed in the table are estimations only, and will vary with sample size and laboratory equipment. The ASTM E776 method did not have specific limits for ranges or detection limits but reported the repeatability (*r*) of an average value of 0.49% to be 0.03%. Of the three bomb combustion preparation techniques, method CEN/TS 15289 appears to be the most sensitive at 50 ppm, which is the limit specified in the method. Five of the ten biomass samples characterized in this project had total chlorine levels below 50 ppm. The only method reviewed that could definitively detect chlorine in all the project samples was ASTM D6721. An interlaboratory study conducted by the Electric Power Research Institute (EPRI) in 2000 that evaluated different methods for Cl and Hg in coal resulted in similar findings where the bomb combustion techniques followed by ion-selective electrode, potentiometric titration, or ion chromatography could not meet the lower level of detection needed for many U.S. coals (12). If low-chlorine biomass fuels are used as alternative energy sources, low detection will be required to meet the MATS rule for HCl emissions.

4.1.5 Methods for Major Elements

The major elements determined in biomass fuels and fossil fuels typically include Al, Ca, Fe, Mg, P, K, Si, Na, and Ti. The analytical results can be reported in a variety of ways: ppm (mg/kg) in the raw fuel, oxide percent in the raw fuel, or oxide percent in the ash. All results in this report are reported as mg/kg in the raw fuel. The CEN/TS 15290 method describes two different approaches: Part A, which is a heated acid digestion of the raw fuel, and Part B, which is a heated acid digestion of the prepared ash at 550°C. This standard allows for the use of several different analytical methods for detection. They are ICP–AES, inductively coupled plasma mass spectrometry (ICP–MS), and atomic absorption spectrometry (AAS). The specification also allows for XRF when validated with suitable reference materials. Unfortunately suitable biomass reference materials are not available in the ranges of concentrations needed for XRF spectrometry. Method ASTM D4326 is an XRF method for coal which calls for ashing the coal at 750°C and fusing the prepared ash with a fluxing agent to produce a glass like material. This method is more suited for coal, due to the higher ashing temperature and the availability of coal standard reference materials. The ASTM D6349 method calls for ashing the material and fusing the ash with a fluxing agent to produce a glass pellet

which is dissolved in acid. Alternatively, the ash can be digested directly in a mixture of acids. The resulting digested solutions are analyzed by ICP–AES.

One major drawback of these methods is the potential loss of alkali and alkaline-earth metals (K, Na, Ca, Mg) in the ashing process. These losses could be significant in the herbaceous type of biomass material, such as switchgrass, corn stover, and wheat straw that typically contain high levels of K. Therefore, it is recommended that a closed vessel (i.e., microwave) acid digestion, as described in CEN/TS 15290 Part A, be done on the raw fuel for determining these metals in biomass. However, the elements Al and Si, are often difficult to dissolve directly in acid and are better solubilized by fusing the ashed material with a fluxing agent as described above. The ashing should be done at 550°C for biomass materials and not the 750°C temperature prescribed for coal. It appears that all three methods reviewed have some drawbacks for accurate determination of all the major elements listed, but slight modifications of the methods as written, or a combination of methods, would result in suitable approaches for determining these elements in biomass.

4.1.6 Methods for Minor and Trace Elements

The elements discussed in these methods include: As, Be, Cd, Cr, Co, Cu, Hg, Mn, Ni, Pb, Sb, Se, Tl, V, and Zn. For method CEN/TS 15297, the sample is digested with a combination of hydrogen peroxide, nitric acid and hydrofluoric acid and heated in a closed vessel. The specification allows for several analytical detection methods. They are ICP–AES, ICP–MS, graphite furnace atomic absorption spectrometry (GFAAS), hydride generation atomic absorption spectrometry, and cold-vapor atomic absorption spectrometry (CVAAS) for Hg. For method ASTM D6357, the sample is ashed at 500°C and the ash is digested with a combination of nitric, hydrochloric, and hydrofluoric acids. The solutions are analyzed by ICP–AES, ICP–MS, or GFAAS. This method does not allow for the determination of Hg and Se, which could be lost during the ashing procedure. ASTM Methods D6414 and D6722 are designated as Hg methods only. D6414 is a closed vessel heated digestion with nitric and hydrochloric acids, followed by CVAAS. D6722 is a direct combustion method where the sample is heated in the presence of oxygen and the Hg is selectively trapped on a gold amalgamator, released, and ultimately detected by atomic absorption. Both ASTM Hg methods have undergone extensive validation for coal through controlled interlaboratory studies that included the analysis of three different coal standard reference materials to determine the accuracy of the methods. These methods may be suitable for biomass materials, but unfortunately, biomass reference materials with certified Hg values are not available at this time to truly validate these methods for biomass materials. The same is true for many of the other trace elements listed in this section. The MATS rule has emissions regulations for eleven of the fifteen trace elements listed, because they're designated as inorganic hazardous air pollutants (HAPs).

4.2   Task 2 – Fuel Selection and Characterization Results

4.2.1   Fuel Selection

As mentioned in Section 3.2.1, one of the criteria for selecting the biomass fuels for this project was to have materials with varying chemical characteristics. The results in the next section will show that this criterion was indeed met.

4.2.2   Characterization Results

4.2.2.1   Proximate Analysis, Ultimate Analysis, and Halogens

The analytical results for the ten project samples are presented in Tables 7 and 8. The data in Table 7 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%. The other halogens, bromine and fluorine, are all below detection limits for the methods employed. There may be a need to develop an alternative method for fluorine to get lower detection limits, since hydrogen fluoride (HF) is one the regulated constituents in the MATS rule. 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. Sulfur dioxide emissions are also regulated under the MATS rule, which makes low-sulfur biomass fuels attractive as an alternative energy source when cofiring with coal.

4.2.2.2   Major Ash Constituents

From an analytical standpoint the results of the nine major ash constituents presented in Table 7 are of particular interest, due to the wide range of concentrations among the different biomass materials. The minimum and maximum values are presented in Table 9. This wide range of concentrations supports the use of methods, other than XRF, due to the lack of standard reference materials that would be needed for calibration. The methods that call for digestion and analysis by ICP–AES are more flexible, because they allow for dilution and standard preparation using aqueous standards that are readily available.

4.2.2.3   Trace Elements

The trace element results are summarized in Table 8. The data show that the majority of the trace elements are below method detection limits for the biomass materials tested in this project. The elements copper, manganese, molybdenum, and zinc, are present in measurable quantities for most of the fuels, which is to be expected since these elements are present in soil as micronutrients and are taken up by the plant.

Further discussion of the biomass fuels analytical results and how they can potentially affect performance in a combustion boiler is presented in Section 4.4.

Table 7. Analytical Results for Project Biomass Fuel Samples[1]

Sample ID	Switchgrass	Corn Stover	Dried Distillers Grains	Sugar Beet Pulp	Wheat Straw	Loblolly Pine	Cottonwood	Aspen	Eucalyptus	Waste Wood Pellets
Proximate Analysis, wt%										
Moisture, as-received	26.76	29.60	10.38	9.45	19.94	32.88	37.58	15.19	28.97	7.75
Ash (550°C)	7.81	6.00	4.23	12.68	6.86	0.78	1.03	1.07	0.41	0.76
Ash (815°C)	8.33	7.16	4.74	13.86	6.91	0.69	0.85	0.95	0.45	0.69
Volatile Matter	75.61	78.30	78.46	72.25	76.46	79.55	82.12	84.63	81.99	82.67
Ultimate Analysis, wt%										
Hydrogen	5.58	5.04	6.69	4.95	5.58	5.85	5.25	5.83	5.54	6.18
Carbon	48.17	45.57	48.97	40.96	41.58	51.79	50.25	49.90	50.20	51.26
Nitrogen	0.63	0.50	4.91	0.97	0.84	0.12	0.09	0.13	0.10	0.06
Sulfur	0.13	0.06	0.97	0.24	0.27	0.02	0.03	0.03	0.01	0.01
Oxygen, calculated	37.69	42.83	34.23	40.20	42.10	41.43	43.36	43.04	43.74	41.72
Calorific Value, MJ/kg	20.9	19.1	21.1	15.9	18.0	20.5	19.4	19.4	19.4	20.3
Calorific Value, Btu/lb	8989	8230	9058	6817	7748	8818	8345	8344	8351	8730
Bulk density, kg/m³	31	29	448	613	29	175	138	108	130	635
Bromine, wt%	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050
Chlorine, wt%	0.0948	0.0066	0.1430	0.0021	0.2000	0.0033	0.0016	0.0042	0.0477	0.0039
Fluorine, wt%	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050
Aluminum, mg/kg	215	1210	21.3	4280	123	338	14.2	8.0	<5	66.6
Calcium, mg/kg	2850	1940	147	10,900	1310	953	2160	2210	587	878
Iron, mg/kg	296	904	243	2310	135	369	72.4	128	58.0	51.5
Magnesium, mg/kg	2460	1580	3410	3210	1170	341	619	533	145	185
Phosphorous, mg/kg	1130	572	9000	539	855	133	320	458	234	22.9
Potassium, mg/kg	8910	6450	11,800	3040	26,300	898	2590	2450	1160	576
Silicon, mg/kg	24,900	21,100	230	41,700	11,100	2050	184	273	578	545
Sodium, mg/kg	48.1	299	764	915	234	69.1	<20	<20	72.8	319
Titanium, mg/kg	21.9	59.4	<2	207	5.0	15.4	2.8	2.1	<2	2.1

[1] Moisture is reported on an as-received basis, and all other parameters are reported on a dry basis.

Table 8. Trace Element Results for Project Biomass Samples, mg/kg dry basis

Sample ID	Switchgrass	Corn Stover	Dried Distillers Grains	Sugar Beet Pulp	Wheat Straw	Loblolly Pine	Cottonwood	Aspen	Eucalyptus	Waste Wood Pellets
Antimony	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Arsenic	<0.1	0.25	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Beryllium	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Cadmium	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Chromium	1.8	3.4	2.2	9.6	0.47	0.73	<0.2	<0.2	<0.2	0.35
Cobalt	0.15	0.25	<0.1	0.80	0.12	4.02	0.34	<0.1	1.01	0.16
Copper	6.80	4.00	4.61	10.2	2.95	1.70	1.43	2.23	1.43	4.09
Lead	<0.5	0.52	<0.5	1.38	<0.5	0.98	<0.5	<0.5	1.85	<0.5
Manganese	66.2	70.0	15.0	121	41.8	74.1	9.78	7.79	16.6	57.8
Mercury	0.0075	0.0042	<0.005	<0.005	0.0066	<0.005	<0.005	<0.005	<0.005	<0.005
Molybdenum	1.98	0.38	0.95	0.46	0.23	<0.1	<0.1	<0.1	<0.1	<0.1
Nickel	1.42	1.94	2.51	3.90	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Thallium	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Tin	<0.5	<0.5	<0.5	<0.5	2.47	<0.5	<0.5	<0.5	<0.5	<0.5
Vanadium	0.58	2.70	<0.1	8.68	0.15	<0.1	<0.1	<0.1	<0.1	<0.1
Zinc	31.0	10.7	53.0	23.2	9.55	9.05	25.2	37.4	2.15	8.22

Table 9. Concentration Ranges for the Major Ash Components

Parameter	Minimum value, mg/kg	Maximum value, mg/kg
Aluminum	<5	4280
Calcium	147	10,900
Iron	51.5	2310
Magnesium	145	3410
Phosphorous	22.9	9000
Potassium	576	26,300
Silicon	184	41,700
Sodium	<20	915
Titanium	<2	207

4.2.3 Interlaboratory Comparison Results

The comparative analytical results of the two laboratories are presented in Tables 10 and 11. The difference in results reported by these labs is presented as relative percent difference (RPD) using the following calculation:

$$RPD = \left[\frac{|a-b|}{\frac{(a+b)}{2}}\right] \times 100 \qquad \text{[Eq. 1]}$$

where:

$a = average\ value\ from\ Lab\ A$

$b = average\ value\ from\ Lab\ B$

RPD was not calculated (NC) when one or both laboratories reported "less than" values.

In general, the agreement between the two laboratories was good. There were a total of 204 paired sets of analyses reported by the laboratories. RPDs could only be calculated for 111 of these pairs because of nonreported values from either one or both of the labs. Of the 111 pairs, less than a quarter (23% or 26 pairs) had RPDs of >20%. The majority of these were reported with the corn stover sample, and the fewest differences and best agreement was with the NJV 94-5 SRM. Although all project samples were ground to a particle size of <1 mm, which is recommended for biomass sample preparation, the NJV 94-5 SRM visually appeared to be ground much finer than the other samples. This difference in particle size, which would result in more heterogeneity for the EERC project samples than for the NJV 94-5 sample, could explain some of the differences in the results from the two laboratories.

Table 10. Results from the Interlaboratory Comparison for the Herbaceous Materials, dry basis

Sample ID	Switchgrass			Corn Stover			Wheat Straw		
	Lab A	Lab B	RPD	Lab A	Lab B	RPD	Lab A	Lab B	RPD
Ash (550°C), wt%	7.81	8.25	5.5	6.00	6.85	13.2	6.9	8.0	15.3
Volatile Matter, wt%	75.61	74.0	2.1	78.30	79.70	1.8	76.46	72.5	5.3
Calorific Value, MJ/kg	20.9	18.56	11.9	19.1	17.91	6.4	18	18.17	0.9
Carbon, wt%	48.17	45.5	5.8	45.57	45.95	0.8	41.58	45.45	8.9
Hydrogen, wt%	5.58	5.9	5.9	5.04	5.80	14.0	5.58	5.8	3.9
Nitrogen, wt%	0.63	0.73	14.7	0.50	0.47	6.2	0.84	0.76	10.0
Sulfur, wt%	0.13	0.11	16.7	0.06	0.04	48.7	0.27	0.175	42.7
Bromine, wt%	<0.0050	<0.005	NC	<0.0050	<0.005	NC	<0.005	<0.005	NC
Chlorine, wt%	0.0948	0.087	8.6	0.0066	0.0074	11.4	0.2	0.18	10.5
Fluorine, wt%	<0.0050	0.018	NC	<0.0050	0.014	NC	<0.005	<0.005	NC
Aluminum, mg/kg	215	130	49.3	1210	890	30.5	123	89	32.1
Calcium, mg/kg	2850	2500	13.1	1940	1500	25.6	1310	1450	10.1
Iron, mg/kg	296	345	15.3	904	340	90.7	135	128	5.3
Magnesium, mg/kg	2460	2100	15.8	1580	1300	19.4	1170	1100	6.2
Phosphorous, mg/kg	1130	735	41.9	572	340	50.9	855	750	13.1
Potassium, mg/kg	8910	7850	12.6	6450	5450	16.8	26300	26000	1.1
Silicon, mg/kg	24,900	25000	0.6	21,100	19000	10.5	11100	14000	23.1
Sodium, mg/kg	48.1	<100	NC	299	<100	NC	234	120	64.4
Titanium, mg/kg	21.9	13	51.0	59.4	17.5	109.0	5	4.25	16.2
Antimony, mg/kg	<0.1	<0.5	NC	<0.1	<0.5	NC	<0.1	<0.5	NC
Arsenic, mg/kg	<0.1	<1	NC	0.25	<1	NC	<0.1	<1	NC
Beryllium, mg/kg	<0.1	<1	NC	<0.1	<1	NC	<0.1	<1	NC
Cadmium, mg/kg	<0.1	<0.2	NC	<0.1	<0.2	NC	<0.1	<0.2	NC
Chromium, mg/kg	1.8	37	181	3.4	22.50	147.5	0.47	2.35	133.3
Cobalt, mg/kg	0.15	<1	NC	0.25	<1	NC	0.12	<1	NC
Copper, mg/kg	6.80	6.6	3.0	4.00	3.45	14.8	2.95	<5	NC
Lead, mg/kg	<0.5	<1	NC	0.52	<1	NC	<0.5	<1	NC
Manganese, mg/kg	66.2	61	9.0	70.0	32.5	73.2	41.8	51	19.8
Mercury, mg/kg	0.0075	<0.02	NC	0.0042	<0.02	NC	0.0082	<0.02	NC
Nickel, mg/kg	1.42	19	173	1.94	6.35	107.9	<0.5	<5	NC
Thallium, mg/kg	<0.1	<1	NC	<0.1	<1	NC	<0.1	<1	NC
Tin, mg/kg	<0.5	<1	NC	<0.5	<1	NC	2.47	<1	NC
Vanadium, mg/kg	<0.5	<1	NC	2.70	<1	NC	0.15	<1	NC
Zinc, mg/kg	31.0	27.5	12.0	10.7	7.10	40.4	9.55	10	4.6

Table 11. Results from the Interlaboratory Comparison for the Wood Materials, dry basis

Sample ID	Eucalyptus			Cottonwood			NJV 94-5 Wood Fuel SRM		
	Lab A	Lab B	RPD	Lab A	Lab B	RPD	Lab A	Lab B	RPD
Ash (550°C), wt%	0.41	0.525	24.6	1.03	1.1	4.4	1.2	1.3	3.3
Volatile Matter, wt%	81.99	84	2.4	82.12	82.7	0.7	77.1	78.7	2.0
Calorific Value, MJ/kg	19.4	20	3.0	19.4	19.67	1.4	21.1	20.63	2.3
Carbon, wt%	50.20	50.15	0.1	50.25	49.7	1.1	52.7	51.6	2.1
Hydrogen, wt%	5.54	6.1	9.6	5.25	5.9	11.4	5.88	6.1	3.7
Nitrogen, wt%	0.10	<0.1	NC	0.09	0.11	20.0	0.17	<0.1	NC
Sulfur, wt%	0.01	0.0215	73.0	0.03	0.033	8.5	0.02	0.023	11.8
Bromine, wt%	<0.0050	<0.005	NC	<0.0050	<0.005	NC	<0.005	<0.005	NC
Chlorine, wt%	0.0477	0.044	8.1	0.0016	<0.005	NC	0.0064	0.0061	5.3
Fluorine, wt%	<0.0050	0.00565	NC	<0.0050	0.010	NC	<0.005	<0.005	NC
Aluminum, mg/kg	<5	<10	NC	14.2	36	86.2	273	260	5.1
Calcium, mg/kg	587	640	8.6	2160	2153	0.3	3234	3400	5.0
Iron, mg/kg	58.0	91.5	44.8	72.4	47	42.3	63.0	50	23.9
Magnesium, mg/kg	145	150	3.4	619	586	5.4	306	310	1.3
Phosphorous, mg/kg	234	220	6.2	320	290	9.8	220	180	19.9
Potassium, mg/kg	1160	1100	5.3	2590	2663	2.8	1039	1020	1.9
Silicon, mg/kg	578	445	26.0	184	161	13.1	246	275	11.3
Sodium, mg/kg	72.8	<100	NC	<20	<100	NC	44.6	<100	NC
Titanium, mg/kg	<2	<1	NC	2.8	2.4	16.8	1.8	1.8	0.0
Antimony, mg/kg	<0.1	<0.5	NC	<0.1	<0.5	NC	<0.1	<0.5	NC
Arsenic, mg/kg	<0.1	<1	NC	<0.1	<1	NC	0.83	<1	NC
Beryllium, mg/kg	<0.1	<1	NC	<0.1	<1	NC	<0.1	<1	NC
Cadmium, mg/kg	<0.1	<0.2	NC	<0.1	<0.2	NC	0.25	0.28	9.6
Chromium, mg/kg	<0.2	7.45	NC	<0.2	<1	NC	0.58	<1	NC
Cobalt, mg/kg	1.01	<1	NC	0.34	<1	NC	0.07	<1	NC
Copper, mg/kg	1.43	<5	NC	1.43	<5	NC	1.7	<5	NC
Lead, mg/kg	1.85	<1	NC	<0.5	<1	NC	0.57	<1	NC
Manganese, mg/kg	16.6	20	18.6	9.78	9.6	1.9	160	180	11.9
Mercury, mg/kg	<0.005	<0.02	NC	<0.005	<0.02	NC	<0.005	<0.02	NC
Nickel, mg/kg	<0.5	2.65	NC	<0.5	<2	NC	0.3	<2	NC
Thallium, mg/kg	<0.1	<1	NC	<0.1	<1	NC	<0.1	<1	NC
Tin, mg/kg	<0.5	<1	NC	<0.5	<1	NC	<0.5	<1	NC
Vanadium, mg/kg	<0.1	<1	NC	<0.1	<1	NC	<0.1	<1	NC
Zinc, mg/kg	2.15	<5	NC	25.2	23.1	8.8	36.3	38	4.6

The laboratories' recovery results of the NJV 94-5 SRM are presented in Table 12. The SRM did not have reference values for all of the parameters that were tested by both laboratories as presented in Tables 9 and 10; therefore, only the results for the reference parameters are reported here. The values presented in parentheses are considered information values, because fewer statistical analyses were used to obtain these values than for the reference values.

The results show that both labs performed very well on the NJV 94-5 wood fuel. Recoveries ranged from 73%–115% for Lab A and 73%–125% for Lab B. The one exception was the chlorine recovery, which was 64% and 61% for Lab A and Lab B, respectively. However, it is worth noting that the chlorine value of 0.010% ± 0.0036% is an informational value, with a confidence interval of ±36%, which indicates that the data used to determine this value in the SRM were highly variable.

The results received from both labs for the NJV 94-5 wood fuel are very encouraging in that the methods used by the labs are suitable for this material and reproducible. These results, however, do not help explain the differences seen with some of the other project samples, especially the corn stover. Perhaps the particle-size differences and heterogeneity were an issue, and one option would be to modify the methods to require a top particle size of 0.5 mm or less.

Table 12. Recovery Results for NJV 94-5 Wood Fuel SRM

Parameter	Reference Value	95% Confidence Interval	Lab A Recovery, %	Lab B Recovery, %
Ash (550°C), wt%	1.22	± 0.040	99	102
Volatile Matter, wt%	(79.2)[1]	± 0.60	97	99
Calorific Value, MJ/kg	20.6	± 0.15	102	100
Carbon, wt%	(51)	± 1.1	103	101
Hydrogen, wt%	(6.04)	± 0.082	97	101
Nitrogen, wt%	(0.17)	± 0.050	97	NC
Sulfur, wt%	0.018	± 0.0039	111	125
Chlorine, wt%	(0.010)	± 0.0036	64	61
Aluminum, mg/kg	260	± 32	105	100
Calcium, mg/kg	3500	± 220	92	97
Iron, mg/kg	70	± 16	90	71
Magnesium, mg/kg	300	± 18	102	103
Phosphorous, mg/kg	210	± 28	105	86
Potassium, mg/kg	900	± 170	115	113
Silicon, mg/kg	(230)	± 37	107	120
Sodium, mg/kg	40	± 12	111	NC
Titanium, mg/kg	(2.4)	± 0.44	75	73
Arsenic, mg/kg	0.8	± 0.24	104	NC
Cadmium, mg/kg	0.27	± 0.028	93	102
Chromium, mg/kg	0.8	± 0.30	73	NC
Copper, mg/kg	2.2	± 0.30	79	NC
Lead, mg/kg	0.68	± 0.025	84	NC
Manganese, mg/kg	210	± 38	76	86
Zinc, mg/kg	38	± 8.5	95	100

[1] ( ) indicate informational values.

4.3 Task 3 – Technology Transfer and Standards Promotion

Throughout the course of this project, the project manager, Carolyn Nyberg, was actively involved in two biomass standards committees, 1) ASABE FPE-709 committee, Biomass Energy and Industrial Products, and the ISO/TC 238, Solid Biofuels. She also attended two major biomass conferences: 1) the International Biomass Conference and Expo in St. Louis, Missouri, May 1–5, 2011, and 2) the Biomass '11 Conference at the Alerus Center in Grand Forks, North Dakota, July 26–27, 2011, where aspects of this project were presented and discussed among biomass colleagues. Although work for this project has been completed, Ms. Nyberg will continue to be involved in the committees mentioned above and will participate in the annual ISO TC 238 meeting in May 2012. This venue will bring together 24 participating countries to discuss and facilitate the development and implementation of international biomass standards, many of which were used in this project.

4.4 Task 4 – Predicting Slagging Behavior of Biomass Fuels

4.4.1 Overall Plant Performance and Emissions

Overall power plant performance and emissions were predicted from the biomass fuel chemical compositions and heating values. Products of combustion calculations were used to predict ash loading in pounds per million British thermal units (lb/MMBtu) for a specified fuel feed rate and uncontrolled (i.e., in the absence of pollution control devices) gaseous SO_2, NO_x, Hg, and chloride emissions. NO_x emissions, however, are more dependent on plant operating conditions; thus their predicted emissions are less precise. CO emissions are highly dependent on plant operating conditions and cannot be estimated. The calculated results of the overall plant performance and emissions are summarized in Table 13.

4.4.1.1 Heating Value, Fuel Feed Rate, and Ash Content

The effect of the biomass on the heating value, fuel feed rate, and ash input was calculated from the Btu content and ultimate analyses of the fuels on an as-received basis. The fuel feed rate and ash feed rate were calculated from the proximate analyses and reported on a lb/MMBtu basis.

Because of the somewhat low heating values compared to an average heating value of 6250 Btu/lb for Falkirk Mine lignite and 6800 Btu/lb for Center Mine lignite, more fuel is required for most of the biomass fuels (13). The exceptions are the dried distillers grains and the waste wood pellets which have moisture contents significantly lower than the other fuels. The cottonwood and eucalyptus have exceptionally low heating values.

The wood fuels have very low ash contents, so much less ash is fed on a MMBtu basis. The grassy biomass ash contents are significantly higher. The dried distillers grains are intermediate in ash content. The sugar beet pulp has a very high ash content, which is probably the result of extraneous soil mixed with the pulp biomass.

Table 13. Calculated Results for Overall Plant Performance and Emissions for Biomass Fuels

Sample ID:	Switchgrass	Corn Stover	Dried Distillers Grains	Sugar Beet Pulp	Wheat Straw	Loblolly Pine	Cottonwood	Aspen	Eucalyptus	Waste wood Pellets
Heating Value, Btu/lb	6584	5794	8118	6173	6203	5919	5209	7077	5932	8053
Ash Content, %	5.72	4.22	3.79	11.48	5.49	0.52	0.64	0.91	0.29	0.70
Fuel Feed Rate, lb/MMBtu	151.9	172.6	123.2	162.0	161.2	169.0	192.0	141.3	168.6	124.2
Ash Feed Rate, lb/MMBtu	8.69	7.29	4.67	18.60	8.85	0.88	1.23	1.28	0.49	0.87
Sulfur, %	0.10	0.04	0.87	0.22	0.22	0.01	0.02	0.03	0.01	0.01
Sulfur, lb/MMBtu	0.14	0.07	1.07	0.35	0.35	0.02	0.04	0.04	0.01	0.01
Nitrogen, %	0.46	0.35	4.40	0.88	0.67	0.08	0.06	0.11	0.07	0.06
Nitrogen, lb/MMBtu	0.70	0.61	5.42	1.42	1.08	0.14	0.11	0.16	0.12	0.07
Chlorine, mg/kg	694	47	1282	19	1601	22	10	36	339	36
Chlorine, lb/MMBtu	0.1055	0.0081	0.1579	0.0030	0.2581	0.0037	0.0019	0.0050	0.0571	0.0045
Mercury, mg/kg	0.0075	0.0042	<0.005	<0.005	0.0066	<0.005	<0.005	<0.005	<0.005	<0.005
Mercury lb/TBtu	7.5071	4.1888	<5	<5	6.5649	<5	<5	<5	<5	<5
Phosphorous, mg/kg	824	402	8062	488	685	89	200	388	166	21
Phosphorous, lb/MMBtu	0.1252	0.0695	0.9931	0.0791	0.1104	0.0151	0.0384	0.0549	0.0280	0.0026
Potassium, mg/kg	6523	4538	10562	2755	21056	603	1619	2079	824	531
Potassium, lb/MMBtu	0.9908	0.7832	1.3011	0.4462	3.3944	0.1018	0.3108	0.2938	0.1390	0.0660
Sodium, mg/kg	35	210	684	828	187	46	10	5	52	294
Sodium, lb/MMBtu	0.0053	0.0363	0.0843	0.1342	0.0302	0.0078	0.0018	0.0008	0.0087	0.0365

4.4.1.2 Fuel Sulfur and Nitrogen Contents

The fuel sulfur is converted almost completely during combustion to sulfur oxides, primarily SO_2. NO_x emissions are highly dependent on plant operating conditions as well as on the amount of nitrogen in the fuel. Approximately half of the total NO_x derives from fuel nitrogen and the other half from thermally generated NO_x. The sulfur- and nitrogen-oxides emission values in Table 13 assume that no control device is present. The woody fuels have very low sulfur contents and, thus, potential SO_2 emissions. The grassy biomasses are somewhat higher. The sulfur content of the dried distillers grains is especially high. The nitrogen concentrations in the biomass fuels follow a similar trend, with the woods being very low and the grassy biomass higher. The dried distillers grains have a very high nitrogen content.

4.4.1.3 Fuel Mercury and Chlorine Contents

Both mercury and chlorine are volatilized during combustion. Mercury is released as elemental mercury at combustion temperatures, and chlorides are converted primarily to gaseous HCl. The calculated mercury and chlorine emission values do not account for the possibility of adsorption on fly ash or removal by a pollution control device.

The mercury concentrations are expressed in pounds of mercury/trillion Btu (lb/TBtu). The woody biomass generally has a low chlorine level, with the eucalyptus being the exception. The dried distillers grains, switchgrass, and wheat straw also have high chlorine contents. Mercury contents are below detection limits for the wood fuels and are very low for the other biomass fuels.

4.4.1.4 Fuel Phosphorous, Potassium, and Sodium Contents

Phosphorous generally produces very fine particles during combustion. Phosphate compounds may vaporize in the combustion flame and then condense in cooler regions of the furnace system homogeneously as single submicron particles or heterogeneously as a coating on existing small particles. Significant amounts of both potassium and sodium are volatilized during combustion and subsequently condense as sulfates, carbonates, or chlorides in the lower temperature regions of a boiler. They have potential for producing low temperature deposition, and the fine phosphorous particles can cause "blinding" of baghouses. The woody biomass fuels have significantly less of these elements than the fuels derived from herbaceous biomass. The dried distillers grains have the highest phosphorous concentration, along with high potassium and sodium. This fuel is expected to cause the most severe low-temperature deposition. The wheat straw has the highest potassium concentration and the sugar beet pulp the highest sodium level. Potassium concentrations in the switchgrass and corn stover fuels are also high. In general, the wood biomass fuels are expected to present fewer problems during combustion.

4.4.2   Equilibrium Thermodynamic Modeling and Viscosity Calculations

4.4.2.1   Results of Thermodynamic Calculations of Viscosity and Liquid Phases

The predicted viscosities and liquid slag concentrations are summarized in Figures 1 and 2 for the biomass fuels. A relatively low viscosity slag containing a high liquid concentration is indicative of a large amount of freely flowing slag that can promote severe ash deposition. A higher slag viscosity with a lower liquid slag concentration is indicative of a smaller amount of nonflowing slag, which usually results in lower ash deposition propensity.

There is, of course, some subjectivity involved in interpreting viscosity graphs but general trends can often be discerned which generally follow what is observed in the boiler. Some of the subjectivity is related to when ash particles begin to form and interact after leaving the combustion flame. When a very low viscosity is observed at a low temperature, as is the case in a relative scenario for the waste wood pellets, the wheat straw, and eucalyptus (Figure 1), this can be indicative of fly ash particles with low-melting-point material, which can remain molten far into the back pass region of boiler. This is not a good scenario for a boiler. The molten ash will more readily stick to furnace heat-transfer tubes in the cooler regions of the boiler forming fouling deposits. However, the amount of low-melting-point material is very low, then fouling may not be as severe as expected, since there isn't sufficient material to coat impacting ash grains and cause them to stick and form heat-transfer-impeding ash deposits. These arguments are used for the rest of ash deposit severity interpretation.
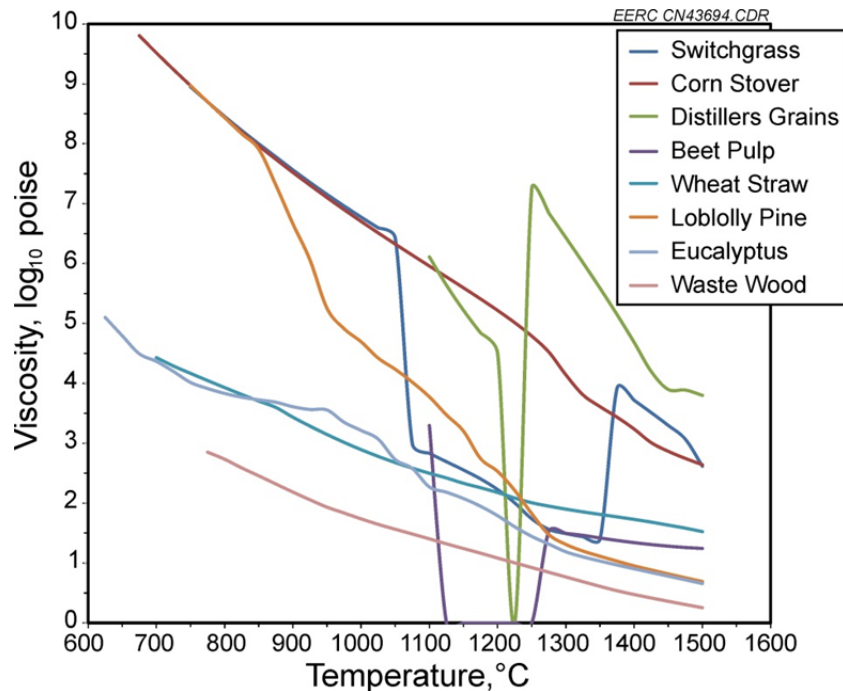
Figure 1. Predicted viscosity for biomass fuels.
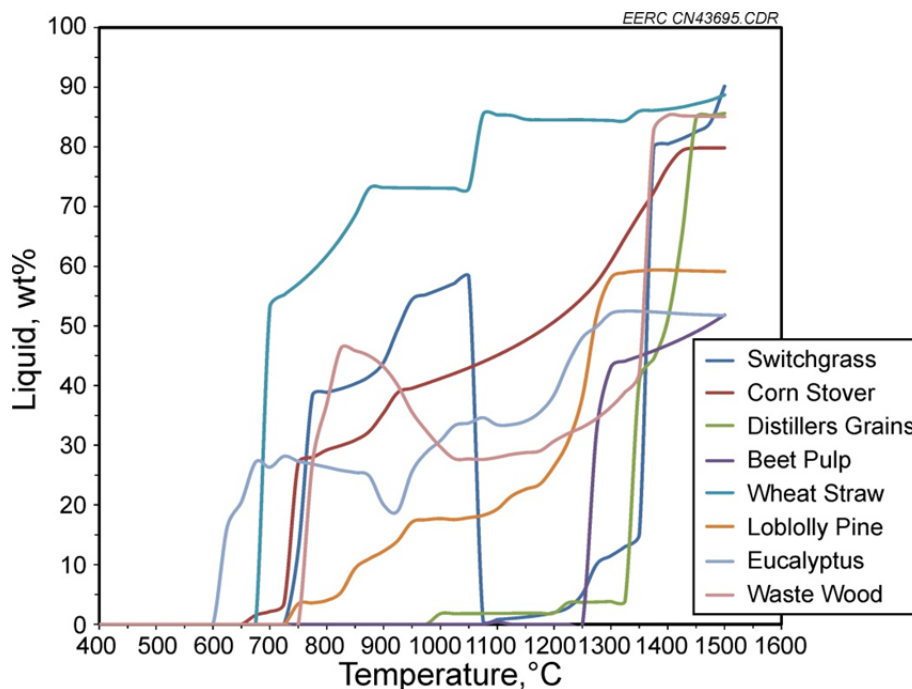
Figure 2. Predicted liquid slag concentrations for biomass fuels.

The corn stover and dried distillers grains have relatively high viscosities of 6.0–5.2 and 6.1–4.5 $\log_{10}$ poise in the normal furnace exit gas temperature (FEGT) range of 2000°–2200°F (1093° to 1204°C). They also have moderate to small amounts of liquid slag (44% and 2%). These fuels should exhibit little or no silicate-based high-temperature fouling. It is noted that the temperature corresponding to the maximum viscosity of 250 poise is the temperature at which slag begins to flow, called the T250 or T_{250} temperature. The waste wood pellets, wheat straw, eucalyptus, and beet pulp may exhibit problematic fouling, since they show a very low viscosity along with high or moderate amounts of liquid slag material commencing at approximately 1400°F (800°C). Specifically, the eucalyptus and the waste wood pellets melts are at the T250 temperature at approximately 1975°F (1079°C) and 1575°F (857°C), respectively, indicative of potentially bad fouling or slagging. The switchgrass may also exhibit silicate-based fouling in the FEGT range, because of its moderate viscosity value and high amount of liquid phase in the critical temperature ranges from burner to back pass. The cottonwood and aspen were not calculated to have any liquid silicate phases, probably because of the small amount of ash and the volatility of potassium which composes a significant portion of their ashes.

The science of looking at relative viscosity curves is especially useful if the particular boiler has experience with some of the fuels. If waste wood typically does not develop ash deposits in the boiler, the viscosity curves agree with that observation; then predicted viscosity plots can be used to plan for different biomass types that might be fired in the boiler. As a disclaimer, viscosity curves should not be the sole source of evaluation. The viscosity analysis should also bear witness to some degree to the ash amounts and ash contents of the biomass fuels. Wheat straw and beet pulp, for example, had the highest ash contents and fairly high levels of alkali, such as potassium and sodium (Table 7), which act as fluxing agents in higher-

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temperature silicate melts. These biomass types also showed the lowest predicted viscosity levels over all temperature ranges; so there is some agreement and validation between composition and viscosity data.

4.4.2.2   *Comparison of Calculated Viscosity and Ash Fusion Temperatures*

Compared in Table 14 are empirical ash fusion temperatures (initial, softening, hemispherical, and fluid) and predicted T_{250}s based on the bulk ash composition and the liquid slag composition predicted by FactSage. Ash fusion temperatures are used as indicators of the fouling and slagging propensity of a fuel ash.

The T_{250}s based on the bulk ash analyses are, with the exception of the wheat straw, well outside the range of the ash fusion temperatures. The T_{250}s based on the viscosities of the liquid slags predicted by FactSage compare more favorably to the ash fusion temperatures for several of the fuels. However, the FactSage calculations severely overpredict temperatures for the formation of liquids from the corn stover and dried distillers grains fuels. Conversely, FactSage calculations for the eucalyptus and waste wood pellets severely underpredict liquid formation temperatures.

4.4.2.3   *Results of Thermodynamic Calculations of Chlorine, Potassium, and Sodium*

The predicted percentages of gaseous chlorine, potassium, and sodium as a function of temperature are presented in Figures 3, 4, and 5, respectively. Condensation, characterized by a decline in gaseous elemental percentage, occurs over a wide range of temperature. As indicated in Figure 3, gaseous chlorine begins to decrease over a temperature range of 932°–1337°F

Table 14. Comparison of Ash Fusion Temperatures with Predicted T_{250} Temperatures

|	Empirical				Calculated	
	Initial Temp., °F	Softening Temp., °F	Hemispherical Temp., °F	Fluid Temp., °F	Bulk Ash T_{250}	Liquid Slag T_{250}
Switchgrass	2015	2184	2328	2485	2547	2149
Corn Stover	2147	2222	2284	2403	2717	>2732
Dried Distillers Grains	1336	1370	1434	1616	<932	>2732
Sugar Beet Pulp	2236	2251	2266	2313	2655	2327
Wheat Straw	1610	1698	1953	2268	1726	2068
Loblolly Pine	2209	2218	2226	2238	2054	2211
Cottonwood	>2800	>2800	>2800	>2800	1062	>2732
Aspen	>2800	>2800	>2800	>2800	<932	>2732
Eucalyptus	>2800	>2800	>2800	>2800	1440	1993
Waste Wood Pellets	2341	2378	2404	2452	1576	1581
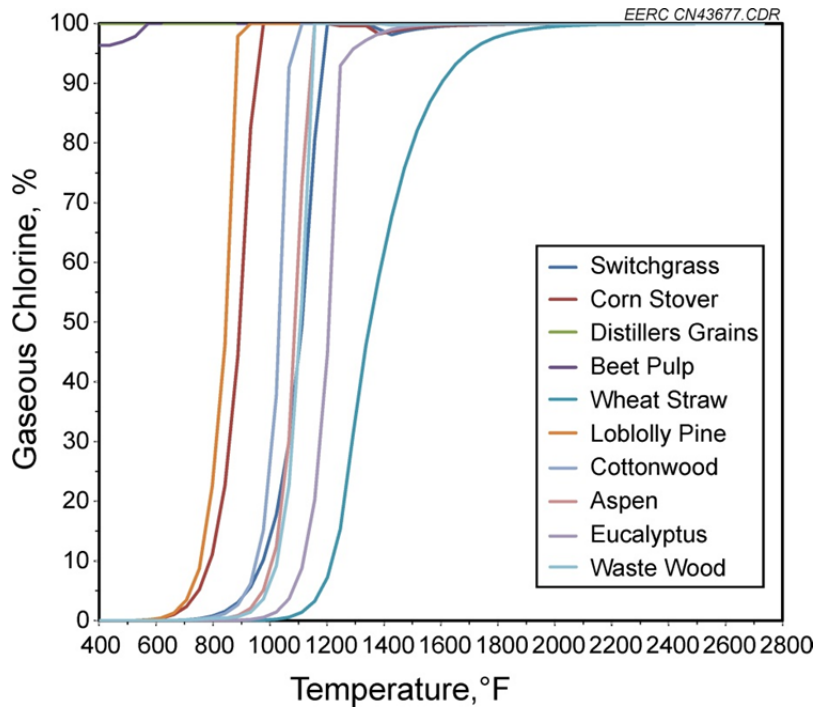
Figure 3. Percentage of gaseous chlorine versus temperature.
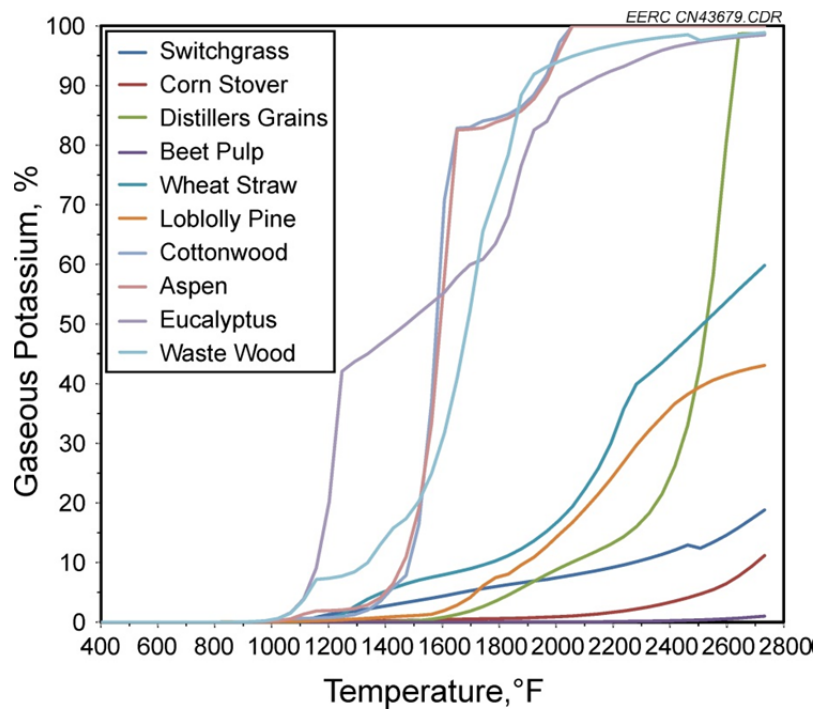

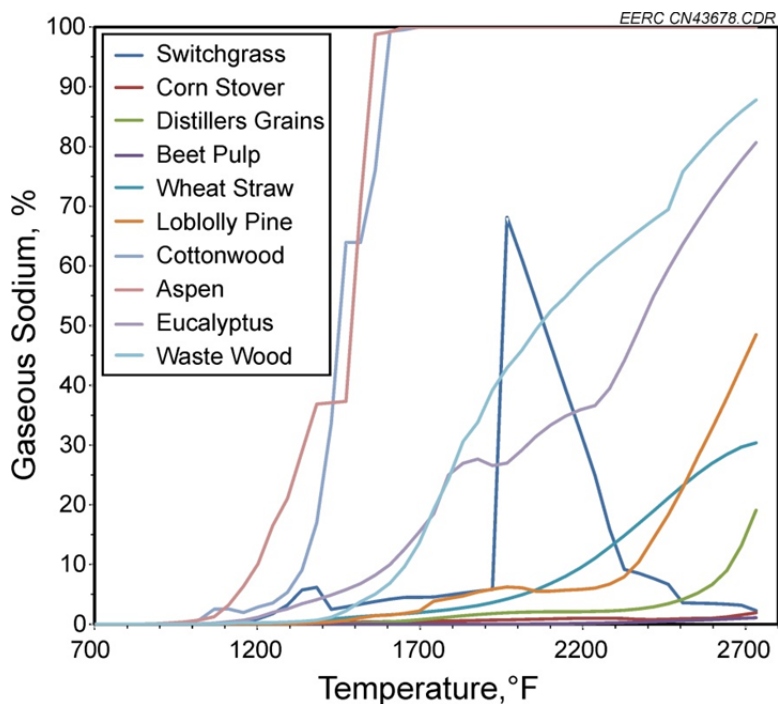Figure 4. Percentage of gaseous potassium versus temperature.

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Figure 5. Percentage of gaseous sodium versus temperature.

(500°–725°C). Wheat straw is the exception, with condensation beginning at a much higher temperature of approximately 1900°F (1038°C). The temperature at which condensation begins is approximately related to the amount of chlorine in the biomass fuels; the higher the chlorine concentration, the higher the condensation temperature. Wheat straw has the highest chlorine and potassium concentrations of all the biomass types analyzed (Table 7). The presence of higher alkali (sodium and potassium) concentrations may also increase the chlorine condensation temperature.

As indicated in Figure 4, the condensation characteristics of potassium in the biomass fuels fall into two general groups. Eucalyptus, aspen, cottonwood, and waste wood potassium condenses at lower temperatures than the herbaceous fuels and loblolly pine. The condensation temperature is approximately related to the concentration of potassium in the fuels.

Sodium also has two general groups of condensation temperatures. Sodium in the cottonwood and aspen fuels are predicted to condense at lower temperatures than the other fuels. The spike in gaseous sodium percentage for the switchgrass is an artifact of the thermodynamic calculation and is probably not representative of the actual characteristics of sodium condensation.

4.4.2.4   Results of Thermodynamic Calculations of Trace Elements

The predicted percentages of various gaseous trace elements are plotted as a function of temperature in Figures 6–19. The following discussion examines the condensation temperature, where the gaseous percentage begins to decline.
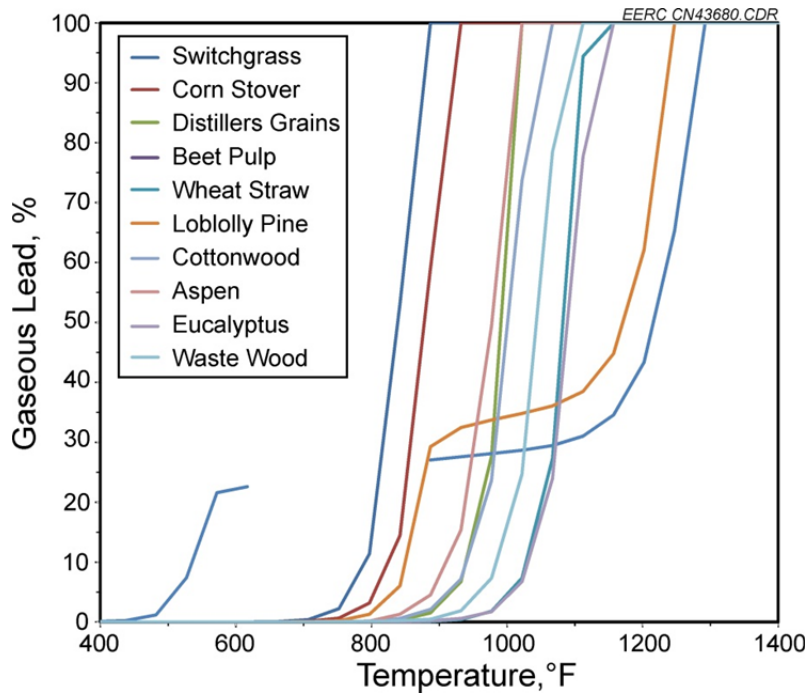
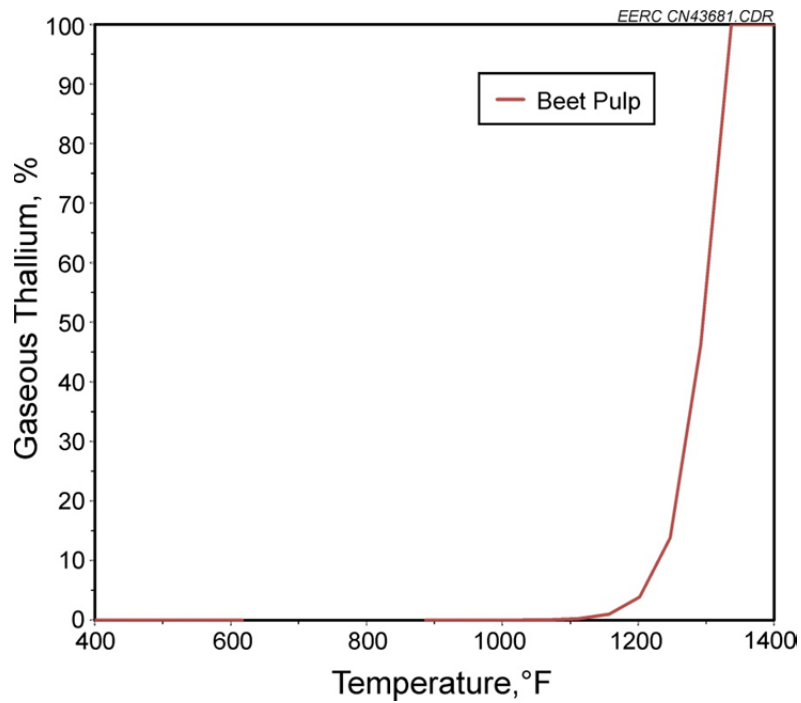Figure 6. Percentage of gaseous lead versus temperature.

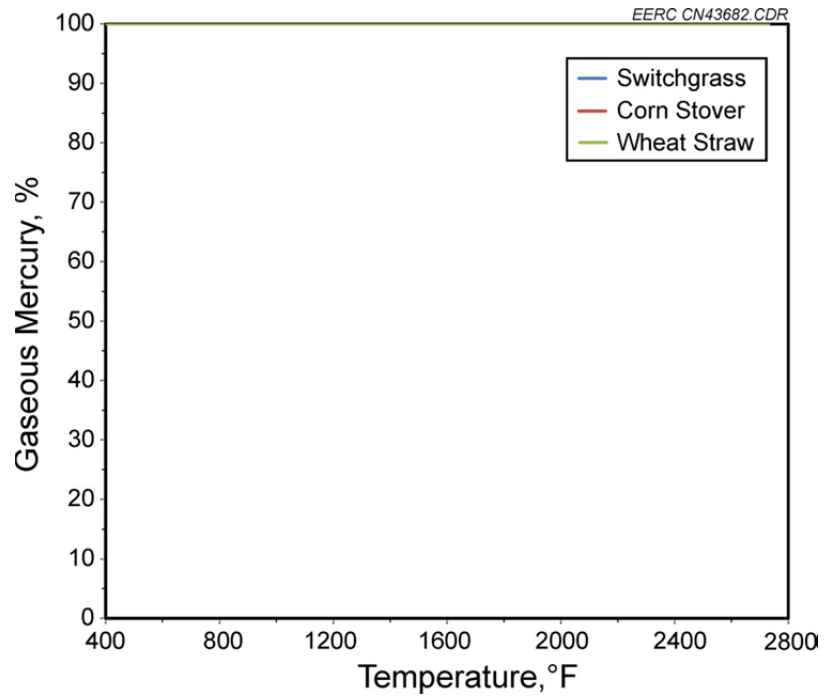Figure 7. Percentage of gaseous thallium versus temperature.

Figure 8. Percentage of gaseous mercury versus temperature.
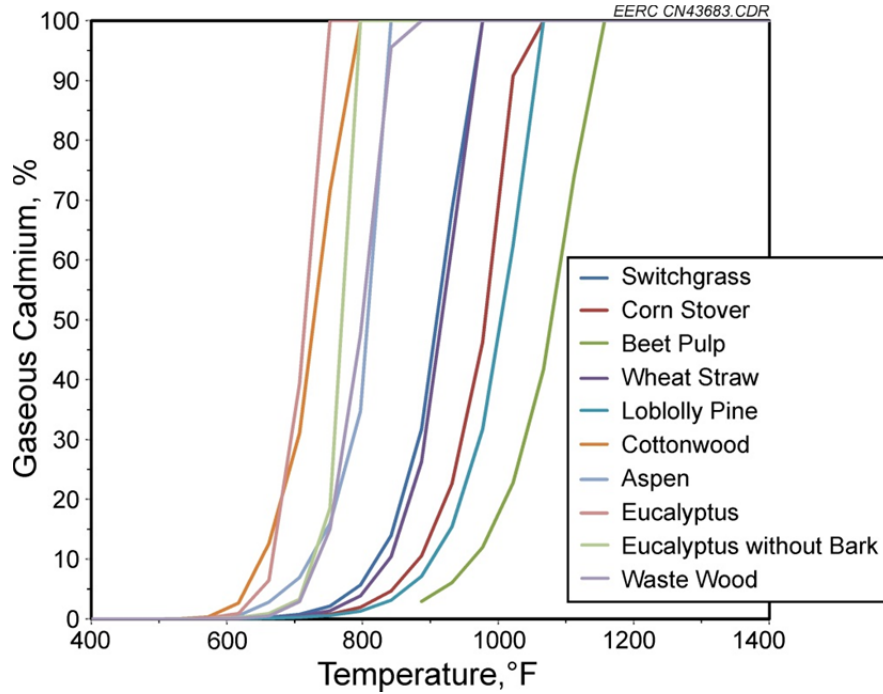

Figure 9. Percentage of gaseous cadmium versus temperature.
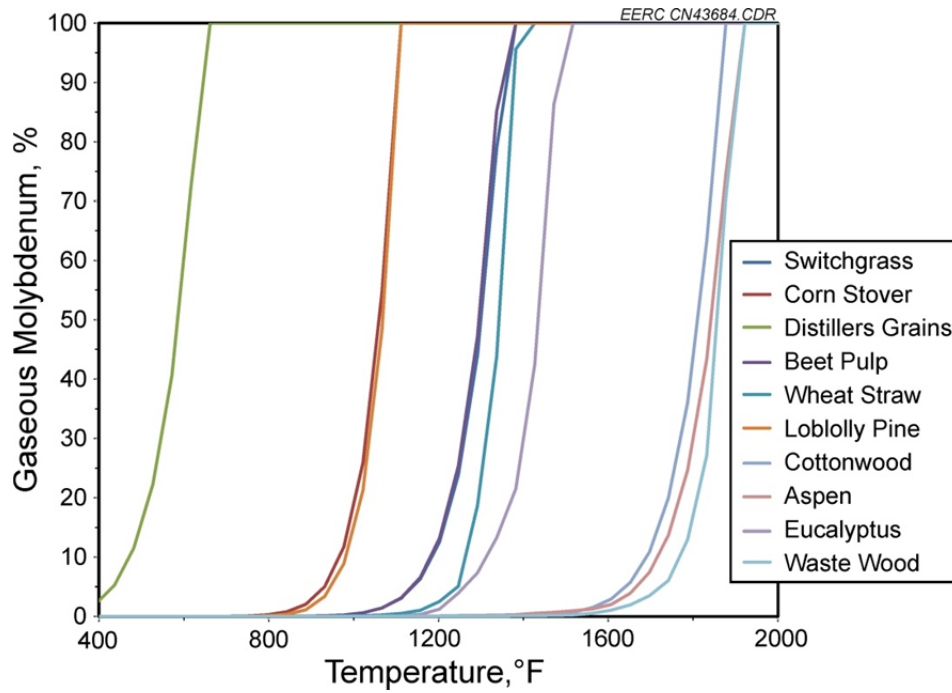
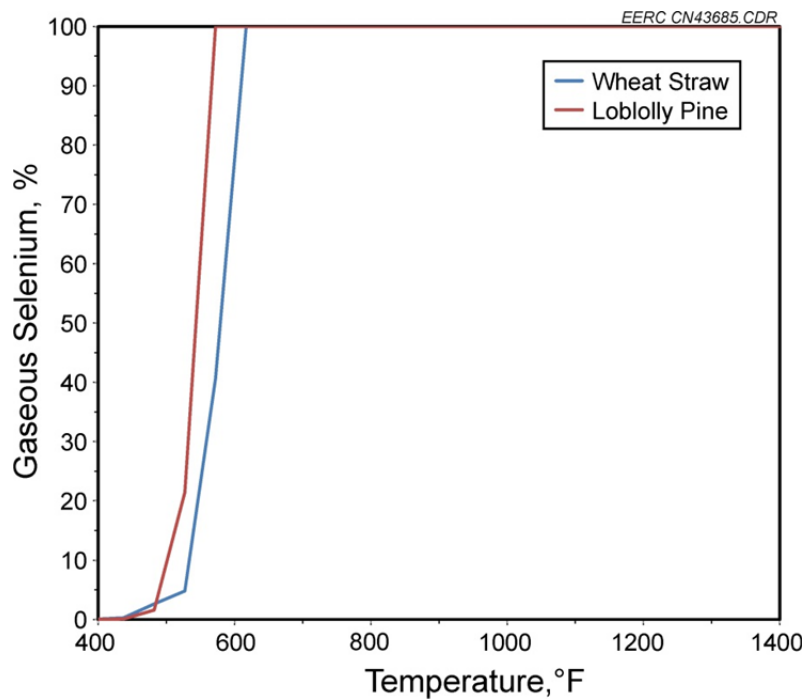Figure 10. Percentage of gaseous molybdenum versus temperature.

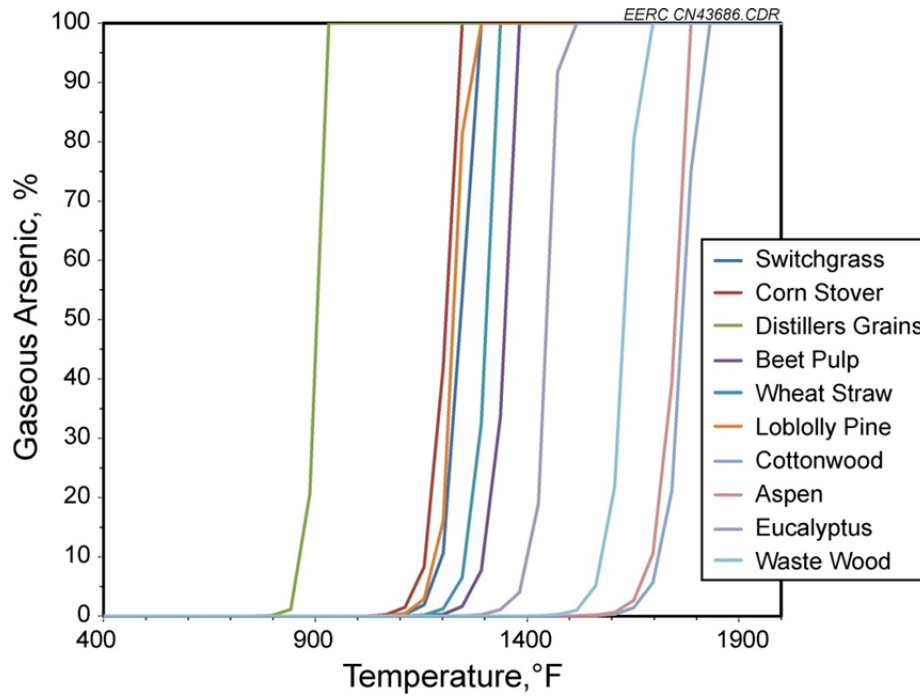Figure 11. Percentage of gaseous selenium versus temperature.

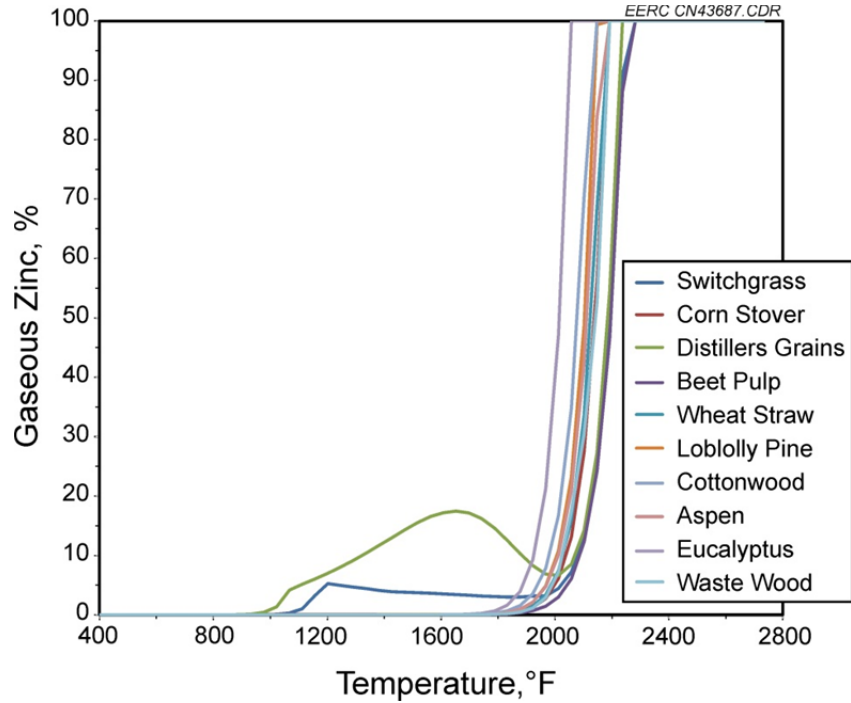Figure 12. Percentage of gaseous arsenic versus temperature.

Figure 13. Percentage of gaseous zinc versus temperature.
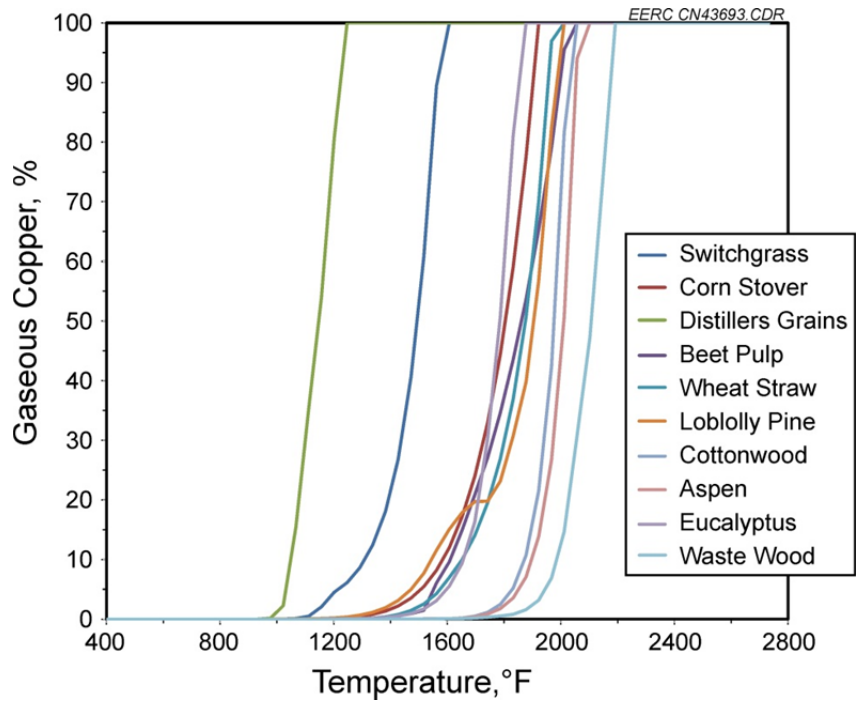
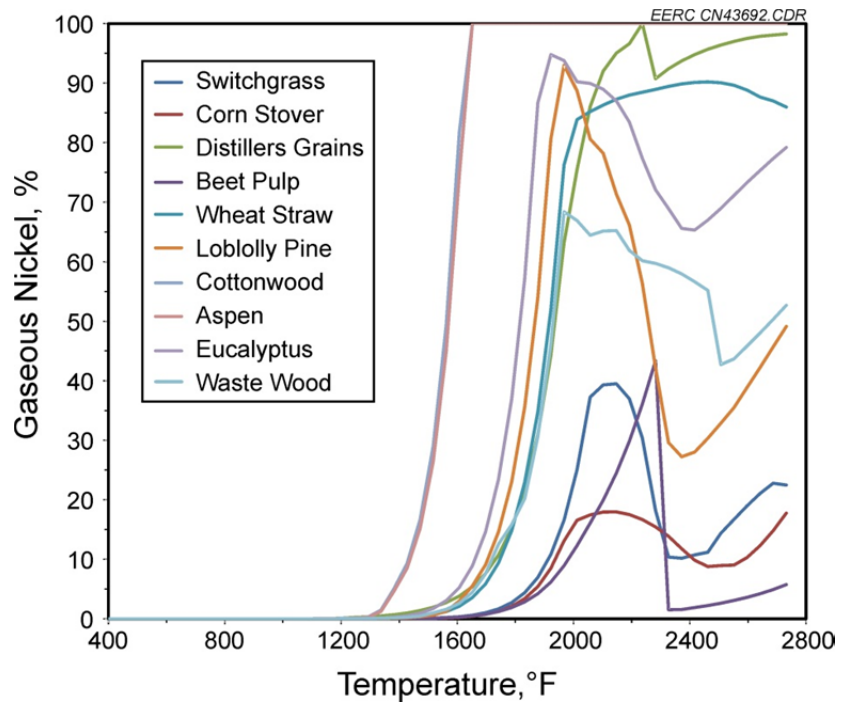Figure 14. Percentage of gaseous copper versus temperature.

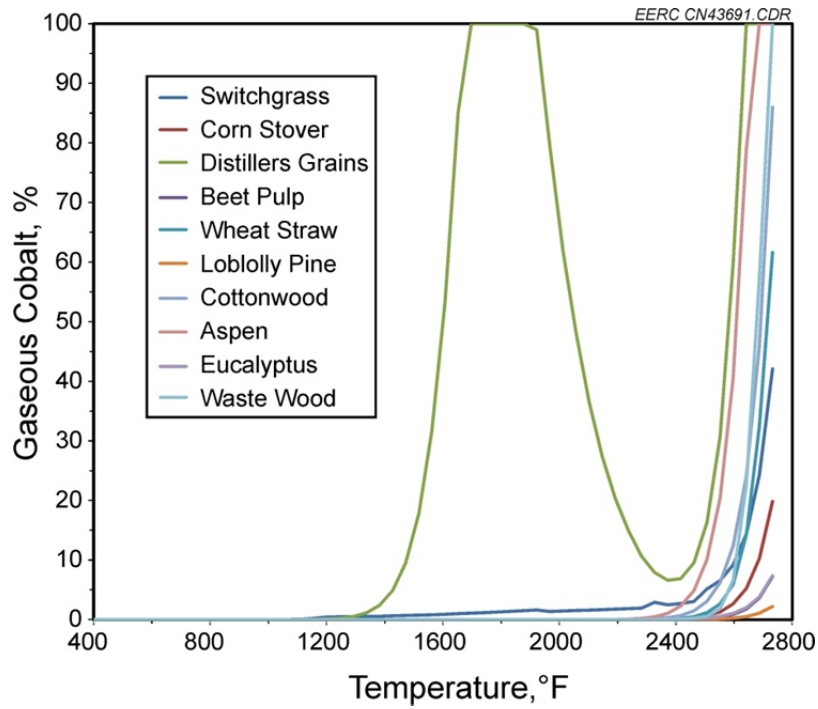Figure 15. Percentage of gaseous nickel versus temperature.

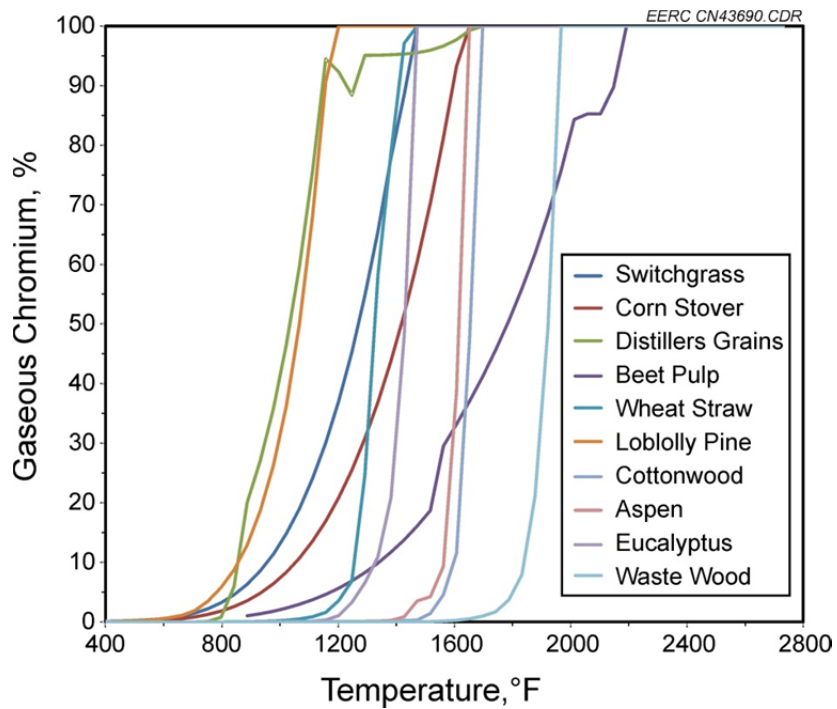Figure 16. Percentage of gaseous cobalt versus temperature.

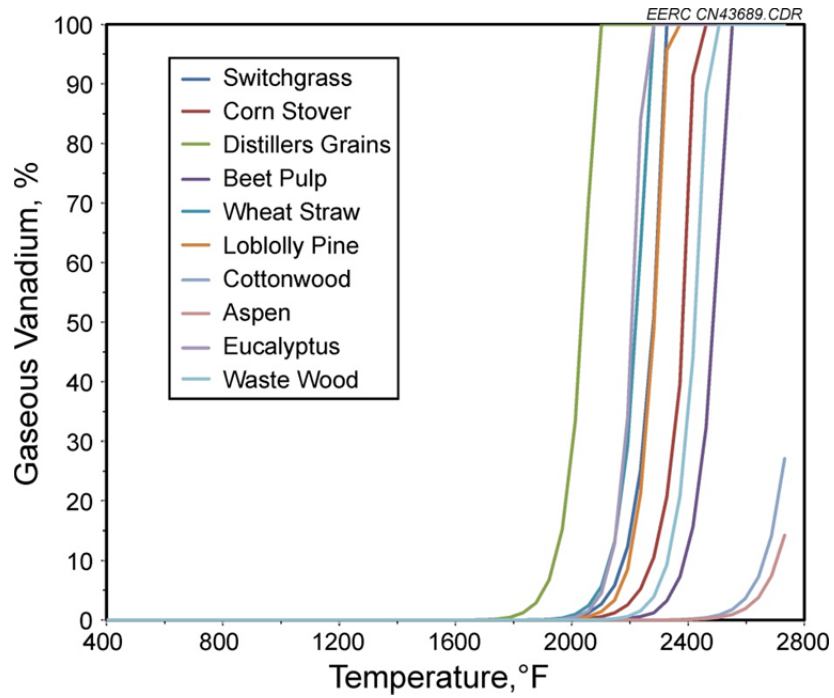Figure 17. Percentage of gaseous chromium versus temperature.

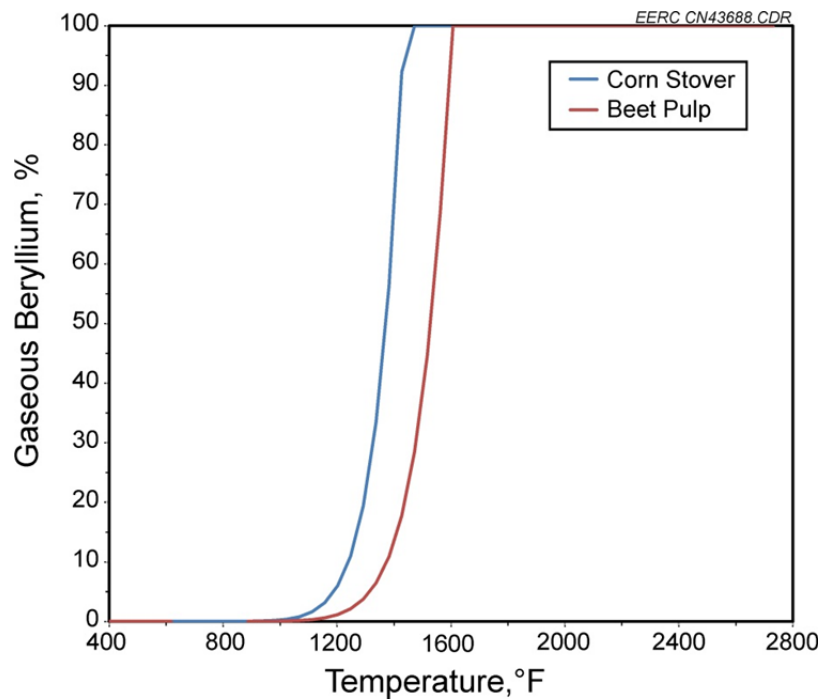Figure 18. Percentage of gaseous vanadium versus temperature.

Figure 19. Percentage of gaseous beryllium versus temperature.

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4.4.2.4.1 Lead

As indicated in Figure 6, lead is predicted to be completely gaseous at ≥1300°F (704°C). The biomass fuel lead condenses over a relatively narrow range from 1292°F (700°C) for the beet pulp to 887°F (475°C) for the switchgrass.

4.4.2.4.2 Thallium

The beet pulp is the only biomass fuel with a detectable thallium concentration. According to Figure 7, thallium begins to condense at 1337°F (725°C).

4.4.2.4.3 Mercury

Only the switchgrass, corn stover, and wheat straw had detectable mercury concentrations. The mercury remains gaseous over the temperature range modeled (Figure 8) primarily as $HgCl_2$, with a small amount of HgO. Both species are soluble and should be removed by wet scrubbing of the flue gas.

4.4.2.4.4 Antimony and Tin

Antimony and tin were below analytical detection limits in the biomass samples.

4.4.2.4.5 Cadmium

No detectable cadmium was found in the dried distillers grains. As indicated in Figure 9, cadmium was predicted to condense from 752°F (400°C) for wheat straw to 1067°F (575°C) for the corn stover and loblolly pine.

4.4.2.4.6 Molybdenum

Molybdenum in the biomass fuels displays three general groups of condensation temperatures in Figure 10. Molybdenum in the cottonwood, aspen, eucalyptus, and waste wood condense from 1872°F (1022°C) to 1922°F (1050°C). In a second group of switchgrass, beet pulp, wheat straw, and eucalyptus, molybdenum condenses from 1382°F (750°C) to 1517°F (825°C). Molybdenum in the corn stover and loblolly pine are predicted to condense at 1112°F (600°C). The dried distillers grains are anomalous, showing a very low molybdenum condensation temperature of 662°F (350°C). The condensation temperatures do not seem to be related to molybdenum concentration and are probably related to the interaction of molybdenum with the other elements present in the fuels.

4.4.2.4.7 Selenium

Only the wheat straw and loblolly pine contained detectable concentrations of selenium. As indicated in Figure 11, selenium is predicted to condense at 616°F (324°C) and 572°F (300°C) from the wheat straw and loblolly pine combustion flue gases, respectively.

4.4.2.4.8 Arsenic

As shown in Figure 12, condensation temperatures for arsenic range from 1787°F (975°C) to 1832°F (1000°C) for the cottonwood, eucalyptus, and aspen fuels, with the waste wood somewhat lower at 1697°F (925°C). Arsenic is predicted to condense from the dried distillers grains combustion flue gas at 932°F (500°C). Arsenic condensation temperatures for the other fuel flue gases cluster in a range from 1247°F (675°C) to 1382°F (750°C).

4.4.2.4.9 Zinc

Zinc (Figure 13) is predicted to condense from most of the biomass fuel combustion flue gases from 2012°F (1100°C) to 2282°F (1250°C). All of the fuels show a generally similar trend of condensation. The anomalous zinc condensation behavior of the switchgrass and dried distillers grains at low temperatures is probably an artifact of the thermodynamic calculations.

4.4.2.4.10 Copper

As shown in Figure 14, the copper condensation temperature is predicted to be highest for the waste wood fuel at 2192°F (1200°C), There are three low copper condensation temperature outliers, dried distillers grains at 1247°F (675°C), switchgrass at 1607°F (875°C), and eucalyptus at 1877°F (1025°C). The other biomass fuels have predicted copper condensation temperatures in the range of 1877°F (1025°C) to 2102°F (1150°C). The temperatures seem to be unrelated to copper concentration.

4.4.2.4.11 Nickel

The predicted nickel condensation temperatures (Figure 15) for aspen, cottonwood, and eucalyptus are lower than for the other fuels at 1652°F (900°C) to 1787°F (975°C). Nickel condensation temperatures for the other biomass fuels range from 1922°F (1050°C) to 2012°F (1100°C).

4.4.2.4.12 Cobalt

As indicated in Figure 16, cobalt is very refractory in the biomass fuels. Effectively, no cobalt remains gaseous at <2327°F (<1275°C). The plot for the dried distillers grains is anomalous, a result of the thermodynamic calculations.

4.4.2.4.13 Manganese

Similar to cobalt, manganese is refractory in the biomass fuels. Although not plotted, gaseous manganese is lacking at <2732°F (<1500°C), the maximum temperature considered in the calculations.

4.4.2.4.14 Chromium

The predicted condensation temperatures for chromium in the biomass fuels (Figure 17) spans a broad range, from 1202°F (650°C) to 2192°F (1200°C), with no definite pattern. The condensation temperatures seem to be unrelated to chromium concentration.

4.4.2.4.15 Vanadium

Vanadium in the aspen, cottonwood, and eucalyptus fuels is predicted to condense, as shown in Figure 18, at >2732°F (1500°C). Vanadium in the dried distillers grains is predicted to condense at 2102°F (1150°C). Vanadium condensation temperatures for the other fuels cluster from 2282°F (1250°C) to 2507°F (1375°C). The vanadium condensation temperatures seem to be unrelated to concentration.

4.4.2.4.16 Beryllium

Only the corn stover and the beet pulp fuels contained beryllium above the analytical detection limit. In Figure 19, beryllium condenses from the corn stover and beet pulp combustion flue gases at 1472°F (800°C) and 1607°F (875°C), respectively.

4.5 Task 5 – Progress Update on the Development of Biomass Standard Reference Materials

Although the efforts of this project didn't coincide with the SRM development efforts at NIST to result in the current availability of biomass certified reference materials, work has now begun at NIST, and biomass reference materials will be available in the near future. NIST is in the process of acquiring large quantities (>100 kg) of at least two different biomass materials, one of which will be a woody biomass. The EERC and others in the biomass industry have provided NIST with valid justification for this development and will continue to follow its progress. EERC researchers will also remain involved in biomass standards development through continued membership in biomass committees.

5.0 SUMMARY

More than 50 analytical methods for biomass materials were collected and reviewed for this project. The methods were obtained from ISO, CEN, ASTM, and ASABE. The final selection was narrowed down to 16 methods for the analysis of the following parameters that are typically associated with fuel quality for combustion systems: 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, selenium, etc.), ash fusibility, and bulk density.

The CEN methods were specifically written for biomass fuels, while most of the ISO and ASTM methods were written for other fuels, such as coal, coke, and refuse-derived fuel.

However, ISO currently has a committee, ISO/TC 238, Solid Biofuels, with six working groups that are reviewing the CEN standards and will adopt many of these standards for publication as ISO standards. The US Technical Advisory Group for ISO/TC 238 is ASABE.

To help evaluate the applicability of these standard test methods to various biomass materials, a total of ten different biomass samples were collected for this project. They included switchgrass, corn stover, wheat straw, dried distillers grains, beet pulp, aspen, cottonwood, eucalyptus, loblolly pine, and waste wood pellets. The intent was to select candidates that are predominantly being used or have the potential to be used in the United States as feedstocks for energy production. The other consideration 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.

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 the materials analyzed, which makes these materials an attractive energy source to help reduce overall HAP emissions.

A small interlaboratory comparison was done with the analysis of five of the ten project samples and one SRM. The results compared well, with the exception of the corn stover sample. The agreement between the laboratories for the NJV 94-5 was very good, as well as the recoveries calculated for both labs. It was suspected that there was more heterogeneity in the project samples than in the SRM, which led to the difference in the results.

The project results were used to help evaluate plant performance of the biomass fuels. The dried distillers grains and waste wood pellets have the highest heating values, slightly greater than 8000 Btu/lb, whereas the cottonwood and eucalyptus have the lowest heating values ($\approx$5100 Btu/lb). The wood fuels have very low ash contents (<1.0 wt%) and the grassy biomass ash contents are significantly higher (4–11 wt%).

The woody biomass fuels have very low sulfur and nitrogen contents and thus potential SO_2 and NO_x emissions ($\leq$0.04 lb/MMBtu and $\leq$0.17 lb/MMBtu, respectively). The grassy biomass fuels contain higher sulfur and nitrogen contents. The sulfur and nitrogen contents of the dried distillers grains are especially high.

The woody biomass fuels generally have low chlorine concentrations (<40 mg/kg), with the eucalyptus being the exception. The dried distillers grains, switchgrass, and wheat straw have the highest chlorine contents (>600 mg/kg). Mercury contents are below detection limits for the wood fuels and are very low ($\leq$0.0075 mg/kg) for the other biomass fuels.

Phosphorous, potassium, and sodium generally participate in low-temperature ash deposition mechanisms in the primary superheater, economizer, and pollution control device regions of a boiler. The woody biomass fuels have significantly less phosphorous, potassium, and sodium contents than the fuels derived from herbaceous biomass. The dried distillers grains

are expected to cause the most severe low-temperature ash deposition problem because they have the highest total concentrations of phosphorous, potassium, and sodium. The wheat straw has the highest potassium concentration and the sugar beet pulp the highest sodium level. Potassium concentrations in the switchgrass and corn stover fuels are also high. In general, the woody biomass fuels are expected to present the lowest propensity for low-temperature fouling.

The corn stover and dried distillers grains fuels are predicted to cause little or no silicate-based high-temperature fouling. The beet pulp, switchgrass, eucalyptus, and waste wood pellet fuels may cause problematic silicate-based fouling based on liquid concentration and viscosity predictions. The cottonwood and aspen are expected to pose no silicate-based fouling, because they lack liquid silicate phases.

Predicted $T_{250}s$, based on bulk ash compositions, did not compare favorably with measured ash fusion temperatures for the biomass fuels. T_{250} predictions based on the FactSage calculated slag compositions were better but still resulted in significant differences from the experimental ash fusion temperatures. It is believed this is due to the volatilization of significant amounts of potassium and sodium from the ash on heating at 815°C, which alters the ash chemistry and melting point.

The condensation of chlorine, potassium, and sodium species is predicted to occur over a wide temperature range. This range is generally below FEGT conditions. Condensation is partially controlled by concentration, with condensation occurring at higher temperatures for higher elemental concentrations. Condensation may also be partially controlled by the presence of other ash components.

With the exception of mercury, all of the trace elements with detectable concentrations were predicted to condense at temperatures of >400°F (>204°C), well above the temperature of flue gas exiting particulate control devices. Depending on the particle size, these trace elements should be removed by particulate control devices. Although gaseous, mercury is predicted to be in the form of chloride and oxide, which would be captured by a wet scrubber.

For the trace elements calculated to exhibit condensation, there is a wide range of condensation temperatures for the individual biomass fuels. This temperature range is probably not representative of trace element condensation but rather interactions with the other elements present in the ash and flue gas. The calculations indicate that there can be a wide variation in the temperature and location at which a particular trace element will condense in a combustion system.

Although the efforts of this project didn't coincide with the SRM development efforts at NIST to result in the current availability of biomass certified reference materials, work has now begun at NIST, and biomass reference materials will be available in the near future. The EERC and others in the biomass industry have provided NIST with valid justification for this development and will continue to follow its progress. EERC researchers will also remain involved in biomass standards development through continued membership in biomass committees.

6.0 REFERENCES

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