PENNSTATE

Feasibility Analysis for Installing a Circulating Fluidized Bed Boiler for Cofiring Multiple Biofuels and Other Wastes with Coal at Penn State University

Fifth Quarterly Technical Progress Report for the Period 06/15/2001 to 09/14/2001

By

Bruce G. Miller and Sharon Falcone Miller
The Energy Institute;

Robert Cooper, Douglas Donovan, John Gaudlip,
Matthew Lapinsky, and William Serencsits
Office of Physical Plant; and

Neil Raskin and Dale Lamke
Foster Wheeler Energy Services, Inc.

October 12, 2001

Work Performed Under Grant No. DE-FG26-00NT40809

For
U.S. Department of Energy
National Energy Technology Laboratory
P.O. Box 10940
Pittsburgh, Pennsylvania 15236

By
The Energy Institute
The Pennsylvania State University
C211 Coal Utilization Laboratory
University Park, Pennsylvania 16802

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DISCLAIMER

EXECUTIVE SUMMARY

The Pennsylvania State University, under contract to the U.S. Department of Energy, National Energy Technology Laboratory is performing a feasibility analysis on installing a state-of-the-art circulating fluidized bed boiler and ceramic filter emission control device at Penn State's University Park campus for cofiring multiple biofuels and other wastes with coal, and developing a test program to evaluate cofiring multiple biofuels and coal-based feedstocks.

The objective of the project is being accomplished using a team that includes personnel from Penn State's Energy Institute, Office of Physical Plant, and College of Agricultural Sciences; Foster Wheeler Energy Services, Inc.; Parsons Energy and Chemicals Group, Inc.; and Cofiring Alternatives.

During this reporting period, work focused on performing the design of the conceptual fluidized bed system, determining the system economics, and preparing a preliminary test plan and budget. In addition, a manuscript was prepared for the 5th Biomass Conference of the Americas.

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1.0 Introduction

The Pennsylvania State University, under contract to the U.S. Department of Energy (DOE), National Energy Technology Laboratory (NETL) is performing a feasibility analysis on installing a state-of-the-art circulating fluidized bed (CFB) boiler and ceramic filter emission control device at Penn State's University Park campus for cofiring multiple biofuels and other wastes with coal, and developing a test program to evaluate cofiring multiple biofuels and coal-based feedstocks. Penn State currently operates an aging stoker-fired steam plant at its University Park campus and has spent considerable resources over the last ten to fifteen years investigating boiler replacements and performing life extension studies. This effort, in combination with a variety of agricultural and other wastes generated at the agricultural-based university and the surrounding rural community, has led Penn State to assemble a team of fluidized bed and cofiring experts to assess the feasibility of installing a CFB boiler for cofiring biomass and other wastes along with coal-based fuels.

The objective of the project is being accomplished using a team that includes personnel from Penn State's Energy Institute, Office of Physical Plant, and College of Agricultural Sciences; Foster Wheeler Energy Services, Inc.; Parsons Energy and Chemicals Group, Inc.; and Cofiring Alternatives.

The CFB boiler system that is being considered in the feasibility analysis is unique in that it:

1) is of compact versus traditional design;
2) includes modules to evaluate ceramic filters, along with fabric filters, for particulate matter control (recent work at Penn State has shown that ceramic filters have potential advantages regarding fine particulate matter and trace elements, i.e., mercury removal);
3) contains an advanced instrumentation package including temperature and pressure sensors, deposition and slagging probes, heat flux meters, and corrosion/erosion panels;
4) contains multi-fuel capabilities (making it a versatile test site for industry and government studies); and
5) is a commercial facility in a rural, agricultural setting that contains an engineering and agricultural-based university.

The state-of-the-art CFB boiler and ceramic filter device allows the University the opportunity to do the following:

- to more economically supply heat to the University Park Campus;
- to reduce the amount of airborne pollutants (i.e., NO_x, SO_2, particulate matter, and potentially trace elements), thus helping to reduce the overall emissions from the University's central heating plant;
- to reduce the amount of agricultural and other waste products produced by the University that must be disposed;
- to help reduce the amount of CO_2 (a greenhouse gas) emissions by combusting waste biofuels; and

- to ultimately serve as a large-scale (commercial demonstration size) test facility for federally- and other outside source-funded research and development projects related to cofiring of biofuels with coal and other coal refuse.

The feasibility analysis assesses: the economics of producing steam; the economics of off-sets such as utilizing multiple biomass and other wastes (i.e., sewage sludge); the value of a unique CFB test facility to perform research for industry, such as Foster Wheeler, and government agencies, such as the DOE; the environmental aspects of the CFB boiler; and the availability of funding from multiple sources including University, state, and federal sources. The feasibility study will also include developing a multiple-year program to test biofuels as the boiler system will be unique in that it will be heavily instrumented and will be able to handle multiple fuels.

1.1 Penn State’s Steam Plants

Penn State University, Office of Physical Plant (OPP) currently operates a coal-fired central steam plant at the University Park Campus. The installed coal-fired capacity is 450,000 lb/h (pph) steam generated by four vibra-grate stoker boilers at 250 psig/540°F, which are used as baseload units. Additional steam generating capacity is available with gas or oil fire in three other boilers, totaling 260,000 pph. Electricity is also produced, as a by-product, with a maximum installed generating capacity of 6,500 kW. Currently at peak operation, which occurs when classes are in session and winter conditions experienced, 420,000 pph of steam are required. Steam requirements during the summer are 125,000 pph while approximately 200,000 pph of steam is required during the spring/fall.

Although the present total steam generating capacity is 710,000 pph, the University prefers not to operate the gas- and oil-fired boilers because the price of the natural gas and fuel oil is significantly higher than that of the coal. Ideally, the University would like to fire only coal and have sufficient coal firing capability to allow for one coal-fired boiler to be down without impacting steam production or forcing the operation of a gas/oil-fired boiler.

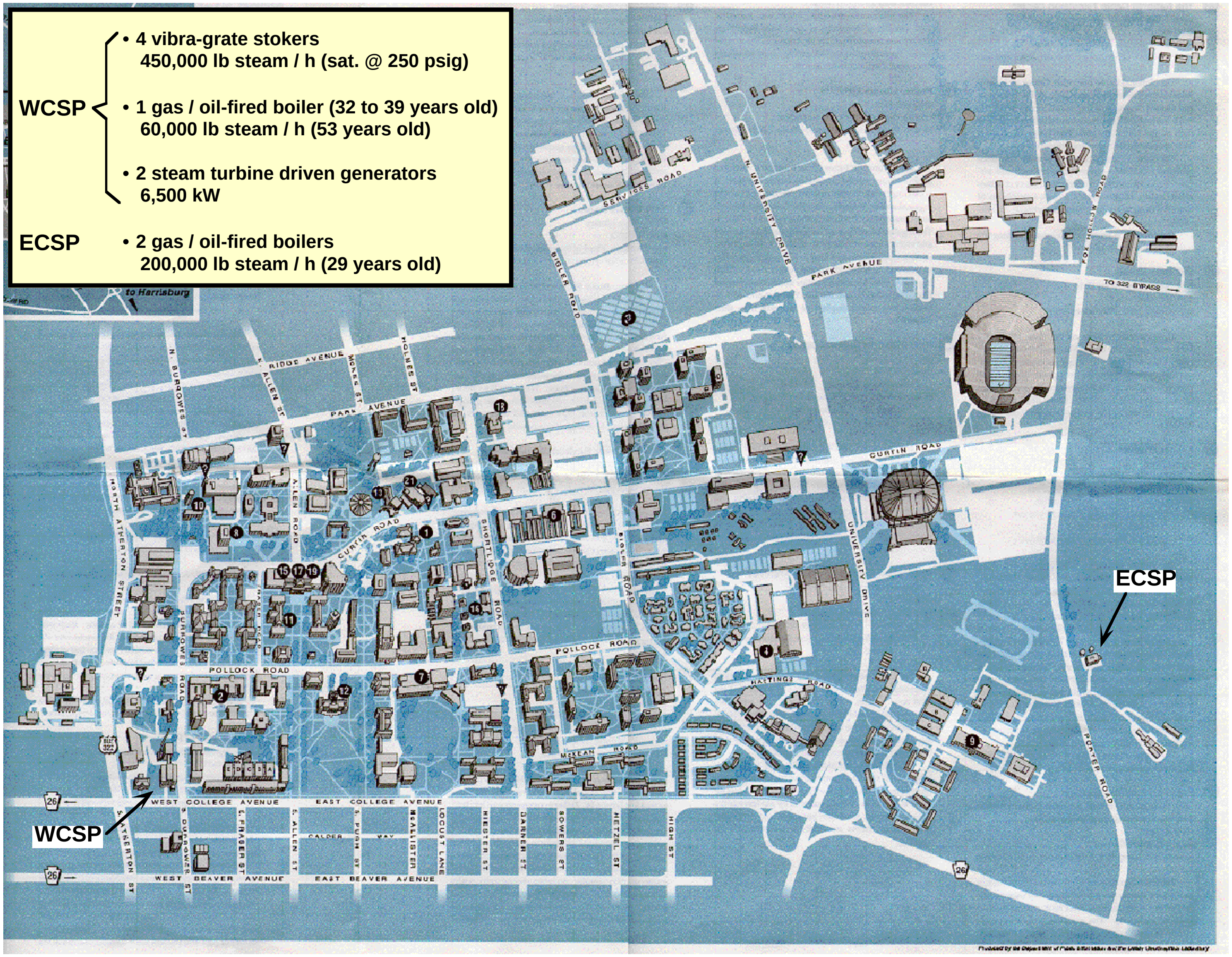
The four stoker-fired boilers at Penn State are all between 33 and 40 years old. When the units were installed (1961 to 1968), the projected life of a typical unit was expected to be approximately 40 years. Since that time, the life of the steam generating units has been reevaluated based on changing technology, economic, and regulatory factors. Life extension studies on many plants have now indicated that economic lives up to 50 to 60 years may be possible depending on the levels of maintenance, type of operation of the units, the cost of competing units, and other parameters related to these factors. Despite this, the University is exploring the possibility of installing a CFB boiler to cofire biomass and other waste streams with coal because of the following benefits:

1) Waste stream utilization. The CFB boiler would be multi-fuel capable with coal being the primary fuel and supplemented with waste streams. Waste stream disposal costs would be eliminated. For example, sewage sludge is currently landfilled at a cost of $47/ton.
2) Lower overall fuel costs. This includes using a lower grade coal including bituminous coal refuse (i.e., gob), growing grasses or crops on University land and cofiring in the boiler, accepting biomass and other wastes from the municipality, and being a test site for industry (e.g., Foster Wheeler) to conduct various fuel tests where the test fuel would be used in place of fuels purchased by the University.
3) Higher efficiency boilers.
4) Lower boiler emissions.
5) Possible alternative to spreading manure on fields and the associated odor problem.
6) Potential external funding source for a boiler replacement project. A recent energy assessment for Penn State showed that a coal-fired cogeneration plant was not economically feasible. However, OPP is reconsidering a boiler replacement because there is the possibility that some of the funding may come from other sources, e.g., industrial sponsorship, state and federal agencies.
7) Research component. By being a test site for industry (e.g., Foster Wheeler), not only would there be a decrease in fuel costs but there is the possibility that other operating costs such as labor could be reduced when industry-funded testing occurs.

Penn State's seven boilers are housed at two locations on campus as shown in Figure 1. The four coal-fired boilers and one small natural gas and oil-fired boiler are located at the West Campus Steam Plant (WCSP). There is not any room for installing additional boilers at this location. Two 100,000 pph of steam boilers, designed for natural gas and No. 2 fuel oil, are located at the East Campus Steam Plant (ECSP). This facility is used for peaking purposes. This location has been identified for future boiler expansion. At this time, OPP is interested in installing a CFB boiler with 200,000 pph of steam capacity at the ECSP. This size of a boiler could be installed without extensive upgrades to the current steam, water, and condensate return infrastructure. Final selection of the boiler size will be determined as part of the feasibility study.

1.2 Project Outline

The work consists of gathering design-related information, collecting and analyzing representative biofuels, coal, and coal refuse samples, developing a conceptual CFB boiler system design, developing a preliminary multiyear test program and associated budget, determining the system design/test program economics, and performing the feasibility study. The work is being performed via the following tasks:



WCSP
- 4 vibra-grate stokers
  450,000 lb steam / h (sat. @ 250 psig)
- 1 gas / oil-fired boiler (32 to 39 years old)
  60,000 lb steam / h (53 years old)
- 2 steam turbine driven generators
  6,500 kW

ECSP
- 2 gas / oil-fired boilers
  200,000 lb steam / h (29 years old)

Figure 1. PENN STATE’S WEST CAMPUS AND EAST CAMPUS STEAM PLANTS

- Task 1. Information and Sample Collection
- Task 2. Biofuels and Biofuel/Coal Characterization
- Task 3. Develop Conceptual Design
- Task 4. Develop Preliminary Test Program/Budget
- Task 5. Determine System/Program Economics
- Task 6. Complete Feasibility Study
- Task 7. Project Management/Reporting

A summary of the activities being performed in each task includes:

Task 1. *Information and Sample Collection*: System requirements and infrastructure information will be assembled by Penn State and provided to Foster Wheeler. In addition, representative samples of biofuel and coal will be collected by Penn State.

Task 2. *Characterize Biofuels and Biofuel/Coal Combinations*: Penn State will characterize the samples collected in Task 1 and Foster Wheeler will use the analyses for assessing issues such as materials handling, deposition, and emissions.

Task 3. *Develop Conceptual Design*: A CFB boiler system will be designed to address the multiple project objectives. Foster Wheeler will perform the conceptual design with input from Penn State and Cofiring Alternatives.

Task 4. *Develop Preliminary Test Program/Budget*: A multiyear test program will be designed and costed to use the state-of-the-art CFB boiler system for investigating a range of issues when cofiring multiple biofuels and possibly other waste materials. Penn State will develop the preliminary test program with consultation from Foster Wheeler and Cofiring Alternatives.

Task 5. *Determine System/Program Economics*: Capital and operating costs will be determined. In addition, the availability of funding for the system and test program will be assessed.

Task 6. *Complete Feasibility Study*: The feasibility study will be completed by incorporating the results from each of the tasks.

Task 7. *Project Management/Reporting*: The project will be managed and reported per DOE’s contractual requirements. Reporting will include the quarterly program/project management and technical progress reports, and a final report.

The status of Tasks 1 through 7 is presented in Sections 2.0 through 8.0, respectively. Activities planned for the next quarterly period are listed in Section 9.0. References and acknowledgments are contained in Sections 10.0 and 11.0, respectively. The project schedule is given in Figure 2, with a description of the milestones contained in Table 1.

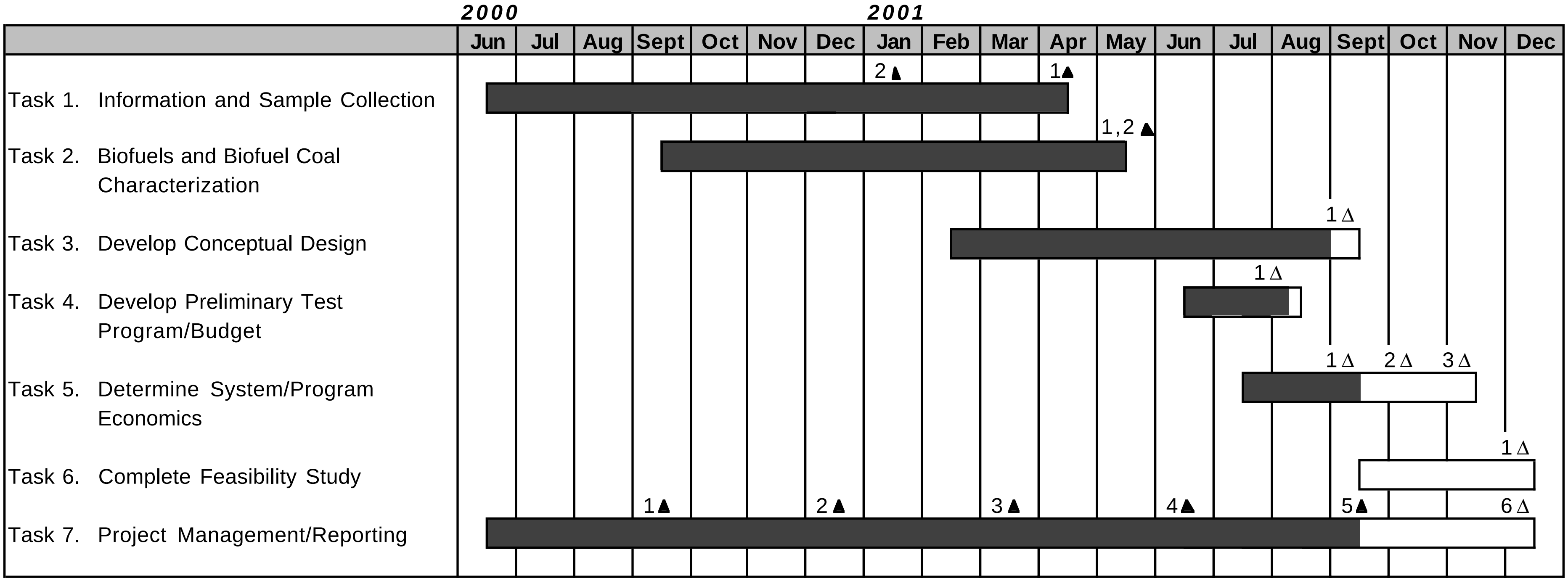


Figure 2. MILESTONE SCHEDULE

Table 1. Description of Milestones

Milestone	Description	Planned Completion Date	Actual Completion Date
Task 1, No. 1	Assemble system requirements and infrastructure information	04/15/01	04/15/01
Task 1, No. 2	Collect representative biofuel and coal samples	11/15/00	01/15/01
Task 2, No. 1	Complete characterization of biofuel samples	05/15/01	05/15/01
Task 2, No. 2	Complete characterization of biofuel/coal samples	05/15/01	05/15/01
Task 3, No. 1	Complete conceptual design	09/15/01	
Task 4, No. 1	Develop preliminary task program/budget	08/15/01	
Task 5, No. 1	Determine capital cost	09/15/01	
Task 5, No. 2	Determine operating costs	10/15/01	
Task 5, No. 3	Assess availability of funding	11/15/01	
Task 6, No. 1	Complete feasibility study	12/15/01	
Task 7, No. 1	Prepare program/project management and technical report 1	09/15/00	10/15/00
Task 7, No. 2	Prepare program/project management and technical report 2	12/15/00	12/15/00
Task 7, No. 3	Prepare program/project management and technical report 3	03/15/01	03/30/01
Task 7, No. 4	Prepare program/project management and technical report 4	06/15/01	07/13/01
Task 7, No. 5	Prepare program/project management and technical report 5	09/15/01	10/12/01
Task 7, No. 6	Prepare program/project management and technical report 6; prepare final report	12/14/01	

2.0 Task 1. Information and Sample Collection

Task 1 has been completed. System requirements and infrastructure information were assembled and provided to Foster Wheeler. This information is currently being used to develop the conceptual design. Representative samples of biofuels were collected by Penn State. Specifics on the samples collected were previously reported (Miller and Jawdy, 2000; Miller et al., 2000). Cofiring Alternatives completed a resource assessment of sawmills and secondary wood processors with wood wastes available for marketing as well as other potential biomass feedstocks for the CFB (Miller et al., 2000; Miller et al., 2001a)

3.0 Task 2. Biofuels and Biofuel/Coal Characterization

Task 2 has been completed. The biofuel analyses, contained in previous quarterly reports (Miller et al., 2000; Miller et al., 2001a), consisted of:

1) Proximate analysis;
2) Ultimate analysis;
3) Higher heating value;
4) Bulk density (where appropriate);
5) Chlorine content (where appropriate); and
6) Rheological characteristics (where appropriate).

In addition, the bulk chemical analysis of the biofuel ashes, stoker bottom and fly ash, and sewage sludge ash was determined. Chemical fractionation analysis was performed on the following samples to determine the mode of occurrence of major and minor elements:

1) Pine shavings;
2) Red oak shavings;
3) Dairy tie-stall manure;
4) Dairy free-stall manure;
5) Miscellaneous manure (mixture of various small-quantity manure streams that are collected at a central storage barn);
6) Sewage sludge;
7) Sheep manure;
8) Reed Canary grass;
9) Bottom ash; and
10) Fly ash.

The results from the spectrochemical and chemical fractionation analyses can be found in Miller et al. (2001b).

4.0 Task 3. Develop Conceptual Design

During this reporting period, work continued on developing the conceptual design. The following work has been completed or is in progress:

- Completed preliminary plant arrangement;
- Finalized equipment requirements with suppliers for the ash handling and fuel(s) feed systems;
- Completed preliminary P&IDs;
- Initiated plant electric load list; and
- Initiated plant input/ output (I/O) list.

5.0 Task 4. Develop Preliminary Test Program/Budget

Work started on Task 4 during this reporting period. A preliminary test program and budget have been developed. The preliminary test program is contained in Appendix A. The budget is being finalized and will be completed during the next quarter.

6.0 Task 5. Determine System/Program Economics

Work in Task 5 continued during this reporting period. Foster Wheeler will provide the system costs to Penn State during October 2001. The results will be incorporated into the feasibility study.

7.0 Task 6. Complete Feasibility Study

No work was performed in Task 6 during this reporting period.

8.0 Task 7. Project Management/Reporting

During this reporting period, DOE's project review meeting was attended in Pittsburgh, Pennsylvania on June 21-22, 2001 and a presentation was given. A manuscript was prepared for the Fifth International Biomass Conference of the Americas that was to be held in September 2001 but now has been postponed to December 2001. The title and authors are "The Occurrence of Inorganic Elements in Various Biomass Material and its Effect on Combustion Behavior," coauthored by Sharon Falcone Miller, Bruce G. Miller, and Curtis M. Jawdy. A copy of the manuscript is attached in Appendix B. In addition, technical reporting was performed per the contractual requirements.

9.0 Next Quarterly Activities

During the next reporting period, the following will be done:

- Complete the conceptual design;
- Complete the cost estimate;

- Complete the preliminary test plan and budget;
- Complete the feasibility study; and
- Prepare the draft final report.

10.0 References

Miller, B.G. and C. Jawdy, "Feasibility Analysis for Installing a Circulating Fluidized Bed Boiler for Cofiring Multiple Biofuels and Other Wastes with Coal at Penn State University First Quarterly Technical Progress Report for the Period 06/15/2000 to 09/14/2000," Prepared for the U.S. Department of Energy National Energy Technology Laboratory, Pittsburgh, Pennsylvania, DE-FG26-00NT40809, October 9, 2000, 40 pages.

Miller, B.G., S. Falcone Miller, C. Jawdy, R. Cooper, D. Donovan, and J.J. Battista, "Feasibility Analysis for Installing a Circulating Fluidized Bed Boiler for Cofiring Multiple Biofuels and Other Wastes with Coal at Penn State University Second Quarterly Technical Progress Report for the Period 09/15/2000 to 12/14/2000," Prepared for the U.S. Department of Energy National Energy Technology Laboratory, Pittsburgh, Pennsylvania, DE-FG26-00NT40809, December 21, 2000, 95 pages.

Miller, B.G., S. Falcone Miller, R. Cooper, D. Donovan, J. Gaudlip, M. Lapinsky, W. Serencsits, N. Raskin, D. Lamke, and J.J. Battista, "Feasibility Analysis for Installing a Circulating Fluidized Bed Boiler for Cofiring Multiple Biofuels and Other Wastes with Coal at Penn State University Third Quarterly Technical Progress Report for the Period 12/15/2000 to 03/14/2001," Prepared for the U.S. Department of Energy National Energy Technology Laboratory, Pittsburgh, Pennsylvania, DE-FG26-00NT40809, March 30, 2001a, 72 pages.

Miller, B.G., S. Falcone Miller, R. Cooper, D. Donovan, J. Gaudlip, M. Lapinsky, W. Serencsits, N. Raskin, and D. Lamke, "Feasibility Analysis for Installing a Circulating Fluidized Bed Boiler for Cofiring Multiple Biofuels and Other Wastes with Coal at Penn State University Fourth Quarterly Technical Progress Report for the Period 03/15/2001 to 06/14/2001," Prepared for the U.S. Department of Energy National Energy Technology Laboratory, Pittsburgh, Pennsylvania, DE-FG26-00NT40809, July 13, 2001b, 22 pages.

11.0 Acknowledgements

Funding for the work was provided by the U.S. Department of Energy under Grant No. DE-FG26-00NT40809. The project is being managed by the U.S. Department of Energy, National Energy Technology Laboratory (Pittsburgh). Philip Goldberg of NETL is the project manager.

Randy Swope from Penn State's College of Agricultural Sciences Farm services and William Lamont from the Horticulture are Department are acknowledged for their assistance in quantifying and sampling various potential feedstocks.

Mike Delallo and Francis Caracappa from Parsons Energy and Chemicals Group, Inc. are acknowledged for their assistance in the system design, costing, and permitting.

APPENDIX A. PRELIMINARY TEST PLAN

Preliminary Test Plan

Introduction

A “Preliminary Test Plan” has been prepared. The plan has not been detailed at this time. This “Preliminary Test Plan” defines a program that Penn State and Foster Wheeler Corporation are proposing at this time. If the decision is made to proceed with the “state-of-the-art” multifuel cofiring capable Compact Circulating Fluidized Bed (CFB) boiler and the test program, a detailed test plan will then be generated. The test program will be a combined engineering – agriculture – science effort. The primary participants (i.e., the Project Team) will be personnel from Penn State’s Office of Physical Plant (OPP), Energy Institute, and College of Agriculture’s farm services, and Foster Wheeler Corporation.

Purpose

The objective of the “Preliminary Test Plan is to establish a viable multifuel cofiring test program in support of OPP’s desire to replace its aging coal-fired fleet of stoker boilers, that are used to supply campus heating, with an environmentally friendly “state of the art” multi-fuel cofiring capable Compact Circulating Fluidized Bed (CFB) boiler. The test program will demonstrate the combustion impacts of multifuel cofiring on the Compact CFB boiler with particular attention to the operational and environmental impacts, as well as issues related to the biofuels themselves. The following operational impacts on the boiler and associated equipment will be evaluated:

- Capacity (ability to meet campus steam demands);
- Efficiency (unburned carbon, air heater exit temperature, excess air requirements, and other losses);
- Heat transfer surfaces;
- Slagging and/or fouling;
- Erosion and/or corrosion;
- Combustion and operational stability and reliability;
- Bed material inventory including quality and sizing;
- Limestone consumption;
- Fly ash and bottom ash collection and removal, and chemical composition and characteristics for commercial uses;
- SCR catalyst life, potential for biofuel constituent poisoning;
- Overall system economics; and
- Additional test and measurement equipment.

Environmental impacts or pollutants that will be evaluated include:

- NO_x;
- SO_x;
- CO_2;
- CO;

- Particulate matter;
- Opacity; and
- Trace elements.

Issues related to the use of the biofuels will also be evaluated. These include:

- Supply reliability;
- Consistency/ quality;
- Transportation – logistics/costs/pollution;
- Storage;
- Preparation;
- Handling – getting the biofuels into the unit; and
- Procurement structure for external biofuel supplies.

OPP is considering the replacement of Penn State's aging steam boilers for the following reasons:

- To more economically supply heat to the University's campus;
- To reduce the amount of airborne pollutants (NO_x, SO_x, particulate matter, and trace elements) presently emitted by the stoker-fired units, thus reducing the overall emissions from the University's central heating plant;
- To reduce the amount of agricultural and other waste products produced by the University that are now being land filled, land applied, and possibly composted in the future;
- To help reduce the amount of CO_2 (a green house gas) by combusting short-term energy crops and waste biofuels that would otherwise be land applied and decomposed to release methane gases into the atmosphere; and
- To potentially serve as a large-scale (commercial demonstration size) test facility for Federally- and industrially-funded research and development projects related to cofiring of biofuels with coals and other coal refuse.

Program Duration and Description

The test program schedule is for eight years and contains fundamental and pilot-scale support and full-scale demonstration and testing. The attached figure shows the schedule for the boiler design, construction, and operation as well as the fundamental and pilot-scale support. The schedule has been developed using January 1, 2002 as the start date based upon December 31, 2001 as the planned date for the completion of the feasibility study. There will be a three-year period starting January 1, 2002 where the basic engineering, final design, and permitting will be completed duringYear 1 and the procurement and construction will be performed during Years 2 and 3. This will be followed by a one-year period of boiler shakedown firing coal and testing various components,Year 4, and two two-year periods of demonstration and testing (Years 5 and 6 and Years 7 and 8). In addition, fundamental and pilot-scale activities will be performed in support of the demonstrations. These will be conducted during Years 1 through 4. For ease of discussion, the test program is presented in four phases:

- Phase I – Fundamental and Pilot-Scale Support;
- Phase II – Boiler Shakedown;
- Phase III – First Two -Year Demonstration/ Test Period; and
- Phase IV – Second Two -Year Demonstration/ Test Period.

Phase I – Fundamental and Pilot-Scale Support

"Fundamental and Pilot-Scale Support" activities will be performed in support of the demonstrations/testing. The activities will include constructing two or more pilot-scale FBC test units to perform a series of studies including, but not limited to, cold-flow modeling, combustion performance and emissions evaluations, deposition and agglomeration assessments through testing and modeling, detailed fuel characterizations (e.g. chemical fractionation analysis), and fuel evaluations. These activities will be performed during Years 1 through 4 and will be performed by a combination of graduate research assistants and Energy Institute and farm services faculty and staff.

It is the intent that during the initial stages of the program, all potential fuels will be evaluated at the pilot-scale before use in the full-scale CFB. This is the modus operandi that The Energy Institute has operated under when performing similar programs for government/industry-funded projects, which consist of demonstration-scale testing in the field (e.g., 35 MW_e cogeneration facility to evaluate sorbent performance of a suite of limestones and dolomites) or using Penn State's demonstration boiler system (i.e., 20 MM Btu/h boiler system integrated in to the University's steam distribution system used to evaluate various coal-based fuels). In both cases, either a bench-scale CFB or a pilot-scale boiler (i.e., 2 MM Btu/h firing rate) were used to ensure that no major complications would be encountered at the larger scale, whether it was system performance or Pennsylvania Department of Protection regulatory compliance. This is especially important in the proposed project since the CFB boiler will be one of Penn State's base-loaded units.

Phase II – Boiler Shakedown

"Boiler Shakedown" will be performed for a period of six months to one year (Year 4 of the test program). This time will be used to shake down the boiler and its related system components, and refine any system components, if required. This time period will also allow the plant operations personnel (i.e., OPP personnel) to become familiar with the boiler and its related system components, and to establish a database archive for coal combustion. As part of this database archive, a full load performance test including stack testing, sampling (coal, limestone, fly ash and bottom ash sampling) and analyses while firing only coal will be conducted prior to commencing the biofuel testing.

It is essential that the existing biofuel transportation, storage and preparation process investigations and testing take place during this time. This will include bench- and pilot-scale testing (see previous section) at campus laboratory facilities as well as at the new boiler installation site. In addition, computer modeling of the various process parameters will also be conducted on campus at various support facilities. The University's diverse professional staff and graduate students will be used to support these efforts as well as outside expertise from the Compact CFB boiler supplier.

The ability to add a by-pass flue gas duct upstream of the baghouse has been included in the basic design of the unit to test the affect of the biofuels on the operation and reliability of emission reduction systems. This duct will be used to allow for either slipstream and/or full-scale testing of various emission reduction systems such as advanced SCR systems, wet/dry scrubbers, and various barrier (including ceramic) filter systems.

The original equipment manufacturer of the Compact CFB boiler and architect/engineering firm that supplied the balance of plant equipment will be retained to perform continuing support to the University during the test period, specifically when plant modifications and/or upgrades are required.

Phase III – First Two-Year Demonstration/ Test Period

Phase III will be for a period of two years (Program Years 5 and 6) to determine the various mixtures of fuels that can be combusted in the Compact CFB boiler without affecting the unit's reliability to produce steam for the campus. During this phase, there will be a more extensive investigation into the biofuels preparation, storage, and conveying systems, in addition to focusing on the various mixtures, methods and quantity of biofuels to inject into the combustion zone of the boiler. The fuels tested in this phase will primarily include those identified in the feasibility study.

Phase IV – Second Two-Year Demonstration/ Test Period

Phase IV is schedule for a period of two years (Program Years 7 and 8). Again, testing of various mixtures of biofuels with coal and/or other waste fuels will be conducted, but as the University's experience base grows, so will their ability to combust more difficult fuel mixtures that may or may not affect the boiler's reliability. These fuels will be selected in conjunction with DOE and may be shipped in from outside of the region. Currently OPP is considering that, at the end of this second test period, a second Compact CFB boiler will have been brought on line to allow the University a greater flexibility in its future test program.

Operational/Design/Reporting Assumptions

Operational Assumptions

The Compact CFB boiler will be maintained and operated by OPP. University professional personnel and graduate students, primarily from The Energy Institute and the Energy and GeoEnvironmental Engineering Department (both within the College of Earth and Mineral Sciences) but also from the College of Agricultural Sciences, will support OPP personnel during testing. However, as with any testing at Penn State, when funded research/testing is being performed for a sponsor, they may have some of their own technical personnel present during the test period. In addition, Foster Wheeler will assist in the program as a project consultant/advisor.

OPP has dictated that the Compact CFB boiler must reliably produce steam per the campus demands. Therefore, the OPP has placed the following conditions on any testing that might be conducted on this new unit:

- Testing can not impair the operation capability or reliability of the Compact CFB boiler to meet the campus steam requirement;
- Testing must by controlled by OPP and testing will be delayed or halted for any reason, if in OPP's opinion, the unit will not be able to meet its obligations to supply steam to the campus;
- Unless a variance is issued, no testing can be commenced that will potentially violate the operating permit for this unit;
- All test programs will be reviewed and approved by OPP prior to their initiation; and
- Strict monitoring procedures of the unit's emissions will be adhered to and recorded.

It should be noted that all testing will be done in a systematic manner following specific rules and regulations as agreed upon between OPP and the Program Manager with input from other members of the Project Team. Prior to performing any test, a test matrix will be developed and agreed to between all of the parties including DOE. This is to ensure that the scope of work to be accomplished during each test has the greatest chance of success, minimizing the potential for costly errors and accidents.

All testing will be conducted to avoid potential upsets in the boiler's operation. The testing will commence with coal firing only. The unit will be stabilized at a load less than its MCR rating. The unit is to operate at this point for a minimum period (usually 8 hours) and a set of baseline data will be taken. Following this period the biofuel(s) to be tested will be introduced into the boiler at minimum quantities and gradually increased to the maximum amount agreed to for the test campaign. Following completion of the test period, the biofuel(s) will be gradually backed out until the minimum amount is reached. At that time, the unit will again be fired only on coal for a minimum period (usually 8 hours) and another baseline set of data taken.

Whenever possible, data acquisition will be done by an automated system. Sampling of fuels, limestone and ashes will be conducted by trained University personnel, either staff from The Energy Institute or OPP operational staff. The following typical data and samples should be collected during each test campaign:

- Electronically available data from the system controls and data logger;
- Manually collected data from the control room or locally mounted instrumentation not normally collected by the data logger;
- Fuel samples – coal and all biofuels;
- Limestone samples; and
- Fly ash and bottom ash samples – besides the standard oxides, the ash samples will be tested for the following trace elements: arsenic, barium, chromium, lead, mercury, and nickel as a minimum.

Design Assumptions

There are specific limitations to the existing CFB unit design as to the variety of biofuels that can be combusted with the present configuration. The Compact CFB boiler plant is designed to receive, store, process and handle the base fuel, i.e., coal, in addition to the limestone, fly ash, and bottom ash. Additionally, a simple biofuel feed train consisting of a “wood” storage silo with double outlet screw feeders has been designed as part of the base system. The screw feeders dump the “wood” fuel onto either of the two coal conveyors. These conveyors direct the fuel mixture through rotary valves directly into the Compact CFB boiler combustion chamber.

Any additional biofuel feed systems requirements will be designed, purchased, constructed, and commissioned as a part of that specific test requiring a modification and/or addition to the existing biofuel feed systems. Thus, the costs to perform such tests must also include the cost for the biofuel feed system modification and/or addition. For example, the manure feeding systems with multiple feeders (e.g., swine waste and solid manures) are part of the proposed test program and their cost estimates will be contained in the budget section.

Special materials for erosion and/or corrosion testing including test coupons, slagging and fouling probes, heat flux meters, etc. must be funded as required for each test that requires such items. This would also include any modifications and/or additions for any existing or new controls and instrumentation. Again, since these are proposed in the test program, their estimated costs will be contained in the budget section.

As mentioned previously, the unit has been designed and laid out to accommodate the addition of an emission reduction system prior to the baghouse. There are two stub duct sections designed into the existing unit’s outlet ducting (upstream of the baghouse) that will allow for either full or slip stream system testing without affecting the integrity of the

Compact CFB boiler to maintain its full load capabilities. Presently, it is envisioned that the following emissions reduction testing will take place:

- Corning honeycombed microfiltration membrane coated barrier filter system – for simultaneous particulate matter and trace element emissions reduction – specifically mercury and lead;
- Advanced SCR system – testing of poison resistant catalyst for NO_x control with units cofiring coal and various biofuels; and
- Electrostatic Precipitators (ESP) – affect of collection efficiency when cofiring coal and various biofuels.

As with the biofuel feed systems and advanced instrumentation packages, the components for the emissions reduction testing have been costed separately from the base unit and will be contained in the budget section.

Reporting

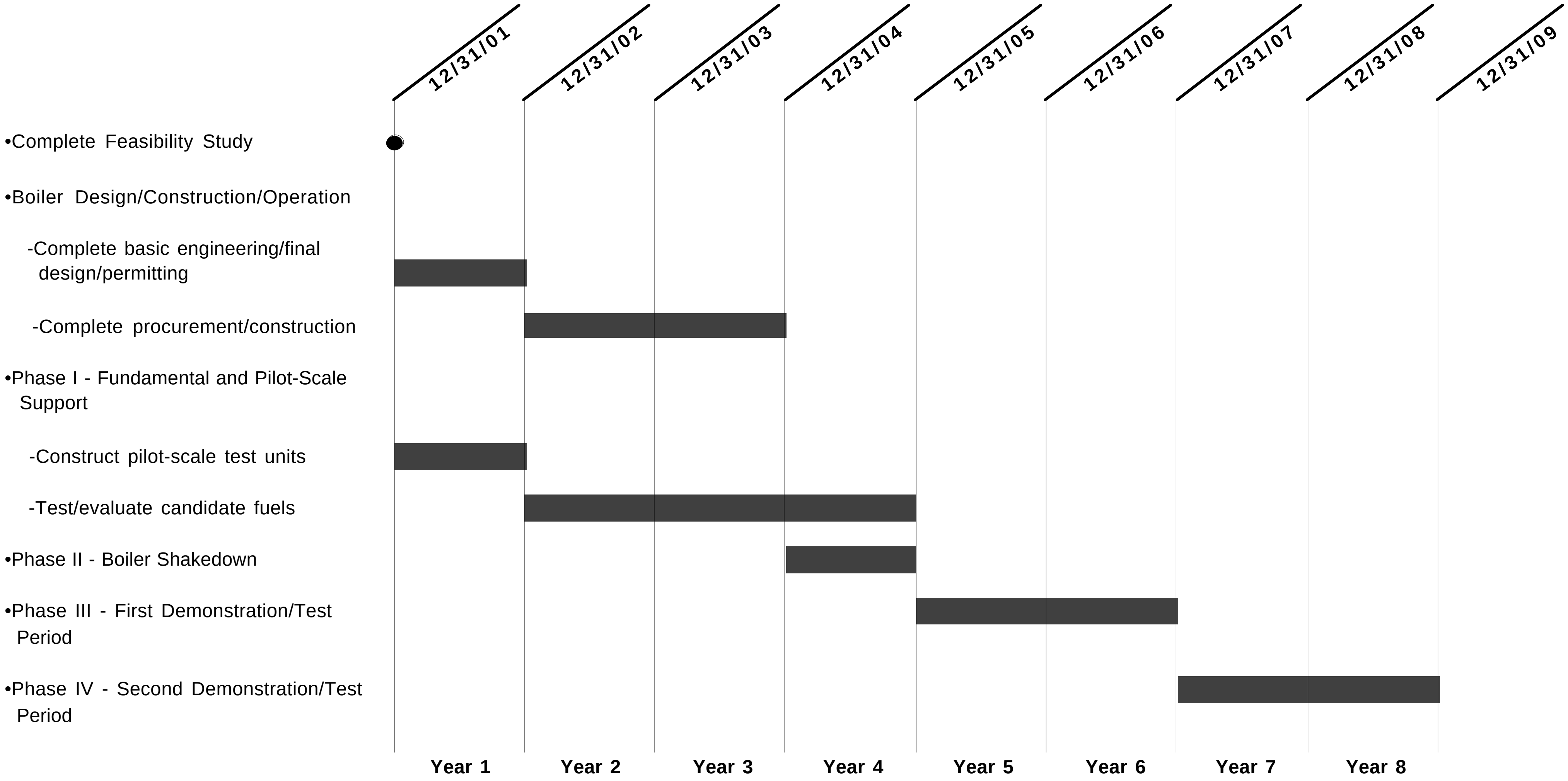
The Project Team, under the direction of the Program Manager, will be responsible for all customer contact as it relates specifically to the preparation and issuance of any test reports. The Program Manager and Project Team are responsible to ensure that all required data and sampling is conducted during each test period as required to fulfill all test and contractual requires. Sufficient data will always be collected to allow for a heat and material balance closure to be performed for each test.

The unit will be inspected (if at all possible) following any major testing phase. This is vital to understand the affects of the biofuels as to slagging and fouling, as well as erosion and corrosion. Note that sootblowing will be kept at a minimum or stopped all together to help define any accelerated rate of slagging or fouling within the unit.

The plant operators and maintenance staff will also keep a daily shift log to record the unit’s (including auxiliary equipment) operational characteristics and maintenance requirements. These might be subjective or quantifiable observations, but they will be recorded for future comparison to the operational teat data. Daily shift logs will also be kept for the biofuel related components, i.e. transportation, storage, preparation, and handling systems.

Photographs will only be taken by University personnel and will be reviewed/approved by the Program Manager to make sure that confidential material is not being published or released to the public.

Test Plan Schedule



APPENDIX B. MANUSCRIPT FOR THE FIFTH INTERNATIONAL BIOMASS CONFERENCE OF THE AMERICAS
Bioenergy and Biobased Products:
Technologies, Markets, and Policies

The Occurrence of Inorganic Elements in Various Biomass Material and its Effect on Combustion Behavior

by

Sharon Falcone Miller, Bruce G. Miller, and Curtis M. Jawdy

The occurrence of inorganic elements in various biofuels and its effect on combustion behavior

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The Pennsylvania State University is performing a feasibility analysis on installing a state-of-the-art circulating fluidized bed (CFB) boiler at Penn State's University Park campus for cofiring multiple biofuels and other wastes with coal. Approximately twenty different biofuels and other waste fuels were identified, collected and analyzed. Chemical fractionation analysis was performed on eleven of the major streams to assess the potential for bed agglomeration. This paper reports the chemical fractionation results for seven biofuels: sheep manure, chicken litter, dairy tie- and free-stall manure, miscellaneous manure (*e.g.,* horse manure), pine shavings and Reed Canary grass. A detailed chemical fractionation methodology is presented that addresses the extremely heterogeneous character of the various components that constitute a biofuel. Results of the chemical fractionation data indicate that $\geq$ 90% of the potassium and sodium in the fuels is present in a water-soluble and/or ion-exchangeable form. Calcium in the fuels is either present in a water soluble/ion-exchangeable form or acid soluble form. Iron is associated in the acid soluble form. Phosphorous is present in a water soluble/ion-exchangeable form. Aluminum and silicon remain in the insoluble portion of the fuel attributed to the presence of straw and dirt from the floor of dairy and poultry barns. Thermodynamic equilibrium modeling via FactSage indicated that biofuel blends cofired with a low-fouling coal do not form significant liquid phases at temperature characteristic of circulating fluid bed combustors (CFBs) (1171K) if the coal provides a significant potion of the thermal input. Biofuels containing little aluminum and minor potassium tend to form liquid $K_2Si_4O_9$ at 1171K. The mass fraction of $K_2Si_4O_9$ formed is very sensitive to the mass fraction of Al_2O_3 present.

Key words: biofuels; chemical fractionation; CFB; Reed Canary grass; manure; pine; thermodynamic modeling; agglomeration

Introduction

The Pennsylvania State University, under contract to the U.S. Department of Energy (DOE), National Energy Technology Laboratory (NETL), is performing a feasibility analysis on installing a state-of-the-art circulating fluidized bed (CFB) boiler and ceramic filter emission control device at Penn State's University Park campus for cofiring multiple biofuels and other wastes with coal, and developing a test program to evaluate cofiring multiple biofuels and coal-based feedstocks. Penn State currently operates an aging stoker-fired steam plant at its University Park campus and has spent considerable resources over the last ten to fifteen years investigating boiler replacements and performing life extension studies. This effort, in combination with a variety of agricultural and other wastes generated at the agricultural-based university and the surrounding rural community, has led Penn State to assemble a team of fluidized bed and cofiring experts to assess the feasibility of installing a CFB boiler for cofiring biomass and other wastes along with coal-based fuels.

The objective of the project is being accomplished using a team that includes personnel from Penn State's Energy Institute, Office of Physical Plant, and College of Agricultural Sciences; Foster Wheeler Energy Services, Inc.; Parsons Energy and Chemicals Group, Inc.; and Cofiring Alternatives.

The CFB boiler system that is being considered in the feasibility analysis is unique in that it:

1) is of compact versus traditional design;
2) includes modules to evaluate ceramic filters, along with fabric filters, for particulate matter control (recent work at Penn State has shown that ceramic filters have potential advantages regarding fine particulate matter and trace elements, *i.e.*, mercury removal);
3) contains an advanced instrumentation package including temperature and pressure sensors, deposition and slagging probes, heat flux meters, and corrosion/erosion panels;
4) contains multifuel capabilities (making it a versatile test site for industry and government studies); and
5) is a commercial facility in a rural, agricultural setting that contains an engineering and agricultural-based university.

The state-of-the-art CFB boiler and ceramic filter device being considered allows the University the opportunity to do the following:

- to more economically supply heat to the University Park Campus;
- to reduce the amount of airborne pollutants (*i.e.*, NO_x, SO_2, particulate matter, and potentially trace elements), thus helping to reduce the overall emissions from the University's central heating plant;
- to reduce the amount of agricultural and other waste products produced by the University that must be disposed;

- to help reduce the amount of CO_2 (a greenhouse gas) emissions by combusting waste biofuels; and
- to ultimately serve as a large-scale (commercial demonstration size) test facility for federally- and other outside source-funded research and development projects related to cofiring of biofuels with coal and other coal refuse.

The feasibility analysis is assessing: the economics of producing steam; the economics of off-sets such as utilizing multiple biomass and other wastes (*i.e.*, sewage sludge); the value of a unique CFB test facility to perform research for industry, such as Foster Wheeler, and government agencies, such as the DOE; the environmental aspects of the CFB boiler; and the availability of funding from multiple sources including University, state, and federal sources. The feasibility study is also including the development of a multiple-year program to test biofuels as the boiler system will be unique in that it will be heavily instrumented and will be able to handle multiple fuels.

Activities that have been completed include: assembling system and infrastructure requirements for the system design, performing a biomass resource assessment, collecting and analyzing representative samples, and assessing materials handling, deposition, and emissions issues. Items in progress include finalizing the conceptual design, developing and costing a multiyear test program to use the CFB boiler system, determining capital and operating costs, assessing availability of funding for the system and test program, and integrating the results into a feasibility study.

It has long been recognized that the mode of occurrence of inorganic elements in fossil fuels has a direct bearing on their behavior during combustion [1-4]. The occurrence of inorganic elements in biofuels is also important. Inorganic species are incorporated in biomass in several ways due to the chemical makeup of the biomass, its origin and the manner in which it is collected for utilization as a fuel. The fuel may be of plant or animal base or a mixture of both due to farming practices (*i.e.,* mixture of manure and bedding). Inorganic species can occur as ion-exchangeable cations, as coordination complexes, and as discrete minerals. In the case of firing a single fuel, such as coal, it is possible to predict ash behavior to avoid system problems. However, it becomes more complex to predict ash behavior in the case of firing multiple fuels in proportions that vary with time, *e.g.,* seasonal changes, and are extremely heterogeneous.

Like low-rank coals, biomass materials often contain significant amounts of alkali metals, *e.g.,* potassium and sodium, and alkaline earth metals, *e.g.,* calcium and magnesium, which are rapidly released into the gas phase and interact with other elements resulting in problems with fouling, slagging and corrosion. In general, potassium and sodium that are associated with the organic structure of the fuel tend to be problematic in that they can contribute to the formation of inorganic phases that have lower melting points. Studies conducted on ash formation during coal combustion show that the incorporation of moderate amounts of alkalis and alkaline earth elements into silicates enhances the coalescence and agglomeration of inorganics due to formation of “sticky” molten phases [2,3,5,6]. The presence of low-melting point phases in a fluidized bed combustor results in the formation of clinkers that can compromise the bed fluidity. It is also important to recognize that the blending of biomass feedstocks and coal does not necessarily result in simply an additive effect of problematic elements. Changes in the feed blend may or may not have devastating effects on system operation. Predicting these effects is based on our understanding of the manner in which the inorganics in fuels interact during combustion and their effect on the chemical and physical properties of the ash and gas phases in the system.

As part of Penn State's resource characterization, the types and quantities of potential feedstocks have been assessed. Approximately twenty different biomass, animal waste, and other wastes were identified, collected and analyzed. These potential feedstocks include the following: animal wastes such as dairy tie-stall and free-stall manure (mixed with leaves and brush to make it stackable), beef manure, horse manure, poultry litter, sheep manure, and swine waste; wood waste and brush; pallets; Reed Canary grass; bottom and fly ash from the stokers; agricultural plastics including horticulture hard plastics and plastic bags, bale tarps, and silo bunker covers; used oil; tires; wood shavings and chips from the surrounding region; coal/paper pulp pellets; and sewage sludge. Details of the resource assessments and results from analysis of all the feedstocks can be found elsewhere [7,8]. Of these feedstocks, chemical fractionation analysis was performed on eleven of the major streams to assess the potential for bed agglomeration. It is the objective of this paper to present the results of characterizing selected biomass fuels via chemical fractionation. The chemical analysis of the fuels is then used to determine the net ash composition of possible fuel blends and their theoretical propensity to form liquid phases during combustion based on thermodynamic modeling.

Methodology

Chemical Fractionation Procedure

The chemical fractionation procedure is based on an element's varying solubility as a result of its occurrence in a fuel. A procedure used to fractionate low-rank coals at the University of North Dakota Energy and Environmental Research Center [9] later modified by Baxter [10] was further modified to better address handling issues particular to biomass fuels. A detailed description of the chemical fractionation procedure is given in the appendix. A schematic representation of the method is shown in Figure 1.

Each step results in a liquid and solid residue sample, which are both analyzed for the following major and minor elements, *i.e.,* Al, Ba, Ca, Fe, K, Mn, Mg, Na, P, Si, Sr, S and Ti, using decoupled argon plasma spectroscopy DCP. Analysis of both the liquid and solid residue was conducted so that a material balance could be performed.

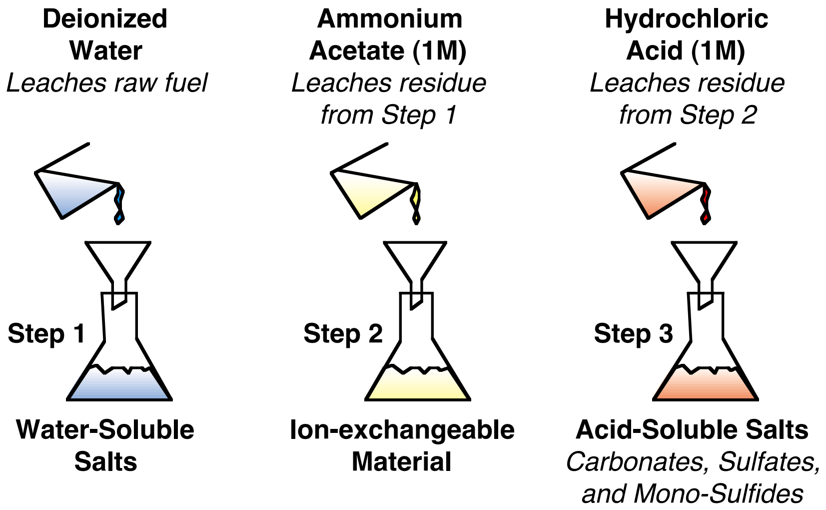

Figure 1. Schematic Representation of the Chemical Fractionation Method

In the first step of leaching, water was used to remove elements that are in a water-soluble form. This consists primarily of water-soluble salts, *e.g.,* alkali sulfates, carbonates, and chlorides. The remainder of the residue from Step 1 was subjected to a second leaching step using ammonium acetate to remove elements that are bound loosely to organic matter, *e.g.,* ion-exchangeable elements such as potassium, calcium, sulfur and sodium. Again, the leachate and a portion of the residue from this step were analyzed for major and minor elements.

The final leaching step used hydrochloric acid to remove element-bearing minerals that exist as acid-soluble salts such as carbonates, sulfates, mono-sulfide minerals, and simple oxides. Again, the leachate and a portion of the residue from this step were analyzed by DCP. The insoluble portion of the fuel is generally made up of silicates and other acid insoluble mineral phases.

Certain biomass fuels are inherently difficult to work with given the chemical fractionation procedure. It is often difficult to obtain a representative sample given the heterogeneous nature of the fuels. As an example, the manure samples consist of a mixture of manure, straw and sand taken from the floor of the two dairy barns and chicken litter is a combination of the chicken manure and the wood shavings that are used as a bed material in the chicken barns. This heterogeneity was noted as a major problem in a round robin study conducted by von Puttkamer et al. [11]. It is also extremely difficult to grind such heterogeneous samples given the different grindability of straw, sand and dried manure. It is also difficult to work with samples that contain material that have inherently different wetabilities and densities, *e.g.,* sand versus straw. Often only the liquid portion of the sample is analyzed due to time and cost considerations. This is not always appropriate as it was observed that material balances for individual elements between the sum of the solid and liquid samples and the original parent was not as good as generally obtained in coal samples. Zevenhoven-Onderwater et al. [12] have also reported such difficulties in obtaining good material balances between analysis of solid and liquid samples. A separate paper is planned to present data generated at Penn State University to address this issue. In short, biomass fuels required special consideration when applying the chemical fractionation procedure. Therefore modifications to the preparation, *e.g.,* cutting and grinding the sample, and filtering steps, *e.g.,* addition of a centrifuge step, were made to accommodate the physical characteristics of the biofuels.

Results and Discussion

Fuel Characterization

Proximate, ultimate and ash analysis of the fuels is given in Table 1. Figures 2 through 10 show the weight percent of selected elements that occur as water soluble and/or ion-exchangeable, acid soluble or insoluble in the different biomass fuels studied.

For purpose of discussion, the water soluble and ion-exchangeable portions are combined as they are both indicative of species that are highly reactive during combustion, *i.e.,* organically-bound or water soluble mineral phases such as carbonates. The combined water soluble and ion-exchangeable portions are referred to as water soluble/ion-exchangeable. Acid soluble elements are usually derived from acid soluble mineral phases, *e.g.,* pyrite and some clays. Insoluble phases are generally minerals such as quartz and aluminosilicates. Many of the insoluble and some of the acid soluble portions are indicative of the presence of dirt and other contaminates that make up the fuel sample and must be considered as part of the total fuel analysis. It should be mentioned that sample reproducibility is also difficult due to variability of the fuels.

Potassium occurs predominately in water soluble/ion-exchangeable forms (Figure 2). In all four manures and the Reed Canary grass, ≥ 95% of the total potassium is water soluble/ion-exchangeable. The pine shavings and chicken litter contained a moderate amount of water soluble/ion-exchangeable potassium with the balance being in the insoluble form. The insoluble potassium in the chicken litter is attributed to the significant amount of wood chips that make up the litter.

Sodium is also present predominately (≥ 90%) in a water soluble/ion-exchangeable form in all of the biomass fuels except for the pine shavings (76%)(Figure 3). The remaining sodium is present mostly in an insoluble form.

Virtually all of the calcium in the fuels is either present as water soluble/ion-exchangeable or acid soluble (Figure 4). Less than 1.6% of the calcium remained in the insoluble portion of the fuel. Unlike potassium and sodium, there was a significant portion of acid soluble calcium ranging from 5.6% to 68%. The plant fuels tended to have significantly less acid soluble calcium (5-6%) than the manure samples (17-68%). Magnesium followed a similar trend as calcium with slightly lower amounts of acid soluble magnesium and some insoluble magnesium present (Figure 5). Interestingly, calcium is not involved in the formation of melt phases predicted by the thermodynamic modeling discussed in the next section.

Table 1. Proximate, ultimate and ash analysis of cofire coal and biomass fuels

	Cofire Coal	Pine Shavings	Reed Canary Grass	Sheep Manure	Dairy Free-Stall	Dairy Tie-Stall Manure	Misc. Manure	Poultry Litter
Moisture	5.0	45.0	65.2	47.8	70.3	69.8	50.5	20.0
Proximate analysis (wt.%, db)								
Volatile matter	24.16	84.7	76.1	65.2	30.6	30.1	21.8	55.3
Ash	14.70	0.1	4.1	20.9	62.3	62.5	73.5	17.0
Fixed carbon	61.14	15.2	19.8	14.0	7.1	7.4	4.8	7.7
Ultimate analysis (wt. %, db)								
Carbon	72.75	49.1	45.8	40.6	22.1	22.6	19.6	38.1
Hydrogen	3.91	6.4	6.1	5.1	2.9	2.9	2.5	5.6
Nitrogen	1.50	0.2	1.0	2.1	1.1	1.1	1.0	3.5
Sulfur	2.27	0.2	0.1	0.6	0.1	0.1	0.1	0.6
Oxygen	4.87	44.0	42.9	30.7	11.5	10.8	3.3	30.9
HHV (Btu/lb, db)	13,118	8,373	7,239	6,895	3,799	8,203	3,114	6,399
HHV (kJ/kg, db)	30,493	19,455	16,828	16,021	8,832	19,070	7,238	14,874
Bulk density (lb/ft^3)	--	11.9	3.12	23.1	50.5	50.5	43.7	--
Bulk density (g/cc)	--	0.10	0.05	0.37	0.81	0.40	0.7	--
Ash Analysis (wt.%)								
Al_2O_3	25.34	13.4	1.66	3.08	0.96	2.26	1.34	9.14
BaO	--	0.15	0.05	0.05	0.02	0.02	0.01	0.05
CaO	2.28	8.75	9.57	12.8	6.38	23.3	3.44	12.7
Fe_2O_3	18.34	5.94	1.47	1.95	1.29	1.37	0.93	4.04
K_2O	2.22	4.94	18.1	23.4	6.75	10.7	1.77	9.94
MgO	0.82	3.35	5.29	5.74	2.65	8.91	1.06	4.01
MnO	--	0.49	0.11	0.17	0.17	0.14	0.03	0.36
Na_2O	0.25	1.38	2.34	4.64	1.32	7.04	0.88	3.60
P_2O_5	0.4	1.44	13.8	9.21	2.90	14.7	2.54	14.0
SiO_2	48.2	57.2	43.0	29.3	74.98	26.0	84.82	39.4
SO_3	0.67	0.05	0.02	5.52	0.04	0.14	0.01	2.58
SrO	--	0.80	0.11	0.03	0.10	0.11	0.14	0.03
TiO_2	--	1.16	4.99	0.20	2.06	5.08	1.20	0.51

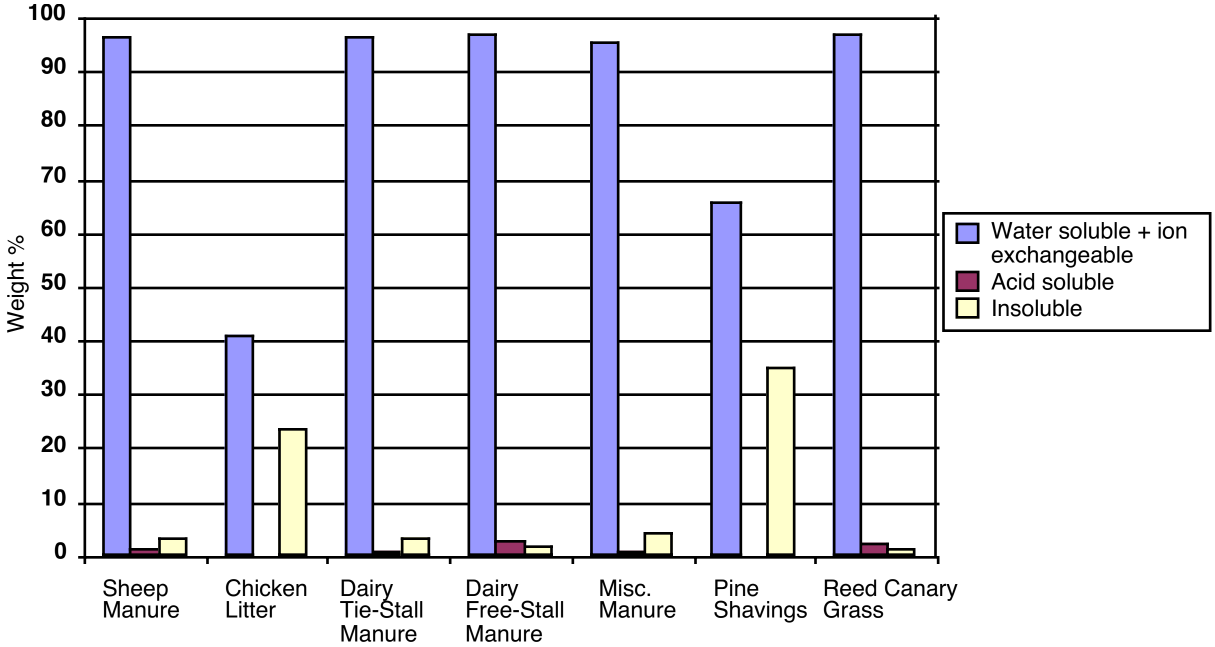

Figure 2. Occurrence of potassium in biofuels

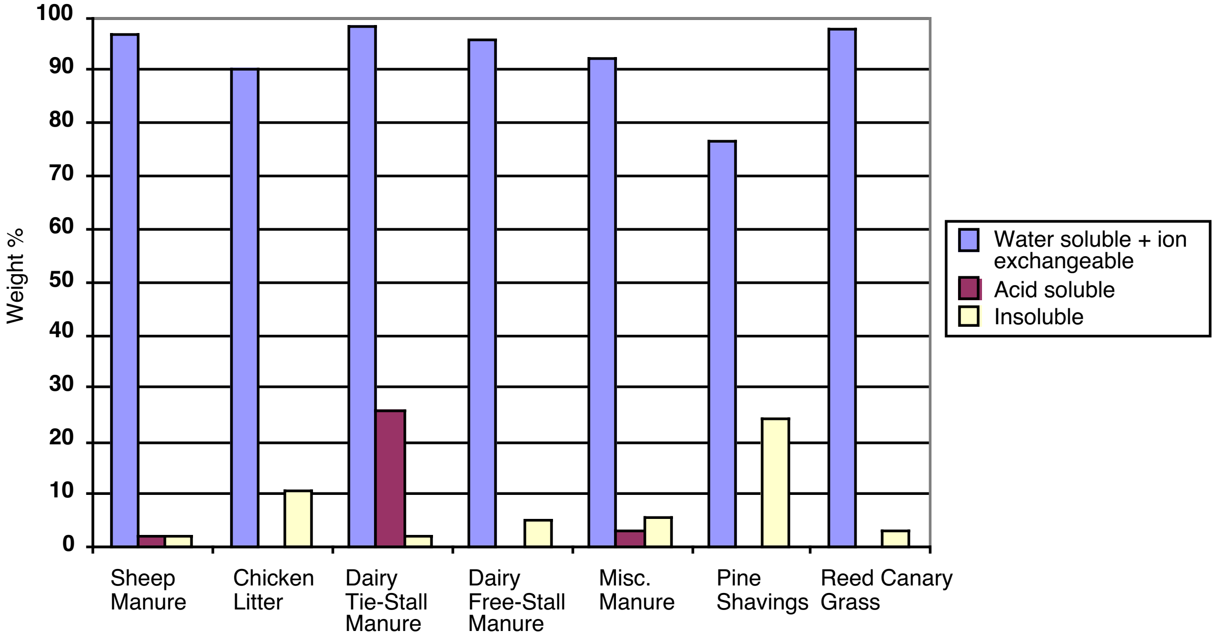

Figure 3. Occurrence of sodium in biofuels

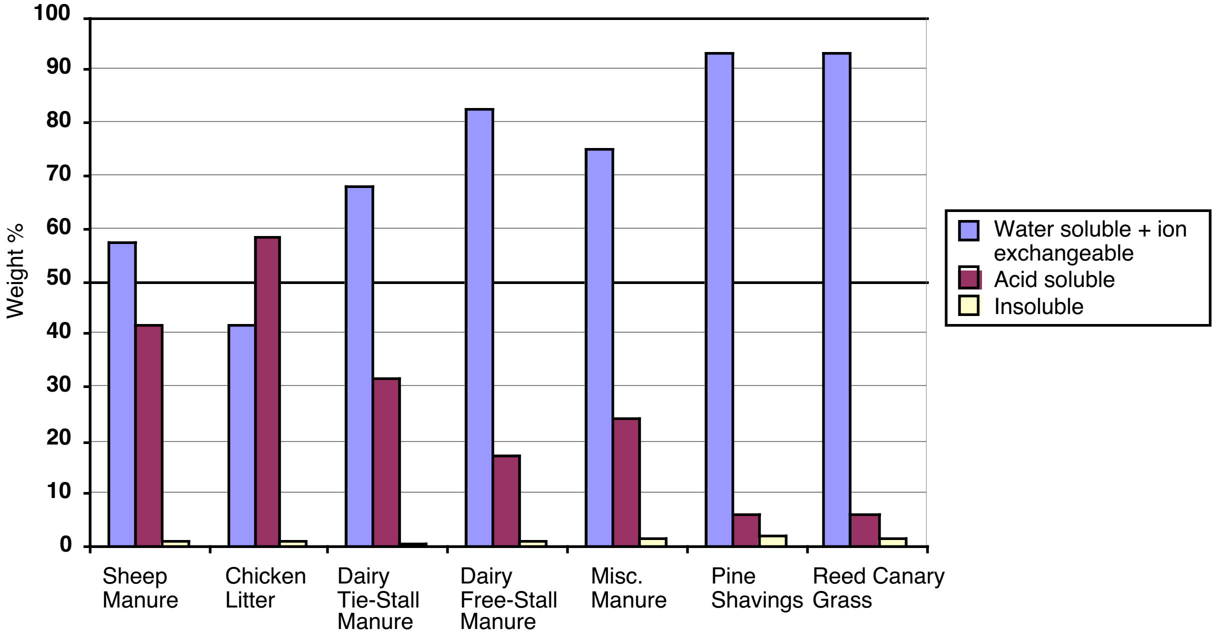

Figure 4. Occurrence of calcium in biofuels

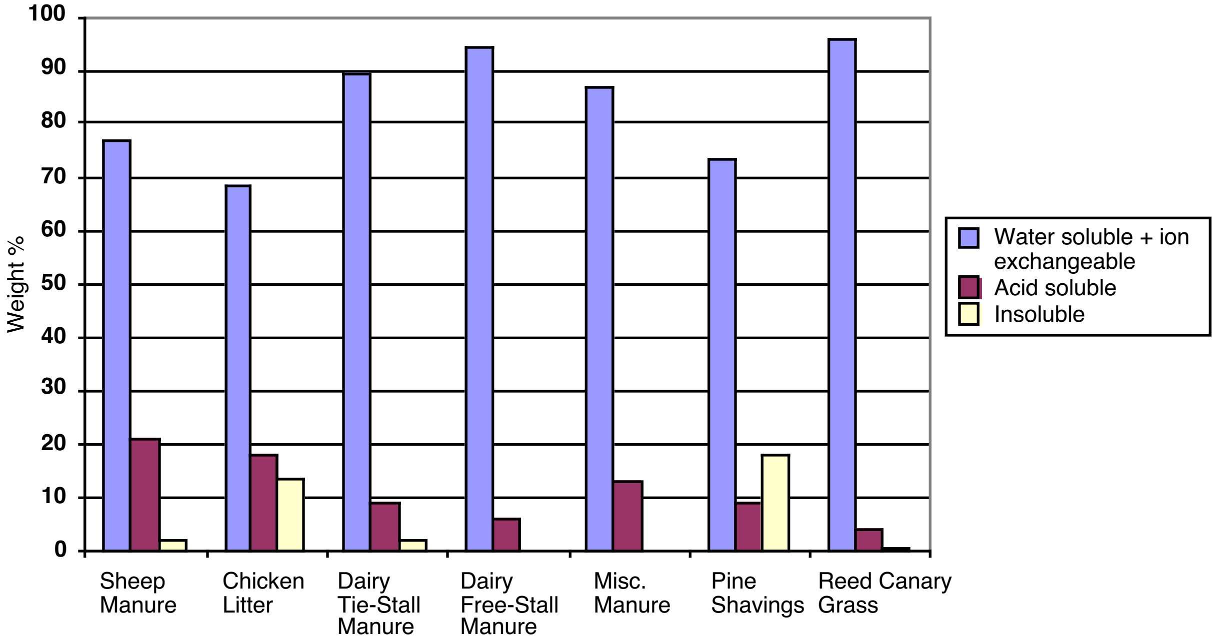

Figure 5. Occurrence of magnesium in biofuels

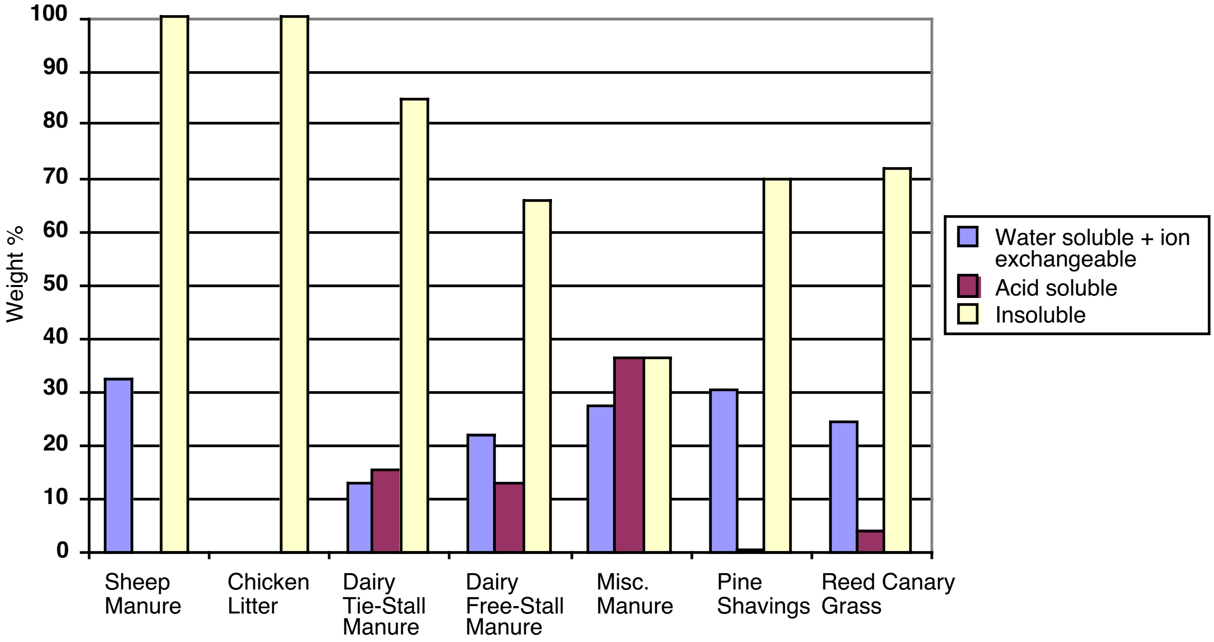

Figure 6. Occurrence of aluminum in biofuels

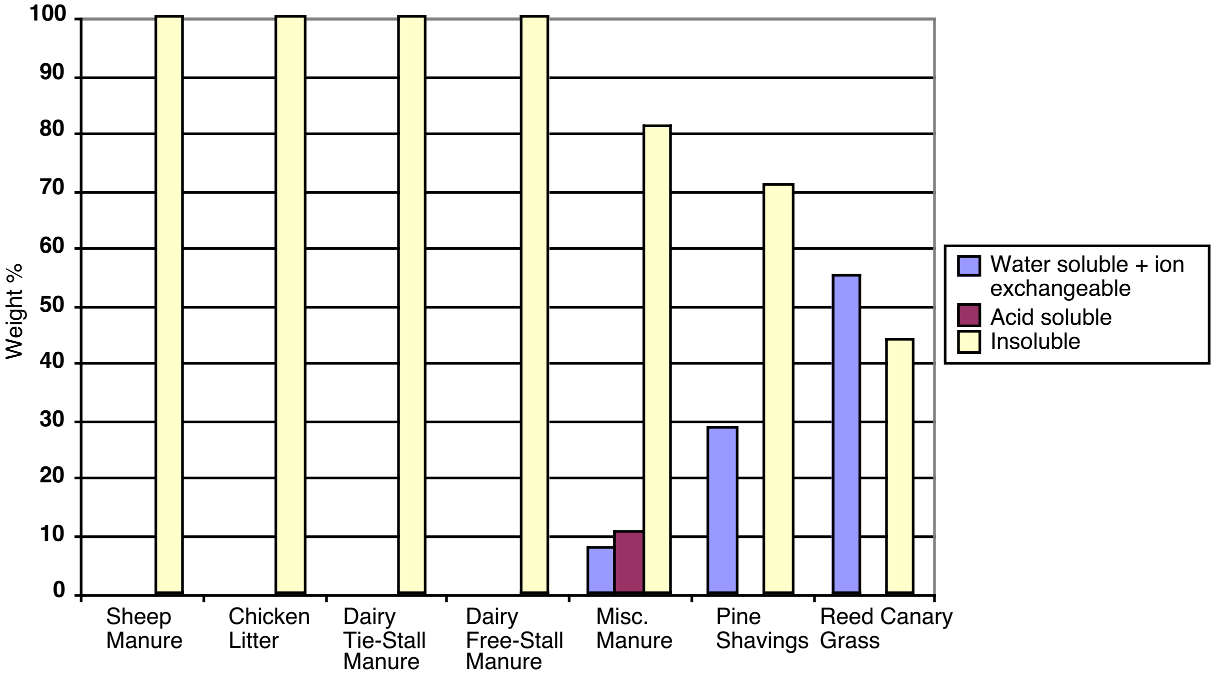

Figure 7. Occurrence of silicon in biofuels

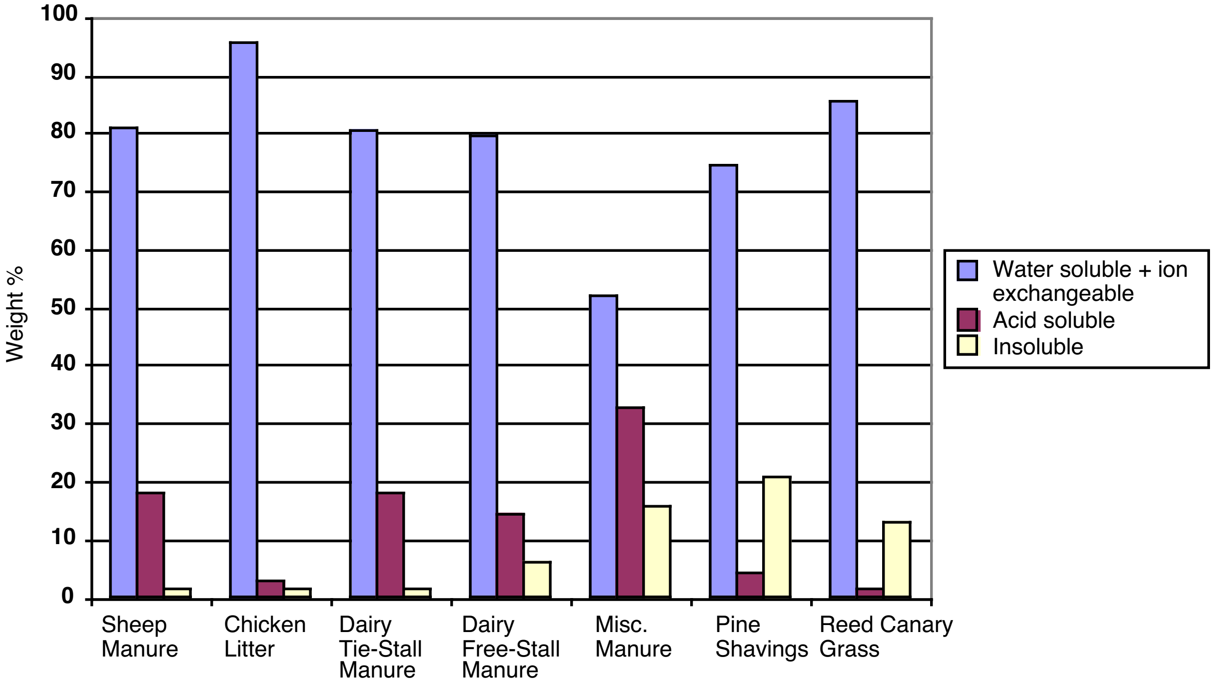

Figure 8. Occurrence of sulfur in biofuels

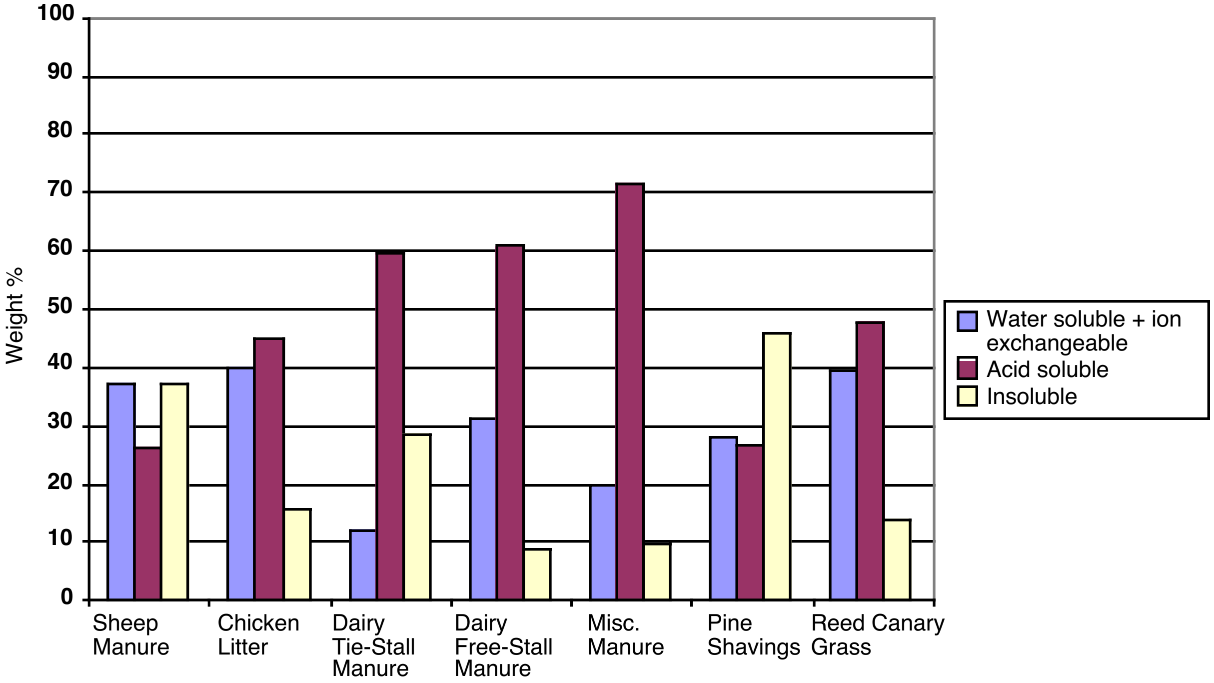

Figure 9. Occurrence of iron in biofuels

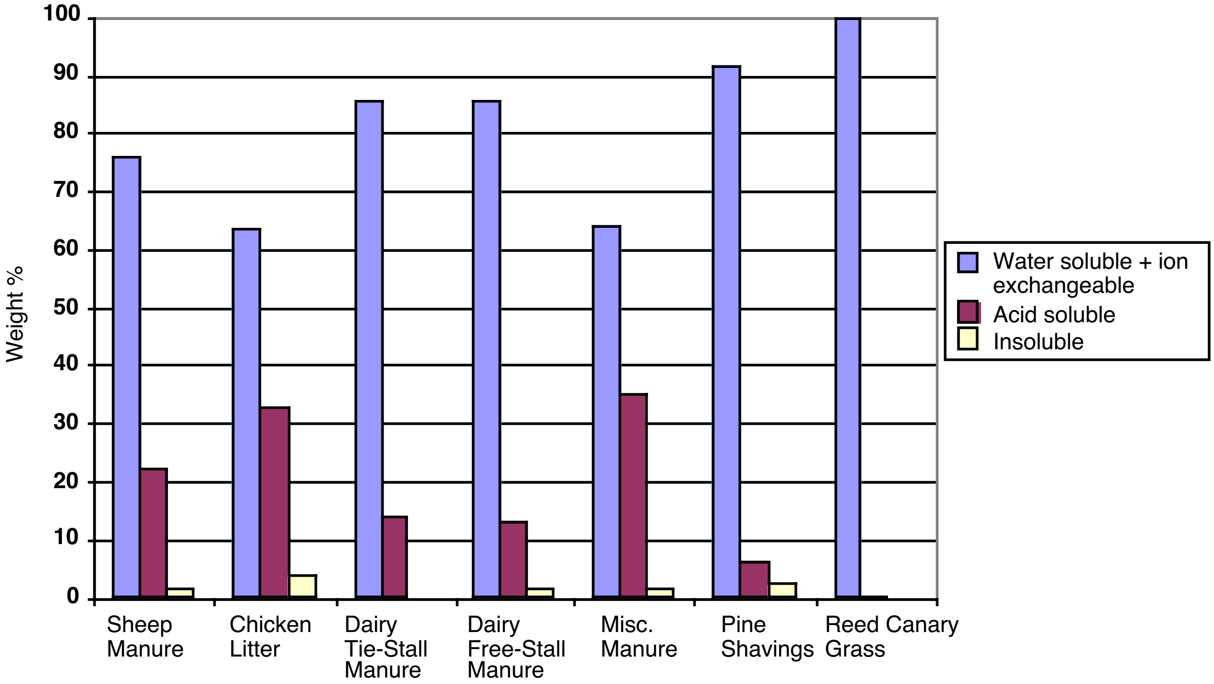

Figure 10. Occurrence of phosphorous in biofuels

Aluminum and silicon are concentrated in the insoluble portion of the fuels (Figures 6 and 7). This is expected given that many of the manure samples also included dirt, *i.e.,* quartz, clay minerals, from the stall as well as hay/straw and sand. There was some water soluble/ion-exchangeable and acid soluble aluminum present in some of the samples (Figure 6). At this time it is unknown what the source of this aluminum could be. Water soluble/ion-exchangeable silicon was measured in the pine shavings and Reed Canary grass. Silicon is not typically found in ion-exchangeable form so no explanation is presented at this time. Material balance of silicon was not very good. This is attributed to the varied contamination of sand/dirt in many of the samples.

Sulfur occurred predominately in the water soluble/ion-exchangeable portion (23-96%)(Figure 8). The percent of sulfur that was acid soluble ranged from 2 to 46%. Iron was the only element present predominately in the form of acid soluble species (26-71%)(Figure 9).

Phosphorous was present predominantly in a water soluble/ion-exchangeable form (≥ 60%) (Figure 10). The difference was found mostly in the acid soluble form ranging from 0.3% in the Reed Canary grass to 34.8% in the miscellaneous manure sample.

In general, a significant portion of the alkali and alkaline earth elements occur in the water soluble/ion-exchangeable portion of the biofuels. Zevenhoven-Onderwater et al. reported similar results for forest residue, *Salix* (low Si) and *Salix* (high Si) [12]. The high percentage of alkali and alkaline earth elements in the water soluble/ion-exchangeable form is cause for concern given their potential for forming molten phases in the bed during CFB combustion. Extraneous quartz is fairly inert within the gas stream in the absence of volatilized alkalis and alkaline earth elements.

Volatilized alkalis and alkaline earth elements can migrate into the silicate structure forming phases that have lower melting points. It is important not only to look at the elemental concentration on a fuel basis but to also consider the interaction of elements at the temperature regime for a given system to better asset potential fuel blends for a particular combustion system.

Thermodynamic Modeling to Predict Inorganic Phases

A series of fuel blends were used as input into a Gibbs free energy minimization program called FactSage developed at the Facility for the Analysis of Chemical Thermodynamics (FACT), Centre for Research in Computational Thermochemistry (CRCT), École Polytechnique de Montréal, Canada, and GTT Technologies [13]. The program calculates equilibrium composition for a given system at a set of defined temperature and/or pressure conditions.

The biomass resource assessment conducted by the Office of Physical Plant and the College of Agricultural Sciences determined the types, quantity and temporal variations of different biomass waste material produced at Penn State's University Park campus. Based on their assessment, an average biofuel and coal fuel blend was identified (Table 2). The coal identified is a medium volatile bituminous coal. The inorganic composition of potential fuel blends is given in Table 3. The average fuel blend composition was used as input into the FactSage Thermodynamic modeling program to determine the state of the inorganic phases present in the bed. An average temperature of 1171K (898°C, 1650°F), to represent an average anticipated bed temperature and a firing-rate of 58.6MW (200MMBtu/hr) were used. The equilibrium phases predicted by FactSage are given in Table 4.

Table 2. Percent thermal input of proposed and theoretical fuel blends based on a firing rate of $58.6MW_t$ (200MMBtu/hr)

% Thermal Input					
Fuel	**Baseline Blend**	**Chicken Litter**	**Manure Blend 1**	**Manure Blend 2**	**Manure-Coal Cofire**
Coal	83.8				84.9
Sewage Sludge	0.4				
Sheep Manure	0.1		59.0	25	3.9
Chicken Litter	0.0	100			
Dairy Tie-Stall Manure	0.4		21.5	25	4.0
Dairy Free-Stall Manure	0.0		8.1	25	3.4
Misc. Manure	0.3		11.7	25	3.9
Red Oak Shavings	8.4				
Pine Shavings	6.5				
Reed Canary Grass	0.2				

Table 3. Inorganic analysis of fuel blends (fuel basis, as-fired)

	Weight %				
Oxide	**Baseline Fuel Blend**	**Chicken Litter**	**Manure Blend 1**	**Manure Blend 2**	**Manure-Coal Cofire**
Al_2O_3	2.29	2.53	0.24	0.17	1.96
BaO	0.00	0.01	0.00	0.00	0.00
CaO	0.43	3.50	0.98	0.64	1.10
Fe_2O_3	1.65	1.12	0.16	0.12	1.35
K_2O	0.23	2.75	1.36	0.63	0.60
MgO	0.11	1.11	0.40	0.24	0.30
MnO	0.00	0.10	0.01	0.01	0.01
Na_2O	0.03	0.99	0.32	0.18	0.20
P_2O_5	0.07	3.86	0.68	0.43	0.63
SiO_2	4.87	10.89	6.38	8.00	8.66
SO_3	0.07	0.71	0.27	0.08	0.13
SrO	0.00	0.01	0.01	0.01	0.01
Ash %	9.78	27.72	10.93	10.67	0.11

Table 4. Inorganic phases predicted at equilibrium at 1171K. All phases are solid unless followed by *(l)* indicating a liquid phase. Liquid phases are also indicated in bold typeface.

	Weight %				
Phase	Baseline Blend	Chicken Litter	Manure Blend 1	Manure Blend 2	Manure-Coal Cofire
SiO_2/tridymite	25.7		11.0	50.0	27.0
$CaAl_2Si_2O_8$/anorthite	19.4				18.7
Fe_2O_3/hematite	17.1		1.7	1.2	9.1
$Al_6Si_2O_{13}$/mullite	14.8				
$KAlSi_2O_6$/leucite	11.1	7.8	10.8	7.3	19.4
$Mg_2Al_4Si_5O_{18}$/cordierite	8.3				
$NaAlSi_3O_8$	2.7				11.8
$CaSO_4$/anhydrite	1.2				1.5
$Ca_3Fe_2Si_3O_{12}$/andradite		25.7			1.1
$MgOCa_2O_2Si_2O_4$/akermanite		13.9			
$Na_2Ca_2Si_3O_9$		29.4			
Mg_2SiO_4/forsterite		8.2			
$K_3Na(SO_4)_2$		7.0			
$Na_2SO_4(l)$		**3.1**			
$CaOMgOSiO_2$/monticellite		4.9			
$K_2Si_4O_9(l)$			**31.0**	**13.3**	
$Na_2Ca_3Si_6O_{16}$			22.2	13.2	
$MgOCaOSi_2O_4$/diopside			15.4	10.0	11.3
$Na_2Mg_2Si_6O_{15}$			8.4	3.3	
K_2SO_4			6.2	1.7	

The most basic scenario was to input the chemical analysis of the fuel blend in the oxide form. It is acknowledged that the elements may or may not be present as oxides. At 1171K (898°C), the phases present in equilibrium are given in Table 4. In some cases, mineral names are assigned to chemical formula. This does not necessary imply any information regarding the crystallinity of the phase but only a match with regard to chemical composition.

In the Baseline Blend fuel, there are no liquid phases present at 1171K. All of the alkali earth elements are tied up in aluminosilicates that have melting points higher than 1171K. The coal provides a significant source of aluminum to favor the formation of aluminosilicates versus silicates that have lower melting points.

At equilibrium at 1171K, the chicken litter fuel contains the liquid phase Na_2SO_4 (3.1 wt. %)(Table 4). The chicken litter contains significant amounts of sodium as compared to the other fuels. The remaining alkali earth elements are divided up into other silicates. Previous work conducted at Penn State University involved combustion studies of chicken litter in a FBC during which significant clinkering occurred in the bed. As is common practice, kaolin clay was added to the fuel feed to reduce the occurrence of clinkering in the bed [14,15]. Kaolinite ($Al_2Si_2O_5(OH)_4$) is the main constituent of kaolin clay. The net effect of the clay is to increase the aluminum in the ash that shifts the equilibrium composition away from the formation of phases having lower melting points. In addition, the kaolin also dilutes the concentration of alkali earth elements. The net effect is to shift the reaction in favor of forming aluminosilicates having higher melting points. Interestingly, calcium is not involved in the formation of melt phases. As mentioned earlier, calcium occurs predominantly in an acid soluble form in the chicken litter. Hald [16] studied the addition of limestone on the formation of liquid phases during combustion of coal and straw and suggested that CaO was only a minor contributor to the formation of melt phases.

The extent to which organically bound alkalis and alkaline earth elements volatilize depends on the combustion temperature, as suggested by the work by Helble et al. [17,18]. However, the volatility of sodium or presence of sodium volatiles in the gas stream decreases with temperature. The reason for this is that at higher temperatures the organically bound sodium will react with silicate particles in the char and will not be released into the gas stream [19,20]. At combustion temperatures less than 1900K, sodium chloride and sodium cations are vaporized from the char. At temperatures greater than 1900K, inherent quartz begins to soften, allowing diffusion of sodium into the silicate structure. This reaction of sodium with inherent silicate particles at high temperatures usually results in the formation of molten silicate particles which ultimately coalesce. The coalescence or agglomeration of silicate particles is greatly enhanced due to the incorporation of alkalis and alkaline earth elements.

Two manure blends utilizing no coal support were run using FactSage. It is recognized that this does not necessarily represent a real life scenario but serves to evaluate the unique nature of biofuels. Each blend consisted of sheep, dairy tie- and dairy free-stall and miscellaneous manure. Manure Blend 1 was based on similar feed rates for the dairy and miscellaneous manures (≈ 6,820 kg/hr) and 13,545 kg/hr feed rate for the sheep manure. The sheep manure has significantly higher levels of potassium, calcium and sodium than the other manures. Manure Blend 2 is based on equal thermal input by the different manures. Manure Blend 1 had significant amounts of liquid phase (≈ 33 wt. %) $K_2Si_4O_9$ *(l)* present at equilibrium. Manure Blend 1 contained approximately twice as much K_2O as Manure Blend 2. Manure Blend 1 had potassium contained within three species: $K_2Si_4O_9$ *(l)* contained 60% of the potassium; $KAlSi_2O_6$ contained 16% of the total potassium and K_2SO_4 contained 24% of the potassium.

Manure Blend 2 had potassium contained within the same three species as Manure Blend 1 with 60% of the potassium in the liquid phase ($K_2Si_4O_9$) which accounted for 13.3 weight percent of the total inorganic material. The high percentage of liquid phase is attributed to the low concentration of Al_2O_3 present in the fuel. Potassium aluminosilicates tend to have higher melting points than potassium silicates. Zevenhoven-Onderwater et al. defined a T_{15} (critical temperature) as the temperature at which 15 weight percent of the ash is present in a molten phase thereby enabling fly ash deposition in the flue gas pass or formation of sticky bottom ash and possible bed sintering and agglomeration [12]. The T_{15} for forest residue was exceeded between 873 and 1133K. The T_{15} for the *Salix* (low Si) was reached between 1113 and 1273K. Salix (high Si) was predicted at temperatures greater than 1303K.

The importance of alkali earth elements in fuels can be demonstrated by the SiO_2-K_2O system (Figure 11).

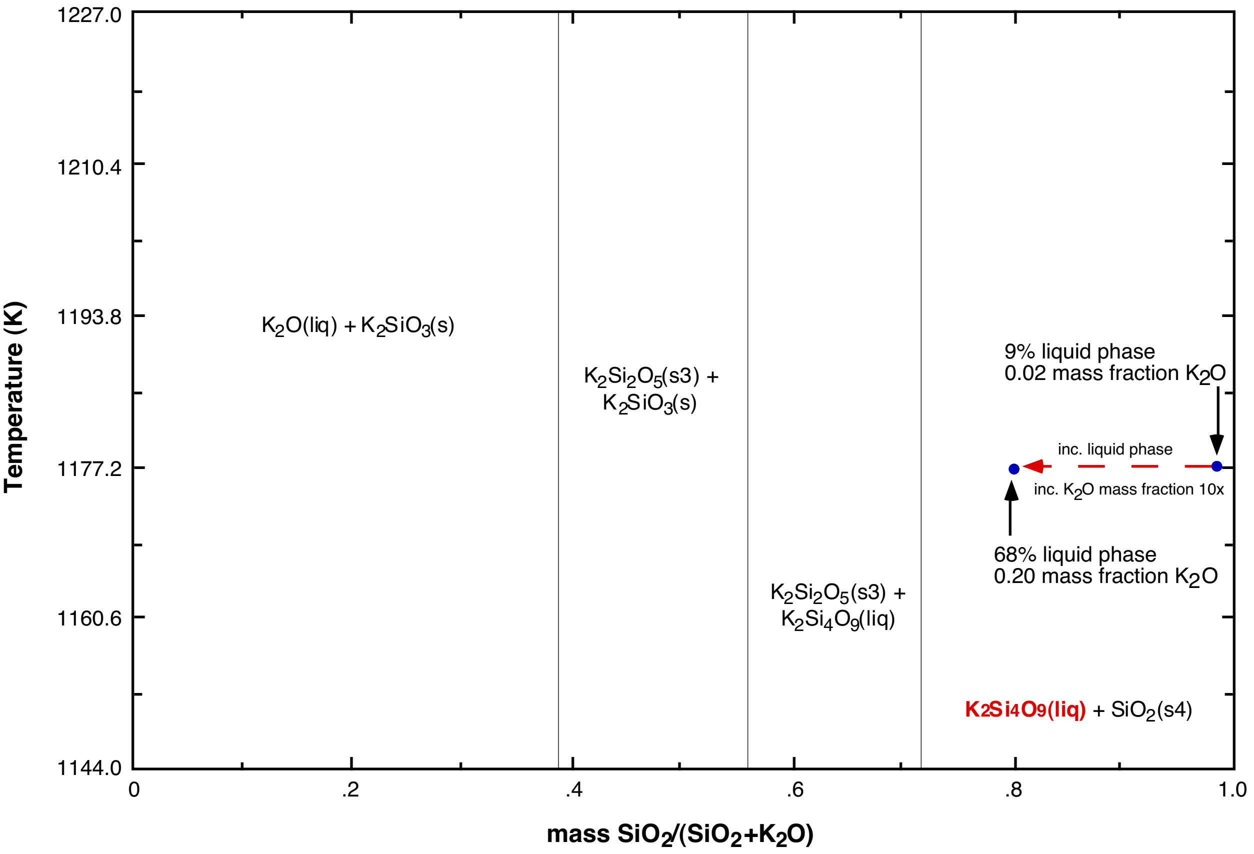

Figure 11. SiO_2-K_2O binary system at equilibrium.

SiO_2 (quartz) has a melting point of 1883K. However, the introduction of a minor amount of K_2O, *e.g.,* 0.02 mass fraction, into the system results in the formation of $K_2Si_4O_9$ *(l)* (9 weight %) at 1171K. $K_2Si_4O_9$ *(l)* is in equilibrium with SiO_2(s4) (tridymite) up to 1732K. An increase in the mass fraction of K_2O to 0.2 increases the mass fraction of the liquid phase to 68% and ultimately leads to the formation of additional potassium silicate melt phases at lower temperatures with tridymite being consumed. Baxter and Jenkins [21] have noted the impact of potassium in depressing the melting point of silicon. Baxter and Jenkins studied straw ash deposits and found that the molten region had a silicon to potassium ratio of less than 4:1 and a ratio over 25:1 in the granular region of the deposit.

It should be noted that the introduction of Al_2O_3 into a system results in a reduction or absence of the $K_2Si_4O_9$ *(l)* phase. In Figure 12 the SiO_2-Al_2O_3 system is shown in which K_2O makes up 0.1 mass fraction of the total system.

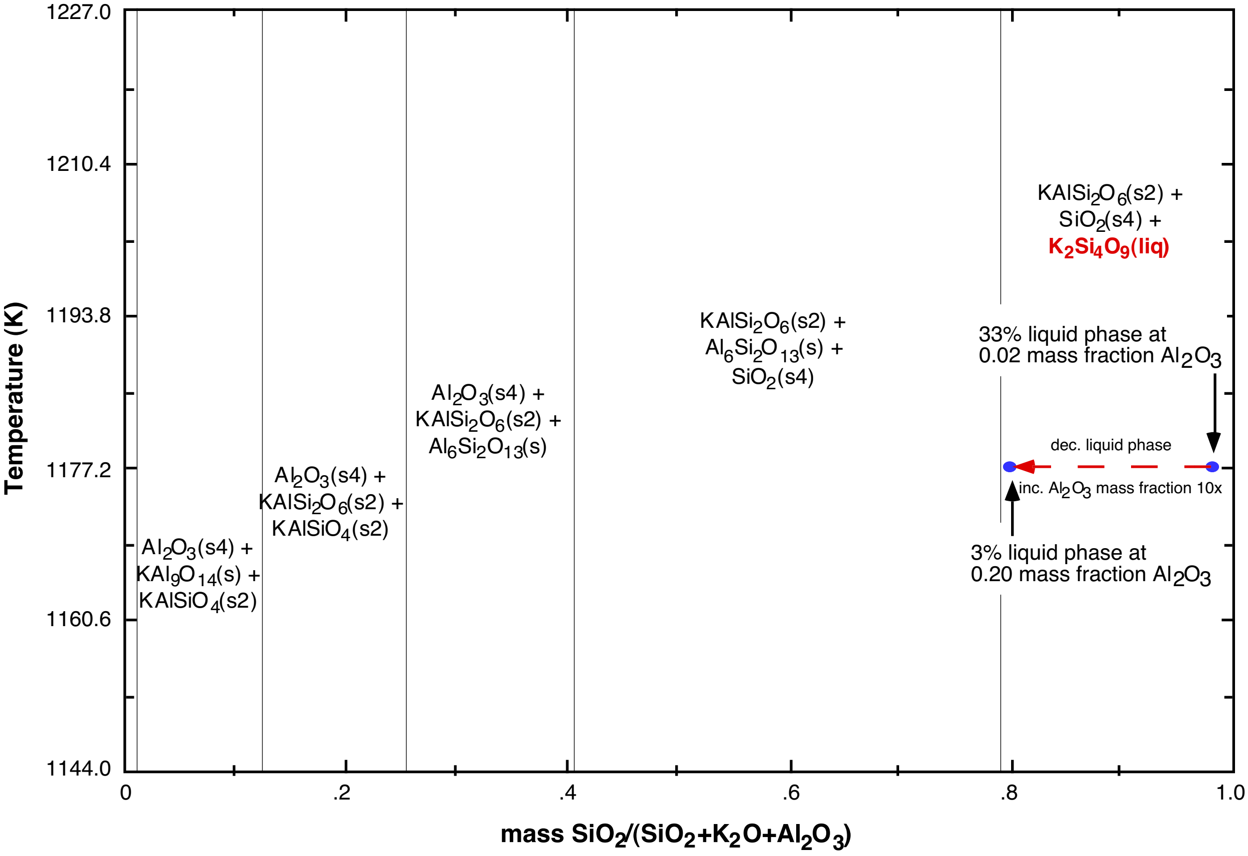

Figure 12. SiO_2-Al_2O_3 binary system at equilibrium and 0.1 mass fraction K_2O.

At 0.02 mass fraction Al_2O_3, the liquid phase accounts for 33% of the total mass at equilibrium. Increasing the mass fraction of Al_2O_3 ten times to 0.20 reduces the mass fraction of liquid phase to 3%. Increasing the mass fraction of Al_2O_3 to 0.22 eliminates the $K_2Si_4O_9$ *(l)* phase. Mullite ($KAlSi_2O_6$) and leucite ($Al_6Si_2O_{13}$) solid phases are in equilibrium with tridymite. The presence of Al_2O_3 in the system favors the formation of potassium aluminosilicates that have higher melting points as compared to potassium silicates. The decrease in liquid phases with increasing aluminum content is precisely what is reflected in the reported inorganic phases in the Baseline Blend with a normalized mass fraction of Al_2O_3 of 31% as compared to the Manure 1 Blend at 3%.

A manure cofire blend was also run in which coal provides 85% of the thermal input. The inorganic composition of the cofire blend is given in Table 3 and the equilibrium composition in Table 4. No liquid phases were calculated to be present at the target temperature of 1171K. In fact no liquid phases were predicted at temperatures up to 1866K (1,593C, 2,900°F). The cofire of coal with the manure blend provides adequate aluminum and silicon to favor the formation of phases that incorporate the alkali earth elements that have higher melting points as compared to phases formed in Manure Blend 1 and 2. A manure cofire in which coal provides 50% of the thermal input was run on FactSage. Interestingly, the equilibrium composition contained a trace (0.6 wt. %) Na_2SO_4 *(l)* at 1171K.

Conclusions

The chemical fractionation methodology described in the appendix was developed as a consequence of the extremely heterogeneous character, *i.e.,* grindability, density and wetability, of the various components that constitute a biofuel. The manner in which biofuels are acquired make it difficult to obtain representative samples or highly reproducible analytical results. This variability is compounded by seasonal variations in the character of biofuels is to be expected. Therefore, fluctuations in biofuel composition should be expected.

Analysis of both leachate and the solid residue was conducted to determine the occurrence of various elements in the biofuels. Potassium occurs predominately in water soluble/ion-exchangeable forms (≥95%) in all four manures and Reed Canary grass. Sodium is also present predominately in water soluble/ion-exchangeable form (≥ 90%) with the remaining sodium present in an insoluble form. Calcium in the fuels is either present in a water soluble/ion-exchangeable form or acid soluble form with the remaining calcium in the insoluble portion of the fuel. Aluminum and silicon remain in the insoluble portion of the fuel. Silicon is attributed to the presence of straw and dirt from the floor of dairy and poultry barns.

The biofuels presented demonstrate the impact that certain elements have on potential clinkering or fouling problems. The FactSage equilibrium calculations suggest that a cofire of biofuels with an appropriate non-fouling coal should not pose any problems in a CFB system given that the coal makes up a majority of the thermal input. Chicken litter was successfully fired in a CFB at Penn State University only after the addition of kaolin clay reduced the presence of low melting phases in the bed. FactSage consistently predicted $K_2Si_4O_9$ *(l)* to be present at 1171K when biofuels having low aluminum levels and significant concentration of alkali earth elements. Only 10% (normalized with respect to SiO_2 and Al_2O_3) of K_2O present in a system was enough to result in the formation of $K_2Si_4O_9$ *(l)* at equilibrium that could compromise a CFB system. Thermodynamically it appears that the baseline cofire blend being evaluated for the CFB boiler for cofiring biomass and other wastes along with coal-based fuels is feasible and that there is flexibility in the biofuel blends that can be handled.

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Appendix. Description Of The Chemical Fractionation Procedure

The following text details the chemical fractionation procedure to determine the mode of occurrence of the mineral components of the biomass feedstocks, coal ashes, and sewage sludge.

Purpose: To determine the occurrence (free, organic, mineral) of the inorganic components in the fuels.

Method: Ground fuel is successively washed with water, ammonium acetate, and hydrochloric acid.

Results: Determined by analyzing both solid and liquid samples taken after each washing step. Mass balance is done to determine the amount of inorganic components lost during each step.

Steps:

1) Dry Fuel

- Fuel are completely dried at 60°C in the large Dispatch oven
- Pyrex pie plates are used for drying (metal tools/containers should be avoided so that contamination will be minimal)

2) Grind Fuel

- Dried fuel is ground to –60 mesh (<250 μm)
- Clean the crusher and pulverizer with compressed air, followed with acetone before every new fuel to be ground
- Cut up fuel if necessary (example: hay)
- Slowly feed to disc crusher
- Feed output from disc crusher to pulverizer
- If necessary, recut and refeed fuel particles that are too large to be fed until they enter the pulverizer
- Remove pulverized fuel from output bin and store in a labeled container in the Dispatch oven until fractionated

3) Clean Glassware

- All glassware and stirrers must be thoroughly cleaned before use as follows:
  clean with scrubber and water
  rinse with deionized water
  rinse with 1M HNO_3 made with deionized water
  rinse with deionized water
  dry on rack

4) Water Wash

- Weigh 120 grams of ground fuel into clean beaker (600 ml for coals, up to 2,000 ml for fluffy biomass)
- Place beaker on stir/heat plate
- Add cleaned stir bar

- Slowly add deionized water and stir with clean glass rod
- Stop adding water when all fuel is wetted and stirring well and heat to 70°C.
- Stir overnight

5) Solid/ Liquid Separation

- Quickly remove beaker from plate and pour mixture into cleaned centrifuge tubes (if the mixture is not stirring as you pour it you will get separation by density and size)
- Centrifuge
- Set up a vacuum filter with Whatman coarse paper (402) and large (1,000 ml) vacuum flask
- Pour supernatant from centrifuge tubes through vacuum filter
- Scrape out solid from centrifuge tubes into a cleaned and labeled Pyrex plate with a clean Teflon coated spatula
- Repeat until beaker is empty
- Scrape solid from Pyrex plate into vacuum filter
- Rinse centrifuge tubes and beaker into vacuum filter
- Rinse solids in vacuum filter with approximately 500 ml of deionized water
- Scrape solids from vacuum funnel back into the Pyrex plate and rinse vacuum funnel with deionized water into plate
- Stir solids thoroughly to mix fractions of different density/size
- Place a small (~15 g) sample of the solids into a sample container, being careful to take a REPRESENTATIVE sample to be submitted for analysis
- Shake up liquid in vacuum flask and put a small sample (~120 ml) in a Nalgene bottle and label to be submitted for analysis
- Measure volume of liquid remaining using a 1,000 ml graduated cylinder and discard this liquid after recording the volume

6) Dry Washed Solids

- Dry solids in Pyrex plate and sample container in Dispatch oven overnight (longer if moisture remains)
- Weigh both bulk solids and sample and record weights

7) Ammonium Acetate Wash

- Repeat water wash procedure using the dried filtrate from the water wash, this time using 1M ammonium acetate made with deionized water
- Heat liquid to 70°C during the stirring phase, checking temperature with a clean thermometer clamped into place on the beaker
- Excess water must be added before you leave for the night to ensure that all the water does not evaporate
- Ammonium acetate wash must be done three times
- Keep the liquid from each washing/centrifuging/filtering step in a labeled container, and take a sample from the combined liquid after the third washing to be submitted for analysis

- Dry the solid after the third washing and remove ~15g to be submitted for analysis
- The remaining solid goes on to the hydrochloric acid step

8) Hydrochloric Acid Wash

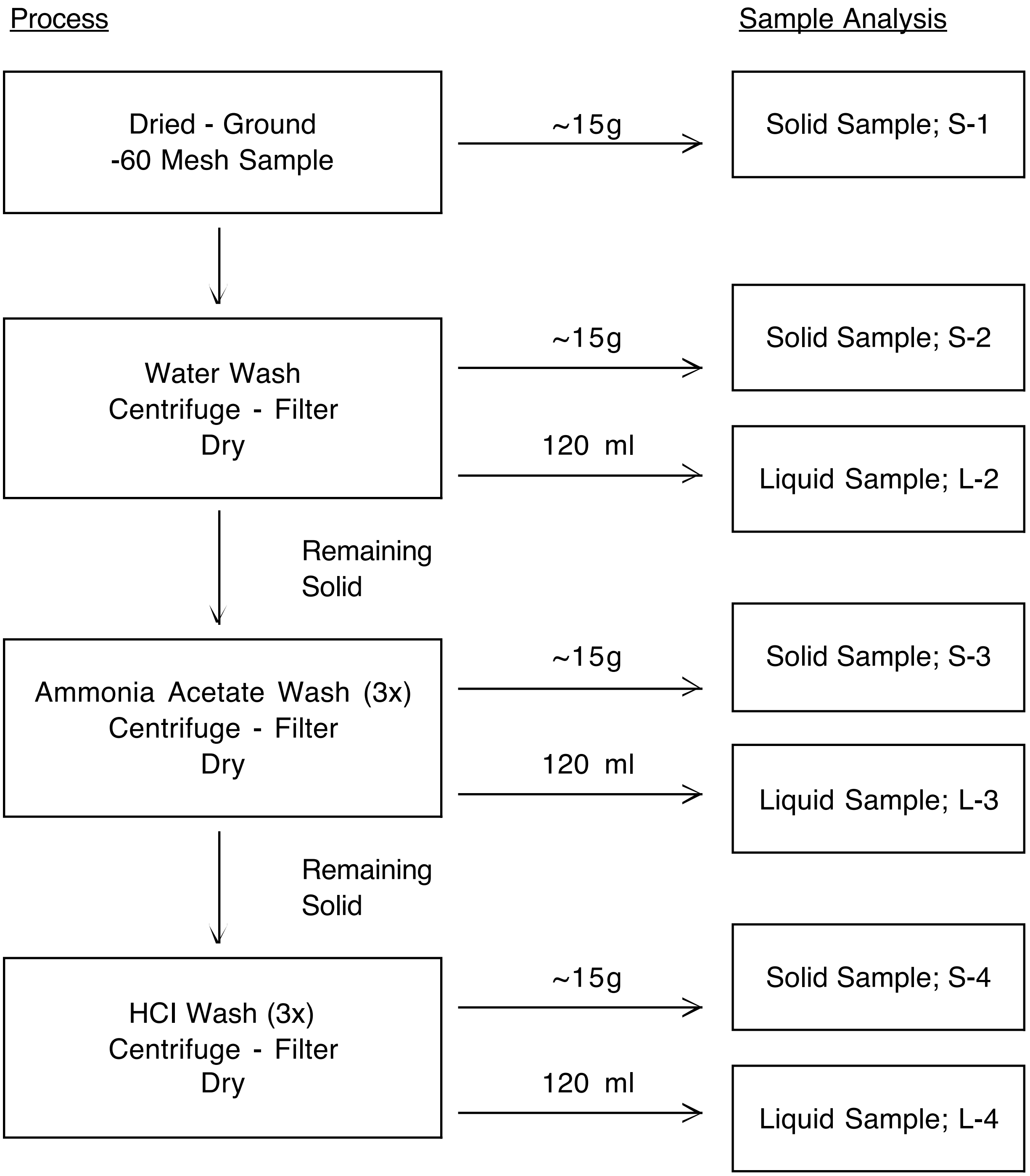
- Repeat the ammonium acetate procedure using 1M HCl rather than ammonium acetate
- Submit ~15g dried solid and 120 ml liquid for analysis

9) Refilter Liquid Samples (if necessary)

- If particulate matter can be seen settled at the bottom of your liquid sample containers, they must be refiltered
- Pass the liquid through a clean vacuum filter set up with a fine Whatman paper and pour back into sample bottle

10) Analyze Samples

- Perform Inductively Coupled Plasma (DCP) spectrometric analysis on all solid and liquid samples



Liquid Samples - add 3% nitric acid.