PENNSTATE

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

Eighth Quarterly Technical Progress Report for the Period 03/15/2002 to 06/14/2002

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 Tom Steitz
Foster Wheeler Energy Services, Inc.

July 12, 2002

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, the final technical design and cost estimate were completed by Foster Wheeler, Foster Wheeler completed a draft report summarizing the design, and Foster Wheeler performed internal reviews and approvals prior to submitting the design package to Penn State.

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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 will allow the University to do the following:

- more economically supply heat to the University Park Campus;
- 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;
- reduce the amount of agricultural and other waste products produced by the University that must be landfilled of land applied;
- reduce the amount of CO_2 (a greenhouse gas) emissions (by combusting waste biofuels); and

- 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.

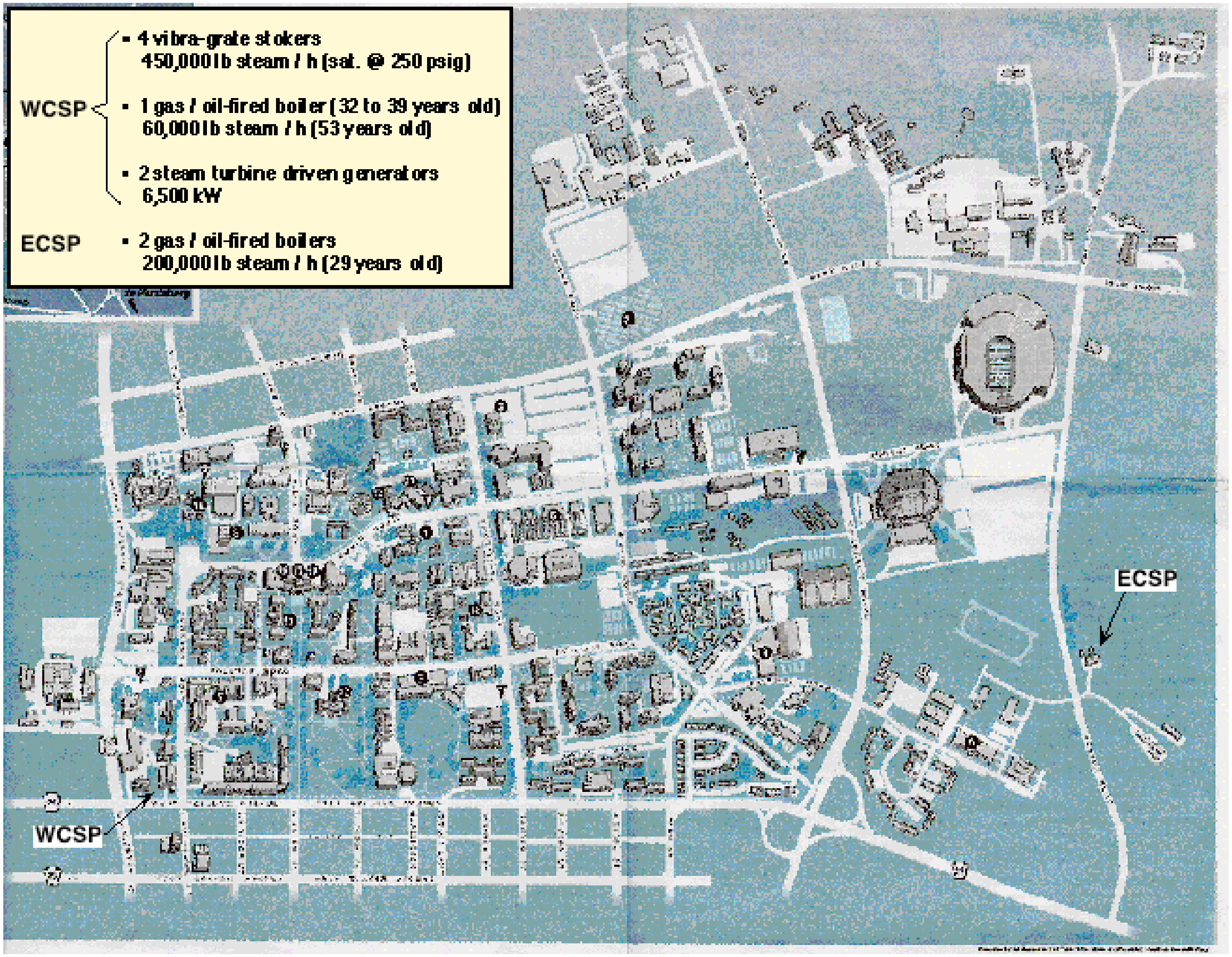
The four stoker-fired boilers at Penn State are all between 33 and 40 years old. When the units were installed (1961 to 1968), the projected life of a typical unit was expected to be approximately 40 years. Since that time, the life of the steam generating units has been reevaluated based on changing 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.

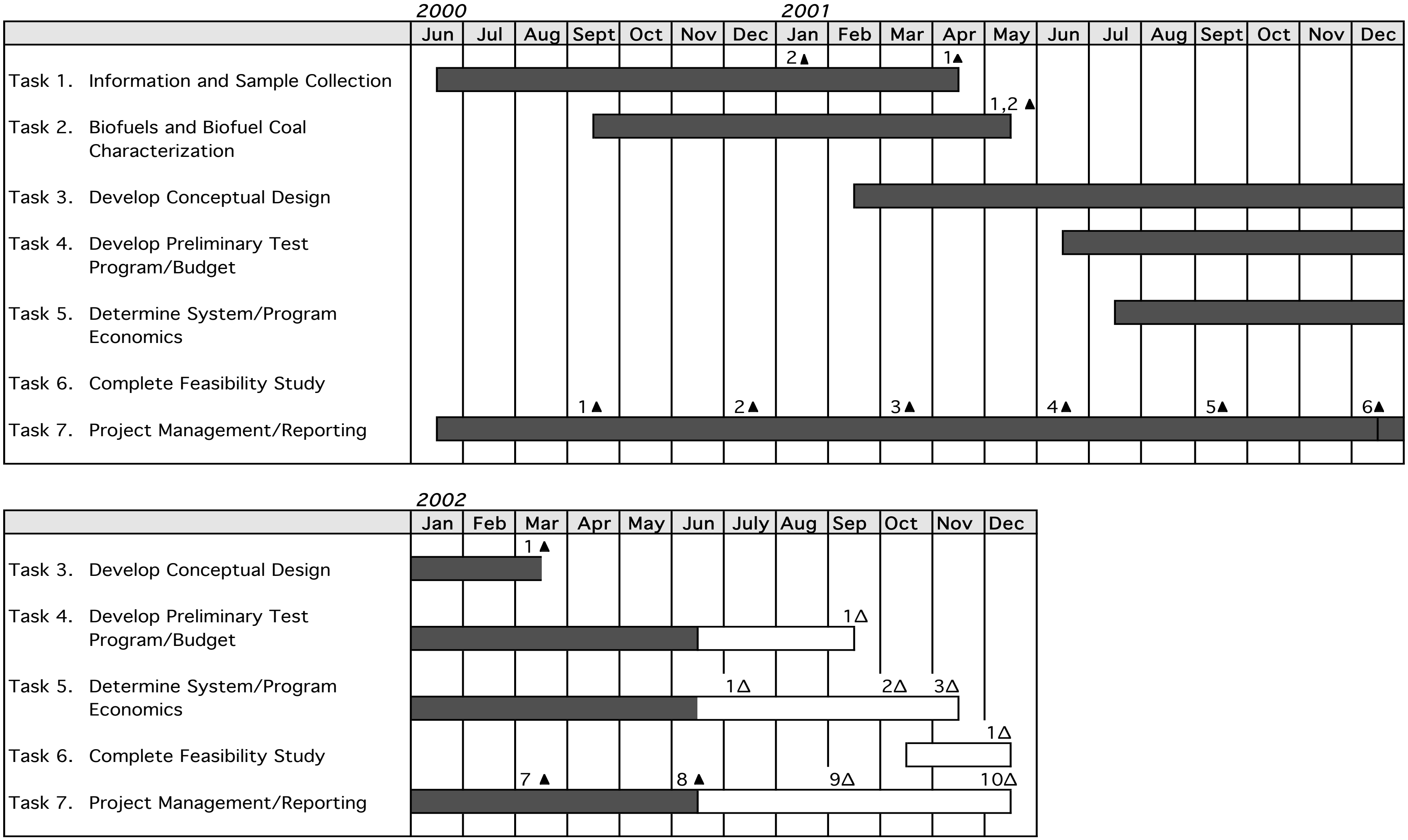


Figure 2. MILESTONE SCHEDULE

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	03/15/02	03/15/02
Task 4, No. 1	Develop preliminary task program/budget	03/15/02	
Task 5, No. 1	Determine capital cost	09/15/02	
Task 5, No. 2	Determine operating costs	10/15/02	
Task 5, No. 3	Assess availability of funding	11/15/02	
Task 6, No. 1	Complete feasibility study	12/14/02	
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	12/15/01	01/18/02
Task 7, No. 7	Prepare program/project management and technical report 7	03/14/02	04/12/02
Task 7, No. 8	Prepare program/project management and technical report 8	06/14/02	07/12/02
Task 7, No. 9	Prepare program/project management and technical report 9	09/14/02	
Task 7, No. 10	Prepare program/project management and technical report 10; prepare final report	12/14/02	

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

The conceptual design was completed by Foster Wheeler during this reporting period. Foster Wheeler will submit the design and cost package to Penn State in July.

5.0 Task 4. Develop Preliminary Test Program/Budget

The budget for the test program 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. The cost estimate was completed but Foster Wheeler is reviewing the numbers internally before submitting them to Penn State. They will be submitted with the design in July 2002.

7.0 Task 6. Complete Feasibility Study

Work continued on Task 6 during this reporting period. Foster Wheeler completed a draft report of the design and cost estimates.

8.0 Task 7. Project Management/Reporting

Technical reporting was performed per the contractual requirements. In addition, work continued on the final report.

A no-cost extension was requested and granted in order to integrate the design and cost package into the feasibility study. The project will be completed by December 2002.

One manuscripts were prepared to be presented at the 2002 International Joint Power Generation Conference in Scottsdale, Arizona on June 24-27, 2002. The title and authors of one manuscript are "The Occurrence of Inorganic Elements in Various Biofuels and its Effect on the Formation of Melt Phases During Combustion," coauthored by Sharon Falcone Miller and Bruce G. Miller. A copy of the manuscript is contained in Appendix A.

9.0 Next Quarterly Activities

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

- Foster Wheeler will submit the design package, cost estimate, and draft final report to Penn State;
- Work will continue on the feasibility study;
- The test plan budget will be prepared
- Penn State will review the design package and generate utility costs;
- Site renderings will be completed; and

- An internal site assessment will be completed.

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

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APPENDIX A. MANUSCRIPT FOR THE 2002 INTERNATIONAL JOINT POWER GENERATION CONFERENCE

The Occurrence of Inorganic Elements in Various Biofuels and its Effect on the Formation of Melt Phases During Combustion

by

Sharon Falcone Miller and Bruce G. Miller

Proceedings for IJPGC’02
2002 International Joint Power Generation Conf.
Phoenix, AZ USA June 24-26,2002

Paper No. IJPGC2002-26177

THE OCCURRENCE OF INORGANIC ELEMENTS IN VARIOUS BIOFUELS AND ITS EFFECT ON THE FORMATION OF MELT PHASES DURING COMBUSTION

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ABSTRACT

The Pennsylvania State University is performing a feasibility analysis on installing a circulating fluidized bed (CFB) boiler at Penn State’s University Park campus for cofiring multiple biofuels and other wastes with coal. Twenty feedstocks are being considered. Chemical fractionation analysis was performed on eleven of the fuels. 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 propensity to form liquid phases during combustion based on thermodynamic modeling. 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. FactSage consistently predicted $K_2Si_4O_9$ *(l)* to be present at 1171K with biofuels having low aluminum levels and significant concentration of alkali earth elements. Only 10% 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.

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.

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.

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. Details of the resource assessments and results from analysis of all the feedstocks can be found elsewhere [7,8]. Of these twenty 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 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.

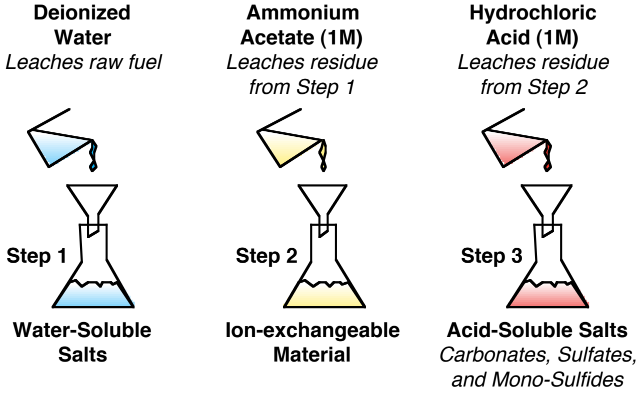

Figure 1. Schematic Representation of the Chemical Fractionation Method

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 7 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. Chlorine and phosphorous (analysis included) are important in the formation of liquid phases but are not discussed at this time due to space constraints.

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%).

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 Manure	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

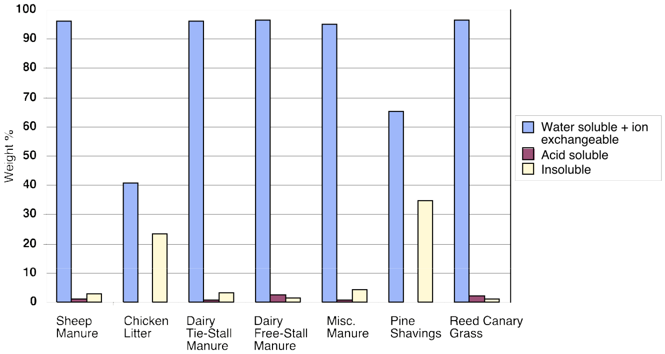

Figure 2. Occurrence of potassium in biofuels

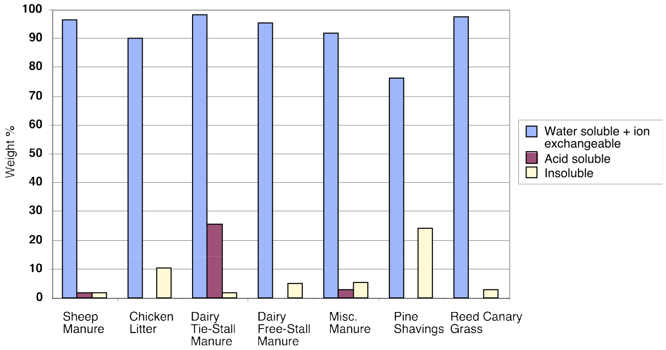

Figure 3. Occurrence of sodium in biofuels

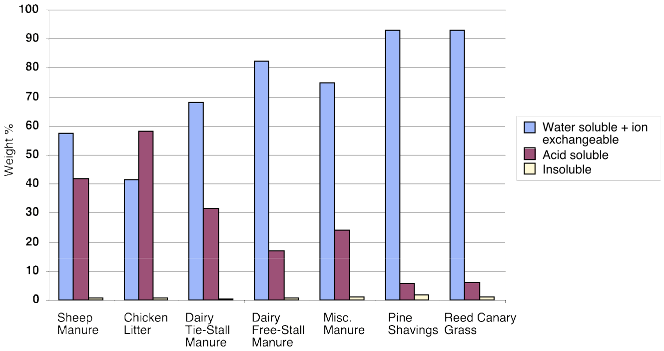

Figure 4. Occurrence of calcium in biofuels

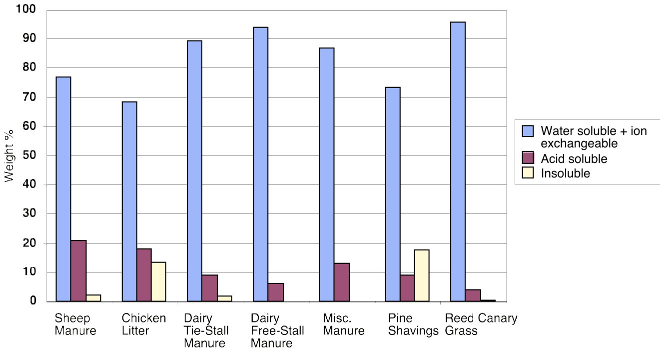

Figure 5. Occurrence of magnesium in biofuels

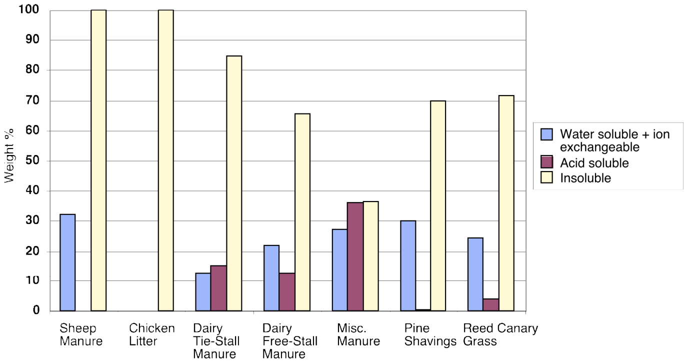

Figure 6. Occurrence of aluminum in biofuels

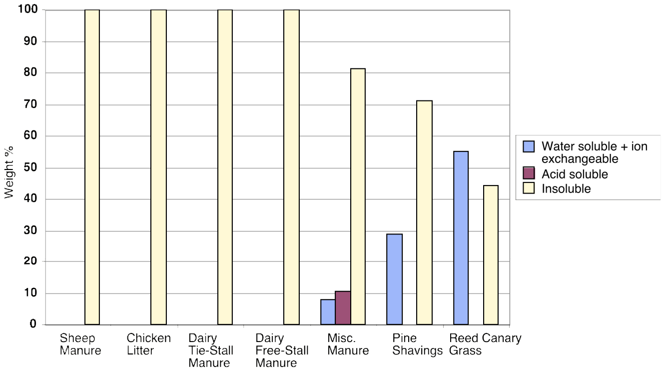

Figure 7. Occurrence of silicon in biofuels

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.

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.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[13]. The program calculates equilibrium composition for a given system at a set of defined temperature and/or pressure conditions. The chemical fractionation results determined the input composition for each fuel blend. Insoluble elements such as silica are fairly inert at lower temperatures typical of a fluid bed. Whereas the water soluble and ion-exchangeable elements are quite reactive.

The biomass resource assessment 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.

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 necessarily imply any information regarding the crystallinity of the phase but only a match with regard to chemical composition.

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	

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. FactSage predicted significant amounts of liquid phase (≈ 33 wt. %) $K_2Si_4O_9$ *(l)* in Manure Blend 1 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 8).

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 FactSage calculation 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 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 9 the SiO_2-Al_2O_3 system as generated by FactSage is shown in which K_2O makes up 0.1 mass fraction of the total system.

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%.

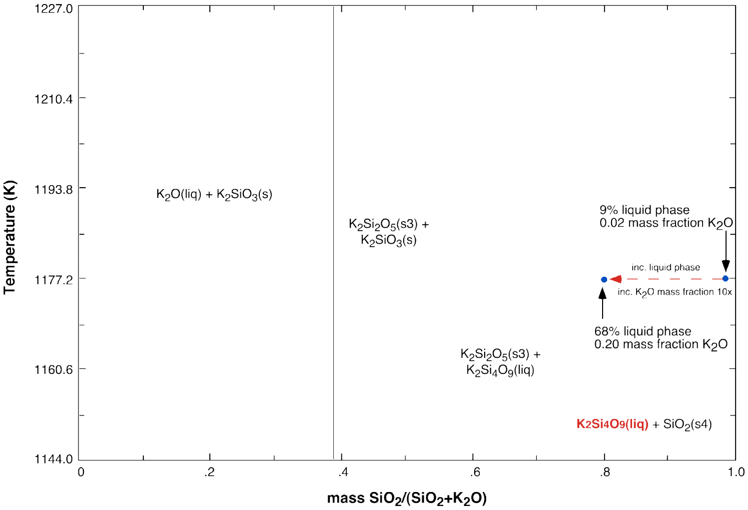

Figure 8. SiO_2-K_2O binary system at equilibrium generated by FactSage

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. 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. %) of Na_2SO_4 *(l)* at 1171K.

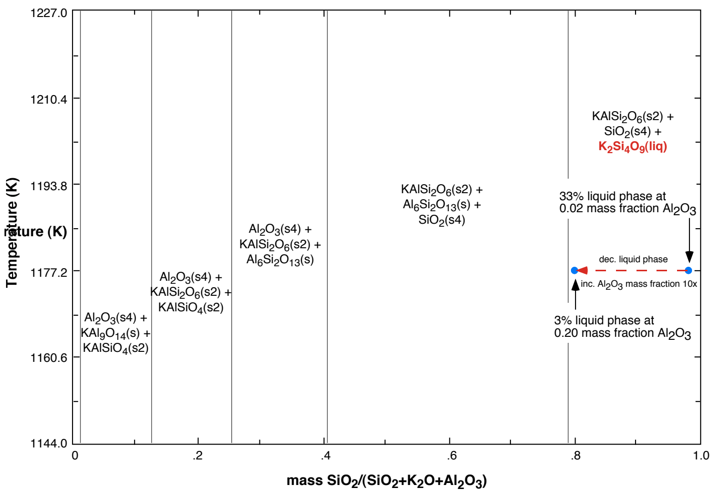

Figure 9. SiO_2- Al_2O_3 binary system at equilibrium and 0.1 mass fraction K2O generated by FactSage

A problem with the generated FactSage diagrams is that they predict much lower temperature at which potassium aluminosilicates liquid phases appear when compared to standard phase diagrams in the literature [22]. The lowest temperature (eutectic) at which liquid phases are present in a SiO_2-K_2O-Al_2O_3 is 1043K in the $K_2O.4SiO_2$ - K_2O. Al_2O_3.6 SiO_2 system. In the $K_2O.2SiO_2$- K_2O. Al_2O_3. $2SiO_2$ system, liquid phases appear at 1196K. However, standard phase diagrams show a decrease in the percent liquid phase with the addition of Al_2O_3 and, conversely, an increase in liquid phase with the addition of K_2O.

CONCLUSIONS

The chemical fractionation methodology 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. 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. FactSage consistently predicted $K_2Si_4O_9$ *(l)* to be present at 1171K with 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. The temperatures at which liquid phases form based on FactSage seem a bit depressed when compared to the literature. It is believed that further scrutiny of the input data and the data base is necessary to resolve this discrepency. 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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REFERENCES

1.Watt JD. 1969. The physical and chemical behaviour of the mineral matter in coal under the conditions met in combustion plant, Part II.BCURA: Leatherhead, England.
2. Raask, Erich, 1985. Mineral impurities in coal combustion, Hemisphere Publishing Corp.: Washington, 484pp.
3. Falcone, SK and Schobert, H.H., "Mineral Transformations during Ashing of Selected Low-Rank Coals," in Mineral Matter and Ash in Coal, KS Vorres, Ed., ACS Symposium Series No. 301, American Chemical Society: Washington, D.C., pp. 114-127, 1986.
4. Schobert HH. 1995. Lignites of North America, Coal Science and Technology 23, Chapter 5, Elsevier: Amsterdam, 678pp.
5. Vorres, K.S., Greenburg, S., and Poeppel, R.B., 1985. "Viscosity of Synthetic Coal Ash Slags," Argonne National Laboratory Report ANL/FE-85-10.
6. Jung, Bongjin, 1990. Viscous Sintering of Coal Ashes in Combustion Systems, PhD Thesis in Fuel Science, The Pennsylvania State University.
7. Miller, BG, Miller, S Falcone, Jawdy, C,M., Cooper, R., Donovan, D., and Battista., J.J. 2000. "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, 95 pages.

8. Miller, BG, Miller, S Falcone, Cooper, R., Donovan, D., Gaudlip, J., Lapinsky, M., Serencsits, W., Raskin, N., Lamke, D., and Battista, J.J. 2001. "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, 72 pages.

9. Benson SA and Holm P. 1985. Comparison of inorganic constituents in three low-rank coals, Ind Chem Engng Prod Res Dev 24:145-149.

10. Baxter LL. 1994. Pollutant emission and deposit formation during combustion of biomass fuel. Livermore, CA.

11. Von Puttkamer, T, Sven UnterberKlaus RG Hein. 2000. Round robin on biomass fuels. ACS National Meeting, Division of Fuel Chemistry, v 45, no 3, August, Washington, DC.

12. Zevenhoven-Onderwater, M.,Blomquist JP, Skrifvars BJ, Backman R, and Hupa M. 2000. The prediction of behavior of ashes from five different solid fuels in fluidized bed combustion. Fuel 79:1353-1361.

13. FACTSage 5.0, 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, Herzogenrath, Germany, released March 2001.

14. Jawdy, CM, Miller, S. Falcone, BG Miller. 2000. "Chicken Litter Combustion Analysis," unpublished internal report.

15. Virr, MJ. 2001. "The Development of a Modular System to Burn Farm Animal Waste to Generate Heat and Power," 16th International Conference on Fluidized Bed Combustion, May 13-16, 2001, Reno, Nevada.

16. Hald, Pia. 1995. The behavior of alkali metals in biomass conversion systems, ACS National Meeting, Division of Fuel Chemistry, v 40, no 3, 210th, August.

17. Helble, JJ, Srinivasachar, S., Boni, A.A., Bool L.E., Gallagher, N.B., Peterson, T.W., Wendt, J.O.L., Huggins, F.E., Shah, N., Huffman, G.P., Graham, K.A., Sarofim, A.F., and Beer, J.M. 1991a. "Mechanisms of Ash Evolution - A Fundamental Study Part II: Bituminous Coals and the Role of Iron and Potassium," Engineering Foundation Conference on Inorganic Transformations and Ash Deposition During Combustion, Palm Coast, Florida.

18. Helble, JJ, Srinivasachar, S., Boni, A.A., Kang, S.G., Graham, K.A., Sarofim, A.F., Beer, J.M., Gallagher, N.B., Bool L.E, TW Peterson, T.W., Wendt, J.O.L., Shah, N., Huggins, F.E., and Huffman, G.P., 1991b. "Mechanisms of Ash Evolution - A Fundamental Study Part I: Low-Rank Coals and the Role of Calcium," Engineering Foundation Conference on Inorganic Transformations and Ash Deposition During Combustion, Palm Coast, Florida.

19. Neville, M and Sarofim, A.F. 1985. "The Fate of Sodium during Pulverized Coal Combustion," Fuel, v. 64, pp. 384-390.

20. Gallagher, NB, Peterson, T.W., and Wendt, J.O.L. 1991."Alkali/Silicate Interactions During Pulverized Coal Combustion," ACS Division of Fuel Chemistry Preprints, v. 36, no. 1, pp. 181-190.

21. Baxter, LL and Jenkins, BM. 1995. Laboratory illustrations of the transformations and deposition of inorganic material in biomass boilers. 210th ACS National Meeting, Fuel Science Division, Chicago, August.

22. Levin, E.M., Robbins, C.R. and McMurdie, H.F. 1964. Phase Diagrams for Ceramists, 5th Printing, 1985, M.K. Reser, Ed., The American Ceramic Society, Inc.: Columbus, Ohio.